



Designation: D3718 – 85a (Reapproved 2022)<sup>e1</sup>

# Standard Test Method for Low Concentrations of Chromium in Paint by Atomic Absorption Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation D3718; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

<sup>e1</sup> NOTE—Footnote 4 was updated editorially in June 2022.

## 1. Scope

1.1 This test method covers the determination of the content of chromium (including chromium oxide) in the range between 0.005 and 1.0 % present in the solids of liquid coatings or in dried films obtained from previously coated substrates. There is no reason to believe that higher levels could not be determined by this test method, provided that appropriate dilutions and adjustments in specimen size and reagent quantities are made.

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

1.3 *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. Specific hazard statements are given in Section 7.*

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

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D1193 Specification for Reagent Water

D2832 Guide for Determining Volatile and Nonvolatile Con-

tent of Paint and Related Coatings

## 3. Summary of Test Method

3.1 The sample of liquid coating or dried film is prepared for analysis by dry ashing at 500 °C followed by digestion with potassium permanganate and sulfuric acid in a polytetrafluoroethylene (PTFE)-lined acid decomposition vessel at an elevated temperature. The chromium in the filtered digestion mixture is determined by atomic absorption spectroscopy.

## 4. Significance and Use

4.1 The permissible level of heavy metals in certain coatings is specified by governmental regulatory agencies. This test method provides a fully documented procedure for determining low concentrations of chromium present in both water- and solvent-reducible coatings to determine compliance.

## 5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, consisting of an atomizer and either a single- or three-slot burner; gas pressure-regulating and metering devices for nitrous oxide (N<sub>2</sub>O) and acetylene; a chromium hollow cathode lamp with a regulated constant current supply; a monochromator and associated optics; a photosensitive detector connected to an electronic amplifier; and a readout device.

5.2 *Muffle Furnace*, maintained at 500 ± 10 °C.

5.3 *Force-Draft Oven*, maintained at 105 ± 2 °C.

5.4 *Acid Decomposition Vessel*, with PTFE digestion cup.<sup>3</sup>

5.5 *Hot Plate*, with variable surface temperature control over the range from 70 to 200 °C.

5.6 *Volumetric Flasks*, 50, 100, and 1000-mL.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The sole source of supply of an acid decomposition cup, (Catalog Number 4745), known to the committee at this time is the Parr Instrument Co., 211 Fifty-third St., Moline, IL 61265. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

5.7 *Pipets*, 5, 10, 15, and 20-mL capacity.

5.8 *Filter Paper*, ashless, medium filtering 15-cm.

5.9 *Paint Shaker*.

5.10 *Crucibles*, wide form, porcelain, approximately 30-mL capacity.<sup>4</sup>

5.11 *Mortar and Pestle*.

5.12 *Paint Draw-Down Bar*.

## 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification **D1193**.

6.3 *Chromium Standard Stock Solution* (1 mg/mL)—Dissolve 3.735 g of potassium chromate ( $K_2CrO_4$ ) in 100 mL of water and dilute to 1 L.

6.4 *Chromium Standard Working Solution* (0.1 mg/mL)—Pipet 10 mL of the chromium standard stock solution into a 100-mL volumetric flask and dilute to volume with water.

6.5 *Oxidizing Solution*—Dissolve 0.2 g of potassium permanganate ( $KMnO_4$ ) in 100 mL of  $H_2SO_4$  (1 + 1). Stir until completely dissolved. The color of this solution is dark brown.

6.6 *Reducing Solution*—Dissolve 1 g of hydroxylamine hydrochloride ( $NH_2OH \cdot HCl$ ) in 100 mL of water.

6.7 *Reagent Blank*—Pipet 5 mL of oxidizing solution into 25 mL of water contained in a 50-mL volumetric flask. Add reducing solution dropwise until the permanganate color has been discharged; then dilute to 50 mL with water.

6.8 *Sulfuric Acid* (1 + 1)—Carefully add 1 volume of concentrated  $H_2SO_4$  (sp gr 1.84) to 1 volume of water.

