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

This standard is issued under the fixed designation D6832; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Editorial corrections were made in October 2013.

1. Scope

1.1 This test method specifies a method for the determination of the time-weighted average mass concentration of hexavalent chromium in workplace air samples.

1.2 The method is applicable to the personal sampling of the inhalable fraction of airborne particles, as defined in ISO 7708, and to area (static) sampling.

1.3 The sample dissolution procedure specifies separate procedures for soluble and insoluble hexavalent chromium.

1.4 The method is applicable to the determination of masses of 0.01 µg to 10 µg of hexavalent chromium per sample without dilution.

1.5 The concentration range for hexavalent chromium in air for which this procedure is applicable is approximately 0.1 µg/m^3 to 100 µg/m^3, assuming 1 m^3 of air sample. The range can be extended upwards by appropriate dilution.

1.6 Interconversion of trivalent and hexavalent chromium species may occur during sampling and sample preparation, but these processes are minimized to the extent possible by the sampling and sample preparation procedures employed.

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

1.8 *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.*

1.9 *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:*[2]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3195 Practice for Rotameter Calibration

D4840 Guide for Sample Chain-of-Custody Procedures

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection

2.2 *ISO Standards:*[3]

ISO 648 Laboratory Glassware—One-mark Pipets

ISO 1042 Laboratory Glassware—One-mark Volumetric Flasks

ISO 3585 Glass Plant, Pipeline and Fittings—Properties of Borosilicate Glass 3.3

ISO 7708 Air Quality—Particle Size Definitions for Health-related Sampling

ISO 8655 Piston and/or Plunger-operated Volumetric Apparatus (6 Parts)

3. Terminology

3.1 For definitions of terms used in this standard test method, refer to Terminology D1356.

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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[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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

4. Summary of Test Method

4.1 A known volume of air is drawn through a filter to collect particulate hexavalent chromium. The sampler is designed to collect the inhalable fraction of airborne particles (see ISO 7708).

4.2 The filter and collected sample are subjected to a dissolution procedure in order to extract hexavalent chromium. The sample dissolution procedure may consist of one (or both) of two techniques: one for soluble and one for insoluble hexavalent chromium.

NOTE 1—If it is desired to measure both soluble as well as total hexavalent chromium, the soluble procedure is used first, and this is followed by the procedure for insoluble hexavalent chromium compounds. Thus, total Cr[VI] is the sum of soluble and insoluble hexavalent chromium compounds. On the other hand, if it is desired to measure total hexavalent chromium without first isolating insoluble Cr[VI] compounds, only the procedure for insoluble Cr[VI] is required (this will dissolve both soluble and insoluble hexavalent chromium compounds).

4.2.1 For dissolution of soluble hexavalent chromium, distilled water with no heating is used to treat the sample. Alternatively, a weakly basic ammonium sulfate/ammonium hydroxide buffer solution with no heating is used to extract soluble forms of hexavalent chromium.

4.2.2 For dissolution of insoluble hexavalent chromium, a basic carbonate buffer solution with heating by a hot plate is used for sample treatment. Alternatively, an ultrasonic bath is used instead of a hot plate.

4.3 Aliquots of sample extracts are subjected to ion chromatography in order to separate extracted hexavalent chromium from trivalent chromium and other metal cations. An ammonium sulfate/ammonium hydroxide eluent solution is used as the mobile phase.

4.4 Following separation, hexavalent chromium is reacted with an acidic solution of 1,5-diphenylcarbazide to form a characteristic violet chromium-diphenylcarbazone complex. Post-column derivatization is used in order to react hexavalent chromium with 1,5-diphenylcarbazide.

4.5 The absorbance of the chromium-diphenylcarbazone complex is measured at 540 nm using visible spectrophotometry. Analytical results are obtained by plotting the measured absorbance as a function of concentration of the chromium-diphenylcarbazone complex.

4.6 The analysis results may be used for the assessment of workplace exposures to hexavalent chromium in air.

5. Significance and Use

5.1 Airborne hexavalent chromium is carcinogenic (**1**),[4] and analytical methods for the measurement of this species in workplace aerosols are desired. Worker exposure to hexavalent chromium occurs primarily through inhalation (**1**), and this test method provides a means for exposure assessment to this highly toxic species. Analytical results from this procedure can be used for regulatory compliance purposes (**2**).

[4] The boldface numbers in parentheses refer to the list of references at the end of this test method.

