Designation: D 5281 – 98

Standard Test Method for Collection and Analysis of Hexavalent Chromium in Ambient Atmospheres[1]

This standard is issued under the fixed designation D 5281; 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 covers the collection and measurement of hexavalent chromium [Cr(VI)] in the ambient atmosphere.

1.2 This test method collects and stabilizes atmospheric hexavalent chromium using an alkaline impinger buffer solution in a wet impingement sampling technique. Lead chromate [$PbCrO_4$], generally considered poorly soluble in water, is soluble in the impinger solution up to 940 µg/L as hexavalent chromium.

1.3 This test method measures hexavalent chromium using an ion chromatographic separation combined with a post separation reaction with a colorimetric reagent and photometric detection.

1.4 This test method is applicable in the range from 0.2 to 100 ng/m^3 of hexavalent chromium in the atmosphere assuming 20 m^3 of air sample. The range can be extended upwards by appropriate dilution.

1.5 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.6 *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:*

D 1193 Specification for Reagent Water[2]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[3]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[3]

D 2914 Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)[3]

D 3195 Practice for Rotameter Calibration[3]

D 3586 Test Method for Chromium in Workplace Atmospheres (Colorimetric Method)[4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *eluent*—the ionic 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

4.1 *Sample Collection:*

4.1.1 Air is drawn at a rate of 15 L/min over a continuous 24-h period through three 500-mL glass impingers (in-line) filled with 0.02 *N* sodium bicarbonate [$NaHCO_3$] "buffer" solution. A target air volume of 20 m^3 is sampled.

4.1.2 Impinger buffer solution has a pH of 8.2 and was selected to prevent hexavalent chromium from being reduced to trivalent chromium [Cr(III)] in an acidic medium during sampling **(4)**.

4.1.3 The impinger buffer solution from each impinger is analyzed for hexavalent chromium.

4.2 *Sample Analysis* **(1, 2, 3, 4)**[5] :

4.2.1 A volume of filtered sample, typically 1 mL, is injected into the eluent flow path and separated by anion exchange using an ammonium sulfate [$(NH_4)_2SO_4$] based eluent.

4.2.2 After separation, the sample is reacted with an acidic solution of diphenylcarbohydrazide. Hexavalent chromium reacts selectively with this reagent to form the characteristic violet colored complex.

4.2.3 The eluent stream passes through a photometric detector for detection of the chromium diphenylcarbohydrazide complex by visible absorbance at 520 nm. Absorbance is proportional to the hexavalent chromium concentration.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] *Annual Book of ASTM Standards,* Vol 11.01.

[3] *Annual Book of ASTM Standards,* Vol 11.03.

[4] Discontinued; *See 1991 Annual Book of ASTM Standards,* Vol 11.03.

[5] The boldface numbers in parentheses refer to a list of references at the end of the text.

5. Significance and Use

5.1 Hexavalent chromium has been shown to be a human respiratory carcinogen in epidemiological studies when humans are exposed to relatively high airborne concentrations. Such high exposures may also induce dermal sensitization to hexavalent chromium in humans **(5)**.

5.2 Ambient atmospheric concentrations of hexavalent chromium are well below detection limits of sampling methods including Test Method D 3586 and NIOSH-7600 **(1)**.

5.3 Objective assessment of ambient atmospheric concentrations of hexavalent chromium provides a means of evaluating exposures to atmospheric hexavalent chromium in a manner that can be related to health-based risk levels. Collecting such actual monitoring data reduces or eliminates the need for theoretical resuspension modeling and provides improved basis for health assessments of potential exposures **(5)**.

5.4 The buffered impinger sampling technique provides pH control of the sampling medium, which stabilizes the oxidation state of hexavalent chromium during sampling **(6)**.

5.5 Ion chromatography provides a means of separating the hexavalent chromium from other species present in the sample, many of which interfere with other detection methods. The combination of this separation with a sensitive colorimetric detection method provides a selective and sensitive analytical method for hexavalent chromium with minimal sample preparation **(4)**.

