

METHOD 218.6

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

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1.0 SCOPE AND APPLICATION

- 1.1 This method provides procedures for determination of dissolved hexavalent chromium (as CrO_4^{2-}) in drinking water, groundwater, and industrial wastewater effluents.

Analyte	Chemical Abstracts Service Registry Number (CASRN)
Hexavalent Chromium (as CrO_4^{2-})	11104-59-9

- 1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.
- 1.3 The method detection limits (MDL) obtained by a single laboratory for hexavalent chromium (Cr (VI)) in 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. A multilaboratory method detection limit (MMDL) in reagent water was determined to be 0.4 µg/L. The IMDL was based upon the within-laboratory standard deviation (s_r) of thirteen paired analyses of samples by thirteen laboratories at an average analyte concentration of 1.4 µg/L.
- 1.4 Samples containing high levels of anionic species such as sulphate 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 24 hours of collection.
- 1.5 This method should be used by analysts experienced in the use of ion chromatography.

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 9-9.5 with a concentrated 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 a high capacity 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 **DEFINITIONS**

- 3.1 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration (Section 7.9).
- 3.2 **Dissolved Analyte** - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.
- 3.3 **Instrument Performance Check (IPC) Solution** - A solution of the method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.4 **Laboratory Duplicates (LD1 and LD2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.5 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.6 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which a known quantity of the 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 results. 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 background concentration.
- 3.7 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.8 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.
- 3.9 **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.
- 3.10 **Quality Control Sample (QCS)** - A solution of the method analyte of known concentration which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a

source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

- 3.11 **Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

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 Reduction of Cr (VI) to Cr (III) can occur in the presence of reducing species in an acidic medium. At pH 6.5 or greater, however, CrO_4^{2-} which is less reactive than HCrO_4^- is the predominant species
- 4.1.3 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulphate, will cause a loss of Cr (VI). The column specified in this method can handle samples containing up to 5% sodium sulphate or 2% sodium chloride². 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 precautions. 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.^{3,4}

6.0 EQUIPMENT AND SUPPLIES

- 6.1 Ion Chromatograph
- 6.1.1 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, eluent or reagent flow path.
- 6.1.2 Helium gas supply (High purity, 99.995%).

- 6.1.3 Pressurized eluent container, plastic, 1 L or 2 L 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 and 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 separating CrO_4^{2-} from other sample constituents (Dionex IonPac AS7 or equivalent).
- 6.1.8 Anion suppressor device: The data presented in this method was generated using a Dionex Anion MicroMembrane Suppressor (P/N 37106). Other suppressor devices may be used provided comparable detection limits are achieved and adequate baseline stability is attained.
- 6.1.9 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.
- 6.1.10 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 labware (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 cleaning 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-lock disposable syringes.
 - 6.2.4 0.45 µm syringe filters.
 - 6.2.5 Storage bottle - High density polypropylene, 1 L 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 units.
- 6.3.4 0.45 μm 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 STANDARDS

- 7.1 Reagents - All chemicals are ACS grade unless otherwise indicated.
 - 7.1.1 Ammonium hydroxide, NH_4OH , (sp.gr. 0.902), (CASRN 1336-21-6).
 - 7.1.2 Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, (CASRN 7783-20-2).
 - 7.1.3 1,5-Diphenylcarbazide, (CASRN 140-22-7).
 - 7.1.4 Methanol, HPLC grade.
 - 7.1.5 Sulfuric acid, concentrated (sp.gr. 1.84).
- 7.2 Reagent 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 Standard Solution - To prepare a 1000 mg/L solution, dissolve 4.501 g of $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ in ASTM Type I water and dilute to 1 L. 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 is used for samples.
- 7.5 Laboratory Fortified Blank (LFB) - To an aliquot of LRB add an aliquot of stock standard (Section 7.3) to produce a final concentration of 100 $\mu\text{g/L}$ 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. A recommended minimum concentration for the QCS is 10 $\mu\text{g/L}$.
- 7.7 Eluent - Dissolve 33 g of ammonium sulphate in 500 mL of ASTM Type I water and add 6.5 mL of ammonium hydroxide. Dilute to 1 L 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 1 L in a volumetric flask. Reagent is stable for four or five days but should be prepared only as needed.