6. Reactions

6.1 Reduction of hexavalent chromium to trivalent species can occur in acidic environments, and also in the presence of organic material or environments having high iron concentrations in air (**3**). Reduction of hexavalent chromium can also occur on filter media (**4**), and efforts should to taken to minimize this contribution to sample loss. Oxidation of trivalent chromium to hexavalent species can occur in strong base and in the presence of air (**5**), so efforts should be taken to minimize these contributions to analytical bias. In plating mist samples and in some welding fume samples, interference from iron may be problematic (**3**).

7. Apparatus

7.1 *Samplers,* designed to collect the inhalable fraction of airborne particles, for use when the exposure limits of interest apply to the inhalable fraction of airborne particles (as defined in ISO 7708).

NOTE 2—In general, personal samples for collection of the inhalable fraction of airborne particles do not exhibit the same size selective characteristics if used for area (static) sampling.

NOTE 3—Consider whether the sample is meant to constitute only that material which is collected on filter material, or whether the sample comprises all particulate that is captured within the sampler (that is, all material on the filter, backup pad (if applicable), and on the inside walls of the sampler). See Appendix X1 for guidance on handling of wall deposits within sampling cassettes.

7.2 *Filters,* of a diameter suitable for use with the samplers (7.1), with a collection efficiency of not less than 99.5 % for particles with a 0.3 µm diffusion diameter (ISO 7708), and compatible with the sample preparation and analysis method.

NOTE 4—Typical filter diameters for personal sampling are 25 mm and 37 mm.

7.2.1 Filters should not react with Cr(VI). The following are acceptable:

7.2.1.1 *Polyvinyl Chloride (PVC) Membrane Filters*, 5 µm pore size or below.

7.2.1.2 *Polyvinyl Fluoride (PVF) Membrane Filters*, 5 µm pore size or below.

7.2.1.3 *Polytetrafluorinated Ethylene (PTFE) Membrane Filters*, 5 µm pore size or below.

7.2.1.4 *Glass Fiber Filters*, binder-free.

7.2.1.5 *Quartz Fiber Filters.*

7.2.1.6 *PVC/Acrylic Copolymer Membrane Filters*, 5 µm pore size or less.

NOTE 5—Several types of filters have been found to cause reduction of hexavalent chromium (**4**). Mixed cellulose ester (MCE) filters may cause significant reduction of hexavalent chromium, and are generally unsuitable. Some PVC filters have been reported to cause hexavalent chromium reduction; this should be investigated prior to choosing PVC filters.

NOTE 6—When sampling chromic acid mist, there is an advantage if the oxidizing potential of hexavalent chromium is lowered, for instance by impregnating the filter with alkali. For example, this can be accomplished by soaking the filter overnight in 1 M sodium hydroxide, and allowing it to dry. This lessens the tendency of Cr(VI) to react with organic compounds in the filter material, or reducing agents and dust present in the sampled air, or both. Filter materials such as PVC and PTFE can be unsuitable for alkali treatment since they tend to be hydrophobic and therefore not easily wetted. PVF and vinyl/acrylic copolymer membrane filters have been found to be suitable for alkali treatment (**3**).

7.3 *Backup Pads,* if necessary for use in the particular sampler employed.

NOTE 7—Cellulose backup pads should not be used for sampling of chromic acid mist, since droplets can penetrate the filter by capillary force, resulting in the possibility of Cr(VI) reduction with the backup pad material. Glass or quartz fiber backup pads could be used, or a mesh comprised of material that is resistant to chromic acid.

7.4 *Sampling Pumps,* with an adjustable flow rate and capable of maintaining the selected flow rate (between 1 and 5 L/min for personal sampling pumps, and between 5 and 400 L/min for high-volume sampling pumps) to within ±5 % of the nominal value throughout the sampling period (up to 8-10 h for personal sampling, or shorter periods for high-volume sampling). For personal sampling the pumps shall be capable of being worn by the worker without impeding normal work activity. Sampling pump flow rates shall be set using either a primary or secondary standard; if a secondary standard is used, it shall be calibrated using a primary standard (see D3195).

NOTE 8—A flow-stabilized pump may be required to maintain the flow rate within the specified limits.

7.5 *Flowmeter, Portable,* capable of measuring the selected volumetric flow rate to within ±2 %, and calibrated against a primary standard (that is, a flowmeter whose accuracy is traceable to primary standards).

