



Designation: **D7614 – 12 D7614 – 20**

# Standard Test Method for Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements<sup>1</sup>

This standard is issued under the fixed designation D7614; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 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 m<sup>3</sup> 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.~~

1.2 This method is applicable to the determination of masses of ~~0.100~~**0.40** to 20.0 ng of hexavalent chromium per sample without dilution. ~~Detection limits vary by instrumentation. Some laboratories may be able to achieve lower detection limits. The lower limit of applicability for this method was determined in a 2019 multi-laboratory detection limit study (1).~~<sup>2</sup>

1.3 This method is applicable ~~for~~to hexavalent chromium measurement in the atmosphere from ~~0.004 ng/m<sup>3</sup>~~**0.019**<sup>3</sup> to 0.926 ng/m<sup>3</sup> assuming a 21.6 m<sup>3</sup> sample volume. ~~The range lower range may be decreased with longer sampling times. The upper 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**.~~

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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~~ safety, health, and ~~health~~ environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>3</sup>

~~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~~

<sup>1</sup> 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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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

<sup>3</sup> 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.

~~D3586D4840 Test Method for Chromium in Workplace Atmospheres (Colorimetric Method)Guide for Sample Chain-of-Custody Procedures (Withdrawn 1990)~~

~~D5281E288 Test Method for Collection and Analysis of Hexavalent Chromium in Ambient AtmospheresSpecification for Laboratory Glass Volumetric Flasks~~

~~D6832E438 Test Method for the Determination of Hexavalent Chromium in Workplace Air by Ion Chromatography and Spectrophotometric Measurement Using 1,5-diphenylcarbazideSpecification for Glasses in Laboratory Apparatus~~

~~E1154 Specification for Piston or Plunger Operated Volumetric Apparatus~~

### 3. Terminology

#### 3.1 ~~Definitions—Definitions:~~

3.1.1 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 ~~acid hardened filters, n—cellulose filters which have been acid-washed and solvent-rinsed by the manufacturer.~~

3.2.2 ~~cassette, n—a cartridge designed to contain a filter through which air is pulled during sample collection. Cassettes may be specific to a brand or model of sampler.~~

3.2.3 ~~chain of custody (COC), n—a document that provides for the traceable transfer of field samples to the analytical laboratory.~~

3.2.4 ~~eluent—eluent, n—the mobile phase used to transport the sample through the ion exchange column chromatograph (IC) system, to include the UV/Vis detector.~~

3.2.5 ~~field data sheet, n—a record that provides a reference document for information directly related to the sample collection event, including pre- and post-calibration data.~~

3.2.6 ~~resolution—quality assurance project plan (QAPP) or project plan, n—the ability of a column to separate constituents under specified test conditions;a document agreed upon by all stakeholders which clearly delineates all aspects of the monitoring project, to include siting of samplers, sampling days and frequency, sampling and analytical protocols and quality assurance elements.~~

### 4. Summary of Test Method ~~(1, (2-42), 3, 4)~~

4.1 ~~This method captures ambient air particulate by pulling a known volume of ambient air through an acid-washed sodium bicarbonate-impregnated cellulose filter. A known volume of air is drawn through a sodium bicarbonate-coated cellulose filter at a rate of 9.0 to 16.0 5.0–16.0 L/min for 24 hours. Particulate hexavalent chromium is stabilized on the impregnated filter.~~

4.2 ~~After sampling, the chain-of-custody forms are appropriately labeled chain of custody forms (COCs) are completed and the filters are placed shipped to the laboratory in a cooler with ice for shipment to the laboratory. or cold packs that will keep filters at ≤0°C. Upon receipt, the filters are placed stored in a freezer before preparation for at ≤0°C prior to sample extraction and analysis.~~

4.3 ~~The filters are extracted in 20 mM sodium bicarbonate. The extract is analyzed by ion chromatography with post-column derivatization using a 1,5-diphenylcarbazide (DPC) post-column reagent. Detection is by ultraviolet/visible light (UV/Vis) detector set at 530 or 540 nm. The extract must be run within 24 hours from the end of extraction.~~

4.4 ~~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, module including mixing coil, and a UV/VIS detector. In the analysis procedure, UV/Vis detector. During analysis, hexavalent chromium exists as chromate due to the near neutral-alkaline pH of the eluent. A minimum of 1000 µL of filtered extract is pumped through an ion exchange column where the hexavalent chromium is separated from other compounds. After separation through the column, the hexavalent chromium-containing eluent stream mixes with the post-column reagent stream. The hexavalent chromium forms a complex with the 1,5-diphenylcarbazide (DPC) which can be 1,5 diphenylcarbazide (DPC) in the post-column reagent. The combined liquid stream then flows through a UV/Vis detector and the resultant diphenylcarbazone complex is detected at 530 or 540 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; instrument responses of standard solutions of known concentration.~~

4.6 ~~Interconversion between trivalent and hexavalent chromium during sampling is minimized by using the sampling, sample recovery, sample extraction, and analytical procedures described in this standard.~~

4.7 ~~The hold time between the date of sample collection and sample extraction is 21 days, stored frozen. The hold time between sample extraction and sample analysis is 24 hours.~~

