diphenylcarbazide in 100 mL of ACS grade methanol. Add 500 mL of reagent water containing 50 mL of 96 percent spectrophotometric grade sulfuric acid. Dilute to 1 liter with reagent water.

7.3.7 Chromium Standard Stock Solution (1000 mg/L). Procure a certified aqueous standard or dissolve 2.829 g of potassium dichromate ($K_2Cr_2O_7$), in reagent water and dilute to 1 liter.

7.3.8 Calibration Standards for ICP or IC/PCR. Prepare calibration standards for ICP or IC/PCR by diluting the Cr standard stock solution (Section 7.3.7) with 0.1 N NaOH or 0.1 N $NaHCO_3$, whichever is used as the impinger absorbing solution, to achieve a matrix similar to the actual field samples. Suggested levels are 0, 50, 100, and 200 µg Cr/L for ICP, and 0, 1, 5, and 10 µg Cr^{+6}/L for IC/PCR.

7.3.9 Calibration Standards for GFAAS. Chromium solutions for GFAAS calibration shall contain 1.0 percent (v/v) HNO_3. The zero standard shall be 1.0 percent (v/v) HNO_3. Calibration standards should be prepared daily by diluting the Cr standard stock solution (Section 7.3.7) with 1.0 percent HNO_3. Use at least four standards to make the calibration curve. Suggested levels are 0, 10, 50, and 100 µg Cr/L.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3, Concentrated. ACS reagent grade or equivalent.

7.4.2 Water. Reagent water that conforms to ASTM Specification D1193–77 or 91 Type II.

7.4.3 HNO_3, 10 percent (v/v). Add by stirring 500 mL of concentrated HNO_3 into a flask containing approximately 4,000 mL of reagent water. Dilute to 5,000 mL with reagent water. Mix well. The reagent shall contain less than 2 µg Cr/L.

8.0 Sample Collection, Preservation, Holding Times, Storage, and Transport

NOTE: Prior to sample collection, consideration should be given to the type of analysis (Cr^{+6} or total Cr) that will be performed. Which analysis option(s) will be performed will determine which sample recovery and storage procedures will be required to process the sample.

8.1 Sample Collection. Same as Method 5 (40 CFR part 60, appendix A), with the following exceptions.

8.1.1 Omit the particulate filter and filter holder from the sampling train. Use a glass nozzle and probe liner instead of stainless steel. Do not heat the probe. Place 100 mL of 0.1 N NaOH or 0.1 N $NaHCO_3$ in each of the first two impingers, and record the data for each run on a data sheet such as shown in Figure 306–2.

8.1.2 Clean all glassware prior to sampling in hot soapy water designed for laboratory cleaning of glassware. Next, rinse the glassware three times with tap water, followed by three additional rinses with reagent water. Then soak the glassware in 10% (v/v) HNO_3 solution for a minimum of 4 hours, rinse three times with reagent water, and allow to air dry. Cover all glassware openings where contamination can occur with Parafilm, or equivalent, until the sampling train is assembled for sampling.

8.1.3 Train Operation. Follow the basic procedures outlined in Method 5 in conjunction with the following instructions. Train sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during a run.

8.2 Sample Recovery. Follow the basic procedures of Method 5, with the exceptions noted.

8.2.1 A particulate filter is not recovered from this train.

8.2.2 Tester shall select either the total Cr or Cr^{+6} sample recovery option.

8.2.3 Samples to be analyzed for both total Cr and Cr^{+6}, shall be recovered using the Cr^{+6} sample option (Section 8.2.6).

8.2.4 A field reagent blank shall be collected for either of the Cr or the Cr^{+6} analysis. If both analyses (Cr and Cr^{+6}) are to be conducted on the samples, collect separate reagent blanks for each analysis.

NOTE: Since particulate matter is not usually present at chromium electroplating and/or chromium anodizing operations, it is not necessary to filter the Cr^{+6} samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr^{+6} solutions, please refer to Method 0061, Determination of Hexavalent Chromium Emissions From Stationary Sources, Section 7.4, Sample Preparation in SW–846 (see Reference 1).

8.2.5 Total Cr Sample Option.

8.2.5.1 Container No. 1. Measure the volume of the liquid in the first, second, and third impingers and quantitatively transfer into a labeled sample container.

8.2.5.2 Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution to rinse the probe nozzle, probe liner, three impingers, and connecting glassware; add this rinse to Container No. 1.

8.2.6 Cr^{+6} Sample Option.

8.2.6.1 Container No. 1. Measure and record the pH of the absorbing solution contained in the *first* impinger at the end of the sampling run using a pH indicator strip. The pH of the solution must be ≥8.5 for NaOH and ≥8.0 for $NaHCO_3$. If it is not, discard the collected sample, increase the normality of the NaOH or $NaHCO_3$ impinger absorbing solution to 0.5 N or to a solution normality approved by the Administrator and collect another air emission sample.

8.2.6.2 After determining the pH of the first impinger solution, combine and measure the volume of the liquid in the first, second, and third impingers and quantitatively transfer into the labeled sample container.

Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution to rinse the probe nozzle, probe liner, three impingers, and connecting glassware: add this rinse to Container No. 1.

8.2.7 Field Reagent Blank.

8.2.7.1 Container No. 2.

8.2.7.2 Place approximately 500 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution into a labeled sample container.

8.3 Sample Preservation, Storage, and Transport.

8.3.1 Total Cr Sample Option. Samples to be analyzed for total Cr need not be refrigerated.

8.3.2 Cr^{+6} Sample Option. Samples to be analyzed for Cr^{+6} must be shipped and stored at 4 °C. Allow Cr^{+6} samples to return to ambient temperature prior to analysis.

8.4 Sample Holding Times.

8.4.1 Total Cr Sample Option. Samples to be analyzed for total Cr shall be analyzed within 60 days of collection.

8.4.2 Cr^{+6} Sample Option. Samples to be analyzed for Cr^{+6} shall be analyzed within 14 days of collection.

9.0 Quality Control

9.1 ICP Quality Control.

9.1.1 ICP Calibration Reference Standards. Prepare a calibration reference standard using the same alkaline matrix as the calibration standards; it should be at least 10 times the instrumental detection limit.

9.1.1.1 This reference standard must be prepared from a different Cr stock solution source than that used for preparation of the calibration curve standards.

9.1.1.2 Prior to sample analysis, analyze at least one reference standard.

9.1.1.3 The calibration reference standard must be measured within 10 percent of it's true value for the curve to be considered valid.

9.1.1.4 The curve must be validated before sample analyses are performed.

9.1.2 ICP Continuing Check Standard.

9.1.2.1 Perform analysis of the check standard with the field samples as described in Section 11.2 (at least after every 10 samples, and at the end of the analytical run).

9.1.2.2 The check standard can either be the mid-range calibration standard or the reference standard. The results of the check standard shall agree within 10 percent of the expected value; if not, terminate the analyses, correct the problem, recalibrate the instrument, and rerun all samples analyzed subsequent to the last acceptable check standard analysis.

9.1.3 ICP Calibration Blank.

9.1.3.1 Perform analysis of the calibration blank with the field samples as described in Section 11.2 (at least after every 10 samples, and at the end of the analytical run).

9.1.3.2 The results of the calibration blank shall agree within three standard deviations of the mean blank value. If not, analyze the calibration blank two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.1.4 ICP Interference Check. Prepare an interference check solution that contains known concentrations of interfering elements that will provide an adequate test of the correction factors in the event of potential spectral interferences.

9.1.4.1 Two potential interferences, iron and manganese, may be prepared as 1000 µg/mL and 200 µg/mL solutions, respectively. The solutions should be prepared in dilute HNO_3 (1–5 percent). Particular care must be used to ensure that the solutions and/or salts used to prepare the solutions are of ICP grade purity (*i.e.*, that no measurable Cr contamination exists in the salts/solutions). Commercially prepared interfering element check standards are available.

9.1.4.2 Verify the interelement correction factors every three months by analyzing the interference check solution. The correction factors are calculated according to the instrument manufacturer's directions. If the interelement correction factors are used properly, no false Cr should be detected.

9.1.4.3 Negative results with an absolute value greater than three (3) times the detection limit are usually the results of the background correction position being set incorrectly. Scan the spectral region to ensure that the correction position has not been placed on an interfering peak.

9.1.5 ICP Duplicate Sample Analysis. Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.1.5.1 As there is no sample preparation required for the ICP analysis, a duplicate analysis is defined as a repeat analysis of one of the field samples. The selected sample shall be analyzed using the same procedures that were used to analyze the original sample.

9.1.5.2 Duplicate sample analyses shall agree within 10 percent of the original measurement value.

9.1.5.3 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value. If agreement is not achieved, perform the duplicate analysis again. If agreement is not achieved the second time, perform corrective action to identify and correct the problem before analyzing the sample for a third time.

9.1.6 ICP Matrix Spiking. Spiked samples shall be prepared and analyzed daily to ensure that there are no matrix effects, that samples and standards have been matrix-matched, and that the laboratory equipment is operating properly.

9.1.6.1 Spiked sample recovery analyses should indicate a recovery for the Cr spike of between 75 and 125 percent.

9.1.6.2 Cr levels in the spiked sample should provide final solution concentrations that are within the linear portion of the calibration curve, as well as, at a concentration level at least: equal to that of the original sample; and, ten (10) times the detection limit.

9.1.6.3 If the spiked sample concentration meets the stated criteria but exceeds the linear calibration range, the spiked sample must be diluted with the field absorbing solution.

9.1.6.4 If the recoveries for the Cr spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.1.7 ICP Field Reagent Blank.

9.1.7.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.1.7.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before reanalyzing the samples.

9.2 GFAAS Quality Control.

9.2.1 GFAAS Calibration Reference Standards. The calibration curve must be verified by using at least one calibration reference standard (made from a reference material or other independent standard material) at or near the mid-range of the calibration curve.

9.2.1.1 The calibration curve must be validated before sample analyses are performed.

9.2.1.2 The calibration reference standard must be measured within 10 percent of its true value for the curve to be considered valid.

9.2.2 GFAAS Continuing Check Standard.

9.2.2.1 Perform analysis of the check standard with the field samples as described in Section 11.4 (at least after every 10 samples, and at the end of the analytical run).

9.2.2.2 These standards are analyzed, in part, to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the check standard may indicate that the graphite tube should be replaced.

9.2.2.3 The check standard may be either the mid-range calibration standard or the reference standard.

9.2.2.4 The results of the check standard shall agree within 10 percent of the expected value.

9.2.2.5 If not, terminate the analyses, correct the problem, recalibrate the instrument, and reanalyze all samples analyzed subsequent to the last acceptable check standard analysis.

9.2.3 GFAAS Calibration Blank.

9.2.3.1 Perform analysis of the calibration blank with the field samples as described in Section 11.4 (at least after every 10 samples, and at the end of the analytical run).

9.2.3.2 The calibration blank is analyzed to monitor the life and performance of the graphite tube as well as the existence of any memory effects. Lack of reproducibility or a significant change in the signal, may indicate that the graphite tube should be replaced.

9.2.3.3 The results of the calibration blank shall agree within three standard deviations of the mean blank value.

9.2.3.4 If not, analyze the calibration blank two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.2.4 GFAAS Duplicate Sample Analysis. Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.2.4.1 A digested aliquot of the selected sample is processed and analyzed using the identical procedures that were used for the whole sample preparation and analytical efforts.

9.2.4.2 Duplicate sample analyses results incorporating duplicate digestions shall agree within 20 percent for sample results exceeding ten (10) times the detection limit.

9.2.4.3 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value.

9.2.4.4 If agreement is not achieved, perform the duplicate analysis again. If agreement is not achieved the second time, perform corrective action to identify and correct the problem before analyzing the sample for a third time.

9.2.5 GFAAS Matrix Spiking.

9.2.5.1 Spiked samples shall be prepared and analyzed daily to ensure that (1) correct procedures are being followed, (2) there are no matrix effects and (3) all equipment is operating properly.

9.2.5.2 Cr spikes are added prior to any sample preparation.

9.2.5.3 Cr levels in the spiked sample should provide final solution concentrations that are within the linear portion of the calibration curve, as well as, at a concentration level at least: equal to that of the original sample; and, ten (10) times the detection limit.

9.2.5.4 Spiked sample recovery analyses should indicate a recovery for the Cr spike of between 75 and 125 percent.

9.2.5.5 If the recoveries for the Cr spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.2.6 GFAAS Method of Standard Additions.

9.2.6.1 Method of Standard Additions. Perform procedures in Section 5.4 of Method 12 (40 CFR Part 60, Appendix A)

9.2.6.2 Whenever sample matrix problems are suspected and standard/sample matrix matching is not possible or whenever a new sample matrix is being analyzed, perform referenced procedures to determine if the method of standard additions is necessary.

9.2.7 GFAAS Field Reagent Blank.

9.2.7.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.2.7.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before reanalyzing the samples.

9.3 IC/PCR Quality Control.

9.3.1 IC/PCR Calibration Reference Standards.

9.3.1.1 Prepare a calibration reference standard at a concentration that is at or near the mid-point of the calibration curve using the same alkaline matrix as the calibration standards. This reference standard should be prepared from a different Cr stock solution than that used to prepare the calibration curve standards. The reference standard is used to verify the accuracy of the calibration curve.

9.3.1.2 The curve must be validated before sample analyses are performed. Prior to sample analysis, analyze at least one reference standard with an expected value within the calibration range.

9.3.1.3 The results of this reference standard analysis must be within 10 percent of the true value of the reference standard for the calibration curve to be considered valid.

9.3.2 IC/PCR Continuing Check Standard and Calibration Blank.

9.3.2.1 Perform analysis of the check standard and the calibration blank with the field samples as described in Section 11.6 (at least after every 10 samples, and at the end of the analytical run).

9.3.2.2 The result from the check standard must be within 10 percent of the expected value.

9.3.2.3 If the 10 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses can be performed.

9.3.2.4 The results of the calibration blank analyses must agree within three standard deviations of the mean blank value.

9.3.2.5 If not, analyze the calibration blank two more times and average the results.

9.3.2.6 If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.3.3 IC/PCR Duplicate Sample Analysis.

9.3.3.1 Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.3.3.2 An aliquot of the selected sample is prepared and analyzed using procedures identical to those used for the emission samples (for example, filtration and/or, if necessary, preconcentration).

9.3.3.3 Duplicate sample injection results shall agree within 10 percent for sample results exceeding ten (10) times the detection limit.

9.3.3.4 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value.

9.3.3.5 If agreement is not achieved, perform the duplicate analysis again.

9.3.3.6 If agreement is not achieved the second time, perform corrective action to identify and correct the problem prior to analyzing the sample for a third time.

9.3.4 ICP/PCR Matrix Spiking. Spiked samples shall be prepared and analyzed with each sample set to ensure that there are no matrix effects, that samples and standards have been matrix-matched, and that the equipment is operating properly.

9.3.4.1 Spiked sample recovery analysis should indicate a recovery of the Cr^{+6} spike between 75 and 125 percent.

9.3.4.2 The spiked sample concentration should be within the linear portion of the calibration curve and should be equal to or greater than the concentration of the original sample. In addition, the spiked sample concentration should be at least ten (10) times the detection limit.

9.3.4.3 If the recoveries for the Cr^{+6} spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.3.5 IC/PCR Field Reagent Blank.

9.3.5.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.3.5.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before reanalyzing the samples.

10.0 Calibration and Standardization

10.1 Sampling Train Calibration. Perform calibrations described in Method 5, (40 CFR part 60, appendix A). The alternate calibration procedures described in Method 5, may also be used.

10.2 ICP Calibration.

10.2.1 Calibrate the instrument according to the instrument manufacturer's recommended procedures, using a calibration blank and three standards for the initial calibration.

10.2.2 Calibration standards should be prepared fresh daily, as described in Section

7.3.8. Be sure that samples and calibration standards are matrix matched. Flush the system with the calibration blank between each standard.

10.2.3 Use the average intensity of multiple exposures (3 or more) for both standardization and sample analysis to reduce random error.

10.2.4 Employing linear regression, calculate the correlation coefficient .

10.2.5 The correlation coefficient must equal or exceed 0.995.

10.2.6 If linearity is not acceptable, prepare and rerun another set of calibration standards or reduce the range of the calibration standards, as necessary.

10.3 GFAAS Calibration.

10.3.1 For instruments that measure directly in concentration, set the instrument software to display the correct concentration, if applicable.

10.3.2 Curve must be linear in order to correctly perform the method of standard additions which is customarily performed automatically with most instrument computer-based data systems.

10.3.3 The calibration curve (direct calibration or standard additions) must be prepared daily with a minimum of a calibration blank and three standards that are prepared fresh daily.

10.3.4 The calibration curve acceptance criteria must equal or exceed 0.995.

10.3.5 If linearity is not acceptable, prepare and rerun another set of calibration standards or reduce the range of calibration standards, as necessary.

10.4 IC/PCR Calibration.

10.4.1 Prepare a calibration curve using the calibration blank and three calibration standards prepared fresh daily as described in Section 7.3.8.

10.4.2 The calibration curve acceptance criteria must equal or exceed 0.995.

10.4.3 If linearity is not acceptable, remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

10.4.4 Analyze the standards with the field samples as described in Section 11.6.

11.0 Analytical Procedures

NOTE: The method determines the chromium concentration in µg Cr/mL. It is important that the analyst measure the field sample volume prior to analyzing the sample. This will allow for conversion of µg Cr/mL to µg Cr/sample.

11.1 ICP Sample Preparation.

11.1.1 The ICP analysis is performed directly on the alkaline impinger solution; acid digestion is not necessary, provided the samples and standards are matrix matched.

11.1.2 The ICP analysis should only be employed when the solution analyzed has a Cr concentration greater than 35 µg/L or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136 or by other commonly accepted analytical procedures.

11.2 ICP Sample Analysis.

11.2.1 The ICP analysis is applicable for the determination of total chromium only.

11.2.2 ICP Blanks. Two types of blanks are required for the ICP analysis.

11.2.2.1 Calibration Blank. The calibration blank is used in establishing the calibration curve. For the calibration blank, use either 0.1 N NaOH or 0.1 N $NaHCO_3$, whichever is used for the impinger absorbing solution. The calibration blank can be prepared fresh in the laboratory; it does not have to be prepared from the same batch of solution that was used in the field. A sufficient quantity should be prepared to flush the system between standards and samples.

11.2.2.2 Field Reagent Blank. The field reagent blank is collected in the field during the testing program. The field reagent blank (Section 8.2.4) is an aliquot of the absorbing solution prepared in Section 7.1.2. The reagent blank is used to assess possible contamination resulting from sample processing.

11.2.3 ICP Instrument Adjustment.

11.2.3.1 Adjust the ICP instrument for proper operating parameters including wavelength, background correction settings (if necessary), and interfering element correction settings (if necessary).

11.2.3.2 The instrument must be allowed to become thermally stable before beginning measurements (usually requiring at least 30 min of operation prior to calibration). During this warmup period, the optical calibration and torch position optimization may be performed (consult the operator's manual).

11.2.4 ICP Instrument Calibration.

11.2.4.1 Calibrate the instrument according to the instrument manufacturer's recommended procedures, and the procedures specified in Section 10.2.

11.2.4.2 Prior to analyzing the field samples, reanalyze the highest calibration standard as if it were a sample.

11.2.4.3 Concentration values obtained should not deviate from the actual values or from the established control limits by more than 5 percent, whichever is lower (see Sections 9.1 and 10.2).

11.2.4.4 If they do, follow the recommendations of the instrument manufacturer to correct the problem.

11.2.5 ICP Operational Quality Control Procedures.

11.2.5.1 Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample or standard.

11.2.5.2 Analyze the continuing check standard and the calibration blank after each batch of 10 samples.

11.2.5.3 Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

11.2.6 ICP Sample Dilution.

11.2.6.1 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive Cr wavelength for which quality control data have already been established.

11.2.6.2 When dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.2.7 Reporting Analytical Results. All analytical results should be reported in μg Cr/mL using three significant figures. Field sample volumes (mL) must be reported also.

11.3 GFAAS Sample Preparation.

11.3.1 GFAAS Acid Digestion. An acid digestion of the alkaline impinger solution is required for the GFAAS analysis.

11.3.1.1 In a beaker, add 10 mL of concentrated HNO_3 to a 100 mL sample aliquot that has been well mixed. Cover the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample to near dryness. Add another 5 mL of concentrated HNO_3 to complete the digestion. Again, carefully reflux the sample volume to near dryness. Rinse the beaker walls and watch glass with reagent water.

11.3.1.2 The final concentration of HNO_3 in the solution should be 1 percent (v/v).

11.3.1.3 Transfer the digested sample to a 50-mL volumetric flask. Add 0.5 mL of concentrated HNO_3 and 1 mL of the 10 μg/mL of $Ca(NO_3)_2$. Dilute to 50 mL with reagent water.

11.3.2 HNO_3 Concentration. A different final volume may be used based on the expected Cr concentration, but the HNO_3 concentration must be maintained at 1 percent (v/v).

11.4 GFAAS Sample Analysis.

11.4.1 The GFAAS analysis is applicable for the determination of total chromium only.

11.4.2 GFAAS Blanks. Two types of blanks are required for the GFAAS analysis.

11.4.2.1 Calibration Blank. The 1.0 percent HNO_3 is the calibration blank which is used in establishing the calibration curve.

