9.4.5 Calculate the percent relative standard deviation (percent RSD) for each analyte using Equation 7, Section 12, substituting the appropriate values for the relative response factors (RRF's) in said equation.

9.4.6 If the percent accuracy (Section 9.4.4) for all analytes is within the range 90 percent to 110 percent and the percent RSD (Section 9.4.5) for all analytes is ≤20 percent, system performance is acceptable and sample analysis may begin. If these criteria are not met for any analyte, then system performance is not acceptable for that analyte and the test must be repeated for those analytes only. Repeated failures indicate a general problem with the measurement system that must be located and corrected. In this case, the entire test, beginning at Section 9.4.1, must be repeated after the problem is corrected.

9.5 Great care must be exercised to maintain the integrity of all standards. It is recommended that all standards be stored at −10 °C to 0 °C in screw-cap amber glass bottles with Teflon liners.

9.6 Unless otherwise specified, all weights are to be recorded within 0.1 mg.

10. Calibration and Standardization.

10.1 Column Baseline Drift. Before each calibration and series of determinations and before the daily calibration check, condition the column using procedures developed by the laboratory or as specified by the column supplier. Operate the GC at initial (i.e., before sample injection) conditions on the lowest attenuation to be used during sample analysis. Adjust the recorder pen to zero on the chart and obtain a baseline for at least one minute. Initiate the GC operating cycle that would be used for sample analysis. On the recorder chart, mark the pen position at the end of the simulated sample analysis cycle. Baseline drift is defined as the absolute difference in the pen positions at the beginning and end of the cycle in the direction perpendicular to the chart movement. Calculate the percent baseline drift by dividing the baseline drift by the chart width representing full-scale deflection and multiply the result by 100.

10.2 Calibration of GC. Bring all stock standards and calibration standards to room temperature while establishing the GC at the determined operating conditions.

10.2.1 Retention Times (RT's) for Individual Compounds.

NOTE: The procedures of this subsection are required only for the initial calibration. However, it is good laboratory practice to follow these procedures for some or all analytes before each calibration. The procedures were written for chromatograms output to a strip chart recorder. More modern instruments (e.g., integrators and electronic data stations) determine and print out or display retention times automatically.

The RT for each analyte should be determined before calibration. This provides a positive identification for each peak observed from the calibration standards. Inject an appropriate volume (see note in Section 11.5.2) of one of the stock reference standards into the gas chromatograph and record on the chart the pen position at the time of the injection (see Section 7.6.1). Dilute an aliquot of the stock reference standard as required in dimethylformamide to achieve a concentration that will result in an on-scale response. Operate the gas chromatograph according to the determined procedures. Select the peak(s) that correspond to the analyte(s) [and internal standard, if used] and measure the retention time(s). If a chart recorder is used, measure the distance(s) on the chart from the injection point to the peak maxima. These distances, divided by the chart speed, are defined as the RT's of the analytes in question. Repeat this process for each of the stock reference standard solutions.

NOTE: If gas chromatography with mass spectrometer detection (GC-MS) is used, a stock reference standard may contain a group of analytes, provided all analytes are adequately separated during the analysis. Mass spectral library matching can be used to identify the analyte associated with each peak in the gas chromatogram. The retention time for the analyte then becomes the retention time of its peak in the chromatogram.

10.2.2 Calibration. The GC must be calibrated using a minimum of three concentration levels of each potential analyte. (See Section 7.7 for instructions on preparation of the calibration standards.) Beginning with the lowest concentration level calibration standard, carry out the analysis procedure as described beginning in Section 11.7. Repeat the procedure for each progressively higher concentration level until all calibration standards have been analyzed.

10.2.2.1 Calculate the RT's for the internal standard and for each analyte in the calibration standards at each concentration level as described in Section 10.2.1. The RT's for the internal standard must not vary by more than 0.10 minutes. Identify each analyte by comparison of the RT's for peak maxima to the RT's determined in Section 10.2.1.

10.2.2.2 Compare the retention times (RT's) for each potential analyte in the calibration standards for each concentration level to the retention times determined in Section 10.2.1. The calibration is not valid unless all RT's for all analytes meet the criteria given in Section 9.3.2.

10.2.2.3 Tabulate the area responses and the concentrations for the internal standard and each analyte in the calibration standards. Calculate the response factor for the

internal standard (RF_{is}) and the response factor for each compound relative to the internal standard (RRF) for each concentration level using Equations 5 and 6, Section 12.

10.2.2.4 Using the RRF's from the calibration, calculate the percent relative standard deviation (percent RSD) for each analyte in the calibration standard using Equation 7, Section 12. The percent RSD for each individual calibration analyte must be *less* than 15 percent. This criterion must be met in order for the calibration to be valid. If the criterion is met, the mean RRF's determined above are to be used until the next calibration.

10.3 Daily Calibration Checks. The calibration curve (Section 10.2.2) must be checked and verified at least once each day that samples are analyzed. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint of the working range and performing the checks in Sections 10.3.1, 10.3.2, and 10.3.3.

10.3.1 For each analyte in the calibration standard, calculate the percent difference in the RRF from the last calibration using Equation 8, Section 12. If the percent difference for each calibration analyte is less than 10 percent, the last calibration curve is assumed to be valid. If the percent difference for any analyte is greater than 5 percent, the analyst should consider this a warning limit. If the percent difference for any one calibration analyte exceeds 10 percent, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new three-point (minimum) calibration must be generated. This criterion must be met before quantitative analysis begins.

10.3.2 If the RF_{is} for the internal standard changes by more than ±20 percent from the last daily calibration check, the system must be inspected for malfunctions and corrections made as appropriate.

10.3.3 The retention times for the internal standard and all calibration check analytes must be evaluated. If the retention time for the internal standard or for any calibration check analyte changes by more than 0.10 min from the last calibration, the system must be inspected for malfunctions and corrections made as required.

11. Procedure

11.1 All samples and standards must be allowed to warm to room temperature before analysis. Observe the given order of ingredient addition to minimize loss of volatiles.

11.2 Bring the GC system to the determined operating conditions and condition the column as described in Section 10.1.

NOTE: The temperature of the injection port may be an especially critical parameter. Information about the proper temperature may be found on the CPDS.

11.3 Perform the daily calibration checks as described in Section 10.3. Samples are not to be analyzed until the criteria in Section 10.3 are met.

11.4 Place the as-received coating sample on a paint shaker, or similar device, and shake the sample for a minimum of 5 minutes to achieve homogenization.

11.5 NOTE: The steps in this section must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory hood free from solvent vapors. All weights must be recorded to the nearest 0.1 mg.

11.5.1 Add 16 g of dimethylformamide to each of two tared vials (A and B) capable of being septum sealed.

11.5.2 To each vial add a weight of coating that will result in the response for the major constituent being in the upper half of the linear range of the calibration curve.

NOTE: The magnitude of the response obviously depends on the amount of sample injected into the GC as specified in Section 11.8. This volume must be the same as used for preparation of the calibration curve, otherwise shifts in compound retention times may occur. If a sample is prepared that results in a response outside the limits of the calibration curve, new samples must be prepared; changing the volume injected to bring the response within the calibration curve limits is not permitted.

11.5.3 Add a weight of internal standard to each vial (A and B) that will result in the response for the internal standard being between 25 percent and 75 percent of the linear range of the calibration curve.

11.5.4 Seal the vials with crimp-on or Mininert® septum seals.

11.6 Shake the vials containing the prepared coating samples for 60 seconds. Allow the vials to stand undisturbed for ten minutes. If solids have not settled out on the bottom after 10 minutes, then centrifuge at 1,000 rpm for 5 minutes. The analyst also has the option of injecting the sample without allowing the solids to settle.

11.7 Analyses should be conducted in the following order: daily calibration check sample, method blank, up to 10 injections from sample vials (*i.e.*, one injection each from up to five pairs of vials, which corresponds to analysis of 5 coating samples).

11.8 Inject the prescribed volume of supernatant from the calibration check sample, the method blank, and the sample vials onto the chromatographic column and record the chromatograms while operating the system under the specified operating conditions.

NOTE: The analyst has the option of injecting the unseparated sample.

12. Data Analysis and Calculations

12.1 Qualitative Analysis. An analyte (e.g., those cited in Section 1.1) is considered tentatively identified if two criteria are satisfied: (1) elution of the sample analyte within ±0.05 min of the average GC retention time of the same analyte in the calibration standard; and (2) either (a) confirmation of the identity of the compound by spectral matching on a gas chromatograph equipped with a mass selective detector or (b) elution of the sample analyte within ±0.05 min of the average GC retention time of the same analyte in the calibration standard analyzed on a dissimilar GC column.

12.1.1 The RT of the sample analyte must meet the criteria specified in Section 9.3.3.

12.1.2 When doubt exists as to the identification of a peak or the resolution of two or more components possibly comprising one peak, additional confirmatory techniques (listed in Section 12.1) must be used.

12.2 Quantitative Analysis. When an analyte has been identified, the quantification of that compound will be based on the internal standard technique.

12.2.1 A single analysis consists of one injection from each of two sample vials (A and B) prepared using the same coating. Calculate the concentration of each identified analyte in the sample as follows:

$$HAP_{wt\%} = 100 \times \frac{(A_x)(W_{is})}{(A_{is})(\overline{RRF_x})(W_x)} \qquad \text{Eq. (1)}$$

where:

$HAP_{wt\%}$ = weight percent of the analyte in coating.
A_x = Area response of the analyte in the sample.
W_{is} = Weight of internal standard added to sample, g.
A_{is} = Area response of the internal standard in the sample.
$\overline{RRF_x}$ = Mean relative response factor for the analyte in the calibration standards.
W_x = Weight of coating added to the sample solution, g.

12.2.2 Report results for duplicate analysis (sample vials A and B) without correction.

12.3 Precision Data. Calculate the percent difference between the measured concentrations of each analyte in vials A and B as follows.

12.3.1 Calculate the weight percent of the analyte in each of the two sample vials as described in Section 12.2.1.

12.3.2 Calculate the percent difference for each analyte as:

$$\%Dif_i = 100 \times \frac{|A_i - B_i|}{\frac{(A_i + B_i)}{2}} \qquad \text{Eq. (2)}$$

where A_i and B_i are the measured concentrations of the analyte in vials A and B.

12.4 Calculate the percent accuracy for analytes in the QCCS (See Section 9.4) as follows:

$$\%\ Accuracy_x = 100 \times \frac{\overline{X}_x}{T_x} \qquad \text{Eq. (3)}$$

where X_x is the mean measured value and T_x is the known true value of the analyte in the QCCS.

12.5 Obtain retention times (RT's) from data station or integrator or, for chromatograms from a chart recorder, calculate the RT's for analytes in the calibration standards (See Section 10.2.2.2) as follows:

$$RT = \frac{\text{Distance from injection to peak maximum}}{\text{Recorder chart speed}} \qquad \text{Eq. (4)}$$

12.6 Calculate the response factor for the internal standard (See Section 10.2.2.3) as follows:

$$RF_{is} = \frac{A_{is}}{C_{is}} \qquad \text{Eq. (5)}$$

where:

A_{is} = Area response of the internal standard.

C_{is} = Weight percent of the internal standard.

12.7 Calculate the relative response factors for analytes in the calibration standards (See Section 10.2.2.3) as follows:

where:

$$RRF_x = \frac{A_x}{RF_{is}\ C_x} \qquad \text{Eq. (6)}$$

RRF_x = Relative response factor for an individual analyte.

A_x = Area response of the analyte being measured.

C_x = Weight percent of the analyte being measured.

12.8 Calculate the percent relative standard deviation of the relative response factors for analytes in the calibration standards (See Section 10.2.2.4) as follows:

$$\%RSD = 100 \times \frac{\sqrt{\dfrac{\sum_{i=1}^{n} \left(RRF_x - \overline{RRF_x}\right)^2}{n-1}}}{\overline{RRF_x}} \qquad \text{Eq. (7)}$$

where:

n = Number of calibration concentration levels used for an analyte.

RRF_x = Individual RRF for an analyte.

$\overline{RRF_x}$ = Mean of all RRF′s for an analyte.

12.9 Calculate the percent difference in the relative response factors between the calibration curve and the daily calibration checks (See Section 10.3) as follows:

$$\%\ \text{Difference} = \frac{\left|\overline{RRF_x} - RRF_c\right|}{\overline{RRF_x}} \times 100 \qquad \text{Eq. (8)}$$

where:

$\overline{RRF}$ = mean relative response factor from last calibration.

RRF = relative response factor from calibration check standard.

13. Measurement of Reaction Byproducts That are HAP [Reserved]

14. Method Performance [Reserved]

15. Pollution Prevention [Reserved]

16. Waste Management

16.1 The coating samples and laboratory standards and reagents may contain compounds which require management as hazardous waste. It is the laboratory's responsibility to ensure all wastes are managed in accordance with all applicable laws and regulations.

16.2 To avoid excessive laboratory waste, obtain only enough sample for laboratory analysis.

16.3 It is recommended that discarded waste coating solids, used rags, used paper towels, and other nonglass or nonsharp waste materials be placed in a plastic bag before disposal. A separate container, designated "For Sharp Objects Only," is recommended for collection of discarded glassware and other sharp-edge items used in the laboratory. It is recommended that unused or excess samples and reagents be placed in a solvent-resistant plastic or metal container with a lid or cover designed for flammable liquids. This container should not be stored in the area where analytical work is performed. It is recommended that a record be kept of all compounds placed in the container for identification of the contents upon disposal.

17. References

1. Clean Air Act Amendments, Public Law 101-549, Titles I-XI, November, 1990.

2. Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph. ASTM Designation D3792-79.

3. Standard Practice for Sampling Liquid Paints and Related Pigment Coatings. ASTM Designation D3925-81.

4. Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph. ASTM Designation D4457-85.

5. Standard Test Method for Determining the Unreacted Monomer Content of Latexes Using Capillary Column Gas Chromatography. ASTM Designation D4827-93.

6. Standard Test Method for Determining Unreacted Monomer Content of Latexes Using Gas-Liquid Chromatography. ASTM Designation D 4747-87.

7. Method 301—"Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR 63, Appendix A.

8. "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."

18. Tables, Diagrams, Flowcharts, and Validation Data

Agency: _____
Inspector: _____
Date/Time: _____
Sample ID#: _____
Source ID: _____
Coating Name/Type: _____
Plant Witness: _____
Type Analysis Required: _____
Special Handling: _____

Sample Container Label

Coating Data

Date: _____
Source: _____

Data	Sample ID No.	Sample ID No.
Coating:		
Supplier Name		
Name and Color of Coating		
Type of Coating (primer, clearcoat, etc.)		
Identification Number for Coating		
Coating Density (lbs/gal)		
Total Volatiles Content (wt percent)		
Water Content (wt percent)		
Exempt Solvents Content (wt percent)		
VOC Content (wt percent)		
Solids Content (vol percent)		
Diluent Properties:		
Name.		
Identification Number		
Diluent Solvent Density (lbs/gal)		
VOC Content (wt percent)		
Water Content (wt percent)		
Exempt Solvent Content (wt percent)		
Diluent/Solvent Ratio (gal diluent solvent/gal coating)		

Stock Reference Standard

Name of Reference Material: _____

Supplier Name: _____

Lot Number: _____

Purity: _____

Name of Solvent Material: *Dimethylformamide* _____

Supplier Name: _____

Lot Number: _____

Purity: _____

Date Prepared: _____

Prepared By: _____

Notebook/page no.: _____

PREPARATION INFORMATION

1. Weight Empty Flask ..... _____,g
2. Weight Plus DMF ..... _____,g
3. Weight Plus Reference Material. _____,g
4. Weight After Made to Volume. _____,g
5. Weight DMF (lines 2–1 + 3–4). _____,g
6. Weight Ref. Material (lines 3–2). _____,g
7. Corrected Weight of Reference Material (line 6 times purity). _____,g

PREPARATION INFORMATION—Continued

8. Fraction Reference Material in Standard (Line 7 ÷ Line 5) soln. _____,g/g
9. Total Volume of Standard Solution. _____, ml
10. Weight Reference Material per ml of Solution (Line 7 ÷ Line 9). _____,g/ml

Laboratory ID No. for this Standard. _____

Expiration Date for this Standard. _____

CALIBRATION STANDARD

Date Prepared: _____

Date Expires: _____

Prepared By: _____

Notebook/page: _____

Calibration Standard Identification No.: _____

PREPARATION INFORMATION

Final Weight Flask Plus Reagents. _____, g

Weight Empty Flask ..... _____, g

Total Weight Of Reagents ..... _____, g

Analyte name [a]	Stock reference standard ID No.	Amount of stock reference standard added (by volume or by weight)				Calculated weight analyte added, g	Weight percent analyte in calibration standard [b]
		Volume added, ml	Amount in standard, g/ml	Weight added, g	Amount in standard, g/g soln		
.							
.							
.							
.							
.							
.							
.							
.							
.							

