

**METHOD 306**  
**DETERMINATION OF CHROMIUM EMISSIONS FROM DECORATIVE AND HARD CHROMIUM**  
**ELECTROPLATING AND 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. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 5.

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Chromium	7440-47-3	See Sec. 13.2

1.2 Applicability. This method applies to the determination of chromium (Cr) in emissions from decorative and hard chrome electroplating facilities, chromium anodizing operations, and continuous chromium plating operations at iron and steel facilities.

1.3 Data Quality Objectives. [Reserved]

2.0 Summary of Method.

2.1 Sampling. An emission sample is extracted isokinetically from the source using an unheated Method 5 sampling train (40 CFR Part 60, Appendix A), with a glass nozzle and probe liner, but with the filter omitted. The sample time shall be at least two hours. The Cr emissions are collected in an alkaline solution containing 0.1 N sodium hydroxide (NaOH) or 0.1 N sodium bicarbonate (NaHCO<sub>3</sub>). The collected samples are recovered using an alkaline solution and are then transported to the laboratory for analysis.

2.2 Analysis.

2.2.1 Total chromium samples with high chromium concentrations ( $\geq 35 \mu\text{g/L}$ ) 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  $\mu\text{g/L}$  or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136.

2.2.2 Alternatively, when lower total chromium concentrations ( $< 35 \mu\text{g/L}$ ) 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.

2.2.3 If it is desirable to determine hexavalent chromium (Cr<sup>+6</sup>) 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<sup>+6</sup>, 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.

3.7 Matrix Modifier - A chemical modification to the sample during GFAAS determinations to ensure that the analyte is not lost during the measurement process (prior to the atomization stage)

3.8 Calibration Reference Standards - Quality control standards used to check the accuracy of the instrument calibration curve prior to sample analysis.

3.9 Continuing Check Standard - Quality control standards used to verify that unacceptable drift in the measurement system has not occurred.

3.10 Calibration Blank - A blank used to verify that there has been no unacceptable shift in the baseline either immediately following calibration or during the course of the analytical measurement.

3.11 Interference Check - An analytical/measurement operation that ascertains whether a measurable interference in the sample exists.

3.12 Interelement Correction Factors - Factors used to correct for interfering elements that produce a false signal (high bias).

3.13 Duplicate Sample Analysis - Either the repeat measurement of a single solution or the measurement of duplicate preparations of the same sample. It is important to be aware of which approach is required for a particular type of measurement. For example, no digestion is required for the ICP determination and the duplicate instrument measurement is therefore adequate whereas duplicate digestion/instrument measurements are required for GFAAS.

3.14 Matrix Spiking - Analytical spikes that have been added to the actual sample matrix either before (Section 9.2.5.2) or after (Section 9.1.6). Spikes added to the sample prior to a preparation technique (e.g., digestion) allow for the assessment of an overall method accuracy while those added after only provide for the measurement accuracy determination.

### 4.0 Interferences.

4.1 ICP Interferences.

4.1.1 ICP Spectral Interferences. Spectral interferences are caused by: overlap of a spectral line from

another element; unresolved overlap of molecular band spectra; background contribution from continuous or recombination phenomena; and, stray light from the line emission of high-concentrated elements. Spectral overlap may be compensated for by correcting the raw data with a computer and measuring the interfering element. At the 267.72 nm Cr analytical wavelength, iron, manganese, and uranium are potential interfering elements. Background and stray light interferences can usually be compensated for by a background correction adjacent to the analytical line. Unresolved overlap requires the selection of an alternative chromium wavelength. Consult the instrument manufacturer's operation manual for interference correction procedures.

4.1.2 ICP Physical Interferences. High levels of dissolved solids in the samples may cause significant inaccuracies due to salt buildup at the nebulizer and torch tips. This problem can be controlled by diluting the sample or by extending the rinse times between sample analyses. Standards shall be prepared in the same solution matrix as the samples (*i.e.*, 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub>).

4.1.3 ICP Chemical Interferences. These include molecular compound formation, ionization effects and solute vaporization effects, and are usually not significant in the ICP procedure, especially if the standards and samples are matrix matched.

#### 4.2 GFAAS Interferences.

4.2.1 GFAAS Chemical Interferences. Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 µg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to the concentrated analyte to ensure a known constant effect. Other matrix modifiers recommended by the instrument manufacturer may also be considered.

