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

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<sup>+6</sup>.

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 ( $\geq 35 \mu\text{g/L}$ ) 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.

2.1.2.2 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.

2.1.2.3 If it is desirable to determine hexavalent chromium ( $\text{Cr}^{+6}$ ) 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  $\text{Cr}^{+6}$ , 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 ( $\text{Cr}^{+3}$ ,  $\text{Cr}^{+6}$ ).

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 ( $\frac{1}{4}$  -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 (  $\frac{1}{4}$  -in.) to 9.5-mm (  $\frac{3}{8}$  -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 (  $\frac{1}{4}$  -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 (  $\frac{3}{32}$  -in.) ID.

6.1.5.2.1 When assembling the first container, place the orifice tip end of the tube approximately 4.8 mm (  $\frac{3}{16}$  -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 (  $\frac{1}{2}$  -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 ( $\frac{1}{2}$  -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 ( $\frac{1}{2}$  -in.) ID glass tube, having an unrestricted opening located 13 mm ( $\frac{1}{2}$  -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 ( $\text{m}^3/\text{min}$ ) or 0.75 cubic feet per minute (cfm).

6.1.7.1 The critical orifice can be constructed by sealing a 2.4-mm ( $\frac{3}{32}$  -in.) ID brass tube approximately 14.3 mm ( $\frac{9}{16}$  -in.) in length inside a second brass tube that is approximately 8 mm ( $\frac{5}{16}$  -in.) ID and 14.3-mm ( $\frac{9}{16}$  -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 ( $\frac{3}{8}$  -in.), 6.4-mm ( $\frac{1}{4}$  -in.) or 3.2-mm ( $\frac{1}{8}$  -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  $\text{H}_g$  (30 in.  $\text{H}_g$ ) vacuum in 25.4 mm  $\text{H}_G$  (1 in.  $\text{H}_g$ ) 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.  $\text{H}_g$  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 ( $\frac{1}{4}$  -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  $\pm 2\%$  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  $\Delta H_{\text{orifice}}$  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  $\pm 2.5$  mm H<sub>g</sub> (0.1 in. H<sub>g</sub>).

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<sub>g</sub> (0.1 in. H<sub>g</sub>) 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<sub>g</sub> 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<sub>3</sub>, 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<sup>+6</sup> 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<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 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 ( $\text{NaHCO}_3$ ) 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 ( $\leq 3$  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 levels  $\leq 10$  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.

7.1.3 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 ( $\text{Cr}^{+6}$  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  $\Delta p$  (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  $\Delta p$  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:

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

Where:

$n$  = Sampling point number.

$\Delta p$  = Average pressure differential across pitot tube, mm H<sub>2</sub>O (in. H<sub>2</sub>O).

$\Delta P_{\text{avg}}$  = Average of  $\Delta p$  values, mm H<sub>2</sub>O (in. H<sub>2</sub>O).

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 thoroughly 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<sub>3</sub>) 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<sub>3</sub> 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  $\leq 0.02$  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  $\geq 15$  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  $\geq 380$  mm Hg ( $\geq 15$  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  $\geq 356$  mm Hg ( $\geq 14$  in. Hg) at sea level and  $\sim 305$  mm Hg ( $\sim 12$  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<sup>+6</sup> sample recovery option. 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 8.2.2).

NOTE: Collect a reagent blank sample for each of the total Cr or the Cr<sup>+6</sup> analytical options. If both analyses (Cr and Cr<sup>+6</sup>) 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<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).

### 8.2.1 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, non-metal 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<sub>3</sub> 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<sup>+6</sup> 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 non-metal 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  $\geq 8.5$  for NaOH and  $\geq 8.0$  for NaHCO<sub>3</sub>. If not, discard the collected sample, increase the concentration of the NaOH or NaHCO<sub>3</sub> 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<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 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<sup>+6</sup> 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<sub>3</sub> 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<sup>+6</sup> Option. Samples that are to be analyzed for Cr<sup>+6</sup> must be shipped and stored at 4 °C (~40 °F).

NOTE: Allow Cr<sup>+6</sup> 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<sup>+6</sup> Option. Samples that are to be analyzed for Cr<sup>+6</sup> 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:

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

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

Where:

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

$P_{\text{std}}$  = 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 +  $t_m$  (°C).

English °R = 460 +  $t_m$  (°F).