[a] Include internal standard(s).
[b] Weight percent = weight analyte added ÷ total weight of reagents.

Quality Control Check Standard

Date Prepared: _____

Date Expires: _____

Prepared By: _____

Notebook/page: _____

Quality Control Check Standard Identification No.: _____

PREPARATION INFORMATION

Final Weight Flask Plus Reagents. _____,g

Weight Empty Flask ..... _____,g

Total Weight Of Reagents ..... _____,g

Analyte name [a]	Stock reference standard ID No.	Amount of stock reference standard added (by volume or by weight)				Calculated weight analyte added, g	Weight percent analyte in QCC standard [b]
		Volume added, ml	Amount in standard, g/ml	Weight added, g	Amount in standard, g/g soln		
.							
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.							

[a] Include internal Standard(s).
[b] Weight percent = weight analyte added ÷ total weight of reagents.

Quality Control Check Standard Analysis

OCCS Identification No. _____

Date OCCS Analyzed: _____

Analyst: _____

QCC Expiration Date: _____

ANALYSIS RESULTS

Analyte	Weight percent determined			Mean Wt percent	Percent accuracx	Percent RSD	Meets criteria in Section 9.4.6	
	Run 1	Run 2	Run 3				Percent accuracy	Percent RSD
.								
.								
.								
.								
.								
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.								
.								
.								
.								

Calibration of Gas Chromatograph

Calibrated By: _____

Calibration Date: _____

PART 1—RETENTION TIMES FOR INDIVIDUAL ANALYTES

Analyte	Stock standard. ID No.	Recorder chart speed		Distance from injection point to peak maximum		Retention time, minutes [a]
		Inches/min.	cm/min.	Inches	Centimeters	
.						
.						
.						
.						
.						
.						
.						
.						
.						

[a] Retention time = distance to peak maxima ÷ chart speed.

CALIBRATION OF GAS CHROMATOGRAPH

Calibrated By: _____

Calibration Date: _____

Part 2—Analysis of Calibration Standards

Analyte	Calib. STD ID No.	Calib. STD ID No.	Calib. STD ID No.
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Name:			
Conc. in STD			
Area Response			
RT			
Internal Standard Name:			
Conc. in STD			
Area Response			
RT			

Calibration of Gas Chromatograph Calibrated By: ____________________

Calibration Date: ____________________

Part 3—Data Analysis for Calibration Standards

Analyte	Calib. STD ID	Calib. STD ID	Calib. STD ID	Mean	percent RSD of RF	Is RT within ±0.05 min of RT for stock? (Y/N)	Is percent RSD <30% (Y/N)
Name:							
RT							
RF							
Name:							
RT							
RF							
Name:							
RT							
RF							
Name:							
RT							
RF							
Name:							
RT							
RF							
Name:							
RT							
RF							
Name:							
RT							
RF							

Daily Calibration Check

Date: _____

Analyst: _____
Calibration Check Standard ID No.:
Expiration Date: _____

Analyte	Retention Time (RT)			Response Factor (RF)		
	Last	This	Difference [a]	Last	This	Difference [b]
.						
.						
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.						
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.						
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.						

[a] Retention time (RT) change (difference) must be less than ±0.10 minutes.
[b] Response factor (RF) change (difference) must be less than 20 percent for each analyte and for the internal standard.

Sample Analysis

Vial A ID No.: _____

Vial B ID No.: _____
Analyzed By: _____
Date: _____

Sample preparation information	Vial A (g)	Vial B (g)
Measured:		
wt empty via.		
wt plus DMF.		
wt plus sample.		
wt plus internal.		
standard.		
Calculated:		
wt DMF.		
wt sample.		
wt internal standard.		

ANALYSIS RESULTS: DUPLICATE SAMPLES

Analyte	Area response		RF	Wt percent in sample		
	Vial A	Vial B		Vial A	Vial B	Average
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.						
.						
.						
.						
.						
.						
.						
.						
.						
.						
.						
Internal Standard.						

METHOD 312A—DETERMINATION OF STYRENE IN LATEX STYRENE-BUTADIENE RUBBER, THROUGH GAS CHROMATOGRAPHY

1. Scope and Application

1.1 This method describes a procedure for determining parts per million (ppm) styrene monomer (CAS No. 100–42–5) in aqueous samples, including latex samples and styrene stripper water.

1.2 The sample is separated in a gas chromatograph equipped with a packed column and a flame ionization detector.

2.0 Summary of Method

2.1 This method utilizes a packed column gas chromatograph with a flame ionization detector to determine the concentration of residual styrene in styrene butadiene rubber (SBR) latex samples.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

4.1 In order to reduce matrix effects and emulsify the styrene, similar styrene free latex is added to the internal standard. There are no known interferences.

4.2 The operating parameters are selected to obtain resolution necessary to determine styrene monomer concentrations in latex.

5.0 Safety

5.1 It is the responsibility of the user of this procedure to establish appropriate safety and health practices.

6.0 Equipment and Supplies

6.1 Adjustable bottle-top dispenser, set to deliver 3 ml. (for internal standard), Brinkmann Dispensette, or equivalent.

6.2 Pipettor, set to 10 ml., Oxford Macroset, or equivalent.

6.3 Volumetric flask, 100-ml, with stopper.

6.4 Hewlett Packard Model 5710A dual channel gas chromatograph equipped with flame ionization detector.

6.4.1 11 ft. × ⅛ in. stainless steel column packed with 10% TCEP on 100/120 mesh Chromosorb P, or equivalent.

6.4.2 Perkin Elmer Model 023 strip chart recorder, or equivalent.

6.5 Helium carrier gas, zero grade.

6.6 Liquid syringe, 25-µl.

6.7 Digital MicroVAX 3100 computer with VG Multichrom software, or equivalent data handling system.

6.6 Wire Screens, circular, 70-mm, 80-mesh diamond weave.

6.7 DEHA—(N,N-Diethyl hydroxylamine), 97 + % purity, CAS No. 3710-84-7

6.8 p-Dioxane, CAS No. 123-91-1

7.0 Reagents and Standards

7.1 Internal standard preparation.

7.1.1 Pipette 5 ml p-dioxane into a 1000-ml volumetric flask and fill to the mark with distilled water and mix thoroughly.

7.2 Calibration solution preparation.

7.2.1 Pipette 10 ml styrene-free latex (eg: NBR latex) into a 100-ml volumetric flask.

7.2.2 Add 3 ml internal standard (section 7.1.1 of this method).

7.2.3 Weigh exactly 10 µl fresh styrene and record the weight.

7.2.4 Inject the styrene into the flask and mix well.

7.2.5 Add 2 drops of DEHA, fill to the mark with water and mix well again.

7.2.6 Calculate concentration of the calibration solution as follows:

mg/l styrene = (mg styrene added)/0.1 L

8.0 Sample Collection, Preservation, and Storage

8.1 A representative SBR emulsion sample should be caught in a clean, dry 6-oz. teflon lined glass container. Close it properly to assure no sample leakage.

8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

9.1 The instrument is calibrated by injecting calibration solution (Section 7.2 of this method) five times.

9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.

9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.3.1 A set of six latex samples shall be collected. Two samples shall be prepared for analysis from each sample. Each sample shall be analyzed in duplicate.

9.3.2 The second set of six latex samples shall be analyzed in duplicate before spiking each sample with approximately 1000 ppm styrene. The spiked samples shall be analyzed in duplicate.

9.3.3 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equations:

where:

$R=\Sigma(R_n)/6$

where:

$R_n = (c_{ns} - c_v)/S_n$

n = sample number

c_{ns} = concentration of compound measured in spiked sample number n.

c_{nu} = concentration of compound measured in unspiked sample number n.

S_n = theoretical concentration of compound spiked into sample n.

9.3.4 A value of R between 0.70 and 1.30 is acceptable.

9.3.5 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration and Instrument Settings

10.1 Injection port temperature, 250 °C.

10.2 Oven temperature, 110 °C, isothermal.

10.3 Carrier gas flow, 25 cc/min.

10.4 Detector temperature, 250 °C.

10.5 Range, 1X.

11.0 Procedure

11.1 Turn on recorder and adjust baseline to zero.

11.2 Prepare sample.

11.2.1 For latex samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask. Pipet 10 ml sample into the flask using the Oxford pipettor, dilute to the 100-ml mark with water, and shake well.

11.2.2 For water samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask and fill to the mark with sample. Shake well.

11.3 Flush syringe with sample.

11.4 Carefully inject 2 µl of sample into the gas chromatograph column injection port and press the start button.

11.5 When the run is complete the computer will print a report of the analysis.

12.0 Data Analysis and Calculation

12.1 For samples that are prepared as in section 11.2.1 of this method:

ppm styrene = A × D

Where:

A = "ppm" readout from computer

D = dilution factor (10 for latex samples)

12.2 For samples that are prepared as in section 11.2.2 of this method, ppm styrene is read directly from the computer.

13.0 Method Performance

13.1 This test has a standard deviation (1) of 3.3 ppm at 100 ppm styrene. The average Spike Recovery from six samples at 1000 ppm Styrene was 96.7 percent. The test method was validated using 926 ppm styrene standard. Six analysis of the same standard provided average 97.7 percent recovery. Note: These are example recoveries and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References and Publications

16.1 40 CFR 63 Appendix A—Method 301 Test Methods Field Validation of Pollutant Measurement

16.2 DSM Copolymer Test Method T-3060, dated October 19, 1995, entitled: *Determination of Residual Styrene in Latex*, Leonard, C.D., Vora, N.M.*et al*

METHOD 312B—DETERMINATION OF RESIDUAL STYRENE IN STYRENE-BUTADIENE (SBR) RUBBER LATEX BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

1.1 This method is applicable to SBR latex solutions.

1.2 This method quantitatively determines residual styrene concentrations in SBR latex solutions at levels from 80 to 1200 ppm.

2.0 Principle of Method

2.1 A weighed sample of a latex solution is coagulated with an ethyl alcohol (EtOH) solution containing a specific amount of alpha-methyl styrene (AMS) as the internal standard. The extract of this coagulation is then injected into a gas chromatograph and separated into individual components. Quantification is achieved by the method of internal standardization.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences [Reserved]

5.0 Safetu

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies

6.1 Analytical balance, 160 g capacity, and 0.1 mg resolution

6.2 Bottles, 2-oz capacity, with poly-cap screw lids

6.3 Mechanical shaker

6.4 Syringe, 10-ul capacity

6.5 Gas chromatograph, Hewlett Packard model 5890A, or equivalent, configured with FID with a megabore jet, splitless injector packed with silanized glass wool.

6.5.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

Injection technique = Splitless
Injector temperature = 225 deg C
Oven temperature = 70 deg C (isothermal)
Detector: temperature = 300 deg C
range = 5
attenuation = 0
Carrier gas: helium = 47 ml/min
Detector gases: hydrogen = 30 ml/min
air = 270 ml/min
make-up = 0 ml/min
Analysis time: = 3.2 min at the specified carrier gas flow rate and column temperature.

6.6 Gas chromatographic column, DB–1, 30 M X 0.53 ID, or equivalent, with a 1.5 micron film thickness.

6.7 Data collection system, Perkin-Elmer/Nelson Series Turbochrom 4 Series 900 Interface, or equivalent.

6.8 Pipet, automatic dispensing, 50-ml capacity, and 2-liter reservoir.

6.9 Flasks, volumetric, class A, 100-ml and 1000-ml capacity.

6.10 Pipet, volumetric delivery, 10-ml capacity, class A.

7.0 Chemicals and Reagents

CHEMICALS:

7.1 Styrene, C8H8, 99 + %, CAS 100–42–5

7.2 Alpha methyl styrene, C9H10, 99%, CAS 98–83–9

7.3 Ethyl alcohol, C2H5OH, denatured formula 2B, CAS 64–17–5

REAGENTS:

7.4 Internal Standard Stock Solution: 5.0 mg/ml AMS in ethyl alcohol.

7.4.1 Into a 100-ml volumetric flask, weigh 0.50 g of AMS to the nearest 0.1 mg.

7.4.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml AMS in ethyl alcohol and will be labeled the AMS STOCK SOLUTION.

7.5 Internal Standard Working Solution: 2500 ug/50 ml of AMS in ethyl alcohol.

7.5.1 Using a 10 ml volumetric pipet, quantitatively transfer 10.0 ml of the AMS STOCK SOLUTION into a 1000-ml volumetric flask.

7.5.2 Dilute to the mark with ethyl alcohol. This solution will contain 2500 ug/50ml of AMS in ethyl alcohol and will be labeled the AMS WORKING SOLUTION.

7.5.3 Transfer the AMS WORKING SOLUTION to the automatic dispensing pipet reservoir.

7.6 Styrene Stock Solution: 5.0 mg/ml styrene in ethyl alcohol.

7.6.1 Into a 100-ml volumetric flask, weigh 0.50 g of styrene to the nearest 0.1 mg.

7.6.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml styrene in ethyl alcohol and will be labeled the STYRENE STOCK SOLUTION.

7.7 Styrene Working Solution: 5000 ug/10 ml of styrene in ethyl alcohol.

7.7.1 Using a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE STOCK SOLUTION into a 100-ml volumetric flask.

7.7.2 Dilute to the mark with ethyl alcohol. This solution will contain 5000 ug/10 ml of styrene in ethyl alcohol and will be labeled the STYRENE WORKING SOLUTION.

8.0 Sample Collection, Preservation and Storage

8.1 Label a 2-oz sample poly-cap lid with the identity, date and time of the sample to be obtained.

8.2 At the sample location, open sample valve for at least 15 seconds to ensure that the sampling pipe has been properly flushed with fresh sample.

8.3 Fill the sample jar to the top (no headspace) with sample, then cap it tightly.

8.4 Deliver sample to the Laboratory for testing within one hour of sampling.

8.5 Laboratory testing will be done within two hours of the sampling time.

8.6 No special storage conditions are required unless the storage time exceeds 2 hours in which case refrigeration of the sample is recommended.

9.0 Quality Control

9.1 For each sample type, 12 samples of SBR latex shall be obtained from the process for the recovery study. Half the vials and caps shall be tared, labeled "spiked", and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared, but are also numbered 1 through 6.

9.2 The six vials labeled "spiked" shall be spiked with an amount of styrene to approximate 50% of the solution's expected residual styrene level.

