no chromium for the calibration blank, with appropriate increases in total chromium concentration for the other calibration standards (see section 4.3.9.). Calibration standards should be prepared fresh daily.

6.3 ICP Calibration. Calibrate the instrument according to the instrument manufacturer's recommended procedures, using a calibration blank and three standards for the initial calibration. Calibration standards should be prepared fresh daily, as described in section 4.3.9. Be sure that samples and calibration standards are matrix matched. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

6.4 IC/PCR Calibration. Prepare a calibration curve using the calibration blank and three calibration standards prepared fresh daily as described in section 4.3.9. Run the standards with the field samples as described in section 5.5.

7. Quality Control

7.1 GFAAS Quality Control

7.1.1 GFAAS Calibration Reference Standards. If a calibration curve is used, it must be verified by use of 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. The calibration reference standard must be measured within 10 percent of it's true value for the curve to be considered valid. The curve must be validated before sample analyses are performed.

7.1.2 GFAAS Check Standards. (a) Run a check standard and a calibration blank after approximately every 10 sample injections, and at the end of the analytical run. These standards are run, 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 indicates that the graphite tube should be replaced. Check standards can 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 reanalyze all samples analyzed subsequent to the last acceptable check standard analysis.

(b) The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis 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.

7.1.3 GFAAS Duplicate Samples. Run one duplicate sample for every 20 samples, (or one per source test, whichever is more frequent). Duplicate samples are brought through the whole sample preparation and analytical process separately. Duplicate samples shall agree within 10 percent.

7.1.4 GFAAS Matrix Spiking. Spiked samples shall be prepared and analyzed daily to ensure that correct procedures are being followed and that all equipment is operating properly. Spiked sample recovery analyses should indicate a recovery for the Cr spike of between 75 and 125 percent. Spikes are added prior to any sample preparation. Cr levels in the spiked sample should provide final solution concentrations that fall within the linear portion of the calibration curve.

7.1.5 GFAAS Method of Standard Additions. Whenever sample matrix problems are suspected and standard/sample matrix matching is not possible or whenever a new sample matrix is being analyzed, the method of standard additions shall be used for the analysis of all extracts. Section 5.4.2 of Method 12 (40 CFR part 60, appendix A) specifies a performance test to determine if the method of standard additions is necessary.

7.1.6 GFAAS Reagent Blank Samples. Analyze a minimum of one matrix-matched reagent blank (section 5.2.2) per sample batch to determine if contamination or memory effects are occurring. The results should agree within three standard deviations of the mean blank value.

7.2 ICP Quality Control.

7.2.1 ICP Interference Check. Prepare an interference check solution to contain known concentrations of interfering elements that will provide an adequate test of the correction factors in the event of potential spectral interferences. Two potential interferences, iron and manganese, may be prepared as 1,000 µg/ml and 200 µg/ml solutions, respectively. The solutions should be prepared in dilute HNO3 (1-5 percent). Particular care must be taken 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. 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 interelement correction factors are used properly, no false Cr should be detected.

7.2.2 **ICP Calibration Reference** Standards. Prepare a calibration reference standard in the same alkaline matrix as the calibration standards; it should be at least 10 times the instrumental detection limit. This reference standard should be prepared from a different Cr stock solution source than that used for preparation of the calibration curve standards and is used to verify the accuracy of the calibration curve. Prior to sample analysis, analyze at least one reference standard. The calibration reference standard must be measured within 10 percent of it's true value for the curve to be considered valid. The curve must be validated before sample analyses are performed.

7.2.3 ICP Check Standards. Run a check standard and a calibration blank after every 10 samples, and at the end of the analytical run. Check standards can 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. The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis 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.

7.2.4 ICP Duplicate Samples. Analyze one duplicate sample for every 20 samples, (or one per source test, whichever is more frequent). Duplicate samples are brought through the whole sample preparation and analytical process. Duplicate samples shall agree within 10 percent.

7.2.5 ICP Reagent Blank Samples. Analyze a minimum of one matrix-matched reagent blank (section 5.2.2) per sample batch to determine if contamination or memory effects are occurring. The results should agree within three standard deviations of the mean blank value.

7.3 IC/PCR Quality Control. 7.3.1 IC/PCR Calibration Reference Standards. Prepare a calibration reference standard in the same alkaline matrix as the calibration standards at a concentration that is at or near the mid-point of the calibration curve. This reference standard should be prepared from a different Cr stock solution source than that used for preparing the calibration curve standards. The reference standard is used to verify the accuracy of the calibration curve. Prior to sample analysis, analyze at least one reference standard. The results of this analysis of the reference standard must be within 10 percent of the true value of the reference standard for the calibration curve to be considered valid. The curve must be validated before sample analyses are performed.

7.3.2 IC/PCR Check Standards. (a) Run the calibration blank and calibration standards with the field samples as described in section 5.5. For each standard, determine the peak areas (recommended) or the peak heights, calculate the average response from the duplicate injections, and plot the average response against the Cr+6 concentration in µg/l. The individual responses for each calibration standard determined before and after field sample analysis must be within 5 percent of the average response for the analysis to be valid. If the 5 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses are performed.

(b) Employing linear regression, calculate a predicted value for each calibration standard using the average response for the duplicate injections. Each predicted value must be within 7 percent of the actual value for the calibration curve to be considered acceptable. If not acceptable, remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

7.3.3 IC/PCR Duplicate Samples. Analyze one duplicate sample for every 20 samples, (or one per source test, whichever is more frequent). Duplicate samples are brought through the whole sample preparation and