6. Interferences

6.1 Reducing agents may reduce hexavalent chromium to trivalent chromium in acidic matrices. Preservation of a pH 7.8 or greater will minimize the effect of these species. The oxidation of trivalent chromium to hexavalent chromium during this test method is unlikely to occur **(6)**.

6.2 By virtue of the chromatographic separation, essentially all interfering species are removed from the hexavalent chromium before detection. The response of 1 mg/L of hexavalent chromium is not affected by 1000 mg/L of chromic ion.

6.3 Interferences may result from overloading of the analytical separator column capacity with high concentrations of anionic species in the sample. Concentrations of chloride ion or sulfate ion up to the equivalent of 2 % NaCl and 5 % Na_2SO_4 do not affect the separation or detection when using a 100-µL sample loop **(2)**.

6.4 Hypochlorite $[OCl^{-1}]$ (100 mg/L) in the buffer solution has been found to cause a positive interference with hexavalent chromium analyses to the extent of 0.3 to 1 µg/L. Hypochlorite (1 mg/L) has also been found, in the presence of 50 µg/L trivalent chromium, to cause a 1.2-µg/L positive interference with hexavalent chromium.

6.5 Permanganate $[MnO_4^{-1}]$ (0.5 µg/L) causes a positive 0.07-µg/L interference with hexavalent chromium.

6.6 No other interferences were observed from 10 µg/L BrO_3^-, MoO_4^{-2}, ClO_4^-, $S_2O_8^{-2}$, VO_4^{-3}, Be^+, Cu^{+2}, Ni^{+2}, Ag^+, Tl^{+3}, V^{+3}, As^{+3}, Ba^{+2}, Cd^{+2}, Co^{+2}, Cr^{+3}, Mo^{+5}, Sb^{+3}, Zn^{+2}, Pb^{+2}, F^-, Cl^-, Br^-, NO_3^-, NO_2^-, $P_2O_6^{-4}$, SO_4^{-2}, 100 mg/L Se, or 1 mg/L Hg **(6)**.

7. Apparatus

7.1 *Sampling Apparatus:*

7.1.1 *Impinger Sampling Train*—For a schematic drawing of the major sampling train components see Fig. 1. The sampling train for collecting particulate matter and hexavalent chromium consists of the following elements:

7.1.1.1 *Impingers*—Three 500-mL impingers (in-line) are used in the sampling train. The first two impingers in the series (A and B) use nozzled impinger inlets with impaction plates. These impingers impinge air at high velocity against the impaction plate creating smaller air bubbles which provide more surface area for air contact with buffer solution. The third impinger (C) has a straight inlet nozzle and no impaction plate.

7.1.1.2 *Impinger Buffer Solution*—0.02 *N* sodium bicarbonate buffer solution (see 8.3.1) is added to the impingers such that: Impinger A = 250 mL, B = 200 mL, and C = 150 mL. These particular impinger sodium bicarbonate solution volumes are recommended to minimize post sample volume disparities between impingers.

7.1.2 The sampling train apparatus is interconnected by the following elements:

7.1.2.1 *Sample Line/Probe*—Sample is drawn from ambient air through a sample line/probe that consists of a 100 to 150-mm polytetrafluoroethylene (PTFE) tube (12-mm (½-in.) outside diameter and 9-mm (⅜-in.) inside diameter). The sample line/probe is inserted into the air inlet of the first Impinger (A).

7.1.2.2 Impingers A, B, and C are interconnected using two glass impinger U-joints. The last impinger in the series (C) is connected to the sample pump by means of vinyl tubing using a glass 0.5π radian (90°) angle impinger joint that adapts the

