METHOD 7195

CHROMIUM, HEXAVALENT (COPRECIPITATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7195 may be used to analyze samples containing more than 5 ug of Cr(VI) per liter. Either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191) can be used with coprecipitation.

2.0 SUMMARY OF METHOD

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate [containing Cr(III)] is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

3.0 INTERFERENCES

3.1 Extracts containing either sulfate or chloride in concentrations above 1,000 mg/L should be diluted prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-mL capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2,000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)2$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 100 mL (1 mL = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 mL glacial acetic acid, CH_3COOH (ACS reagent grade), to 100 mL with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 mL concentrated ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution, add 1 mL of 30% H_2O_2 and 1 mL concentrated HNO_3 and dilute to 100 mL with Type II water (1 mL = 5.0 mg trivalent chromium). Prepare fresh monthly, or as needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Transfer a 50-mL portion of the sample to a 100-mL Griffin beaker and adjust to a pH of 3.5 ± 0.3 by adding volumes of 10% acetic acid dropwise. Proceed immediately to Step 7.2, taking no longer than 15 min between these steps.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH should be used to readjust the pH to 3.5 ± 0.3.

7.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube. Add 100 uL of the lead nitrate solution, stopper the tube, mix the sample, and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 mL glacial acetic acid, stopper, and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100 uL of ammonium sulfate solution, stopper, and mix.

7.5 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 2,000 rpm in small increments over a period of 5 min. Hold at 2,000 rpm for 1 min.

NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging, remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care, the supernate can be withdrawn to within approximately 0.1 mL above the precipitate. Wash the precipitate with 5 mL Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

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

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

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

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary, use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7197, Chelation/Extraction, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

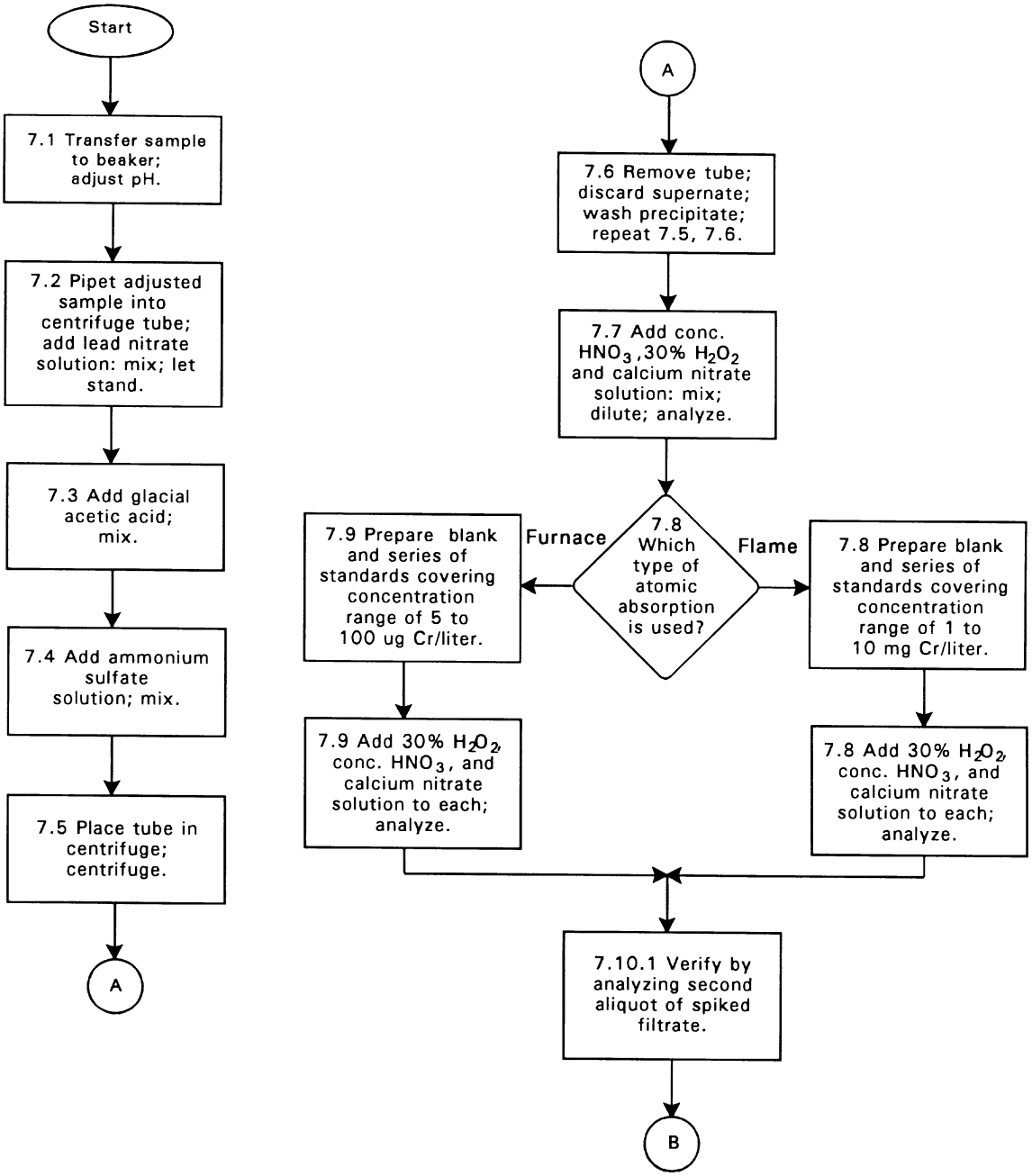
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

