

REVISIONS

## METHOD 7196

### HEXAVALENT CHROMIUM: COLORIMETRY

#### 1.0 Scope and Application

1.1 Method 7196 is used to determine the concentration of hexavalent chromium Cr(VI) in Extraction Procedure (EP) extracts and groundwaters. This method may be used for certain domestic and industrial wastes provided no interfering substances are present (See paragraph 3.1).

1.2 Method 7196 may be used to analyze samples containing up to 50 mg of Cr(VI) per liter.

#### 2.0 Summary of Method

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product and its absorbance is measured photometrically at 540 nm.

#### 3.0 Interferences

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/l of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/liter may produce a yellow color but the ferric iron color is not strong and no difficulty is normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

#### 4.0 Apparatus and Materials

4.1 Colorimetric equipment. One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

## METHOD 7196

### HEXAVALENT CHROMIUM: COLORIMETRIC METHOD

#### 1.0 Scope and Application

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium Cr(VI) in Extraction Procedure toxicity characteristic (EP) extracts and groundwaters. This method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present (See paragraph 3.1).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

#### 2.0 Summary of Method

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4.2 Separatory funnels: 125-ml, Squibb form, with glass or teflon stopcock and stopper.

### 5.0 Reagents

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

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate,  $K_2Cr_2O_7$  (analytical reagent grade), in Type II water and dilute to 1 liter (1 ml = 50  $\mu$ g Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 ml potassium dichromate stock solution to 100 ml (1 ml = 5  $\mu$ g Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 ml of distilled reagent grade or spectrograde-quality sulfuric acid,  $H_2SO_4$ , to 100 ml with Type II water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 ml acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

### 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 Section One 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, the samples and extracts should be stored at 4° C until analyzed.

### 7.0 Procedure

7.1 Color development and measurement: Transfer 95 ml of the extract to be tested to a 100-ml volumetric flask. Add 2.0 ml diphenylcarbazide solution and mix. Add  $H_2SO_4$  solution to give a pH of  $2 \pm 0.5$ , dilute to 100 ml with Type II water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use Type II water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of

a blank carried through the method (see also note below). From the corrected absorbance, determine the mg/l of chromium present by reference to the calibration curve. NOTE: If the solution is turbid after dilution to 100 ml in 7.1 above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

## 7.2 Preparation of calibration curve

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet chromium standard solution (5  $\mu\text{g/ml}$ ) in measured volumes ranging from 2.00 to 20.0 ml into 250-ml beakers or conical flasks. This will result in standard concentrations ranging from 0.5 to 50 mg/l Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell, and measure the absorbance at 540 nm. As reference, use distilled water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/l of Cr(VI).

## 7.3 Verification

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. 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  $\mu\text{g Cr(VI)/liter}$ . To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 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.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (coprecipitation or chelation/extraction) should be used.



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7.4 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 made 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 and the waste is not hazardous by reason of the Cr(VI) concentration in the EP extract.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 If none of the analytical methods approved for this analysis yield valid results, and if the sample contains total chromium in excess of the threshold concentration allowed for hexavalent chromium, the sample will be considered to exhibit the characteristic of EP toxicity unless exempted according to the provisions of 40 CFR 261.4(b)(6).

### 8.0 Quality Control

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

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

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

8.4 Analyze check standards after approximately every 15 samples.

8.5 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.6 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.7 The method of standard additions 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.