## 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, a carcinogen and industrial toxin.~~ Hexavalent chromium is a known inhalation irritant and is associated with respiratory cancer ~~((45)).~~

5.2 Ambient atmospheric concentrations of hexavalent chromium are well below the detection limits of standard sampling methods, including Test Methods~~previous analytical methods utilized for the D3586 and determination of D5281 (hexavalent chromium (52)).~~

5.3 Ambient atmospheric concentrations of hexavalent chromium provides provide a means of evaluating exposures in a manner that can be related to health-based risk levels. Collecting actual monitoring data provides~~The data for samples collected in situ provide an improved basis for health assessments of potential exposures ((25)).~~

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

5.5 This test method assumes that field and laboratory personnel are familiar with low volume ambient air sampling and hexavalent chromium analysis by ion chromatography with post-column derivatization. This method should not be performed for regulatory or compliance purposes until the field and laboratory personnel have demonstrated the ability to collect and analyze samples in such a manner as to pass the quality control requirements found in Section 13.

## 6. Interferences

6.1 Sodium carbonate, if when used as the stabilizing medium for the hexavalent chromium to impregnate the sampling filters, was observed to cause interferences with the analysis ~~((43)).~~

6.2 Higher concentrations of the sodium bicarbonate impregnating impregnation solution (8.9) may cause flow restrictions during ambient air sampling ~~((43)).~~

6.3 The use of an impregnated filter (11.2.2) of smaller pore size has been shown to cause definite flow restrictions during ambient air ~~sampling sampling (3).~~

6.4 Several types of filters have been determined reported by multiple laboratories to contain trace amounts of hexavalent chromium which will leach out with time, are detectable using this method. A variety of filters filter matrices including polyvinyl chloride (PVC), Quartz, quartz, and mixed cellulose esters (MCE) were found to have high concentrations of hexavalent chromium and can not cannot be used for low level ambient methods.~~Cr<sup>6+</sup> Cellulose determinations filters (1 can be acid washed and alkali treated in order to stabilize and retain the hexavalent chromium following method specifications (, 4)).~~

6.5 Conversion of trivalent chromium to hexavalent chromium has been reported when the extraction temperature exceeds 24°C. This may be minimized by chilling the sonication bath water, or by using a mechanical shaker (wrist action (7.9.1) or orbital (7.9.2)) at room temperature (4).

6.6 Conversion of trivalent to hexavalent chromium has been reported in unfiltered extracts stored at room temperature (6). This is minimized by filtering the extracts immediately after extraction and storing them refrigerated at ≤4°C.

6.7 Trivalent iron, tetravalent titanium, pentavalent vanadium and hexavalent molybdenum form peaks on analytical systems utilizing Thermo AS7 separatory columns. Trivalent iron elutes off immediately prior to hexavalent chromium. In large enough quantities, the trivalent iron may completely obscure the hexavalent chromium peak. The peaks elute in the following chronological order: tetravalent titanium, hexavalent molybdenum, pentavalent vanadium, trivalent iron, hexavalent chromium (6).

6.8 Other published methods have reported copper, nickel, and mercury as interferences (7, 8).

6.9 Oxidizers such as acid fumes and reducing agents such as divalent iron are known to cause interconversion between the hexavalent and trivalent state (5, 9). The use of impregnated filters and room temperature extraction techniques may minimize the amount of interconversion.

6.10 In ambient airsheds, accuracy of data depends on whether interconversion occurs in the airshed itself, that is, in situ, or whether the conversion is a direct result of sampling or analytical processes (6). In the airshed, any interconversion that occurs is not considered an interferent. Interconversion that is an artifact of sampling or analysis is considered an interferent. During sampling, a particle may be exposed to a much larger volume of ambient gasses than it would be if it were not trapped on a filter with gasses being drawn over its surface. During analysis, some compounds may be solubilized into the extract that, in the air shed, would be isolated from the hexavalent chromium. Once solubilized out of the particle(s) and into the extraction solution, these interferent compounds may then react with the hexavalent or trivalent chromium. Deducing whether interconversion is occurring in situ, during sampling, or during analysis, is not currently feasible, although mechanisms are described in this method to attempt to limit interconversion.

## 7. Apparatus

7.1 *Sampling System*, capable of accurately and precisely sampling 9.0 to 16.0 L/min at flow rates of 5.0–16.0 L/min.

NOTE 1—An example of a sampling system for ambient air consists of a filter, an air inlet, a cassette with filter, a flow meter, a vacuum 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 consistent and constant flow rate over a sampling period of up to 24 hours. Sampling pump flow rates shall be calibrated before sampling begins. (See Practice D3195 and Section 10.)

7.1.2 *Polytetrafluoroethylene (PTFE) filter holder*, *Filter cassette*, needed for some sampling systems to hold the sample filter. All sampling systems shall have PTFE screens ensure the filter does not contact any metal at any point in order to minimize the potential of hexavalent chromium contamination.