7.6 *Ancillary Equipment:*

7.6.1 *Flexible Tubing,* of a diameter suitable for making a leak-proof connection from the sampler to the sampling pump.

7.6.2 *Belts or Harnesses,* to which the sampling pump can be conveniently fixed for personal sampling (except where sampling pumps are small enough to fit inside workers' pockets).

7.6.3 *Flat-Tipped Forceps,* plastic or plastic-tipped, for loading and unloading filters into or out of samplers.

7.6.4 *Filter Transport Cassettes,* or similar, if required, in which to transport samples for laboratory analysis.

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

7.7 *Analytical or Laboratory Apparatus*
Ordinary laboratory apparatus, and:

7.7.1 *Glassware,* made of borosilicate glass 3.3 and complying with the requirements of ISO 3585.

7.7.1.1 *Beakers,* of capacities between 50 mL and 2 L.

7.7.1.2 *Watch Glasses,* to fit the beakers.

7.7.1.3 *One-Mark Pipets,* complying with the requirements of ISO 648.

7.7.1.4 *One-Mark Volumetric Flasks,* of capacities between 10 mL and 1000 mL, complying with the requirements of ISO 1042.

7.7.1.5 *Piston-Operated Volumetric Apparatus,* complying with the requirements of ISO 8655. Pipettors, as an alternative to one-mark pipets for the preparation of standard solutions, calibration solutions, and dilution of samples. Dispensors, for dispensing acids.

7.7.2 *Hot Plate,* thermostatically controlled, capable of maintaining a surface temperature of approximately 135°C; for hot plate extraction of insoluble hexavalent chromium compounds.

7.7.3 *Sonicator,* minimum power output 0.5 W/cm^2, for use in the ultrasonic extraction of insoluble hexavalent chromium compounds.

7.7.4 *Ion Chromatograph,* having the following components:

NOTE 9—The following components should be comprised, to the extent possible, of inert materials.

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

7.7.4.2 *Injection Valve*—A low dead-volume valve, (1 mL or less), nonmetallic, that will allow the loading of sample contents into the eluant stream. Sample loops of up to 1 mL volume will provide enhanced detection limits.

NOTE 10—Either an autosampler or a manual injection system, or both, is (are) acceptable.

7.7.4.3 *Guard Column*—A column placed before the separator column (7.7.4.4) to protect the separator column from fouling by particles or strongly adsorbed organic constituents.

7.7.4.4 *Separator Column*—A column packed with high capacity pellicular anion exchange resin that is suitable for resolving hexavalent chromium from other metals and cations.

7.7.4.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent solution against a back pressure of up to 40 kPa.

7.7.4.6 *Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams with minimal band spreading.

7.7.4.7 *Detector*—A low-volume flow-through visible absorbance detector with a nonmetallic flow path.

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

NOTE 11—The use of an automated system is recommended.

7.7.5 *Eluant Reservior*—A container suitable for storing eluant solution.

7.7.6 *Syringe Filter,* 0.45 µm, for sample filtration prior to analysis. The filter material shall be chemically inert.

7.7.7 *Syringe,* equipped with a male fitting and a capacity of at least 1 mL; or auto sampler module with like specifications.

8. Reagents

8.1 For the analysis of hexavalent chromium, use only reagents of recognized analytical grade, and only water as specified in (8.1.1).

8.1.1 *Water,* complying with the requirements of ASTM Type 1 water (as specified in Specification D1193: electrical conductivity less than 0.1 mS/m and resistivity greater than 0.01 M-Ω-m at 25°C).

8.1.2 *Sulfuric acid (H_2SO_4),* concentrated, specific gravity ~1.84 g/mL, ~98 % (m/m).

8.1.3 *Nitric aAcid (HNO_3),* concentrated, specific gravity ~1.42 g/mL, 69-71 % (m/m).

8.1.4 *Nitric acid wash solution (1 % HNO_3)*—Dilute 10 mL of concentrated nitric acid (8.1.3) to 1 litre with water (8.1.1).

8.1.5 *Sodium carbonate (Na_2CO_3),* anhydrous, purity greater than 99.9 % (m/m).

8.1.6 *Sodium hydroxide (NaOH),* pellets, purity greater than 99.5 % (m/m).

8.1.7 *Ammonium sulfate ($(NH_4)_2SO_4$),* purity greater than 99.5 % (m/m).

