

Standard Methods for the Examination of Water and Wastewater

3500-Cr CHROMIUM*#(1)

3500-Cr A. Introduction

1. Occurrence and Significance

Chromium (Cr) is the first element in Group VIB in the periodic table; it has an atomic number of 24, an atomic weight of 51.99, and valences of 1 through 6. The average abundance of Cr in the earth's crust is 122 ppm; in soils Cr ranges from 11 to 22 ppm; in streams it averages about 1 µg/L, and in groundwaters it is generally 100 µg/L. Chromium is found chiefly in chrome-iron ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). Chromium is used in alloys, in electroplating, and in pigments. Chromate compounds frequently are added to cooling water for corrosion control.

In natural waters trivalent chromium exists as Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_4^-$; in the hexavalent form chromium exists as CrO_4^{2-} and as $\text{Cr}_2\text{O}_7^{2-}$. Cr^{3+} would be expected to form strong complexes with amines, and would be adsorbed by clay minerals. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water.

Chromium is considered nonessential for plants, but an essential trace element for animals. Hexavalent compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The chromium guidelines for natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level for chromium). The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 µg/L. The U.S. EPA primary drinking water standard MCL is 0.1 mg/L for total chromium.

2. Selection of Method

The colorimetric method (B) is useful for the determination of hexavalent chromium in a natural or treated water in the range from 100 to 1000 µg/L. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell paths. The ion chromatographic method with photometric detection (C) is suitable for determining dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. The electrothermal atomic absorption spectrometric method (Section 3113B) is suitable for determining low levels of total chromium (< 50 µg/L) in water and wastewater, and the flame atomic absorption spectrometric methods (Section 3111B and Section 3111C) and the inductively coupled plasma methods (Section 3120 and Section 3125) are appropriate for measuring concentrations up to milligram-per-liter levels.

3. Sample Handling

If only the dissolved metal content is desired, filter sample through a 0.45-µm membrane

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filter at time of collection, and after filtration acidify filtrate with conc nitric acid (HNO_3) to $\text{pH} < 2$. If only dissolved hexavalent chromium is desired, adjust pH of filtrate to 8 or above with 1N sodium hydroxide solution and refrigerate. If the total chromium content is desired, acidify unfiltered sample at time of collection with conc HNO_3 to $\text{pH} < 2$. If total hexavalent chromium is desired, adjust the pH of unfiltered sample to 8 or above with 1N sodium hydroxide and refrigerate.

3500-Cr B. Colorimetric Method

1. General Discussion

a. *Principle:* This procedure measures only hexavalent chromium (Cr^{6+}). Therefore, to determine total chromium convert all the chromium to the hexavalent state by oxidation with potassium permanganate. NOTE: The oxidation process may not provide total conversion of all chromium species to Cr^{6+} .¹⁻³ For total chromium determination, acid-digest the sample (see Section 3030) and follow with a suitable instrumental analysis technique. The hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet colored complex of unknown composition is produced. The reaction is very sensitive, the molar absorptivity based on chromium being about $40\,000\text{ L g}^{-1}\text{ cm}^{-1}$ at 540 nm. To determine total chromium, digest the sample with a sulfuric-nitric acid mixture and then oxidize with potassium permanganate before reacting with the diphenylcarbazide.

b. *Interferences:* The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent but the intensities are much lower than that for chromium at the specified pH . Concentrations as high as 200 mg Mo or Hg/L can be tolerated. Vanadium interferes strongly but concentrations up to 10 times that of chromium will not cause trouble. Potential interference from permanganate is eliminated by prior reduction with azide. Iron in concentrations greater than 1 mg/L may produce a yellow color but the ferric ion (Fe^{3+}) color is not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength. Interfering amounts of molybdenum, vanadium, iron, and copper can be removed by extraction of the cupferrates of these metals into chloroform (CHCl_3). A procedure for this extraction is provided but do not use it unless necessary, because residual cupferron and CHCl_3 in the aqueous solution complicate the later oxidation. Therefore, follow the extraction by additional treatment with acid fuming to decompose these compounds.