7.1.2.1 *Polytetrafluoroethylene (PTFE) filter cassette*, all components of this cassette which contact the sample stream are composed of PTFE. The inlet of the cassette is a mixing chamber to prevent particulate from accumulating only in the center of the filter. The filter support screen is composed of PTFE. The outlet of the cassette has a large enough gas volume to ensure consistent vacuum across the surface of the filter. The inlet and outlet halves of the cassette are joined with a threaded coupling ring. The inlet and outlet stems are protected with vinyl caps. The filter is entirely encased within the cassette. During sampling, the cassette inlet faces the ground, and a glass funnel is attached to the inlet to prevent any precipitation from being entrained in the sample gas stream. See Fig. 2.

7.1.2.2 *Federal Reference Method (FRM) filter cassette*, this cassette is typically composed of a hard plastic such as high density polyethylene (HDPE) or acetal homopolymer resin. The filter support screen is typically composed of stainless steel, although aluminum screens are available. The use of a polyester drain disc between the filter and the metal support screen ensures that the filter does not contact metal at any point in time.

7.1.2.3 *Secondary cassette containers*, to minimize contamination risks during shipment of cassettes. For PTFE cassettes, this may consist of a 500 mL wide-mouth plastic bottle. For FRM cassettes, this may consist of an anti-static bag or a clear plastic mailer, both designed to hold FRM cassettes. Tertiary containers, if used, may consist of plastic freezer bags.

7.1.3 *Filters*, 47 mm, 37 mm, or other suitably sized ashless, cellulose filters. These filters must be acid washed before use to remove any residual chromium. Filters which have been acid-washed by the manufacturer are commercially available and are commonly referred to as “acid hardened cellulose” by the manufacturers.

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*:

7.1.4 *Glass funnel assembly*, *funnel*, for use with the PTFE filter holders used cassettes. (See Fig. 2 with Sampling System Type A. These funnels are used to protect the filters from precipitation.)

7.1.5 *Flow control device*, capable of controlling and measuring selected volumetric sample gas 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 standard, see Practice D3195 and Section 10.)

7.1.6 *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 determine the total amount of time the sampler was in operation.

7.1.7 *Freezer*, for storage of filters before and after sampling. Freezer temperatures must be maintained below  $-18^{\circ}\text{C}$  at all times. A field freezer is not required, but highly recommended. The laboratory must have a freezer. All freezers must have a means of monitoring the freezer temperature 7 days per week, such as a max/min thermometer. If a max/min thermometer is used, it must be NIST-traceable and within its calibration expiration date.

7.1.8 *Ice cooler*, *Cooler and cold packs (or dry ice)*, for transport of filters to and from the sampling site. Cold packs may be any form which can maintain a temperature of  $<0^{\circ}\text{C}$  for the duration of time that the filters are contained in the cooler.

7.1.9 *Flexible tubing*, for use with flow calibration (see sampling system (10.1.47.1).

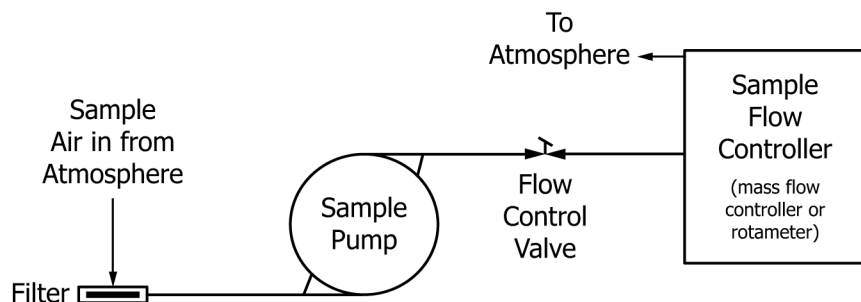


FIG. 1 Hexavalent Chromium Sampling System in Ambient Air

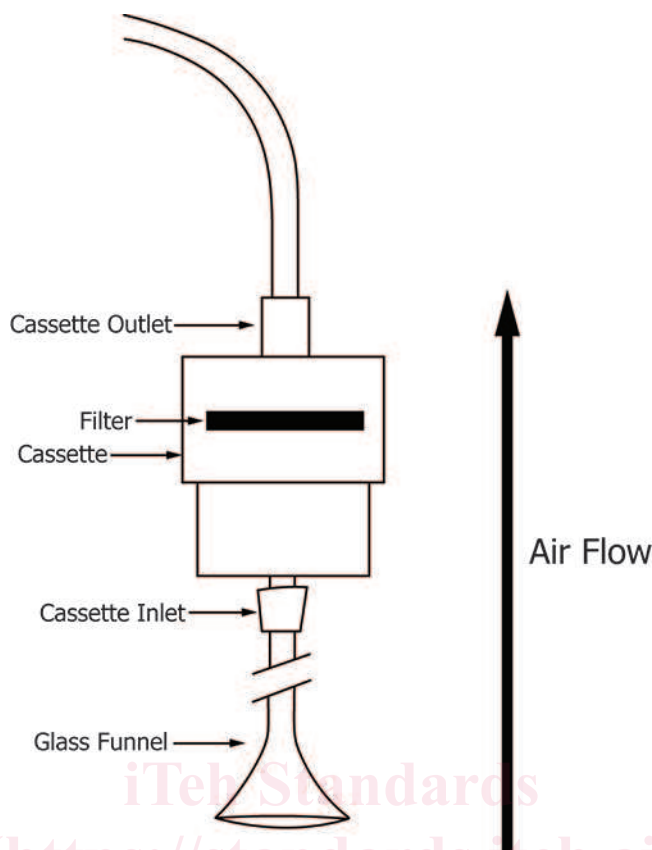


FIG. 32 Ion Chromatography Determination Diagram of Hexavalent Chromium PTFE Filter Cassette Assembly

7.1.10 Calibration system, soap bubble, rotameter, or mass flow calibration system Calibration system, soap bubble, rotameter or mass flow calibration system to calibrate flow meters (see (10.1)).