8.1.8 *Ammonia (NH_3),* concentrated, specific gravity ~0.90 g/mL, ~29 % (m/m).

8.1.9 *1,5-diphenylcarbazide ($C_6H_5NHNHCONHNHC_6H_5$),* purity greater than 98 % (m/m).

8.1.10 *Methanol (CH_3OH),* HPLC grade.

8.1.11 *Potassium dichromate ($K_2Cr_2O_7$),* purity greater than 99.9 % (m/m).

8.1.12 *Extraction solutions.*

NOTE 12—Extraction solutions other than those specified may be used, if desired, provided that it can be demonstrated that the performance of the measuring procedure is not impaired.

8.1.12.1 *Extraction solution for insoluble Cr(VI) compounds,* 2 % (m/v) sodium hydroxide/3 % (m/v) sodium carbonate: Dissolve 20 g of sodium hydroxide pellets (8.1.6) and 30 g of sodium carbonate (8.1.5) in 250 mL of water (8.1.1), swirl to mix, and allow to cool. Quantitatively transfer the solution to a one litre volumetric flask, dilute to the mark with water (8.1.1), stopper and mix thoroughly.

8.1.12.2 Extraction solutions for soluble Cr(VI) compounds, either of the following:

(1) Water (8.1.1), or

(2) Extraction buffer, ammonium sulfate/ammonium hydroxide buffer solution (0.05 M $(NH_4)_2SO_4$/0.05 M NH_4OH, pH ~8): Dissolve 6.6 g of ammonium sulfate ($(NH_4)_2SO_4$) (8.1.7) in about 500 mL of water. Add 3.25 mL of concentrated ammonium hydroxide (NH_4OH) (8.1.8). Mix well and dilute to 1 litre with water (8.1.1) in a one-mark volumetric flask. Stopper and mix thoroughly.

NOTE 13—This extraction buffer will dissolve water-soluble Cr(VI), for example, potassium chromate, and it may dissolve Cr(VI) compounds which are not water-soluble, for example, strontium chromate. However, this buffer will not dissolve insoluble Cr(VI) compounds such as lead chromate and barium chromate. The use of this extraction buffer serves to stabilize chromium species in solution (for example, trivalent and hexavalent) and thereby reduces interconversion rates of trivalent and hexavalent chromium valence states.

8.1.13 *Eluant Solutions:*

8.1.13.1 *Eluant concentrate,* 2.0 M ammonium sulfate, $(NH_4)_2SO_4$/1 M ammonium hydroxide, NH_4OH: Dissolve 264 g of ammonium sulfate ($(NH_4)_2SO_4$) (8.1.7) in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide (NH_4OH) (8.1.8). Mix well and dilute to 1 litre with water (8.1.1) in a one-mark volumetric flask. Stopper and mix thoroughly.

8.1.13.2 *Eluant solution,* 0.20 M ammonium sulfate, $(NH_4)_2SO_4$/0.1 M ammonium hydroxide, NH_4OH: Add 100 mL of eluant concentrate (8.1.13.1) to a 1-litre one-mark volumetric flask and dilute to volume with water (8.1.1). Stopper and mix thoroughly.

8.1.14 *pH Indicator papers,* suitable for measuring the pH of sample solutions (pH 8.0 ± 0.5) and the pH of effluent from the spectrophotometric detector (pH 2.0 or lower).

8.1.15 *Hexavalent Chromium Standard Solutions:*

8.1.15.1 *Hexavalent Chromium Stock Standard Solution (~1000 µg Cr/l)*—Use a commercially available hexavalent chromium standard solution with a certified concentration. Observe the manufacturer's expiration date or recommended shelf life. Alternatively, dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$) (which has been dried at 105°C for 1 h and then cooled in a dessicator) in water (8.1.1). Dilute with water (8.1.1) to 100 mL in a one-mark volumetric flask, stopper and mix thoroughly.

NOTE 14—Potassium chromate (K_2CrO_4) can be used as an alternative to potassium dichromate for the preparation of hexavalent chromium standard solutions.

8.1.15.2 *Hexavalent Chromium Working Standard Solution (1000 µg Cr/l)*—Pipet 1.00 mL of the chromium stock solution (8.1.15.1) into a 1-litre one-mark volumetric flask and dilute to volume with water (8.1.1). Stopper and mix thoroughly. Prepare this solution fresh monthly.

