Designation: D7614 – 12

Standard Test Method for Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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^3 ambient air (at 15 L/min for 24 hours) through a sodium bicarbonate cellulose acid washed filter. Atmospheric hexavalent chromium is stabilized on the alkaline coated filter.

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

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

1.5 This method is applicable for hexavalent chromium measurement in the atmosphere from 0.004 ng/m^3 to 0.926 ng/m^3 assuming a 21.6 m^3 sample volume. The range can be increased using appropriate dilutions.

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

1.7 The corresponding method for workplace air samples is ASTM Test Method D6832.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4840 Guide for Sample Chain-of-Custody Procedures

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D3195 Practice for Rotameter Calibration

D3586 Test Method for Chromium in Workplace Atmospheres (Colorimetric Method) (Withdrawn 1990)[3]

D5281 Test Method for Collection and Analysis of Hexavalent Chromium in Ambient Atmospheres (Withdrawn 2014)[3]

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

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

4. Summary of Test Method (1, 2, 3, 4)[4]

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

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

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

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

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

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

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

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

5. Significance and Use

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

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

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

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

6. Interferences

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

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

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

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

7. Apparatus

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

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

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

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

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

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

7.1.4 *Sample pump:*

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

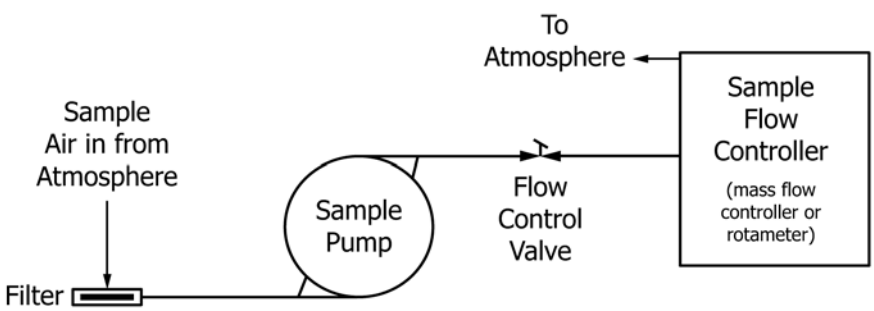

FIG. 1 Hexavalent Chromium Sampling System in Ambient Air

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

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

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

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

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

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

7.2 *Analytical System:*

7.2.1 *Ion chromatograph* shall have the following components:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8. Reagents

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

8.1.1 *Water,* complying with the requirements of ASTM Type I deionized water (DI water) as specified in Specification D1193 (>18 MΩ-cm).

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

8.1.3 *Ammonium hydroxide (NH_4)OH,* reagent grade, 28.0–30.0 % NH_4 basis, specific gravity 0.99 (g/cm^3).

8.1.4 *1,5-diphenylcarbazide ($C_{13}N_4O$),* ACS crystalline (DPC).

8.1.5 *Methanol (CH_3OH),* HPLC grade, 0.2 micron filtered, greater than 99.9 % purity, 0.79 (g/cm^3).

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

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

8.1.8 *Potassium dichromate ($K_2Cr_2O_7$),* 99.99+ % purity based on trace metals, crystalline. Before use it should be dried at 105°C for 1 hour then cooled in a dessicator. See 8.1.12.1 for instructions on preparing standard solutions.

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

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

8.1.11 *Post-Column Derivatizing Reagent (PCR),* in a 50 mL volumetric flask, dissolve 0.25 gm of 1,5-diphenylcarbazide (see 8.1.4) in 50 mL of HPLC-grade methanol (see 8.1.5). Sonicate until DPC goes into solution. In a 500 mL volumentric 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.

8.1.12 *Hexavalent Chromium Standard Solutions :*

8.1.12.1 *Hexavalent Chromium Stock Standard Solution (~1000 µg/mL Cr^{6+}),*—stock hexavalent chromium standards are available commercially or can be prepared by diluting 0.283 grams of potassium dichromate (see 8.1.8) with DI water (see 8.1.1) in a 100 mL volumetric flask. Dilute to volume with 20 mM sodium bicarbonate extraction solution, stopper and mix thoroughly.