9.3 The spiked samples shall be shaken for several hours and allowed to cool to room temperature before analysis.

9.4 The six samples of unspiked solution shall be coagulated and a mean styrene value shall be determined, along with the standard deviation, and the percent relative standard deviation.

9.5 The six samples of the spiked solution shall be coagulated and the results of the analyses shall be determined using the following equations:

$M_r = M_s - M_u$

$R = M_r/S$

where:

M_u = Mean value of styrene in the unspiked sample

M_s = Measured amount of styrene in the spiked sample

M_r = Measured amount of the spiked compound

S = Amount of styrene added to the spiked sample

R = Fraction of spiked styrene recovered

9.6 A value of R between 0.70 and 1.30 is acceptable.

9.7 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

10.1 Using a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE WORKING SOLUTION (section 7.7.2 of this method) into a 2-oz bottle.

10.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer

50.0 ml of the internal standard solution into the 2-oz bottle.

10.3 Cap the 2-oz bottle and swirl. This is the calibration standard, which contains 5000 µg of styrene and 2500 µg of AMS.

10.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 µl of the calibration standard.

10.5 Obtain the peak areas and calculate the relative response factor as described in the calculations section (section 12.1 of this method).

11.0 Procedure

11.1 Into a tared 2-oz bottle, weigh 10.0 g of latex to the nearest 0.1 g.

11.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer 50.0 ml of the internal standard solution into the 2-oz bottle.

11.3 Cap the bottle. Using a mechanical shaker, shake the bottle for at least one minute or until coagulation of the latex is complete as indicated by a clear solvent.

11.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 ul of the liquor.

11.5 Obtain the peak areas and calculate the concentration of styrene in the latex as described in the calculations section (Section 12.2 of this method).

12.0 Calculations

12.1 Calibration:

$RF = (W_x \times A_{is}) / (W_{is} \times A_x)$

where:

RF = the relative response factor for styrene

W_x = the weight (ug) of styrene

A_{is} = the area of AMS

W_{is} = the weight (ug) of AMS

A_x = the area of styrene

12.2 Procedure:

$ppm_{styrene} = (A_x\ RF \times W_{is}) / (A_{is} \times W_s)$

where:

$ppm_{styrene}$ = parts per million of styrene in the latex

A_x = the area of styrene

RF = the response factor for styrene

W_{is} = the weight (ug) of AMS

A_{is} = the area of AMS

W_s = the weight (g) of the latex sample

12.3 Correct for recovery (R) as determined by section 9.0 of this method.

13.0 Precision

13.1 Precision for the method was determined at the 80, 144, 590, and 1160 ppm levels. The standard deviations were 0.8, 1.5, 5 and 9 ppm respectively. The percent relative standard deviations (%RSD) were 1% or less at all levels. Five degrees of freedom were used for all precision data except at the 80 ppm level, where nine degrees of freedom were used. Note: These are example results and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 Discard liquid chemical waste into the chemical waste drum.

15.2 Discard latex sample waste into the latex waste drum.

15.3 Discard polymer waste into the polymer waste container.

16.0 References

16.1 This method is based on Goodyear Chemical Division Test Method E-889.

METHOD 312C—DETERMINATION OF RESIDUAL STYRENE IN SBR LATEX PRODUCED BY EMULSION POLYMERIZATION

1.0 Scope

1.1 This method is applicable for determining the amount of residual styrene in SBR latex as produced in the emulsion polymerization process.

2.0 Principle of Method

2.1 A weighed sample of latex is coagulated in 2-propanol which contains alpha-methyl styrene as an Internal Standard. The extract from the coagulation will contain the alpha-methyl styrene as the Internal Standard and the residual styrene from the latex. The extract is analyzed by a Gas Chromatograph. Percent styrene is calculated by relating the area of the styrene peak to the area of the Internal Standard peak of known concentration.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences [Reserved]

5.0 Safety

5.1 When using solvents, avoid contact with skin and eyes. Wear hand and eye protection. Wash thoroughly after use.

5.2 Avoid overexposure to solvent vapors. Handle only in well ventilated areas.

6.0 Equipment and Supplies

6.1 *Gas Chromatograph*—Hewlett Packard 5890, Series II with flame ionization detector, or equivalent.

Column—HP 19095F-123, 30m × 0.53mm, or equivalent. Substrate HP FFAP (cross-linked) film thickness 1 micrometer. Glass

injector port liners with silanized glass wool plug.

Integrator—HP 3396, Series II, or equivalent.

6.2 Wrist action shaker

6.3 Automatic dispenser

6.4 Automatic pipet, calibrated to deliver 5.0 ±0.01 grams of latex

6.5 Four-ounce wide-mouth bottles with foil lined lids

6.6 Crimp cap vials, 2ml, teflon lined septa

6.7 Disposable pipets

6.8 Qualitative filter paper

6.9 Cap crimper

6.10 Analytical balance

6.11 10ml pipette

6.12 Two-inch funnel

7.0 Reagents and Standards

7.1 2-Propanol (HP2C grade)

7.2 Alpha methyl styrene (99 + % purity)

7.3 Styrene (99 + % purity)

7.4 Zero air

7.5 Hydrogen (chromatographic grade)

7.6 Helium

7.7 Internal Standard preparation

7.7.1 Weigh 5.000–5.005 grams of alpha-methyl styrene into a 100ml volumetric flask and bring to mark with 2-propanol to make Stock "A" Solution.

NOTE: Shelf life—6 months.

7.7.2 Pipette 10ml of Stock "A" Solution into a 100ml volumetric flask and bring to mark with 2-propanol to prepare Stock "B" Solution.

7.7.3 Pipette 10ml of the Stock "B" solution to a 1000ml volumetric flask and bring to the mark with 2-propanol. This will be the Internal Standard Solution (0.00005 grams/ml).

7.8 Certification of Internal Standard—Each batch of Stock "B" Solution will be certified to confirm concentration.

7.8.1 Prepare a Standard Styrene Control Solution in 2-propanol by the following method:

7.8.1.1 Weigh 5.000 ±.005g of styrene to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "A" Solution.

7.8.1.2 Pipette 10ml of Styrene Stock "A" Solution to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "B" Solution.

7.8.1.3 Pipette 10ml of Styrene Stock "B" soluion to a 250ml volumtric flask and fill to mark wtih 2-propanol to make the Certification Solution.

7.8.2 Certify Alpha-Methyl Styrene Stock "B" Solution.

7.8.2.1 Pipette 5ml of the Certification Solution and 25ml of the Alpha Methyl Styrene Internal Standard Solution to a 4-oz. bottle, cap and shake well.

7.8.2.2 Analyze the resulting mixture by GC using the residual styrene method. (11.4–11.6 of this method)

7.8.2.3 Calculate the weight of alpha methyl styrene present in the 25ml aliquat of the new Alpha Methyl Styrene Standard by the following equation:

$W_x = F_x \, x W_{is}(A_x/A_{is})$

Where

A_x = Peak area of alpha methyl styrene

A_{is} = Peak area of styrene

W_x = Weight of alpha methyl styrene

W_{is} = Weight of styrene (.00100)

F_x = Analyzed response factor = 1

The Alpha Methyl Styrene Stock Solution used to prepare the Internal Standard Solution may be considered certified if the weight of alpha methyl styrene analyzed by this method is within the range of .00121g to .00129g.

8.0 Sampling

8.1 Collect a latex sample in a capped container. Cap the bottle and identify the sample as to location and time.

8.2 Deliver sample to Laboratory for testing within one hour.

8.3 Laboratory will test within two hours.

8.4 No special storage conditions are required.

9.0 Quality Control

9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks, and spiked samples to demonstrate continued performance.

9.1.1 When the method is first set up, a calibration is run and the recovery efficiency for each type of sample must be determined.

9.1.2 If new types of samples are being analyzed, then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the composition of the matrix.

9.2 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.2.1 In determining the recovery efficiency, the quadruplet sampling system shall be used. Six sets of samples (for a total of 24) shall be taken. In each quadruplet set, half of the samples (two out of the four) shall be spiked with styrene.

9.2.2 Prepare the samples as described in section 8 of this method. To the vials labeled "spiked", add a known amount of styrene that is expected to be present in the latex.

9.2.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of styrene reported for each pair of spiked and unspiked samples with the same vial number.

9.2.4 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equation:

$R = \Sigma(R_n)/12$

Where: n = sample number

$R_n = (M_s - M_u)/S$

M_s = total mass of compound (styrene) measured in spiked sample (μg)

M_u = total mass of compound (styrene) measured in unspiked sample (μg)

S = theoretical mass of compound (styrene) spiked into sample (μg)

R = fraction of spiked compound (styrene) recovered

9.2.5 A different R value should be obtained for each sample type. A value of R between 0.70 and 1.30 is acceptable.

9.2.6 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

A styrene control sample will be tested weekly to confirm the FID response and calibration.

10.1 Using the Styrene Certification Solution prepared in 7.8.1, perform test analysis as described in 7.8.2 using the equation in 7.8.2.3 to calculate results.

10.2 Calculate the weight of styrene in the styrene control sample using the following equation:

$W_{sty} = (F_x \times A_{sty} \times W_{is})A_{is}$

The instrument can be considered calibrated if the weight of the styrene analyzed is within range of 0.00097–0.00103gms.

11.0 Procedure

11.1 Using an auto pipet, add 25ml of Internal Standard Solution to a 4 oz. wide-mouth bottle.

11.2 Using a calibrated auto pipet, add 5.0 ±0.01g latex to the bottle containing the 25ml of Internal Standard Solution.

11.3 Cap the bottle and place on the wrist action shaker. Shake the sample for a minimum of five minutes using the timer on the shaker. Remove from shaker.

11.4 Using a disposable pipet, fill the 2ml sample vial with the clear alcohol extract. (If the extract is not clear, it should be filtered using a funnel and filter paper.) Cap and seal the vial.

11.5 Place the sample in the autosampler tray and start the GC and Integrator. The sample will be injected into the GC by the auto-injector, and the Integrator will print the results.

11.6 *Gas Chromatograph Conditions*

Oven Temp—70 °C
Injector Temp—225 °C
Detector Temp—275 °C
Helium Pressure—500 KPA
Column Head Pressure—70 KPA
Makeup Gas—30 ml/min.
Column—HP 19095F—123, 30m × 0.53mm Substrate: HP—FFAP (cross-linked) 1 micrometer film thickness

12.0 Calculations

12.1 The integrator is programmed to do the following calculation at the end of the analysis:

$\%ResidualStyrene = (A_x \times W_{is})/(A_{is} \times W_x) \times F_x \times 100$

Where:

A_x = Peak area of styrene

A_{is} = Peak area of internal standard

W_x = Weight of sample = 5g

W_{is} = Weight of internal std. = 0.00125g

F_x = Analyzed response factor = 1.0

12.2 The response factor is determined by analyzing a solution of 0.02g of styrene and 0.02g of alpha methyl styrene in 100ml of 2-propanol. Calculate the factor by the following equation:

$F_x = (W_x \times A_{is})/(W_{is} \times A_x)$

Where:

W_x = Weight of styrene

A_x = Peak area of styrene

W_{is} = Weight of alpha methyl styrene

A_{is} = Peak area of alpha methyl styrene

13.0 Method Performance

13.1 Performance must be determined for each sample type by following the procedures in section 9 of this method.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References [Reserved]

METHOD 313A—DETERMINATION OF RESIDUAL HYDROCARBONS IN RUBBER CRUMB

1.0 Scope and Application

1.1 This method determines residual toluene and styrene in stripper crumb of the of the following types of rubber: polybutadiene (PBR) and styrene/butadiene rubber (SBR), both derived from solution polymerization processes that utilize toluene as the polymerization solvent.

1.2 The method is applicable to a wide range of concentrations of toluene and styrene provided that calibration standards cover the desired range. It is applicable at least over the range of 0.01 to 10.0 % residual toluene and from 0.1 to 3.0 % residual styrene. It is probably applicable over a wider range, but this must be verified prior to use.

1.3 The method may also be applicable to other process samples as long as they are of a similar composition to stripper crumb. See section 3.1 of this method for a description of stripper crumb.

2.0 Summary of Method

2.1 The wet crumb is placed in a sealed vial and run on a headspace sampler which heats the vial to a specified temperature for a specific time and then injects a known volume of vapor into a capillary GC. The concentration of each component in the vapor is proportional to the level of that component in the crumb sample and does not depend on water content of the crumb.

2.2 Identification of each component is performed by comparing the retention times to those of known standards.

2.3 Results are calculated by the external standard method since injections are all performed in an identical manner. The response for each component is compared with that obtained from dosed samples of crumb.

2.4 Measured results of each compound are corrected by dividing each by the average recovery efficiency determined for the same compound in the same sample type.

3.0 Definitions

3.1 Stripper crumb refers to pieces of rubber resulting from the steam stripping of a toluene solution of the same polymer in a water slurry. The primary component of this will be polymer with lesser amounts of entrained water and residual toluene and other hydrocarbons. The amounts of hydrocarbons present must be such that the crumb is a solid material, generally less that 10 % of the dry rubber weight.

4.0 Interferences

4.1 Contamination is not normally a problem since samples are sealed into vials immediately on sampling.

4.2 Cross contamination in the headspace sampler should not be a problem if the correct sampler settings are used. This should be verified by running a blank sample immediately following a normal or high sample. Settings may be modified if necessary if this proves to be a problem, or a blank sample may be inserted between samples.

4.3 Interferences may occur if volatile hydrocarbons are present which have retention times close to that of the components of interest. Since the solvent makeup of the processes involved are normally fairly well defined this should not be a problem. If it is found to be the case, switching to a different chromatographic column will probably resolve the situation.

5.0 Safety

5.1 The chemicals specified in this method should all be handled according to standard laboratory practices as well as any special precautions that may be listed in the MSDS for that compound.

5.2 Sampling of strippers or other process streams may involve high pressures and temperatures or may have the potential for exposure to chemical fumes. Only personnel who have been trained in the specific sampling procedures required for that process should perform this operation. An understanding of the process involved is necessary. Proper personal protective equipment should be worn. Any sampling devices should be inspected prior to use. A detailed sampling procedure which specifies exactly how to obtain the sample must be written and followed.

6.0 Equipment and Supplies

6.1 Hewlett Packard (HP) 7694 Headspace sampler, or equivalent, with the following conditions:

Times (min.): GC cycle time 6.0 , vial equilibration 30.0 , pressurization 0.25 , loop fill 0.25, loop equilibration 0.05 , inject 0.25
Temperatures (deg C): oven 70, loop 80, transfer line 90
Pressurization gas: He @ 16 psi

6.2 HP 5890 Series II capillary gas chromatograph, or equivalent, with the following conditions:

Column: Supelco SPB–1, or equivalent, 15m × .25mm × .25 μ film
Carrier: He @ 6 psi
Run time: 4 minutes
Oven: 70 deg C isothermal
Injector: 200 deg C split ratio 50:1
Detector: FID @ 220 deg C

6.3 HP Chemstation consisting of computer, printer and Chemstation software, or an equivalent chromatographic data system.

6.4 20 ml headspace vials with caps and septa.