$T_{\text{std}}$  = Standard absolute temperature,

Metric = 293 °K.

English = 528 °R.

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

$V_{m(\text{std}),\text{mfg}}$  = 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:

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

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., manufacturer'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  $\sim 0.75$  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  $\mu\text{g Cr/mL}$ . It is important that the analyst measure the volume of the field sample prior to analyzing the sample. This will allow for conversion of  $\mu\text{g Cr/mL}$  to  $\mu\text{g Cr/sample}$ .

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,  $\mu g$  Cr/mL.

$C_{Cr}$  = Concentration of Cr in stack gas, dry basis, corrected to standard conditions  $\mu g/dscm$  ( $gr/dscf$ ).

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,  $\mu g$  ( $gr$ ).

$M_s$  = Molecular weight of wet stack gas, wet basis,  $g/g\text{-mole}$ , ( $lb/lb\text{-mole}$ ); 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,  $^{\circ}C$  ( $^{\circ}F$ ).

$T_m$  = Absolute average dry gas meter temperature:

Metric  $^{\circ}\text{K} = 273 + t_m (^{\circ}\text{C})$ .

English  $^{\circ}\text{R} = 460 + t_m (^{\circ}\text{F})$ .

$t_s$  = Average stack temperature,  $^{\circ}\text{C}$  ( $^{\circ}\text{F}$ ).

$T_s$  = Absolute average stack gas temperature: Metric  $^{\circ}\text{K} = 273 + t_s (^{\circ}\text{C})$ . English  $^{\circ}\text{R} = 460 + t_s (^{\circ}\text{F})$ .

$T_{\text{std}}$  = Standard absolute temperature: Metric =  $293 ^{\circ}\text{K}$ . English =  $528 ^{\circ}\text{R}$ .

$V_{\text{ad}}$  = Volume of sample aliquot after digestion (mL).

$V_{\text{af}}$  = Volume of sample aliquot after dilution (mL).

$V_{\text{bd}}$  = Volume of sample aliquot submitted to digestion (mL).

$V_{\text{bf}}$  = Volume of sample aliquot before dilution (mL).

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

$V_{\text{mL}}$  = Volume of impinger contents plus rinses (mL).

$V_{\text{m(std)}}$  = 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).

$\Delta p$  = Velocity head measured by the Type S pitot tube, cm  $\text{H}_2\text{O}$  (in.  $\text{H}_2\text{O}$ ).

$\Delta p_{\text{avg}}$  = Average of  $\Delta p$  values, mm  $\text{H}_2\text{O}$  (in.  $\text{H}_2\text{O}$ ).

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:

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

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.

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

12.5 Total Cr in Sample. Calculate  $M_{Cr}$ , the total  $\mu\text{g}$  Cr in each sample, using the following equation:

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

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:

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

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  $\mu\text{g}/\text{dscm}$  ( $\mu\text{g}/\text{dscf}$ ) on a dry basis, corrected to standard conditions, using the following equation:

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

NOTE: To convert  $\mu\text{g}/\text{dscm}$  ( $\mu\text{g}/\text{dscf}$ ) to  $\text{mg}/\text{dscm}$  ( $\text{mg}/\text{dscf}$ ), divide by 1000.

12.8 Stack Gas Velocity.

12.8.1  $K_p$  = Velocity equation constant:

$$\text{Metric } K_p = 34.97 \frac{m}{\text{sec}} \left[ \frac{(\text{g/g-mole})(\text{mm Hg})}{(^{\circ}\text{K})(\text{mm H}_2\text{O})} \right]^{1/2}$$

$$\text{English } K_p = 85.49 \frac{ft}{\text{sec}} \left[ \frac{(\text{lb/lb-mole})(\text{in. Hg})}{(^{\circ}\text{R})(\text{in. H}_2\text{O})} \right]^{1/2}$$

12.8.2 Average Stack Gas Velocity.

$$\begin{aligned}
 v_s &= K_p C_p \left( \sqrt{\Delta P} \right)_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}} \\
 &= 34.97 C_p \left( \sqrt{\Delta P} \right)_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}} \quad \text{Eq. 306A-9}
 \end{aligned}$$

12.9 Cross sectional area of stack.

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

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:

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

Where:

3600 = Conversion factor, sec/hr.