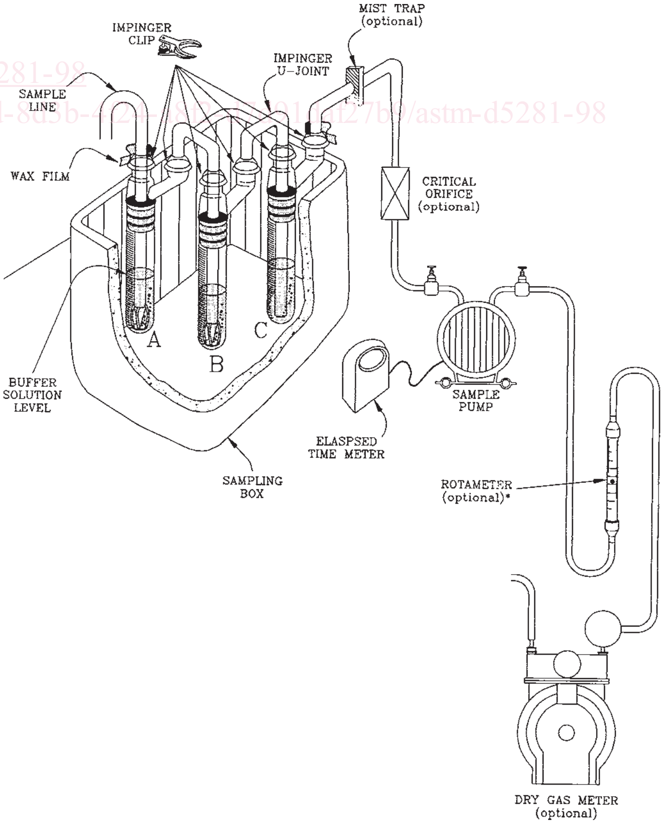

FIG. 1 Diagram of a Sampling Train and Sampling Apparatus

impinger to wax film tubing (see 7.1.3). Impinger clips, wax, and wax film wraps are used to secure all impinger connections and prevent sampling train leaks.

7.1.3 *Sampling Box*—A pre-assembled impinger sampling box holds the impinger sampling train and is designed so that the sample line/probe protrudes outside the box and bends downward. The sample box is fitted with vinyl tubing (14-mm (9⁄16-in.) outside diameter and 9-mm (3⁄8-in.) inside diameter) that connects the impinger sampling train to a sample pump (see 7.1.2.2). The vinyl tubing is fitted with an in-line rotameter to facilitate sampling train operational checks.

7.1.3.1 An in-line rotameter fitted on the sample box facilitates operational checks of the sampling system. The rotameter is a glass variable area flow meter capable of measuring flowrates between 10 and 15 L/min, calibrated in accordance with Practice D 3195.

7.1.3.2 *Leakless Sample Pump*—A vane-axial electrically operated sampling pump capable of drawing 10 to 18 L/min of air through the sampling train over 24 h is suitable.

7.1.3.3 *Flow Control Device*—Air flowrate control can be enhanced using a critical orifice or dry gas meter in accordance with Test Methods D 2914. Protect the orifice or gas meter from particulate matter (see 11.2.6).

7.1.4 *Bubble Meter*—The bubble meter is used as a primary method of sampling train air flowrate calibration (see 10.1) and shall be capable of reading sampling air flowrates of 2 to 30 L/min. Connect the bubble meter to the sample line/probe with a flexible rubber tube.

7.1.5 An elapsed time meter is placed in line with the sample pump to assist in detection of electrical interruptions that could have occurred over the 24 h interval.

7.1.6 *Stop Watch or Timer*.

7.1.7 *pH Meter,* to measure the pH of the impinger buffer solution.

7.1.8 *Refrigerator or Ice Cooler,* for storage of samples prior to shipment to the laboratory (see 11.4).

7.1.9 *Ice Cooler,* for transport of samples to the laboratory (see 11.4).

7.1.10 *Meteorological Weather Station or Weather Data Service,* to determine ambient temperature, pressure, relative humidity, wind speed and direction, and precipitation (see 11.2.7). This information may be useful to interpret data, but is not required to correct data for standard conditions.

7.2 *Analytical Apparatus* **(4)**:

7.2.1 *Ion Chromatograph*—The ion chromatograph shall have the following components as shown in Fig. 2.

7.2.1.1 *Pump,* capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 15 to 150 MPa (200 to 2000 lb/in.^{2}).