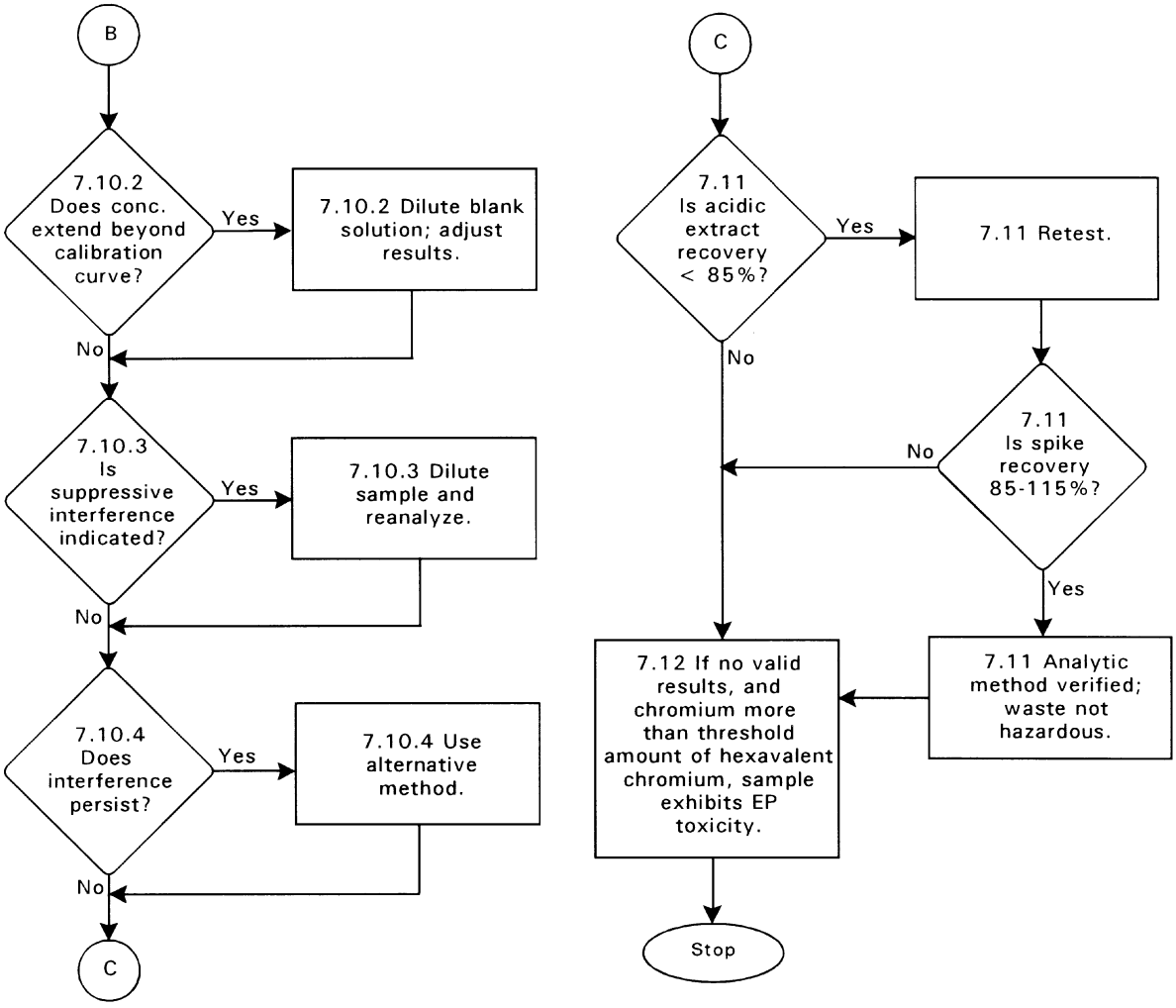
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.5 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.5.


Start
7.1 Transfer sample to beaker; adjust pH.
7.2 Pipet adjusted sample into centrifuge tube; add lead nitrate solution: mix; let stand.
7.3 Add glacial acetic acid; mix.
7.4 Add ammonium sulfate solution; mix.
7.5 Place tube in centrifuge; centrifuge.
A
A
7.6 Remove tube; discard supernate; wash precipitate; repeat 7.5, 7.6.
7.7 Add conc. HNO_3, 30% H_2O_2 and calcium nitrate solution: mix; dilute; analyze.
7.8 Which type of atomic absorption is used?
Furnace
Flame
7.9 Prepare blank and series of standards covering concentration range of 5 to 100 ug Cr/liter.
7.8 Prepare blank and series of standards covering concentration range of 1 to 10 mg Cr/liter.
7.9 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.8 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.10.1 Verify by analyzing second aliquot of spiked filtrate.
B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7.10.2 Does conc. extend beyond calibration curve?
Yes
7.10.2 Dilute blank solution; adjust results.
No
7.10.3 Is suppressive interference indicated?
Yes
7.10.3 Dilute sample and reanalyze.
No
7.10.4 Does interference persist?
Yes
7.10.4 Use alternative method.
No
C
C
7.11 Is acidic extract recovery < 85%?
Yes
7.11 Retest.
No
7.11 Is spike recovery 85-115%?
No
Yes
7.11 Analytic method verified; waste not hazardous.
7.12 If no valid results, and chromium more than threshold amount of hexavalent chromium, sample exhibits EP toxicity.
Stop