11.4.2.2 Field Reagent Blank. An aliquot of the 0.1 N NaOH solution or the 0.1 N $NaHCO_3$ prepared in Section 7.1.2 is collected for the field reagent blank. The field reagent blank is used to assess possible contamination resulting from processing the sample.

11.4.2.2.1 The reagent blank must be subjected to the entire series of sample preparation and analytical procedures, including the acid digestion.

11.4.2.2.2 The reagent blank's final solution must contain the same acid concentration as the sample solutions.

11.4.3 GFAAS Instrument Adjustment.

11.4.3.1 The 357.9 nm wavelength line shall be used.

11.4.3.2 Follow the manufacturer's instructions for all other spectrophotometer operating parameters.

11.4.4 Furnace Operational Parameters. Parameters suggested by the manufacturer should be employed as guidelines.

11.4.4.1 Temperature-sensing mechanisms and temperature controllers can vary between instruments and/or with time; the validity of the furnace operating parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher-than-necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized.

11.4.4.2 Similar verification of furnace operating parameters may be required for complex sample matrices (consult instrument manual for additional information). Calibrate the GFAAS system following the procedures specified in Section 10.3.

11.4.5 GFAAS Operational Quality Control Procedures.

11.4.5.1 Introduce a measured aliquot of digested sample into the furnace and atomize.

11.4.5.2 If the measured concentration exceeds the calibration range, the sample should be diluted with the calibration blank solution (1.0 percent HNO_3) and reanalyzed.

11.4.5.3 Consult the operator's manual for suggested injection volumes. The use of multiple injections can improve accuracy and assist in detecting furnace pipetting errors.

11.4.5.4 Analyze a minimum of one matrix-matched reagent blank per sample batch to determine if contamination or any memory effects are occurring.

11.4.5.5 Analyze a calibration blank and a continuing check standard after approximately every batch of 10 sample injections.

11.4.6 GFAAS Sample Dilution.

11.4.6.1 Dilute and reanalyze samples that are more concentrated than the instrument calibration range.

11.4.6.2 If dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.4.7 Reporting Analytical Results.

11.4.7.1 Calculate the Cr concentrations by the method of standard additions (see operator's manual) or, from direct calibration. All dilution and/or concentration factors must be used when calculating the results.

11.4.7.2 Analytical results should be reported in μg Cr/mL using three significant figures. Field sample volumes (mL) must be reported also.

11.5 IC/PCR Sample Preparation.

11.5.1 Sample pH. Measure and record the sample pH prior to analysis.

11.5.2 Sample Filtration. Prior to preconcentration and/or analysis, filter all field samples through a 0.45-μm filter. The

filtration step should be conducted just prior to sample injection/analysis.

11.5.2.1 Use a portion of the sample to rinse the syringe filtration unit and acetate filter and then collect the required volume of filtrate.

11.5.2.2 Retain the filter if total Cr is to be determined also.

11.5.3 Sample Preconcentration (older instruments).

11.5.3.1 For older instruments, a preconcentration system may be used in conjunction with the IC/PCR to increase sensitivity for trace levels of Cr^{+6}.

11.5.3.2 The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent, followed by removal of the analyte from the absorbent (consult instrument manual).

11.5.3.3 For a manual system, position the injection valve so that the eluent displaces the concentrated Cr^{+6} sample, transferring it from the preconcentration column and onto the IC anion separation column.

11.6 IC/PCR Sample Analyses.

11.6.1 The IC/PCR analysis is applicable for hexavalent chromium measurements only.

11.6.2 IC/PCR Blanks. Two types of blanks are required for the IC/PCR analysis.

11.6.2.1 Calibration Blank. The calibration blank is used in establishing the analytical curve. For the calibration blank, use either 0.1 N NaOH or 0.1 N $NaHCO_3$, whichever is used for the impinger solution. The calibration blank can be prepared fresh in the laboratory; it does not have to be prepared from the same batch of absorbing solution that is used in the field.

11.6.2.2 Field Reagent Blank. An aliquot of the 0.1 N NaOH solution or the 0.1 N $NaHCO_3$ solution prepared in Section 7.1.2 is collected for the field reagent blank. The field reagent blank is used to assess possible contamination resulting from processing the sample.

11.6.3 Stabilized Baseline. Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent and post-column reagent flow rates according to the manufacturers recommendations.

NOTE: As long as the ratio of eluent flow rate to PCR flow rate remains constant, the standard curve should remain linear. Inject a sample of reagent water to ensure that no Cr^{+6} appears in the water blank.

11.6.4 Sample Injection Loop. Size of injection loop is based on standard/sample concentrations and the selected attenuator setting.

11.6.4.1 A 50-µL loop is normally sufficient for most higher concentrations.

11.6.4.2 The sample volume used to load the injection loop should be at least 10 times the loop size so that all tubing in contact with the sample is thoroughly flushed with the new sample to prevent cross contamination.

11.6.5 IC/PCR Instrument Calibration.

11.6.5.1 First, inject the calibration standards prepared, as described in Section 7.3.8 to correspond to the appropriate concentration range, starting with the lowest standard first.

11.6.5.2 Check the performance of the instrument and verify the calibration using data gathered from analyses of laboratory blanks, calibration standards, and a quality control sample.

11.6.5.3 Verify the calibration by analyzing a calibration reference standard. If the measured concentration exceeds the established value by more than 10 percent, perform a second analysis. If the measured concentration still exceeds the established value by more than 10 percent, terminate the analysis until the problem can be identified and corrected.

11.6.6 IC/PCR Instrument Operation.

11.6.6.1 Inject the calibration reference standard (as described in Section 9.3.1), followed by the field reagent blank (Section 8.2.4), and the field samples.

11.6.6.1.1 Standards (and QC standards) and samples are injected into the sample loop of the desired size (use a larger size loop for greater sensitivity). The Cr^{+6} is collected on the resin bed of the column.

11.6.6.1.2 After separation from other sample components, the Cr^{+6} forms a specific complex in the post-column reactor with the DPC reaction solution, and the complex is detected by visible absorbance at a maximum wavelength of 540 nm.

11.6.6.1.3 The amount of absorbance measured is proportional to the concentration of the Cr^{+6} complex formed.

11.6.6.1.4 The IC retention time and the absorbance of the Cr^{+6} complex with known Cr^{+6} standards analyzed under identical conditions must be compared to provide both qualitative and quantitative analyses.

11.6.6.1.5 If a sample peak appears near the expected retention time of the Cr^{+6} ion, spike the sample according to Section 9.3.4 to verify peak identity.

11.6.7 IC/PCR Operational Quality Control Procedures.

11.6.7.1 Samples should be at a pH ≥8.5 for NaOH and ≥8.0 if using $NaHCO_3$; document any discrepancies.

11.6.7.2 Refrigerated samples should be allowed to equilibrate to ambient temperature prior to preparation and analysis.

11.6.7.3 Repeat the injection of the calibration standards at the end of the analytical run to assess instrument drift. Measure areas or heights of the Cr^{+6}/DPC complex chromatogram peaks.

11.6.7.4 To ensure the precision of the sample injection (manual or autosampler), the response for the second set of injected

standards must be within 10 percent of the average response.

11.6.7.5 If the 10 percent criteria duplicate injection cannot be achieved, identify the source of the problem and rerun the calibration standards.

11.6.7.6 Use peak areas or peak heights from the injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentrations of the field samples.

11.6.8 IC/PCR Sample Dilution.

11.6.8.1 Samples having concentrations higher than the established calibration range must be diluted into the calibration range and re-analyzed.

11.6.8.2 If dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.6.9 Reporting Analytical Results. Results should be reported in µg Cr^{+6}/mL using three significant figures. Field sample volumes (mL) must be reported also.

12.0 Data Analysis and Calculations

12.1 Pretest Calculations.

12.1.1 Pretest Protocol (Site Test Plan).

12.1.1.1 The pretest protocol should define and address the test data quality objectives (DQOs), with all assumptions, that will be required by the end user (enforcement authority); what data are needed? why are the data needed? how will the data be used? what are method detection limits? and what are estimated target analyte levels for the following test parameters.

12.1.1.1.1 Estimated source concentration for total chromium and/or Cr^{+6}.

12.1.1.1.2 Estimated minimum sampling time and/or volume required to meet method detection limit requirements (Appendix B 40 CFR Part 136) for measurement of total chromium and/or Cr^{+6}.

12.1.1.1.3 Demonstrate that planned sampling parameters will meet DQOs. The protocol must demonstrate that the planned sampling parameters calculated by the tester will meet the needs of the source and the enforcement authority.

12.1.1.2 The pre-test protocol should include information on equipment, logistics, personnel, process operation, and other resources necessary for an efficient and coordinated test.

12.1.1.3 At a minimum, the pre-test protocol should identify and be approved by the source, the tester, the analytical laboratory, and the regulatory enforcement authority. The tester should not proceed with the compliance testing before obtaining approval from the enforcement authority.

12.1.2 Post Test Calculations.

12.1.2.1 Perform the calculations, retaining one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1.2.2 Nomenclature.

C_S = Concentration of Cr in sample solution, µg Cr/mL.

C_{cc} = Concentration of Cr in stack gas, dry basis, corrected to standard conditions, mg/dscm.

D = Digestion factor, dimension less.

F = Dilution factor, dimension less.

M_{Cr} = Total Cr in each sample, µg.

V_{ad} = Volume of sample aliquot after digestion, mL.

V_{af} = Volume of sample aliquot after dilution, mL.

V_{bd} = Volume of sample aliquot submitted to digestion, mL.

V_{bf} = Volume of sample aliquot before dilution, mL.

V_{soln} = Volume of impinger contents plus rinses, mL.

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

12.1.2.3 Dilution Factor. The dilution factor is the ratio of the volume of sample aliquot after dilution to the volume before dilution. This ratio is given by the following equation:

$$F = \frac{V_{af}}{V_{bf}} \quad \text{Eq. 306-1}$$

12.1.2.4 Digestion Factor. The digestion factor is the ratio of the volume of sample aliquot after digestion to the volume before digestion. This ratio is given by Equation 306–2.

$$D = \frac{V_{ad}}{V_{bd}} \quad \text{Eq. 306-2}$$

12.1.2.5 Total Cr in Sample. Calculate MCr, the total µg Cr in each sample, using the following equation:

$$M_{cr} = V_{mL} \times C_S \times F \times D \qquad \text{Eq. 306-3}$$

12.1.2.6 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. Same as Method 5.

12.1.2.7 Dry Gas Volume, Volume of Water Vapor, Moisture Content. Same as Method 5.

12.1.2.8 Cr Emission Concentration (C_{Cr}). Calculate C_{Cr}, the Cr concentration in the stack gas, in mg/dscm on a dry basis, corrected to standard conditions using the following equation:

$$C_{Cr} = \frac{M_{Cr}}{V_{m(std)}} \times 10^{-3} \frac{mg}{\mu g} \qquad \text{Eq. 306-4}$$

12.1.2.9 Isokinetic Variation, Acceptable Results. Same as Method 5.

13.0 Method Performance

13.1 Range. The recommended working range for all of the three analytical techniques starts at five times the analytical detection limit (see also Section 13.2.2). The upper limit of all three techniques can be extended indefinitely by appropriate dilution.

13.2 Sensitivity.

13.2.1 Analytical Sensitivity. The estimated instrumental detection limits listed are provided as a guide for an instrumental limit. The actual method detection limits are sample and instrument dependent and may vary as the sample matrix varies.

13.2.1.2 ICP Analytical Sensitivity. The minimum estimated detection limits for ICP, as reported in Method 6010A and the recently revised Method 6010B of SW–846 (Reference 1), are 7.0 µg Cr/L and 4.7 µg Cr/L, respectively.

13.2.1.3 GFAAS Analytical Sensitivity. The minimum estimated detection limit for GFAAS, as reported in Methods 7000A and 7191 of SW–846 (Reference 1), is 1 µg Cr/L.

13.2.1.4 IC/PCR Analytical Sensitivity. The minimum detection limit for IC/PCR with a preconcentrator, as reported in Methods 0061 and 7199 of SW–846 (Reference 1), is 0.05 µg Cr^{+6}/L.

1.3.2.1.5 Determination of Detection Limits. The laboratory performing the Cr^{+6} measurements must determine the method detection limit on a quarterly basis using a suitable procedure such as that found in 40 CFR, Part 136, Appendix B. The determination should be made on samples in the appropriate alkaline matrix. Normally this involves the preparation (if applicable) and consecutive measurement of seven (7) separate aliquots of a sample with a concentration <5 times the expected detection limit. The detection limit is 3.14 times the standard deviation of these results.

13.2.2 In-stack Sensitivity. The in-stack sensitivity depends upon the analytical detection limit, the volume of stack gas sampled, the total volume of the impinger absorbing solution plus the rinses, and, in some cases, dilution or concentration factors from sample preparation. Using the analytical detection limits given in Sections 13.2.1.1, 13.2.1.2, and 13.2.1.3; a stack gas sample volume of 1.7 dscm; a total liquid sample volume of 500 mL; and the digestion concentration factor of ½ for the GFAAS analysis; the corresponding in-stack detection limits are 0.0014 mg Cr/dscm to 0.0021 mg Cr/dscm for ICP, 0.00015 mg Cr/dscm for GFAAS, and 0.000015 mg Cr^{+6}/dscm for IC/PCR with preconcentration.

NOTE: It is recommended that the concentration of Cr in the analytical solutions be at least five times the analytical detection limit to optimize sensitivity in the analyses. Using this guideline and the same assumptions for impinger sample volume, stack gas sample volume, and the digestion concentration factor for the GFAAS analysis (500 mL,1.7 dscm, and 1/2, respectively), the recommended minimum stack concentrations for optimum sensitivity are 0.0068 mg Cr/dscm to 0.0103 mg Cr/dscm for ICP, 0.00074 mg Cr/dscm for GFAAS, and 0.000074 mg Cr^{+6}/dscm for IC/PCR with preconcentration. If required, the in-stack detection limits can be improved by either increasing the stack gas sample volume, further reducing the volume of the digested sample for GFAAS, improving the analytical detection limits, or any combination of the three.

13.3 Precision.

13.3.1 The following precision data have been reported for the three analytical methods. In each case, when the sampling precision is combined with the reported analytical precision, the resulting overall precision may decrease.

13.3.2 Bias data is also reported for GFAAS.

13.4 ICP Precision.

13.4.1 As reported in Method 6010B of SW–846 (Reference 1), in an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid/distilled water matrices that had been spiked with various metal concentrates. For true values of 10, 50, and 150 μg Cr/L; the mean reported values were 10, 50, and 149 μg Cr/L; and the mean percent relative standard deviations were 18, 3.3, and 3.8 percent, respectively.

13.4.2 In another multi laboratory study cited in Method 6010B, a mean relative standard of 8.2 percent was reported for an aqueous sample concentration of approximately 3750 μg Cr/L.

13.5 GFAAS Precision. As reported in Method 7191 of SW–846 (Reference 1), in a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 μg Cr/L, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97 percent, 101 percent, and 102 percent, respectively.

13.6 IC/PCR Precision. As reported in Methods 0061 and 7199 of SW–846 (Reference 1), the precision of IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 μg/dscm of total Cr was 25 percent and 9 percent, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of C^{+6} the precision was 20 percent.

14.0 Pollution Prevention

14.1 The only materials used in this method that could be considered pollutants are the chromium standards used for instrument calibration and acids used in the cleaning of the collection and measurement containers/labware, in the preparation of standards, and in the acid digestion of samples. Both reagents can be stored in the same waste container.

14.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

14.3 To the extent possible, the containers/vessels used to collect and prepare samples should be cleaned and reused to minimize the generation of solid waste.

15.0 Waste Management

15.1 It is the responsibility of the laboratory and the sampling team to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

15.2 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better—Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW–846, Third Edition," as amended by Updates I, II, IIA, IIB, and III. Document No. 955–001–000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

2. Cox, X.B., R.W. Linton, and F.E. Butler. Determination of Chromium Speciation in Environmental Particles—A Multi-technique Study of Ferrochrome Smelter Dust. Accepted for publication in Environmental Science and Technology.

3. Same as Section 17.0 of Method 5, References 2, 3, 4, 5, and 7.

4. California Air Resources Board, "Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources." Method 425, September 12, 1990.

5. *The Merck Index*. Eleventh Edition. Merck & Co., Inc., 1989.

6. Walpole, R.E., and R.H. Myers. "Probability and Statistics for Scientists and Engineering." 3rd Edition. MacMillan Publishing Co., NewYork, N.Y., 1985.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

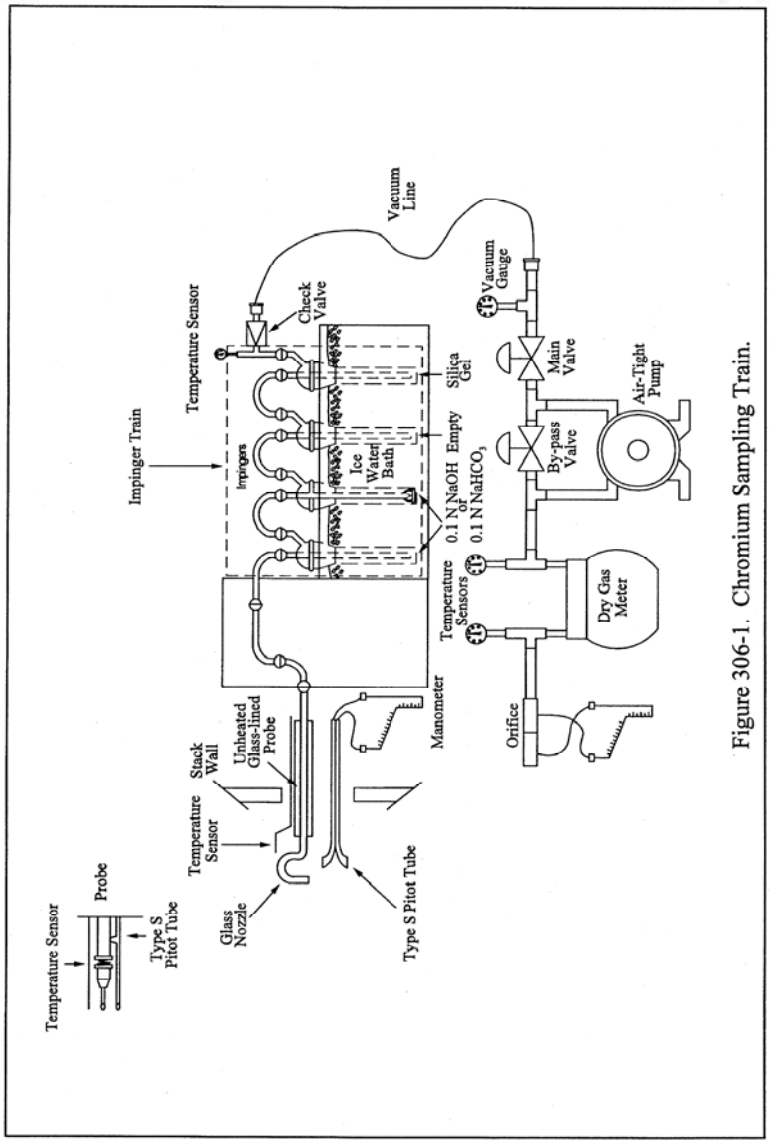


Figure 306-1. Chromium Sampling Train.

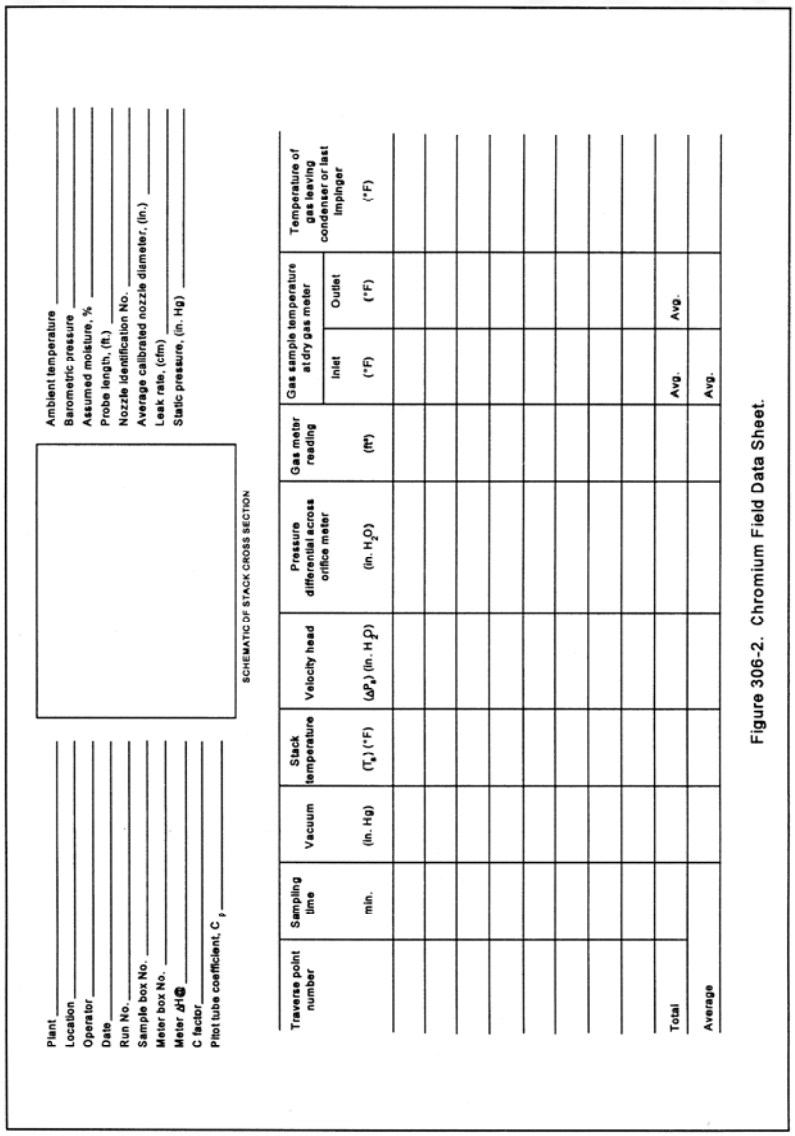


Figure 306-2. Chromium Field Data Sheet.