4.2.2 GFAAS Cyanide Band Interferences. Nitrogen should not be used as the purge gas due to cyanide band interference.

4.2.3 GFAAS Spectral Interferences. Background correction may be required because of possible significant levels of nonspecific absorption and scattering at the 357.9 nm analytical wavelength.

4.2.4 GFAAS Background Interferences. Zeeman or Smith-Hieftje background correction is recommended for interferences resulting from high levels of dissolved solids in the alkaline impinger solutions.

#### 4.3 IC/PCR Interferences.

4.3.1 IC/PCR Chemical Interferences. Components in the sample matrix may cause Cr<sup>+6</sup> to convert to trivalent chromium (Cr<sup>+3</sup>) or cause Cr<sup>+3</sup> to convert to Cr<sup>+6</sup>. The chromatographic separation of Cr<sup>+6</sup> using ion chromatography reduces the potential for other metals to interfere with the post column reaction. For the IC/PCR analysis, only compounds that coelute with Cr<sup>+6</sup> and affect the diphenylcarbazide reaction will cause interference.

4.3.2 IC/PCR Background Interferences. Periodic analyses of reagent water blanks are used to demonstrate that the analytical system is essentially free of contamination. Sample cross-contamination can occur when high-level and low-level samples or standards are analyzed alternately and can be eliminated by thorough purging of the sample loop. Purging of the sample can easily be achieved by increasing the injection volume to ten times the size of the sample loop.

#### 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.

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

## 6.0 Equipment and Supplies.

### 6.1 Sampling Train.

6.1.1 A schematic of the sampling train used in this method is shown in Figure 306-1. The train is the same as shown in Method 5, Section 6.0 (40 CFR Part 60, Appendix A) except that the probe liner is unheated, the particulate filter is omitted, and quartz or borosilicate glass must be used for the probe nozzle and liner in place of stainless steel.

6.1.2 Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended over metal fittings to prevent contamination. If desired, a single combined probe nozzle and liner may be used, but such a single glass assembly is not a requirement of this methodology.

6.1.3 Use 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub> in the impingers in place of water.

6.1.4 Operating and maintenance procedures for the sampling train are described in APTD-0576 of Method 5. Users should read the APTD-0576 document and adopt the outlined procedures.

6.1.5 Similar collection systems which have been approved by the Administrator may be used.

6.2 Sample Recovery. Same as Method 5, [40 CFR Part 60, Appendix A], with the following exceptions:

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

6.2.2 Sample Recovery Solution. Use 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub>, whichever is used as the impinger absorbing solution, in place of acetone to recover the sample.

6.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 250 mL, 500 mL or 1,000 mL.

### 6.3 Analysis.

6.3.1 General. For analysis, the following equipment is needed.

6.3.1.1 Phillips Beakers. (Phillips beakers are preferred, but regular beakers may also be used.)

6.3.1.2 Hot Plate.

6.3.1.3 Volumetric Flasks. Class A, various sizes as appropriate.

6.3.1.4 Assorted Pipettes.

6.3.2 Analysis by ICP.

6.3.2.1 ICP Spectrometer. Computer-controlled emission spectrometer with background correction and radio frequency generator.

6.3.2.2 Argon Gas Supply. Welding grade or better.

### 6.3.3 Analysis by GFAAS.

#### 6.3.3.1 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

#### 6.3.3.2 Graphite Furnace Atomic Absorption Spectrophotometer.

#### 6.3.3.3 Furnace Autosampler

### 6.3.4 Analysis by IC/PCR.

6.3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post-column reagent delivery and mixing system, and a visible detector, capable of operating at 520 nm-540 nm, all with a non-metallic (or inert) flow path. An electronic peak area mode is recommended, but other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in Section 10.4 can be satisfied. A sample loading system is required if preconcentration is employed.

6.3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) non-metallic column with anion separation characteristics and a high loading capacity designed for separation of metal chelating compounds to prevent metal interference. Resolution described in Section 11.6 must be obtained. A non-metallic guard column with the same ion-exchange material is recommended.

6.3.4.3 Preconcentration Column (for older instruments). An HPIC non-metallic column with acceptable anion retention characteristics and sample loading rates must be used as described in Section 11.6.

#### 6.3.4.4 Filtration Apparatus for IC/PCR.

6.3.4.4.1 Teflon, or equivalent, filter holder to accommodate 0.45- $\mu$ m acetate, or equivalent, filter, if needed to remove insoluble particulate matter.

