5.3.2 Sample Analysis by GFAAS. (a) The 357.9-nm wavelength line shall be used. Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

(b) Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments and/or with time, the validity of the furnace 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. Similar verification of furnace parameters may be required for complex sample matrices. Calibrate the GFAAS system following the procedures specified in section 6.

(c) Inject a measured aliquot of digested sample into the furnace and atomize. If the concentration found exceeds the calibration range, the sample should be diluted with the calibration blank solution (1.0 percent HNO₃) and reanalyzed. Consult the operator's manual for suggested injection volumes. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

(d) Analyze a minimum of one matrixmatched reagent blank per sample batch to determine if contamination or any memory effects are occurring. Analyze a calibration blank and a midpoint calibration check standard after approximately every 10 sample injections.

(e) Calculate the Cr concentrations:

(1) By the method of standard additions (see operator's manual),

(2) From the calibration curve, or
(3) Directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. All results should be reported in μg

Cr/ml with up to three significant figures. 5.4 Sample Analysis by ICP. (a) The ICP measurement is performed directly on the alkaline impinger solution; acid digestion is not necessary provided the samples and standards are matrix matched. However, ICP should only be used when the solution analyzed has a Cr concentration greater than $35 \mu g/l$.

(b) 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 sample processing. Use either 0.1 N NaOH or 0.1 N NaHCO₃, whichever was used for the impinger absorbing solution, for the calibration blank. The calibration blank can be prepared fresh in the laboratory; it does not have to be from the same batch of solution that was used in the field. Prepare a sufficient quantity to flush the system between standards and samples. The reagent blank (section 5.2.2) is a sample of the impinger solution used for sample collection that is collected in the field during the testing program.

(c) Set up the instrument with proper operating parameters including wavelength,

background correction settings (if necessary), and interfering element correction settings (if necessary). The instrument must be allowed to become thermally stable before beginning performance of 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).

(d) Calibrate the instrument according to the instrument manufacturer's recommended procedures, and the procedures specified in section 6.3. Before analyzing the samples, reanalyze the highest calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5 percent, or the established control limits, whichever is lower (see sections 6 and 7). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

(e) Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample or standard. Analyze the midpoint calibration standard and the calibration blank after each 10 samples. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

(f) 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 are already established.

(g) If dilutions are performed, the appropriate factors must be applied to sample values. All results should be reported in μ g Cr/ml with up to three significant figures.

5.5 Sample Analyses by IC/PCR. (a) The Cr⁺⁶ content of the sample filtrate is determined by IC/PCR. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

(b) Prior to preconcentration and/or analysis, filter all field samples through a 0.45- μ m filter. This filtration should be conducted just prior to sample injection/analysis.

(c) The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent (as described in section 3.4.3.3), followed by removal of the analyte from the absorbent. Inject the sample into a sample loop of the desired size (use repeated loadings or a larger size loop for greater sensitivity). The Cr⁺⁶ is collected on the resin bed of the column. Switch the injection valve so that the eluent displaces the concentrated Cr⁺⁶ sample, moving it off the preconcentration column and onto the IC anion separation column. After separation from other sample components, the Cr+6 forms a specific complex in the post-column reactor with the DPC reaction solution, and the complex is detected by visible absorbance at a wavelength of 520 nm. The amount of absorbance measured is proportional to the concentration of the Cr+6 complex formed. Compare the IC retention time and the absorbance of the Cr⁺⁶ complex with known Cr+6 standards analyzed under identical conditions to provide both qualitative and quantitative analyses.

(d) 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 sample processing. Use either 0.1 N NaOH or 0.1 N NaHCO₃, whichever was used for the impinger solution, for the calibration blank. The calibration blank can be prepared fresh in the laboratory; it does not have to be from the same batch of solution that was used in the field. The reagent blank (section 5.2.2) is a sample of the impinger solution used for sample collection that is collected in the field during the testing program.

(e) Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent flow rate at approximately 1 ml/min and the post-column reagent flow rate at approximately 0.5 ml/min. Note: As long as the ratio of eluent flow rate to PCR flow rate remains constant, the standard curve should remain linear. Inject a sample of reagent water to ensure that no Cr^{+6} appears in the water blank.

(f) First, inject the calibration standards prepared, as described in section 4.3.9 to cover the appropriate concentration range, starting with the lowest standard first. Next, inject, in duplicate, the calibration reference standard (as described in section 7.3.1), followed by the reagent blank (section 5.2.2), and the field samples. Finally, repeat the injection of the calibration standards to assess instrument drift. Measure areas or heights of the Cr+6/DPC complex chromatogram peaks. The response for replicate, consecutive injections of samples must be within 5 percent of the average response, or the injection should be repeated until the 5 percent criterion can be met. Use the average response (peak areas or heights) from the duplicate injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentrations of the field samples employing the average response from the duplicate injections.

6. Calibration

6.1 Sampling Train Calibration. Perform all of the calibrations described in Method 5, section 5 (40 CFR part 60, appendix A). The alternate calibration procedures described in section 7 of Method 5 (40 CFR part 60, appendix A) may also be used.

6.2 GFAAS Calibration. Either run a series of chromium standards and a calibration blank and construct a calibration curve by plotting the concentrations of the standards against the absorbencies, or using the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration, if applicable. This is customarily performed automatically with most instrument computer-based data systems.

6.2.1 GFAAS Calibration Curve. If a calibration curve is used, it should be prepared daily with a minimum of a calibration blank and three standards. Calibration standards for total chromium should start with 1 percent v/v HNO₃ with