METHOD 306A—DETERMINATION OF CHROMIUM EMISSIONS FROM DECORATIVE AND HARD CHROMIUM ELECTROPLATING AND CHROMIUM ANODIZING OPERATIONS

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 40 CFR Part 60, Appendix A and in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306.

1.0 Scope and Application

1.1 Analyte. Chromium. CAS Number (7440–47–3).

1.2 Applicability.

1.2.1 This method applies to the determination of chromium (Cr) in emissions from decorative and hard chromium electroplating facilities, chromium anodizing operations, and continuous chromium plating at iron and steel facilities. The method is less expensive and less complex to conduct than Method 306. Correctly applied, the precision and bias of the sample results should be comparable to those obtained with the isokinetic Method 306. This method is applicable for the determination of air emissions under nominal ambient moisture, temperature, and pressure conditions.

1.2.2 The method is also applicable to electroplating and anodizing sources controlled by wet scrubbers.

1.3 Data Quality Objectives.

1.3.1 Pretest Protocol.

1.3.1.1 The pretest protocol should define and address the test data quality objectives (DQOs), with all assumptions, that will be required by the end user (enforcement authority); what data are needed? why are the data needed? how will data be used? what are method detection limits? and what are estimated target analyte levels for the following test parameters.

1.3.1.1.1 Estimated source concentration for total chromium and/or Cr^{+6}.

1.3.1.1.2 Estimated minimum sampling time and/or volume required to meet method detection limit requirements (Appendix B 40 CFR Part 136) for measurement of total chromium and/or Cr^{+6}.

1.3.1.1.3 Demonstrate that planned sampling parameters will meet DQOs. The protocol must demonstrate that the planned sampling parameters calculated by the tester will meet the needs of the source and the enforcement authority.

1.3.1.2 The pre-test protocol should include information on equipment, logistics, personnel, process operation, and other resources necessary for an efficient and coordinated performance test.

1.3.1.3 At a minimum, the pre-test protocol should identify and be approved by the source, the tester, the analytical laboratory, and the regulatory enforcement authority. The tester should not proceed with the compliance testing before obtaining approval from the enforcement authority.

2.0 Summary of Method

2.1 Sampling.

2.1.1 An emission sample is extracted from the source at a constant sampling rate determined by a critical orifice and collected in a sampling train composed of a probe and impingers. The proportional sampling time at the cross sectional traverse points is varied according to the stack gas velocity at each point. The total sample time must be at least two hours.

2.1.2 The chromium emission concentration is determined by the same analytical procedures described in Method 306: inductively-coupled plasma emission spectrometry (ICP), graphite furnace atomic absorption spectrometry (GFAAS), or ion chromatography with a post-column reactor (IC/PCR).

2.1.2.1 Total chromium samples with high chromium concentrations (≥35 μg/L) may be analyzed using inductively coupled plasma emission spectrometry (ICP) at 267.72 nm.

NOTE: The ICP analysis is applicable for this method only when the solution analyzed has a Cr concentration greater than or equal to 35 μg/L or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136.

2.1.2.2 Alternatively, when lower total chromium concentrations (<35 μg/L) are encountered, a portion of the alkaline sample solution may be digested with nitric acid and analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) at 357.9 nm.

2.1.2.3 If it is desirable to determine hexavalent chromium (Cr^{+6}) emissions, the samples may be analyzed using an ion chromatograph equipped with a post-column reactor (IC/PCR) and a visible wavelength detector. To increase sensitivity for trace levels of Cr^{+6}, a preconcentration system may be used in conjunction with the IC/PCR.

3.0 Definitions

3.1 *Total Chromium*—measured chromium content that includes both major chromium oxidation states (Cr + 3, Cr + 6).

3.2 *May*—Implies an optional operation.

3.3 *Digestion*—The analytical operation involving the complete (or nearly complete) dissolution of the sample in order to ensure the complete solubilization of the element (analyte) to be measured.

3.4 *Interferences*—Physical, chemical, or spectral phenomena that may produce a high or low bias in the analytical result.

3.5 *Analytical System*—All components of the analytical process including the sample digestion and measurement apparatus.

3.6 *Sample Recovery*—The quantitative transfer of sample from the collection apparatus to the sample preparation (digestion, etc.) apparatus. This term should not be confused with analytical recovery.

4.0 Interferences

4.1 Same as in Method 306, Section 4.0.

5.0 Safety

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

5.2 Chromium and some chromium compounds have been listed as carcinogens although Chromium (III) compounds show little or no toxicity. Chromium is a skin and respiratory irritant.

6.0 Equipment and Supplies

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

6.1 Sampling Train. A schematic of the sampling train is shown in Figure 306A–1. The individual components of the train are available commercially, however, some fabrication and assembly are required.

6.1.1 Probe Nozzle/Tubing and Sheath.

6.1.1.1 Use approximately 6.4-mm (¼-in.) inside diameter (ID) glass or rigid plastic tubing approximately 20 cm (8 in.) in length with a short 90 degree bend at one end to form the sampling nozzle. Grind a slight taper on the nozzle end before making the bend. Attach the nozzle to flexible tubing of sufficient length to enable collection of a sample from the stack.

6.1.1.2 Use a straight piece of larger diameter rigid tubing (such as metal conduit or plastic water pipe) to form a sheath that begins about 2.5 cm (1 in.) from the 90 ° bend on the nozzle and encases and supports the flexible tubing.

6.1.2 Type S Pitot Tube. Same as Method 2, Section 6.1 (40 CFR Part 60, Appendix A).

6.1.3 Temperature Sensor.

6.1.3.1 A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other sensor capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature.

6.1.3.2 The temperature sensor shall either be positioned near the center of the stack, or be attached to the pitot tube as directed in Section 6.3 of Method 2.

6.1.4 Sample Train Connectors.

6.1.4.1 Use thick wall flexible plastic tubing (polyethylene, polypropylene, or polyvinyl chloride) – 6.4-mm (¼-in.) to 9.5-mm (⅜-in.) ID to connect the train components.

6.1.4.2 A combination of rigid plastic tubing and thin wall flexible tubing may be used as long as tubing walls do not collapse when leak-checking the train. Metal tubing cannot be used.

6.1.5 Impingers. Three, one-quart capacity, glass canning jars with vacuum seal lids, or three Greenburg-Smith (GS) design impingers connected in series, or equivalent, may be used.

6.1.5.1 One-quart glass canning jar. Three separate jar containers are required: (1) the first jar contains the absorbing solution; (2) the second is empty and is used to collect any reagent carried over from the first container; and (3) the third contains the desiccant drying agent.

6.1.5.2 Canning Jar Connectors. The jar containers are connected by leak-tight inlet and outlet tubes installed in the lids of each container for assembly with the train. The tubes may be made of – 6.4 mm (¼-in.) ID glass or rigid plastic tubing. For the inlet tube of the first impinger, heat the glass or plastic tubing and draw until the tubing separates. Fabricate the necked tip to form an orifice tip that is approximately 2.4 mm (3⁄32-in.) ID.

6.1.5.2.1 When assembling the first container, place the orifice tip end of the tube approximately 4.8 mm (3⁄16-in.) above the inside bottom of the jar.

6.1.5.2.2 For the second container, the inlet tube need not be drawn and sized, but the tip should be approximately 25 mm (1 in.) above the bottom of the jar.

6.1.5.2.3 The inlet tube of the third container should extend to approximately 12.7 mm (½-in.) above the bottom of the jar.

6.1.5.2.4 Extend the outlet tube for each container approximately 50 mm (2 in.) above the jar lid and downward through the lid, approximately 12.7 mm (½-in.) beneath the bottom of the lid.

6.1.5.3 Greenburg-Smith Impingers. Three separate impingers of the Greenburg-Smith (GS) design as described in Section 6.0 of Method 5 are required. The first GS impinger shall have a standard tip (orifice/plate), and the second and third GS impingers shall be modified by replacing the orifice/plate tube with a 13 mm (½-in.) ID glass tube, having an unrestricted opening located 13 mm (½-in.) from the bottom of the outer flask.

6.1.5.4 Greenburg-Smith Connectors. The GS impingers shall be connected by leak-free ground glass "U" tube connectors or by leak-free non-contaminating flexible tubing. The first impinger shall contain the absorbing solution, the second is empty and the third contains the desiccant drying agent.

6.1.6 Manometer. Inclined/vertical type, or equivalent device, as described in Section 6.2 of Method 2 (40 CFR Part 60, Appendix A).

6.1.7 Critical Orifice. The critical orifice is a small restriction in the sample line that is located upstream of the vacuum pump. The orifice produces a constant sampling flow rate that is approximately 0.021 cubic meters per minute (m^3/min) or 0.75 cubic feet per minute (cfm).

6.1.7.1 The critical orifice can be constructed by sealing a 2.4-mm (3⁄32-in.) ID brass tube approximately 14.3 mm (9⁄16-in.) in length inside a second brass tube that is approximately 8 mm (5⁄16-in.) ID and 14.3-mm (9⁄16-in.) in length .

6.1.7.2 Materials other than brass can be used to construct the critical orifice as long as the flow through the sampling train can be maintained at approximately 0.021 cubic meter per minute (0.75) cfm.

6.1.8 Connecting Hardware. Standard pipe and fittings, 9.5-mm (⅜-in.), 6.4-mm (¼-in.)

or 3.2-mm (⅛-in.) ID, may be used to assemble the vacuum pump, dry gas meter and other sampling train components.

6.1.9 Vacuum Gauge. Capable of measuring approximately 760 mm H_g (30 in. H_g) vacuum in 25.4 mm H_G (1 in. H_g) increments. Locate vacuum gauge between the critical orifice and the vacuum pump.

6.1.10 Pump Oiler. A glass oil reservoir with a wick mounted at the vacuum pump inlet that lubricates the pump vanes. The oiler should be an in-line type and not vented to the atmosphere. See EMTIC Guideline Document No. GD-041.WPD for additional information.

6.1.11 Vacuum Pump. Gast Model 0522–V103–G18DX, or equivalent, capable of delivering at least 1.5 cfm at 15 in. H_g vacuum.

6.1.12 Oil Trap/Muffler. An empty glass oil reservoir without wick mounted at the pump outlet to control the pump noise and prevent oil from reaching the dry gas meter.

6.1.13 By-pass Fine Adjust Valve (Optional). Needle valve assembly 6.4-mm (¼-in.), Whitey 1 RF 4–A, or equivalent, that allows for adjustment of the train vacuum.

6.1.13.1 A fine-adjustment valve is positioned in the optional pump by-pass system that allows the gas flow to recirculate through the pump. This by-pass system allows the tester to control/reduce the maximum leak-check vacuum pressure produced by the pump.

6.1.13.1.1 The tester must conduct the post test leak check at a vacuum equal to or greater than the maximum vacuum encountered during the sampling run.

6.1.13.1.2 The pump by-pass assembly is not required, but is recommended if the tester intends to leak-check the 306A train at the vacuum experienced during a run.

6.1.14 Dry Gas Meter. An Equimeter Model 110 test meter or, equivalent with temperature sensor(s) installed (inlet/outlet) to monitor the meter temperature. If only one temperature sensor is installed, locate the sensor at the outlet side of the meter. The dry gas meter must be capable of measuring the gaseous volume to within ±2% of the true volume.

NOTE: The Method 306 sampling train is also commercially available and may be used to perform the Method 306A tests. The sampling train may be assembled as specified in Method 306A with the sampling rate being operated at the delta $H_@$ specified for the calibrated orifice located in the meter box. The Method 306 train is then operated as described in Method 306A.

6.2 Barometer. Mercury aneroid barometer, or other barometer equivalent, capable of measuring atmospheric pressure to within ±2.5 mm H_g (0.1 in. H_g).

6.2.1 A preliminary check of the barometer shall be made against a mercury-in-glass reference barometer or its equivalent.

6.2.2 Tester may elect to obtain the absolute barometric pressure from a nearby National Weather Service station.

6.2.2.1 The station value (which is the absolute barometric pressure) must be adjusted for elevation differences between the weather station and the sampling location. Either subtract 2.5 mm H_g (0.1 in. H_g) from the station value per 30 m (100 ft) of elevation increase or add the same for an elevation decrease.

6.2.2.2 If the field barometer cannot be adjusted to agree within 0.1 in. H_g of the reference barometric, repair or discard the unit. The barometer pressure measurement shall be recorded on the sampling data sheet.

6.3 Sample Recovery. Same as Method 5, Section 6.2 (40 CFR Part 60, Appendix A), with the following exceptions:

6.3.1 Probe-Liner and Probe-Nozzle Brushes. Brushes are not necessary for sample recovery. If a probe brush is used, it must be non-metallic.

6.3.2 Wash Bottles. Polyethylene wash bottle, for sample recovery absorbing solution.

6.3.3 Sample Recovery Solution. Use 0.1 N NaOH or 0.1 N $NaHCO_3$, whichever is used as the impinger absorbing solution, to replace the acetone.

6.3.4 Sample Storage Containers.

6.3.4.1 Glass Canning Jar. The first canning jar container of the sampling train may serve as the sample shipping container. A new lid and sealing plastic wrap shall be substituted for the container lid assembly.

6.3.4.2 Polyethylene or Glass Containers. Transfer the Greenburg-Smith impinger contents to precleaned polyethylene or glass containers. The samples shall be stored and shipped in 250-mL, 500-mL or 1000-mL polyethylene or glass containers with leak-free, non metal screw caps.

6.3.5 pH Indicator Strip, for Cr^{+6} Samples. pH indicator strips, or equivalent, capable of determining the pH of solutions between the range of 7 and 12, at 0.5 pH increments.

6.3.6 Plastic Storage Containers. Air tight containers to store silica gel.

6.4 Analysis. Same as Method 306, Section 6.3.

7.0 Reagents and Standards.

NOTE: Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). Where such specifications are not available, use the best available grade. It is recommended, but not required, that reagents be checked by the appropriate analysis prior to field use to assure that contamination is below the analytical detection limit for the ICP or GFAAS total chromium analysis; and that contamination is below the analytical detection limit for

Cr^{+6} using IC/PCR for direct injection or, if selected, preconcentration.

7.1 Sampling.

7.1.1 Water. Reagent water that conforms to ASTM Specification D1193 Type II (incorporated by reference see §63.14). All references to water in the method refer to reagent water unless otherwise specified. It is recommended that water blanks be checked prior to preparing the sampling reagents to ensure that the Cr content is less than three (3) times the anticipated detection limit of the analytical method.

7.1.2 Sodium Hydroxide (NaOH) Absorbing Solution, 0.1 N. Dissolve 4.0 g of sodium hydroxide in 1 liter of water to obtain a pH of approximately 8.5.

7.1.3 Sodium Bicarbonate ($NaHCO_3$) Absorbing Solution, 0.1 N. Dissolve approximately 8.5 g of sodium bicarbonate in 1 liter of water to obtain a pH of approximately 8.3.

7.1.4 Chromium Contamination.

7.1.4.1 The absorbing solution shall not exceed the QC criteria noted in Method 306, Section 7.1.1 (≤3 times the instrument detection limit).

7.1.4.2 When the Cr^{+6} content in the field samples exceeds the blank concentration by at least a factor of ten (10), Cr^{+6} blank levels ≤10 times the detection limit will be allowed.

NOTE: At sources with high concentrations of acids and/or SO_2, the concentration of NaOH or $NaHCO_3$ should be ≥0.5 N to insure that the pH of the solution remains at or above 8.5 for NaOH and 8.0 for $NaHCO_3$ during and after sampling.

7.1.3 Desiccant. Silica Gel, 6–16 mesh, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.2 Sample Recovery. Same as Method 306, Section 7.2.

7.3 Sample Preparation and Analysis. Same as Method 306, Section 7.3.

7.4 Glassware Cleaning Reagents. Same as Method 306, Section 7.4.

8.0 Sample Collection, Recovery, Preservation, Holding Times, Storage, and Transport

NOTE: Prior to sample collection, consideration should be given as to the type of analysis (Cr^{+6} or total Cr) that will be performed. Deciding which analysis will be performed will enable the tester to determine which appropriate sample recovery and storage procedures will be required to process the sample.

8.1 Sample Collection.

8.1.1 Pretest Preparation.

8.1.1.1 Selection of Measurement Site. Locate the sampling ports as specified in Section 11.0 of Method 1 (40 CFR Part 60, Appendix A).

8.1.1.2 Location of Traverse Points.

8.1.1.2.1 Locate the traverse points as specified in Section 11.0 of Method 1 (40 CFR Part 60, Appendix A). Use a total of 24 sampling points for round ducts and 24 or 25 points for rectangular ducts. Mark the pitot and sampling probe to identify the sample traversing points.

8.1.1.2.2 For round ducts less than 12 inches in diameter, use a total of 16 points.

8.1.1.3 Velocity Pressure Traverse. Perform an initial velocity traverse before obtaining samples. The Figure 306A–2 data sheet may be used to record velocity traverse data.

8.1.1.3.1 To demonstrate that the flow rate is constant over several days of testing, perform complete traverses at the beginning and end of each day's test effort, and calculate the deviation of the flow rate for each daily period. The beginning and end flow rates are considered constant if the deviation does not exceed 10 percent. If the flow rate exceeds the 10 percent criteria, either correct the inconsistent flow rate problem, or obtain the Administrator's approval for the test results.

8.1.1.3.2 Perform traverses as specified in Section 8.0 of Method 2, but record only the Δp (velocity pressure) values for each sampling point. If a mass emission rate is desired, stack velocity pressures shall be recorded before and after each test, and an average stack velocity pressure determined for the testing period.

8.1.1.4 Verification of Absence of Cyclonic Flow. Check for cyclonic flow during the initial traverse to verify that it does not exist. Perform the cyclonic flow check as specified in Section 11.4 of Method 1 (40 CFR Part 60, Appendix A).

8.1.1.4.1 If cyclonic flow is present, verify that the absolute average angle of the tangential flow does not exceed 20 degrees. If the average value exceeds 20 degrees at the sampling location, the flow condition in the stack is unacceptable for testing.

8.1.1.4.2 Alternative procedures, subject to approval of the Administrator, *e.g.*, installing straightening vanes to eliminate the cyclonic flow, must be implemented prior to conducting the testing.

8.1.1.5 Stack Gas Moisture Measurements. *Not required.* Measuring the moisture content is optional when a mass emission rate is to be calculated.

8.1.1.5.1 The tester may elect to either measure the actual stack gas moisture during the sampling run or utilize a nominal moisture value of 2 percent.

8.1.1.5.2 For additional information on determining sampling train moisture, please refer to Method 4 (40 CFR Part 60, Appendix A).

8.1.1.6 Stack Temperature Measurements. If a mass emission rate is to be calculated, a temperature sensor must be placed either near the center of the stack, or attached to the pitot tube as described in Section 8.3 of Method 2. Stack temperature measurements,

shall be recorded before and after each test, and an average stack temperature determined for the testing period.

8.1.1.7 Point Sampling Times. Since the sampling rate of the train (0.75 cfm) is maintained constant by the critical orifice, it is necessary to calculate specific sampling times for each traverse point in order to obtain a proportional sample.

8.1.1.7.1 If the sampling period (3 runs) is to be completed in a single day, the point sampling times shall be calculated only once.

8.1.1.7.2 If the sampling period is to occur over several days, the sampling times must be calculated daily using the initial velocity pressure data recorded for that day. Determine the average of the Δp values obtained during the velocity traverse (Figure 306A–2).

8.1.1.7.3 If the stack diameter is less than 12 inches, use 7.5 minutes in place of 5 minutes in the equation and 16 sampling points instead of 24 or 25 points. Calculate the sampling times for each traverse point using the following equation:

$$\text{Minutes at point n} = \frac{\sqrt{\Delta p \text{ at Point n}}}{\left(\sqrt{\Delta p}\right)_{avg}} \times 5 \text{ min.} \qquad \text{Eq. 306A-1}$$

Where:

n = Sampling point number.

Δp = Average pressure differential across pitot tube, mm H_2O (in. H_2O).

ΔP_{avg} = Average of Δp values, mm H_2O (in. H_2O).

NOTE: Convert the decimal fractions for minutes to seconds.

8.1.1.8 Pretest Preparation. It is recommended, but not required, that all items which will be in contact with the sample be cleaned prior to performing the testing to avoid possible sample contamination (positive chromium bias). These items include, but are not limited to: Sampling probe, connecting tubing, impingers, and jar containers.