7.2 Analytical System: system, ion chromatograph, with the following components:

NOTE 2—A wide variety of instrumentation is commercially available. Follow the instrument manufacturer's guidelines for allowable instrument component operating pressures and other instrument-specific operational requirements.

7.2.1 Pump, capable of delivering a constant flow of eluent at the rate recommended by the manufacturer.

7.2.2 Guard column, placed before the separatory column to remove particulate and organic contaminants from samples.

7.2.3 Separatory column, packed with a high capacity, high efficiency, hydrophobic, anion exchange resin capable of separating hexavalent chromium from other metallic cations.

7.2.4 Post-column reagent module, capable of delivering a constant flow of post-column reagent at one third of the rate of the eluent flow rate. The module may consist of a pneumatic delivery system or a pump, as long as the ratio of post-column reagent flow to eluent flow is consistent and the eluent flow rate is three-times the post-column reagent flow rate. It is imperative that the ratio of eluent to post-column reagent be 3:1 to ensure that the pH upon mixing of the two liquid streams is such that the diphenylcarbazide can complex to the fullest extent possible during post-column derivatization.

7.2.5 Ion chromatograph Reaction coil, shall have the following components: capable of mixing two flowing liquid streams with minimal band spreading.

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.

7.2.6 UV/Vis detector, flow through cell with UV/Vis absorbance detector. The detection wavelength for hexavalent chromium following this method is 530 or 540 nm, whichever has the greatest response for a 1 ng/mL standard on a given ion chromatography system.

7.2.7 Injection valve, with non-metallic flow path composed of a largely inert material such as polyethylethylketone (PEEK).

7.2.8 Sample loop, minimum volume of 1 mL (1000 µL).

7.2.9 Autosampler with suitable autosampler vials and caps, to provide consistent operation with better precision of retention times.

7.2.10 Acquisition software, as provided by instrument manufacturer.

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, Specification E1154 for laboratory glassware/pipettes-piston operated volumetric devices.

7.4 Glassware, Volumetric flasks, made of borosilicate glass, which should comply with ISO 3585 for 100 mL, 200 mL, 1 L, and 2 L, which comply with Specification E288 borosilicate glass and Specification E438.

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 for reagent preparation. Must have accurate readability to 0.0010.1 mg.

7.6 Centrifuge tubes/Extraction vessels with caps, 14 mL disposable polystyrene round bottom tubes with snap caps for sample preparation-disposable plastic (polystyrene, polypropylene, or polyethylene) tubes or cups with tightly fitting caps and a minimum working volume of 10 mL. Vessels must have sufficient depth to ensure that filters are fully submerged in extraction solution during extraction.

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

7.8 Nitrogen purged Glove box (2)-Impregnation area, 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 with clean airshed and surfaces such as:

7.8.1 Option 1—Nitrogen purged glove boxes (2) one box to be used to prepare the filters before sampling, the second box to be used to prepare the filters for post-sampling extraction and analysis. The boxes must be airtight with a double-layered closed gasket system and contain suspended plastic-coated screens to hold filters during preparation. Purge the boxes with ultra-pure nitrogen.

7.8.2 Option 2—Dedicated filter handling room, maintained largely dust free, equipped with HEPA filtered HVAC system and HEPA filtered laminar flow hood. Similar to that described in EPA PM2.5 Guidance Document 2.12 (10).

7.8.3 Option 3—Any clean area in which filters are cleaned, impregnated, dried, and handled in such a manner as to pass the 10 % prescreening requirements described in 11.2.2.5.

7.9 Ultrasonicator, to be used for standard preparation-reagent preparation, standard preparation when standards are not purchased commercially, and filter extraction if using extraction Option 1 (11.5.2.1).

7.9.1 (Optional) wrist action shaker, for filter extraction Option 2, operating at 385 oscillations/minute with a tilt of 7.5°.

7.9.2 (Optional) orbital shaker, for filter extraction Option 3, operating at a minimum of 200 RPM.

7.10 Disposable PVC gloves, for sample handling and prevention of sample contamination-contamination during sampling and analysis. Nitrile and latex gloves react with the post-column DPC reagent to form a color that absorbs at 530 or 540 nm (6). Use of gloves made from any material other than PVC must be carefully considered with regard to the likelihood of contamination of the filter.

7.11 Forceps, Polytetrafluoroethylene (PTFE) or plastic, for handling filters. Clean forceps prior to each use with reagent water or ethanol.

7.12 Thermometer or thermocouple, NIST-traceable, for measuring temperature of the localized environment before and after sample extraction.

