



Standard Test Method for Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements¹

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1. Scope

1.1 This test method specifies a procedure for the sampling and analysis of airborne particulate matter for hexavalent chromium in ambient air samples.

1.2 The method involves drawing 21.6 m³ ambient air (at 15 L/min for 24 hours) through a sodium bicarbonate cellulose acid washed filter. Atmospheric hexavalent chromium is stabilized on the alkaline coated filter.

1.3 This method uses ion chromatography with post-column derivatization with 1,5-diphenylcarbazide (DPC) and a Ultraviolet/Visible (UV/VIS) detector.

1.4 This method is applicable to the determination of masses of 0.10 to 20.0 ng of hexavalent chromium per sample without dilution.

1.5 This method is applicable for hexavalent chromium measurement in the atmosphere from 0.004 ng/m³ to 0.926 ng/m³ assuming a 21.6 m³ sample volume. The range can be increased using appropriate dilutions.

1.6 Interconversion of trivalent and hexavalent chromium during sampling is minimized to the extent possible by using these sampling procedures.

1.7 The corresponding method for workplace air samples is ASTM Test Method [D6832](#).

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *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.*

¹ This test method is under the jurisdiction of ASTM Committee [D22](#) on Air Quality and is the direct responsibility of Subcommittee [D22.03](#) on Ambient Atmospheres and Source Emissions.

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2. Referenced Documents

2.1 *ASTM Standards*:²

D4840 [Guide for Sample Chain-of-Custody Procedures](#)

[D1193 Specification for Reagent Water](#)

[D1356 Terminology Relating to Sampling and Analysis of Atmospheres](#)

[D1357 Practice for Planning the Sampling of the Ambient Atmosphere](#)

[D3195 Practice for Rotameter Calibration](#)

[D3586 Test Method for Chromium in Workplace Atmospheres \(Colorimetric Method\) \(Withdrawn 1990\)](#)³

[D5281 Test Method for Collection and Analysis of Hexavalent Chromium in Ambient Atmospheres \(Withdrawn 2014\)](#)³

[D6832 Test Method for the Determination of Hexavalent Chromium in Workplace Air by Ion Chromatography and Spectrophotometric Measurement Using 1,5-diphenylcarbazide](#)

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology [D1356](#).

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *eluent*—the 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 (1, 2, 3, 4)⁴

4.1 A known volume of air is drawn through a sodium bicarbonate coated cellulose filter at a rate of 9.0 to 16.0 L/min for 24 hours.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ The boldface numbers in parentheses refer to a list of references at the end of this standard.

4.2 After sampling, the chain-of-custody forms are appropriately labeled and the filters are placed in a cooler with ice for shipment to the laboratory. Upon receipt, the filters are placed in a freezer before preparation for analysis.

4.3 The filters are extracted in sodium bicarbonate by means of sonication for one hour. The extract is analyzed by ion chromatography using a system comprised of a guard column, an analytical column, a post-column derivatization module, and a UV/VIS detector. In the analysis procedure, hexavalent chromium exists as chromate due to the near neutral pH of the eluent. After separation through the column, the hexavalent chromium forms a complex with the 1,5-diphenylcarbazide (DPC) which can be detected at 530 nm.

4.4 One blank filter, per 10 samples prepared, is also desorbed and analyzed in accordance with 4.3.

4.5 Hexavalent chromium is identified and quantified by comparing its retention time and peak area to the corresponding standard solutions.

5. Significance and Use

5.1 Hexavalent chromium is anthropogenic from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxic and cancer-causing substance. Hexavalent chromium is a known inhalation irritant and associated with respiratory cancer (4).

5.2 Ambient concentrations of hexavalent chromium are well below detection limits of standard sampling methods, including Test Methods D3586 and D5281 (5).

5.3 Ambient atmospheric concentrations of hexavalent chromium provides a means of evaluating exposures in a manner that can be related to health-based risk levels. Collecting actual monitoring data provides improved basis for health assessments of potential exposures (2).

5.4 This test method provides step-by-step instructions for sampling and analysis of hexavalent chromium collected on sodium bicarbonate coated cellulose filters exposed to ambient air.

6. Interferences

6.1 Sodium carbonate, if used as the stabilizing medium for the hexavalent chromium filters, was observed to cause interferences with the analysis (4).

6.2 Higher concentrations of the sodium bicarbonate impregnating solution may cause flow restrictions during ambient air sampling (4).

6.3 The use of an impregnated filter of smaller pore size has been shown to cause definite flow restrictions during ambient air sampling.