7.2.1.2 *Injection Valve*—A low dead-volume valve that will allow the loading of a sample contents into the eluent stream. Sample loops of up to 1 mL will provide enhanced detection limits. Smaller sample loops will result in proportionally higher detection limits.

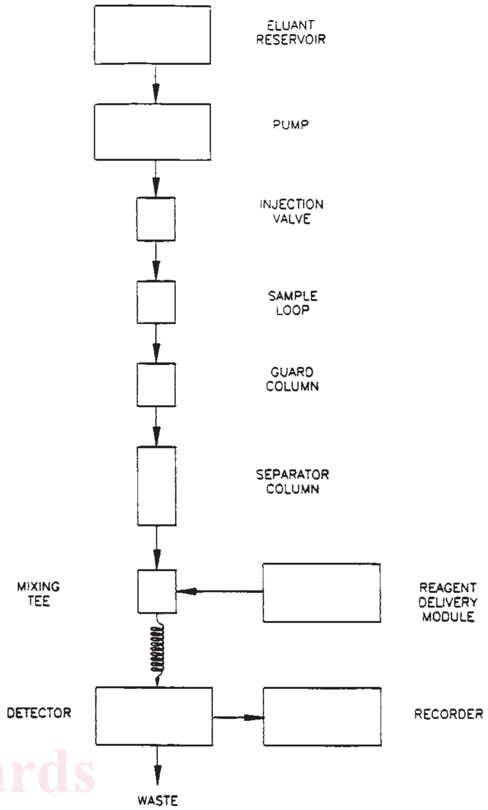

FIG. 2 Diagram of an Ion Chromatograph Using Post-Column Reagent Addition and Photometric Detection

7.2.1.3 *Guard Column*—A column placed before the separator column to protect the separator column from fouling by particles or strongly absorbed organic constituents.

7.2.1.4 *Separator Column*—A column packed with high capacity pellicular anion exchange resin that is suitable for resolving hexavalent chromium from a sample containing high total dissolved solids (for example, 3 % Na_2SO_4).

7.2.1.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 40 kPa (6.0 lb/in.^{2}).

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

7.2.1.7 *Detector*—A low-volume, flow-through visible absorbance detector with a nonmetallic 1-cm flow path. The detection wavelength for hexavalent chromium is 520 nm.

7.2.1.8 *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.

7.2.2 *Eluent Reservoir*—A container suitable for storing eluent.

7.2.3 *0.45 µm syringe filter,* for sample filtration prior to analysis (see 11.5.7).

7.2.4 *Syringe*—A syringe equipped with a male fitting and a capacity of at least 1 mL or auto sampler module (see 11.5.8).

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6]

8.2 *Purity of Water*—Water shall be Type II reagent water conforming to Specification D 1193.

8.3 *Sampling Reagents and Materials:*

8.3.1 *Impinger Buffer Solution*—0.02 N sodium bicarbonate buffer solution: dissolve 1.67 g of sodium bicarbonate ($NaHCO_3$) in 1 L of reagent water.

8.3.2 *Impinger Buffer Solution Spike*—Prepared in 0.5, 1, and 10-µg/L concentrations by diluting appropriate volumes of the 1000 µg/L hexavalent chromium standard (see 8.2.2) in the buffer solution (see 8.3.1).

8.3.3 *1 % Nitric Acid Wash Solution*—Dilute 10 mL of concentrated reagent grade nitric (HNO_3) acid, sp gr 1.42, to 1 L with water.

8.4 *Ion Chromatography Eluents:*

8.4.1 *Eluent Concentrate* (2.0 *M* $(NH_4)_2SO_4$, 1.0 *M* NH_4OH)—Dissolve 264 g of ammonium sulfate $(NH_4)_2SO_4$ in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide (NH_4OH—sp gr 0.90). Mix well and dilute to 1 L in a volumetric flask.

8.4.2 *Eluent* (0.20 M $(NH_4)_2SO_4$, 0.1 M NH_4OH)—Add 100 mL of eluent concentrate (see 8.4.1) to a 1-L flask and dilute to volume with water.