7.13 Extract storage containers, disposable plastic (polystyrene, polypropylene, or polyethylene) tubes with tightly fitting caps and a minimum working volume of 10 mL.

7.14 Plastic syringe with Luer-Lok fitting and liquid sealed plunger, 10 mL, for filtering extracts after extraction.

7.15 Luer-Lok syringe filter, 0.2 µm pore size, for filtering extracts after extraction.

7.16 pH strips, full range, for checking pH of cleaned filters if following filter cleaning Option 1.

7.17 Drain Discs (only required if using FRM cassettes), polyester, chemically inert, binder free, for preventing filter from contacting metal support screen if using FRM cassettes.

## 8. Reagents

8.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification **D1193**.

8.3 Reagent Water, ASTM Type I,  $\geq 18.2 \text{ M}\Omega$ .

8.4 Ammonium sulfate  $((\text{NH}_4)_2\text{SO}_4)$ , 99.999 % purity based on trace metals.

8.5 Ammonium hydroxide  $(\text{NH}_4\text{OH})$ , reagent grade, 28.0–30.0 %  $\text{NH}_4$ , specific gravity  $0.899 \text{ g/cm}^3$ .

8.6 1,5-diphenylcarbazide (DPC), crystalline. When fully dissolved in methanol, no visible particulate should be present and solution should be colorless.

8.7 Methanol  $(\text{CH}_3\text{OH})$ , HPLC grade, greater than 99.9 % purity, specific gravity  $0.79 \text{ g/cm}^3$ .

8.8 Sulfuric acid  $(\text{H}_2\text{SO}_4)$ , concentrated, specific gravity  $1.84 \text{ g/cm}^3$ .

8.9 Sodium bicarbonate  $(\text{NaHCO}_3)$ , 99.5+ % purity.

8.10 Potassium dichromate  $(\text{K}_2\text{Cr}_2\text{O}_7)$ , 99.99+ % purity based on trace metals, crystalline. For use in preparing standards. Dry at  $105^\circ\text{C}$  for 1 hour then cool in a desiccator prior to use. Alternatively, potassium chromate  $(\text{K}_2\text{Cr}_2\text{O}_4)$  may be used (see **Note 3**).

8.11 Sodium Bicarbonate Extraction Solution (20 mM), in a 2 L volumetric flask, dissolve 3.36 g of sodium bicarbonate (8.9) in reagent water (8.3). Dilute to volume with reagent water and mix thoroughly.

8.12 Eluent, 250 mM ammonium sulfate (8.4)/100 mM ammonium hydroxide (8.5)—In a 2 L volumetric flask, dissolve 66 g of ammonium sulfate in approximately 1500 mL reagent water (8.3). Add 13 mL of ammonium hydroxide. Dilute to volume with reagent water and mix thoroughly. Other eluents or eluent concentrations are acceptable if all quality control samples meet their acceptance criteria.

8.13 Post-Column Derivatization Reagent, in a 500 mL volumetric flask, add approximately 300 mL of reagent water (8.3), then carefully add 14 mL of concentrated sulfuric acid (8.8) and mix thoroughly. Allow to cool after mixing. In a 50 mL volumetric flask, dissolve 0.25 g of 1,5-diphenylcarbazide (8.6) in 50 mL of HPLC-grade methanol (8.7). Sonication may be used to facilitate DPC dissolution. Add DPC-methanol solution to sulfuric acid solution. Dilute to 500 mL with reagent water and mix thoroughly. Depending on laboratory conditions, this reagent may be stable for up to seven days. It is suspected that exposure to UV light can increase the rate of degradation of this reagent. Do not use if the reagent is darker than dark honey in color.

8.14 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**). Standard Solutions:

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  $(\text{NH}_4)_2\text{SO}_4$ , 99.999 % purity based on trace metals, specific gravity 1.77 (g/mL).

8.1.3 Ammonium hydroxide  $(\text{NH}_4)\text{OH}$ , reagent grade, 28.0–30.0 %  $\text{NH}_4$  basis, specific gravity  $0.99 \text{ (g/cm}^3\text{)}$ .

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

8.1.5 Methanol  $(\text{CH}_3\text{OH})$ , HPLC grade, 0.2 micron filtered, greater than 99.9 % purity,  $0.79 \text{ (g/cm}^3\text{)}$ .

8.1.6 Sulfuric acid  $(\text{H}_2\text{SO}_4)$ , concentrated, 99.999 % purity based on trace metals, specific gravity 1.84 (g/mL).

8.1.7 Sodium bicarbonate  $(\text{NaHCO}_3)$ , 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  $105^\circ\text{C}$  for 1 hour then cooled in a desiccator. 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.

<sup>4</sup> The last approved version ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, of this historical standard is referenced on [www.astm.org](http://www.astm.org); American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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.

8.14.1 *Hexavalent Chromium Standard Solutions: Primary and Secondary Stock Standard Solutions (~1000 µg/mL Cr<sup>6+</sup>)*, stock hexavalent chromium standards are available commercially or can be prepared by dissolving 0.283 g of potassium dichromate (8.10) in 20 mM sodium bicarbonate extraction solution (8.11) in a 100 mL volumetric flask. Dilute to volume with 20 mM sodium bicarbonate extraction solution and mix thoroughly.