2. Apparatus

a. *Colorimetric equipment:* One of the following is required:

- 1) *Spectrophotometer*, for use at 540 nm, with a light path of 1 cm or longer.
- 2) *Filter photometer*, providing a light path of 1 cm or longer and equipped with a greenish yellow filter having maximum transmittance near 540 nm.

b. *Separatory funnels*, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

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c. Acid-washed glassware: New and unscratched glassware will minimize chromium adsorption on glass surfaces during the oxidation procedure. Do not use glassware previously treated with chromic acid. Thoroughly clean other used glassware and new glassware with nitric or hydrochloric acid to remove chromium traces.

3. Reagents

Use reagent water (see Section 1080) for reagent preparation and analytical procedure.

a. Stock chromium solution: Dissolve 141.4 mg $\text{K}_2\text{Cr}_2\text{O}_7$ in water and dilute to 100 mL; 1.00 mL = 500 μg Cr.

b. Standard chromium solution: Dilute 1.00 mL stock chromium solution to 100 mL; 1.00 mL = 5.00 μg Cr.

c. Nitric acid, HNO_3 , conc.

d. Sulfuric acid, H_2SO_4 , conc, 18N, and 6N.

e. Sulfuric acid, H_2SO_4 , 0.2N: Dilute 17 mL 6N H_2SO_4 to 500 mL with water.

f. Phosphoric acid, H_3PO_4 , conc.

g. Methyl orange indicator solution.

h. Hydrogen peroxide, H_2O_2 , 30%.

i. Ammonium hydroxide, NH_4OH , conc.

j. Potassium permanganate solution: Dissolve 4 g KMnO_4 in 100 mL water.

k. Sodium azide solution: Dissolve 0.5 g NaN_3 in 100 mL water.

l. Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 mL acetone. Store in a brown bottle. Discard when solution becomes discolored.

m. Chloroform, CHCl_3 : Avoid or redistill material that comes in containers with metal or metal-lined caps.

n. Cupferron solution: Dissolve 5 g cupferron, $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$, in 95 mL water.

o. Sodium hydroxide, 1N: Dissolve 40 g NaOH in 1 L water. Store in plastic bottle.

4. Procedure

a. Preparation of calibration curve: To compensate for possible slight losses of chromium during digestion or other analytical operations, treat standards by the same procedure as the sample. Accordingly, pipet measured volumes of standard chromium solution (5 $\mu\text{g}/\text{mL}$) ranging from 2.00 to 20.0 mL, to give standards for 10 to 100 μg Cr, into 250-mL beakers or conical flasks. Depending on pretreatment used in ¶ b below, proceed with subsequent treatment of standards as if they were samples, also carrying out cupferron treatment of standards if this is required for samples.

Develop color as for samples, transfer a suitable portion of each colored solution to a 1-cm absorption cell, and measure absorbance at 540 nm, using reagent water as reference.

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Correct absorbance readings of standards by subtracting absorbance of a reagent blank carried through the method.

Construct a calibration curve by plotting corrected absorbance values against micrograms chromium in 102 mL final volume.

b. Treatment of sample: If sample has been filtered and/or only hexavalent chromium is desired, start analysis within 24 h of collection and proceed to ¶ 4e. NOTE: Recent evidence⁴ suggests that preserved samples can be held for 30 d without substantial changes to Cr⁶⁺ concentrations. If total dissolved chromium is desired and there are interfering amounts of molybdenum, vanadium, copper, or iron present, proceed to ¶ 4c. If interferences are not present, proceed to ¶ 4d.

