

**METHOD #: 218.3** Approved for NPDES and SDWA (Issued 1978)  
**TITLE:** Chromium (AA, Chelation Extraction)  
**ANALYTE:** CAS # Cr Chromium 7440-47-3  
**INSTRUMENTATION:** AA  
**STORET No.** 01034

## 1.0 Scope and Application

- 1.1 This method covers the determination of total chromium in drinking, surface and saline waters. The method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present. (See 3.1)
- 1.2 The method may be used to analyze samples containing from 1.0 to 25  $\mu\text{g}$  of chromium per liter.
- 1.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

## 2.0 Summary of the Method

- 2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) following oxidation of trivalent chromium. The chelate is extracted with methyl isobutyl ketone (MIBK) and aspirated into the flame of the atomic absorption spectrophotometer.
- 2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform as described in section 9.2 of the atomic absorption text found in this manual.

## 3.0 Interferences

- 3.1 High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.

## 4.0 Instrumental Parameters (General)

- 4.1 Chromium hollow cathode lamp.
- 4.2 Wavelength: 357.9 nm
- 4.3 Fuel: Acetylene
- 4.4 Oxidant: Air
- 4.5 Type of flame: Fuel rich (adjust for organic solvent).

## 5.0 Reagents

- 5.1 Ammonium pyrrolidine dithiocarbamate (APDC) solution. Dissolve 1.0 g

- APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.
- 5.2 Bromophenol blue indicator solution: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.
  - 5.3 Potassium dichromate standard solution, 1.0 mL = 0.08 mg Cr: Dissolve 0.2263 g dried analytical reagent grade  $K_2Cr_2O_7$  in demineralized water and make up to 1000 mL.
  - 5.4 Trivalent chromium stock solution, 1.0 mL = 0.002 mg  $Cr^{+3}$ : Pipet 5.00 mL of the potassium dichromate standard solution (5.3) into an Erlenmeyer flask. Add approximately 15 mg  $Na_2SO_3$  and 0.5 mL concentrated  $HNO_3$ . Gently evaporate to dryness; strong heating reoxidizes the chromium. Add 0.5 mL concentrated  $HNO_3$  and again evaporate to dryness to destroy any excess sulfite. Take up in 1 mL concentrated  $HNO_3$  with warming and dilute to 200.0 mL with demineralized water.
  - 5.5 Trivalent chromium working solution, 1.0 mL = 0.005 mg  $Cr^{+3}$ : Immediately before use, dilute 25.0 mL of trivalent chromium stock solution (5.4) to 100.0 mL with demineralized water.
  - 5.6 Potassium permanganate, 0.1 N: Dissolve 0.32 g potassium permanganate in 100 mL demineralized water.
  - 5.7 Sodium azide, 0.1%: Dissolve 100 mg sodium azide in demineralized water and dilute to 100 mL.
  - 5.8 Methyl isobutyl ketone (MIBK).
  - 5.9 Sodium hydroxide solution, 1 M: Dissolve 40 g NaOH in demineralized water and dilute to 1 liter.
  - 5.10 Sulfuric acid, 0.12 M: Slowly add 6.5 mL concentrated  $H_2SO_4$  (sp gr 1.84) to demineralized water and dilute to 1 liter.

## 6.0 Procedure

- 6.1 Pipet a volume of sample containing less than  $2.5\mu g$  chromium (100 mL maximum) into a 200 mL volumetric flask, and adjust the volume to approximately 100 mL. The pH must be 2.0 or less. Add concentrated  $HNO_3$  if necessary.
- 6.2 Acidify a liter of demineralized water with 1.5 mL concentrated  $HNO_3$ . Prepare a blank and sufficient standards using trivalent chromium and adjust volumes to approximately 100 mL with the acidified demineralized water.
- 6.3 Add 0.1 N  $KMnO_4$  dropwise to both standards and samples until a faint pink color persists.
- 6.4 Heat on a steam bath for 20 minutes. If the color disappears, add additional  $KMnO_4$  solution dropwise to maintain a slight excess.
- 6.5 While still on the steam bath, add sodium azide solution dropwise until the  $KMnO_4$  color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.
- 6.6 Transfer the flasks to a water bath and cool to room temperature.
- 6.7 Remove from the water bath and filter (through Whatman No. 40 filter paper or equivalent) any sample which has a brownish precipitate or coloration which may interfere with the pH adjustment.
- 6.8 Add 2.0 mL of 1 M NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1 M NaOH dropwise to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12 M

H<sub>2</sub>SO<sub>4</sub> dropwise until the blue color just disappears, then add 2.0 mL in excess. The pH at this point will be 2.4.

- 6.9 The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.
- 6.10 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.
- 6.11 Add 10.0 mL MIBK and shake vigorously for 3 minutes.
- 6.12 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.
- 6.13 Aspirate the ketone layer, record the instrument reading for each sample and standard against the blank. Repeat, and average the duplicate results.

## 7.0 Calculations

- 7.1 Determine the  $\mu\text{g/L}$  Cr in each sample from a plot of the instrument readings of standards. A working curve must be prepared with each set of samples. Report Cr concentrations as follows: Less than 10  $\mu\text{g/L}$ , nearest  $\mu\text{g/L}$ ; 10  $\mu\text{g/L}$  and above, two significant figures.

## 8.0 Precision and Accuracy

- 8.1 Precision and accuracy data are not available at this time.

## 9.0 Reference

- 9.1 Atomic Absorption Newsletter 6, p. 128 (1967).