3.3.4.4 0.45-µm Filter Cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

## 4. Reagents

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.

4.1 Sampling.

4.1.1 Water. Reagent water that conforms to ASTM Specification D1193-77, Type II (incorporated by reference—see § 63.14). It is recommended that water blanks be checked prior to preparing sampling reagents to ensure that the Cr content is less than the analytical detection limit.

4.1.2 Sodium Hydroxide (NaOH) Absorbing Solution, 0.1 N or Sodium Bicarbonate (NaHCO<sub>3</sub>) Absorbing Solution, 0.1 N. Dissolve 4.0 g of sodium hydroxide in 1 l of water, or dissolve 8.5 g of sodium bicarbonate in 1 l of water.

4.2 Sample Recovery.

4.2.1 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub>. See section 4.1.2. Use the same solution for recovery as was used in the impingers.

4.2.2 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 intervals.

4.3 Sample Preparation and Analysis.

4.3.1 Nitric Acid (HNO<sub>3</sub>), Concentrated, for GFAAS. Trace metals grade or better HNO<sub>3</sub> must be used for reagent preparation. The ACS reagent grade HNO<sub>3</sub> is acceptable for cleaning glassware.

4.3.2  $\dot{\text{HNO}}_3$ , 1.0 percent (v/v), for GFAAS. Add, with stirring, 10 ml of concentrated  $HNO_3$  to 800 ml of water. Dilute to 1,000 ml with water. This reagent shall contain less than 0.001 mg Cr/l.

4.3.3 Calcium Nitrate Ca( $NO_3$ )2 Solution (10 µg Ca/ml) for GFAAS. Prepare the solution by weighing 36 mg of Ca( $NO_3$ )<sub>2</sub> into a 1 l volumetric flask. Dilute with water to 1 l.

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

**4**.3.5 Chromatographic Eluent, for IC/ PCR. The eluent used in the analytical system is ammonium sulfate based. Prepare by adding 6.5 ml of 29 percent ammonium hydroxide (NH<sub>4</sub>OH) and 33 g of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) to 500 ml of reagent water. Dilute to 1 l with reagent water and mix well. Other combinations of eluents and/ or columns may be employed provided peak resolution, as described in section 5.5, repeatability and linearity, as described in section 6.4.1, and analytical sensitivity are acceptable.

4.3.6 Post-Column Reagent, for IC/PCR. An effective post-column reagent for use with the chromatographic eluent described in section 4.3.5 is a diphenylcarbazide (DPC) based system. Dissolve 0.5 g of 1,5diphenylcarbazide 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 l with reagent water.

4.3.7 Chromium Štandard Stock Solution (1,000 mg/l). Procure a certified aqueous standard or dissolve 2.829 g of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>,) in water and dilute to 1 l.

4.3.8 Calibration Standards for GFAAS. Chromium solutions for GFAAS calibration shall be prepared to contain 1.0 percent (v/ v) HNO<sub>3</sub>. The zero standard shall be 1.0 percent (v/v) HNO<sub>3</sub>. Calibration standards should be prepared daily by diluting the Cr standard stock solution (section 4.3.7) with 1.0 percent HNO<sub>3</sub>. Use at least four standards to make the calibration curve. Suggested levels are 0, 5, 50, and 100 µg Cr/l.

4.3.9 Calibration Standards for ICP or IC/ PCR. Prepare calibration standards for ICP or IC/ PCR. Prepare calibration standards for ICP or IC/PCR by diluting the Cr standard stock solution (section 4.3.7) with 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub>, whichever was used as the impinger absorbing solution, to achieve a matrix similar to the actual field samples. Suggested levels are 0, 25, 50, and 100 µg Cr/ I for ICP, and 0, 0.5, 5, and 10 µg Cr<sup>+6</sup>/I for IC/PCR.

4.4 Glassware Cleaning Reagents.

4.4.1 HNO<sub>3</sub>, Concentrated. The ACS reagent grade or equivalent.
4.4.2 Water. Reagent water that conforms

4.4.2 Water. Reagent water that conforms to ASTM Specification D1193–77, Type II, (incorporated by reference—see § 63.14).