6.5 Headspace vial crimper.

6.6 Microliter pipetting syringes.

6.7 Drying oven at 100 deg C vented into cold trap or other means of trapping hydrocarbons released.

6.8 Laboratory shaker or tumbler suitable for the headspace vials.

6.9 Personal protective equipment required for sampling the process such as rubber gloves and face and eye protection.

7.0 Reagents and Standards

7.1 Toluene, 99.9 + % purity, HPLC grade.

7.2 Styrene, 99.9 + % purity, HPLC grade.

7.3 Dry rubber of same type as the stripper crumb samples.

8.0 Sample Collection, Preservation and Storage

8.1 Collect a sample of crumb in a manner appropriate for the process equipment being sampled.

8.1.1 If conditions permit, this may be done by passing a stream of the crumb slurry through a strainer, thus separating the crumb from the water. Allow the water to drain freely, do not attempt to squeeze any water from the crumb. Results will not depend on the exact water content of the samples. Immediately place several pieces of crumb directly into a headspace vial. This should be done with rubber gloves to protect the hands from both the heat and from contact with residual hydrocarbons. The vial should be between ¼ and ⅓ full. Results do not depend on sample size as long as there is sufficient sample to reach an equilibrium vapor pressure in the headspace of the vial. Cap and seal the vial. Prepare each sample at least in duplicate. This is to minimize the effect of the variation that naturally occurs in the composition of non homogeneous crumb. The free water is not analyzed by this method and should be disposed of appropriately along with any unused rubber crumb.

8.1.2 Alternatively the process can be sampled in a specially constructed sealed bomb which can then be transported to the laboratory. The bomb is then cooled to ambient temperature by applying a stream of running water. The bomb can then be opened and the crumb separated from the water and the vials filled as described in section 8.1.1 of this method. The bomb may be stored up to 8 hours prior to transferring the crumb into vials.

8.2 The sealed headspace vials may be run immediately or may be stored up to 72 hours prior to running. It is possible that even longer storage times may be acceptable, but this must be verified for the particular type of sample being analyzed (see section 9.2.3 of this method). The main concern here is that some types of rubber eventually may flow, thus compacting the crumb so that the surface area is reduced. This may have some effect on the headspace equilibration.

9.0 Quality Control

9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks and spiked samples to demonstrate continued performance.

9.1.1 When the method is first set up a calibration is run (described in section 10 of this method) and an initial demonstration of method capability is performed (described in section 9.2 of this method). Also recovery efficiency for each type of sample must be determined (see section 9.4 of this method).

9.1.2 It is permissible to modify this method in order to improve separations or make other improvements, provided that all performance specifications are met. Each time a modification to the method is made it is necessary to repeat the calibration (section 10 of this method), the demonstration of method performance (section 9.2 of this method) and the recovery efficiency for each type of sample (section 9.4 of this method).

9.1.3 Ongoing performance should be monitored by running a spiked rubber standard. If this test fails to demonstrate that the analysis is in control, then corrective action must be taken. This method is described in section 9.3 of this method.

9.1.4 If new types of samples are being analyzed then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the composition of the matrix.

9.2 Initial demonstration of method capability to establish the accuracy and precision of the method. This is to be run following the calibration described in section 10 of this method.

9.2.1 Prepare a series of identical spiked rubber standards as described in section 9.3 of this method. A sufficient number to determine statistical information on the test should be run. Ten may be a suitable number, depending on the quality control methodology used at the laboratory running the tests. These are run in the same manner as unknown samples (see section 11 of this method).

9.2.2 Determine mean and standard deviation for the results. Use these to determine the capability of the method and to calculate suitable control limits for the ongoing performance check which will utilize the same standards.

9.2.3 Prepare several additional spiked rubber standards and run 2 each day to determine the suitability of storage of the samples for 24, 48 and 72 hours or longer if longer storage times are desired.

9.3 A spiked rubber standard should be run on a regular basis to verify system performance. This would probably be done daily if samples are run daily. This is prepared in the same manner as the calibration standards (section 10.1 of this method), except that only one concentration of toluene and styrene is prepared. Choose concentrations of toluene and styrene that fall in the middle of the range expected in the stripper crumb and then do not change these unless there is a major change in the composition of the unknowns. If it becomes necessary to change the composition of this standard the initial performance demonstration must be repeated with the new standard (section 9.2 of this method).

9.3.1 Each day prepare one spiked rubber standard to be run the following day. The dry rubber may be prepared in bulk and stored for any length of time consistent with the shelf life of the product. The addition of water and hydrocarbons must be performed daily and all the steps described under section 10.1 of this method must be followed.

9.3.2 Run the spiked rubber standard prepared the previous day. Record the results and plot on an appropriate control chart or other means of determining statistical control.

9.3.3 If the results for the standard indicate that the test is out of control then corrective action must be taken. This may include a check on procedures, instrument settings, maintenance or recalibration. Samples may be stored (see section 8.2 of this method) until compliance is demonstrated.

9.4 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.4.1 For each sample type collect 12 samples from the process (section 8.1 of this method). This should be done when the process is operating in a normal manner and residual hydrocarbon levels are in the normal range. Half the vials and caps should be tared, labeled "spiked" and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared but are also numbered 1 through 6. Immediately on sampling, the vials should be capped to prevent loss of volatiles. Allow all the samples to cool completely to ambient temperature. Reweigh each of the vials labeled "spiked" to determine the weight of wet crumb inside.

9.4.2 The dry weight of rubber present in the wet crumb is estimated by multiplying the weight of wet crumb by the fraction of nonvolatiles typical for the sample. If this is not known, an additional quantity of crumb may be sampled, weighed, dried in an oven and reweighed to determine the fraction of volatiles and nonvolatiles prior to starting this procedure.

9.4.3 To the vials labeled "spiked" add an amount of a mixture of toluene and styrene that is between 40 and 60 % of the amount expected in the crumb. This is done by removing the cap, adding the mixture by syringe, touching the tip of the needle to the sample in order to remove the drop and then immediately recapping the vials. The mixture is not added through the septum, because a punctured septum may leak and vent vapors as the vial is heated. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. The exact dry weight of rubber present and the concentration of residual toluene and styrene are not known at this time so an exact calculation of the concentration of hydrocarbons is not possible until the test is completed.

9.4.4 Place all the vials onto a shaker or tumbler for 24 ±2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

9.4.5 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials. Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

9.4.6 Run the spiked and unspiked samples in the normal manner. Record the concentrations of toluene and styrene reported for each pair of spiked and unspiked samples with the same vial number.

9.4.7 Open each of the vials labeled "spiked", remove all the rubber crumb and place it into a tarred drying pan. Place in a 100 deg C oven for two hours, cool and reweigh. Subtract the weight of the tare to give the dry weight of rubber in each spiked vial. Calculate the concentration of toluene and styrene spiked into each vial as percent of dry rubber weight. This will be slightly different for each vial since the weights of dry rubber will be different.

9.4.8 For each hydrocarbon calculate the average recovery efficiency (R) using the following equations:

$R = R\_\Sigma(P_n)/6$ (average of the 6 individual R_n values)

Where:

$R_n = (C_{ns} - C_{nu}) / S_n$

Where:

n = vial number

Cns = concentration of compound measured in spiked sample number n.

Cnu = concentration of compound measured in unspiked sample number n.

Sn = theoretical concentration of compound spiked into sample n calculated in step 9.4.7

9.4.9 A different R value should be obtained for each compound (styrene and toluene) and for each sample type.

9.4.10 A value of R between 0.70 and 1.30 is acceptable.

9.4.11 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type (see section 12.2 of this method.)

10.0 Calibration

10.1 Calibration standards are prepared by dosing known amounts of the hydrocarbons of interest into vials containing known amounts of rubber and water.

10.1.1 Cut a sufficient quantity of dry rubber of the same type as will be analyzed into pieces about the same size as that of the crumb. Place these in a single layer on a piece of aluminum foil or other suitable surface and place into a forced air oven at 100 °C for four hours. This is to remove any residual hydrocarbons that may be present. This step may be performed in advance.

10.1.2 Into each of a series of vials add 3.0 g of the dry rubber.

10.1.3 Into each vial add 1.0 ml distilled water or an amount that is close to the

amount that will be present in the unknowns. The exact amount of water present does not have much effect on the analysis, but it is necessary to have a saturated environment. The water will also aid in the uniform distribution of the spiked hydrocarbons over the surface of the rubber after the vials are placed on the shaker (in step 10.1.5 of this method).

10.1.4 Into each vial add varying amounts of toluene and styrene by microliter syringe and cap the vials immediately to prevent loss. The tip of the needle should be carefully touched to the rubber in order to transfer the last drop to the rubber. Toluene and styrene may first be mixed together in suitable proportions and added together if desired. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. Concentrations of added hydrocarbons are calculated as percent of the dry rubber weight. At least 5 standards should be prepared with the amounts of hydrocarbons added being calculated to cover the entire range possible in the unknowns. Retain two samples with no added hydrocarbons as blanks.

10.1.5 Place all the vials onto a shaker or tumbler for 24 ±2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

10.1.6 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials. Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

10.2 Run the standards and blanks in the same manner as described for unknowns (section 11 of this method), starting with a blank, then in order of increasing hydrocarbon content and ending with the other blank.

10.3 Verify that the blanks are sufficiently free from toluene and styrene or any interfering hydrocarbons.

10.3.1 It is possible that trace levels may be present even in dry product. If levels are high enough that they will interfere with the calibration then the drying procedure in section 10.1.1 of this method should be reviewed and modified as needed to ensure that suitable standards can be prepared.

10.3.2 It is possible that the final blank is contaminated by the previous standard. If this is the case review and modify the sampler parameters as needed to eliminate this problem. If necessary it is possible to run blank samples between regular samples in order to reduce this problem, though it should not be necessary if the sampler is properly set up.

10.4 Enter the amounts of toluene and styrene added to each of the samples (as calculated in section 10.1.4 of this method) into the calibration table and perform a calibration utilizing the external standard method of analysis.

10.5 At low concentrations the calibration should be close to linear. If a wide range of levels are to be determined it may be desirable to apply a nonlinear calibration to get the best fit.

11.0 Procedure

11.1 Place the vials in the tray of the headspace sampler. Enter the starting and ending positions through the console of the sampler. For unknown samples each is run in duplicate to minimize the effect of variations in crumb composition. If excessive variation is noted it may be desirable to run more than two of each sample.

11.2 Make sure the correct method is loaded on the Chemstation. Turn on the gas flows and light the FID flame.

11.3 Start the sequence on the Chemstation. Press the START button on the headspace unit. The samples will be automatically injected after equilibrating for 30 minutes in the oven. As each sample is completed the Chemstation will calculate and print out the results as percent toluene and styrene in the crumb based on the dry weight of rubber.

12.0 Data Analysis and Calculations

12.1 For each set of duplicate samples calculate the average of the measured concentration of toluene and styrene. If more than two replicates of each sample are run calculate the average over all replicates.

12.2 For each sample correct the measured amounts of toluene and styrene using the following equation:

Corrected Result = C_m/R

Where:

C_m = Average measured concentration for that compound.

R = Recovery efficiency for that compound in the same sample type (see section 9.4 of this method)

12.3 Report the recovery efficiency (R) and the corrected results of toluene and styrene for each sample.

13.0 Method Performance

13.1 This method can be very sensitive and reproducible. The actual performance depends largely on the exact nature of the samples being analyzed. Actual performance must be determined by each laboratory for each sample type.

13.2 The main source of variation is the actual variation in the composition of non homogeneous crumb in a stripping system and the small sample sizes employed here. It

therefore is the responsibility of each laboratory to determine the optimum number of replicates of each sample required to obtain accurate results.

14.0 Pollution Prevention

14.1 Samples should be kept sealed when possible in order to prevent evaporation of hydrocarbons.

14.2 When drying of samples is required it should be done in an oven which vents into a suitable device that can trap the hydrocarbons released.

14.3 Dispose of samples as described in section 15.

15.0 Waste Management

15.1 Excess stripper crumb and water as well as the contents of the used sample vials should be properly disposed of in accordance with local and federal regulations.

15.2 Preferably this will be accomplished by having a system of returning unused and spent samples to the process.

16.0 References

16.1 "HP 7694 Headspace Sampler—Operating and Service Manual", Hewlett-Packard Company, publication number G1290-90310, June 1993.

METHOD 313B—THE DETERMINATION OF RESIDUAL HYDROCARBON IN SOLUTION POLYMERS BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

1.1 This method is applicable to solution polymerized polybutadiene (PBD).

1.2 This method quantitatively determines n-hexane in wet crumb polymer at levels from 0.08 to 0.15% by weight.

1.3 This method may be extended to the determination of other hydrocarbons in solution produced polymers with proper experimentation and documentation.

2.0 Principle of Method

2.1 A weighed sample of polymer is dissolved in chloroform and the cement is coagulated with an isopropyl alcohol solution containing a specific amount of alpha-methyl styrene (AMS) as the internal standard. The extract of this coagulation is then injected into a gas chromatograph and separated into individual components. Quantification is achieved by the method of internal standardization.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies

6.1 Analytical balance, 160 g capacity, 0.1 mg resolution

6.2 Bottles, 2-oz capacity with poly-cap screw lids

6.3 Mechanical shaker

6.4 Syringe, 10-ul capacity

6.5 Syringe, 2.5-ml capacity, with 22 gauge 1.25 inch needle, PP/PE material, disposable

6.6 Gas chromatograph, Hewlett-Packard model 5890, or equivalent, configured with FID, split injector packed with silanized glass wool.

6.6.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

6.6.2 Injector parameters:

Injection technique = Split
Injector split flow = 86 ml/min
Injector temperature = 225 deg C

6.6.3 Oven temperature program:

Initial temperature = 40 deg C
Initial time = 6 min
Program rate = 10 deg C/min
Upper limit temperature = 175 deg C
Upper limit interval = 10 min

6.6.4 Detector parameters:

Detector temperature = 300 deg C
Hydrogen flow = 30 ml/min
Air flow = 350 ml/min
Nitrogen make up = 26 ml/min

6.7 Gas chromatographic columns: SE-54 (5%-phenyl) (1%-vinyl)-methylpolysiloxane, 15 M × 0.53 mm ID with a 1.2 micron film thickness, and a Carbowax 20M (polyethylene glycol), 15 M × 0.53 mm ID with a 1.2 micron film thickness.

6.7.1 Column assembly: using a 0.53 mm ID butt connector union, join the 15 M × 0.53 mm SE-54 column to the 15 M × 0.53 mm Carbowax 20M. The SE-54 column will be inserted into the injector and the Carbowax 20M inserted into the detector after they have been joined.

6.7.2 Column parameters:

Helium flow = 2.8 ml/min
Helium headpressure = 2 psig

6.8 Centrifuge

6.9 Data collection system, Hewlett-Packard Model 3396, or equivalent

6.10 Pipet, 25-ml capacity, automatic dispensing, and 2 liter reservoir

6.11 Pipet, 2-ml capacity, volumetric delivery, class A

6.12 Flasks, 100 and 1000-ml capacity, volumetric, class A

6.13 Vial, serum, 50-ml capacity, red rubber septa and crimp ring seals

6.14 Sample collection basket fabricated out of wire mesh to allow for drainage

7.0 Chemicals and Reagents

CHEMICALS:

7.1 alpha-Methyl Styrene, C9H10, 99 + % purity, CAS 98-83-9

7.2 n-Hexane, C6H14, 99 + % purity, CAS 110-54-3

7.3 Isopropyl alcohol, C3H8O 99.5 + % purity, reagent grade, CAS 67-63-0

7.4 Chloroform, CHCl3, 99% min., CAS 67-66-3

REAGENTS:

7.5 Internal Standard Stock Solution: 10 mg/25 ml AMS in isopropyl alcohol.

7.5.1 Into a 25-ml beaker, weigh 0.4 g of AMS to the nearest 0.1 mg.

7.5.2 Quantitatively transfer this AMS into a 1-L volumetric flask. Dilute to the mark with isopropyl alcohol.

7.5.3 Transfer this solution to the automatic dispensing pipet reservoir. This will be labeled the AMS STOCK SOLUTION.

7.6 n-Hexane Stock Solution: 13mg/2ml hexane in isopropyl alcohol.