NOTE 3—Potassium chromate (K_2CrO_4) can be used as an alternative to potassium dichromate for the preparation of the hexavalent chromium stock standard solution.

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.

8.1.13 *Nitric Acid (HNO_3),* concentrated, 70 % redistilled, 99.999+ % purity based on trace metals, specific gravity 1.4 (g/mL).

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.

8.1.14 *Sodium Bicarbonate Impregnating Solution (1.2 M),* dissolve 5 g of sodium bicarbonate (see 8.1.7) in DI water (see 8.1.1) in a 500 L volumetric flask. Mix well and dilute to mark. Stopper and mix thoroughly.

9. Sampling

9.1 Samples are collected using an individual filter apparatus and flow control device.

9.2 A flow control device(s) is used to maintain a relatively constant sample flow rate through each sample filter over a specific sampling period. 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 connecting lines between the filter assembly and the sampling pump should be kept 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 The following steps are provided for operation of a typical collection system while collecting a sample

9.4.1 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).

9.4.2 With 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.

9.4.3 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.

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.

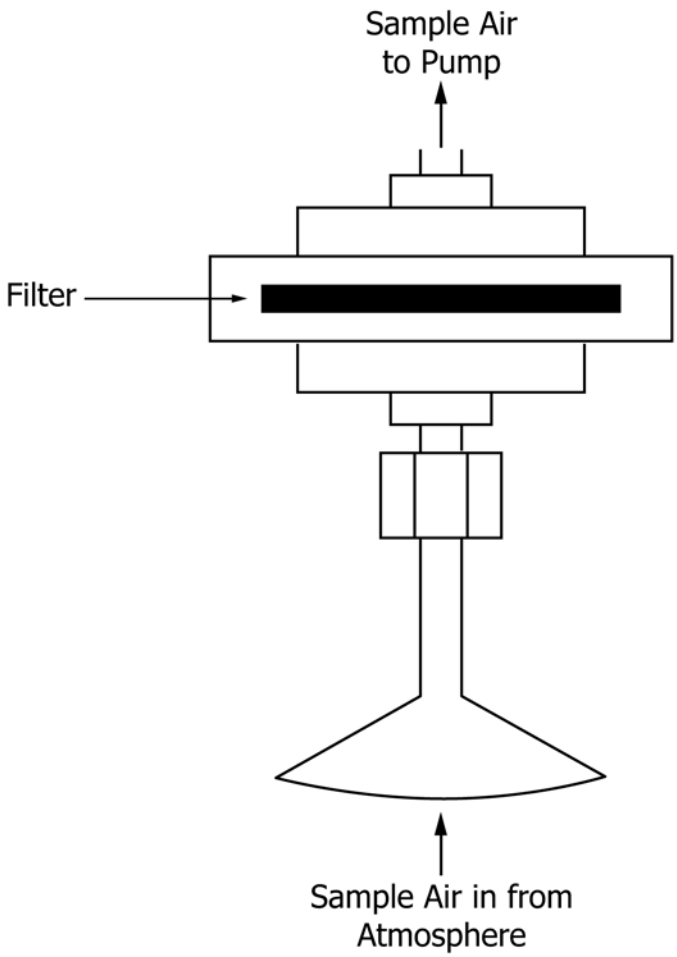

FIG. 2 Hexavalent Chromium Filter Assembly (Preloaded in Laboratory)

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). Generic procedures are provided in 10.1.3 to 10.1.7.

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

10.1.4 Turn the sampler pump on and allow it to stabilize. After the flow rate has stabilized, attach the calibration devise to the inlet by means of flexible tubing (see 7.1.10).

10.1.5 Check system for leaks by restricting the flow at the cartridge inlet. Turn sampler on and visually check that the flow does not increase above 0 L/min. If flow increases above 0 L/min then retighten the tubing and recheck. If the leak is still detected, replace the sampling tubing with clean decontaminated apparatus.