8.1.1.8.1 Sample train components should be: (1) Rinsed with hot tap water; (2) washed with hot soapy water; (3) rinsed with tap water; (4) rinsed with reagent water; (5) soaked in a 10 percent (v/v) nitric acid solution for at least four hours; and (6) rinsed throughly with reagent water before use.

8.1.1.8.2 At a minimum, the tester should, rinse the probe, connecting tubing, and first and second impingers twice with either 0.1 N sodium hydroxide (NaOH) or 0.1 N sodium bicarbonate ($NaHCO_3$) and discard the rinse solution.

8.1.1.8.3 If separate sample shipping containers are to be used, these also should be precleaned using the specified cleaning procedures.

8.1.1.9 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 306A–1. Secure the nozzle-liner assembly to the outer sheath to prevent movement when sampling.

8.1.1.9.1 Place 250 mL of 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution into the first jar container or impinger. The second jar/impinger is to remain empty. Place 6 to 16 mesh indicating silica gel, or equivalent desiccant into the third jar/impinger until the container is half full (~ 300 to 400 g).

8.1.1.9.2 Place a small cotton ball in the outlet exit tube of the third jar to collect small silica gel particles that may dislodge and impair the pump and/or gas meter.

8.1.1.10 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedures shall be performed: (1) Place the jar/impinger containers into an ice bath and wait 10 minutes for the ice to cool the containers before performing the leak check and/or start sampling; (2) to perform the leak check, seal the nozzle using a piece of clear plastic wrap placed over the end of a finger and switch on the pump; and (3) the train system leak rate should not exceed 0.02 cfm at a vacuum of 380 mm Hg (15 in. Hg) or greater. If the leak rate does exceed the 0.02 cfm requirement, identify and repair the leak area and perform the leak check again.

NOTE: Use caution when releasing the vacuum following the leak check. Always allow air to slowly flow through the nozzle end of the train system while the pump is still operating. Switching off the pump with vacuum on the system may result in the silica gel being pulled into the second jar container.

8.1.1.11 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., jar container) exchange becomes necessary, a leak-check shall be conducted *immediately before* the component exchange is made. The leak-check shall be performed according to the procedure outlined in Section 8.1.1.10 of this method. If the leakage rate is found to be ≤0.02 cfm at the maximum operating vacuum, the results are acceptable. If,

however, a higher leak rate is obtained, either record the leakage rate and correct the sample volume as shown in Section 12.3 of Method 5 or void the sample and initiate a replacement run. Following the component change, leak-checks are optional, but are recommended as are the pretest leak-checks.

8.1.1.12 Post Test Leak Check. Remove the probe assembly and flexible tubing from the first jar/impinger container. Seal the inlet tube of the first container using clear plastic wrap and switch on the pump. The vacuum in the line between the pump and the critical orifice must be ≥15 in. Hg. Record the vacuum gauge measurement along with the leak rate observed on the train system.

8.1.1.12.1 If the leak rate does not exceed 0.02 cfm, the results are acceptable and no sample volume correction is necessary.

8.1.1.12.2 If, however, a higher leak rate is obtained (>0.02 cfm), the tester shall either record the leakage rate and correct the sample volume as shown in Section 12.3 of Method 5, or void the sampling run and initiate a replacement run. After completing the leak-check, slowly release the vacuum at the first container while the pump is still operating. Afterwards, switch-off the pump.

8.1.2 Sample Train Operation.

8.1.2.1 Data Recording. Record all pertinent process and sampling data on the data sheet (see Figure 306A–3). Ensure that the process operation is suitable for sample collection.

8.1.2.2 Starting the Test. Place the probe/nozzle into the duct at the first sampling point and switch on the pump. Start the sampling using the time interval calculated for the first point. When the first point sampling time has been completed, move to the second point and continue to sample for the time interval calculated for that point; sample each point on the traverse in this manner. Maintain ice around the sample containers during the run.

8.1.2.3 Critical Flow. The sample line between the critical orifice and the pump must operate at a vacuum of ≥380 mm Hg (≥15 in. Hg) in order for critical flow to be maintained. This vacuum must be monitored and documented using the vacuum gauge located between the critical orifice and the pump.

NOTE: Theoretically, critical flow for air occurs when the ratio of the orifice outlet absolute pressure to the orifice inlet absolute pressure is less than a factor of 0.53. This means that the system vacuum should be at least ≥356 mm Hg (≥14 in. Hg) at sea level and ~ 305 mm Hg (~ 12 in. Hg) at higher elevations.

8.1.2.4 Completion of Test.

8.1.2.4.1 Circular Stacks. Complete the first port traverse and switch off the pump. Testers may opt to perform a leak-check between the port changes to verify the leak rate however, this is not mandatory. Move the sampling train to the next sampling port and repeat the sequence. Be sure to record the final dry gas meter reading after completing the test run. After performing the post test leak check, disconnect the jar/impinger containers from the pump and meter assembly and transport the probe, connecting tubing, and containers to the sample recovery area.

8.1.2.4.2 Rectangle Stacks. Complete each port traverse as per the instructions provided in 8.1.2.4.1.

NOTE: If an approximate mass emission rate is to be calculated, measure and record the stack velocity pressure and temperature before and after the test run.

8.2 Sample Recovery. After the train has been transferred to the sample recovery area, disconnect the tubing that connects the jar/impingers. The tester shall select either the total Cr or Cr^{+6} sample recovery option. Samples to be analyzed for both total Cr and Cr^{+6} shall be recovered using the Cr^{+6} sample option (Section 8.2.2).

NOTE: Collect a reagent blank sample for each of the total Cr or the Cr^{+6} analytical options. If both analyses (Cr and Cr^{+6}) are to be conducted on the samples, collect separate reagent blanks for each analysis. Also, since particulate matter is not usually present at chromium electroplating and/or chromium anodizing operations, it is not necessary to filter the Cr^{+6} samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr^{+6} solutions, please refer to Method 0061, Determination of Hexavalent Chromium Emissions from Stationary Sources, Section 7.4, Sample Preparation in SW–846 (see Reference 1).

8.2.1 Total Cr Sample Option.

8.2.1.1 Shipping Container No. 1. The first jar container may either be used to store and transport the sample, or if GS impingers are used, samples may be stored and shipped in precleaned 250-mL, 500-mL or 1000-mL polyethylene or glass bottles with leak-free, nonmetal screw caps.

8.2.1.1.1 Unscrew the lid from the first jar/impinger container.

8.2.1.1.2 Lift the inner tube assembly almost out of the container, and using the wash bottle containing fresh absorbing solution, rinse the outside of the tube that was immersed in the container solution; rinse the inside of the tube as well, by rinsing twice from the top of the tube down through the inner tube into the container.

8.2.1.2 Recover the contents of the second jar/impinger container by removing the lid and pouring any contents into the first shipping container.

8.2.1.2.1 Rinse twice, using fresh absorbing solution, the inner walls of the second container including the inside and outside of the inner tube.

8.2.1.2.2 Rinse the connecting tubing between the first and second sample containers with absorbing solution and place the rinses into the first container.

8.2.1.3 Position the nozzle, probe and connecting plastic tubing in a vertical position so that the tubing forms a "U".

8.2.1.3.1 Using the wash bottle, partially fill the tubing with fresh absorbing solution. Raise and lower the end of the plastic tubing several times to allow the solution to contact the internal surfaces. Do not allow the solution to overflow or part of the sample will be lost. Place the nozzle end of the probe over the mouth of the first container and elevate the plastic tubing so that the solution flows into the sample container.

8.2.1.3.2 Repeat the probe/tubing sample recovery procedure but allow the solution to flow out the opposite end of the plastic tubing into the sample container. Repeat the entire sample recovery procedure once again.

8.2.1.4 Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution during the rinsing of the probe nozzle, probe liner, sample containers, and connecting tubing.

8.2.1.5 Place a piece of clear plastic wrap over the mouth of the sample jar to seal the shipping container. Use a standard lid and band assembly to seal and secure the sample in the jar.

8.2.1.5.1 Label the jar clearly to identify its contents, sample number and date.

8.2.1.5.2 Mark the height of the liquid level on the container to identify any losses during shipping and handling.

8.2.1.5.3 Prepare a chain-of-custody sheet to accompany the sample to the laboratory.

8.2.2 Cr^{+6} Sample Option.

8.2.2.1 Shipping Container No. 1. The first jar container may either be used to store and transport the sample, or if GS impingers are used, samples may be stored and shipped in precleaned 250-mL, 500-mL or 1000-mL polyethylene or glass bottles with leak-free nonmetal screw caps.

8.2.2.1.1 Unscrew and remove the lid from the first jar container.

8.2.2.1.2 Measure and record the pH of the solution in the first container by using a pH indicator strip. The pH of the solution must be ≥8.5 for NaOH and ≥8.0 for $NaHCO_3$. If not, discard the collected sample, increase the concentration of the NaOH or NaHCO3 absorbing solution to 0.5 M and collect another air emission sample.

8.2.2.2 After measuring the pH of the first container, follow sample recovery procedures described in Sections 8.2.1.1 through 8.2.1.5.

NOTE: Since particulate matter is not usually present at chromium electroplating and/or chromium anodizing facilities, it is not necessary to filter the Cr^{+6} samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr^{+6} solutions, please refer to the EPA Method 0061, Determination of Hexavalent Chromium Emissions from Stationary Sources, Section 7.4, Sample Preparation in SW–846 (see Reference 5) for procedure.

8.2.3 Silica Gel Container. Observe the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition/color on the field data sheet. Do not use water or other liquids to remove and transfer the silica gel.

8.2.4 Total Cr and/or Cr^{+6} Reagent Blank.

8.2.4.1 Shipping Container No. 2. Place approximately 500 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution in a precleaned, labeled sample container and include with the field samples for analysis.

8.3 Sample Preservation, Storage, and Transport.

8.3.1 Total Cr Option. Samples that are to be analyzed for total Cr need not be refrigerated.

8.3.2 Cr^{+6} Option. Samples that are to be analyzed for Cr^{+6} must be shipped and stored at 4 °C (~40 °F).

NOTE: Allow Cr^{+6} samples to return to ambient temperature prior to analysis.

8.4 Sample Holding Times.

8.4.1 Total Cr Option. Samples that are to be analyzed for total chromium must be analyzed within 60 days of collection.

8.4.2 Cr^{+6} Option. Samples that are to be analyzed for Cr^{+6} must be analyzed within 14 days of collection.

9.0 Quality Control

9.1 Same as Method 306, Section 9.0.

10.0 Calibration and Standardization

NOTE: Tester shall maintain a performance log of all calibration results.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedures outlined in Section 10.1 of Method 2.

10.2 Temperature Sensor. Use the procedure in Section 10.3 of Method 2 to calibrate the in-stack temperature sensor.

10.3 Metering System.

10.3.1 Sample Train Dry Gas Meter Calibration. Calibrations may be performed as described in Section 16.2 of Method 5 by either the manufacturer, a firm who provides calibration services, or the tester.

10.3.2 Dry Gas Meter Calibration Coefficient (Y_m). The meter calibration coefficient (Y_m) must be determined prior to the initial use of the meter, and following each field test program. If the dry gas meter is new, the manufacturer will have specified the Y_m value for the meter. This Y_m value can be used as the pretest value for the first test. For subsequent tests, the tester must use the Y_m value established during the pretest calibration.

10.3.3 Calibration Orifice. The manufacturer may have included a calibration orifice and a summary spreadsheet with the meter that may be used for calibration purposes. The spreadsheet will provide data necessary to determine the calibration for the orifice and meter (standard cubic feet volume, sample time, etc.). These data were produced when the initial Y_m value was determined for the meter.

10.3.4 Y_m Meter Value Verification or Meter Calibration.

10.3.4.1 The Y_m meter value may be determined by replacing the sampling train critical orifice with the calibration orifice. Replace the critical orifice assembly by installing the calibration orifice in the same location. The inlet side of the calibration orifice is to be left open to the atmosphere and is *not* to be reconnected to the sample train during the calibration procedure.

10.3.4.2 If the vacuum pump is cold, switch on the pump and allow it to operate (become warm) for several minutes prior to starting the calibration. After stopping the pump, record the initial dry gas meter volume and meter temperature.

10.3.4.3 Perform the calibration for the number of minutes specified by the manufacturer's data sheet (usually 5 minutes). Stop the pump and record the final dry gas meter volume and temperature. Subtract the start volume from the stop volume to obtain the V_m and average the meter temperatures (t_m).

10.3.5 Y_m Value Calculation. Y_m is the calculated value for the dry gas meter. Calculate Y_m using the following equation:

$$Y_m = \frac{V_{m(std),mfg}}{V_m\left(\frac{T_{std}}{P_{std}}\right)\left(\frac{P_{bar}}{T_m}\right)}$$

$$Y_m = \frac{V_{m(std),mfg}\,T_m}{17.64\,V_m\,P_{bar}} \qquad \text{Eq. 306A - 2}$$

Where:

P_{bar} = Barometric pressure at meter, mm Hg, (in. Hg).

P_{std} = Standard absolute pressure,

Metric = 760 mm Hg.

English = 29.92 in. Hg.

t_m = Average dry gas meter temperature, °C, (°F).

T_m = Absolute average dry gas meter temperature,

Metric °K = 273 + tm (°C).

English °R = 460 + t_m (°F).

T_{std} = Standard absolute temperature,

Metric = 293 °K.

English = 528 °R.

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

$V_{m(std),mfg}$ = Volume of gas sample measured by manufacture's calibrated orifice and dry gas meter, corrected to standard conditions (pressure/temperature) dscm (dscf).

Y_m = Dry gas meter calibration factor, (dimensionless).

10.3.6 Y_m Comparison. Compare the Y_m value provided by the manufacturer (Section 10.3.3) or the pretest Y_m value to the post test Y_m value using the following equation:

$$\frac{Y_m(\text{manufacturer's or pretest value})}{Y_m(\text{post-test value})} \qquad \text{Eq. 306A - 3}$$

10.3.6.1 If this ratio is between 0.95 and 1.05, the designated Y_m value for the meter is acceptable for use in later calculations.

10.3.6.1.1 If the value is outside the specified range, the test series shall either be: 1) voided and the samples discarded; or 2) calculations for the test series shall be conducted using whichever meter coefficient value (i.e., manufacturers's/pretest Y_m value or post test Y_m value) produces the lowest sample volume.

10.3.6.1.2 If the post test dry gas meter Y_m value differs by more than 5% as compared to the pretest value, either perform the calibration again to determine acceptability or return the meter to the manufacturer for recalibration.

10.3.6.1.3 The calibration may also be conducted as specified in Section 10.3 or Section 16.0 of Method 5 (40 CFR Part 60, Appendix A), except that it is only necessary to check the calibration at one flow rate of ~ 0.75 cfm.

10.3.6.1.4 The calibration of the dry gas meter must be verified after each field test program using the same procedures.

NOTE: The tester may elect to use the Y_m post test value for the next pretest Y_m value; e.g., Test 1 post test Y_m value and Test 2 pretest Y_m value would be the same.

10.4 Barometer. Calibrate against a mercury barometer that has been corrected for temperature and elevation.

10.5 ICP Spectrometer Calibration. Same as Method 306, Section 10.2.

10.6 GFAA Spectrometer Calibration. Same as Method 306, Section 10.3.

10.7 IC/PCR Calibration. Same as Method 306, Section 10.4.

11.0 Analytical Procedures

NOTE: The method determines the chromium concentration in µg Cr/mL. It is important that the analyst measure the volume of the field sample prior to analyzing the sample. This will allow for conversion of µg Cr/mL to µg Cr/sample.

11.1 Analysis. Refer to Method 306 for sample preparation and analysis procedures.

12.0 Data Analysis and Calculations

12.1 Calculations. Perform the calculations, retaining one extra decimal point beyond that of the acquired data. When reporting final results, round number of figures consistent with the original data.

12.2 Nomenclature.

A = Cross-sectional area of stack, m_2 (ft_2).
B_{ws} = Water vapor in gas stream, proportion by volume, dimensionless (assume 2 percent moisture = 0.02).
C_p = Pitot tube coefficient; "S" type pitot coefficient usually 0.840, dimensionless.
C_S = Concentration of Cr in sample solution, µg Cr/mL.
C_{Cr} = Concentration of Cr in stack gas, dry basis, corrected to standard conditions µg/dscm (gr/dscf).
d = Diameter of stack, m (ft).
D = Digestion factor, dimensionless.
ER = Approximate mass emission rate, mg/hr (lb/hr).
F = Dilution factor, dimensionless.
L = Length of a square or rectangular duct, m (ft).
M_{Cr} = Total Cr in each sample, µg (gr).
M_s = Molecular weight of wet stack gas, wet basis, g/g-mole, (lb/lb-mole); in a nominal gas stream at 2% moisture the value is 28.62.
P_{bar} = Barometric pressure at sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure; in this case, usually the same value as the barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure:
Metric = 760 mm Hg.
English = 29.92 in. Hg.
Q_{std} = Average stack gas volumetric flow, dry, corrected to standard conditions, dscm/hr (dscf/hr).
t_m = Average dry gas meter temperature, °C (°F).
T_m = Absolute average dry gas meter temperature:
Metric °K = 273 + t_m (°C).
English °R = 460 + t_m (°F).
t_s = Average stack temperature, °C (°F).
T_s = Absolute average stack gas temperature: Metric °K = 273 + t_s (°C). English °R = 460 + t_s (°F).
T_{std} = Standard absolute temperature: Metric = 293 °K, English = 528 °R.
V_{ad} = Volume of sample aliquot after digestion (mL).
V_{af} = Volume of sample aliquot after dilution (mL).
V_{bd} = Volume of sample aliquot submitted to digestion (mL).
V_{bf} = Volume of sample aliquot before dilution (mL).
V_m = Volume of gas sample as measured (actual, dry) by dry gas meter, dcm (dcf).
V_{mL} = Volume of impinger contents plus rinses (mL).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions (temperature/pressure), dscm (dscf).
v_s = Stack gas average velocity, calculated by Method 2, Equation 2–9, m/sec (ft/sec).
W = Width of a square or rectangular duct, m (ft).
Y_m = Dry gas meter calibration factor, (dimensionless).
Δp = Velocity head measured by the Type S pitot tube, cm H_2O (in. H_2O).
Δp_{avg} = Average of Δp values, mm H_2O (in. H_2O).

12.3 Dilution Factor. The dilution factor is the ratio of the volume of sample aliquot after dilution to the volume before dilution. The dilution factor is usually calculated by the laboratory. This ratio is derived by the following equation:

$$F = \frac{V_{af}}{V_{bf}} \qquad \text{Eq. 306A-4}$$

12.4 Digestion Factor. The digestion factor is the ratio of the volume of sample aliquot after digestion to the volume before digestion. The digestion factor is usually calculated by the laboratory. This ratio is derived by the following equation.

$$D = \frac{V_{ad}}{V_{bd}} \qquad \text{Eq. 306A-5}$$

12.5 Total Cr in Sample. Calculate M_{Cr}, the total μg Cr in each sample, using the following equation:

$$M_{Cr} = V_{mL} \times C_S \times F \times D \qquad \text{Eq. 306A-6}$$

12.6 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) using the following equation:

$$V_{m(std)} = V_m Y_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K_1 V_m Y_m \left(\frac{P_{bar}}{T_m}\right) \qquad \text{Eq. 306A-7}$$

Where:

K_1 = Metric units—0.3855 °K/mm Hg.
English units—17.64 °R/in. Hg.

12.7 Cr Emission Concentration (C_{Cr}). Calculate C_{Cr}, the Cr concentration in the stack gas, in μg/dscm (μg/dscf) on a dry basis, corrected to standard conditions, using the following equation:

$$C_{Cr} = \frac{M_{Cr}}{V_{m(std)}} \qquad \text{Eq. 306A-8}$$

NOTE: To convert μg/dscm (μg/dscf) to mg/dscm (mg/dscf), divide by 1000.

12.8 Stack Gas Velocity.

12.8.1 K_p = Velocity equation constant:

$$\text{Metric } K_p = 34.97 \frac{m}{sec}\left[\frac{(g/g\text{-mole})(\text{mm Hg})}{(^\circ K)(\text{mm } H_2O)}\right]^{1/2}$$

$$\text{English } K_p = 85.49 \frac{ft}{sec}\left[\frac{(lb/lb\text{-mole})(\text{in. Hg})}{(^\circ R)(\text{in. } H_2O)}\right]^{1/2}$$

12.8.2 Average Stack Gas Velocity.

$$v_s = K_p C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}}$$

$$= 34.97\ C_p \left(\sqrt{\Delta p}\right)_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}} \qquad \text{Eq. 306A-9}$$

12.9 Cross sectional area of stack.

$$A = \frac{\Pi d^2}{4} \text{ or } A = LW \qquad \text{Eq. 306A-10}$$

12.10 Average Stack Gas Dry Volumetric Flow Rate.

NOTE: The emission rate may be based on a nominal stack moisture content of 2 percent (0.02). To calculate an emission rate, the tester may elect to use either the nominal stack gas moisture value or the actual stack gas moisture collected during the sampling run.