7.6.1 Into a 100-ml volumetric flask, weigh 0.65 g of n-hexane to the nearest 0.1 mg.

7.6.2 Dilute to the mark with isopropyl alcohol. This solution will be labeled the n-HEXANE STOCK SOLUTION.

8.0 Sample Collection, Preservation and Storage

8.1 A sampling device similar to Figure 1 is used to collect a non-vented crumb rubber sample at a location that is after the stripping operation but before the sample is exposed to the atmosphere.

8.2 The crumb rubber is allowed to cool before opening the sampling device and removing the sample.

8.3 The sampling device is opened and the crumb rubber sample is collected in the sampling basket.

8.4 One pound of crumb rubber sample is placed into a polyethylene bag. The bag is labeled with the time, date and sample location.

8.5 The sample should be delivered to the laboratory for testing within one hour of sampling.

8.6 Laboratory testing will be done within 3 hours of the sampling time.

8.7 No special storage conditions are required unless the storage time exceeds 3 hours in which case refrigeration of the samples is recommended.

9.0 Quality Control

9.1 For each sample type, 12 samples shall be obtained from the process for the recovery study. Half of the vials and caps shall be tared, labeled "spiked", and numbered 1 through 6. The other vials shall be labeled "unspiked" and need not be tared, but are also numbered 1 through 6.

9.2 Determine the % moisture content of the crumb sample. After determining the % moisture content, the correction factor for calculating the dry crumb weight can be determined by using the equation in section 12.2 of this method.

9.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of the n-hexane content of the mixed hexane reported for each pair of spiked and unspiked samples.

9.4 For the recovery study, each sample of crumb shall be dissolved in chloroform containing a known amount of mixed hexane solvent.

9.5 For each hydrocarbon, calculate the recovery efficiency (R) using the following equations:

$M_r = M_s - M_u$

$R = M_r/S$

Where:

M_u = Measured amount of compound in the unspiked sample

M_s = Measured amount of compound in the spiked sample

M_r = Measured amount of the spiked compound

S = Amount of compound added to the spiked sample

R = Fraction of spiked compound recovered

9.6 Normally a value of R between 0.70 and 1.30 is acceptable.

9.7 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

10.1 Using the AMS STOCK SOLUTION equipped with the automatic dispensing pipet (7.5.3 of this method), transfer 25.0 ml of the internal standard solution into an uncapped 50-ml serum vial.

10.2 Using a 2.0 ml volumetric pipet, quantitatively transfer 2.0 ml of the n-HEXANE STOCK SOLUTION (7.6.2 of this method) into the 50-ml serum vial and cap. This solution will be labeled the CALIBRATION SOLUTION.

10.3 Using the conditions prescribed (6.6 of this method), inject 1 µl of the supernate.

10.4 Obtain the peak areas and calculate the response factor as described in the calculations section (12.1 of this method).

11.0 Procedure

11.1 Determination of Dry Polymer Weight

11.1.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.1.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.1.3 A suitable gravimetric measurement should be made on a sample of this wet crumb to determine the correction factor needed to calculate the dry polymer weight.

11.2 Determination of n-Hexane in Wet Crumb

11.2.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.2.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.2.3 Into a tared 2 oz bottle, weigh 1.5 g of wet polymer to the nearest 0.1 mg.

11.2.4 Add 25 ml of chloroform to the 2 oz bottle and cap.

11.2.5 Using a mechanical shaker, shake the bottle until the polymer dissolves.

11.2.6 Using the autodispensing pipet, add 25.0 ml of the AMS STOCK SOLUTION (7.5.3 of this method) to the dissolved polymer solution and cap.

11.2.7 Using a mechanical shaker, shake the bottle for 10 minutes to coagulate the dissolved polymer.

11.2.8 Centrifuge the sample for 3 minutes at 2000 rpm.

11.2.9 Using the conditions prescribed (6.6 of this method), chromatograph 1 µl of the supernate.

11.2.10 Obtain the peak areas and calculate the concentration of the component of interest as described in the calculations (12.2 of this method).

12.0 Calculations

12.1 Calibration:

$RF_x = (W_x \times A_{is}) / (W_{is} \times A_x)$

Where:

RF_x = the relative response factor for n-hexane

W_x = the weight (g) of n-hexane in the CALIBRATION SOLUTION

A_{is} = the area of AMS

W_{is} = the weight (g) of AMS in the CALIBRATION SOLUTION

A_x = the area of n-hexane

12.2 Procedure:

12.2.1 Correction Factor for calculating dry crumb weight.

F = 1—(% moisture / 100)

Where:

F = Correction factor for calculating dry crumb weight

% moisture determined by appropriate method

12.2.2 Moisture adjustment for chromatographic determination.

$W_s = F \times W_c$

Where:

W_s = the weight (g) of the dry polymer corrected for moisture

F = Correction factor for calculating dry crumb weight

W_c = the weight (g) of the wet crumb in section 9.6

12.2.3 Concentration (ppm) of hexane in the wet crumb.

$ppm_x = (A_x * RF_x * W_{is} * 10000) / (A_{is} * W_s)$

Where:

ppm_x = parts per million of n-hexane in the polymer

A_x = the area of n-hexane

RF_x = the relative response factor for n-hexane

W_{is} = the weight (g) of AMS in the sample solution

A_{is} = the area of AMS

W_s = the weight (g) of the dry polymer corrected for moisture

13.0 Method Performance

13.1 Precision for the method was determined at the 0.08% level.

The standard deviation was 0.01 and the percent relative standard deviation (RSD) was 16.3 % with five degrees of freedom.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 Discard liquid chemical waste into the chemical waste drum.

15.2 Discard polymer waste into the polymer waste container.

16.0 References

16.1 This method is based on Goodyear Chemical Division Test Method E–964.

METHOD 315—DETERMINATION OF PARTICULATE AND METHYLENE CHLORIDE EXTRACTABLE MATTER (MCEM) FROM SELECTED SOURCES AT PRIMARY ALUMINUM PRODUCTION FACILITIES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5 of 40 CFR part 60, appendix A.

1.0 Scope and Application

1.1 Analytes. Particulate matter (PM). No CAS number assigned. Methylene chloride extractable matter (MCEM). No CAS number assigned.

1.2 Applicability. This method is applicable for the simultaneous determination of PM and MCEM when specified in an applicable regulation. This method was developed by consensus with the Aluminum Association and the U.S. Environmental Protection Agency (EPA) and has limited precision estimates for MCEM; it should have similar precision to Method 5 for PM in 40 CFR part 60, appendix A since the procedures are similar for PM.

1.3 Data quality objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter and MCEM are withdrawn isokinetically from the source. PM is collected on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses on the probe and is subsequently removed in an acetone rinse or on the filter at or above the filtration temperature, is determined gravimetrically after removal of uncombined water. MCEM is then determined by adding a methylene chloride rinse of the probe and filter holder, extracting the condensable hydrocarbons collected in the impinger water, adding an acetone rinse followed by a methylene chloride rinse of the sampling train components after the filter and before the silica gel impinger, and determining residue gravimetrically after evaporating the solvents.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the EPA.

6.1 Sample collection. The following items are required for sample collection:

6.1.1 Sampling train. A schematic of the sampling train used in this method is shown in Figure 5–1, Method 5, 40 CFR part 60, appendix A–3. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0 of this method); commercial models of this train are also available. For changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, Method 5, 40 CFR part 60, appendix A–3, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0 of this method). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. The use of grease for sealing sampling train components is not recommended because many greases are soluble in methylene chloride. The sampling train consists of the following components:

6.1.1.1 Probe nozzle. Glass or glass lined with sharp, tapered leading edge. The angle of taper shall be ≤30 °, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in.) inside diameter (ID) in increments of 0.16 cm (1/16 in.). Larger nozzle sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in section 10.0 of this method.

6.1.1.2 Probe liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature at the exit end during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and using the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of

liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1,500 °F) and for quartz glass it is 1,500 °C (2,700 °F).

6.1.1.3 Pitot tube. Type S, as described in section 6.1 of Method 2, 40 CFR part 60, appendix A, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1 of Method 5, 40 CFR part 60, appendix A) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–6b, 40 CFR part 60, appendix A) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2, 40 CFR part 60, appendix A.

6.1.1.4 Differential pressure gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2, 40 CFR part 60, appendix A. One manometer shall be used for velocity head (Dp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter heating system. Any heating system capable of maintaining a temperature around the filter holder of 120 ±14 °C (248 ±25 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3 °C (5.4 °F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD–0581 may be used.

6.1.1.7 Temperature sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas, and the temperature around the filter holder can be regulated and monitored during sampling.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: four glass impingers connected in series with leak-free ground glass fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water (section 8.3.1 of this method), the third shall be empty, and the fourth shall contain a known weight of silica gel or equivalent desiccant. A temperature sensor capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring.

6.1.1.9 Metering system. Vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature to within 3 °C (5.4 °F), dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1 of Method 5, 40 CFR part 60, appendix A. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains using metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg.

NOTE: The barometric reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm (0.1 in) Hg per 30 m (100 ft) elevation increase or plus 2.5 mm (0.1 in) Hg per 30 m (100 ft) elevation decrease.

6.1.3 Gas density determination equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, 40 CFR part 60, appendix A, and gas analyzer, if necessary, as described in Method 3, 40 CFR part 60, appendix A. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4, 40 CFR part 60, appendix A). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be

attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample recovery. The following items are required for sample recovery:

6.2.1 Probe-liner and probe-nozzle brushes. Nylon or Teflon® bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, nylon, Teflon®, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash bottles. Glass wash bottles are recommended. Polyethylene or tetrafluoroethylene (TFE) wash bottles may be used, but they may introduce a positive bias due to contamination from the bottle. It is recommended that acetone not be stored in polyethylene or TFE bottles for longer than a month.

6.2.3 Glass sample storage containers. Chemically resistant, borosilicate glass bottles, for acetone and methylene chloride washes and impinger water, 500 ml or 1,000 ml. Screw-cap liners shall either be rubber-backed Teflon® or shall be constructed so as to be leak-free and resistant to chemical attack by acetone or methylene chloride. (Narrow-mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri dishes. For filter samples, glass, unless otherwise specified by the Administrator.

6.2.5 Graduated cylinder and/or balance. To measure condensed water, acetone wash and methylene chloride wash used during field recovery of the samples, to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any such balance is suitable for use here and in section 6.3.4 of this method.

6.2.6 Plastic storage containers. Air-tight containers to store silica gel.

6.2.7 Funnel and rubber policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample analysis. The following equipment is required for sample analysis:

6.3.1 Glass or Teflon® weighing dishes.

6.3.2 Desiccator. It is recommended that fresh desiccant be used to minimize the chance for positive bias due to absorption of organic material during drying.

6.3.3 Analytical balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature sensor. To measure the temperature of the laboratory environment.

6.3.8 Buchner fritted funnel. 30 ml size, fine (<50 micron)-porosity fritted glass.

6.3.9 Pressure filtration apparatus.

6.3.10 Aluminum dish. Flat bottom, smooth sides, and flanged top, 18 mm deep and with an inside diameter of approximately 60 mm.

7.0 Reagents and Standards

7.1 Sample collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–95A (incorporated by reference in §63.841 of this part). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 of this method may be used to select the appropriate filter.

7.1.2 Silica gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed ice.

7.1.5 Stopcock grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon® sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator. [Caution: Many stopcock greases are methylene chloride-soluble. Use sparingly and carefully remove prior to recovery to prevent contamination of the MCEM analysis.]

7.2 Sample recovery. The following reagents are required for sample recovery:

7.2.1 Acetone. Acetone with blank values <1 ppm, by weight residue, is required. Acetone blanks may be run prior to field use, and only acetone with low blank values may be used. In no case shall a blank value of greater than 1E–06 of the weight of acetone used be subtracted from the sample weight.

NOTE: This is more restrictive than Method 5, 40 CFR part 60, appendix A. At least one vendor (Supelco Incorporated located in Bellefonte, Pennsylvania) lists <1 mg/l as residue for its Environmental Analysis Solvents.

7.2.2 Methylene chloride. Methylene chloride with a blank value <1.5 ppm, by weight, residue. Methylene chloride blanks may be run prior to field use, and only methylene

chloride with low blank values may be used. In no case shall a blank value of greater than 1.6E–06 of the weight of methylene chloride used be subtracted from the sample weight.

NOTE: A least one vendor quotes <1 mg/l for Environmental Analysis Solvents-grade methylene chloride.

7.3 Sample analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.1 of this method.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.3.3 Methylene chloride. Same as in section 7.2.2 of this method.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

8.1 Pretest preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Weigh several 200 g to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel need not be preweighed but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 A batch of glass fiber filters, no more than 50 at a time, should placed in a soxhlet extraction apparatus and extracted using methylene chloride for at least 16 hours. After extraction, check filters visually against light for irregularities, flaws, or pinhole leaks. Label the shipping containers (glass or plastic petri dishes), and keep the filters in these containers at all times except during sampling and weighing.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., <0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for longer than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 104 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1, 40 CFR part 60, appendix A or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2, 40 CFR part 60, appendix A; it is recommended that a leak check of the pitot lines (see section 8.1 of Method 2, 40 CFR part 60, appendix A) be performed. Determine the moisture content using Approximation Method 4 (section 1.2 of Method 4, 40 CFR part 60, appendix A) or its alternatives to make isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in section 8.6 of Method 2, 40 CFR part 60, appendix A; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.2 of Method 2, 40 CFR part 60, appendix A).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that: (1) The sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator); and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to eliminate timekeeping errors.

8.2.6 In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of sampling train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just

prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass liners are used, install the selected nozzle using a Viton A 0-ring when stack temperatures are less than 260 °C (500 °F) and an asbestos string gasket when temperatures are higher. See APTD–0576 for details. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as in Figure 5-1 of Method 5, 40 CFR part 60, appendix A, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-check procedures.

8.4.1 Leak check of metering system shown in Figure 5-1 of Method 5, 40 CFR part 60, appendix A. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2 of Method 5, 40 CFR part 60, appendix A): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for 1 minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest leak check. A pretest leak-check is recommended but not required. If the pretest leak-check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A 0-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum. (See NOTE in section 8.4.2.1 of this method). Then connect the probe to the train and perform the leak check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. *Do not* reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak check as shown below and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak checks during sample run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 of this method, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is

less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method or void the sample run.

NOTE: Immediately after component changes, leak checks are optional; if such leak checks are done, the procedure outlined in section 8.4.2 of this method should be used.

8.4.4 Post-test leak check. A leak check is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2 of this method, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume, as shown in section 12.4 of this method, or void the sampling run.

8.5 Sampling train operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120 14 °C (248 25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5, 40 CFR part 60, appendix A. Be sure to record the initial reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings indicated by Figure 5-2 of Method 5, 40 CFR part 60, appendix A at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap and verify that the filter and probe heating systems are up to temperature and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 # 0.02 and the stack gas equivalent density (dry molecular weight) is 29 ±4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above-stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0 of this method) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (height of impinger stem), close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1, 40 CFR part 60, appendix A or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3 of this method). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used in all trains, in which case the front-half catches from the individual

trains may be combined (as may the impinger catches) and one analysis of the front-half catch and one analysis of the impinger catch may be performed.

8.5.9 At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM reading, and then conduct a post-test leak check, as outlined in section 8.4.4 of this method. Also leak-check the pitot lines as described in section 8.1 of Method 2, 40 CFR part 60, appendix A. The lines must pass this leak check in order to validate the velocity head data.

8.6 Calculation of percent isokinetic. Calculate percent isokinetic (see Calculations, section 12.12 of this method) to determine whether a run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult the Administrator for possible variance on the isokinetic rates.