6.9 *Sulfuric Acid* (5 % volume per volume)—Carefully add 50 mL of concentrated  $H_2SO_4$  (sp gr 1.84) to 500 mL of water and dilute to 1 L.

## 7. Hazards

7.1 Use care in handling concentrated  $H_2SO_4$  because it is corrosive and may cause severe burns of the skin or eyes. Refer to suppliers' Material Safety Data Sheet.

<sup>4</sup> Wide form 30-mL porcelain crucibles are available from multiple suppliers, such as #66136 from CoorsTek.

<sup>5</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2 The National Institute for Occupational Safety and Health has stated that hexavalent chromium compounds are hazardous to health. Care should be exercised in preparation of a sample for test. The wearing of a respirator and rubber or synthetic gloves is recommended. In case of contact, wash thoroughly with soap and water. Mixtures containing hexavalent chromium compounds should not be flushed down a drain but disposed of as hazardous waste.

7.3 Use only a rubber bulb aspirator for pipetting liquids.

## 8. Calibration and Standardization

8.1 Prepare 50-mL quantities of at least four standard solutions bracketing the expected chromium concentration in the sample to be tested. To suitable aliquots of the 100-ppm chromium standard working solution, add 10 mL of the oxidizing solution with a pipet, followed by the dropwise addition of reducing solution until the permanganate color has been discharged, then dilute to 50 mL with water.

8.2 Operational instructions for atomic absorption spectrophotometers vary with different models. Consult the manufacturer's literature for establishing optimum conditions for the specific instrument used.

8.3 Turn the instrument on and set the wavelength to the 357.9-nm chromium line. Apply the recommended current to the chromium hollow-cathode lamp. Allow the instrument to warm up for about 15 min and set the slit width. Adjust the nitrous oxide and acetylene pressures and ignite the burner according to instructions.

8.4 Aspirate water to rinse the atomizer chamber. Aspirate a standard solution and make any necessary readjustment in instrument parameters to obtain maximum absorption. Zero the instrument while aspirating reagent blank solution (6.7). Aspirate each of the appropriate standard solutions and record the corresponding instrument readings. Aspirate water between each standard.

8.5 Transfer a 25-mL aliquot from each of the standard solutions prepared in 8.1 to 50-mL volumetric flasks and dilute to volume with water. Repeat the steps outlined in 8.4 for the diluted aliquot solutions.

8.6 Construct a calibration curve on linear graph paper by plotting the absorbance versus concentration (micrograms per millilitre) for each set of standard solutions.

NOTE 1—To obtain maximum accuracy one should complete calibration and standardization just prior to sample analysis.

## 9. Procedure

9.1 If the sample is a liquid coating, mix it until homogeneous, preferably on a mechanical paint shaker. Determine the nonvolatile content in accordance with Guide **D2832**.

9.2 Determine the ash content of the material under test in duplicate.

9.2.1 Weigh to the nearest 0.1 mg approximately 5 g of liquid coating or 3 g of dried film into each of two tared porcelain crucibles.

NOTE 2—Recover dried paint films from previously coated substrates (being careful not to remove any underlying material from the substrate)

or prepare in the laboratory from liquid samples. For the laboratory preparation, flow some of the well-mixed sample onto a clean glass plate. The use of a paint draw-down bar is recommended to obtain a uniform film thickness not exceeding 2 mils (50  $\mu\text{m}$ ). Allow the film to dry in an oven at 105 °C for a minimum of 1 h. Scrape the dried film off the glass plate, preferably with a single-edge razor blade.

9.2.2 Place the crucibles containing the liquid coating on the hot plate and slowly increase the temperature until the material is dried. With some types of coatings, an initial oven-drying at 105 °C may be necessary to remove solvents without incurring losses due to spattering.

9.2.3 When the specimen appears to be dry, or when starting with a dried film, gradually increase the temperature of the hot plate until the material chars.

9.2.4 After charring is complete, place the crucibles in the muffle furnace and ash at 500 °C.

9.2.5 When the ashing appears to be complete (approximately 1 to 2 h), remove the crucibles from the muffle furnace and allow to cool to room temperature in a desiccator. Weigh and calculate the mean value for the percent ash.