Volumetric Flow Rate Equation:

$$Q_{std} = 3600\left(1 - B_{ws}\right) v_s A \left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 306A-11}$$

Where:
3600 = Conversion factor, sec/hr.

$$Q_{std} = 62{,}234\ v_s A \left(\frac{P_s}{T_{s(avg)}}\right) \qquad \text{Eq. 306A-12}$$

NOTE: To convert Q_{std} from dscm/hr (dscf/hr) to dscm/min (dscf/min), divide Q_{std} by 60.

12.11 Mass emission rate, mg/hr (lb/hr):

$$ER = C_{cr} \times Q_{std} \times 10^{-3}\ (mg/hr) \qquad \text{Eq. 306A-13}$$

$$ER = C_{cr} \times Q_{std} \times 1.43 \times 10^{-4}\ (lb/hr) \qquad \text{Eq. 306A-14}$$

13.0 Method Performance

13.1 Range. The recommended working range for all of the three analytical techniques starts at five times the analytical detection limit (see also Method 306, Section 13.2.2). The upper limit of all three techniques can be extended indefinitely by appropriate dilution.

13.2 Sensitivity.

13.2.1 Analytical Sensitivity. The estimated instrumental detection limits listed are provided as a guide for an instrumental limit. The actual method detection limits

are sample and instrument dependent and may vary as the sample matrix varies.

13.2.1.1 ICP Analytical Sensitivity. The minimum estimated detection limits for ICP, as reported in Method 6010A and the recently revised Method 6010B of SW–846 (Reference 1), are 7.0 μg Cr/L and 4.7 μg Cr/L, respectively.

13.2.1.2 GFAAS Analytical Sensitivity. The minimum estimated detection limit for GFAAS, as reported in Methods 7000A and 7191 of SW–846 (Reference 1), is 1.0 μg Cr/L.

13.2.1.3 IC/PCR Analytical Sensitivity. The minimum detection limit for IC/PCR with a preconcentrator, as reported in Methods 0061 and 7199 of SW–846 (Reference 1), is 0.05 μg Cr^{+6}/L.

13.2.2 In-stack Sensitivity. The in-stack sensitivity depends upon the analytical detection limit, the volume of stack gas sampled, and the total volume of the impinger absorbing solution plus the rinses. Using the analytical detection limits given in Sections 13.2.1.1, 13.2.1.2, and 13.2.1.3; a stack gas sample volume of 1.7 dscm; and a total liquid sample volume of 500 mL; the corresponding in-stack detection limits are 0.0014 mg Cr/dscm to 0.0021 mg Cr/dscm for ICP, 0.00029 mg Cr/dscm for GFAAS, and 0.000015 mg Cr^{+3}/dscm for IC/PCR with preconcentration.

NOTE: It is recommended that the concentration of Cr in the analytical solutions be at least five times the analytical detection limit to optimize sensitivity in the analyses. Using this guideline and the same assumptions for impinger sample volume and stack gas sample volume (500 mL and 1.7 dscm, respectively), the recommended minimum stack concentrations for optimum sensitivity are 0.0068 mg Cr/dscm to 0.0103 mg Cr/dscm for ICP, 0.0015 mg Cr/dscm for GFAAS, and 0.000074 mg Cr^{+6} dscm for IC/PCR with preconcentration. If required, the in-stack detection limits can be improved by either increasing the sampling time, the stack gas sample volume, reducing the volume of the digested sample for GFAAS, improving the analytical detection limits, or any combination of the three.

13.3 Precision.

13.3.1 The following precision data have been reported for the three analytical methods. In each case, when the sampling precision is combined with the reported analytical precision, the resulting overall precision may decrease.

13.3.2 Bias data is also reported for GFAAS.

13.4 ICP Precision.

13.4.1 As reported in Method 6010B of SW–846 (Reference 1), in an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid/distilled water matrices that had been spiked with various metal concentrates. For true values of 10, 50, and 150 μg Cr/L; the mean reported values were 10, 50, and 149 μg Cr/L; and the mean percent relative standard deviations were 18, 3.3, and 3.8 percent, respectively.

13.4.2 In another multilaboratory study cited in Method 6010B, a mean relative standard of 8.2 percent was reported for an aqueous sample concentration of approximately 3750 μg Cr/L.

13.5 GFAAS Precision. As reported in Method 7191 of SW–846 (Reference 1), in a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 μg Cr/L, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97 percent, 101 percent, and 102 percent, respectively.

13.6 IC/PCR Precision. As reported in Methods 0061 and 7199 of SW–846 (Reference 1), the precision of IC/PCR with sample preconcentration is 5 to 10 percent; the overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 μg/dscm of total Cr is 25 percent and 9 percent, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6} the precision is 20 percent.

14.0 Pollution Prevention

14.1 The only materials used in this method that could be considered pollutants are the chromium standards used for instrument calibration and acids used in the cleaning of the collection and measurement containers/labware, in the preparation of standards, and in the acid digestion of samples. Both reagents can be stored in the same waste container.

14.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

14.3 To the extent possible, the containers/vessels used to collect and prepare samples should be cleaned and reused to minimize the generation of solid waste.

15.0 Waste Management

15.1 It is the responsibility of the laboratory and the sampling team to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

15.2 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

1. F.R. Clay, Memo, Impinger Collection Efficiency—Mason Jars vs. Greenburg-Smith Impingers, Dec. 1989.

2. Segall, R.R., W.G. DeWees, F.R. Clay, and J.W. Brown. Development of Screening Methods for Use in Chromium Emissions Measurement and Regulations Enforcement. In: Proceedings of the 1989 EPA/A&WMA International Symposium-Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP–13, EPA Report No. 600/9–89–060, p. 785.

3. Clay, F.R., Chromium Sampling Method. In: Proceedings of the 1990 EPA/A&WMA International Symposium-Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP–17, EPA Report No. 600/9–90–026, p. 576.

4. Clay, F.R., Proposed Sampling Method 306A for the Determination of Hexavalent Chromium Emissions from Electroplating and Anodizing Facilities. In: Proceedings of the 1992 EPA/A&WMA International Symposium-Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP–25, EPA Report No. 600/R–92/131, p. 209.

5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW–846, Third Edition as amended by Updates I, II, IIA, IIB, and III. Document No. 955–001–000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

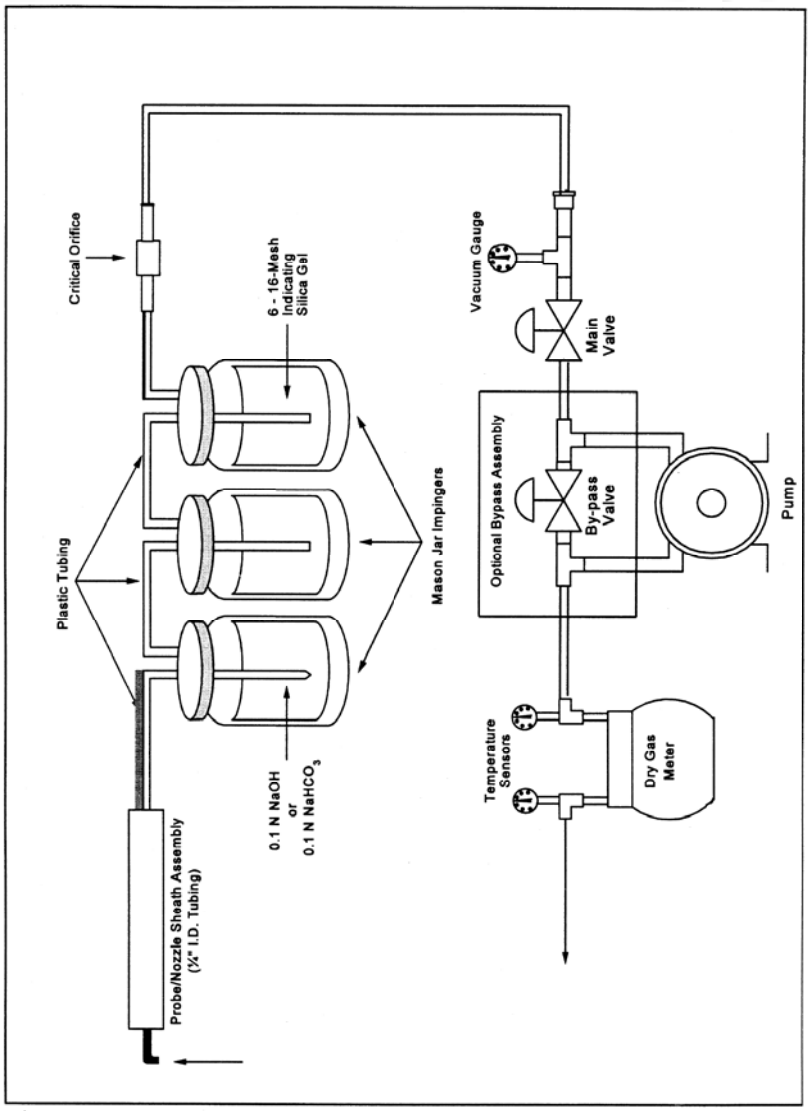
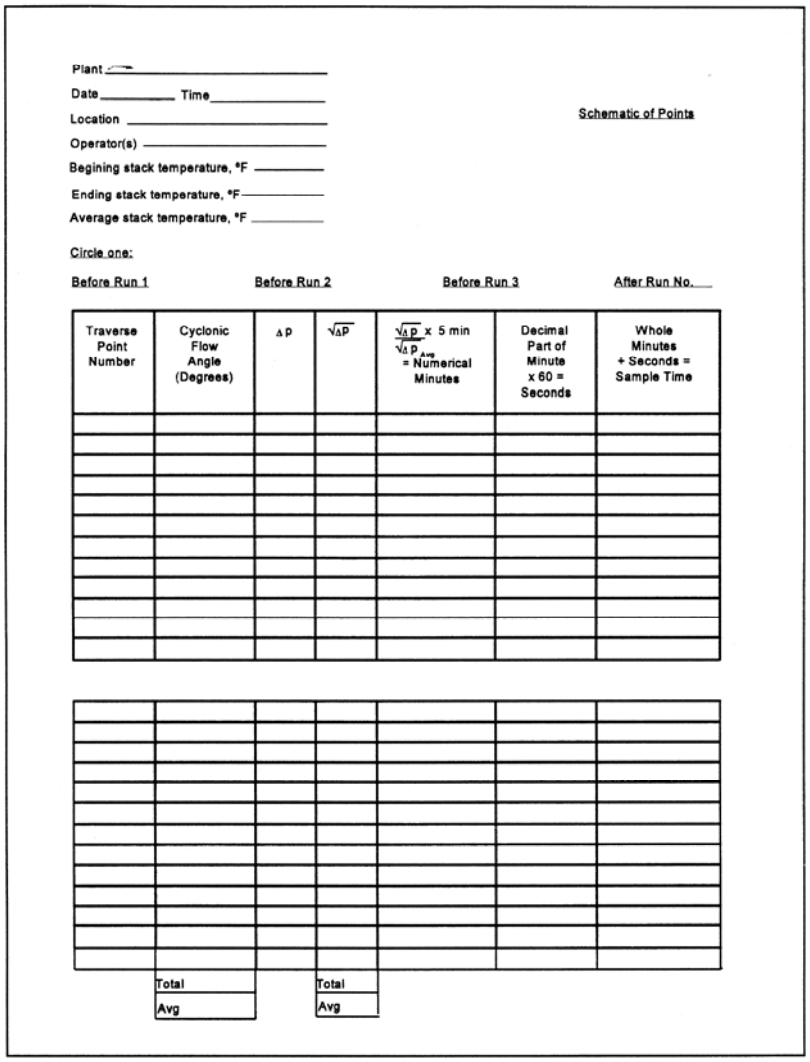


Figure 306A-1. Method 306A Sampling Train.



Plant _____

Date _____ Time _____

Location _____

Operator(s) _____

Begining stack temperature, °F _____

Ending stack temperature, °F _____

Average stack temperature, °F _____

Schematic of Points

Circle one:

Before Run 1 Before Run 2 Before Run 3 After Run No. ___

Traverse Point Number	Cyclonic Flow Angle (Degrees)	Δp	$\sqrt{\Delta P}$	$\frac{\sqrt{\Delta p}}{\sqrt{\Delta p_{Ave}}}$ x 5 min = Numerical Minutes	Decimal Part of Minute x 60 = Seconds	Whole Minutes + Seconds = Sample Time

	Total		Total			
	Avg		Avg			

Figure 306A-2. Velocity Traverse and Point Sample Time Calculation Sheet.

Plant _____ Date _____ Run Number _____

Sampling Site _____ Operator _____

Total Cr catch, M, μg _____ Stack radius, r, in. _____

Avg dry gas meter temp, T_m, °F _____ Avg delta p, Δ p in., H_2O _____

Meter correction factor, Y_m _____ Stack temp, T_s, °F _____

Meter volume, V_m, ft^3 _____ Leak rate before run, cfm _____

Barometric press, P_{bar}, in. Hg _____ Leak rate after run, cfm _____

Start clock time _____ Stop meter volume, ft^3 _____

Stop clock time _____ Start meter volume, ft^3 _____

POINT NO	SAMPLE (MIN/SEC)	GAS METER TEMP (F)		CRITICAL ORIFICE VACUUM IN. HG	POINT NO	SAMPLE (MIN/SEC)	GAS METER TEMP (F)		CRITICAL ORIFICE VACUUM IN. HG
	TOTAL					TOTAL			
		AVG					AVG		

REMARKS _____

Figure 306A-3. Chromium Constant Sampling Rate Field Data Sheet.

METHOD 306B—SURFACE TENSION MEASUREMENT FOR TANKS USED AT DECORATIVE CHROMIUM ELECTROPLATING AND CHROMIUM ANODIZING 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 40 CFR Part 60, Appendix A and in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306.

1.0 Scope and Application

1.1 Analyte. Not applicable.

1.2 Applicability. This method is applicable to all chromium electroplating and chromium anodizing operations, and continuous chromium plating at iron and steel facilities where a wetting agent is used in the tank as the primary mechanism for reducing emissions from the surface of the plating solution.

2.0 Summary of Method

2.1 During an electroplating or anodizing operation, gas bubbles generated during the process rise to the surface of the liquid and burst. Upon bursting, tiny droplets of chromic acid become entrained in ambient air. The addition of a wetting agent to the tank bath reduces the surface tension of the liquid and diminishes the formation of these droplets.

2.2 This method determines the surface tension of the bath using a stalagmometer or a tensiometer to confirm that there is sufficient wetting agent present.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

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

6.0 Equipment and Supplies

6.1 Stalagmometer. Any commercially available stalagmometer or equivalent surface tension measuring device may be used to measure the surface tension of the plating or anodizing tank liquid provided the procedures specified in Section 11.1.2 are followed.

6.2 Tensiometer. A tensiometer may be used to measure the surface tension of the tank liquid provided the procedures specified in ASTM Method D 1331–89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents (incorporated by reference—see §63.14) are followed.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Sample Recovery, Sample Preservation, Sample Holding Times, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Procedure. The surface tension of the tank bath may be measured using a tensiometer, stalagmometer, or any other equivalent surface tension measuring device for measuring surface tension in dynes per centimeter.

11.1.1 If a tensiometer is used, the procedures specified in ASTM Method D 1331–89 must be followed.

11.1.2 If a stalagmometer is used, the procedures specified in Sections 11.1.2.1 through 11.1.2.3 must be followed.

11.1.2.1 Check the stalagmometer for visual signs of damage. If the stalagmometer appears to be chipped, cracked, or otherwise in disrepair, the instrument shall not be used.

11.1.2.2 Using distilled or deionized water and following the procedures provided by the manufacturer, count the number of drops corresponding to the distilled/deionized water liquid volume between the upper and lower etched marks on the stalagmometer. If the number of drops for the distilled/deionized water is not within ±1 drop of the number indicated on the instrument, the stalagmometer must be cleaned, using the procedures specified in Section 11.1.3 of this method, before using the instrument to measure the surface tension of the tank liquid.

11.1.2.2.1 If the stalagmometer must be cleaned, as indicated in Section 11.1.2.2, repeat the procedure specified in Section 11.1.2.2 before proceeding.

11.1.2.2.2 If, after cleaning and performing the procedure in Section 11.1.2.2, the number of drops indicated for the distilled/deionized water is not within ±1 drop of the number indicated on the instrument, either use the number of drops corresponding to the distilled/deionized water volume as the reference number of drops, or replace the instrument.

11.1.2.3 Determine the surface tension of the tank liquid using the procedures specified by the manufacturer of the stalagmometer.

11.1.3 *Stalagmometer cleaning procedures.* The procedures specified in Sections 11.1.3.1 through 11.1.3.10 shall be used for cleaning a stalagmometer, as required by Section 11.1.2.2.

11.1.3.1 Set up the stalagmometer on its stand in a fume hood.

11.1.3.2 Place a clean 150 (mL) beaker underneath the stalagmometer and fill the beaker with reagent grade concentrated nitric acid.

11.1.3.3 Immerse the bottom tip of the stalagmometer (approximately 1 centimeter (0.5 inches)) into the beaker.

11.1.3.4 Squeeze the rubber bulb and pinch at the arrow up (1) position to collapse.

11.1.3.5 Place the bulb end securely on top end of stalagmometer and carefully draw the nitric acid by pinching the arrow up (1) position until the level is above the top etched line.

11.1.3.6 Allow the nitric acid to remain in stalagmometer for 5 minutes, then carefully remove the bulb, allowing the acid to completely drain.

11.1.3.7 Fill a clean 150 mL beaker with distilled or deionized water.

11.1.3.8 Using the rubber bulb per the instructions in Sections 11.1.3.4 and 11.1.3.5, rinse and drain stalagmometer with deionized or distilled water.

11.1.3.9 Fill a clean 150 mL beaker with isopropyl alcohol.

11.1.3.10 Again using the rubber bulb per the instructions in Sections 11.1.3.4 and 11.1.3.5, rinse and drain stalagmometer twice with isopropyl alcohol and allow the stalagmometer to dry completely.

11.2 Frequency of Measurements.

11.2.1 Measurements of the bath surface tension are performed using a progressive system which decreases the frequency of surface tension measurements required when the proper surface tension is maintained.

11.2.1.1 Initially, following the compliance date, surface tension measurements must be conducted once every 4 hours of tank operation for the first 40 hours of tank operation.

11.2.1.2 Once there are no exceedances during a period of 40 hours of tank operation, measurements may be conducted once every 8 hours of tank operation.

11.2.1.3 Once there are no exceedances during a second period of 40 consecutive hours of tank operation, measurements may be conducted once every 40 hours of tank operation on an on-going basis, until an exceedance occurs. The maximum time interval for measurements is once every 40 hours of tank operation.

11.2.2 If a measurement of the surface tension of the solution is above the 40 dynes per centimeter limit when measured using a stalagmometer, above 33 dynes per centimeter when measured using a tensiometer, or above an alternate surface tension limit established during the performance test, the time interval shall revert back to the original monitoring schedule of once every 4 hours. A subsequent decrease in frequency would then be allowed according to Section 11.2.1.

12.0 Data Analysis and Calculations

12.1 Log Book of Surface Tension Measurements and Fume Suppressant Additions.

12.1.1 The surface tension of the plating or anodizing tank bath must be measured as specified in Section 11.2.

12.1.2 The measurements must be recorded in the log book. In addition to the record of surface tension measurements, the frequency of fume suppressant maintenance additions and the amount of fume suppressant added during each maintenance addition must be recorded in the log book.

12.1.3 The log book will be readily available for inspection by regulatory personnel.

12.2 Instructions for Apparatus Used in Measuring Surface Tension.

12.2.1 Included with the log book must be a copy of the instructions for the apparatus used for measuring the surface tension of the plating or anodizing bath.

12.2.2 If a tensiometer is used, a copy of ASTM Method D 1331–89 must be included with the log book.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 307—DETERMINATION OF EMISSIONS FROM HALOGENATED SOLVENT VAPOR CLEANING MACHINES USING A LIQUID LEVEL PROCEDURE

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of the halogenated solvent emissions from solvent vapor cleaners in the idling mode.

1.2 Principle. The solvent level in the solvent cleaning machine is measured using inclined liquid level indicators. The change in liquid level corresponds directly to the amount of solvent lost from the solvent cleaning machine.

2. Apparatus

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

2.1 Inclined Liquid Level Indicator. A schematic of the inclined liquid level indicators used in this method is shown in figure 307–1; two inclined liquid level indicators having 0.05 centimeters divisions or smaller shall be used. The liquid level indicators shall be made of glass, Teflon, or any similar material that will not react with the solvent

being used. A 6-inch by 1-inch slope is recommended; however the slope may vary depending on the size and design of the solvent cleaning machine.

NOTE: It is important that the inclined liquid level indicators be constructed with ease of reading in mind. The inclined liquid level indicators should also be mounted so that they can be raised or lowered if necessary to suit the solvent cleaning machine size.

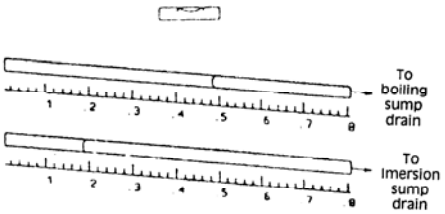


Figure 307-1. Inclined Liquid Level Indicator Apparatus.

2.2 Horizontal Indicator. Device to check the inclined liquid level indicators orientation relative to horizontal.

2.3 Velocity Meter. Hotwire and vane anemometers, or other devices capable of measuring the flow rates ranging from 0 to 15.2 meters per minute across the solvent cleaning machine.

