

METHOD #: 218.4 Approved for NPDES (Issued 1978)
TITLE: Chromium, Hexavalent (AA, Chelation Extraction)
ANALYTE: CAS # Cr Chromium Hexavalent 7440-47-3
INSTRUMENTATION: AA
STORET No. 01032

1.0 Scope and Application

- 1.1 This method covers the determination of dissolved hexavalent chromium in drinking, surface and saline waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present. (See 4. 1.)
- 1.2 The method may be used to analyze samples containing from 10 to 250 μg of chromium per liter.

2.0 Summary of the Method

- 2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is 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. A pH of 2. 3 must be maintained throughout the extraction.
- 2.3 The diphenylcarbazide colorimetric procedure as found on p. 192 of "Standard Methods for the Examination of Water and Wastewater", 14th edition, 1975, may also be used.

3.0 Sample Handling and Preservation

- 3.1 Stability of hexavalent chromium is not completely understood at this time. Therefore, the chelation and extraction should be carried out as soon as possible.
- 3.2 To retard the chemical activity of hexavalent chromium, the sample should be transported and stored until time of analysis at 4°C.

4.0 Interferences

- 4.1 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.

5.0 Instrumental Parameters (General)

- 5.1 Chromium hollow cathode lamp.
- 5.2 Wavelength: 357.9 nm
- 5.3 Fuel: Acetylene
- 5.4 Oxidant: Air
- 5.5 Type of Flame: Fuel rich (adjust for organic solvent)

6.0 Reagents

- 6.1 Ammonium pyrrolidine dithiocarbamate (APDC) solution. Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.
- 6.2 Bromophenol blue indicator solution: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.
- 6.3 Chromium standard solution I, 1.0 mL = 100 μg Cr: Dissolve 0.2829 g pure, dried $\text{K}_2\text{Cr}_2\text{O}_7$ in demineralized water and dilute to 1000 mL.
- 6.4 Chromium standard solution II, 1.0 mL = 10.0 μg Cr: Dilute 100 mL chromium standard solution I to 1000 mL with demineralized water.
- 6.5 Chromium standard solution III, 1.0 mL = 0.10 μg Cr: Dilute 10.0 mL chromium standard solution II to 1000 mL with demineralized water.
- 6.6 Methyl isobutyl ketone (MIBK).
- 6.7 Sodium hydroxide solution, 1 M: Dissolve 40 g NaOH in demineralized water and dilute to 1 liter.
- 6.8 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.

7.0 Procedure

- 7.1 Pipet a volume of sample containing less than 25 μg chromium (100 mL maximum) into a 200 mL volumetric flask, and adjust the volume to approximately 100 mL.
- 7.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 mL.
- 7.3 Add 2 drops bromophenol blue indicator solution. (The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.)
- 7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.
- 7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.
- 7.6 Add 10.0 mL MIBK and shake vigorously for 3 minutes.
- 7.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.
- 7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

8.0 Calculations

- 8.1 Determine the $\mu\text{g}/\text{L}$ CR^{+6} in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples. Report CR^{+6} concentrations as follows: Less than 10 $\mu\text{g}/\text{L}$, nearest $\mu\text{g}/\text{L}$; 10 $\mu\text{g}/\text{L}$ and

above, two significant figures.

9.0 Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using the (PDCA) extraction procedure and Cincinnati Ohio tap water spiked at a concentration of $50_{\mu\text{g}} \text{ CR}^{+6}/\text{L}$ the standard deviation was ± 2.6 with a mean recovery of 96%.