10.1.6 Attach the calibration flow check apparatus to the cartridge inlet.

10.1.7 Adjust the sample pump so that the flow rate is at 13, 14, 15, and 16 L/min. Record an average of at least three calibration readings for each flow rate in a sampler log book. Note the sampler ID, date, time, and initials of the person performing the calibration.

10.2 *Analytical Calibration:*

10.2.1 Prepare the initial calibration ranges from 0.05 to 2 ng/mL of hexavalent chromium as described in 8.1.12.3.

10.2.2 Determine the analytical instrument hexavalent chromium response for each standard using the procedure described in 11.5.

10.2.3 Prepare a calibration curve using a linear plot of the peak area as a function of standard concentration by the regression analysis of least squares. The acceptable coefficient of determination (R2) shall be greater than 0.995 with the RSD < 10%.

10.2.4 Use the same procedure to determine the sample results (see 10.2.3).

10.2.5 Calibrate instrument daily or with each analysis batch not to exceed 24 hours.

10.2.6 As part of the quality assurance program in the evaluation of the data, calibration verification from a secondary source at an intermediate concentration (0.5 ng/mL) is run as a check of the precision of the instrument and calibration.

10.2.7 An Initial Calibration Verification (ICV) should be analyzed after the initial calibration and Continuing Calibration Verifications (CCV) should be analyzed after every ten injections. The recovery criteria are 85-115 %.

10.2.7.1 Prepare the calibration verification standards at 0.5 ng/mL as described in 8.1.12.3 using a secondary source standard.

11. Procedure

11.1 *Filter Preparation:*

11.1.1 Soak filters in an Acid Bath Solution (see 8.1.13.1) for a minimum of 16 and a maximum of 24 hours.

11.1.2 Rinse filters thoroughly with DI water (see 8.1.1). Check pH of the filters by placing a pH strip on top of the wet filter. The pH should match the pH of the DI water. Discard the tested filter.

11.1.3 Dry the filters completely on a screen rack in a nitrogen-purged glove box (see 7.8) for approximately five hours. Filter appearance will become stiff and curled after they have dried.

11.1.4 Soak the filters in the Sodium Bicarbonate impregnating solution (see 8.1.14) overnight.

11.1.5 Replace the Acid Bath Solution (see 8.1.13.1) and the Sodium Bicarbonate impregnating solution (see 8.1.14) daily. The filters will not become clean enough for sampling if the solutions are reused more than twice.

NOTE 7—If the filters are not completely dry before placing them in the impregnating solution, the solution will become dilute and the filters will not collect samples as efficiently.

11.1.6 Dry the filters completely on a screen rack in a nitrogen-purged glove box for approximately 5 hours. Filter appearance will become stiff and curled after they have dried.

11.1.7 Place dried filters into Petri dishes (see 7.8). Place the petri dishes into freezer bags labeled with a unique batch number and store in a freezer until needed.

11.1.8 Analyze 10 % of the filters to verify cleanliness. If one filter has a detectible amount (greater than zero), the whole batch is discarded and a new batch is prepared.

11.1.9 Whenever the filters are handled, clean PTFE coated or plastic tweezers are used with disposable gloves. All filter preparation is completed in the glove box as it is being purged with pure nitrogen.

NOTE 8—The filters are stored in the freezer until shipped in the field or used to prepare spikes or blanks during analysis. The filters are frozen to prevent the sodium bicarbonate from reacting with possible interfering substances present in the air.

11.2 *Shipment and Storage of the Filters:*

11.2.1 The laboratory will need to determine whether the filters used for filter holders (see Fig. 2) or install the filters in the field.

11.2.2 Filters are placed in the PTFE filter holders (see Fig. 2) or in petri dishes (dependent on sampler type). The filter holders are labeled, and a chain of custody is provided.

11.2.3 The filters are shipped to the field in a cooler packed with ice packs to keep the filters frozen.

11.2.4 The filters holder/dishes, gloves, and chain of custodies are sent to the field approximately 1-2 weeks in advance. The filters should be stored in freezers in the field.

11.3 *Sample Collection:*

11.3.1 Assemble the sampling system.

11.3.2 Document all information required about the site information on the chain of custody form. This information should include at a minimum: 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.