3. Procedure

3.1 Connection of the Inclined Liquid Level Indicator. Connect one of the inclined liquid level indicators to the boiling sump drain and the other inclined liquid level indicator to the immersion sump drain using Teflon tubing and the appropriate fittings. A schematic diagram is shown in figure 307–2.

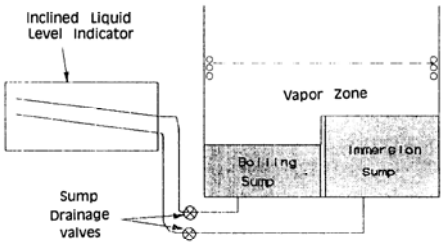


Figure 307-2. Solvent Cleaner Test Setup.

3.2 Positioning of Velocity Meter. Position the velocity meter so that it measures the flow rate of the air passing directly across the solvent cleaning machine.

3.3 Level the Inclined Liquid Level Indicators.

3.4 Initial Inclined Liquid Level Indicator Readings. Open the sump drainage valves. Allow the solvent cleaning machine to operate long enough for the vapor zone to form and the system to stabilize (check with manufacturer). Record the inclined liquid level indicators readings and the starting time on the data sheet. A sample data sheet is provided in figure 307–3.

Date _____

Run _____

Solvent type _____

Solvent density, g/m^3 (lb/ft^3) _____

Length of boiling sump (S_B), m (ft) _____

Width of boiling sump (W_B), m (ft) _____

Length of immersion sump (S_I), m (ft) _____

Width of immersion sump (W_I), m (ft) _____

Length of solvent vapor/air interface (S_V), m (ft) _____

Width of solvent vapor/air interface (W_V), m (ft) _____

Clock time	Boiling sump reading	Immersion sump reading	Flow rate reading

Figure 307–3. Data sheet.

3.5 Final Inclined Liquid Level Indicator Readings. At the end of the 16-hour test run, check to make sure the inclined liquid level indicators are level; if not, make the necessary adjustments. Record the final inclined liquid level indicators readings and time.

3.6 Determination of Solvent Vapor/Air Interface Area for Each Sump. Determine the area of the solvent/air interface of the individual sumps. Whenever possible, physically measure these dimensions, rather than using factory specifications. A schematic of the dimensions of a solvent cleaning machine is provided in figure 307–4.

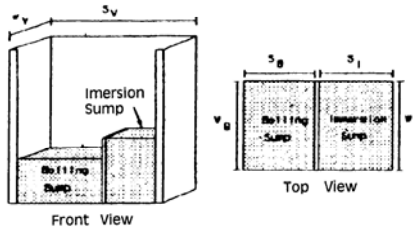


Figure 307-4. Solvent Cleaner Dimensions.

4. Calculations

4.1 Nomenclature.

A_B = area of boiling sump interface, m^2 (ft^2).
A_I = area of immersion sump interface, m^2 (ft^2).
A_V = area of solvent/air interface, m^2 (ft^2).
E = emission rate, kg/m^2-hr (lb/ft^2-hr).
K = 100,000 cm . g/m . kg for metric units.
= 12 in./ft for English units.
L_{Bf} = final boiling sump inclined liquid level indicators reading, cm (in.).
L_{Bi} = initial boiling sump inclined liquid level indicators reading, cm (in.).
L_{If} = final immersion sump inclined liquid level indicators reading, cm (in.).
L_{Ii} = initial immersion sump inclined liquid level indicators reading, cm (in.).
S_B = length of the boiling sump, m (ft).
S_I = length of the immersion sump, m (ft).
S_V = length of the solvent vapor/air interface, m (ft).
W_B = width of the boiling sump, m (ft).
W_I = width of the immersion sump, m (ft).
W_V = width of the solvent vapor/air interface, m (ft).
ρ = density of solvent, g/m3 (lb/ft3).
θ = test time, hr.

4.2 Area of Sump Interfaces. Calculate the areas of the boiling and immersion sump interfaces as follows:

$A_B = S_B W_B$ Eq. 307–1
$A_I = S_I W_I$ Eq. 307–2

4.3 Area of Solvent/Air Interface. Calculate the area of the solvent vapor/air interface as follows:

$A_V = S_V W_V$ Eq. 307–3

4.4 Emission Rate. Calculate the emission rate as follows:

$$E = \frac{\left(L_{B_f} - L_{B_i}\right)\rho A_B + \left(L_{I_f} - L_{I_i}\right)\rho A_I}{K A_V \theta}$$

Eq. 307-4

METHOD 308—PROCEDURE FOR DETERMINATION OF METHANOL EMISSION FROM STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte. Methanol. Chemical Abstract Service (CAS) No. 67–56–1.

1.2 Applicability. This method applies to the measurement of methanol emissions from specified stationary sources.

2.0 Summary of Method

A gas sample is extracted from the sampling point in the stack. The methanol is collected in deionized distilled water and adsorbed on silica gel. The sample is returned to the laboratory where the methanol in the water fraction is separated from other organic compounds with a gas chromatograph

(GC) and is then measured by a flame ionization detector (FID). The fraction adsorbed on silica gel is extracted with an aqueous solution of n-propanol and is then separated and measured by GC/FID.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

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

5.2 Methanol Characteristics. Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation.

6.0 Equipment and Supplies

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

6.1.1 Sampling Train. The sampling train is shown in Figure 308–1 and component parts are discussed below.

6.1.1.1 Probe. Teflon®, approximately 6-millimeter (mm) (0.24 inch) outside diameter.

6.1.1.2 Impinger. A 30-milliliter (ml) midget impinger. The impinger must be connected with leak-free glass connectors. Silicone grease may not be used to lubricate the connectors.

6.1.1.3 Adsorbent Tube. Glass tubes packed with the required amount of the specified adsorbent.

6.1.1.4 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.5 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the sampling train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

6.1.1.6 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of up to 1000 milliliter per minute (ml/min). Alternatively, the tester may use a critical orifice to set the flow rate.

6.1.1.7 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).

6.1.1.8 Barometer. Mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 inch) Hg. See the NOTE in Method 5 (40 CFR part 60, appendix A), section 6.1.2.

6.1.1.9 Vacuum Gauge and Rotameter. At least 760-mm (30-inch) Hg gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

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

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml, two.

6.2.2 Sample Vials. Glass, 40-ml, with Teflon®-lined septa, to store impinger samples (one per sample).

6.2.3 Graduated Cylinder. 100-ml size.

6.3 Analysis. The following are required for analysis:

6.3.1 Gas Chromatograph. GC with an FID, programmable temperature control, and heated liquid injection port.

6.3.2 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

6.3.3 Flow Meter. To monitor accurately sample loop flow rate of 100 ml/min.

6.3.4 Regulators. Two-stage regulators used on gas cylinders for GC and for cylinder standards.

6.3.5 Recorder. To record, integrate, and store chromatograms.

6.3.6 Syringes. 1.0- and 10-microliter (l) size, calibrated, for injecting samples.

6.3.7 Tubing Fittings. Stainless steel, to plumb GC and gas cylinders.

6.3.8 Vials. Two 5.0-ml glass vials with screw caps fitted with Teflon®-lined septa for each sample.

6.3.9 Pipettes. Volumetric type, assorted sizes for preparing calibration standards.

6.3.10 Volumetric Flasks. Assorted sizes for preparing calibration standards.

6.3.11 Vials. Glass 40-ml with Teflon®-lined septa, to store calibration standards (one per standard).

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sampling. The following are required for sampling:

7.1.1 Water. Deionized distilled to conform to the American Society for Testing and Materials (ASTM) Specification D 1193–77, Type 3. At the option of the analyst, the potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Silica Gel. Deactivated chromatographic grade 20/40 mesh silica gel packed in glass adsorbent tubes. The silica

gel is packed in two sections. The front section contains 520 milligrams (mg) of silica gel, and the back section contains 260 mg.

7.2 Analysis. The following are required for analysis:

7.2.1 Water. Same as specified in section 7.1.1.

7.2.2 n-Propanol, 3 Percent. Mix 3 ml of n-propanol with 97 ml of water.

7.2.3 Methanol Stock Standard. Prepare a methanol stock standard by weighing 1 gram of methanol into a 100-ml volumetric flask. Dilute to 100 ml with water.

7.2.3.1 Methanol Working Standard. Prepare a methanol working standard by pipetting 1 ml of the methanol stock standard into a 100-ml volumetric flask. Dilute the solution to 100 ml with water.

7.2.3.2 Methanol Standards For Impinger Samples. Prepare a series of methanol standards by pipetting 1, 2, 5, 10, and 25 ml of methanol working standard solution respectively into five 50-ml volumetric flasks. Dilute the solutions to 50 ml with water. These standards will have 2, 4, 10, 20, and 50 µg/ml of methanol, respectively. After preparation, transfer the solutions to 40-ml glass vials capped with Teflon® septa and store the vials under refrigeration. Discard any excess solution.

7.2.3.3 Methanol Standards for Adsorbent Tube Samples. Prepare a series of methanol standards by first pipetting 10 ml of the methanol working standard into a 100-ml volumetric flask and diluting the contents to exactly 100 ml with 3 percent n-propanol solution. This standard will contain 10 µg/ml of methanol. Pipette 5, 15, and 25 ml of this standard, respectively, into four 50-ml volumetric flasks. Dilute each solution to 50 ml with 3 percent n-propanol solution. These standards will have 1, 3, and 5 µg/ml of methanol, respectively. Transfer all four standards into 40-ml glass vials capped with Teflon®-lined septa and store under refrigeration. Discard any excess solution.

7.2.4 GC Column. Capillary column, 30 meters (100 feet) long with an inside diameter (ID) of 0.53 mm (0.02 inch), coated with DB 624 to a film thickness of 3.0 micrometers, (µm) or an equivalent column. Alternatively, a 30-meter capillary column coated with polyethylene glycol to a film thickness of 1 µm such as AT-WAX or its equivalent.

7.2.5 Helium. Ultra high purity.

7.2.6 Hydrogen. Zero grade.

7.2.7 Oxygen. Zero grade.

8.0 Procedure

8.1 Sampling. The following items are required for sampling:

8.1.1 Preparation of Collection Train. Measure 20 ml of water into the midget impinger. The adsorbent tube must contain 520 mg of silica gel in the front section and 260 mg of silica gel in the backup section. Assemble the train as shown in Figure 308–1. An optional, second impinger that is left empty may be placed in front of the water-containing impinger to act as a condensate trap. Place crushed ice and water around the impinger.

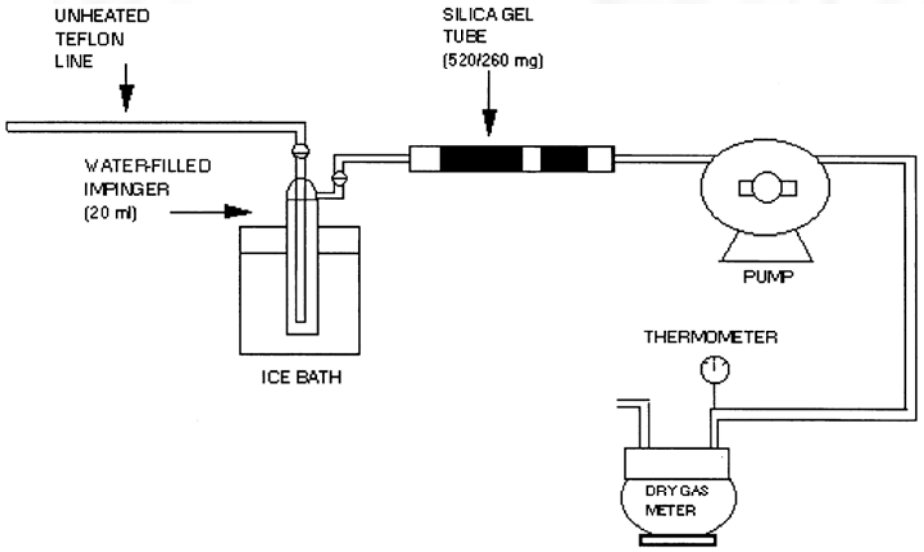


Figure 308.1. Sampling train schematic

8.1.2 Leak Check. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0-to 40-ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm (10 inch) Hg, and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3 Sample Collection. Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the Teflon® tubing at the sampling point, connect the tubing to the impinger, and start the pump. Adjust the sample flow to a constant rate between 200 and 1000 ml/min as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings (DGM, temperatures at DGM and at impinger outlet, and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less. At the conclusion of each run,

turn off the pump, remove the Teflon® tubing from the stack, and record the final readings. Conduct a leak check as in section 8.1.2. (This leak check is mandatory.) If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.2 Sample Recovery. The following items are required for sample recovery:

8.2.1 Impinger. Disconnect the impinger. Pour the contents of the midget impinger into a graduated cylinder. Rinse the midget impinger and the connecting tubes with water, and add the rinses to the graduated cylinder. Record the sample volume. Transfer the sample to a glass vial and cap with a Teflon® septum. Discard any excess sample. Place the samples in an ice chest for shipment to the laboratory.

8.2.2. Adsorbent Tubes. Seal the silica gel adsorbent tubes and place them in an ice chest for shipment to the laboratory.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures. The following quality control measures are required:

Section	Quality control measure	Effect
8.1.2, 8.1.3, 10.1.	Sampling equipment leak check and calibration.	Ensures accurate measurement of sample volume.
10.2	GC calibration	Ensures precision of GC analysis.

10.0 Calibration and Standardization

10.1 Metering System. The following items are required for the metering system:

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, first leak-check the metering system (drying tube, needle valve, pump, rotameter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube, and pull a vacuum of 250 mm (10 inch) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Next, remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet test meter (e.g., 1 liter per revolution (0.035 cubic feet per revolution)) to the inlet of the drying tube. Make three independent calibrations runs, using at least five revolutions of the DGM per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y-value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

10.1.2 Posttest Calibration Check. After each field test series, conduct a calibration check as in section 10.1.1 above, except for the following variations: (a) The leak check is not to be conducted, (b) three, or more revolutions of the DGM may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in section 10.1.1), then the DGM volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in section 10.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

10.1.3 Temperature Sensors. Calibrate 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.

10.1.4 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

10.1.5 Barometer. Calibrate against a mercury barometer.

10.2 Gas Chromatograph. The following procedures are required for the gas chromatograph:

10.2.1 Initial Calibration. Inject 1 µl of each of the standards prepared in sections 7.2.3.3 and 7.2.3.4 into the GC and record the response. Repeat the injections for each standard until two successive injections agree within 5 percent. Using the mean response for each calibration standard, prepare a linear least squares equation relating the response to the mass of methanol in the sample. Perform the calibration before analyzing each set of samples.

10.2.2 Continuing Calibration. At the beginning of each day, analyze the mid level calibration standard as described in section 10.5.1. The response from the daily analysis must agree with the response from the initial calibration within 10 percent. If it does not, the initial calibration must be repeated.

11.0 Analytical Procedure

11.1 Gas Chromatograph Operating Conditions. The following operating conditions are required for the GC:

11.1.1 Injector. Configured for capillary column, splitless, 200 °C (392 °F).

11.1.2 Carrier. Helium at 10 ml/min.

11.1.3 Oven. Initially at 45 °C for 3 minutes; then raise by 10 °C to 70 °C; then raise by 70 °C/min to 200 °C.

11.2 Impinger Sample. Inject 1 µl of the stored sample into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

11.3 Silica Gel Adsorbent Sample. The following items are required for the silica gel adsorbent samples:

11.3.1 Preparation of Samples. Extract the front and backup sections of the adsorbent tube separately. With a file, score the glass adsorbent tube in front of the first section of silica gel. Break the tube open. Remove and discard the glass wool. Transfer the first section of the silica gel to a 5-ml glass vial and stopper the vial. Remove the spacer between the first and second section of the adsorbent tube and discard it. Transfer the second section of silica gel to a separate 5-ml glass vial and stopper the vial.

11.3.2 Desorption of Samples. Add 3 ml of the 10 percent n-propanol solution to each of the stoppered vials and shake or vibrate the vials for 30 minutes.

11.3.3 Inject a 1-µl aliquot of the diluted sample from each vial into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{af} = Concentration of methanol in the front of the adsorbent tube, µg/ml.

C_{ab} = Concentration of methanol in the back of the adsorbent tube, µg/ml.

C_i = Concentration of methanol in the impinger portion of the sample train, µg/ml.

E = Mass emission rate of methanol, µg/hr (lb/hr).

M_{tot} = Total mass of methanol collected in the sample train, µg.

P_{bar} = Barometric pressure at the exit orifice of the DGM, mm Hg (in. Hg).

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

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

T_m = Average DGM absolute temperature, degrees K (°R).

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

V_{af} = Volume of front half adsorbent sample, ml.

V_{ab} = Volume of back half adsorbent sample, ml.

V_i = Volume of impinger sample, ml.

V_m = Dry gas volume as measured by the DGM, dry cubic meters (dcm), dry cubic feet (dcf).

$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dry standard cubic meters (dscm), dry standard cubic feet (dscf).

12.2 Mass of Methanol. Calculate the total mass of methanol collected in the sampling train using Equation 308–1.

$$M_{tot} = V_i C_i + V_{af} C_{af} + V_{ab} C_{ab} \qquad \text{Equation 308-1}$$

12.3 Dry Sample Gas Volume, Corrected to Standard Conditions. Calculate the volume of gas sampled at standard conditions using Equation 308–2.

$$V_m(std) = \frac{V_m Y T_{std} P_{bar}}{T_m P_{std}} \qquad \text{Equation 308-2}$$

12.4 Mass Emission Rate of Methanol. Calculate the mass emission rate of methanol using Equation 308–3.

$$E = \frac{M_{tot} Q_{sd}}{V_{m(std)}}$$ Equation 308-3

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Bibliography

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17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 310A—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

1.1 This method is used to analyze any crumb rubber or water samples for residual hexane content.

1.2 The sample is heated in a sealed bottle with an internal standard and the vapor is analyzed by gas chromatography.

2.0 Summary of Method

2.1 This method, utilizing a capillary column gas chromatograph with a flame ionization detector, determines the concentration of residual hexane in rubber crumb samples.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

4.1 There are no known interferences.

5.0 Safety

5.1 It is the responsibility of the user of this procedure to establish safety and health practices applicable to their specific operation.

6.0 Equipment and Supplies

6.1 Gas Chromatograph with a flame ionization detector and data handling station equipped with a capillary column 30 meters long.

6.2 Chromatograph conditions for Sigma 1:

6.2.1 Helium pressure: 50# inlet A, 14# aux

6.2.2 Carrier flow: 25 cc/min

6.2.3 Range switch: 100x

6.2.4 DB: 1 capillary column

6.3 Chromatograph conditions for Hewlett-Packard GC:

6.3.1 Initial temperature: 40 °C

6.3.2 Initial time: 8 min

6.3.3 Rate: 0

6.3.4 Range: 2

6.3.5 DB: 1705 capillary column

6.4 Septum bottles and stoppers

6.5 Gas Syringe—0.5 cc

7.0 Reagents and Standards

7.1 Chloroform, 99.9 + %, A.S.C. HPLC grade

8.0 Sample Collection, Preservation, and Storage

8.1 A representative sample should be caught in a clean 8 oz. container with a secure lid.

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 10.2 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 Determine the percent hexane in three separate dried rubber crumb samples.

9.3.2 Weigh a portion of each crumb sample into separate sample bottles and add a known amount of hexane (10 microliters) by microliter syringe and 20 microliters of internal standard. Analyze each by the described procedure and calculate the percent recovery of the known added hexane.

9.3.3 Repeat the previous step using twice the hexane level (20 microliters), analyze and calculate the percent recovery of the known added hexane.

9.3.4 Set up two additional sets of samples using 10 microliters and 20 microliters of hexane as before, but add an amount of water equal to the dry crumb used. Analyze and calculate percent recovery to show the effect of free water on the results obtained.

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

9.3.6 R shall be 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 Calibrate the chromatograph using a standard made by injecting 10 µl of fresh hexane and 20 µl of chloroform into a sealed septum bottle. This standard will be 0.6 wt.% *total* hexane based on 1 gram of dry rubber.

10.2 Analyze the hexane used and calculate the percentage of each hexane isomer (2-methylpentane, 3-methylpentane, n-hexane, and methylcyclo-pentane). Enter these percentages into the method calibration table.

10.3 Heat the standard bottle for 30 minutes in a 105 °C oven.

10.4 Inject about 0.25 cc of vapor into the gas chromatograph and after the analysis is finished, calibrate according to the procedures described by the instrument manufacturer.

11.0 Procedure

11.1 Using a cold mill set at a wide roller gap (125–150 mm), mill about 250 grams of crumb two times to homogenize the sample.

11.2 Weigh about 2 grams of wet crumb into a septum bottle and cap with a septum ring. Add 20 µl of chloroform with a syringe and place in a 105 °C oven for 45 minutes.

11.3 Run the moisture content on a separate portion of the sample and calculate the grams of dry rubber put into the septum bottle.

11.4 Set up the data station on the required method and enter the dry rubber weight in the sample weight field.

11.5 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

11.6 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

11.7 To analyze water samples, pipet 5 ml of sample into the septum bottle, cap and add 20 µl of chloroform. Place in a 105 °C oven for 30 minutes.