8.14.1.1 *Hexavalent Chromium Stock Standard Solution (~1000 µg/mL Cr<sup>6+</sup>)*,—Prepare two separate 1000 µg/mL Cr<sup>6+</sup> stock hexavalent chromium standards are available commercially or can be prepared by diluting 0.283 grams of potassium dichromate (see solutions or obtain two commercially prepared stock solutions from separate sources. When a second manufacturer is not available, a primary stock solution from the same manufacturer, but from a different manufacturing lot, may be used. The primary stock standard is used exclusively for 8.1.8) with DI water (see calibration standards. The secondary stock 8.1.1) in a 100 mL volumetric flask. Dilute to volume with standard is used for all quality control standards and samples (Section 13.20) mM (11 sodium)-bicarbonate extraction solution, stopper and mix thoroughly.

NOTE 3—Potassium chromate (K<sub>2</sub>CrO<sub>4</sub>) can may be used as an alternative to potassium dichromate for the preparation of the hexavalent chromium stock standard solution. 0.373 g of K<sub>2</sub>CrO<sub>4</sub> are needed to make ~100 mL of ~1000 µg/mL Cr<sub>6</sub>.

NOTE 4—Two primary stock solutions should be prepared and/or obtained from separate sources. One is to be used exclusively for the calibration standards and the other for the laboratory control samples (LCS) and calibration verification.

8.1.12.2 *Hexavalent Chromium Working Standard Solution*, to be prepared in the 20 mM sodium bicarbonate extraction solution. The working standard solution is at 1000 ng/mL. Dilute 100 µL of the stock standard solution (see 8.1.12.1) with extraction solution (see 8.1.9) in a 100 mL volumetric flask. Dilute to volume, stopper and mix thoroughly. The working standard solution is stable for up to one month.

8.1.12.3 *Hexavalent Chromium Calibration Solutions*, to be prepared in the 20 mM sodium bicarbonate extraction solution. Standards are prepared in 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0 ng/L concentrations by diluting appropriate volumes of the 1000 ng/mL working standard solution (see 8.1.12.2) with the 20 mM sodium bicarbonate extraction solution (see 8.1.9). The calibration standards are prepared after the working stock standard is prepared. They are stable for one month and should be analyzed every day samples are prepared.

8.14.2 *Hexavalent Chromium Intermediate Primary Standard Solution*, 1000 ng/mL, to be prepared in 20 mM sodium bicarbonate extraction solution. In a 100 mL volumetric flask, add approximately 75 mL extraction solution (8.11) and 100 µL of the primary source stock standard solution (8.14.1). Dilute to volume with 20 mM sodium bicarbonate solution and mix thoroughly. Depending on the laboratory environment, the intermediate primary standard solution can be stable for up to twelve months.

8.14.3 *Hexavalent Chromium Calibration Solutions*, to be prepared in 20 mM sodium bicarbonate extraction solution. A minimum of six standards are prepared to span the range of 0.04 to 2.0 ng/mL by diluting appropriate volumes of the 1000 ng/mL intermediate standard solution (8.14.2) with 20 mM sodium bicarbonate extraction solution (8.11). Depending on the laboratory environment, the calibration standard solutions can be stable for up to twelve months.

NOTE 4—Calibration standard concentrations below 0.04 ng/mL may be used if the laboratory's analytical system has a lower detection limit than that determined in the 2019 multi-laboratory study (1). For NELAC accredited laboratories, the lowest calibration standard must be at the lowest concentration reported to the client without qualifiers (11).

8.14.4 *Hexavalent Chromium Intermediate Secondary Standard Solution*, 1000 ng/mL, to be prepared in 20 mM sodium bicarbonate extraction solution. In a 100 mL volumetric flask, add approximately 75 mL extraction solution (8.11) and 100 µL of the secondary source stock standard solution (8.14.1) pending on the laboratory environment, the working intermediate standard solution can be stable for up to twelve months.

8.14.5 *Nitric Acid (HNO<sub>3</sub> Hexavalent Chromium Initial<sub>3</sub>) and Continuing Calibration Verification Standard Solution*, concentrated, 70% redistilled, 99.999+ % purity based concentration at or below the mid-point of the calibration curve, to be prepared in 20 mM sodium bicarbonate extraction solution. In a 100 mL volumetric flask, add approximately 75 mL extraction solution (8.11) and the appropriate amount of the intermediate secondary source standard solution (8.14.4 on trace metals, specific gravity 1.4 (g/mL)). Dilute to volume with 20 mM sodium bicarbonate solution and mix thoroughly. Depending on laboratory environment, the secondary working standard solution can be stable for up to twelve months.

8.1.13.1 *Acid Bath Solution (10% Nitric Acid)*, add 50 mL 99.999+ % nitric acid (see 8.1.13) to approximately 500 mL DI water (see 8.1.1) in a volumetric flask. Dilute to mark with DI water, stopper and mix well.

8.14.6 *Trivalent Chromium Stock Standard Solution (~1000 µg/mL Cr<sup>3+</sup>)*, stock trivalent chromium standards are available commercially. The standard must be verified to contain negligible amounts of Cr<sup>6+</sup> prior to use for this method.