11.3.3 *Sample collection using filter holders (see Fig. 2).*

11.3.3.1 Remove the plugs from the inlet and outlet of the pre-loaded filter holder. Insert the funnel stem into the inlet fitting of the filter holder.

11.3.3.2 Connect the outlet of the pre-loaded filter holder and funnel assembly to the PTFE tube that connects to the sample pump. If a collocated sample is scheduled, connect the outlet of the collocated pre-loaded filter holder and funnel assembly to the collocated PTFE connecting tube.

11.3.3.3 Program the sampler to initiate flow through the entire sampling system and adjust the sample collection flow rate to 15.0 L/min.

11.3.3.4 Allow flow to continue for approximately two minutes while the system attains operating temperature. After two minutes, readjust the flow rate to 15.0 Lpm if necessary. Document the flow rate on the chain of custody (see 11.3.2).

11.3.3.5 Program the sampler to collect the 24 hour sample on the designated sample date.

11.3.4 *Sample collection when loading filters at the field:*

11.3.4.1 Remove the filter from the petri dish and attach it to the inlet of the sampler.

11.3.4.2 Program the start date and time, and the inlet flow, using mass flow controllers, into the sampler's microprocessor.

11.3.4.3 After collection, each sampler will automatically stop. Elapsed time, target flow rate, and other sampling information are noted on a chain of custody forms.

11.3.5 *Sample recovery from field:*

11.3.5.1 Sample recovery must be performed as soon as possible on the day after the scheduled collection event to prevent hexavalent chromium conversion to trivalent chromium.

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

11.3.5.3 Document the final flow, recovery date, and total elapsed time on the chain of custody form.

NOTE 9—Because it is desirable to retain any particulate matter that may be adhered/attached to the sample filter, great care must be taken to shake/jostle the filter as little as possible throughout the sample recovery process.

11.3.5.4 Disassemble the filter from the sampler.

11.3.5.5 Document any/all remaining required information on the chain of custody forms.

11.3.5.6 Repackage the filter and chain of custody forms quickly and place the package(s) in a clean, uncontaminated freezer.

11.3.5.7 Return the package(s) to the laboratory in a cooler with ice packs.

11.4 *Filter Extraction:*

NOTE 10—Due to the oxidation/reduction and conversion problems of Cr^{3+} and C^{r6+}, the extraction should be performed immediately prior to analysis. Hexavalent chromium concentrations in the extracts have been shown to decrease significantly with time if left at ambient conditions. If the extracts are placed in temperatures below 18°F, however, the solution concentrations are stable. Therefore, it is important that the ion chromatograph analysis system is calibrated and ready for analysis.

11.4.1 Remove the exposed filter from the petri dish or filter holder using disposable gloves (see 7.10). Fold the filter and place it in a 14 mL disposable polystyrene centrifuge tube (see 7.6) and add 10 mL of sodium bicarbonate extraction solution (see 8.1.9). Cap the tube tightly with plastic snap caps.

11.4.2 Place the tubes in a PTFE coated test tube rack. Place the tube rack in the ultrasonicator (see 7.9) for one hour.

11.4.3 After 1 hour of sonication, remove the tubes and place 5 mL of the sample extract into a to a 5-mL disposable autosampler vial. Extracts are stored in a refrigerator until all analysis of samples is complete.

11.5 *Hexavalent Chromium Analysis:*

11.5.1 Set-up the ion chromatograph (see 7.2) in accordance with the manufacturer's instructions.

11.5.2 Install the guard column (see 7.2.1.2) and the separator columns (see 7.2.1.3) in the ion chromatograph.

11.5.3 Install a 1 mL sample loop on the injection valve (see 7.2.1.6) on the ion chromatograph.

11.5.4 Adjust the eluent (see 8.1.10) flow rate to 1.0 mL/minute. Adjust the 1,5-diphenylcarbazide reagent (see 8.1.11) until the flow rate is 0.33 mL/minute.