11.8 Enter 5 grams into the sample weight field.

11.9 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

11.10 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

12.0 Data Analysis and Calculation

12.1 For samples that are prepared as in section 11 of this method, ppm n-hexane is read directly from the computer.

12.2 The formulas for calculation of the results are as follows:

$ppm_{hexane} = (A_{hexane} \times R_{hexane})/(A_{is} \times R_{is})$

Where:

A_{hexane} = area of hexane

R_{hexane} = response of hexane

A_{is} = area of the internal standard

R_{is} = response of the internal standard

% hexane in crumb = (ppm_{hexane}/sample amount)100

12.3 Correct the results by the value of R (as determined in sections 9.3.4, 9.3.5, and 9.3.6 of this method).

13.0 Method Performance

13.1 The test has a standard deviation of 0.14 wt% at 0.66 wt% hexane. Spike recovery of 12 samples at two levels of hexane averaged 102.3%. Note: Recovery must be determined for each type of sample. The values given here are meant to be examples of method performance.

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 DSM Copolymer Test Method T–3380.

METHOD 310B—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

Analyte	CAS No.	Matrix	Method sensitivity (5.5g sample size)
Hexane	110–54–3	Rubber crumb	.01 wt%.

Analyte	CAS No.	Matrix	Method sensitivity (5.5g sample size)
Applicable Termonomer		Rubber crumb	.001 wt%.

1.1 Data Quality Objectives:

In the production of ethylene-propylene terpolymer crumb rubber, the polymer is recovered from solution by flashing off the solvent with steam and hot water. The resulting water-crumb slurry is then pumped to the finishing units. Certain amounts of solvent (hexane being the most commonly used solvent) and diene monomer remain in the crumb. The analyst uses the following procedure to determine those amounts.

2.0 Summary of Method

2.1 The crumb rubber sample is dissolved in toluene to which heptane has been added as an internal standard. Acetone is then added to this solution to precipitate the crumb, and the supernatant is analyzed for hexane and diene by a gas chromatograph equipped with a flame ionization detector (FID).

3.0 Definitions

3.1 Included in text as needed.

4.0 Interferences

4.1 None known.

4.2 Benzene, introduced as a contaminant in the toluene solvent, elutes between methyl cyclopentane and cyclohexane. However, the benzene peak is completely resolved.

4.3 2,2-dimethyl pentane, a minor component of the hexane used in our process, elutes just prior to methyl cyclopentane. It is included as "hexane" in the analysis whether it is integrated separately or included in the methyl cyclopentane peak.

5.0 Safety

5.1 This procedure does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

5.2 Chemicals used in this analysis are flammable and hazardous (see specific toxicity information below). Avoid contact with sources of ignition during sample prep. All handling should be done beneath a hood. Playtex or nitrile gloves recommended.

5.3 Hexane is toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. May cause irritation on contact with skin or eyes. May cause damage to kidneys.

5.4 Termonomer may be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Causes skin irritation.

5.5 Toluene is harmful or fatal if swallowed. Vapor harmful if inhaled. Symptoms: headache, dizziness, hallucinations, distorted perceptions, changes in motor activity, nausea, diarrhea, respiratory irritation, central nervous system depression, unconsciousness, liver, kidney and lung damage. Contact can cause severe eye irritation. May cause skin irritation. Causes irritation of eyes, nose, and throat.

5.6 Acetone, at high concentrations or prolonged overexposure, may cause headache, dizziness, irritation of eyes and respiratory tract, loss of strength, and narcosis. Eye contact causes severe irritation; skin contact may cause mild irritation. Concentrations of 20,000 ppm are immediately dangerous to life and health.

5.7 Heptane is harmful if inhaled or swallowed. May be harmful if absorbed through the skin. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated exposure to skin causes defatting and dermatitis.

5.8 The steam oven used to dry the polymer in this procedure is set at 110 °C. Wear leather gloves when removing bottles from the oven.

6.0 Equipment and Supplies

6.1 4000-ml volumetric flask

6.2 100-ml volumetric pipette

6.3 1000-ml volumetric flask

6.4 8-oz. French Square sample bottles with plastic-lined caps

6.5 Top-loading balance

6.6 Laboratory shaker

6.7 Laboratory oven set at 110 °C (steam oven)

6.8 Gas chromatograph, Hewlett-Packard 5890A, or equivalent, interfaced with HP 7673A (or equivalent) autosampler (equipped with nanoliter adapter and robotic arm), and HP 3396 series II or 3392A (or equivalent) integrator/controller.

6.9 GC column, capillary type, 50m × 0.53mm, methyl silicone, 5 micron film thickness, Quadrex, or equivalent.

6.10 Computerized data acquisition system, such as CIS/CALS

6.11 Crimp-top sample vials and HP p/n 5181–1211 crimp caps, or screw-top autosampler vials and screw tops.

6.12 Glass syringes, 5-ml, with "Luer-lock" fitting

6.13 Filters, PTFE, .45 μm pore size, Gelman Acrodisc or equivalent, to fit on Luer-lock syringes (in 6.12, above).

7.0 Reagents and Standards

7.1 Reagent toluene, EM Science Omnisolv (or equivalent)

Purity Check: Prior to using any bottle of reagent toluene, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each (note that an area of 15 is equivalent to less than 0.01 wt% in a 10g sample).

7.2 Reagent acetone, EM Science Omnisolv HR-GC (or equivalent)

Purity Check: Prior to using any bottle of reagent acetone, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each.

7.3 Reagent heptane, Aldrich Chemical Gold Label, Cat #15,487-3 (or equivalent)

Purity Check: Prior to using any bottle of reagent heptane, analyze it according to section 11.2 of this method. Use the bottle only if hexane and termonomer peak areas are less than 5 each.

7.4 Internal standard solution—used as a concentrate for preparation of the more dilute Polymer Dissolving Solution. It contains 12.00g heptane/100ml of solution which is 120.0g per liter.

Preparation of internal standard solution (polymer dissolving stock solution):

Action	Notes
7.4.1 Tare a clean, dry 1-liter volumetric flask on the balance. Record the weight to three places.	If the 1-liter volumetric flask is too tall to fit in the balance case, you can shield the flask from drafts by inverting a paint bucket with a hole cut in the bottom over the balance cover. Allow the neck of the flask to project through the hole in the bucket.
7.4.2 Weigh 120.00 g of n-heptane into the flask. Record the total weight of the flask and heptane as well as the weight of heptane added.	Use 99 + % n-heptane from Aldrich or Janssen Chimica.
7.4.3 Fill the flask close to the mark with toluene, about 1 to 2" below the mark.	Use EM Science Omnisolve toluene, Grade TX0737–1, or equivalent.
7.4.4 Shake the flask vigorously to mix the contents	Allow any bubbles to clear before proceeding to the next step.
7.4.5 Top off the flask to the mark with toluene. Shake vigorously, as in section 7.4.4 of this method, to mix well.	
7.4.6 Weigh the flask containing the solution on the three place balance record the weight	
7.4.7 Transfer the contents of the flask to a 1 qt Boston round bottle.	Discard any excess solution
7.4.8 Label the bottle with the identity of the contents, the weights of heptane and toluene used, the date of preparation and the preparer's name.	Be sure to include the words *"Hexane in Crumb Polymer Dissolving Stock Solution"* on the label.
7.4.9 Refrigerate the completed blend for the use of the routine Technicians.	

7.5 Polymer Dissolving Solution ("PDS")—Heptane (as internal standard) in toluene. This solution contains 0.3g of heptane internal standard per 100 ml of solution.

7.5.1 Preparation of Polymer Dissolving Solution. Fill a 4,000-ml volumetric flask about ¾ full with toluene.

7.5.2 Add 100 ml of the internal standard solution (section 7.4 of this method) to the flask using the 100ml pipette.

7.5.3 Fill the flask to the mark with toluene. Discard any excess.

7.5.4 Add a large magnetic stirring bar to the flask and mix by stirring.

7.5.5 Transfer the polymer solvent solution to the one-gallon labeled container with 50ml volumetric dispenser attached.

7.5.6 Purity Check: Analyze according to section 11.2. *NOTE:* You must "precipitate" the sample with an equal part of acetone (thus duplicating actual test conditions—see section 11.1 of this method, sample prep) before analyzing. Analyze the reagent 3 times to quantify the C_6 and termonomer interferences. Inspect the results to ensure good agreement among the three runs (within 10%).

7.5.7 Tag the bottle with the following information:

POLYMER DISSOLVING SOLUTION FOR C_6 IN CRUMB ANALYSIS
PREPARER'S NAME
DATE
CALS FILE ID'S OF THE THREE ANALYSES FOR PURITY (from section 7.5.6 of this method)

7.6 Quality Control Solution: the quality control solution is prepared by adding specific amounts of mixed hexanes (barge hexane), n-nonane and termonomer to some polymer dissolving solution. Nonane elutes in the same approximate time region as termonomer and is used to quantify in that region because it has a longer shelf life.

Termonomer, having a high tendency to polymerize, is used in the QC solution only to ensure that both termonomer isomers elute at the proper time.

First, a concentrated stock solution is prepared; the final QC solution can then be prepared by diluting the stock solution.

7.6.1 In preparation of stock solution, fill a 1-liter volumetric flask partially with polymer dissolving solution (PDS)—see section 7.5 of this method. Add 20.0 ml barge hexane, 5.0 ml n-nonane, and 3 ml termonomer. Finish filling the volumetric to the mark with PDS.

7.6.2 In preparation of quality control solution, dilute the quality control stock solution (above) precisely 1:10 with PDS, i.e. 10 ml of stock solution made up to 100 ml (volumetric flask) with PDS. Pour the solution into a 4 oz. Boston round bottle and store in the refrigerator.

8.0 Sample Collection, Preservation and Storage

8.1 Line up facility to catch crumb samples. The facility is a special facility where the sample is drawn.

8.1.1 Ensure that the cock valve beneath facility is closed.

8.1.2 Line up the system from the slurry line cock valve to the cock valve at the nozzle on the stripper.

8.1.3 Allow the system to flush through facility for a period of 30 seconds.

8.2 Catch a slurry crumb sample.

8.2.1 Simultaneously close the cock valves upstream and downstream of facility.

8.2.2 Close the cock valve beneath the slurry line in service.

8.2.3 Line up the cooling tower water through the sample bomb water jacket to the sewer for a minimum of 30 minutes.

8.2.4 Place the sample catching basket beneath facility and open the cock valve underneath the bomb to retrieve the rubber crumb.

8.2.5 If no rubber falls by gravity into the basket, line up nitrogen to the bleeder upstream of the sample bomb and force the rubber into the basket.

8.2.6 Close the cock valve underneath the sample bomb.

8.3 Fill a plastic "Whirl-pak" sample bag with slurry crumb and send it to the lab immediately.

8.4 Once the sample reaches the lab, it should be prepped as soon as possible to avoid hexane loss through evaporation. Samples which have lain untouched for more than 30 minutes should be discarded.

9.0 Quality Control

Quality control is monitored via a computer program that tracks analyses of a prepared QC sample (from section 7.6.2 of this method). The QC sample result is entered daily into the program, which plots the result as a data point on a statistical chart. If the data point does not satisfy the "in-control" criteria (as defined by the lab quality facilitator), an "out-of-control" flag appears, mandating corrective action.

In addition, the area of the n-heptane peak is monitored so that any errors in making up the polymer dissolving solution will be caught and corrected. Refer to section 12.4 of this method.

9.1 Fill an autosampler vial with the quality control solution (from section 7.6.2 of this method) and analyze on the GC as normal (per section 11 of this method).

9.2 Add the concentrations of the 5 hexane isomers as they appear on the CALS printout. Also include the 2,2-dimethyl-pentane peak just ahead of the methyl cyclopentane (the fourth major isomer) peak in the event that the peak integration split this peak out. Do not include the benzene peak in the sum. Note the nonane concentration. Record both results (total hexane and nonane) in the QC computer program. If out of control, and GC appears to be functioning within normal parameters, reanalyze a fresh control sample. If the fresh QC is not in control, check stock solution for contaminants or make up a new QC sample with the toluene currently in use. If instrument remains out-of-control, more thorough GC troubleshooting may be needed.

Also, verify that the instrument has detected both isomers of termonomer (quantification not necessary—see section 7.0 of this method).

9.3 Recovery efficiency must be determined for high ethylene concentration, low ethylene concentration, E-P terpolymer, or oil extended samples and whenever modifications are made to the method. Recovery shall be between 70 and 130 percent. All test results must be corrected by the recovery efficiency value (R).

9.3.1 Approximately 10 grams of wet EPDM crumb (equivalent to about 5 grams of dry rubber) shall be added to six sample bottles containing 100 ml of hexane in crumb polymer dissolving solution (toluene containing 0.3 gram n-heptane/100 ml solution). The polymer shall be dissolved by agitating the bottles on a shaker for 4 hours. The polymer shall be precipitated using 100 ml acetone.

9.3.2 The supernatant liquid shall be decanted from the polymer. Care shall be taken to remove as much of the liquid phase from the sample as possible to minimize the effect of retained liquid phase upon the next cycle of the analysis. The supernatant liquid shall be analyzed by gas chromatography using an internal standard quantitation method with heptane as the internal standard.

9.3.3 The precipitated polymer from the steps described above shall be redissolved using toluene as the solvent. No heptane shall be added to the sample in the second

dissolving step. The toluene solvent and acetone precipitant shall be determined to be free of interfering compounds.

9.3.4 The rubber which was dissolved in the toluene shall be precipitated with acetone as before, and the supernatant liquid decanted from the precipitated polymer. The liquid shall be analyzed by gas chromatography and the rubber phase dried in a steam-oven to determine the final polymer weight.

9.3.5 The ratios of the areas of the hexane peaks and of the heptane internal standard peak shall be calculated for each of the six samples in the two analysis cycles outlined above. The area ratios of the total hexane to heptane (R1) shall be determined for the two analysis cycles of the sample set. The ratio of the values of R1 from the second analysis cycle to the first cycle shall be determined to give a second ratio (R2).

10.0 Calibration and Standardization

The procedure for preparing a Quality Control sample with the internal standard in it is outlined in section 7.6 of this method.

10.1 The relative FID response factors for n-heptane, the internal standard, versus the various hexane isomers and termonomer are relatively constant and should seldom need to be altered. However Baseline construction is a most critical factor in the production of good data. For this reason, close attention should be paid to peak integration. Procedures for handling peak integration will depend upon the data system used.

10.2 If recalibration of the analysis is needed, make up a calibration blend of the internal standard and the analytes as detailed below and analyze it using the analytical method used for the samples.

10.2.1 Weigh 5 g heptane into a tared scintillation vial to five places.

10.2.2 Add 0.2 ml termonomer to the vial and reweigh.

10.2.3 Add 0.5 ml hexane to the vial and reweigh.

10.2.4 Cap, and shake vigorously to mix.

10.2.5 Calculate the weights of termonomer and of hexane added and divide their weights by the weight of the n-heptane added. The result is the known of given value for the calibration.

10.2.6 Add 0.4 ml of this mixture to a mixture of 100 ml toluene and 100 ml of acetone. Cap and shake vigorously to mix.

10.2.7 Analyze the sample.

10.2.8 Divide the termonomer area and the total areas of the hexane peaks by the n-heptane area. This result is the "found" value for the calibration.

10.2.9 Divide the appropriate "known" value from 10.2.5 by the found value from 10.2.8. The result is the response factor for the analyte in question. Previous work has shown that the standard deviation of the calibration method is about 1% relative.

11.0 Procedure

11.1 SAMPLE PREPARATION

11.1.1 Tare an 8oz sample bottle—Tag attached, cap off; record weight and sample ID on tag in pencil.

11.1.2 Place crumb sample in bottle: RLA–3: 10 g (gives a dry wt. of ~5.5 g).

11.1.3 Dispense 100ml of PDS into each bottle. SAMPLE SHOULD BE PLACED INTO SOLUTION ASAP TO AVOID HEXANE LOSS—Using "Dispensette" pipettor. *Before dispensing, "purge" the dispensette (25% of its volume) into a waste bottle to eliminate any voids.*

11.1.4 Tightly cap bottles and load samples into shaker.

11.1.5 Insure that "ON-OFF" switch on the shaker itself is "ON."

11.1.6 Locate shaker timer. Insure that toggle switch atop timer control box is in the middle ("off") position. If display reads "04:00" (4 hours), move toggle switch to the left position. Shaker should begin operating.

11.1.7 After shaker stops, add 100 ml acetone to each sample to precipitate polymer. Shake minimum of 5 minutes on shaker—Vistalon sample may not have fully dissolved; nevertheless, for purposes of consistency, 4 hours is the agreed-upon dissolving time.

11.1.8 Using a 5-ml glass Luer-lock syringe and Acrodisc filter, filter some of the supernatant liquid into an autosampler vial; crimp the vial and load it into the GC autosampler for analysis (section 11.2 of this method)—The samples are filtered to prevent polymer buildup in the GC. Clean the syringes in toluene.

11.1.9 Decant remaining supernatant into a hydrocarbon waste sink, being careful not to discard any of the polymer. Place bottle of precipitate into the steam oven and dry for six hours—Some grades of Vistalon produce very small particles in the precipitate, thus making complete decanting impossible without discarding some polymer. In this case, decant as much as possible and put into the oven as is, allowing the oven to drive off remaining supernatant (this practice is avoided for environmental reasons). WARNING: OVEN IS HOT—110 °C (230 °F).

11.1.10 Cool, weigh and record final weight of bottle.

11.2 GC ANALYSIS

11.2.1 Initiate the CALS computer channel.

11.2.2 Enter the correct instrument method into the GC's integrator.

11.2.3 Load sample vial(s) into autosampler.

11.2.4 Start the integrator.

11.2.5 When analysis is complete, plot CALS run to check baseline skim.

12.0 Data Analysis and Calculations

12.1 Add the concentrations of the hexane peaks as they appear on the CALS printout. Do not include the benzene peak in the sum.

12.2 Subtract any hexane interferences found in the PDS (see section 7.5.6 of this method); record the result.

12.3 Note the termonomer concentration on the CALS printout. Subtract any termonomer interference found in the PDS and record this result in a "% termonomer by GC" column in a logbook.

12.4 Record the area (from CALS printout) of the heptane internal standard peak in a "C7 area" column in the logbook. This helps track instrument performance over the long term.

12.5 After obtaining the final dry weight of polymer used (Section 11.1.10 of this method), record that result in a "dry wt." column of the logbook (for oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

12.6 Divide the %C6 by the dry weight to obtain the total PHR hexane in crumb. Similarly, divide the % termonomer by the dry weight to obtain the total PHR termonomer in crumb. Note that PHR is an abbreviation for "parts per hundred". Record both the hexane and termonomer results in the logbook.

12.7 Correct all results by the recovery efficiency value (R).

13.0 Method Performance

13.1 The method has been shown to provide 100% recovery of the hexane analyte. The method was found to give a 6% relative standard deviation when the same six portions of the same sample were carried through the procedure. Note: These values are examples; each sample type, as specified in Section 9.3, must be tested for sample recovery.

14.0 Pollution Prevention

14.1 Dispose of all hydrocarbon liquids in the appropriate disposal sink system; never pour hydrocarbons down a water sink.

14.2 As discussed in section 11.1.9 of this method, the analyst can minimize venting hydrocarbon vapor to the atmosphere by decanting as much hydrocarbon liquid as possible before oven drying.

15.0 Waste Management

15.1 The Technician conducting the analysis should follow the proper waste management practices for their laboratory location.

16.0 References

16.1 Baton Rouge Chemical Plant Analytical Procedure no. BRCP 1302

16.2 Material Safety Data Sheets (from chemical vendors) for hexane, ENB, toluene, acetone, and heptane

METHOD 310C—DETERMINATION OF RESIDUAL N-HEXANE IN EPDM RUBBER THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

1.1 This method describes a procedure for the determination of residual hexane in EPDM wet crumb rubber in the 0.01—2% range by solvent extraction of the hexane followed by gas chromatographic analysis where the hexane is detected by flame ionization and quantified via an internal standard.

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

2.0 Summary

2.1 Residual hexane contained in wet pieces of EPDM polymer is extracted with MIBK. A known amount of an internal standard (IS) is added to the extract which is subsequently analyzed via gas chromatography where the hexane and IS are separated and detected utilizing a megabore column and flame ionization detection (FID). From the response to the hexane and the IS, the amount of hexane in the EPDM polymer is calculated.

3.0 Definitions

3.1 Hexane—refers to n-hexane

3.2 Heptane—refers to n-heptane

3.3 MIBK—methyl isobutyl ketone (4 methyl 2—Pentanone)

4.0 Interferences

4.1 Material eluting at or near the hexane and/or the IS will cause erroneous results. Prior to extraction, solvent blanks must be analyzed to confirm the absence of interfering peaks.

5.0 Safety

5.1 Review Material Safety Data Sheets of the chemicals used in this method.

6.0 Equipment and Supplies

6.1 4 oz round glass jar with a wide mouth screw cap lid.

6.2 Vacuum oven.

6.3 50 ml pipettes.

6.4 A gas chromatograph with an auto sampler and a 50 meter, 0.53 ID, methyl silicone column with 5 micron phase thickness.

6.5 Shaker, large enough to hold 10, 4 oz. jars.

6.6 1000 and 4000 ml volumetric flasks.
6.7 Electronic integrator or equivalent data system.
6.8 GC autosampler vials.
6.9 50 uL syringe.