- 7.9 Buffer Solution - Dissolve 33 g of ammonium sulphate 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 sample collection, 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 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 adding dropwise a solution of the buffer, periodically checking the pH with the pH meter. Approximately 10 mL 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 must be analyzed within 24 hours of collection.

9.0 QUALITY CONTROL

- 9.1 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, and 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.
- 9.2 Initial Demonstration of Performance (mandatory)
- 9.2.1 The initial demonstration of performance is used to characterize instrument performance (MDLs and linear dynamic range) and laboratory performance prior to sample analyses.
- 9.2.2 Method detection limit (MDL) -- A MDL should be established using reagent water 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 concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (s)$$

where:

t = Student's t value for n-1 degrees of freedom at the 99% confidence level; t = 3.143 for six degrees of freedom

s = standard deviation of the replicate analyses

The MDL must be sufficient to detect Cr (VI) at the required level according to compliance monitoring regulation (Section 1.2). The MDL should be determined annually, when a new operator begins work or whenever there is a change in instrument analytical hardware or operating conditions.

- 9.2.3 Linear dynamic range (LDR) -- The LDR should be determined by analyzing a minimum of seven calibration standards ranging in concentration from 1-5,000 µg/L across all sensitivity settings of the spectrophotometer. Normalize responses by dividing the response by the sensitivity setting multiplier. Perform the linear regression of normalized response vs. concentration and obtain the constants m and b , where m is the slope of the line and b is the y-intercept. Incrementally analyze standards of higher concentration until the measured absorbance response, R , of a standard no longer yields a calculated concentration, C_c , that is $\pm 10\%$ of the known concentration, C , where $C_c = (R - b)/m$. That concentration defines the upper limit of the LDR for your instrument and analytical operating conditions. Samples having a concentration that is $\geq 90\%$ of the upper limit of the LDR must be diluted to fall within the bounds of the current calibration curve concentration range and reanalyzed.

9.3 Assessing Laboratory Performance (mandatory)

- 9.3.1 The laboratory must analyze at least one LRB (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 contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.
- 9.3.2 The laboratory must analyze at least one LFB (Section 7.5) with each set of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of Cr (VI) falls outside the control limits (Section 9.3.3), then the procedure is judged out of control, and the source of the problem should be identified and resolved before continuing the analysis.
- 9.3.3 Until sufficient data become available (usually a minimum of 20-30 analyses), assess laboratory performance against recovery limits of 90-110%. When sufficient internal performance data becomes available, develop control limits from the percent mean recovery (\bar{x}) and the standard deviation(s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\begin{aligned}\text{UPPER CONTROL LIMIT} &= \bar{x} + 3s \\ \text{LOWER CONTROL LIMIT} &= \bar{x} - 3s\end{aligned}$$

- 9.3.4 To verify that the instrument is properly calibrated on a continuing basis, run a LRB and a IPC (Section 3.3) after every 10 analyses. The results of analyses of standards will indicate whether the calibration remains valid. If the measured concentration of the IPC (a midpoint calibration standard) deviates from the true concentration by

more than $\pm 5\%$, perform another analysis of the LPC. If the discrepancy is still $\pm 5\%$ of the known concentration then the instrument must be recalibrated and the previous 10 samples reanalyzed. The instrument response from the calibration check may be used for recalibration purposes.

- 9.3.5 Quality control sample (QCS) - Each quarter, the laboratory should analyze one or more QCS. If criteria provided with the QCS are not within $\pm 10\%$ of the stated value, corrective action must be taken and documented.

9.4 Assessing Analyte Recovery and Data Quality

- 9.4.1 The laboratory must add a known amount of Cr (VI) to a minimum of 10% of samples. The concentration level can be the same as that of the laboratory fortified blank (Section 7.5).
- 9.4.2 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 Section 9.3.3 for the analysis of LFBs. Fortified recovery calculations are not required if the concentration of Cr (VI) added is less than 2X the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

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

where:

- R = percent recovery
C_F = fortified sample concentration
C = sample background concentration
F = concentration equivalent of Cr (VI) added to sample

- 9.4.3 If the recovery of Cr (VI) falls outside control limits established in Section 9.3.3 and the recovery obtained for the LFB was shown to be in control (Section 9.3), 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'.

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Establish IC 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 of the post column reagent (Section 7.8) from the detector is 2.0 mL/min. This requires manual adjustment and measurement of the final flow rate 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.

