



Designation: D7614 – 20

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

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 (ϵ) 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 This method is applicable to the determination of masses of 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).²

1.3 This method is applicable to hexavalent chromium measurement in the atmosphere from 0.019 to 0.926 ng/m³ assuming a 21.6 m³ sample volume. The lower range may be decreased with longer sampling times. The upper range can be increased using appropriate dilutions.

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, health, and 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.*

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

2. Referenced Documents

2.1 *ASTM Standards*:³

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

D4840 Guide for Sample Chain-of-Custody Procedures

E288 Specification for Laboratory Glass Volumetric Flasks

E438 Specification for Glasses in Laboratory Apparatus

E1154 Specification for Piston or Plunger Operated Volumetric Apparatus

3. Terminology

3.1 *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, n*—the mobile phase used to transport the sample through the ion 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 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.

3.2.6 *quality assurance project plan (QAPP) or project plan, n*—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 (2-4)

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 at a rate of 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 (COCs) are completed and the filters are shipped to the laboratory in a cooler with ice or cold packs that will keep filters at $\leq 0^{\circ}\text{C}$. Upon receipt, the filters are stored in a freezer at $\leq 0^{\circ}\text{C}$ 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 extract is analyzed by ion chromatography using a system comprised of a guard column, an analytical column, a post-column derivatization module including mixing coil, and a UV/Vis detector. During analysis, hexavalent chromium exists as chromate due to the 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) 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.

4.5 Hexavalent chromium is identified and quantified by comparing its retention time and peak area to the corresponding 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 a carcinogen and industrial toxin. Hexavalent chromium is a known inhalation irritant and is associated with respiratory cancer (5).

5.2 Ambient atmospheric concentrations of hexavalent chromium are well below the detection limits of previous analytical methods utilized for the determination of hexavalent chromium (2).

5.3 Ambient atmospheric concentrations of hexavalent chromium provide a means of evaluating exposures in a manner that can be related to health-based risk levels. The data for samples collected in situ provide an improved basis for health assessments of potential exposures (5).

5.4 This test method provides step-by-step instructions for the sampling and analysis of 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, when used to impregnate the sampling filters, was observed to cause interferences with the analysis (3).

6.2 Higher concentrations of the sodium bicarbonate impregnation solution (8.9) may cause flow restrictions during ambient air sampling (3).

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

6.4 Several types of filters have been reported by multiple laboratories to contain trace amounts of hexavalent chromium which are detectable using this method. A variety of filter matrices including polyvinyl chloride (PVC), quartz, and mixed cellulose esters (MCE) were found to have high concentrations of hexavalent chromium and cannot be used for low level ambient Cr^{6+} determinations (1, 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 $\leq 4^{\circ}\text{C}$.

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 interferents (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 sampling at flow rates of 5.0–16.0 L/min.

NOTE 1—An example of a sampling system for ambient air consists of an air inlet, a cassette with filter, a flow meter, a vacuum pump, a timer and a power supply as shown in Fig. 1.

7.1.1 *Sampling pumps*, with an adjustable flow rate, capable of maintaining a consistent and constant flow rate over a sampling period of up to 24 hours. Sampling pump flow rates must be calibrated before sampling begins. (See Practice D3195 and Section 10.)

7.1.2 *Filter cassette*, to hold the sample filter. All sampling systems shall 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.

7.1.4 *Glass funnel*, for use with the PTFE filter cassettes. (See Fig. 2.)

7.1.5 *Flow control device*, capable of controlling and measuring selected sample gas flow rates to within $\pm 2\%$. Rotameter control devices must be calibrated against a primary