8.7 Sample recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone and methylene chloride used for cleanup as blanks. Take 200 ml of each solvent directly from the wash bottle being used and place it in glass sample containers labeled "acetone blank" and "methylene chloride blank," respectively.

8.7.6 Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces are wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe, hold a sample container under the lower end of the probe, and catch any acetone and PM that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-described manner at least six times, since metal probes have small crevices in which PM can be entrapped. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 After ensuring that all joints have been wiped clean of silicone grease, clean the

inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone also (if applicable).

8.7.6.2.6 After rinsing the nozzle, probe, and front half of the filter holder with acetone, repeat the entire procedure with methylene chloride and save in a separate No. 2M container.

8.7.6.2.7 After acetone and methylene chloride washings and PM have been collected in the proper sample containers, tighten the lid on the sample containers so that acetone and methylene chloride will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label each container to identify clearly its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal the container. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3 of this method.

8.7.6.4 Impinger water. Treat the impingers as follows:

8.7.6.4.1 Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

8.7.6.4.2 Following the determination of the volume of liquid present, rinse the back half of the train with water, add it to the impinger catch, and store it in a container labeled 3W (water).

8.7.6.4.3 Following the water rinse, rinse the back half of the train with acetone to remove the excess water to enhance subsequent organic recovery with methylene chloride and quantitatively recover to a container labeled 3S (solvent) followed by at least three sequential rinsings with aliquots of methylene chloride. Quantitatively recover to the same container labeled 3S. Record separately the amount of both acetone and methylene chloride used to the nearest 1 ml or 0.5g.

NOTE: Because the subsequent analytical finish is gravimetric, it is okay to recover both solvents to the same container. This would not be recommended if other analytical finishes were required.

8.8 Sample transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous quality control measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6.	Sampling and equipment leak check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume metering system checks. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter orifice check. Using the calibration data obtained during the calibration procedure described in section 10.3 of this method, determine the ΔH_a for the metering system orifice. The ΔH_a is the orifice pressure differential in units of in. H_20 that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH_a is calculated as follows:

$$\Delta H_a = 0..0319\,\Delta H \frac{T_m \Theta^2}{P_{bar} Y^2 V_m^2}$$

Where

0.0319 = (0.0567 in. Hg/ °R)(0.75 cfm)^2;

ΔH = Average pressure differential across the orifice meter, in. H_20;

T_m = Absolute average DGM temperature, °R;

Θ = Total sampling time, min;

P_{bar} = Barometric pressure, in. Hg;

Y = DGM calibration factor, dimensionless;

V_m = Volume of gas sample as measured by DGM, dcf.

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the ΔH_a pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\,T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

Where

Y_c = DGM calibration check value, dimensionless;

10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97\,Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated critical orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a quality control check by following the procedure of section 16.2 of this method.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot tube assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2, 40 CFR part 60, appendix A.

10.3 Metering system.

10.3.1 Calibration prior to use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5-5 of Method 5, 40 CFR part 60, appendix A. The wet test meter should have a capacity of 30 liters/revolution (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading, as expected in field use, to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m^3 (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5-6 of Method 5, 40 CFR part 60, appendix A, and calculate Y (the DGM calibration factor) and ΔH_a (the orifice calibration factor) at each orifice setting, as shown on Figure 5-6 of Method 5, 40 CFR part 60, appendix A. Allowable tolerances for individual Y and ΔH_a values are given in Figure 5-6 of Method 5, 40 CFR part 60, appendix A. Use the average of the Y values in the calculations in section 12 of this method.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak check procedure will not detect leakages within the pump. For these cases the following leak check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and DGM volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

10.3.2 Calibration after use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test) with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as previously detailed.

NOTE: Alternative procedures, e.g., rechecking the orifice meter coefficient, may be used, subject to the approval of the Administrator.

10.3.3 Acceptable variation in calibration. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, either the test series shall be voided or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe heater calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature sensors. Use the procedure in Section 10.3 of Method 2, 40 CFR part 60, appendix A–1 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.6 Barometer. Calibrate against a mercury barometer.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 315–1 of this method.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1.

11.2.1.1 PM analysis. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings (overnight desiccation is a common practice). If a third weighing is required and it agrees within ±0.5 mg, then the results of the second weighing should be used. For quality assurance purposes, record and report each individual weighing; if more than three weighings are required, note this in the results for the subsequent MCEM results.

11.2.1.2 MCEM analysis. Transfer the filter and contents quantitatively into a beaker. Add 100 ml of methylene chloride and cover with aluminum foil. Sonicate for 3 minutes then allow to stand for 20 minutes. Set up the filtration apparatus. Decant the solution into a clean Buchner fritted funnel. Immediately pressure filter the solution through the tube into another clean, dry beaker. Continue decanting and pressure filtration until all the solvent is transferred. Rinse the beaker and filter with 10 to 20 ml methylene chloride, decant into the Buchner fritted funnel and pressure filter. Place the beaker on a low-temperature hot plate (maximum 40 °C) and slowly evaporate almost to dryness. Transfer the remaining last few milliliters of solution quantitatively from the beaker (using at least three aliquots of methylene chloride rinse) to a tared clean dry aluminum dish and evaporate to complete dryness. Remove from heat once solvent is evaporated. Reweigh the dish after a 30-minute equilibrium in the balance room and determine the weight to the nearest 0.1 mg. Conduct a methylene chloride blank run in an identical fashion.

11.2.2 Container No. 2.

11.2.2.1 PM analysis. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to 1 ±0.5 g. Transfer the contents to a tared 250 ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.2.2 MCEM analysis. Add 25 ml methylene chloride to the beaker and cover with aluminum foil. Sonicate for 3 minutes then allow to stand for 20 minutes; combine with contents of Container No. 2M and pressure filter and evaporate as described for Container 1 in section 11.2.1.2 of this method.

Notes for MCEM Analysis

1. Light finger pressure only is necessary on 24/40 adaptor. A Chemplast adapter #15055–240 has been found satisfactory.

2. Avoid aluminum dishes made with fluted sides, as these may promote solvent "creep," resulting in possible sample loss.

3. If multiple samples are being run, rinse the Buchner fritted funnel twice between samples with 5 ml solvent using pressure filtration. After the second rinse, continue the flow of air until the glass frit is completely

dry. Clean the Buchner fritted funnels thoroughly after filtering five or six samples.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Container 3W (impinger water).

11.2.4.1 MCEM analysis. Transfer the solution into a 1,000 ml separatory funnel quantitatively with methylene chloride washes. Add enough solvent to total approximately 50 ml, if necessary. Shake the funnel for 1 minute, allow the phases to separate, and drain the solvent layer into a 250 ml beaker. Repeat the extraction twice. Evaporate with low heat (less than 40 °C) until near dryness. Transfer the remaining few milliliters of solvent quantitatively with small solvent washes into a clean, dry, tared aluminum dish and evaporate to dryness. Remove from heat once solvent is evaporated. Reweigh the dish after a 30-minute equilibration in the balance room and determine the weight to the nearest 0.1 mg.

11.2.5 Container 3S (solvent).

11.2.5.1 MCEM analysis. Transfer the mixed solvent to 250 ml beaker(s). Evaporate and weigh following the procedures detailed for container 3W in section 11.2.4 of this method.

11.2.6 Blank containers. Measure the distilled water, acetone, or methylene chloride in each container either volumetrically or gravimetrically. Transfer the "solvent" to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. (Conduct a solvent blank on the distilled deionized water blank in an identical fashion to that described in section 11.2.4.1 of this method.) Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Containers No. 2, 3W, and 3M as well as the blank containers may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone and methylene chloride are highly flammable and have a low flash point.

12.0 Data Analysis and Calculations

12.1 Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.2 Nomenclature.

A_n = Cross-sectional area of nozzle, m^3 (ft^3).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/g.

C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (I = 1, 2, 3...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

m_a = Mass of residue of acetone after evaporation, mg.

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(°K) (g-mole)] '61' 21.85 [(in. Hg)(ft^3)]/[(°R)(lb-mole)'61'].

T_m = Absolute average dry gas meter (DGM) temperature (see Figure 5–2 of Method 5, 40 CFR part 60, appendix A), °K (°R).

T_s = Absolute average stack gas temperature (see Figure 5–2 of Method 5, 40 CFR part 60, appendix A), °K(°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_t = Volume of methylene chloride blank, ml.

V_{tw} = Volume of methylene chloride used in wash, ml.

V_{lc} = Total volume liquid collected in impingers and silica gel (see Figure 5–3 of Method 5, 40 CFR part 60, appendix A), ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack gas velocity, calculated by Equation 2–9 in Method 2, 40 CFR part 60, appendix A, using data obtained from Method 5, 40 CFR part 60, appendix A, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5–2 of Method 5, 40 CFR part 60, appendix A), mm H_2O (in H_2O).

ρ_a = Density of acetone, 785.1 mg/ml (or see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

ρ_t = Density of methylene chloride, 1316.8 mg/ml (or see label on bottle).

Θ = Total sampling time, min.

Θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

Θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

Θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

12.3 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5–2 of Method 5, 40 CFR part 60, appendix A).

12.4 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in Hg) by using Equation 315–1.

$$V = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} = V = K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m} \qquad \text{Eq. 315-1}$$

Where

K_1 = 0.3858 °K/mm Hg for metric units,

= 17.64 °R/in Hg for English units.

NOTE: Equation 315–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 315–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 315–1 with the expression:

$[V_m-(L_p-L_a)\,\Theta]$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 315–1 by the expression:

$$\left[V_m - (L_1 - L_a)\,\Theta_1 - \sum_{i=2}^{n}(L_i - L_a)\,\Theta_i - (L_p - L_a)\,\Theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.5 Volume of water vapor condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} = K_2 V_{1c} \qquad \text{Eq. 315-2}$$

Where

K_2 = 0.001333 m^3/ml for metric units;

= 0.04706 ft^3/ml for English units.

12.6 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 315-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 315-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated

conditions is given in section 4.0 of Method 4, 40 CFR part 60, appendix A. For the purposes of this method, the average stack gas temperature from Figure 5–2 of Method 5, 40 CFR part 60, appendix A may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.7 Acetone blank concentration.

$$C_a = \frac{M_a}{V_a \rho_a} \qquad \text{Eq. 315-4}$$

12.8 Acetone wash blank.

$W_a = C_a V_{aw} \rho a$ *Eq. 315–5*

12.9 Total particulate weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank associated with these two containers (see Figure 315–1).

NOTE: Refer to section 8.5.8 of this method to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.10 Particulate concentration.

$c_s = K_3\ m_n/V_{m(std)}$ Eq. 315–6

where

K = 0.001 g/mg for metric units;
= 0.0154 gr/mg for English units.

12.11 Conversion factors.

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.12 Isokinetic variation.

12.12.1 Calculation from raw data.

$$I = \frac{100\ T_s \left| K_4 V_{lc} + \left(\frac{V_m Y}{T_m}\right)\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right.}{60\ \Theta\ V_s P_s A_n} \qquad \text{Eq. 315-7}$$

where

K_4 = 0.003454 [(mm Hg)(m^3)]/[(ml)(°K)] for metric units;
= 0.002669 [(in Hg)(ft^3)]/[(ml)(°R)] for English units.

12.12.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std}\ 100}{T_{std} V_s \Theta A_n P_s\ 60\left(1 - B_{ws}\right)} = K_5 \frac{T_s V_{m(std)}}{P_s V_s A_n \Theta\left(1 - B_{ws}\right)} \qquad \text{Eq. 315-8}$$

where

K_5 = 4.320 for metric units;
= 0.09450 for English units.

12.12.3 Acceptable results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM or MCEM results are low in comparison to the standard, and "I" is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in the Bibliography may be used to make acceptability judgments. If "I" is judged to be unacceptable, reject the results, and repeat the test.

12.13 Stack gas velocity and volumetric flow rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 5.2 and 5.3 of Method 2, 40 CFR part 60, appendix A.

12.14 MCEM results. Determine the MCEM concentration from the results from Containers 1, 2, 2M, 3W, and 3S less the acetone, methylene chloride, and filter blanks value as determined in the following equation:

$m_{mcem} = Sm_{total} - w_a - w_t - f_b$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry gas meter as a calibration standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 16.1 of this method, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard dry gas meter calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity, e.g., 3 liters/rev (0.1 ft^3/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and be capable of measuring volume to within 1.0 percent; wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7 of Method 5, 40 CFR part 60, appendix A. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm H_2O [4 in. H_2O] at a flow rate of 30 liters/min [1 cfm]). This can be accomplished by using large-diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8 of Method 5, 40 CFR part 60, appendix A). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, q. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{\left(t_w + t_{std}\right)\Theta} \qquad \text{Eq. 315-9}$$

$$Y_{ds} = \frac{V_w \left(T_{ds} + T_{std}\right) P_{bar}}{V_{ds}\left(T_w + T_{std}\right)\left(P_{bar} + \frac{\Delta p}{13.6}\right)} \qquad \text{Eq. 315-10}$$

Where

K_1 = 0.3858 for international system of units (SI); 17.64 for English units;

P_{bar} = Barometric pressure, mm Hg (in Hg);

V_w = Wet test meter volume, liter (ft^3);

t_w = Average wet test meter temperature, °C (°F);

t_{std} = 273 °C for SI units; 460 °F for English units;

Θ = Run time, min;

t_{ds} = Average dry gas meter temperature, °C (°F);

V_{ds} = Dry gas meter volume, liter (ft^3);

Δp = Dry gas meter inlet differential pressure, mm H_2O (in H_2O).

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard dry gas meter recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates (suggested rates are 14 and 28 liters/min [0.5 and 1.0 cfm]). Calculate the meter coefficients for these two points, and compare the

values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

6.2 Critical orifices as calibration standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 10.3 of this method, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of critical orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubing that has been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices; i.e., a critical vacuum can be obtained, as described in section 7.2.2.2.3 of Method 5, 40 CFR part 60, appendix A. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 315-1 give the approximate flow rates indicated in the table.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 × 20 mm sleeve type, into a 0.5 in Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9 of Method 5, 40 CFR part 60, appendix A.

16.2.2 Critical orifice calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 of this method to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of meter box. The critical orifices must be calibrated in the same configuration as they will be used; i.e., there should be no connections to the inlet of the orifice.

16.2.2.1.1 Before calibrating the meter box, leak-check the system as follows: Fully open the coarse adjust valve and completely close the bypass valve. Plug the inlet. Then turn on the pump and determine whether there is any leakage. The leakage rate shall be zero; i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 5.6 of Method 5, 40 CFR part 60, appendix A for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn 0-rings, etc. and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 5.3 of Method 5, 40 CFR part 60, appendix A. Make sure that the wet test meter meets the requirements stated in section 7.1.1.1 of Method 5, 40 CFR part 60, appendix A. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of critical orifices. Set up the apparatus as shown in Figure 5-10 of Method 5, 40 CFR part 60, appendix A.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak-check the system as in section 7.2.2.1.1 of Method 5, 40 CFR part 60, appendix A. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: turn on the pump, fully open the coarse adjust valve, and adjust the bypass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, DH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2 of this method. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K'. Record the information listed in Figure 5-11 of Method 5, 40 CFR part 60, appendix A.

16.2.2.2.6 Calculate K' using Equation 315-11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6}\right) T_{amb}^{\frac{1}{2}}}{P_{bar} T_m \Theta} \qquad \text{Eq. 315-11}$$

where

K' = Critical orifice coefficient, $[m^3)(°K)^{1/2}]/[(mm\ Hg)(min)]$ $[(ft^3)(°R)^{1/2})]/[(in.\ Hg)(min)]$

T_{amb} = Absolute ambient temperature, °K (°R).