If sample is unfiltered and total chromium is desired, digest with HNO₃ and H₂SO₄ as in Section 3030G. If interferences are present, proceed to ¶ 4c, ¶ 4d, and ¶ 4e. If there are no interferences, proceed to ¶ 4d and ¶ 4e.

c. Removal of molybdenum, vanadium, iron, and copper with cupferron: Pipet a portion of sample containing 10 to 100 µg Cr into a 125-mL separatory funnel. Dilute to about 40 mL with water and chill in an ice bath. Add 5 mL ice-cold cupferron solution, shake well, and let stand in ice bath for 1 min. Extract in separatory funnel with three successive 5-mL portions of CHCl₃; shake each portion thoroughly with aqueous solution, let layers separate, and withdraw and discard CHCl₃ extract. Transfer extracted aqueous solution to a 125-mL conical flask. Wash separatory funnel with a small amount of water and add wash water to flask. Boil for about 5 min to volatilize CHCl₃ and cool. Add 5 mL HNO₃ and 3 mL H₂SO₄. Boil samples to the appearance of SO₃ fumes. Cool slightly, carefully add 5 mL HNO₃, and again boil to fumes to complete decomposition of organic matter. Cool, wash sides of flask, and boil once more to SO₃ fumes, assuming elimination of all HNO₃. Cool and add 25 mL water.

d. Oxidation of trivalent chromium: Pipet a portion of digested sample with or without interferences removed, and containing 10 to 100 µg Cr, into a 125-mL conical flask. Add several drops of methyl orange indicator, then add conc NH₄OH until solution just begins to turn yellow. Add 1 + 1 H₂SO₄ dropwise until it is acidic, plus 1 mL (20 drops) in excess. Adjust volume to about 40 mL, add two or more acid-washed glass beads, and heat to boiling. Add 2 drops KMnO₄ solution to give a dark red color. If fading occurs, add KMnO₄ dropwise to maintain an excess of about 2 drops. Boil for 2 min longer. Add 1 mL NaN₃ solution and continue boiling gently. If red color does not fade completely after boiling for approximately 30 s, add another 1 mL NaN₃ solution. Continue boiling for 1 min after color has faded completely, then cool.

e. Color development and measurement: Add 0.25 mL (5 drops) H₃PO₄. Use 0.2N H₂SO₄ and a pH meter to adjust solution to pH 1.0 ± 0.3. NOTE: Recent work⁵ identifies the optimum pH range for color development to be 1.6 to 2.2; the matter of optimum pH range is currently being considered by *Standard Methods*. Transfer solution to a 100-mL volumetric

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flask, dilute to 100 mL, and mix. Add 2.0 mL diphenylcarbazide solution, mix, and let stand 5 to 10 min for full color development. Transfer an appropriate portion to a 1-cm absorption cell and measure its absorbance at 540 nm, using reagent water as reference. Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method (see also note below). From the corrected absorbance, determine micrograms chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in ¶ e above, take an absorbance reading before adding carbazide reagent and correct absorbance reading of final colored solution by subtracting the absorbance measured previously.

5. Calculation

For digested samples:

$$\text{mg Cr/L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{A \times B} \times 100$$

where:

A = mL original sample, and

B = mL portion from 100 mL digested sample.

For undigested samples:

$$\text{mg Cr/L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{A}$$

6. Precision and Bias

Collaborative test data from 16 laboratories were obtained on reagent water, tap water, 10% NaCl solution, treated water from synthetic organic industrial waste, EPA extraction leachate, process water, lake water, and effluent from a steel pickle liquor treatment plant.⁶ The test data yielded the following relationships:

Reagent water:

$$S_t = 0.037x + 0.006$$

$$S_o = 0.022x + 0.004$$

Drinking or wastewater:

$$S_t = 0.067x + 0.004$$

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$$S_o = 0.037x + 0.002$$

Leachate:

$$S_t = 0.032x + 0.007$$

$$S_o = 0.017x + 0.004$$

where:

S_t = overall precision,

S_o = single-operator precision, and

x = chromium concentration, mg/L.

7. References

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8. Bibliography

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Endnotes

1 (Popup - Footnote)

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