11.5.5 Set the UV/VIS detector to 530 nm.

11.5.6 Allow the system to equilibrate for 10 to 45 minutes.

11.5.7 Inject 1 mL of the filtered sample through the sample port using an appropriate syringe or autosampler (see 7.2.1.8) into the eluent stream and note the injection time on the chromatogram (see Fig. 3).

12. Calculation

12.1 *Sampling:*

12.1.1 Calculate the sample air volume (V_s), in m^3 using the sample time and average flow rate as follows:

$$V_s(m^3) = \frac{F_s + F_e}{2} \times T_s \times \frac{1m^3}{1000L} \quad (1)$$

where:

F_s = start flow rate (L/minute)
F_e = ending flow rate (L/minute), and
T_s = total sampling time, minutes.

12.1.2 The final sample air flow rate is determined by the average pre-and post-sampling air flow rates in m^3 (see 10.1).

12.1.3 Record the final sample air volume sampled in m^3 on the sample chain of custody.

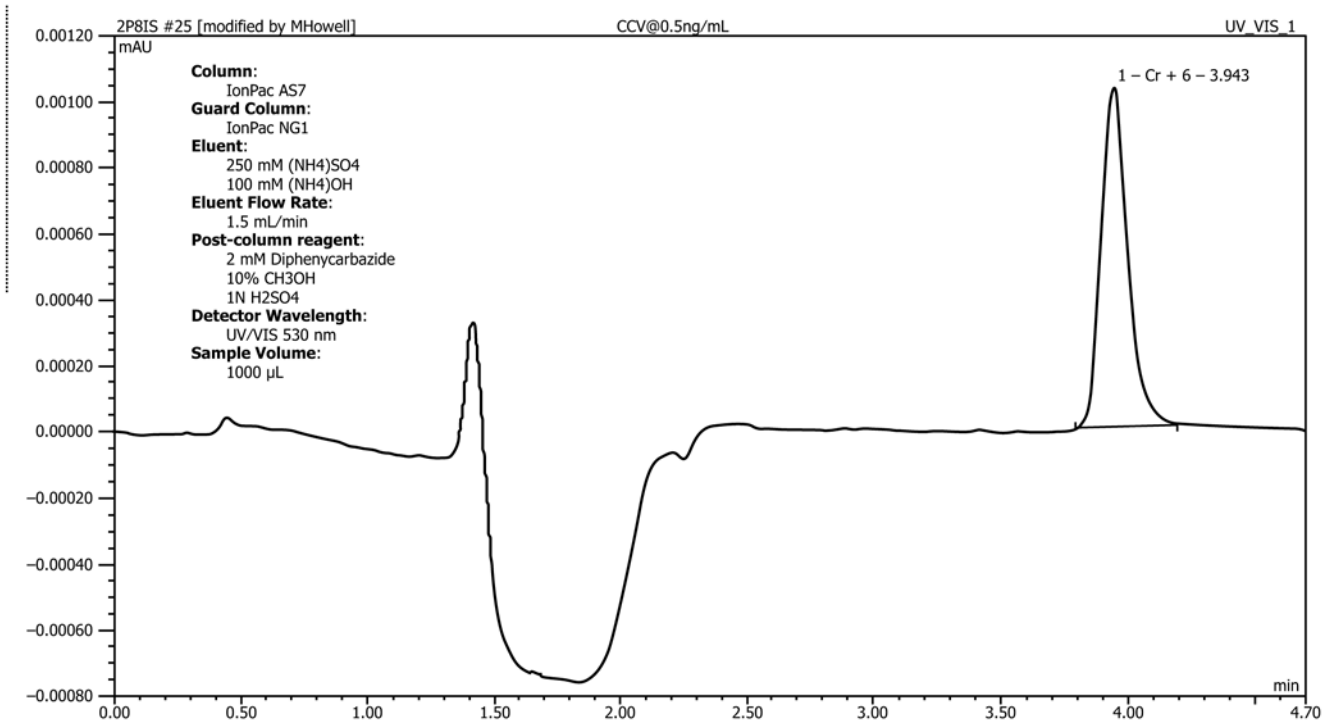

FIG. 3 Ion Chromatography Determination of Hexavalent Chromium

12.2 *Analytical:*

12.2.1 Determine the hexavalent chromium concentration in ng/mL, using the same method that was used in the calibration step (see 10.2).

