METHOD #: 218.6 Recommended for Approval for NPDES (August, 1991)

TITLE: Determination Of Dissolved Hexavalent Chromium In Drinking Water, Groundwater And Industrial Wastewater Effluents By Ion Chromatography

ANALYTE: CAS # Chromium 7440-47-3, Cr

INSTRUMENTATION: IC

1.0 Scope and Application

1.1 This method provides procedures for the determinatbn of dissolved hexavalent chromium in drinking water, groundwater and industrial wastewater effluents.

1.2 The Method Detection Limits (MDL, defined in Sectin 3) for the above matrices are listed in Table 1. The MDL obtained by an individual laboratory for a specific matrix may differ from those listed depending on the nature of the sample and the instrumentation used.

1.3 Samples containing high levels of anionic species such as suHate and chloride may cause column overload. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) toCr(III). Samples must be stored at 4°C and analyzed within twenty-four hours of collection.

1.4 This method should be used by analysts experienced in the use of ion chromatography and the interpretatbn of ion chromatograms.

2.0 Summary of Method

2.1 An aqueous sample is filtered through a 0.45 um filter and the filtrate is adjusted to a pH of 9 to 9.5 with a buffer solution. A measured volume of the sample (50-250 µL) is introduced into the ion chromatograph. A guard column removes organics from the sample before the Cr(VI) as CrO_4^{2-} is separated on an anion exchange separator column. Post-Column derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex a 530 nm.

3.0 Definitions

3.1 Dissolved--Material that will pass through a 0.45 um membrane filter.

3.2 Method Detection Limit (MDL)- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte (1).

3.3 Linear Dynamic Range- The concentratbn range over which the analytical working curve remains linear.

3.4 Laboratory Reagent Blank (LRB)- An aliquot of reagent water that is treated exactly like a sample including exposure to all glassware, equipment, solvents and reagents that are used with samples. The LRB is used to determine if the method analyte is present in the laboratory environment, the reagents or apparatus.

3.5 Stock Standard Solution- A concentrated, certified standard solution of the method analyte. The stock standard solution is used to prepare calibration standards.

3.6 Calibration Standard (CAL)- A solution prepared from the stock standard and used to calibrate the instrument response with respect to analyte concentration.

3.7 Laboratory FonHied Blank (LFB)- An aliquot of reagent water to which a known quantity of method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is within accepted control limits.

3.8 Laboratory Fortified Sample Matrix (LFM)- An aliquot of an environmental sample to which a known quantity of method analyte is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical result. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for the concentration found.

3.9 Quality Control Sample (QCS)- A solution containing a known concentration of analyte prepared by a laboratory other than the laboratory performing the analysis. The sample is used to check laboratory performance.

3.10 Laboratory Duplicates (LD)- Two albuots of the same sample that ara treated exactly the same throughout preparative and analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures.

3.11 Laboratory Performance Check Standards (LPC)- A solution of the analyte prepared in the laboratory by making appropriate dilutions of the stock standard in reagent water. The LPC is used to evaluate the performance of the instrument system within a given calibration Curve.

4.0 Interferences

4.1 Interferences which affect the accurate determination of Cr(VI) may come from several sources.

4.1.1 Contamination- A trace amount of Cr is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess for potential Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact of caustic or acidic reagents or samples with stainless steel or pigmented material.

4.1.2 Oxidation of soluble Cr(III) to Cr(VI) can occur in an alkaline medium in the presence of oxidants such as Fe(III) and oxidized Mn or as a result of the aeration that occurs in most extraction procedures (2-5).

4.1.3 Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. At a pH of 6.5 or greater, however, $HCrO_4^{-1}$ is converted to CrO_4^{2-} which is less reactive than the $HCrO_4^{-1}$.

4.1.4 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulfate, will cause a loss of Cr(VI). The column specified in this method can handle samples containing up to 5% sodium sulfate or 2% sodium chloride (6). Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

5.0 Safety

5.1 Hexavalent chromium is toxic and a suspected carcinogen and should be handled with appropriate precautbns (3,4). Extreme care should be exercised when weighing the salt for preparation of the stock standard. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of chemicals specified in this method. A reference file of material safety data sheets should also be available to all personnel involved in the chemical analysis (7,8).

6.0 Apparatus and Equipment

6.1 Ion Chromatograph

6.1.1 Instrument equipped with a pump capable of withstanding a minimum backpressure of 2000 psi and capable of delivering a constant flow in the range of 1-5 mL/min and containing no metal parts in the sample, eluent or reagent flow path.