7.0 Reagents and Standards

7.1 Reagent grade Methyl-Iso-Butyl-Ketone (MIBK)
7.2 n-heptane, 99% + purity
7.3 n-hexane, 99% + purity

8.0 Sample Collection

8.1 Trap a sample of the EPDM crumb slurry in the sampling apparatus. Allow the crumb slurry to circulate through the sampling apparatus for 5 minutes; then close off the values at the bottom and top of the sampling apparatus, trapping the crumb slurry. Run cooling water through the water jacket for a minimum of 30 minutes. Expel the cooled crumb slurry into a sample catching basket. If the crumb does not fall by gravity, force it out with demineralized water or nitrogen. Send the crumb slurry to the lab for analysis.

9.0 Quality Control

9.1 The Royalene crumb sample is extracted three times with MIBK containing an internal standard. The hexane from each extraction is added together to obtain a total hexane content. The percent hexane in the first extraction is then calculated and used as the recovery factor for the analysis.
9.2 Follow this test method through section 11.4 of the method. After removing the sample of the first extraction to be run on the gas chromatograph, drain off the remainder of the extraction solvent, retaining the crumb sample in the sample jar. Rinse the crumb with demineralized water to remove any MIBK left on the surface of the crumb. Repeat the extraction procedure with fresh MIBK with internal standard two more times.
9.3 After the third extraction, proceed to section 11.5 of this method and obtain the percent hexane in each extraction. Use the sample weight obtained in section 12.1 of this method to calculate the percent hexane in each of the extracts.
9.4 Add the percent hexane obtained from the three extractions for a total percent hexane in the sample.
9.5 Use the following equations to determine the recovery factor (R):
% Recovery of the first extraction = (% hexane in the first extract/total % hexane) × 100
Recovery Factor (R) = (% Hexane Recovered in the first extract)/100

10.0 Calibration

10.1 Preparation of Internal Standard (IS) solution:
Accuracy weigh 30 grams of n-heptane into a 1000 ml volumetric flask. Dilute to the mark with reagent grade MIBK. Label this Solution "A". Pipette 100 mls. of Solution A into a 4 liter volumetric flask. Fill the flask to the mark with reagent MIBK. Label this Solution "B". Solution "B" will have a concentration of 0.75 mg/ml of heptane.
10.2 Preparation of Hexane Standard Solution (HS):
Using a 50 uL syringe, weigh by difference, 20 mg of n-hexane into a 50 ml volumetric flask containing approximately 40 ml of Solution B. Fill the flask to the mark with Solution B and mix well.
10.3 Conditions for GC analysis of standards and samples:
Temperature:
Initial = 40 °C
Final = 150 °C
Injector = 160 °C
Detector = 280 °C
Program Rate = 5.0 °C/min
Initial Time = 5 minutes Final Time = 6 minutes
Flow Rate = 5.0 ml/min
Sensitivity = detector response must be adjusted to keep the hexane and IS on scale.
10.4 Fill an autosampler vial with the HS, analyze it three times and calculate a Hexane Relative Response Factor (RF) as follows:

$$RF = (A_{IS} \times C_{HS} \times P_{HS})/(A_{HS} \times C_{IS} \times P_{IS}) \quad (1)$$

Where:
A_{IS} = Area of IS peak (Heptane)
A_{HS} = Area of peak (Hexane Standard)
C_{HS} = Mg of Hexane/50 ml HS
C_{IS} = Mg of Heptane/50 ml IS Solution B
P_{IS} = Purity of the IS n-heptane
P_{HS} = Purity of the HS n-hexane

11.0 Procedure

11.1 Weight 10 grams of wet crumb into a tared (W1), wide mouth 4 oz. jar.
11.2 Pipette 50 ml of Solution B into the jar with the wet crumb rubber.
11.3 Screw the cap on tightly and place it on a shaker for 4 hours.
11.4 Remove the sample from the shaker and fill an autosampler vial with the MIBK extract.
11.5 Analyze the sample two times.
11.6 Analyze the HS twice, followed by the samples. Inject the HS twice at the end of each 10 samples or at the end of the run.

12.0 Calculations

12.1 Drain off the remainder of the MIBK extract from the polymer in the 4 oz. jar. Retain all the polymer in the jar. Place the uncovered jar and polymer in a heated vacuum oven until the polymer is dry. Reweigh the jar and polymer (W2) and calculate the dried sample weight of the polymer as follows:
Dried SW = W2—W1 (2)

12.2 Should the polymer be oil extended, pipette 10 ml of the MIBK extract into a tared evaporating dish (W1) and evaporate to dryness on a steam plate.

Reweigh the evaporating dish containing the extracted oil (W2). Calculate the oil content of the polymer as follows:

Gram of oil extracted = 5 (W2—W1) (3)

% Hexane in polymer = $(A_s \times RF \times C_{IS} \times P_{IS})/(A_{IS} \times SW)$ (4)

Where:

A_s = Area of sample hexane sample peak.
A_{IS} = Area of IS peak in sample.
C_{IS} = Concentration of IS in 50 ml.
P_{IS} = Purity of IS.
SW = Weight of dried rubber after extraction. (For oil extended polymer, the amount of oil extracted is added to the dry rubber weight).
% Corrected Hexane = (% Hexane in Polymer)/R (5)
R = Recovery factor determined in section 9 of this method.

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 311—ANALYSIS OF HAZARDOUS AIR POLLUTANT COMPOUNDS IN PAINTS AND COATINGS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH

1. Scope and Application

1.1 Applicability. This method is applicable for determination of most compounds designated by the U.S. Environmental Protection Agency as volatile hazardous air pollutants (HAP's) (See Reference 1) that are contained in paints and coatings. Styrene, ethyl acrylate, and methyl methacrylate can be measured by ASTM D 4827–93 or ASTM D 4747–87. Formaldehyde can be measured by ASTM PS 9–94 or ASTM D 1979–91. Toluene diisocyanate can be measured in urethane prepolymers by ASTM D 3432–89. Method 311 applies only to those volatile HAP's which are added to the coating when it is manufactured, not to those which may form as the coating cures (reaction products or cure volatiles). A separate or modified test procedure must be used to measure these reaction products or cure volatiles in order to determine the total volatile HAP emissions from a coating. Cure volatiles are a significant component of the total HAP content of some coatings. The term "coating" used in this method shall be understood to mean paints and coatings.

1.2 Principle. The method uses the principle of gas chromatographic separation and quantification using a detector that responds to concentration differences. Because there are many potential analytical systems or sets of operating conditions that may represent useable methods for determining the concentrations of the compounds cited in Section 1.1 in the applicable matrices, all systems that employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the prescribed quality control, calibration, and method performance requirements are met. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

2. Summary of Method

Whole coating is added to dimethylformamide and a suitable internal standard compound is added. An aliquot of the sample mixture is injected onto a chromatographic column containing a stationary phase that separates the analytes from each other and from other volatile compounds contained in the sample. The concentrations of the analytes are determined by comparing the detector responses for the sample to the responses obtained using known concentrations of the analytes.

3. Definitions [Reserved]

4. Interferences

4.1 Coating samples of unknown composition may contain the compound used as the internal standard. Whether or not this is the case may be determined by following the procedures of Section 11 and deleting the addition of the internal standard specified in Section 11.5.3. If necessary, a different internal standard may be used.

4.2 The GC column and operating conditions developed for one coating formulation may not ensure adequate resolution of target analytes for other coating formulations. Some formulations may contain nontarget analytes that coelute with target analytes. If there is any doubt about the identification or resolution of any gas chromatograph (GC) peak, it may be necessary to analyze the sample using a different GC column or different GC operating conditions.

4.3 Cross-contamination may occur whenever high-level and low-level samples are analyzed sequentially. The order of sample

analyses specified in Section 11.7 is designed to minimize this problem.

4.4 Cross-contamination may also occur if the devices used to transfer coating during the sample preparation process or for injecting the sample into the GC are not adequately cleaned between uses. All such devices should be cleaned with acetone or other suitable solvent and checked for plugs or cracks before and after each use.

5. Safety

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

5.2 Dimethylformamide is harmful if inhaled or absorbed through the skin. The user should obtain relevant health and safety information from the manufacturer. Dimethylformamide should be used only with adequate ventilation. Avoid contact with skin, eyes, and clothing. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. If eyes are affected, consult a physician. Remove and wash contaminated clothing before reuse.

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

6. Equipment and Supplies

NOTE: Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

6.1 Sample Collection.

6.1.1 Sampling Containers. Dual-seal sampling containers, four to eight fluid ounce capacity, should be used to collect the samples. Glass sample bottles or plastic containers with volatile organic compound (VOC) impermeable walls must be used for corrosive substances (*e.g.*, etch primers and certain coating catalysts such as methyl ethyl ketone (MEK) peroxide). Sample containers, caps, and inner seal liners must be inert to the compounds in the sample and must be selected on a case-by-case basis.

6.1.1.1 Other routine sampling supplies needed include waterproof marking pens, tubing, scrappers/spatulas, clean rags, paper towels, cooler/ice, long handle tongs, and mixing/stirring paddles.

6.1.2 Personal safety equipment needed includes eye protection, respiratory protection, a hard hat, gloves, steel toe shoes, etc.

6.1.3 Shipping supplies needed include shipping boxes, packing material, shipping labels, strapping tape, etc.

6.1.4 Data recording forms and labels needed include coating data sheets and sample can labels.

NOTE: The actual requirements will depend upon the conditions existing at the source sampled.

6.2 Laboratory Equipment and Supplies.

6.2.1 Gas Chromatograph (GC). Any instrument equipped with a flame ionization detector and capable of being temperature programmed may be used. Optionally, other types of detectors (e.g., a mass spectrometer), and any necessary interfaces, may be used provided that the detector system yields an appropriate and reproducible response to the analytes in the injected sample. Autosampler injection may be used, if available.

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

6.2.3 Column. The column must be constructed of materials that do not react with components of the sample (*e.g.*, fused silica, stainless steel, glass). The column should be of appropriate physical dimensions (*e.g.*, length, internal diameter) and contain sufficient suitable stationary phase to allow separation of the analytes. DB–5, DB-Wax, and FFAP columns are commonly used for paint analysis; however, it is the responsibility of each analyst to select appropriate columns and stationary phases.

6.2.4 Tube and Tube Fittings. Supplies to connect the GC and gas cylinders.

6.2.5 Pressure Regulators. Devices used to regulate the pressure between gas cylinders and the GC.

6.2.6 Flow Meter. A device used to determine the carrier gas flow rate through the GC. Either a digital flow meter or a soap film bubble meter may be used to measure gas flow rates.

6.2.7 Septa. Seals on the GC injection port through which liquid or gas samples can be injected using a syringe.

6.2.8 Liquid Charging Devices. Devices used to inject samples into the GC such as clean and graduated 1, 5, and 10 microliter (µl) capacity syringes.

6.2.9 Vials. Containers that can be sealed with a septum in which samples may be prepared or stored. The recommended size is 25 ml capacity. Mininert® valves have been found satisfactory and are available from Pierce Chemical Company, Rockford, Illinois.

6.2.10 Balance. Device used to determine the weights of standards and samples. An analytical balance capable of accurately weighing to 0.0001 g is required.

7. Reagents and Standards

7.1 Purity of Reagents. Reagent grade chemicals shall be used in all tests. Unless otherwise specified, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of determination.

7.2 Carrier Gas. Helium carrier gas shall have a purity of 99.995 percent or higher. High purity nitrogen may also be used. Other carrier gases that are appropriate for the column system and analyte may also be used. Ultra-high purity grade hydrogen gas and zero-grade air shall be used for the flame ionization detector.

7.3 Dimethylformamide (DMF). Solvent for all standards and samples. Some other suitable solvent may be used if DMF is not compatible with the sample or coelutes with a target analyte.

NOTE: DMF may coelute with ethylbenzene or p-xylene under the conditions described in the note under Section 6.2.3.

7.4 Internal Standard Materials. The internal standard material is used in the quantitation of the analytes for this method. It shall be gas chromatography spectrophotometric quality or, if this grade is not available, the highest quality available. Obtain the assay for the internal standard material and maintain at that purity during use. The recommended internal standard material is 1-propanol; however, selection of an appropriate internal standard material for the particular coating and GC conditions used is the responsibility of each analyst.

7.5 Reference Standard Materials. The reference standard materials are the chemicals cited in Section 1.1 which are of known identity and purity and which are used to assist in the identification and quantification of the analytes of this method. They shall be the highest quality available. Obtain the assays for the reference standard materials and maintain at those purities during use.

7.6 Stock Reference Standards. Stock reference standards are dilutions of the reference standard materials that may be used on a daily basis to prepare calibration standards, calibration check standards, and quality control check standards. Stock reference standards may be prepared from the reference standard materials or purchased as certified solutions.

7.6.1 Stock reference standards should be prepared in dimethylformamide for each analyte expected in the coating samples to be analyzed. The concentrations of analytes in the stock reference standards are not specified but must be adequate to prepare the calibration standards required in the method. A stock reference standard may contain more than one analyte provided all analytes are chemically compatible and no analytes coelute. The actual concentrations prepared must be known to within 0.1 percent (e.g., 0.1000 ±0.0001 g/g solution). The following procedure is suggested. Place about 35 ml of dimethylformamide into a tared ground-glass stoppered 50 ml volumetric flask. Weigh the flask to the nearest 0.1 mg. Add 12.5 g of the reference standard material and reweigh the flask. Dilute to volume with dimethylformamide and reweigh. Stopper the flask and mix the contents by inverting the flask several times. Calculate the concentration in grams per gram of solution from the net gain in weights, correcting for the assayed purity of the reference standard material.

NOTE: Although a glass-stoppered volumetric flask is convenient, any suitable glass container may be used because stock reference standards are prepared by weight.

7.6.2 Transfer the stock reference standard solution into one or more Teflon-sealed screw-cap bottles. Store, with minimal headspace, at −10 °C to 0 °C and protect from light.

7.6.3 Prepare fresh stock reference standards every six months, or sooner if analysis results from daily calibration check standards indicate a problem. Fresh stock reference standards for very volatile HAP's may have to be prepared more frequently.

7.7 Calibration Standards. Calibration standards are used to determine the response of the detector to known amounts of reference material. Calibration standards must be prepared at a minimum of three concentration levels from the stock reference standards (see Section 7.6). Prepare the calibration standards in dimethylformamide (see Section 7.3). The lowest concentration standard should contain a concentration of analyte equivalent either to a concentration of no more than 0.01% of the analyte in a coating or to a concentration that is lower than the actual concentration of the analyte in the coating, whichever concentration is higher. The highest concentration standard

should contain a concentration of analyte equivalent to slightly more than the highest concentration expected for the analyte in a coating. The remaining calibration standard should contain a concentration of analyte roughly at the midpoint of the range defined by the lowest and highest concentration calibration standards. The concentration range of the standards should thus correspond to the expected range of analyte concentrations in the prepared coating samples (see Section 11.5). Each calibration standard should contain each analyte for detection by this method expected in the actual coating samples (e.g., some or all of the compounds listed in Section 1.1 may be included). Each calibration standard should also contain an appropriate amount of internal standard material (response for the internal standard material is within 25 to 75 percent of full scale on the attenuation setting for the particular reference standard concentration level). Calibration Standards should be stored for 1 week only in sealed vials with minimal headspace. If the stock reference standards were prepared as specified in Section 7.6, the calibration standards may be prepared by either weighing each addition of the stock reference standard or by adding known volumes of the stock reference standard and calculating the mass of the standard reference material added. Alternative 1 (Section 7.7.1) specifies the procedure to be followed when the stock reference standard is added by volume. Alternative 2 (Section 7.7.2) specifies the procedure to be followed when the stock reference standard is added by weight.

NOTE: To assist with determining the appropriate amount of internal standard to add, as required here and in other sections of this method, the analyst may find it advantageous to prepare a curve showing the area response versus the amount of internal standard injected into the GC.

7.7.1 Preparation Alternative 1. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert® valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of each stock reference standard using new pipets (or pipet tips) for each stock reference standard. Reweigh the vial and seal it. Using the known weights of the standard reference materials per ml in the stock reference standards, the volumes added, and the total weight of all reagents added to the vial, calculate the weight percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

7.7.2 Preparation Alternative 2. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert® valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of a stock reference standard using a new pipet (or pipet tip) and reweigh the vial. Repeat this process for each stock reference standard to be added. Seal the vial after obtaining the final weight. Using the known weight percents of the standard reference materials in the stock reference standards, the weights of the stock reference standards added, and the total weight of all reagents added to the vial, calculate the weight percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

8. Sample Collection, Preservation, Transport, and Storage

8.1 Copies of material safety data sheets (MSDS's) for each sample should be obtained prior to sampling. The MSDS's contain information on the ingredients, and physical and chemical properties data. The MSDS's also contain recommendations for proper handling or required safety precautions. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

8.2 A copy of the blender's worksheet can be requested to obtain data on the exact coating being sampled. A blank coating data sheet form (see Section 18) may also be used. The manufacturer's formulation information from the product data sheet should also be obtained.

8.3 Prior to sample collection, thoroughly mix the coating to ensure that a representative, homogeneous sample is obtained. It is preferred that this be accomplished using a coating can shaker or similar device; however, when necessary, this may be accomplished using mechanical agitation or circulation systems.

8.3.1 Water-thinned coatings tend to incorporate or entrain air bubbles if stirred too vigorously; mix these types of coatings slowly and only as long as necessary to homogenize.

8.3.2 Each component of multicomponent coatings that harden when mixed must be sampled separately. The component mix ratios must be obtained at the facility at the time of sampling and submitted to the analytical laboratory.

8.4 Sample Collection. Samples must be collected in a manner that prevents or minimizes loss of volatile components and that does not contaminate the coating reservoir. A suggested procedure is as follows. Select a sample collection container which has a capacity at least 25 percent greater than the container in which the sample is to be transported. Make sure both sample containers are clean and dry. Using clean, long-handled tongs, turn the sample collection container upside down and lower it into the coating reservoir. The mouth of the sample collection container should be at approximately the midpoint of the reservoir (do not take the sample from the top surface). Turn the sample collection container over and slowly bring it to the top of the coating reservoir. Rapidly pour the collected coating into the sample container, filling it completely. It is important to fill the sample container completely to avoid any loss of volatiles due to volatilization into the headspace. Return any unused coating to the reservoir or dispose as appropriate.

NOTE: If a company requests a set of samples for its own analysis, a separate set of samples, using new sample containers, should be taken at the same time.

8.5 Once the sample is collected, place the sample container on a firm surface and insert the inner seal in the container by placing the seal inside the rim of the container, inverting a screw cap, and pressing down on the screw cap which will evenly force the inner seal into the container for a tight fit. Using clean towels or rags, remove all residual coating material from the outside of the sample container after inserting the inner seal. Screw the cap onto the container.

8.5.1 Affix a sample label (see Section 18) clearly identifying the sample, date collected, and person collecting the sample.

8.5.2 Prepare the sample for transportation to the laboratory. The sample should be maintained at the coating's recommended storage temperature specified on the Material Safety Data Sheet, or, if no temperature is specified, the sample should be maintained within the range of 5 °C to 38 °C.

8.9 The shipping container should adhere to U.S. Department of Transportation specification DOT 12–B. Coating samples are considered hazardous materials; appropriate shipping procedures should be followed.

9. Quality Control

9.1 Laboratories using this method should operate a formal quality control program. The minimum requirements of the program should consist of an initial demonstration of laboratory capability and an ongoing analysis of blanks and quality control samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. When results indicate atypical method performance, a quality control check standard (see Section 9.4) must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.2 Before processing any samples, the analyst must demonstrate, through analysis of a reagent blank, that there are no interferences from the analytical system, glassware, and reagents that would bias the sample analysis results. Each time a set of analytical samples is processed or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.3 Required instrument quality control parameters are found in the following sections:

9.3.1 Baseline stability must be demonstrated to be ≤5 percent of full scale using the procedures given in Section 10.1.

9.3.2 The GC calibration is not valid unless the retention time (RT) for each analyte at each concentration is within ±0.05 min of the retention time measured for that analyte in the stock standard.

9.3.3 The retention time (RT) of any sample analyte must be within ±0.05 min of the average RT of the analyte in the calibration standards for the analyte to be considered tentatively identified.

9.3.4 The GC system must be calibrated as specified in Section 10.2.

9.3.5 A one-point daily calibration check must be performed as specified in Section 10.3.

9.4 To establish the ability to generate results having acceptable accuracy and precision, the analyst must perform the following operations.

9.4.1 Prepare a quality control check standard (QCCS) containing each analyte expected in the coating samples at a concentration expected to result in a response between 25 percent and 75 percent of the limits of the calibration curve when the sample is prepared as described in Section 11.5. The QCCS may be prepared from reference standard materials or purchased as certified solutions. If prepared in the laboratory, the QCCS must be prepared independently from the calibration standards.

9.4.2 Analyze three aliquots of the QCCS according to the method beginning in Section 11.5.3 and calculate the weight percent of each analyte using Equation 1, Section 12.

9.4.3 Calculate the mean weight percent ($\bar{X}$) for each analyte from the three results obtained in Section 9.4.2.

9.4.4 Calculate the percent accuracy for each analyte using the known concentrations (Ti) in the QCCS using Equation 3, Section 12.