reducing the volume of the digested sample for GFAAS, improving the analytical detection limits, or any combination of the three.

2.3 Precision. The following precision data have been reported for the three analytical methods. In the case of the GFAAS there is also bias data. In all cases, when sampling precision is combined with analytical precision, the resulting overall precision may be lower.

2.3.1 GFÅAS Precision. As reported in Method 7191 of SW–846, in a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 μ 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.

2.3.2 ICP Precision. As reported in Method 6010A of SW–846, in an EPA roundrobin 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.

2.3.3 IC/PCR Precision. As reported in 40 CFR part 266, appendix IX, the precision of the IC/PCR with sample preconcentration is 5 to 10 percent; the overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 µg/dscm of total Cr is 25 percent and 9 percent for Cr^{+6} and total Cr, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6} the precision is 20 percent.

2.4 Interferences.

2.4.1 GFAAS 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 suitable. Nitrogen should not be used as the purge gas due to cvanide band interference. Background correction may be required because of possible significant levels of nonspecific absorption and scattering at the 357.9 nm analytical wavelength. Zeeman or Smith-Hieftje background correction is recommended to correct for interferences due to high levels of dissolved solids in the alkaline impinger solutions.

2.4.2 ICP Interferences.

2.4.2.1 ICP Spectral Interferences. (a) Spectral interferences are caused by:

(1) Overlap of a spectral line from another element;

(2) Unresolved overlap of molecular band spectra;

(3) Background contribution from continuous or recombination phenomena; and (4) Stray light from the line emission of high-concentration elements.

(b) Spectral overlap may be compensated for by computer correcting the raw data after monitoring 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 Cr wavelength. Consult the instrument manufacturer's operation manual for interference correction procedures.

2.4.2.2 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 providing for extended rinse times between sample analyses. Standards are prepared in the same matrix as the samples (i.e., 0.1 N NaOH or 0.1 N NaHCO₃).

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

2.4.3 IC/PCR Interferences. Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr+3) or cause Cr+3 to convert to Cr+6. The chromatographic separation of Cr⁺⁶ 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⁺⁶ and affect the diphenylcarbazide reaction will cause interference. Periodic analyses of reagent water blanks are used to demonstrate that the analytical system is essentially free of contamination. Sample crosscontamination that can occur when highlevel and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be achieved by increasing the injection volume of the samples to ten times the size of the sample loop.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 306-1. The train is the same as Method 5, section 2.1 (40 CFR part 60, appendix A), except that the filter is omitted, and quartz or borosilicate glass must be used for the probe nozzle and liner in place of stainless steel. It is not necessary to heat the probe liner. 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 piece is not a requirement of this methodology. Use 0.1 N NaOH or 0.1 N NaHCO₃ in the impingers in place of water.

3.2 Sample Recovery. Same as Method 5, section 2.2 (40 CFR part 60, appendix A), with the following exceptions:

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

3.2.2 Sample Recovery Solution. Use 0.1 N NaOH or 0.1 N NaHCO₃, whichever was used as the impinger absorbing solution, in place of acetone to recover the sample.

3.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 500 ml or 1,000 ml.

3.2.4 Filtration Apparatus for IC/PCR. Teflon, or equivalent, filter holder and 0.45 μ m acetate, or equivalent, filter.

3.3 Analysis. For analysis, the following equipment is needed.

3.3.1 General.

3.3.1.1 Phillips Beakers. (Phillips beakers are preferred, but regular beakers can also be used.)

3.3.1.2 Hot Plate.

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

3.3.1.4 Assorted Pipettes.

3.3.2 Analysis by GFAAS.

3.3.2.1 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

3.3.2.2 Graphite Furnace Atomic

Absorption Spectrophotometer.

3.3.3 Analysis by ICP.

3.3.3.1 ICP Spectrometer. Computercontrolled emission spectrometer with background correction and radio frequency generator.

3.3.3.2 Argon Gas Supply. Welding grade or better.

3.3.4 Analysis by IC/PCR.

3.3.4.1 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, all with a nonmetallic (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 6.4.1 can be satisfied. A sample loading system will be required if preconcentration is employed.

3.3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) nonmetallic 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 5.5 must be obtained. A nonmetallic guard column with the same ion-exchange material is recommended.

3.3.4.3 Preconcentration Column. An HPIC nonmetallic column with acceptable anion retention characteristics and sample loading rates as described in section 5.5.

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