8.14.7 *Sodium Bicarbonate Impregnating Solution (1.2 M)*, *Trivalent Chromium Working Standard Solution*, dissolve 5 g of sodium bicarbonate (see 1000 ng/mL, to be prepared in reagent water. In a 100 mL volumetric flask, add approximately 75 mL reagent water (8.1.78.3) in DI water (see and 100 µL of 8.1.1) in a 500 mL volumetric flask. the trivalent chromium stock standard solution (8.14.6 Mix well and dilute to mark. Stopper). Dilute to volume with reagent water and mix thoroughly. Depending on the laboratory environment, the working standard solution can be stable for up to twelve months. A small amount of concentrated nitric acid (<1% volume-to-volume) may be added to prevent conversion of Cr<sup>3+</sup> to Cr<sup>6+</sup>.

8.15 *Nitric Acid (HNO<sub>3</sub>)*, concentrated, trace metals grade, specific gravity 1.4 (g/cm<sup>3</sup>).

8.16 *Acid Bath Solution (10 % Nitric Acid)*, in a 1 L volumetric flask, add approximately 500 mL reagent water (8.3) and 50 mL concentrated nitric acid (8.15), in that order. Dilute to volume with reagent water and mix well. This solution is only required if using filter cleaning protocol Option 1 (11.2.1.1).

8.17 *Sodium Bicarbonate Impregnation Solution (0.12M)*, in a 500 mL volumetric flask, dissolve 5.0 g of sodium bicarbonate (8.9) in reagent water (8.3). Sonication may be used to facilitate dissolution. Dilute to volume with reagent water and mix thoroughly.

## 9. Sampling

9.1 ~~Samples are collected using an individual filter apparatus~~ Collect samples using a pre-prepared filter (11.2.2) contained in a cassette (7.1.2) suitable for the Sampling System being employed. (See 11.1 through 11.4.) Wear gloves (7.10 and flow control device-) when handling the filter cassettes, both pre- and post-sample collection.

9.2 ~~A flow control device(s) is used~~ For each sample, use a flow control device to maintain a relatively constant sample flow rate through each sample filter over a specific sampling period, of 5–16 L/min over 24 hours. The flow device can be a mass flow controller or a rotameter. ~~A nominal flow rate of 9.0 to 16.0 L/min is applied for sample collection.~~

9.3 During operation, the control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of the sample collection period. ~~The~~ Ensure the connecting lines between the filter assembly-cassette (7.1.2) and the sampling pump should (7.1.1 be kept-), if any, are as short as possible to minimize the system residence time. If a rotameter is used, it should be calibrated in the field to determine true readings (see 10.1).

9.4 Prior to use, calibrate all sampling system components described in Section 10, “Calibration and Standardization.” If a rotameter is used, calibrate it in the field to determine true readings (10.1).

9.5 The following steps are provided for operation of a typical collection sampling system while collecting a sample sample:

9.5.1 Set the sampling system to the desired sample collection flow rate(s) (that is, referencing the corresponding ambient calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event): Assemble the sampling system.

9.5.2 If performing field loading of filters into cassettes (7.1.2), wear gloves (7.10) and use PTFE or plastic forceps (8.11) when removing filters from petri dishes and placing them into filter cassettes. Load the filters as described in 11.3.

9.5.3 Document all required site information on the field data sheet. Include, at a minimum, the following: site location, operator, filter set-up date, scheduled collection date, initial rotameter or mass flow controller reading, programmed start and end times, and any additional comments deemed necessary.

9.5.4 *Sample Collection Using PTFE Cassettes* With (7.1.2.1 disposable gloves, attach the prepared filter assembly to the inlet ) (see Fig. 2) of the probe or place the prepared filter into the filter holder, depending on the type of sampler.):

NOTE 5—One filter to collect a single sample, two filters for collocated samples.

9.5.4.1 Remove the caps from the inlet and outlet of the pre-loaded filter cassette. Attach the funnel stem (7.1.4) to the inlet fitting of the cassette with tubing and tighten securely.

9.5.4.2 Connect the outlet of the cassette (7.1.2) and funnel assembly to the PTFE tube (7.1.9) that connects to the sample pump (7.1.1). If a collocated sample is scheduled, connect the outlet of the collocated cassette to the collocated PTFE connecting tube. (See Note 17.)

9.5.4.3 Program the sampler to initiate flow through the entire sampling system. Adjust the sample collection flow rate to the intended flow rate to be used during sampling.

9.5.4.4 Allow the flow to continue for approximately two minutes while the system attains operating temperature. After two minutes, verify that the flow rate matches the intended flow rate from 9.5.4.3; re-adjust if necessary. Document the flow rate on the field data sheet.

9.5.4.5 Program the sampler to collect a 24-hour sample on the designated sample date.

9.5.5 *Sample Collection Using FRM Cassettes (7.1.2.2)*:

9.5.5.1 Equip the sampling system with a pre-loaded FRM cassette per the Manufacturer’s guidelines for the sampling system being employed.