9.3 Transfer each ash to a clean, dry mortar and grind to a fine, uniform powder. Weigh to the nearest 0.1 mg, 0.02 to 0.2 g of each ash directly into separate decomposition vessel inserts.

NOTE 3—For a material containing 50 ppm (mg/kg) of chromium based on the solids and having 50 % ash and 70 % nonvolatile material, 0.2 g of ash extracted and diluted to 50 mL will contain 0.28  $\mu\text{g}$  of chromium per millilitre, and for one containing 10 000 ppm, 0.02 g of ash extracted and diluted to 100 mL will contain 2.8  $\mu\text{g}$  of chromium per millilitre. To ensure complete recovery of chromium, do not use more than 0.05 g of ash for materials that are known or suspected to contain over 1000 ppm of chromium based on the solids.

9.4 Pipet exactly 10 mL of oxidizing solution into the cup. Swirl gently to facilitate mixing. Place the vessel in a circulating oven at 105 °C for 1½ h.

9.5 Remove the vessel from the oven and allow to cool slowly to ambient temperature. Do *not* cool by placing the vessel in a refrigerator or freezer, or by submerging it in a cooling liquid. When cooled, carefully unseal the vessel in a fume hood.

NOTE 4—When the vessel is disassembled, if the solution does not show the presence of excess permanganate, repeat the digestion using a smaller weight of ash.

9.6 Quantitatively filter the contents through filter paper directly into a 50 or 100-mL volumetric flask. Rinse the digestion cup several times with water, transferring any insoluble material to the filter paper. Wash the filter paper several times with small volumes of water. Add hydroxylamine hydrochloride solution dropwise to the filtrate until the permanganate color has been discharged, then dilute to volume with water.

9.7 Aspirate each test solution and determine the absorbance in the same manner in which the instrument was calibrated. Determine the concentration of chromium in micrograms per millilitre from the appropriate calibration curve. If the absorbance is above the range covered by the calibration curve, dilute an aliquot of the test solutions to a suitable volume with H<sub>2</sub>SO<sub>4</sub> (5 % volume per volume) and repeat the determinations.

NOTE 5—The method of standard additions may be used to improve the accuracy of the analysis. This test method is particularly recommended for use with unknown samples where matrix effects may be potentially significant. For a detailed description of the procedure and calculations used in the method of standard additions, consult a standard text on atomic absorption spectroscopy or the instruction manual provided by the instrument manufacturer.

## 10. Calculation

10.1 Calculate the mean concentration of chromium in the nonvolatile portion of the sample as follows:

$$\text{Chromium, ppm (mg/kg) in nonvolatile} = (C \times F \times A \times V) / (S \times NV) \quad (1)$$

where:

- C* = concentration of chromium in the aspirated test solution,  $\mu\text{g/mL}$ ,
- F* = dilution factor from 9.7 (volume diluted to volume of aliquot),
- A* = mean percent ash as determined in 9.2.5,
- V* = volume diluted to in 9.6 (50 or 100 mL),
- S* = weight of ash, and
- NV* = percent nonvolatile of paint sample (use 100 if sample was a dried film).

## 11. Report

11.1 Report the chromium content of the nonvolatile portion of the sample tested and whether the analysis was conducted on a liquid coating or a dried film.

## 12. Precision and Bias<sup>6</sup>

12.1 The precision estimates are based on an interlaboratory study in which six different laboratories analyzed in duplicate, on two different days, four samples of water-reducible paints and four samples of solvent-reducible paints containing from 50 to 10 000 ppm (mg/kg) chromium. The within-laboratory coefficient of variation was found to be 4.9 % relative at 39 degrees of freedom and the between-laboratory coefficient of variation was 8.5 % relative at 31 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

12.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 14 % relative.

12.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 24 % relative.

12.2 *Bias*—The mean of duplicate determinations within any laboratory should be within 17 % relative of true value.

## 13. Keywords

13.1 AAS; chromium; low concentration of antimony in paints

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1012. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).