6.4 Several types of filters have been determined to contain trace amounts of chromium which will leach out with time. A variety of filters including polyvinyl chloride (PVC), Quartz, and mixed cellulose esters (MCE) were found to have high concentrations of chromium and can not be used for low level ambient methods. Cellulose filters can be acid washed and alkali treated in order to stabilize and retain the hexavalent chromium following method specifications (4).

7. Apparatus

7.1 *Sampling System*, capable of accurately and precisely sampling 9.0 to 16.0 L/min.

NOTE 1—An example of a sampling system for ambient air consists of a filter inlet, a flow meter, a vacuum gage/pump, a timer and a power supply as shown in Fig. 1. In operation, ambient air is drawn through the filter assembly with a vacuum pump at a fixed flow rate between 9 to 16 L/min.

7.1.1 *Sampling pumps*, with an adjustable flow rate capable of maintaining a flow rate between 9.0 and 16.0 L/min through a sampling period of up to 24 hours. Sampling pump flow rates shall be calibrated before sampling begins. (See Practice D3195.)

7.1.2 *Polytetrafluoroethylene (PTFE) filter holder*, needed for some sampling systems. All sampling systems shall have PTFE screens in order to minimize the potential of hexavalent chromium contamination.

7.1.3 *Filters*, 47 mm ashless, cellulose filters. These filters must be acid washed before use to remove any residual chromium.

NOTE 2—Finding filters that are free of Chromium can be challenging because of the low detections determined when following this method. Cellulose filters can be acid washed and sodium bicarbonate treated in order to stabilize the hexavalent chromium following method specifications (4).

7.1.4 *Sample pump*:

7.1.5 *Glass funnel assembly*, for use with the PTFE filter holders used with Sampling System Type A. These funnels are used to protect the filters from precipitation.

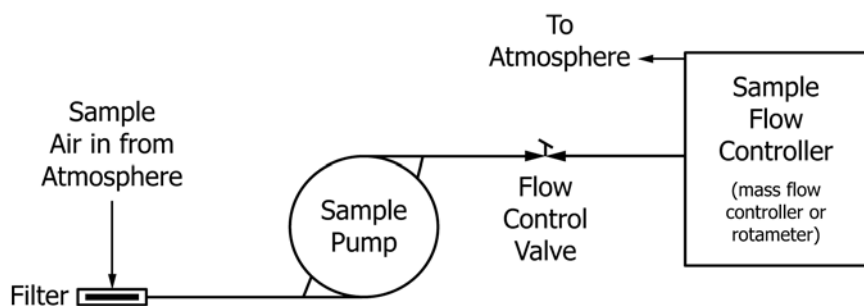


FIG. 1 Hexavalent Chromium Sampling System in Ambient Air

7.1.6 *Flow control device*, capable of controlling and measuring selected volumetric flow rates to within $\pm 2\%$. Rotameter control devices should be calibrated against a primary standard (that is, a flowmeter whose accuracy is traceable to a primary standard. (See Practice [D3195](#).)

7.1.7 *Elapsed timer*, to be placed in line with the sample pump to assist in detection of electrical interruptions that could occur over the 24 hour time interval.

7.1.8 *Freezer*, for storage of filters before and after sampling. Freezer temperatures must be maintained below -18°C .

7.1.9 *Ice cooler*, for transport of filters to and from the sampling site.

7.1.10 *Flexible tubing*, for use with flow calibration (see [10.1.4](#)).

7.1.11 Calibration system, soap bubble, rotameter or mass flow calibration system to calibrate flow meters (see [10.1](#)).

7.2 Analytical System:

7.2.1 *Ion chromatograph* shall have the following components:

7.2.1.1 *Pump*, capable of delivering a constant flow of in the range of 1 to 5 mL/min (millilitre/minute) at a pressure of 15 to 150 MPa.

7.2.1.2 *Guard column*, placed before the separator column to remove particulate contaminants and highly adsorptive compounds from samples, prolonging analytical column life.

7.2.1.3 *Separator column*, packed with a high capacity, high efficiency, hydrophobic, anion exchange column

7.2.1.4 *Post column reagent module*, capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 40 kPa.

7.2.1.5 *Reaction coil*, capable of mixing two flowing streams with minimal band spreading.

7.2.1.6 *UV/VIS detector*, low volume, flow through visible absorbance detector with a nonmetallic 1-cm flow path. The detection wavelength for hexavalent chromium is 530 nm.

7.2.1.7 *Injection valve*, to ensure compatibility with aqueous and reverse-phase eluents and protect sensitive samples from metallic contamination. Sample loops of up to 1 mL will provide enhanced detection limits.