8.1.15.3 *Hexavalent Chromium Calibration Solutions*—Prepare a minimum of five calibration solutions in the concentration range of 0.02 to 5 µg/L by diluting appropriate pipetted volumes of the 1000 µg/L standard solution (8.1.15.2) in the appropriate extraction solution (8.1.12). Prepare these solutions fresh daily.

8.1.16 *1,5-Diphenylcarbazide Reagent Solution*—Dissolve 0.125 g of 1,5-diphenylcarbazide (8.1.9) in 25 mL of methanol (8.1.10). Add about 100 mL of water (8.1.1) containing 5.6 mL of concentrated sulfuric acid (8.1.2). Dilute with water (8.1.1) to 250 mL in a one-mark volumetric flask, stopper and mix thoroughly. Prepare this solution fresh daily.

NOTE 15—Other suitable solvents, such as acetone, may be used for the preparation of the 1,5-diphenylcarbazide reagent solution (if desired).

9. Sampling

NOTE 16—For information on strategies for the sampling of workplace atmospheres, consult Guide E1370.

9.1 *Sampling Procedure:*

9.1.1 *Selection and Use of Samplers:*

9.1.1.1 Select a sampler designed for collection of the inhalable fraction of airborne particles, as defined in ISO 7708.

NOTE 17—If possible, samplers selected should be manufactured from conducting material, since samplers comprised of non-conducting material have electrostatic properties that can adversely influence representative sampling.

9.1.1.2 Use the samplers at their designed flow rate (between 1 and 5 L/min), and in accordance with the manufacturer's instructions, so that they collect the inhalable fraction of airborne particles.

9.1.2 *Sampling Period:*

9.1.2.1 Select a sampling period long enough to ensure that the amount of hexavalent chromium collected is adequate to enable hexavalent chromium in air concentrations to be determined at the required level (see Guide E1370). Ideally, the sampling period should be for the entire workday.

9.1.2.2 In calculating the minimum sampling time required it is necessary to consider the selected flow rate and the lower limit of the recommended analytical working range of the method.

9.1.2.3 The sampling time shall not be so long as to risk overloading of the filter with particulate material. This is a concern when high concentrations of hexavalent chromium in air are anticipated.

NOTE 18—If filter overloading is an observed or suspected problem and it is desired to sample for the entire workday, it may be necessary to collect consecutive samples.

9.2 *Preparation of Sampling Equipment:*

9.2.1 Perform the following in an area where contamination from hexavalent chromium is known to be at a minimum:

9.2.1.1 Clean the samplers before use by soaking them in detergent solution, rinsing them thoroughly with water, and then drying them.

9.2.1.2 Load the filters into clean, dry samplers. Handle the filters only with clean flat-tipped forceps and gloved hands. Seal each loaded filter with tape or shrink-wrap in order to secure the individual sections of the sampler. Cap the inlet and outlet of each sampler with a cover or plug to protect the filter and interior of the sampler from contamination.

NOTE 19—Samplers that are pre-loaded with filters are available commercially from a number of vendors.

9.2.1.3 Remove the protective cover or plugs from a loaded sampler. Connect the sampling pump to the loaded sampler using flexible tubing, and ensure that there are no leaks. Turn on the pump, and allow for an appropriate warm-up period (if necessary). Set the selected flow rate with an accuracy of ±5 % using the calibrated flowmeter. Finally, turn off the pump and reseal the sampler.

9.3 *Collection of Samples:*

9.3.1 For personal monitoring, fix the sampler to the clothing of the worker, and place within the workers breathing zone (see Terminology D1356). Attach the sampling pump to the worker as appropriate, to minimize inconvenience. For fixed location sampling, select a suitable desired sampling site.

9.3.2 When ready to initiate sampling, remove the cover or plug from the inlet of the sampler and turn on the pump to begin sampling. Record the time and initial pump flow rate.

9.3.3 Since it is possible for filters to become clogged, monitor the performance of the sampler frequently, that is, a minimum of once per hour. Measure the flow rate with an accuracy of ±5 % using the calibrated flowmeter, and record the measured value.

9.3.4 At the end of the sampling period, terminate sampling, and measure the flow rate with an accuracy of ±5 % using the calibrated flowmeter. Consider the sample to be invalid if the flow rate was not maintained to within ±5 % of the nominal value throughout the sampling period. Record the volumetric flow rate and the time, and calculate the duration of the sampling period.