16.2.2.2.7 Average the K′ values. The individual K′ values should not differ by more than ±0.5 percent from the average.

16.2.3 Using the critical orifices as calibration standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in sections 7.2.2.2.1 to 7.2.2.2.5 of Method 5, 40 CFR part 60, appendix A. Record the information listed in Figure 5–12 of Method 5, 40 CFR part 60, appendix A.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$V_{m(std)} = K_1\ V_m\ [P_{bar} + (\Delta H/13.6)]/T_m$ *Eq. 315–12*

$V_{cr(std)} = K'\ (P_{bar}\ \Theta)/T_{amb}^{1/2}$ *Eq. 315–13*

$Y = V_{cr(std)}/V_{m(std)}$ *Eq. 315–14*

where

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K' = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 7.2.2.2 of Method 5, 40 CFR part 60, appendix A.

17.0 References

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 315–1. FLOW RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS.

Gauge/length (cm)	Flow rate (liters/min)	Gauge/length (cm)	Flow rate (liters/min)
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	115/10.2	10.48

FIGURE 315–1. PARTICULATE AND MCEM ANALYSES

Particulate Analysis

Plant	
Date	
Run No.	
Filter No.	
Amount liquid lost during transport	
Acetone blank volume (ml)	
Acetone blank concentration (Eq. 315–4) (mg/mg)	
Acetone wash blank (Eq. 315–5) (mg)	

%	Final weight (mg)	Tare weight (mg)	Weight gain (mg)
Container No. 1			
Container No. 2			
Total			
Less Acetone blank			
Weight of particulate matter			

Moisture Analysis	Final volume (mg)	Initial volume (mg)	Liquid collected (mg)
Impingers	Note 1	Note 1	
Silica gel			
Total			

NOTE 1: Convert volume of water to weight by multiplying by the density of water (1 g/ml).

Container No.	Final weight (mg)	Tare of aluminum dish (mg)	Weight gain	Acetone wash volume (ml)	Methylene chloride wash volume (ml)
MCEM Analysis					
1.					
2 + 2M.					
3W.					
3S.					
Total			$\sum m_{total}$	$\sum V_{aw}$	$\sum V_{tw}$

Less acetone wash blank (mg) (not to exceed 1 mg/l of acetone used).	$w_a = c_a p_a \sum V_{aw}$
Less methylene chloride wash blank (mg) (not to exceed 1.5 mg/l of methylene chloride used).	$w_t = c_t p_t \sum V_{tw}$

Less filter blank (mg) (not to exceed . . . (mg/filter)	F_b
MCEM weight (mg)	$m_{MCEOM} = \sum m_{total} - w_a - w_i - f_b$

METHOD 316—SAMPLING AND ANALYSIS FOR FORMALDEHYDE EMISSIONS FROM STATIONARY SOURCES IN THE MINERAL WOOL AND WOOL FIBERGLASS INDUSTRIES

1.0 Introduction

This method is applicable to the determination of formaldehyde, CAS Registry number 50–00–0, from stationary sources in the mineral wool and wool fiber glass industries. High purity water is used to collect the formaldehyde. The formaldehyde concentrations in the stack samples are determined using the modified pararosaniline method. Formaldehyde can be detected as low as 8.8×10^{10} lbs/cu ft (11.3 ppbv) or as high as 1.8×10^{3} lbs/cu ft (23,000,000 ppbv), at standard conditions over a 1 hour sampling period, sampling approximately 30 cu ft.

2.0 Summary of Method

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in high purity water. Formaldehyde present in the emissions is highly soluble in high purity water. The high purity water containing formaldehyde is then analyzed using the modified pararosaniline method. Formaldehyde in the sample reacts with acidic pararosaniline, and the sodium sulfite, forming a purple chromophore. The intensity of the purple color, measured spectrophotometrically, provides an accurate and precise measure of the formaldehyde concentration in the sample.

3.0 Definitions

See the definitions in the General Provisions of this Subpart.

4.0 Interferences

Sulfite and cyanide in solution interfere with the pararosaniline method. A procedure to overcome the interference by each compound has been described by Miksch, et al.

5.0 Safety [Reserved]

6.0 Apparatus and Materials

6.1 A schematic of the sampling train is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5, 40 CFR part 60, appendix A, procedures.

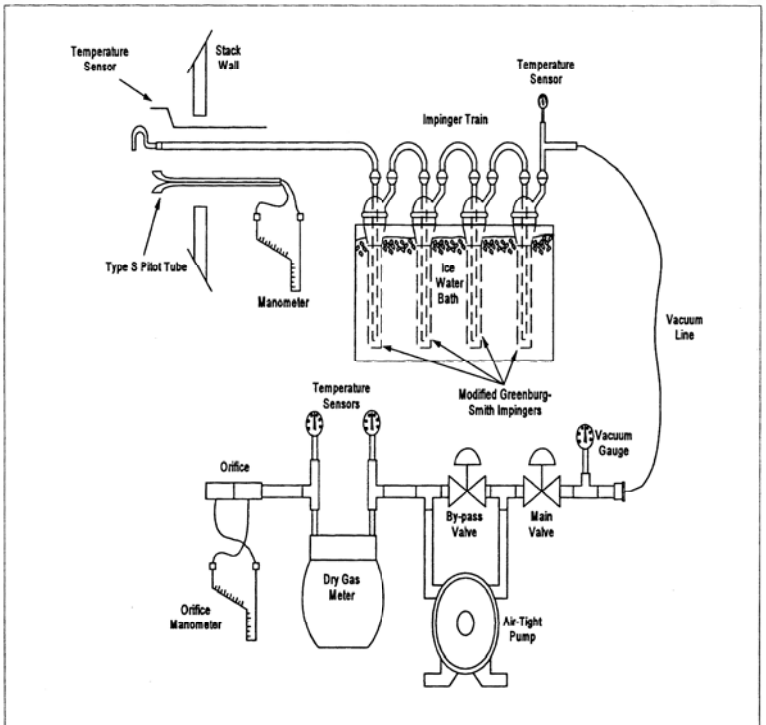

Figure 1. Sampling Train.

The sampling train consists of the following components: probe nozzle, probe liner, pitot tube, differential pressure gauge, impingers, metering system, barometer, and gas density determination equipment.

6.1.1 Probe Nozzle: Quartz, glass, or stainless steel with sharp, tapered (30 ° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm (1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedure outlined in Section 10.1.

6.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The probe shall be maintained at a temperature of 120 °C ±14 °C (248 °F ±25 °F).

6.1.3 Pitot Tube: The pitot tube shall be Type S, as described in Section 2.1 of EPA Method 2, 40 CFR part 60, appendix A, or any other appropriate device. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Figure 2–6b, EPA Method 2, 40 CFR part 60, appendix A) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2, 40 CFR part 60, appendix A.

6.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.

6.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameters (1/2 in) glass tube extending to 1.3 cm (1/2 in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Place a thermometer capable of measuring temperature

to within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

6.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperatures within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1 percent, and related equipment as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0–999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2 percent. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

6.1.7 Barometer: The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase (rate is plus 2.5 mm Hg per 30 m (100 ft) of elevation decrease).

6.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.3 of EPA Method 2, 40 CFR part 60, appendix A), and gas analyzer, if necessary (as described in EPA Method 3, 40 CFR part 60, appendix A). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the top of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot openings (see Figure 2–7, EPA Method 2, 40 CFR part 60, appendix A). As a second alternative, if a difference of no more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

6.2 Sample Recovery

6.2.1 Probe Liner: Probe nozzle and brushes; bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon™, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

6.2.2 Wash Bottles: One wash bottle is required. Polyethylene, Teflon™, or glass wash bottles may be used for sample recovery.

6.2.3 Graduated Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not >2 ml. Laboratory balances capable of weighing to ±0.5 g are required.

6.2.4 Polyethylene Storage Containers: 500 ml wide-mouth polyethylene bottles are required to store impinger water samples.

6.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid the transfer of material into and out of containers in the field.

6.3 Sample Analysis

6.3.1 Spectrophotometer—B&L 70, 710, 2000, etc., or equivalent; 1 cm pathlength cuvette holder.

6.3.2 Disposable polystyrene cuvettes, pathlengh 1 cm, volume of about 4.5 ml.

6.3.3 Pipettors—Fixed-volume Oxford pipet (250 µl; 500 µl; 1000 µl); adjustable volume Oxford or equivalent pipettor 1–5 ml model, set to 2.50 ml.

6.3.4 Pipet tips for pipettors above.

6.3.5 Parafilm, 2 ° wide; cut into about 1'' squares.

7.0 Reagents

7.1 High purity water: All references to water in this method refer to high purity water (ASTM Type I water or equivalent). The water purity will dictate the lower limits of formaldehyde quantification.

7.2 Silica Gel: Silica gel shall be indicting type, 6–16 mesh. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

7.3 Crushed Ice: Quantities ranging from 10–50 lbs may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

7.4 Quaternary ammonium compound stock solution: Prepare a stock solution of dodecyltrimethylammonium chloride (98 percent minimum assay, reagent grade) by dissolving 1.0 gram in 1000 ml water. This solution contains nominally 1000 µg/ml quaternary ammonium compound, and is used as a biocide for some sources which are prone to microbial contamination.

7.5 Pararosaniline: Weigh 0.16 grams pararosaniline (free base; assay of 95 percent or greater, C.I. 42500; Sigma P7632 has been found to be acceptable) into a 100 ml flask. Exercise care, since pararosaniline is a dye and will stain. Using a wash bottle with high-purity water, rinse the walls of the flask. Add no more than 25 ml water. Then,

carefully add 20 ml of concentrated hydrochloric acid to the flask. The flask will become warm after the addition of acid. Add a magnetic stir bar to the flask, cap, and place on a magnetic stirrer for approximately 4 hours. Then, add additional water so the total volume is 100 ml. This solution is stable for several months when stored tightly capped at room temperature.

7.6 Sodium sulfite: Weigh 0.10 grams anhydrous sodium sulfite into a 100 ml flask. Dilute to the mark with high purity water. Invert 15–20 times to mix and dissolve the sodium sulfite. This solution must be prepared fresh every day.

7.7 Formaldehyde standard solution: Pipet exactly 2.70 ml of 37 percent formaldehyde solution into a 1000 ml volumetric flask which contains about 500 ml of high-purity water. Dilute to the mark with high-purity water. This solution contains nominally 1000 µg/ml of formaldehyde, and is used to prepare the working formaldehyde standards. The exact formaldehyde concentration may be determined if needed by suitable modification of the sodium sulfite method (Reference: J.F. Walker, Formaldehyde (Third Edition), 1964.). The 1000 µg/ml formaldehyde stock solution is stable for at least a year if kept tightly closed, with the neck of the flask sealed with Parafilm. Store at room temperature.

7.8 Working formaldehyde standards: Pipet exactly 10.0 ml of the 1000 µg/ml formaldehyde stock solution into a 100 ml volumetric flask which is about half full of high-purity water. Dilute to the mark with high-purity water, and invert 15–20 times to mix thoroughly. This solution contains nominally 100 µg/ml formaldehyde. Prepare the working standards from this 100 µg/ml standard solution and using the Oxford pipets:

Working standard, µ/mL	µL or 100 µg/mL solution	Volumetric flask volume (dilute to mark with water)
0.250	250	100
0.500	500	100
1.00	1000	100
2.00	2000	100
3.00	1500	50

The 100 µg/ml stock solution is stable for 4 weeks if kept refrigerated between analyses. The working standards (0.25–3.00 µg/ml) should be prepared fresh every day, consistent with good laboratory practice for trace analysis. If the laboratory water is not of sufficient purity, it may be necessary to prepare the working standards every day. The laboratory must establish that the working standards are stable—DO NOT assume that your working standards are stable for more than a day unless you have verified this by actual testing for several series of working standards.

8.0 Sample Collection

8.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.2 Laboratory Preparation

8.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD–0576, unless otherwise specified.

8.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

8.3 Preliminary Field Determinations

8.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1, 40 CFR part 60, appendix A, or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2, 40 CFR part 60, appendix A. A leak-check of the pitot lines according to Section 3.1 of EPA Method 2, 40 CFR part 60, appendix A, must be performed. Determine the stack gas moisture content using EPA Approximation Method 4,40 CFR part 60, appendix A, or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, 40 CFR part 60, appendix A, Section 3.6. If integrated EPA Method 3, 40 CFR part 60, appendix A, sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 l/min (1.0 cfm). During the run do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A).

8.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

8.3.4 A minimum of 30 cu ft of sample volume is suggested for emission sources with stack concentrations not greater than 23,000,000 ppbv. Additional sample volume shall be collected as necessitated by the capacity of the water reagent and analytical detection limit constraint. Reduced sample volume may be collected as long as the final concentration of formaldehyde in the stack

sample is greater than 10 (ten) times the detection limit.

8.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1, 40 CFR part 60, appendix A. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.

8.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculations of concentrations.

8.4 Preparation of Collection Train

8.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon™ film or aluminum foil until just prior to assembly or until sampling is about to begin.

8.4.2 Place 100 ml of water in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of water per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD–0576 for details. Other connection systems utilizing either 316 stainless steel or Teflon™ ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.4.4 Assemble the train as shown in Figure 1. During assembly, a very light coating of silicone grease may be used on ground-glass joints of the impingers, but the silicone grease should be limited to the outer portion (see APTD–0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon™ tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

8.4.5 Place crushed ice all around the impingers.

8.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

8.5 Leak-Check Procedures

8.5.1 Pre-test Leak-check: Recommended, but not required. If the tester elects to conduct the pre-test leak-check, the following procedure shall be used.

8.5.1.1 After the sampling train has been assembled, turn on and set probe heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton-a O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in Hg) vacuum.

NOTE: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

If a woven glass fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum may be used if this lower vacuum is not exceeded during the test.) Next connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in Hg) vacuum. Leakage rates in excess of (a) 4 percent of the average sampling rate or (b) 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

8.5.1.2 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak-check at this higher vacuum or end the leak-check, as described below, and start over.

8.5.1.3 When the leak-check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

8.5.2 Leak-checks During Sampling Run:

8.5.2.1 If, during the sampling run, a component change (e.g., impinger) becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure described in Section 10.3.3, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.0057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

8.5.2.2 Immediately after component changes, leak-checks are optional. If performed, the procedure described in section 8.5.1.1 shall be used.

8.5.3 Post-test Leak-check:

8.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as the pre-test leak-check, except that the post-test leak-check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

8.6 Sampling Train Operation

8.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, below 28 l/min (1.0 cfm). Maintain a temperature around the probe of 120 °C ±14 °C (248 ° ±25 °F).

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Figure 2 - Fornaldehyde Field Data

Plant . . . . . .

Location . . . . . .

Operator . . . . . .

Date . . . . . .

Run No . . . . . .

Sample box No . . . . . .

Meter box No . . . . . .

Meter ΔH . . . . . .

C Factor . . . . . .

Pitot tube coefficient, Op

SCHEMATIC OF STACK CROSS SECTION

Ambient temperature . . . . . .

Barometric pressure . . . . . .

Assumed moisture, percent . . . .

Probe length, m (ft) . . . . . .

Nozzle Identification No . . . .

Average calibrated nozzle

diameter, cm (in.) . . . . . .

Probe heater setting . . . . . .

Leak rate, m^3/min (cfm) . . . . .

Probe liner material . . . . . .

Static pressure, mm Hg (in. Hg) .

Filter No. . . . . .