9.5.5.2 Program the sampler to initiate flow through the entire sampling system. Adjust the sample collection flow rate to the intended flow rate to be used during sampling.

9.5.5.3 Allow the flow to continue for approximately two minutes while the system attains operating temperature. After two minutes, verify that the flow rate matches the intended flow rate from 9.5.5.2; re-adjust if necessary. Document the flow rate on the field data sheet.

9.5.5.4 Program the sampler to collect a 24-hour sample on the designated sample date.

9.5.6 Record the start and end time of the collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate. *Sample Recovery:*

9.5.6.1 Wear gloves (7.10) to remove the filter cassette (7.1.2.2) from the sampler. Retrieve the sample as soon as possible and no later than 12 hours after the sampling system has completed the run. If removing the filter from the filter cassette in the field, wear gloves and use only PTFE or plastic forceps (8.11).

NOTE 5—Timely recovery of samples from the sampler is necessary to prevent possible interconversion between Cr<sup>3+</sup> and Cr<sup>6+</sup>. To avoid recovery timing issues, alternative sampling days or sampling start and end times may be used if approved by the regulator or the facility, or both, or if specified as such in a QAPP (that is, Sampler 1 start time 0700 hours, Sampler 2 start time 0730 hours, Sampler 3 start time 0800 hours).

9.5.6.2 For systems equipped with rotameters (7.1.5), verify the final flow by turning on the system and taking a reading after a two-minute warm-up period.

9.5.6.3 Document the final flow, sample recovery date, and total elapsed run time on the field data sheet.

9.5.6.4 Record the start and end time of the sample collection event and the corresponding flow rate on the sampling field data sheet. Record the sample event name, sample type, location, and collection date and time on the field data sheet as well as any remaining required information and observations pertaining to the samples. Place the completed data sheet (if paper sheets are used) in the cooler with the samples. If electronic field data sheets are used, save the file to an appropriate device to avoid accidental deletion.

9.5.6.5 Carefully remove the sample filter cassette (7.1.2.2) and funnel (if used) (7.1.4) from the sampling system and gently place the cassette in a clean secondary container (7.1.2.3). Limit any jarring or sudden movements of the cassettes while removing it from the samplers. See Note 6. Place the secondary container containing the sample cassette into a cooler containing ice packs or dry ice.

NOTE 6—Limitation of shaking, jarring, or jostling of the filter or filter cassette during the sample recovery process is to prevent the loss of particulate matter from the sample filter.

9.5.6.6 If a freezer (7.1.7) is available for storage in the field, the cooler temperature is acceptable as long as the transit time of the filter cassette between removal from the sampling system to placement into the field freezer is less than one hour and the ice packs are still ≤0°C or dry ice (if used) is still visibly present.

9.5.6.7 If a freezer (7.1.7) is not available in the field, the cooler (7.1.8) must maintain a temperature of ≤0°C for the duration of the time that the filter or cassette is contained within the cooler, whether the cooler is being used for storage in the field or shipment to the laboratory.

9.5.6.8 Ship the filters or filter cassettes to the laboratory as described in 11.4.

9.4.4 After the run is complete, and using disposable gloves, remove each sample filter (that is, one at a time). The sample event name, sample type, location, and collection date should be recorded on the field data sheet.

9.4.5 Place the entire filter assembly, its funnel (if used), and the completed data sheet into a cooler with ice packs, and return to the laboratory for analysis using overnight service.

9.4.6 Because of the potential for filter contamination, Field Blank (FB) samples must be taken at a rate of 10 % of the sampling schedule, however more blanks should be performed if results are detected at concentrations greater than the detection limit.

9.4.7 Upon receipt at the laboratory, the sample is logged into the laboratory data management system and the sample container is stored in a freezer until preparation for analysis.

NOTE 6—Samples can remain for up to three days after sampling if the ambient temperature is ≤60°F (15). Otherwise, it is imperative that samples are recovered from the field the day after an event, regardless of weekends or holidays. To avoid recovery date issues, alternate sampling days could be approved in advance.

## 10. Calibration and Standardization

10.1 *Sampling Calibration*, required for samplers equipped with rotameters.

10.1.1 Calibrate sample air flow rate using a primary method of calibration at the beginning and end of sampling period.

10.1.2 Use a rotameter, a soap bubbler or a mass flow calibrator system for calibration (see (7.1.9, 7.1.10)). Generic procedures are provided in 10.1.3 through 10.1.6.

10.1.3 Wear disposable gloves (see (7.10)) during calibration to prevent sampler contamination.

10.1.4 Install a filter cassette (7.1.2) containing a filter in the same manner as performed during routine sampling. Void this filter when calibration is complete.

10.1.5 Turn the sampler pump on and allow it to stabilize. After the flow rate has stabilized, attach the calibration device to the inlet by means of flexible tubing (see Leak check the system: 7.1.10).

10.1.5.1 Turn on the pump (7.1.1) and allow it to stabilize.

10.1.5.2 Check the system for leaks by blocking the flow at the cassette inlet (PTFE cassettes (7.1.2.1)) or sampling system inlet (FRM cassettes (7.1.2.2)) and visually checking that flow is not occurring. If flow is detected, seek and eliminate the leak(s).