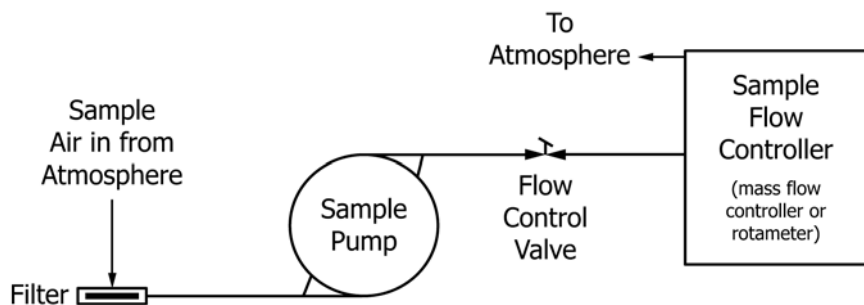


FIG. 1 Hexavalent Chromium Sampling System in Ambient Air

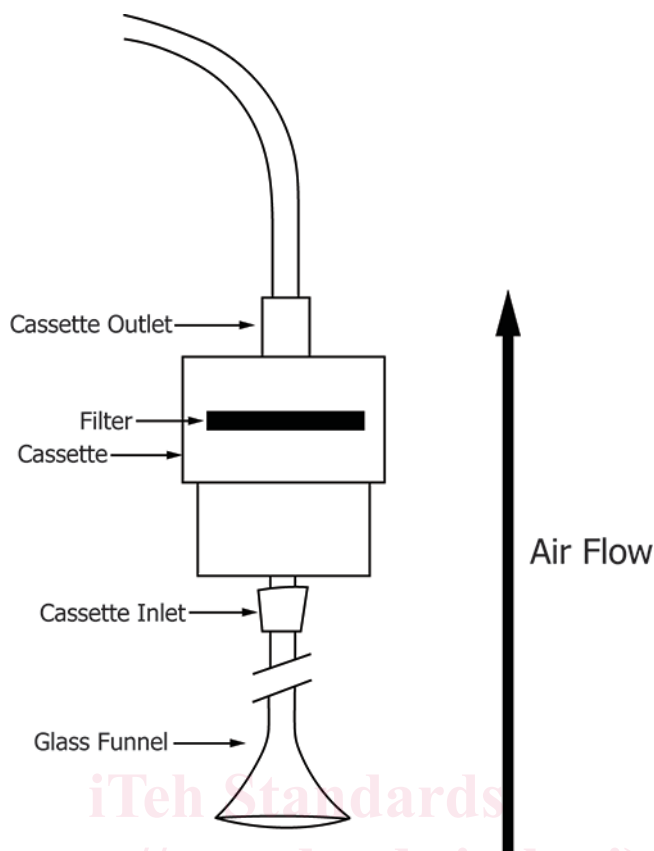


FIG. 2 Diagram of Hexavalent Chromium PTFE Filter Cassette Assembly

standard (that is, a flowmeter whose accuracy is traceable to a primary standard, see Practice D3195 and Section 10.)

7.1.6 *Elapsed timer*, to be placed in line with the sample pump to 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 0°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 *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°C for the duration of time that the filters are contained in the cooler.

7.1.9 *Flexible tubing*, for use with sampling system (7.1).

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

7.2 *Analytical 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 *Reaction coil*, capable of mixing two flowing liquid streams with minimal band spreading.

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 polyethylene glycol (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 Specification E1154 for piston operated volumetric devices.

7.4 *Volumetric flasks*, made of borosilicate glass, 100 mL, 200 mL, 1 L, and 2 L, which comply with Specification E288 and Specification E438.

7.5 *Analytical balance*, for reagent preparation. Must have accurate readability to 0.1 mg.

7.6 *Extraction vessels with caps*, 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*, disposable plastic, for storage of the acid-washed, sodium bicarbonate-impregnated filters.

7.8 *Impregnation area*, 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 PM_{2.5} 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 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 prevention of sample 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.⁴ 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, ≥18.2 MΩ.

8.4 *Ammonium sulfate ((NH₄)₂SO₄)*, 99.999 % purity based on trace metals.

8.5 *Ammonium hydroxide (NH₄OH)*, reagent grade, 28.0–30.0 % NH₄, specific gravity 0.899 g/cm³.

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 (CH₃OH)*, HPLC grade, greater than 99.9 % purity, specific gravity 0.79 g/cm³.

8.8 *Sulfuric acid (H₂SO₄)*, concentrated, specific gravity 1.84 g/cm³.

8.9 *Sodium bicarbonate (NaHCO₃)*, 99.5+ % purity.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

8.10 *Potassium dichromate* ($K_2Cr_2O_7$), 99.99+ % purity based on trace metals, crystalline. For use in preparing standards. Dry at 105°C for 1 hour then cool in a desiccator prior to use. Alternatively, potassium chromate ($K_2Cr_2O_4$) 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-diphenylcarbazine (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 *Standard Solutions:*

8.14.1 *Hexavalent Chromium Primary and Secondary Stock Standard Solutions* (~1000 $\mu\text{g/mL Cr}^{6+}$), 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 Prepare two separate 1000 $\mu\text{g/mL Cr}^{6+}$ stock 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 calibration standards. The secondary stock standard is used for all quality control standards and samples (Section 13) (11).

NOTE 3—Potassium chromate (K_2CrO_4) may be used as an alternative to potassium dichromate for the preparation of the hexavalent chromium stock standard solution. 0.373 g of K_2CrO_4 are needed to make ~100 mL of ~1000 $\mu\text{g/mL Cr}^{6+}$.

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 *Hexavalent Chromium Initial and Continuing Calibration Verification Standard Solution*, 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). 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.

8.14.6 *Trivalent Chromium Stock Standard Solution* (~1000 $\mu\text{g/mL Cr}^{3+}$), stock trivalent chromium standards are available commercially. The standard must be verified to contain negligible amounts of Cr^{6+} prior to use for this method.

8.14.7 *Trivalent Chromium Working Standard Solution*, 1000 ng/mL, to be prepared in reagent water. In a 100 mL volumetric flask, add approximately 75 mL reagent water (8.3) and 100 μL of the trivalent chromium stock standard solution (8.14.6). 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^{3+} to Cr^{6+} .

8.15 *Nitric Acid* (HNO_3), concentrated, trace metals grade, specific gravity 1.4 (g/cm^3).

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