Traverse point number	Sampling time (θ) min.	Vacuum mm Hg (in. Hg)	Stack temperature (T) °C (°F)	Velocity head (ΔP) mm (in) H_2O	Pressure differential across orifice meter mm H_2O (in. H_2O)	Gas sample volume m^3 (ft^3)	Gas sample temperature at dry gas meter		Filter holder temperature °C (°F)	Temperature of gas leaving condenser or last impinger °C (°F)
							Inlet °C (°F)	Outlet °C (°F)		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Total	.....	.....	.....	.....	.....	.....	Avg.	Avg.	.....	.....
Average	.....	.....	.....	.....	.....	.....	Avg.	.....	.....	.....

8.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the probe heating system are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ±0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ±4. APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

8.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, a low vacuum on the train may have to be started prior to entering the stack.

8.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

8.6.6 Traverse the stack cross section, as required by EPA Method 1, 40 CFR part 60, appendix A, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

8.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of <20 °C (68 °F) at the silica gel outlet.

8.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or trains may also be used for sampling when the capacity of a single train is exceeded.

8.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

8.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Also, check the pitot lines as described in EPA Method 2, 40 CFR part 60, appendix A. The lines must pass this leak-check in order to validate the velocity-head data.

8.6.11 Calculate percent isokineticity (see Method 2) to determine whether the run was valid or another test should be made.

8.7 Sample Preservation and Handling

8.7.1 Samples from most sources applicable to this method have acceptable holding times using normal handling practices (shipping samples iced, storing in refrigerator at 2 °C until analysis). However, forming section stacks and other sources using waste water sprays may be subject to microbial contamination. For these sources, a biocide (quaternary ammonium compound solution) may be added to collected samples to improve sample stability and method ruggedness.

8.7.2 Sample holding time: Samples should be analyzed within 14 days of collection. Samples must be refrigerated/kept cold for the entire period preceding analysis. After

the samples have been brought to room temperature for analysis, any analyses needed should be performed on the same day. Repeated cycles of warming the samples to room temperature/refrigerating/rewarming, then analyzing again, etc., have not been investigated in depth to evaluate if analyte levels remain stable for all sources.

8.7.3 Additional studies will be performed to evaluate whether longer sample holding times are feasible for this method.

8.8 Sample Recovery

8.8.1 Preparation:

8.8.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.

8.8.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon™ caps, or caps of other inert materials may be used to seal all openings.

8.8.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.

8.8.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

8.8.1.5 Save a portion of the washing solution (high purity water) used for cleanup as a blank.

8.8.2 Sample Containers:

8.8.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the combined impinger solution from the graduated cylinder into the polyethylene bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first three impingers, and impinger connectors) with water. Use less than 400 ml for the entire waste (250 ml would be better, if possible). Add the rinse water to the sample container.

8.8.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with water from a wash bottle. Brush with a bristle brush and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok (or equivalent) fitting with water in a similar way.

8.8.2.1.2 Rinse the probe liner with water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a bristle brush. Hold the probe in an inclined position, and squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. Rinse the brush with water and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as describe above.

NOTE: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

8.8.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of water for each rinse, and brush each surface to which the sample is exposed with a bristle brush to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush, using water.

8.8.2.1.4 After all water washing and particulate matter have been collected in the sample container, tighten the lid so the sample will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

8.8.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

8.8.2.2 Container 2: Sample Blank. Prepare a blank by using a polyethylene container and adding a volume of water equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

8.8.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent

and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon™ caps maybe used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

8.8.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Putting sample bottles in Zip-Lock™ bags can aid in maintaining the integrity of the sample labels. Sample containers should be placed vertically to avoid leakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory. It is critical that samples be chilled immediately after recovery. If the source is susceptible to microbial contamination from wash water (e.g. forming section stack), add biocide as directed in section 8.2.5.

8.8.2.5 A quaternary ammonium compound can be used as a biocide to stabilize samples against microbial degradation following collection. Using the stock quaternary ammonium compound (QAC) solution; add 2.5 ml QAC solution for every 100 ml of recovered sample volume (estimate of volume is satisfactory) immediately after collection. The total volume of QAC solution must be accurately known and recorded, to correct for any dilution caused by the QAC solution addition.

8.8.3 Sample Preparation for Analysis 8.8.3.1 The sample should be refrigerated if the analysis will not be performed on the day of sampling. Allow the sample to warm at room temperature for about two hours (if it has been refrigerated) prior to analyzing.

8.8.3.2 Analyze the sample by the pararosaniline method, as described in Section 11. If the color-developed sample has an absorbance above the highest standard, a suitable dilution in high purity water should be prepared and analyzed.

9.0 Quality Control

9.1 Sampling: See EPA Manual 600/4-77-02b for Method 5 quality control.

9.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, and procedure validations. The positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

9.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recover water, and water reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.

9.2.2 Blank Correction: The field blank formaldehyde concentrations will be subtracted from the appropriate sample formaldehyde concentrations. Blank formaldehyde concentrations above 0.25 μg/ml should be considered suspect, and subtraction from the sample formaldehyde concentrations should be performed in a manner acceptable to the Administrator.

9.2.3 Method Blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

10 Calibration

10.1 Probe Nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in). When the nozzle becomes nicked or corroded, it shall be repaired and calibrated, or replaced with a calibrated nozzle before use. Each nozzle must be permanently and uniquely identified.

10.2 Pitot Tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

10.3 Metering System

10.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576.

Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not delete leakages with the pump. For these cases, the following leak-check procedure will apply: Make a ten-minute calibration run at 0.00057 m^3/min (0.02 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

10.3.2 After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD–0576.

10.3.3 Leak-check of metering system: The portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13–18 cm (5–7 in) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

NOTE: If the dry-gas meter coefficient values obtained before and after a test series differ by >5 percent, either the test series must be voided or calculations for test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe Heater: The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD–0576. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used.

10.5 Temperature gauges: Use the procedure in Section 4.3 of EPA Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.6 Barometer: Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in Hg) of the mercury barometer. Alternately, if a National Weather Service Station (NWSS) is located at the same altitude above sea level as the test site, the barometric pressure reported by the NWSS may be used.

10.7 Balance: Calibrate the balance before each test series, using Class S standard weights. The weights must be within ±0.5 percent of the standards, or the balance must be adjusted to meet these limits.

11.0 Procedure for Analysis

The working formaldehyde standards (0.25, 0.50, 1.0, 2.0, and 3.0 μg/ml) are analyzed and a calibration curve is calculated for each day's analysis. The standards should be analyzed first to ensure that the method is working properly prior to analyzing the samples. In addition, a sample of the high-purity water should also be analyzed and used as a "0" formaldehyde standard.

The procedure for analysis of samples and standards is identical: Using the pipet set to 2.50 ml, pipet 2.50 ml of the solution to be analyzed into a polystyrene cuvette. Using the 250 μl pipet, pipet 250 μl of the pararosaniline reagent solution into the cuvette. Seal the top of the cuvette with a Parafilm square and shake at least 30 seconds to ensure the solution in the cuvette is well-mixed. Peel back a corner of the Parafilm so the next reagent can be added. Using the 250 μl pipet, pipet 250 μl of the sodium sulfite reagent solution into the cuvette. Reseal the cuvette with the Parafilm, and again shake for about 30 seconds to mix the solution in the cuvette. Record the time of addition of the sodium sulfite and let the color develop at room temperature for 60 minutes. Set the spectrophotometer to 570 nm and set to read in Absorbance Units. The spectrophotometer should be equipped with a holder for the 1-cm pathlength cuvettes. Place cuvette(s) containing high-purity water in the spectrophotometer and adjust to read 0.000 AU.

After the 60 minutes color development period, read the standard and samples in the spectrophotometer. Record the absorbance reading for each cuvette. The calibration curve is calculated by linear regression, with the formaldehyde concentration as the "x" coordinate of the pair, and the absorbance reading as the "y" coordinate. The procedure is very reproducible, and typically will yield

values similar to these for the calibration curve:

Correlation Coefficient: 0.9999
Slope: 0.50
Y-Intercept: 0.090

The formaldehyde concentration of the samples can be found by using the trend-line feature of the calculator or computer program used for the linear regression. For example, the TI-55 calculators use the "X" key (this gives the predicted formaldehyde concentration for the value of the absorbance you key in for the sample). Multiply the formaldehyde concentration from the sample by the dilution factor, if any, for the sample to give the formaldehyde concentration of the original, undiluted, sample (units will be micrograms/ml).

11.1 Notes on the Pararosaniline Procedure

11.1.1 The pararosaniline method is temperature-sensitive. However, the small fluctuations typical of a laboratory will not significantly affect the results.

11.1.2 The calibration curve is linear to beyond 4 "µg/ml" formaldehyde, however, a research-grade spectrophotometer is required to reproducibly read the high absorbance values. Consult your instrument manual to evaluate the capability of the spectrophotometer.

11.1.3 The quality of the laboratory water used to prepare standards and make dilutions is critical. It is important that the cautions given in the Reagents section be observed. This procedure allows quantitation of formaldehyde at very low levels, and thus it is imperative to avoid contamination from other sources of formaldehyde and to exercise the degree of care required for trace analyses.

11.1.4 The analyst should become familiar with the operation of the Oxford or equivalent pipettors before using them for an analysis. Follow the instructions of the manufacturer; one can pipet water into a tared container on any analytical balance to check pipet accuracy and precision. This will also establish if the proper technique is being used. Always use a new tip for each pipetting operation.

11.1.5 This procedure follows the recommendations of ASTM Standard Guide D 3614, reading all solutions versus water in the reference cell. This allows the absorbance of the blank to be tracked on a daily basis. Refer to ASTM D 3614 for more information.

12.0 Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Calculations of Total Formaldehyde

12.1.1 To determine the total formaldehyde in mg, use the following equation if biocide was not used:

Total mg formaldehyde=

$$C_d \times V \times DF \times 0.001 \text{ mg/µg}$$

Where:

C_d = measured conc. formaldehyde, µg/ml
V = total volume of stack sample, ml
DF = dilution factor

12.1.2 To determine the total formaldehyde in mg, use the following equation if biocide was used:

Total mg formaldehyde=

$$\frac{C_d \times V}{(V - B) \times DF \times 0.001 \text{ mg/µg}}$$

Where:

C_d = measured conc. formaldehyde, µg/ml
V = total volume of stack sample, ml
B = total volume of biocide added to sample, ml
DF = dilution factor

12.2 Formaldehyde concentration (mg/m³) in stack gas. Determine the formaldehyde concentration (mg/m³) in the stack gas using the following equation: Formaldehyde concentration (mg/m³) =

$$\frac{K \times [\text{total formaldehyde, mg}]}{V_m(\text{std})}$$

Where:

K = 35.31 cu ft/m³ for V_m (std) in English units, or
K = 1.00 m³/m³ for V_m (std) in metric units
V_m (std) = volume of gas sample measured by a dry gas meter, corrected to standard conditions, dscm (dscf)

12.3 Average dry gas meter temperature and average orifice pressure drop are obtained from the data sheet.

12.4 Dry Gas Volume: Calculate V_m (std) and adjust for leakage, if necessary, using the equation in Section 6.3 of EPA Method 5, 40 CFR part 60, appendix A.

12.5 Volume of Water Vapor and Moisture Content: Calculated the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA Method 5.

13.0 Method Performance

The precision of this method is estimated to be better than ±5 percent, expressed as ±the percent relative standard deviation.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

R.R. Miksch, et al., Analytical Chemistry, November 1981, 53 pp. 2118–2123.
J.F. Walker, Formaldehyde, Third Edition, 1964.

US EPA 40 CFR, part 60, Appendix A, Test Methods 1–5

METHOD 318—EXTRACTIVE FTIR METHOD FOR THE MEASUREMENT OF EMISSIONS FROM THE MINERAL WOOL AND WOOL FIBERGLASS INDUSTRIES

1.0 Scope and Application

This method has been validated and approved for mineral wool and wool fiberglass sources. This method may not be applied to other source categories without validation and approval by the Administrator according to the procedures in Test Method 301, 40 CFR part 63, appendix A. For sources seeking to apply FTIR to other source categories, Test Method 320 (40 CFR part 63, appendix A) may be utilized.

1.1 Scope. The analytes measured by this method and their CAS numbers are:

Carbon Monoxide 630–08–0
Carbonyl Sulfide 463–58–1
Formaldehyde 50–00–0
Methanol 1455–13–6
Phenol 108–95–2

1.2 Applicability

1.2.1 This method is applicable for the determination of formaldehyde, phenol, methanol, carbonyl sulfide (COS) and carbon monoxide (CO) concentrations in controlled and uncontrolled emissions from manufacturing processes using phenolic resins. The compounds are analyzed in the mid-infrared spectral region (about 400 to 4000 cm−1 or 25 to 2.5 μm). Suggested analytical regions are given below (Table 1). Slight deviations from these recommended regions may be necessary due to variations in moisture content and ammonia concentration from source to source.

TABLE 1—EXAMPLE ANALYTICAL REGIONS

Compound	Analytical region (cm−1) FL_m – FU_m	Potential interferants
Formaldehyde	2840.93 – 2679.83	Water, Methane.
Phenol	1231.32 – 1131.47	Water, Ammonia, Methane.
Methanol	1041.56 – 1019.95	Water, Ammonia.
COS[a]	2028.4 – 2091.9	Water, CO_2 CO.
CO[a]	2092.1 – 2191.8	Water, CO_2, COS.

[a] Suggested analytical regions assume about 15 percent moisture and CO_2, and that COS and CO have about the same absorbance (in the range of 10 to 50 ppm). If CO and COS are hundreds of ppm or higher, then CO_2 and moisture interference is reduced. If CO or COS is present at high concentration and the other at low concentration, then a shorter cell pathlength may be necessary to measure the high concentration component.

1.2.2 This method does not apply when: (a) Polymerization of formaldehyde occurs, (b) moisture condenses in either the sampling system or the instrumentation, and (c) when moisture content of the gas stream is so high relative to the analyte concentrations that it causes severe spectral interference.

1.3 Method Range and Sensitivity

1.3.1 The analytical range is a function of instrumental design and composition of the gas stream. Theoretical detection limits depend, in part, on (a) the absorption coefficient of the compound in the analytical frequency region, (b) the spectral resolution, (c) interferometer sampling time, (d) detector sensitivity and response, and (e) absorption pathlength.

1.3.2 Practically, there is no upper limit to the range. The practical lower detection limit is usually higher than the theoretical value, and depends on (a) moisture content of the flue gas, (b) presence of interferants, and (c) losses in the sampling system. In general, a 22 meter pathlength cell in a suitable sampling system can achieve practical detection limits of 1.5 ppm for three compounds (formaldehyde, phenol, and methanol) at moisture levels up to 15 percent by volume. Sources with uncontrolled emissions of CO and COS may require a 4 meter pathlength cell due to high concentration levels. For these two compounds, make sure absorbance of highest concentration component is <1.0.

1.4 Data Quality Objectives

1.4.1 In designing or configuring the system, the analyst first sets the data quality objectives, i.e., the desired lower detection limit (DL_i) and the desired analytical uncertainty (AU_i) for each compound. The instrumental parameters (factors b, c, d, and e in Section 1.3.1) are then chosen to meet these requirements, using Appendix D of the FTIR Protocol.

1.4.2 Data quality for each application is determined, in part, by measuring the RMS (Root Mean Square) noise level in each analytical spectral region (Appendix C of the FTIR Protocol). The RMS noise is defined as the RMSD (Root Mean Square Deviation) of the absorbance values in an analytical region from the mean absorbance value of the region. Appendix D of the FTIR Protocol defines the MAU_{im} (minimum analyte uncertainty of the ith analyte in the mth analytical region). The MAU is the minimum analyte concentration for which the analytical uncertainty limit (AU_i) can be maintained: if the measured analyte concentration is less than MAU_i, then data quality is unacceptable. Table 2 gives some example