4.4.3 HNO<sub>3</sub>, 10 percent (v/v). Add with stirring 500 ml of concentrated HNO<sub>3</sub> to a flask containing approximately 4,000 ml of water. Dilute to 5,000 ml with water. Mix well. The reagent shall contain less than 2  $\mu$ g Cr/l.

## 5. Procedure

5.1 Sampling. (a) Same as Method 5, section 4.1 (40 CFR part 60, appendix A), except omit the filter and filter holder from the sampling train, use a glass nozzle and probe liner, do not heat the probe, place 100 ml of 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub> in each of the first two impingers, and record the data for each run on a data sheet such as the one shown in Figure 306–2.

(b) 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 all glassware in 10 percent (v/v) HNO<sub>3</sub> solution for a minimum of 4 hours, rinse three times with reagent water, and allowed to air dry. Cover all glassware openings where contamination can occur with Parafilm, or equivalent, until the sampling train is assembled for sampling.

(c) If the sample is going to be analyzed for  $Cr^{+6}$  using IC/PCR, determine the pH of the solution in the first impinger at the end of the sampling run using a pH indicator strip. The pH of the solution should be greater than 8.5. If not, the concentration of the NaOH or NaHCO<sub>3</sub> impinger absorbing solution should be increased to 0.5 N and the sample should be rerun.

5.2 Sample Recovery. Follow the basic procedures of Method 5, section 4.2, with the

exceptions noted below; a filter is not recovered from this train.

5.2.1 Container No. 1. Measure the volume of the liquid in the first, second, and third impingers and quantitatively transfer into a labelled sample container. Use approximately 200 to 300 ml of 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub> to rinse the probe nozzle, probe liner, three impingers, and connecting glassware; add this rinse to the same container.

5.2.2 Container No. 2 (Reagent Blank). Place approximately 500 ml of 0.1 N NaOH or 0.1 N NaHCO<sub>3</sub> absorbing solution in a labeled sample container.

5.2.3 Sample Filtration for IC/PCR. If the sample is to be analyzed for  $Cr^{+6}$  by IC/PCR, it must be filtered immediately following recovery to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process. Filter the entire contents of Container No. 1 through a 0.45- $\mu$ m acetate filter (or equivalent), and collect the filtrate in a 1,000 ml graduated cylinder. Rinse the sample container with reagent water three separate times, pass these rinses through the filtrate. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container.

5.2.4 Sample Preservation. Refrigerate samples upon receipt. (Containers Nos. 1 and 2).

5.3 Sample Preparation and Analysis for GFAAS. For analysis by GFAAS, an acid digestion of the alkaline impinger solution is required. Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to assess possible contamination resulting from the sample processing. The 1.0 percent HNO<sub>3</sub> is the calibration blank. The 0.1 N NaOH solution or the 0.1 N NaHCO<sub>3</sub> from section 5.2.2 is the reagent blank. The reagent blank must be carried through the complete analytical procedure, including the acid digestion, and must contain the same acid concentration in the final solution as the sample solutions.

5.3.1 Acid Digestion for GFAAS. (a) In a beaker, add 10 ml of concentrated HNO<sub>3</sub> to a sample aliquot of 100 ml taken for analysis. Cover the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample down to near dryness. Add another 5 ml of concentrated HNO<sub>3</sub> to complete the digestion. Carefully reflux the sample volume down to near dryness. Wash down the beaker walls and watch glass with reagent water. The final concentration of HNO<sub>3</sub> in the solution should be 1 percent (v/v). Transfer the digested sample to a 50 ml volumetric flask. Add 0.5 ml of concentrated HNO<sub>3</sub>, and 1 ml of the 10 µg/ml of Ca (NO<sub>3</sub>)<sub>2</sub>.

(b) Dilute to 50 ml with reagent water. A different final volume may be used, based on the expected Cr concentration, but the  $HNO_3$  concentration must be maintained at 1 percent (v/v).

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