NOTE 20—If an integral timer is used, check the reading on the integral timer. Consider the sample to be invalid if this and the calculated sampling time do not agree to within ±5 %, since this suggests that the sampling pump was not operating throughout the entire sampling period.

9.3.5 Reseal the sampler and disconnect it from the sampling pump.

9.3.6 Record sample identity and all relevant sampling data. Calculate the average flow rate by averaging the flow rate measurements taken before and after (and perhaps during) the sampling period. Compute the volume of air sampled in litres by multiplying the mean flow rate (in L/min) by the sampling time (min).

9.3.7 For each batch of ten samples (or less), submit for analysis at least two unused filters (blanks) from the same lot used for sample collection. Subject these blank filters to exactly the same handling procedures as the samples, but draw no air through them.

9.4 *Transportation:*

9.4.1 For samplers having an internal filter cassette, remove the filter cassette from each sampler and place within a transport cover.

NOTE 21—Transport covers are normally supplied by the manufacturer

9.4.2 For samplers of the disposable cassette type, transport samples in the samplers from which they were collected.

NOTE 22—Samples may be placed in an ice cooler so that they are kept refrigerated during transport.

9.4.3 Samples shall be transported to the laboratory for analysis in such a manner to prevent contamination and damage to the samples in transit. Samples shall be individually and unambiguously labeled to ensure proper handling.

9.4.4 Avoid exposing filter samples to plasticizers that may cause reduction of Cr(VI).

9.4.5 Follow sampling chain of custody procedures in accordance with Guide D4840 to ensure sample traceability. Ensure that the documentation that accompanies the samples is suitable for a "chain of custody" to be established.

10. Preparation of Apparatus

10.1 *Cleaning of Glassware:*

NOTE 23—Perform all of the following while wearing gloves.

10.1.1 Before use, clean all glassware to remove any residual grease or chemicals by first soaking in laboratory detergent solution and then rinsing thoroughly with water.

10.1.2 After initial cleaning with detergent and water, clean all beakers with nitric acid. This can be accomplished by either soaking for a minimum of 24 h in concentrated nitric acid, or by the following procedure: fill beakers to one-third capacity with concentrated nitric acid, and then heat them at a hot plate surface temperature of 140°C in a fume hood until most of the liquid has evaporated, and allow to cool. Rinse beakers thoroughly with water.

10.1.3 Glassware that has been previously subjected to the entire cleaning procedure described in the previous steps, and which has been reserved for the analysis of hexavalent chromium, can be cleaned adequately by rinsing with nitric acid wash solution and then with water.

10.2 *Instrumental Set-Up:*

10.2.1 Set up the ion chromatograph in accordance with manufacturer's instructions.

10.2.2 Install the organic guard column and separator columns in the ion chromatograph.

10.2.3 Install a 1 mL sample loop on the injection valve of the ion chromatograph.

10.2.4 Adjust the eluant flow rate to that recommended by the manufacturer of the instrument. Increase the flow of the diphenylcarbazide (DPC) reagent solution until the flow rate reaches that recommended by the instrument manufacturer.

NOTE 24—It is recommended that the ratio of the flow rate of the DPC reagent solution to that of the eluent remain the same.

10.2.5 Measure the pH of the detector effluent, and ensure that the effluent pH is 2 (by addition of sulfuric or hydrochloric acid) or lower.

NOTE 25—pH needs to be strongly acidic to ensure a quantitative reaction of DPC with Cr(VI).

10.2.6 Adjust the visible detector to read at 540 nm.

10.2.7 After the flow rates are adjusted, allow the system to equilibrate for at least 15 min.

11. Procedure

11.1 *Preparation of Sample and Blank Solutions*—Samples and blanks shall be prepared for subsequent analysis by using either a procedure for soluble hexavalent chromium or a procedure for insoluble hexavalent chromium. The former procedure entails extraction in water or sulfate buffer solution, while the latter involves hot plate digestion in carbonate extraction buffer solution.

NOTE 26—Perform all of the following while wearing gloves.

11.1.1 *Procedure for Soluble Hexavalent Chromium:*

NOTE 27—The following may be conducted using plastic labware.

11.1.1.1 Open each sampler or sample container, and transfer each filter sample or blank into a clean, labeled 50 mL beaker using nonmetallic flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample, wash any particulate matter adhering to the internal surfaces into the beaker using a minimum volume of water (see 8.1.1) or extraction buffer (see 8.1.12.2).