NOTE 11—Analytical chromatographic software will calculate sample concentrations based on the calibration values entered into the program. These systems do not need manual calibrations.

12.2.2 For samples that have been diluted, calculate the original hexavalent chromium concentrations in ng/mL by the following:

$$Final\ Concentration(ng/mL) = \frac{(C \times F)}{V} \quad (2)$$

where:

C = hexavalent chromium in ng/mL, read from the calibration curve (see 10.2),
F = volume of diluted sample in mL, and
V = volume of undiluted sample in mL.

12.3 *Reporting Results:*

12.3.1 Determine the hexavalent chromium sample concentration in ng/m^3 by the following:

$$Final\ Concentration(ng/m^3) = \frac{(C_f \times V_f)}{V_s} \quad (3)$$

where:

C_f = final analytical concentration in ng/mL,
V_f = final preparation volume in mL, and
V_s = sample air volume in m^3.

13. Precision and Bias

13.1 Precision has been determined for this test method based on collocated sample tests (**6**).

NOTE 12—Collocated samples are two samples collected at the same point in time and space and can be considered identical. These samples are collected using two separate samplers.

13.1.1 The sampling precision of these samples are determined from analysis of collocate samples using the pooled coefficient of variation (CV). The CV ranges between 266 collocated samples from 0.5 to 18.4 %. The pooled coefficient of variation of these tests was 10.3 %.

13.1.2 The analytical precision of these samples are determined by analyzing collocated samples in replicate. From 206 replicate analyses, the CV ranges from 1.0 to 11.7 %. The pooled coefficient of variation of these tests was 4.4 %.

13.1.3 Precision concentrations ranged from <0.01 ng/m^3 to 0.02 ng/m^3.

13.2 Bias can not be determined for this method because there is not a particulate reference standard. The test method accuracy was assessed as a function of a liquid spikes on the sodium bicarbonate coated filters (see 11.1). In these tests, four sets of filters were spike at 1 ng/mL hexavalent chromium. The spike recovery ranged from 95.6 to 112 % and the mean was 104 %.

13.3 Accuracy has been determined for this method based on audit samples performed on 29 audit samples over a period of 3 years at three separate laboratories. Recoveries ranged from 79.7 % to 120 % with an 99.9 % average and a standard deviation of 9.8 %. Theoretical spiked concentrations ranged from 0.37 to 1000 ng/filter.

13.4 The analytical method detection limit (MDL) was determined every year according to the procedure in 40 CFR, Part 136, Appendix B. A standard is spiked onto at least seven prepared filters at a concentration three times the estimated

detection limit. These filters are extracted according to the method outlined (see 11.4). The method detection limit ranged from 0.0024 ng/m^3 to 0.0065 ng/m^3 (based on 21.6 m^3 sample volume) over a five year range (2007 to 2011) (**7**).

13.5 *Sample Collection and Stability:*

13.5.1 Filter contamination, cellulose, binderless quartz, PVC, and PTFE filters were tested to determine the cleanest available with the best collection efficiency (**4**). Cellulose and PTFE filters demonstrated the cleanest media, whereas the PVC and binderless quartz showed increases over the calibration range after a minimum of six days. Because the PTFE is hydrophobic, the cellulose filters were considered the best collection media however certain preservation procedures that must be followed before acceptable sample results should be reported, including,

13.5.2 The filters must be acid washed, rinsed and dried before coating them with the sodium bicarbonate to prevent hexavalent chromium background. Using this method however, does not lengthen the collection or storage hold time (**4**).

13.5.3 All samples must be retrieved from the field within one day after the sample has been collected to prevent hexavalent chromium negative bias (loss) (up to 20 % on the first day) (**8**).

13.5.4 All samples must be frozen after collection to reduce the risk of hexavalent chromium loss (**8**).

13.6 *Sample Collection Quality Control (**9**):*

13.6.1 Filters which have been dropped or become contaminated with any foreign matter (that is, dirt, finger marks, ink, liquids, etc.) are invalid.

