



Designation: D 5257 – 97

## Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5257; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers procedures for the determination of dissolved hexavalent chromium in waste water, surface water, and drinking water.

1.2 The precision and bias of this test method has been tested in reagent water and industrial waste water and has been found suitable over the range of approximately 1 to 1000  $\mu\text{g/L}$ . See **Table 1** for details. Higher levels can be determined by appropriate dilution.

1.3 Samples containing very high levels of anionic species (that is, chloride, sulfate, etc.) may cause column overload. Samples containing high levels of reducing species (that is, sulfides, sulfites, etc.) may cause reduction of Cr(VI) to Cr(III). This can be minimized by buffering the sample to a pH of 9 to 9.5, filtering it, storing it at 4°C and analyzing it within 24 h.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1066 Practice for Sampling Steam<sup>2</sup>

D 1129 Terminology Relating to Water<sup>2</sup>

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>2</sup>

D 1193 Specification for Reagent Water<sup>2</sup>

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>

D3370 Practices for Sampling Water from Closed Conduits

#### 2.2 EPA Standard:

EPA Method 218.6 Determination of Dissolved Hexavalent

**TABLE 1 Determination of Precision and Bias for Hexavalent Chromium**

| Water Matrix | Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | $S_r$ | $S_o^A$ | Bias, % |
|--------------|-------------------------------|-------------------------------|-------|---------|---------|
| Reagent      | 1.2                           | 1.40                          | 0.16  | 0.15    | + 16.6  |
|              | 1.6                           | 1.87                          | 0.65  | ...     | + 16.9  |
|              | 6.0                           | 6.68                          | 1.03  | 0.53    | + 11.3  |
|              | 8.0                           | 8.64                          | 1.10  | ...     | + 8.0   |
|              | 16.0                          | 17.4                          | 2.25  | 0.77    | + 8.8   |
|              | 20.0                          | 21.4                          | 2.31  | ...     | + 7.0   |
|              | 100                           | 101                           | 1.91  | 3.76    | + 1.0   |
|              | 140                           | 143                           | 5.52  | ...     | + 2.1   |
|              | 800                           | 819                           | 24.3  | 12.7    | + 2.4   |
|              | 960                           | 966                           | 18.5  | ...     | + 7.3   |
| Waste        | 6.0                           | 5.63                          | 1.17  | 0.55    | -6.2    |
|              | 8.0                           | 7.31                          | 1.91  | ...     | -8.6    |
|              | 16.0                          | 15.1                          | 2.70  | 1.85    | -5.6    |
|              | 20.0                          | 19.8                          | 1.01  | ...     | -1.0    |
|              | 100                           | 98.9                          | 4.36  | 3.31    | -1.1    |
|              | 140                           | 138                           | 8.39  | ...     | -1.4    |
|              | 800                           | 796                           | 60.6  | 27.1    | -0.5    |
|              | 960                           | 944                           | 72.1  | ...     | -1.7    |

<sup>A</sup>Each Youden pair was used to calculate one lab data point,  $S_o$ .

Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *eluant*—the ionic mobile phase used to transport the sample through the ion exchange column.

3.2.2 *resolution*—the ability of a column to separate constituents under specified test conditions.

### 4. Summary of Test Method

4.1 A fixed volume of buffered and filtered sample, typically 100  $\mu\text{L}$ , is injected into the eluant flow path and separated by anion exchange using an ammonium sulfate based eluant.

4.2 After separation, the sample is reacted with an acidic solution of diphenylcarbohydrazide. Hexavalent chromium reacts selectively with this reagent to form the characteristic violet colored complex.

<sup>3</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

4.3 The eluant stream passes through a photometric detector for detection of the chromium diphenylcarbohydrazide complex by visible absorbance at 530 nm. Absorbance is proportional to the hexavalent chromium concentration.

## 5. Significance and Use

5.1 Hexavalent chromium salts are used extensively in the metal finishing and plating industries, in the leather industry as a tanning agent, and in the manufacture of paints, dyes, explosives, and ceramics. Trivalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industry, and in photography. Chromium, in either oxidation state, may be present in waste water from these industries and may also be discharged from chromate-treated cooling waters.

5.2 Hexavalent chromium is toxic to humans, animals, and aquatic life. It can produce lung tumors when inhaled and readily induces skin sensitization. It is not known whether cancer will result from ingestion of chromium in any of its valence states.

5.3 Ion chromatography provides a means of separating the hexavalent chromium from other species present in the sample, many of which interfere with other detection methods. The combination of this separation with a sensitive colorimetric detection method provides a selective and sensitive analytical method for hexavalent chromium with minimal sample preparation.

