METHOD #: 218.5 Test Method (December 1982)

TITLE: Chromium, Dissolved Hexavalent (AA, Furnace Technique)

ANALYTE: CAS # Cr Chromium 7440-47-3

INSTRUMENTATION: AA

1.0 Scope and Application

1.1 This method covers the determination of dissolved hexavalent chromium (CR^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interfering substances are taken into account. (See 4.1.)

1.2 The method may be used to analyze samples containing from 5 to 100 ug of CR^{6+} per liter. The range of the method may be extended upward by dilution.

2.0 Summary of Method

2.1 The method is based on the separation of CR^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate is drawn off and the CR^{6+} precipitate resolubilized in nitric acid as trivalent chromium (CR^{3+}) and quantified by furnace atomic absorption.

2.2 Hexavalent chromium may also be analyzed by the chelation/ extraction technique (see Method 218.4 or the procedure described in 9.2 of the Atomic Absorption methods found in this manual).

3.0 Sample Handling and Preservation

3.1 For sample handling, cleaning glassware and the filtration procedure see part 4.1 of the Atomic Absorption Method section of this manual.

3.2 The sample must not be preserved by acidification, but instead transported and stored until time of analysis at 4°C.

3.3 Stability of CR^{6+} in environmental samples is n of completely understood at this time. The chemical nature of the sample matrix can have a definite affect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.

4.0 Interferences

4.1 The possible interference from other elements which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/liter should be diluted before analysis.

4.3 The potential reduction of CR^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present the sample aliquot taken for analysis should be neutralized and aerated before beginning.

5.0 Instrument Parameters (General)

5.1 Drying Time and Temp: 30 sec - 25°C.
5.2 Ashing Time and Temp: 30 sec -1000°C.
5.3 Atomizing Time and Temp: 10 sec - 2700°C.
5.4 Purge Gas Atmosphere: Argon
5.5 Wavelength: 357.9nm
5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6.0 Special Apparatus

6.1 Glassware
6.1.1 Filtering flask, heavy wall, 1 liter capacity
6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass stoppered, 10 mL capacity
6.1.3 Pasteur pipets, borosilicate glass, 5 3/4 inches.
6.2 Centrifuge: any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.
6.3 pH Meter: a wide variety of instruments are commercially available and suitable for this work.
6.4 Test Tube Mixer: any mixer capable of thorough vortex is acceptable.

7.0 Reagents

7.1 Lead Nitrate Solution: Dissolve 33.1 grams of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.
7.2 Ammonium Sulfate Solution: Dissolve 2.7 grams of ammonium sulfate, $(NH4)_2SO_4$ analytical reagent grade), in deionized distilled water and dilute to 100 mL.
7.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \bullet 4H_20$ (analytical reagent grade), in. deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.
7.4 Nitric Acid, conc.: Distilled reagent grade or equivalent to spectrograde quality.
7.5 Acetic Acid, Glacial: ACS reagent grade.
7.5.1 Acetic Acid, 10%(v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.
7.6 Ammonium Hydroxide, 10%(v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.
7.7 Hydrogen Peroxide, 30%: ACS reagent grade.
7.8 Potassium Dichromate Standard Solution: Dissolve 2.8285 grams of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 liter. 1 mL = 1 mg Cr (1000 mg/L)
7.9 Trivalent Chromium Working Stock Solution: To 50 mL of the potassium dichromate standard solution (7.8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc. HNO_3 (7.4) and dilute to 100 mL with deionized distilled water 1 mL = 0.5 mg CR^{3+} Prepare fresh monthly or as needed.

8.0 Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the CR^{3+} working stock (7.9) that will adequately bracket the sample. The normal working range covers a concentration range of 5 to 100 µg Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL CONC HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standard should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.) and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20/µL injection, continuous flow purge gas and non-pyrolytic graphite. The use of simultaneous background correction is required for both calibration and sample analysis.

9.0 Procedure

9.1 Transfer a 50 mL portion of the filtered sample to a 100mL Griffin beaker and adjust to pH 3.5 ± 0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.
Note: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to < 3, 10% NH_40H (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10 mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100 µL of the lead nitrate solution (7.1), stopper the tube, mix the sample and allow to stand for 3 min.

9.3 After the formation of lead chromate, retain the CR^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 mL ammonium sulfate solution (7.2), stopper and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Centrifuge the sample at 2000 rpm for 10 min.
Note 2: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging remove the tube and draw off the supernate using the apparatus detailed in Figure 1. As the pasteur pipet is lowered into the tube the supernate is sucked into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100 uL 30% H_2O_2 (7.7) and 100 uL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10mL, mix and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

10.0 Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation

is present. This must be accomplished by analyzing a second 10mL aliquot of the pH adjusted filtrate (9.1) spiked with CR^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30 ug CR^{6+}/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11.0 Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)

11.4 The method of standard addition should not be required in as much as the CR^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

11.5 Data to be entered into STORET (No. 01032) must be reported as µg/L.

12.0 Precision and Accuracy

12.1 In a single laboratory (EMSL) using a mixed industrial-domestic waste effluent containing 22 ug CR^{6+}/L and spiked with a concentration of 50 ug CR^{6+}/L the standard deviations were ± 1.0 and ± 2.7, respectively with a spike recovery of 94%.

12.2 Recoveries of a 40 ug CR^{6+}/L spike in diluted tannery and plating waste effluents were 96% and 93%, respectively.

12.3 Using Cincinnati, Ohio tap water spiked at concentrations of 5,10, and 50 ug CR^{6+}/L the standard deviations were ± 0.7, ± 0.6, and ± 0.6, respectively. Spike recovery at all three levels was 102%.

12.4 A 1000 ug CR^{3+}/L standard solution analyzed by this method yielded a result of 8 ug CR^{6+}/L with a relative standard deviation of 19%.

12.5 The data from 5 µg CR^{6+}/L tap water spike was used to calculate method detection limit (MDL) with 99% confidence as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Sclence and Technology. Vol. 15, Number 12, page 1426, December 1981. The calculated MDL for Cincinnati drinking water is 2.3 µg/L.