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

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):

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

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

### 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<sup>+6</sup>/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<sup>+36</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 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<sup>+6</sup> 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  $\mu\text{g Cr/L}$ ; the mean reported values were 10, 50, and 149  $\mu\text{g Cr/L}$ ; 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  $\mu\text{g Cr/L}$ .

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  $\mu\text{g Cr/L}$ , the standard deviations were  $\pm 0.1$ ,  $\pm 0.2$ , and  $\pm 0.8$ , 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  $\text{Cr}^{+6}$  and 3.5  $\mu\text{g/dscm}$  of total Cr is 25 percent and 9 percent, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of  $\text{Cr}^{+6}$  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*

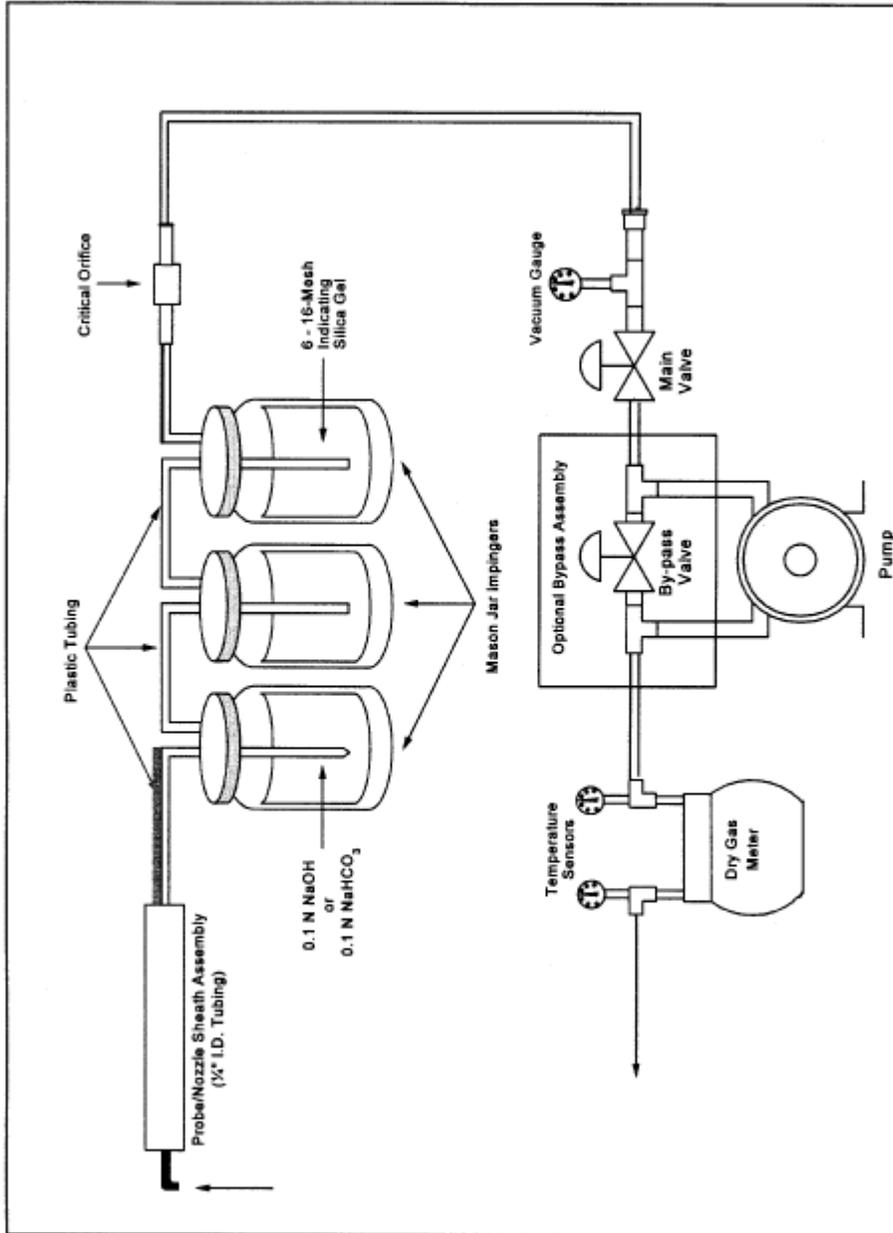


Figure 306A-1. Method 306A Sampling Train.