13.6.2 Filters with tears or pinholes which occurred before or during sampling are invalid.

13.6.3 If the start and stop flow rates differ more than ±10 % the filter is invalid.

13.6.4 Filter samples collected by the samplers which operate less than 23 hours or more than 25 hours are invalid, for 24 hour samples.

13.6.5 If a power failure occurs during a sample run which causes the stop time or sample duration requirements to be violated, the sample is invalid.

13.6.6 Field Blank (FB) samples must be taken at a rate of 10 % of the sampling schedule, however more blanks should be preformed if results are detected at concentrations greater than the detection limit. The FB fails if the concentration is higher than 3 times the calculated method detection limit. If the FB fails, the site will be notified and another FB will be taken. If no reason for failure is identified the corresponding sample concentration values must be flagged in the data report. Additional FBs must be collected until the problem is corrected.

13.7 *Analytical Quality Control (**9**):*

13.7.1 *Calibration Verification Sample,* analyze an ICV immediately following the calibration and a CCV after every 10 injections and at the end of the analysis batch. The recovery criteria are 85-115 % recovery.

13.7.2 *Calibration Blank Samples,* analyze an initial calibration blank (ICB) prepared from the 20 mM sodium bicarbonate solution after the ICV. Analyze continuing calibration blanks (CCB) after every CCV and at the end of the sequence to verify that no contamination is occurring during the analysis. The acceptance criterion is less than the MDL.

13.7.3 *Method Blank Samples,* prepare and analyze a method blank (MB) sample with every 10 samples. A MB is prepared and analyzed with the samples and contains a blank filter and 20 mM sodium bicarbonate solution. The acceptance criterion is less than the MDL.

13.7.4 *Method Spike,* analyze a method spike to determine that the matrix effects from the filters after every ten samples. A method spike is prepared by spiking a liquid standard on a blank filter, allowing it to dry, and preparing and analyzing with the samples. The acceptance criterion for the method spike is 80-120 % recovery.

14. Keywords

14.1 ambient; ambient atmospheres; atmospheres; chromium; hexavalent chromium; ion chromatography; sampling

REFERENCES

(1) California Air Resources Board, Standard Operating Procedure for the Analysis of Hexavalent Chromium at Ambient Atmospheric Levels by Ion Chromatography, MLD039, Revision 3. March 2002.

(2) RTI, 1988. Research Triangle Institute The Fate of Hexavalent Chromium in the Atmosphere. Prepared for California Air Resources Board, Sacramento, CA.

(3) Dionex Technical Note, Determination of Chromium by Ion Chromatography. TN 24, July 1991.

(4) Swift, J.; Merrill, R.; Tedder, D. Hexavalent Chromium Method Development. J. Homolya, Work Assignment Manager, U.S. Environmental Protection Agency, Research Triangle Park, NC.

(5) Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC), Special Report by Eastern Research Group under EPA Contract 68-D-00-264, Research Triangle Park, NC, 2008.

(6) Molina, D., and Abell, M. T., NIOSH Manual of Analytical Methods, 3rd. ed., Method No. 7600, National Institute of Occupational Safety and Health (NIOSH), Pub. No. 84-100, Cincinnati, OH, 1984.

(7) Swift, J.; Howell, M..; Tedder, D. Collection and Analysis of Hexavalent Chromium in Ambient Air. Presented at NEMC in Washington, DC (August, 2006) and the QA EPA Region 6 Conference in Dallas, TX (October, 2006).

(8) ERG, 2006. Eastern Research Group, Inc. "2006 Urban Air Toxics Monitoring Program (UATMP) Final Report." Internet address: http://www.epa.gov/ttn/amtic/uatm.html

(9) ERG, 2008. Eastern Research Group, Inc. "Support for the EPA National Monitoring Programs (NMOC, UATMP, PAMS, HAPs and NATTS) Quality Assurance Project Plan", Special Report by Eastern Research Group under EPA Contract 68-D-03-049, Research Triangle Park, NC, 2008.