8.4.3 *Diphenylcarbohydrazide Reagent*—Dissolve 0.5 g of 1,5-diphenylcarbohydrazide in 100 mL of reagent grade methanol. Add to about 500 mL of water containing 28 mL of 96 % sulfuric acid (sp gr 1.84). Dilute with water to 1 L in a volumetric flask.

8.5 *Calibration Standards:*

8.5.1 *Hexavalent Chromium Solution, Stock* (1000 mg Cr/L)—Dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$) that has been dried at 105°C for 1 h, in water. Dilute to 100 mL in a volumetric flask.

8.5.2 *Hexavalent Chromium Solution, Standard* (1000 µg Cr/L)—Pipet 1.00 mL of the chromium stock solution (see 8.5.1) into a 1-L volumetric flask and dilute to volume with water.

8.5.3 *Hexavalent Chromium Solution, Calibration Standards*—Standards are prepared in 5, 1, 0.5, 0.05, and 0.02-µg/L concentrations by diluting appropriate volumes of the 1000-µg/L standard in the impinger buffer solution (see 8.3.1).

9. Sampling

9.1 Select a sampling location to provide information on the possible impact of site activities, conditions, and possible human exposures. Collect both upwind and downwind ambient air samples.

9.2 To assess ambient environmental concentrations of hexavalent chromium, collect samples with a target air volume of 20 m^3 over a continuous 24-h sampling interval.

9.3 *Field Quality Assurance and Control Samples (QA/QC):*

9.3.1 Field QA/QC samples collected include: one impinger field blank for every sampling period (see 11.1.2.4 and 12.3.2).

9.4 Sampling collection and analytical procedures are described in Section 11.

9.5 For general information on sampling refer to Practice D 1357.

10. Calibration and Standardization

10.1 *Sampling Calibration:*

10.1.1 Calibrate sample air flowrate using a primary method of calibration at the beginning (pre-calibration) and end (post-calibration) of each sampling session as follows. The beginning and end air flowrates shall not vary by more than ±30 % (see 11.2.6). The final sample flowrate is an average of the pre- and post-sample calibrations **(7)**. Perform maintenance and repairs to calibration equipment in accordance with the manufacturer's instructions, and keep records for documentation.

10.1.2 Use a soap bubble meter (see 7.1.4), rotameter (see 7.1.3.1), or both, for sample calibration. Procedures for sample calibration using a soap bubble meter are provided in 10.1.3 to 10.1.8.

10.1.3 Wear latex gloves during sample calibration procedures to prevent sample contamination.

10.1.4 Activate the sample pump (see 7.1.3.2) and allow it to stabilize. After the pump flowrate stabilizes, attach the sampling train to the pump by means of the vinyl tubing (see 7.1.3).

10.1.5 Check the sample train for leaks by pressurizing the sample impinger train. This can be accomplished by restricting flow through the train at the air inlet, while being careful not to draw buffer solution into the sample pump or from Impinger A to B, or B to C. When the impinger train is pressurized, inspect each impinger for signs of bubbling. If bubbling is observed, inspect the connections (see 7.1.2.1 and 7.1.2.1) for leaks. These connecting joints may require additional wax or wax film wrapping, or both, (see 7.1.2.2). If bubbling does not cease, replace the sampling train with clean decontaminated apparatus.

10.1.6 Attach the bubble meter to the air line/probe of the sampling train, and prime the bubble meter flow cell with bubble solution by drawing repeated films through the cell until a single film travels the distance.

10.1.7 Adjust the sample pump so that the sample flowrate is 15 L/min (±30 %). Record the average of at least three calibration runs in a sample log book. Note the time and date, and set the elapsed timer to zero.

10.2 *Analytical Calibration:*

10.2.1 Prepare hexavalent chromium solution standards as described in 8.5.3.

10.2.2 Determine the analytical instrument chromium response for each of the standards using the procedure defined in 11.5.

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[6] *Reagent Chemicals, American Chemical Society Specifications,* 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.