11.1.1.2 Add ~6 mL of water (8.1.1; 8.1.12.2(1)) or ammonium sulfate/ammonium hydroxide extraction buffer (8.1.12.2(2)) to the beakers and swirl gently to mix the contents. Ensure that the sample-loaded sides of the filters remain completely immersed. Cover the beakers with watch glasses.

11.1.1.3 Allow the immersed filters to sit for one hour at room temperature, swirling/agitating occasionally.

NOTE 28—Alternative temperatures, for example, 37°C (**6**), may be used if desired.

11.1.1.4 Remove the filters from the beakers with flat-tipped forceps, carefully washing all surfaces with an additional 1 to 2 mL of water. Discard the filters.

11.1.1.5 Remove particles in the solutions by filtration or centrifugation.

11.1.1.6 Quantitatively transfer the solutions containing extracted soluble hexavalent chromium to 10-mL one-mark volumetric flasks. Rinse all surfaces with a minimum volume of water, and ensure that the rinsate is transferred to the volumetric flask.

11.1.1.7 Adjust the pH to 8 ± 0.2 with a minimum amount of buffer concentrate (2 M ammonium sulfate/1 M ammonium hydroxide). Account for any significant change in volume.

NOTE 29—This is needed for subsequent ion chromatographic analysis. The slightly basic nature of the solution stabilizes both Cr(III) and Cr(VI) species.

11.1.1.8 Dilute to the mark with water.

11.1.2 *Procedure for Total Hexavalent Chromium:*

NOTE 30—As an alternative to hot plate dissolution of Cr(VI), ultrasonic extraction may be used.

11.1.2.1 Open each sampler or sample container, and transfer each filter sample or blank into a clean, labeled 50 mL beaker using flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample, wash any particulate matter adhering to the internal surfaces into the beaker using a minimum volume of extraction buffer solution (see 8.1.12.1).

11.1.2.2 Add 10 mL of extraction solution (8.1.12.1), 2 % (m/v) sodium hydroxide/3 % (m/v) sodium carbonate 0.05 (pH 13), to each beaker containing filter samples or blanks. Ensure that the filters are completely immersed in the extraction solution.

11.1.2.3 Place the beakers containing the filters and extraction solution on a hot plate that is preheated to a surface temperature of 135°C, and heat the solutions with occasional swirling for 60 to 90 min. Do not allow solutions to boil over or evaporate to dryness.

NOTE 31—Evaporation to dryness can cause unwanted interconversion of Cr(VI) and Cr(III) species. For example, aereal oxidation may cause oxidation of Cr(III) to Cr(VI).

11.1.2.4 Remove the beakers from the hot plate and allow them to cool to room temperature.

11.1.2.5 Carefully rinse each watch glass and the insides of each beaker with water, and transfer each solution quantitatively to a 10 mL one-mark volumetric flask. Remove any undissolved particulate by filtration or centrifugation.

11.1.2.6 Check the pH and, if necessary, adjust the pH to 13 ± 0.2 with a minimum amount of extraction solution (8.1.12.1) or sulfuric acid.

NOTE 32—It is important that the buffer solution be slightly basic, as this pH stabilizes both Cr(III) and Cr(VI) species.

11.1.2.7 Dilute to the mark with water.

11.1.3 *Procedure for Insoluble Chromium:*

11.1.3.1 If it is desired to determine insoluble Cr(VI), follow the above procedures for determining soluble Cr(VI) (11.1.1) and total Cr(VI) (11.1.2), respectively (in sequence).

11.1.3.2 Insoluble Cr(VI) is determined by the difference in results obtained for total Cr(VI) and soluble Cr(VI): [Insoluble Cr(VI)] = [Total Cr(VI)] - [Soluble Cr(VI)].

11.2 *Instrumental Analysis:*

11.3 *Analysis of Calibration Solutions:*

11.3.1 Remove a portion (2-5 mL) of each calibration solution, and filter it through a 0.45 µm syringe filter.

11.3.2 Inject 1 mL of filtered calibration solution into the ion chromatographic system, using an appropriate syringe or auto sampler, into the eluant stream, and mark the injection time on the chromatogram recorder.

11.3.3 Determine the absorbance for hexavalent chromium response for each of the calibration standards, using either peak height (in absorbance) or peak area (peak magnitude × time)