METHOD 7199

DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

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

1.2 The method detection limits 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 sulfate and chloride may cause column overload. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(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 in the interpretation of ion chromatograms.

2.0 SUMMARY OF METHOD

2.1 An aqueous sample is filtered through a 0.45 µm 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 at 530 nm.

3.0 INTERFERENCES

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

3.1.1 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 or caustic or acidic reagents of samples with stainless steel or pigmented material.

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

3.1.3 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 (1). Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

4.0 APPARATUS AND MATERIALS

4.1 Ion Chromatograph.

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

4.1.2 Helium gas supply (High purity, 99.995%).

4.1.3 Pressurized eluant container, plastic, one or two liter size.

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

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

4.1.6 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).

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

4.1.8 Postcolumn reactor - Mixing tee, or membrane reactor, with reaction coil. Must be compatible with flows from 0 to 2 mL/min.

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

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

4.2 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 Reagent water. Alternative cleaning procedures are permitted, provided that adequate cleanliness can be demonstrated through the analysis of method blanks.

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

4.2.1 Volumetric flasks and a graduated cylinder - of acceptable precision and accuracy.

4.2.2 Assorted calibrated pipettes - of acceptable precision and accuracy.

4.2.3 Disposable syringes - 10-mL, with male luer-lock fittings.

4.2.4 Syringe filters - 0.45-µm.

4.2.5 Storage bottle - high density polypropylene, 1-L capacity.

4.2.6 pH meter - to read pH range 0 - 14 with accuracy ± 0.03 pH.

4.2.7 Filter discs - 0.45-µm pore, 7.3-cm diameter (Gelman Acro 50A, Mfr. No. 4262, or equivalent).

4.2.8 Plastic syringe filtration unit (Baxter Scientific, Cat. No. 1240 IN, or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1.1 Ammonium hydroxide, NH_4OH (sp.gr. 0.902) (CAS RN 1336-21-6).

5.1.2 Ammonium sulfate, $(NH_4)_2\ SO_4$ (CAS RN 7783-20-2).

5.1.3 1,5-Diphenylcarbazide (CAS RN 140-22-7).

5.1.4 Methanol, HPLC grade.

5.1.5 Sulfuric acid, concentrated (sp.gr. 1.84).

5.2 Reagent water. Reagent water shall be interference-free and should conform to the performance specifications of ASTM Type I water. All references to water in the method refer to reagent water unless otherwise specified. A definition of reagent water can be found in Chapter One.

5.3 Cr(VI) Stock Solution (1000 mg/L). Dissolve 4.501 g of $Na_2CrO_4 \cdot 4H_2O$ in reagent water and dilute to one liter. Transfer to a polypropylene storage container.

5.4 Quality control sample (QCS). Obtained and prepared from an independent source (EPA, NIST or from a commercial source). Dilute an aliquot according to the instructions and analyze with samples. If an EPA or NIST reference sample is not available, a mid-range standard, prepared from an independent commercial source, may be used.

5.5 Eluant. Dissolve 33 g of ammonium sulfate in 500 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to one liter with reagent water. Degass the solution with helium gas for 5-10 minutes prior to use.

5.6 Post-column reagent. Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of HPLC grade methanol in a 1000 mL volumetric flask. In a separate container, add 28 mL of 98% sulfuric acid into 500 mL of reagent water, mix, and degass with helium gas for 5-10 minutes prior to adding to the diphenylcarbazide solution. Dilute to volume with reagent water. Reagent is stable for four or five days, but should only be prepared in one liter quantities as needed.

5.7 Buffer Solution. Dissolve 33 g of ammonium sulfate in 75 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with reagent water. Degass the solution with helium gas for 5-10 minutes prior to use.

5.8 Dilution Water. A batch of reagent grade water must be prepared by adjusting the pH within the range of 9-9.5 using the buffer solution. Use this solution for diluting working standards and high level samples.

5.9 Helium Gas.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 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.

6.2 For the determination of dissolved Cr(VI), the sample should be filtered through a 0.45-µm 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 dropwise addition of buffer solution (Section 5.7), periodically checking the pH with the pH meter or narrow pH-range pH paper. If salts are formed as a result of the pH adjustment, the filtrate must be filtered again prior to analysis. Approximately 10 mL of sample are sufficient for three IC analyses.

6.3 Ship and store the samples at 4°C in 125-mL narrow-mouth, high-density polypropylene containers, or equivalent. Bring to ambient temperature prior to analysis. Samples should be analyzed within 24 hours of collection.

7.0 PROCEDURE

7.1 Sample preparation. Allow pH-adjusted samples to equilibrate to ambient temperature prior to analysis. Samples that have not been pH adjusted should be adjusted as described in Section 6.2.

7.2 Calibration. Calibrate the instrument using a minimum of a calibration blank and three calibration standards bracketing the anticipated concentration range of the samples. The calibration range must cover no more than two orders of magnitude. Calibration standards should be prepared from the Cr(VI) stock standard (Section 5.3) by appropriate dilution using the dilution water (Section 5.8) in volumetric flasks.

7.2.1 Establish ion chromatographic operating conditions as indicated in Table 2 or as instructed by the instrument manufacturer. The flow rate of the eluant 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.