## 6. Interferences

6.1 By virtue of the chromatographic separation essentially all interfering species are removed from the hexavalent chromium before detection.

6.2 Interferences may result from overloading of the analytical column capacity with high concentrations of anionic species in the sample. Concentrations of chloride ion or sulfate ion up to the equivalent of 1 % NaCl and 3 %  $\text{Na}_2\text{SO}_4$  do not affect the separation or detection when using an anion exchange column and a 100  $\mu\text{L}$  sample loop.

6.3 The response of 1 mg/L of hexavalent chromium is not affected by 1 g/L of chromic ion.

6.4 Reducing species may reduce hexavalent chromium in acidic matrices. Preservation at a pH 9 to 9.5 will minimize the effect of these species.

6.5 Trace amounts of Cr are sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this test method to adjust the pH of samples, reagent blanks should be analyzed to assess the potential for Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact with caustic or acidic reagents with chromium containing stainless steel or pigmented materials.

## 7. Apparatus

7.1 *Ion Chromatograph*—An ion chromatograph having the following components configured as shown in Fig. 1.

7.1.1 *Pump*, capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 200 to 2000 psi.

7.1.2 *Injection Valve*—A high pressure, low dead volume valve that allows introduction of 50 to 250  $\mu\text{L}$  of sample into the eluant stream at up to 2000 psi.

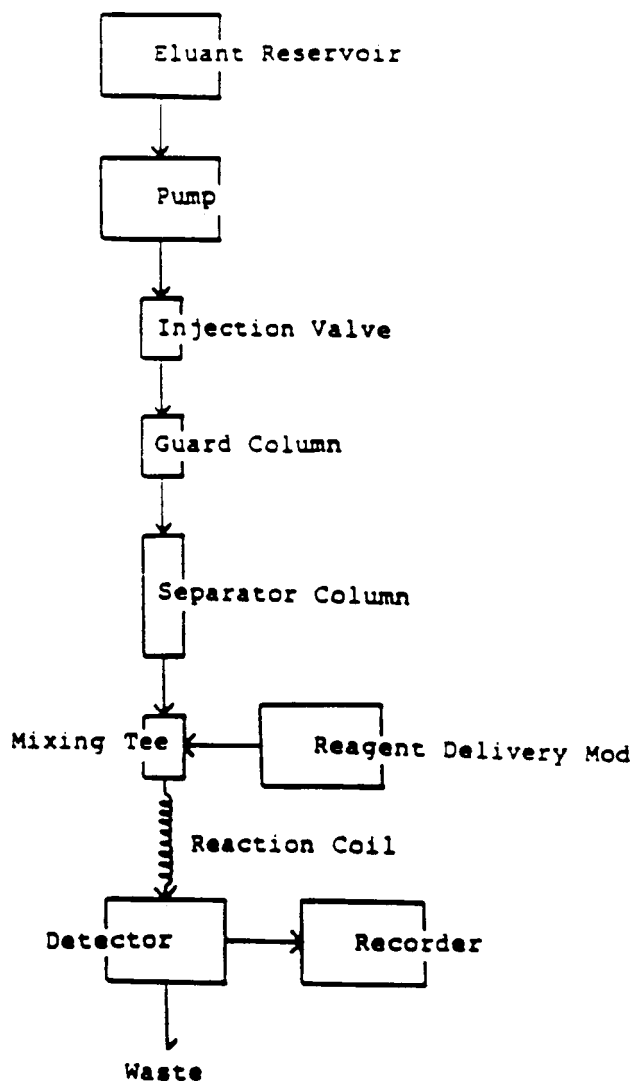


**FIG. 1 Diagram of an Ion Chromatograph Using Post-Column Reagent Addition and Photometric Detection**

7.1.3 *Guard Column*—A column placed before the separator column to protect the separator column from fouling by particles or strongly absorbed organic constituents.

7.1.4 *Analytical Column*—A liquid chromatographic column packed with a polymeric anion exchange resin capable of separating chromate from other anions in a sample containing high total dissolved solids (for example 3 %  $\text{Na}_2\text{SO}_4$ ).

7.1.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 60 psi.

7.1.6 *Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams providing a sufficient reaction time for post column reaction with minimal band spreading.

7.1.7 *Detector*—A low-volume, flow-through UV-visible absorbance detector with a non-metallic flow path. The recommended detection wavelength for hexavalent chromium is 530 nm.

7.2 *Recorder, Integrator, Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.