6.1.2 Helium gas supply (high purity, 99.995%).

6.1.3 Pressurized eluent container, plastic, one or two liter size.

6.1.4 Sample loops of various sizes (50-250µL).

6.1.5 A pressurized reagent delivery module with a mixing tee and beaded mixing coil.

6.1.6 Guard Column- A column placed before the separator column containing a sorbent capable of removing strongly absorbing organics and particles that would otherwise damage the separator column (Dionex IonPac NG1 or equivalent).

6.1.7 Separator Column- A column packed with a high capacity anion exchange resin capable of resolving CrO_4^{2-} from other sample constituents (Dionex IonPac AS7 or equivalent).

6.1.8 A low-volume flow-through cell visible lamp detector containing no metal parts in contact with the eluent flow path. Detection wavelength is at 530 nm.

6.1.9 Recorder, integrator or computer for receiving analog or digital signals for recording detector response (peak height or area) as a function of time.

6.2 Labware- All reusable glassware (glass, quartz, polyethylene, Teflon, etc.) including the sample containers should be soaked overnight in laboratory grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9) followed by rinsing with tap water and ASTM Type I water.

NOTE: chromic acid must not be used for the cleaning of glassware.

6.2.1 Glassware- Class A volumetric flasks and a graduated cylinder.

6.2.2 Assorted Class A calibrated pipettes.

6.2.3 10 mL male luer-bck disposable syringes.

6.2.4 0.45 µm syringe filters.

6.2.5 Storage bottle--high density polypropylene, 1 liter capacity.

6.3 Sample Processing Equipment

6.3.1 Liquid sample transport containers- high density polypropylene, 125 mL capacity.

6.3.2 Supply of dry ice or refrigerant packing and styrofoam shipment boxes.
6.3.3 pH meter- to read pH range 0-14 with accuracy ± 0.03 pH.
6.3.4 0.45 um filter discs, 7.3 cm diameter (Gelman Acro 50A, Mfr. No.4262 or equivalent)
6.3.5 Plastic syringe filtration unit (Baxter Scientific, Cat. No. 1240 IN or equivalent).

7.0 Reagents and Consumable Materials

7.1 Reagents- All chemicals are ACS grade unless otherwise indicated.
7.1.1 Ammonium hydroxide, NH_4OH, (sp.gr. 0.902), (CAS RN 1336-21-6).
7.1.2 Ammonium sulfate, NH_2SO_4, (CAS RN 7783-20-2).
7.1.3 1,5 Diphenylcarbazide, (CAS RN 1 40-22-7).
7.1.4 Methanol, HPLC grade.
7.1.5 Sulfuric acid, concentrated (sp.gr. 1.84).
7.2 Water- For all sample preparations and dilutions, ASTM Type I water (ASTM D1193) is required. Suitable water may be obtained by passing distilled water through a mixed bed of anion and cation exchange resins.
7.3 Cr(VI) Stock Solution- Dissolve 4,501 g of Na2CrO4*4H2O in ASTM Type I water and dilute to one liter. Transfer to a polypropylene storage container.
7.4 Laboratory Reagent Blank (LRB)- Aqueous LRBs can be prepared by adjusting the pH of ASTM Type I water to 9-9.5 with the same volume of buffer as was used for the samples.
7.5 Laboratory Fortified Blank (LFB)- To an aliquot of reagent blank add an aliquot of stock standard to produce a final concentration of 100 µg/L of Cr(VI). The LFB must be carried through the entire sample preparation and analysis scheme.
7.6 Quality Control Sample (QCS)- A quality control sample must be obtained from an outside laboratory. Dilute an aliquot according to instructions and analyze with samples.
7.7 Eluent- Dissolve 33 g of ammonium sulfate in 500 mL of ASTM Type I water and add 6.5 mL of ammonium hydroxide. Dilute to one liter with ASTM Type I water.
7.8 Post-column Reagent- Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of HPLC grade methanol. Add to about 500 mL of ASTM Type I water containing 28 mL of 98% sulfuric acid while stirring. Dilute with ASTM Type I water to one liter in a volumetric flask. Reagent is stable for four or five days but should only be prepared in one liter quantities as needed.
7.9 Buffer Solution- Dissolve 33 g of ammonium sulfate in 75 mL of ASTM Type I water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with ASTM Type I water.

8.0 Sample Collection, Preservation and Storage

8.1 Prior to the collection of the sample, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration and pH adjustment should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For the determination of dissolved Cr(VI), the sample should be filtered through a 0.45 um filter. Use a portion of the sample to rinse the syringe filtration unit and filter and then collect the required volume of filtrate. Adjust the pH of the sample to 9-9.5 by adding dropwise a solution of the buffer, periodically checking the pH with the pH meter. Approximately 10 mLs of sample are sufficient for three IC analyses.