7.2.2 Injection loop size is chosen based on standard and sample concentrations and the selected attenuator setting. A 250-µL loop was used to establish the method detection limits in Table 1. A 50-µL loop is normally sufficient for higher concentrations. The sample volume used to load 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.

7.2.3 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.

7.3 Instrument performance. Check the performance of the instrument and verify the calibration using data gathered from analyses of laboratory blanks, calibration standards and the quality control sample.

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

7.3.2 To verify that the instrument is properly calibrated on a continuing basis, run a laboratory blank and a calibration check standard every ten analyses. If the measured concentration of the analyte deviates from the true concentration by more than ± 10%, re-analyze the calibration check standard. If this check standard deviates by more than ± 10%, 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. Refer to Section 7.2 for instrument calibration procedures.

7.4 Sample Analysis. Draw into a new, unused syringe approximately 3 mL of sample and attach a syringe filter to the syringe. Discard 0.5 mL through the filter and load the remaining sample (equal to at least 10X the sample loop volume) into sample loop. Samples having concentrations higher than the established calibration range must be diluted into the calibration range and re-analyzed. Each sample should be injected twice and the Relative Standard Deviation of the duplicates should be less than 20% or the sample data must be qualified.

7.5 Calculations.

7.5.1 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.

7.5.2 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.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate quality control procedures.

8.2 All quality control data should be maintained and available for easy reference or inspection.

8.3 Calibration curves should be composed of a minimum of a blank and three standards.

8.4 Samples exceeding the highest calibration standard must be diluted and re-analyzed.

8.5 A minimum of one method blank sample per sample batch must be analyzed to check for contamination. A method blank is reagent water prepared by adjusting the pH to between 9 and 9.5 with the same volume of buffer as used for the samples.

8.6 A minimum of one duplicate sample and one matrix spike sample per sample batch must be analyzed for each analytical batch to check for duplicate precision and matrix-spike recovery.

8.7 A quality control sample (QCS) must be analyzed at the beginning of each analytical run to validate the instrument calibration.

9.0 METHOD PERFORMANCE

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

9.2 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 were determined.

9.3 Pooled Precision and Accuracy: This method was tested by 21 volunteer laboratories in a joint study by USEPA and the American Society for Testing and Materials (ASTM). Mean recovery and accuracy for Cr(VI) (as CrO_4^{2-}) was determined from the retained data of 13 laboratories in reagent water, drinking water, groundwater, and various industrial wastewaters. For reagent water, the mean recovery and the overall and single-analyst relative standard deviations were 105%, 7.8%, and 3.9%, respectively. Table 4 contains the linear equations that describe the single-analyst standard deviation and mean recovery of Cr(VI) in reagent water.

10.0 REFERENCES

1. Dionex Technical Note No. 26, May 1990.

2. 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. 1426-1435.

3. Edgell, K., Longbottom, J., and Joyce, R., "Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography: Collaborative Study", (Internal EPA report, 1992).

4. Arar, Elizabeth J., and Pfaff, John D., "Determination of Dissolved Hexavalent Chromium in Industrial Wastewater Effluents by Ion Chromatography and Post-Column Derivatization with Diphenylcarbazide", Journal of Chromatography, 546 (1991) 335-340.

TABLE 1
METHOD DETECTION LIMIT FOR Cr(VI)

Matrix Type	Retention Time (min)	Method Detection Limit[(a)] µg/L
Reagent Water	3.8	0.4
Drinking Water	3.8	0.3
Ground Water	3.8	0.3
Primary Sewage Wastewater	3.8	0.3
Electroplating Wastewater	3.8	0.3

[(a)] MDL concentrations are computed for final analysis solution (Section 8.2.2)

TABLE 2
ION CHROMATOGRAPHIC CONDITIONS

Columns:	Guard Column - Dionex Ionpac NGI Separator Column - Dionex IonPac AS7
Eluant:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4 Flow Rate = 1.5 mL/min
Post-Column Reagent:	2mM Diphenylcarbohydrazide 10% v/v CH_3OH 1 N H_2SO_4 Flow rate = 0.5 mL/min
Detector:	Visible 530 nm

TABLE 3
SINGLE-LABORATORY PRECISION AND ACCURACY

Sample Type	Cr(VI) (µg/L)[a]	Percent Mean 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	100	100	0.7
Wastewater	1000	104	2.7
Electroplating	100	99	0.4
Wastewater	1000	101	0.4

[a] Sample spiked at this concentration level.
[b] RPD - relative percent difference between duplicates.

TABLE 4
SINGLE-ANALYST PRECISION, OVERALL PRECISION AND RECOVERY
FROM MULTILABORATORY STUDY

	Reagent Water (6-960 µg/L)	Matrix Water (6-960 µg/L)
Mean Recovery	X = 1.020C + 0.592	X = 0.989C - 0.411
Overall Standard Deviation	S_R= 0.035X + 0.893	S_R= 0.059X + 1.055
Single-Analyst Standard-Deviation	S_R= 0.021X + 0.375	S_R= 0.041X + 0.393

X = Mean concentration; µg/L, exclusive of outliers.
C = True value, µg/L.
S_R= Overall standard deviation.
S_R= Single-Analyst standard deviation.

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