6.3.4.4.2 0.45- $\mu$ m Filter Cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

## 7.0 Reagents and Standards.

**NOTE:** Unless otherwise indicated, all reagents should 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. Reagents should 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<sup>+6</sup> using IC/PCR for direct injection or, if selected, preconcentration.

### 7.1 Sampling.

7.1.1 Water. Reagent water that conforms to ASTM Specification D1193-77 or 91 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<sub>3</sub>) 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 Section 7.1.1 ( $\leq 3$  times the instrument detection limit).

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

**NOTE:** At sources with high concentrations of acids and/or  $\text{SO}_2$ , the concentration of NaOH or  $\text{NaHCO}_3$  should be  $\geq 0.5$  N to insure that the pH of the solution remains at or above 8.5 for NaOH and 8.0 for  $\text{NaHCO}_3$  during and after sampling.

#### 7.1.5 Silica Gel. Same as in Method 5.

#### 7.2 Sample Recovery.

7.2.1 0.1 N NaOH or 0.1 N  $\text{NaHCO}_3$ . Use the same solution for the sample recovery that is used for the impinger absorbing solution.

7.2.2 pH Indicator Strip, for IC/PCR. pH indicator capable of determining the pH of solutions between the pH range of 7 and 12, at 0.5 pH increments.

#### 7.3 Sample Preparation and Analysis.

7.3.1 Nitric Acid ( $\text{HNO}_3$ ), Concentrated, for GFAAS. Trace metals grade or better  $\text{HNO}_3$  must be used for reagent preparation. The ACS reagent grade  $\text{HNO}_3$  is acceptable for cleaning glassware.

7.3.2  $\text{HNO}_3$ , 1.0% (v/v), for GFAAS. Prepare, by slowly stirring, 10 mL of concentrated  $\text{HNO}_3$  into 800 mL of reagent water. Dilute to 1,000 mL with reagent water. The solution shall contain less than 0.001 mg Cr/L.

7.3.3 Calcium Nitrate  $\text{Ca}(\text{NO}_3)_2$  Solution (10  $\mu\text{g}$  Ca/mL) for GFAAS analysis. Prepare the solution by weighing 40.9 mg of  $\text{Ca}(\text{NO}_3)_2$  into a 1 liter volumetric flask. Dilute with reagent water to 1 liter.

7.3.4 Matrix Modifier, for GFAAS. See instrument manufacturer's manual for suggested matrix modifier.

7.3.5 Chromatographic Eluent, for IC/PCR. The eluent used in the analytical system is ammonium sulfate based.

7.3.5.1 Prepare by adding 6.5 mL of 29 percent ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and 33 g of ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) to 500 mL of reagent water. Dilute to 1 liter with reagent water and mix well.

7.3.5.2 Other combinations of eluents and/or columns may be employed provided peak resolution, repeatability, linearity, and analytical sensitivity as described in Sections 9.3 and 11.6 are acceptable.

7.3.6 Post-Column Reagent, for IC/PCR. An effective post-column reagent for use with the chromatographic eluent described in Section 7.3.5 is a diphenylcarbazide (DPC)-based system. Dissolve 0.5 g of 1,5-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  $\mu$ g Cr/L for ICP, and 0, 1, 5, and 10  $\mu$ g  $Cr^{+6}$ /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  $\mu$ g 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  $\mu$ g Cr/L.

#### 7.5 Quality Assurance Audit Samples.

7.5.1 When making compliance determinations, and upon availability, audit samples shall be obtained from the appropriate EPA regional Office or from the responsible enforcement authority and analyzed in conjunction with the field samples.

7.5.2 If EPA or National Institute of Standards and Technology (NIST) reference audit sample are not available, a mid-range standard, prepared from an independent commercial source, may be used.

**NOTE:** To order audit samples, contact the responsible enforcement authority at least 30 days prior to the test date to allow sufficient time for the audit sample to be delivered.

#### 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 (See Figures 306-3 and 306-4).

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<sub>3</sub> 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<sup>3</sup>/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<sup>+6</sup> sample recovery option.

8.2.3 Samples to be analyzed for both total Cr and Cr<sup>+6</sup>, shall be recovered using the Cr<sup>+6</sup> sample option (Section 8.2.6).