7.2.1.8 *Autosampler (optional)*, to provide consistent operation with precise quality assurance.

7.2.1.9 *Acquisition software*, where the instrument is controlled and data are collected and processed using the instrument chromatography software and computer.

7.3 *Fully adjustable, air-displacement pipets*, for small-volume dispensing of aqueous fluids of moderate viscosity and density. Pipets should comply with ISO 648, for laboratory glassware/pipettes.

7.4 *Glassware*, made of borosilicate glass, which should comply with ISO 3585 for borosilicate glass.

7.4.1 *Volumetric flasks*, 100 mL, 200 mL, 1 L, and 2 L, which should comply with ISO 1042 for laboratory glassware/one-mark volumetric flasks.

7.5 *Analytical balance*, to provide reliable performance and accurate readability to 0.001 mg.

7.6 *Centrifuge tubes with caps*, 14 mL disposable polystyrene round bottom tubes with snap caps for sample preparation.

7.7 *Petri dishes*, 47 millimetre (mm) disposable plastic units to be used in the storage of the acid washed, sodium bicarbonate coated filters.

7.8 *Nitrogen purged Glove box (2)*, one box to be use to prepare the filters before sampling. The second box should be used to prepare the filters for analysis. The boxes should be sealed airtight with a double-layered closed gasket system and contain suspended plastic coated screens to hold filters during preparation. The boxes should be purged with ultra-pure nitrogen.

7.9 *Ultrasonicator*, to be used for standard preparation.

7.10 *Disposable gloves*, for sample handling and prevention of sample contamination.

8. Reagents

8.1 For the analysis of low level hexavalent chromium, only use reagents of the highest recognized analytical grade and water as specified in (see [8.1.1](#)).

8.1.1 *Water*, complying with the requirements of ASTM Type I deionized water (DI water) as specified in Specification [D1193](#) ($>18\text{ M}\Omega\text{-cm}$).

8.1.2 *Ammonium sulfate* (NH_4) SO_4 , 99.999 % purity based on trace metals, specific gravity 1.77 (g/mL).

8.1.3 *Ammonium hydroxide* (NH_4) OH , reagent grade, 28.0–30.0 % NH_4 basis, specific gravity 0.99 (g/cm³).

8.1.4 *1,5-diphenylcarbazide* ($\text{C}_{13}\text{N}_4\text{O}$), ACS crystalline (DPC).

8.1.5 *Methanol* (CH_3OH), HPLC grade, 0.2 micron filtered, greater than 99.9 % purity, 0.79 (g/cm³).

8.1.6 *Sulfuric acid* (H_2SO_4), concentrated, 99.999 % purity based on trace metals, specific gravity 1.84 (g/mL).

8.1.7 *Sodium bicarbonate* (NaHCO_3), greater than 99.5 % purity.

8.1.8 *Potassium dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$), 99.99+ % purity based on trace metals, crystalline. Before use it should be dried at 105°C for 1 hour then cooled in a dessicator. See [8.1.12.1](#) for instructions on preparing standard solutions.

8.1.9 *Sodium Bicarbonate Extraction Solution (20 mM)*, dissolve 3.36 grams (g) of sodium bicarbonate (see [8.1.7](#)) in DI water (see [8.1.1](#)) in a 2.0 L volumetric flask. Mix well and dilute to mark. Stopper and mix thoroughly.

8.1.10 *Eluent Stock*, 250 mM ammonium sulfate (see [8.1.2](#)) and 100 mM ammonium hydroxide (see [8.1.3](#)): dissolve 66 g of ammonium sulfate in ~ 1000 mL DI water (see [8.1.1](#)) in a 2 L volumetric flask. Add 7 mL of ammonium hydroxide and dilute to volume with DI water. Stopper and mix thoroughly.

8.1.11 *Post-Column Derivatizing Reagent (PCR)*, in a 50 mL volumetric flask, dissolve 0.25 gm of 1,5-diphenylcarbazide (see [8.1.4](#)) in 50 mL of HPLC-grade methanol (see [8.1.5](#)). Sonicate until DPC goes into solution. In a 500 mL volumetric flask add approximately 300 mL of DI water (see [8.1.1](#)). Carefully add 14 mL of 99.999 % sulfuric acid (see [8.1.6](#)) to the DI water, allow to cool after mixing. Add DPC-methanol solution to sulfuric acid solution. Dilute to 500 mL with DI water, stopper and mix thoroughly. This reagent is stable for four or five days. To minimize waste, it should be prepared in 500 mL quantities as needed.