Chromium, atomic emission spectrometry, dc plasma

Parameters and Codes:
Chromium, dissolved, I-1229-87 (µg/L as Cr): 01030
Chromium, whole water recoverable, I-3229-87 (µg/L as Cr): 01034
Chromium, suspended recoverable, I-7229-87 (µg/L as Cr): 01031

1. Application

1.1 This method is used to analyze samples of finished water, natural water, industrial water, and water-suspended sediment containing from 1 to 10,000 µg/L of chromium. Sample solutions containing more than 10,000 µg/L chromium or with specific conductances greater than 10,000 µS/cm must be diluted. This method was implemented in the National Water Quality Laboratory in December 1987.

1.2 Suspended recoverable chromium is calculated by subtracting dissolved chromium from whole water recoverable chromium.

1.3 Recoverable chromium in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

2. Summary of method

Chromium is determined by a direct-reading emission spectrometer that uses a dc argon plasma as an excitation source (Johnson and others, 1979a, 1979b). A solution of lithium chloride, sulfuric acid, and glycerin is added to samples and standards to provide a common background matrix and to compensate for viscosity changes. The liquid solution then is converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma by way of a plastic spray chamber and Pyrex injection tube. Chromium is determined on the average of three replicate exposures using a 5-second integrated intensity. A standard solution and a blank are used to calibrate the instrument.

3. Interferences

Stray-light from calcium emission from the 422.7-nm wavelength raises the background at the 425.4-nm chromium wavelength causing positive interference. This interference can be corrected by using a two-point background correction technique. Calcium concentrations as large as 1,500 mg/L can be tolerated. Samples exceeding this concentration need to be diluted.

4. Apparatus

4.1 *Spectrometer,* Beckman, Spectraspan VI with dc argon plasma or equivalent, with Echelle optics, printer, autosampler, and peristaltic pump.

4.2 Refer to manufacturer's manual to optimize instrument for the following:

Plasma viewing position	0
Gas	Argon
Sleeve pressure	50 lb/in^2
Nebulizer pressure	25 lb/in^2
Entrance slit	25x300 µm
Exit slit	50x300 µm
Voltage	800 V
Wavelength	425.435 nrn

5. Reagents

5.1 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Chromium standard solution I*, 1 mL = 1,000 µg Cr: Dissolve 1.000 g chromium powder in a minimum of 6*M* HCl. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCl and dilute to 1,000 mL with water. Store in plastic bottle.

5.3 *Chromium standard solution II*, 1.00 mL = 100 µg Cr: Dilute 100 mL chromium standard solution I to 1,000 mL with water. Store in plastic bottle.

5.4 *Chromium working solution,* 1.00 mL = 10.0 µg Cr: Dilute 100 mL chromium standard solution II to 1,000 mL with water. Store in plastic bottle.

5.5 *Glycerin,* USP.

5.6 *Hydrochloric acid,* concentrated (sp gr 1.19), Ultrex or equivalent.

5.7 *Hydrochloric acid, 6M:* Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL water, and dilute to 1 L with water.

5.8 *Lithium chloride,* LiCl, reagent grade.

5.9 *Matrix modifier:* Dissolve 367 g LiCl in 1,000 mL water. Allow the solution to cool. Transfer to a 4-L polyethylene container, and while stirring add 2,000 mL of glycerin. In a Teflon beaker slowly add with stirring 500 mL concentrated H_2SO_4 to 400 mL water. When the dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl solution. Dilute to 4,000 mL with water.

5.10 *Sulfuric acid,* concentrated (sp gr 1.84), Ultrex or equivalent.

6. Procedure

6.1 Pipet 10.0 mL sample into a disposable plastic test tube.

6.2 Pipet 10.0 mL blank and working solution into plastic test tubes.

6.3 Add 2.0 mL matrix modifier to the sample, blank, and working solution.

6.4 Place plastic caps on the tubes and mix well.

6.5 Refer to manufacturer's manual for computer-operating and wavelength-optimization procedures. Use the prepared blank and chromium working solution for instrument calibration and all subsequent recalibrations.

6.6 Refer to manufacturer's manual for autosampler-operating procedures. Pour samples in autosampler tray, positioning a blank and working solution after every eight samples. Begin analysis (NOTE 1).

NOTE 1. Because of thermal instability inherent with the high-resolution spectrometer, repeak the analytical line if the chromium standard drifts more than 4 percent.

7. Calculations

7.1 The computer system is designed so that the blank and the 10,000 µg/L of chromium standard solution are used to establish a two-point calibration curve. The system will convert instrument intensity readings to analytical concentrations. The printer display includes the blank and working solution instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

7.2 Obtain the micrograms per liter of dissolved or whole water recoverable chromium in each sample from the printer.

7.3 To determine micrograms per liter of suspended recoverable chromium, subtract dissolved chromium concentrations from whole water recoverable chromium concentrations.

8. Report

Report concentrations of chromium, dissolved (01030), whole water recoverable (01034), and suspended recoverable (01031), as follows: less than 100 µg/L, nearest microgram per liter; 100 µg/L and greater, two significant figures.

9. Precision

9.1 Precision for dissolved chromium, on the basis of five determinations by a single operator over a five-day period, expressed in standard deviation and in percentage relative standard deviation, is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
3.47	0.96	27.7
11.0	.45	4.1
18.5	.20	1.1
78.5	.90	1.1
158	2.0	1.3
205	2.6	1.3
410	8.3	2.0
505	5.2	1.0
616	9.6	1.6
743	14	1.9

9.2 Precision for whole water recoverable chromium, on the basis of 10 determinations by a single operator over a five-day period, expressed in standard deviation and in percentage relative standard deviation, is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
2.34	0.37	5.8
3.19	.38	1.9
5.83	.30	5.1
23.7	1.19	5.0

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., 1979a, Determination of trace elements in natural waters by the D.C. argon plasma, multielement atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197-212.

______1979b, Evaluation of spectral interferences associated with a direct current plasma-multielement atomic emission spectrometer (DCP-MAES) system: Applied Spectroscopy, v. 33, p. 451-456.