8.2.4 A field reagent blank shall be collected for either of the Cr or the Cr<sup>+6</sup> analysis. If both analyses (Cr and Cr<sup>+6</sup>) 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<sup>+6</sup> samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr<sup>+6</sup> 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<sub>3</sub> 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<sup>+6</sup> 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  $\geq 8.5$  for NaOH and  $\geq 8.0$  for NaHCO<sub>3</sub>. If it is not, discard the collected sample, increase the normality of the NaOH or NaHCO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sup>+6</sup> Sample Option.** Samples to be analyzed for Cr<sup>+6</sup> must be shipped and stored at 4°C. Allow Cr<sup>+6</sup> 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<sup>+6</sup> Sample Option.** Samples to be analyzed for Cr<sup>+6</sup> 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 its 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<sub>3</sub> (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.

#### 9.1.8 Audit Sample Analysis.

9.1.8.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

9.1.8.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.1.8.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

#### 9.1.9 Audit Sample Results.

9.1.9.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.1.9.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

9.1.9.3 The concentrations of the audit samples obtained by the analyst shall agree within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.1.9.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

#### 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.

9.2.8 Audit Sample Analysis.

9.2.8.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

9.2.8.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.2.8.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

9.2.9 Audit Sample Results.

9.2.9.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.2.9.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

9.2.9.3 The concentrations of the audit samples obtained by the analyst shall agree within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.2.9.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

### 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<sup>+6</sup> 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<sup>+6</sup> 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.

9.3.6 Audit Sample Analysis.

9.3.6.1 When the method is used to analyze samples to demonstrate compliance with source emission regulation, an audit sample must be analyzed, subject to availability.

9.3.6.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.3.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

9.3.7 Audit Sample Results.

9.3.7.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.3.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period. 9.3.7.3 The concentrations of the audit samples obtained by the analyst shall agree within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.3.7.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

#### 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  $\mu\text{g Cr/mL}$ . It is important that the analyst measure the field sample volume prior to analyzing the sample. This will allow for conversion of  $\mu\text{g Cr/mL}$  to  $\mu\text{g Cr/sample}$ .

### 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  $35 \mu\text{g/L}$  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  $\text{NaHCO}_3$ , 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  $\mu\text{g Cr/mL}$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  and 1 mL of the 10  $\mu\text{g/mL}$  of  $\text{Ca}(\text{NO}_3)_2$ . Dilute to 50 mL with reagent water.

11.3.2  $\text{HNO}_3$  Concentration. A different final volume may be used based on the expected Cr concentration, but the  $\text{HNO}_3$  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  $\text{HNO}_3$  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<sub>3</sub> 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<sub>3</sub>) 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  $\mu\text{g Cr/mL}$  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- $\mu\text{m}$  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  $\text{Cr}^{+6}$ .

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  $\text{Cr}^{+6}$  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  $\text{NaHCO}_3$ , 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  $\text{NaHCO}_3$  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  $\text{Cr}^{+6}$  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- $\mu$ L 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  $\text{Cr}^{+6}$  is collected on the resin bed of the column.

11.6.6.1.2 After separation from other sample components, the  $\text{Cr}^{+6}$  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  $\text{Cr}^{+6}$  complex formed.

11.6.6.1.4 The IC retention time and the absorbance of the  $\text{Cr}^{+6}$  complex with known  $\text{Cr}^{+6}$  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  $\text{Cr}^{+6}$  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  $\geq 8.5$  for NaOH and  $\geq 8.0$  if using  $\text{NaHCO}_3$ ; 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  $\text{Cr}^{+6}$ /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  $\mu\text{g Cr}^{+6}/\text{mL}$  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  $\text{Cr}^{+6}$ .

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  $\text{Cr}^{+6}$ .

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,  $\mu\text{g Cr}/\text{mL}$ .

$C_{Cr}$	=	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, ìg.
$V_{ad}$	=	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.
$V_{mL}$	=	Volume of impinger contents plus rinses, mL.
$V_{m(std)}$	=	Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm.

$$F = \frac{V_{af}}{V_{bf}}$$

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:

12.1.2.4 Digestion Factor. The digestion factor is the ratio of the volume of sample aliquot after

$$D = \frac{V_{ad}}{V_{bd}}$$

digestion to the volume before digestion. This ratio is given by Equation 306-2.

$$M_{Cr} = V_{mL} \times C_S \times F \times D$$

12.1.2.5 Total Cr in Sample. Calculate  $M_{Cr}$ , the total ìg Cr in each sample, using the following equation:

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

$$C_{Cr} = \frac{M_{Cr}}{V_{m(std)}} \times 10^{-3} \frac{\text{mg}}{\text{mg}}$$

mg/dscm on a dry basis, corrected to standard conditions using the following equation:

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<sup>+6</sup>/L.**

13.2.1.5 Determination of Detection Limits. The laboratory performing the Cr<sup>+6</sup> 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 1/2 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<sup>+6</sup>/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<sup>+6</sup>/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 pre-concentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr<sup>+6</sup> 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 Cr<sup>+6</sup> 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.