8.3 Ship and store the samples at 4°C. Bring to ambient temperature prior to analysis. Samples should be analyzed within twenty-four hours of collection.

9.0 Calibratlon

9.1 Calibration- At the time samples are analyzed a calibration should be performed using a minimum of three calibration solutbns that bracket the anticipated concentratbn range of the samples. Calibration standards should be prepared from the stock standard (Sectbn 7.3) by appropriate dilution with ASTM Type I water (Sectbn 7.2) in volumetric flasks. The solution should be adjusted to a pH of 9-9.5 with the buffer solution (Section 7.9) prior to final dilution.

9.1.1 Establish ion chromatographic operating conditions as indicated in Table 2. The flow rate of the eluent pump is set at 1.5 mL/min and the pressure of the reagent delivery module adjusted so that the final flow rate from the detector is 2.0 mL/min. This requires manual adjustment and measurement of the final flow using a graduated cylinder and a stop watch. A warm up period of approximately 30 minutes after the flow rate has been adjusted is recommended and the flow rate should be checked prior to calibration and sample analysis.

9.1.2 Injection loop size is chosen based on standard and sample concentrations and the selected attenuator setting. A 250 uL loop was used to establish the method detection limits in Table 1. A 50 uL loop is normally sufficient for higher concentrations. The sample volume used to had the injection loop should be at least 10 times the loop size so that all tubing in contact with sample is thoroughly flushed with new sample to prevent cross contamination.

9.1.3 A calibration curve of analyte response (peak height or area) versus analyte concentration should be constructed. The coefficient of correlation for the curve should be 0.999 or greater.

9.2 Instrument Performance- Check the performance of the instrument and verify the calibration using data gathered trom analyses of laboratory blanks, calibration standards and the quality control sample.

9.2.1 After the calibration has been established, it should be verified by analyzing the QCS (Section 7.6). If the measured value of the QCS exceeds ± 10% of the established value, a second analysis should be performed. If the value still exceed the established value, the analysis should be terminated until the source of the problem is identified and corrected.

9.2.2 To verify that the instrument is properly calibrated on a continuing basis, run an LRB and an LPC after every ten analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the measured concentration of the analyte deviates from the true concentration by more than ± 5%, the instrument must be

recalibrated and the previous ten samples re-analyzed. The instrument response from the calibration check may be used for recalibration purposes.

10.0 Quality Control

10.1 Each laboratory using this method is required to operate a formal Quality Control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

10.2 Initial Demonstration of Performance

10.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) for analyses conducted by this method.

10.2.2 Method Detection Limit (MDL)- Method Detection Limit should be established using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine the MDL value, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentratbn values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (s)$$

where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.143 for seven replicates].

s = standard deviation of the replicate analyses.

10.2.3 Linear dynamic range- linear dynamic ranges are governed by Beer's Law. A set of at least five standards covering the estimated linear range should be prepared fresh from the stock solution and one analysis of each performed. A log vs. log plot of peak height vs. analyte concentration having a slope between 0.98 and 1.02 will indicate linearity (7). The linear dynamic range for this method covered four orders of magnitude (1 µg/L to 10,000 µg/L) when peak height was used.

10.3 Assessing Laboratory Perforrnance Reagent and Fortified Blanks

10.3.1 Laboratory Reagent Blank (LRB)- the laboratory must analyze at least one reagent blank (Section 7.4) with each set of samples. Reagent blank data are used to assess contamination from a laboratory environment. If the Cr(VI) value in the reagent blank exceeds the determined MDL, then laboratory or reagent contaminatbn should be suspected. Any determined source of contaminatbn should be corrected and the samples re-analyzed.

10.3.2 Laboratory Fortified Biank (LFB)- the laboratory must analyze at least one fortified blank (Section 7.5) with each set of sarnples. Calculate accuracy as percent recovery (see 10.4.2). If the recovery of Cr(VI) falls outside the control limits (see10.3.3), then the procedure is judged out of control, and the source of the problem should be identified and resolved before continuing the analysis.

10.3.3 Until sufficient data become available (usually a minimum of twenty to thirty analyses), the laboratory should assess laboratory performance against recovery limits of 90-110%. When sufficient internal performance data becomes available, develop control limits from the percent mean recovery (x) and the standard deviation (s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

Upper Control Limit = x + 3s

Lower Control Limit = x - 3s

10.4 Assessing Analyte Recovery- Laboratory Fortified Sample Matrix

10.4.1 The laboratory must add a known amount of Cr(VI) to a minimum of 10% of the routine samples. The concentration level can be the same as that of the laboratory fortified blank (Section 7.5) for liquid samples.