- 10.2 Injection sample loop size should be chosen based on anticipated sample concentrations and the selected sensitivity setting of the spectrophotometer. 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 sample 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 minimize cross-contamination.
- 10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.
- 10.4 The recommended calibration routine is given in Section 11.3.

11.0 PROCEDURE

- 11.1 Filtered, pH adjusted samples at 4°C should be brought to ambient temperature prior to analysis.
- 11.2 Initiate instrument operating configuration described in Section 10.0 and Table 2.
- 11.3 Calibration - Before samples are analyzed a calibration should be performed using a minimum of three calibration solutions that bracket the anticipated concentration range of the samples. Calibration standards should be prepared from the stock standard (Section 7.3) by appropriate dilution with ASTM Type I water (Section 7.2) in volumetric flasks. The solution should be adjusted to pH 9-9.5 with the buffer solution (Section 7.9) prior to final dilution.
- 11.4 Construct a calibration curve of analyte response (peak height or area) versus analyte concentration over a concentration range of one or two orders of magnitude. The calibration range should bracket the anticipated concentration range of samples. The coefficient of correlation (r) for the curve should be 0.999 or greater.
- 11.5 Draw into a new, unused syringe (Section 6.2.3) approximately 3 mL of sample. Inject 10X the volume of the sample loop into the injection valve of the IC. Sample concentrations that exceed the calibration range must be diluted and reanalyzed.
- 11.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4.

12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 The sample concentration can be calculated from the calibration curve. Report values in µg/L. Sample concentrations must be corrected for any Cr (VI) contamination found in the LRB.
- 12.2 The QC data obtained during sample analyses provide an indication of the quality of sample data and should be reported with sample results.

13.0 METHOD PERFORMANCE

- 13.1 Instrumental operating conditions used for single-laboratory testing of the method are summarized in Table 2. MDLs for dissolved Cr (VI) in five matrix waters are listed in Table 1.
- 13.2 Single-analyst precision and accuracy data for five matrix waters, drinking water, deionized water, groundwater, treated municipal sewage wastewater, and treated electroplating wastewater are listed in Table 3.
- 13.3 Pooled Precision and Accuracy: This method was tested by 21 volunteer laboratories in a joint study by the 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, ground water, 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. For the other matrices combined, the same values were 96.7%, 11.9% and 6.3%, respectively. Table 4 contains the linear equations that describe the single-analyst standard deviation, overall standard deviation and mean recovery of Cr (VI) in reagent water and matrix water.

14.0 POLLUTION PREVENTION

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Management for Waste Reduction”, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

- 15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rule and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in the Section 14.2.

16.0 REFERENCES

1. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A. and Budde, W.L. "Trace Analyses for Wastewaters", Environ. Sci. and Technol., Vol.15, No.12, 1981, pp.1426-1435.
2. Dionex Technical Note No. 26, May 1990.
3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986.
4. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. METHOD DETECTION LIMIT FOR CR (VI)

Maxtrix Type	Conc. Used to Compute MDL µg/L	MDL µg/L
Reagent Water	1	0.4
Drinking Water	2	0.3
Ground Water	2	0.3
Primary Sewage Wastewater	2	0.3
Electroplating Wastewater	2	0.3

TABLE 2. ION CHROMATOGRAPHIC CONDITIONS

Columns:	Guard Column - Dionex IonPac NG1 Separator Column - Dionex IonPac AS7
Eluent:	250 mM (NH ₄) ₂ SO ₄ 100 mM NH ₄ OH Flow rate = 1.5 mL/min.
Post-Column Reagent:	2 mM Diphenylcarbohydrazide 10% v/v CH ₃ OH 1 N H ₂ SO ₄ Flow rate = 0.5 mL/min.
Detector:	Visible 530 nm
Retention Time:	3.8 minutes

TABLE 3. SINGLE ANALYST PRECISION AND ACCURACY

Sample Type	Cr (VI) (µg/L) ^a	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 Effluent	1000	104	2.7
Electroplating	100	99	0.4
Wastewater Effluent	1000	101	0.4

^aSample fortified at this concentration level.

^bRPD - 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	$S_r = 0.021X + 0.375$	$S_r = 0.041X + 0.393$
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X	Mean concentration, µg/L, exclusive of outliers.	
C	True value, µg/L.	
S _R	Overall standard deviation.	
S _r	Single-analyst standard deviation.	