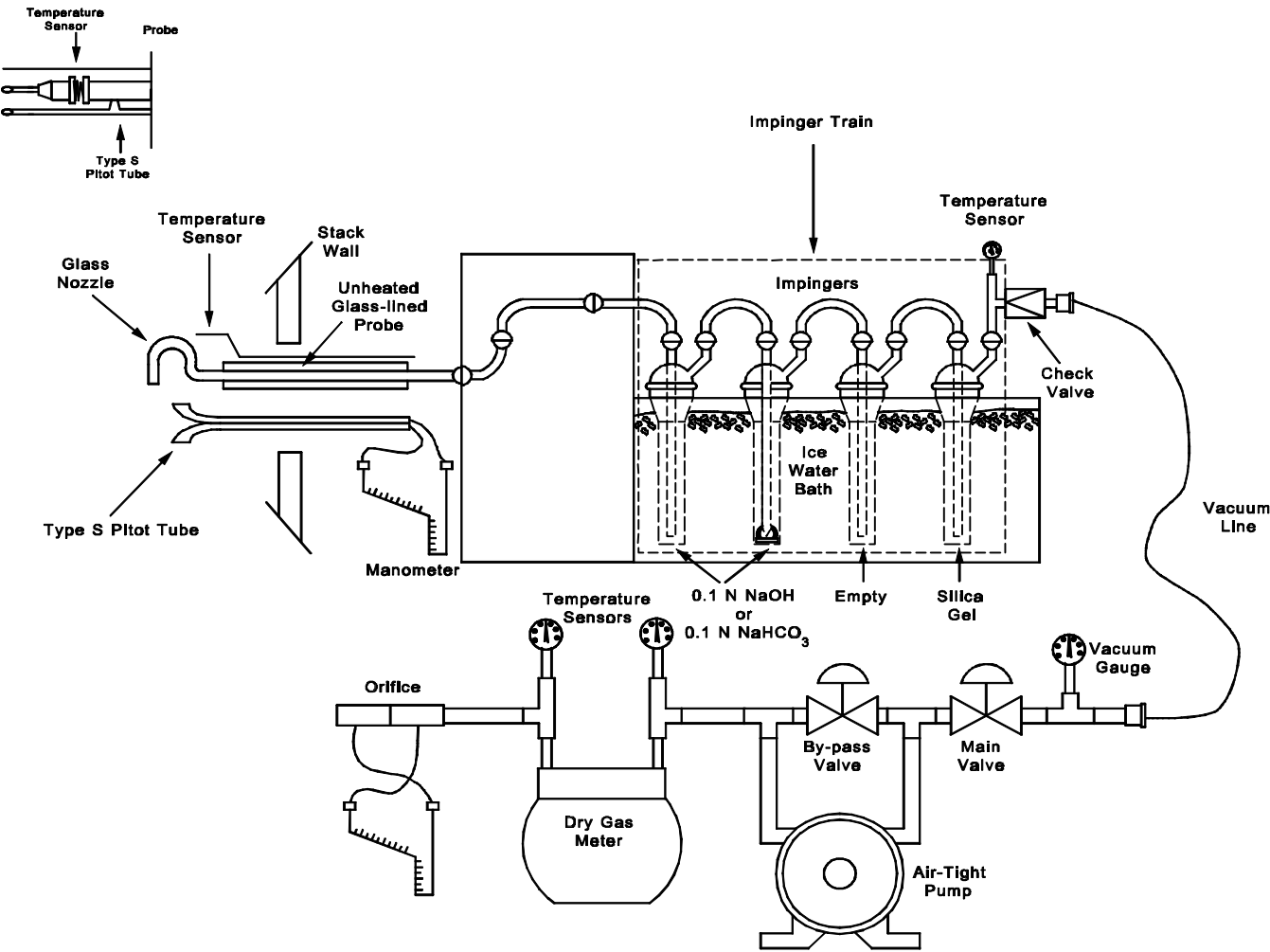


Figure 306-1. Chromium Sampling Train.