10.4.2 Calculate the percent recovery for Cr(VI) corrected for background concentration measured in the unfortified sample, and compare this value to the control limits established in Section10.3.3 for the analysis of LFBs. Fortified recovery calculations are not required if the fortified concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{(C_F - C) \times 100}{F}$$

Where:

R = percent recovery.

C_F = fortified sample concentration.

C = sample baekground concentration.

F = concentration equivalent of Cr(VI) added to sample.

10.4.3 If the reeovery of Cr(VI) falls outside control limits, while the reeovery obtained for the LFB was shown to be in control (Section 10.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for Cr(VI) in the unfortified sample must be labelled "suspect matrix".

10.5 Quality Control Sample (QCS)- Each quarter, the laboratory should analyze one or more QCS (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

11.0 Procedure

11.1 Sample Preparation Filtered, pH adjusted samples at 4°C should be brought to ambient temperature prior to analysis.

11.2 Initiate instrument operating configuration and calibrate (Section 9).

11.3 Draw into a new, unused syringe (6.2.3) approximately 3 mL of sample and attach a syringe filter to the syringe. Discard 0.5 mL through the filter and load 10X the sample loop volume. Samples having concentrations higher than the established linear dynamic range should be diluted into the calibration range and re-analyzed.

12.0 Calculatlons

12.1 From the calibration curve the concentration of the sample can be determined. For the above procedure, if there is no dilution, the concentration of the sample should be reported as µg/L. Data should be corrected for any Cr(VI) contamination found in reagent blanks.

12.2 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 Precision and Accuracy

13.1 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 2. Dissolved Cr(VI) method detection limits determined using the procedure in 10.2.2 are listed in Table 1.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 3 for five water samples representing drinking water, deionized water, groundwater, treated municipal sewage wastewater and treated electroplating wastewater. Samples were fortified with 100 and 1000 µg/L of Cr(VI) and recoveries determine (Section 10.4.2).

14.0 References

1. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A. and Budde, W.L., "Trace Analyses for Wastewaters," Environmental Science and Technology, Vol. 15, No. 12,1981, PP. 14261435.
2. Bartlett, R. and James, B., "Behavior of Chromium in Soils: ill. Oxidation," J. Environ. Qual., Vol. 8, No. 1,1979, pp. 31-35.
3. Zatka, V.J., "Speciation of Hexavalent Chromium in Welding Fumes Interference by Air Oxidation of Chromium," Am. Ind. Hyg. Assoc.J., Vol. 46, No. 7,1985, pp. 327-331.
4. Pedersen, B., Thomsen, E. and Stern, R.M., "Some Problems in Sampling, Analysis and Evaluation of Welding Fumes Containing Cr(VI)", Ann. Occup. HYg., Vol. 31, No. 3,1987, pp.325-338.
5. Messman, J.D., Churchwell, M.E., et. al. Determination of Stable Valence States of Chromium in Aqueous and Solid Waste Matrices - Experimental Verification of Chemical Behavior. EPA/600/S4-86/039, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1987, 112 pp.
6. Dionex Technical Note No. 26, May 1990.

7. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administratbn, Federal Register, July 24, 1986.
8. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.
9. Johnson, D.C., Anal. Chim. Acta, Vol. 204, No. 1 1988.

Table 1. Method Detection Limit for Cr(VI)

Matrix Type	Conc. used to compute MDL (µg/L)	Method Detection Limit (a) (µg/L)
Reagent Water	1	0.4
Drinking Water	2	0.3
Ground Water	2	0.3
Primary Sewage Wastewater	2	0.3
ElectroplatingWastewater	2	0.8

(a) MDL concentrations are computed for final analysis solution (Section 11.2).

Table 2. Ion Chromatographic Conditions

Columns:	Guard Column - Dionex IonPac NG1 Separator Column - Dionex IonPac AS7
Eluent:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4OH Flow rate - 1.5 mL/min
Post-Column Reagent:	2 mM Diphenylcarbohydrazide 10% v/v CH_3OH 1 N H_2SO_4 Flow rate - 0.5 mL/min
Detector:	Visible 530 nm
Retention Time:	3.8 min.

Table 3. Single- Laboratory Precision and Accuracy

Sample Type	Percent Mean Cr(VI) [a] (µg/L)	Recovery	RPD [b]
Reagent Water	100	100	0.8
	1000	100	0.0
Drinking Water	100	105	6.7
	1000	98	1.5
Ground Water	100	98	0.0
	1000	96	0.8
Primary Sewage Wastewater	100	100	0.7
	1000	104	2.7
Electroplating Wastewater	100	99	0.4
	1000	101	0.4

(a) Sample fortified at this concentration level.
(b) RPD - relative percent difference between duplicates.