



Standard Test Method for Lead and Chromium in Air Particulate Filter Samples of Lead Chromate Type Pigment Dusts by Atomic Absorption Spectroscopy¹

This standard is issued under the fixed designation D 4358; 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 determines amounts of lead and chromium in residues obtained from air sampling of lead chromate and lead silico-chromate type pigment dusts. It is not applicable to all pigment dusts or to paint overspray samples of any kind.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

3. Summary of Test Method

3.1 The filter containing the air particulate sample is dissolved with nitric acid followed by treatment with 50 % aqueous ammonium acetate solution. The solution is transferred to a volumetric flask and lead and chromium determined by atomic absorption.

4. Significance and Use

4.1 This test method covers only the analysis of the pigment dusts on filters, the results being expressed as micrograms of lead and of chromium. Sampling procedures are not a part of this test method, nor are those calculations that are required to convert the results to concentration of lead and chromium in

the sampled air, as required by the U.S. Occupational Safety and Health Act (OSHA).

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, consisting of an atomizer and burner; gas pressure regulating and metering devices for air, acetylene, and nitrous oxide; provision for hollow cathode source lamps with regulated constant current supply; a monochromator with associated optics; a photodetector; an amplifier; and digital or analog readout system.

5.2 *Lead Hollow Cathode Lamp* or electrodeless discharge source lamp.

5.3 *Chromium Hollow Cathode Source Lamp*.

5.4 *Volumetric Flasks*, 10-mL.

6. Reagents and Materials

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 Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ 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 **D 1193**.

6.3 *Ammonium Acetate Solution (50 % W/V aqueous)*—Dissolve 250 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) in water and dilute to 500 mL.

6.4 *Nitric Acid (sp gr 1.50)*—Concentrated nitric acid (HNO_3).

6.5 *Nitric Acid, (1 + 3)*—Dilute 1 part concentrated nitric acid with 3 parts water.

¹ 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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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 *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.

6.6 *Lead, Standard Stock Solution (1000 µg/mL)*—Dissolve 0.1599 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in 50 mL of water containing 20 mL of concentrated HNO_3 and 10 mL of 50 % ammonium acetate solution, and dilute to 100 mL with water.

6.7 *Chromium, Standard Stock Solution (1000 µg/mL)*—Dissolve 0.3734 g of potassium chromate (K_2CrO_4) in 50 mL water containing 5 mL of concentrated HNO_3 and dilute to 100 mL with water.

6.8 *Filter Blank*—Millipore 0.8-µm pore size, 37-mm diameter, mixed esters of cellulose, Type AA white, plain, or equivalent.

6.9 *Hydrogen Peroxide*—30 % (H_2O_2).

7. Calibration and Standardization

7.1 Good atomic absorption practice requires that the test solutions being analyzed be aspirated into the flame interspersed between or at least contiguous to aspiration of the calibration standards. The formal separation of calibration and analysis is for clarity of the methodology only and such separation should not be made in practice.

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

7.3 Insert the lead source lamp into the appropriate holder. Turn on the instrument and apply the current recommended by the manufacturer to the source lamp. Allow the lead source lamp a 10-min warmup. Adjust the wavelength to 283.3 nm, set the slit to 0.7-nm bandpass, and maximize the transmitted energy by fine adjustment of the wavelength.

7.4 Prepare fresh standard solutions each day containing 0.5, 1.0, 2.0, 5.0, and 10.0 ppm lead by appropriate dilutions of the 1000 µg/mL stock standard. 20 mL of concentrated HNO_3 and 2 mL of 50 % ammonium acetate should be added in each case per 100 mL of final dilution.

7.5 Adjust the air and acetylene pressure or flow rates and ignite the burner according to the instruction manual. Adjust the acetylene to give a rich flame. Allow a few minutes to equilibrate.

7.6 Aspirate water to rinse the atomizer chamber. Aspirate the 10 ppm standard and make any necessary readjustment in instrument parameters to obtain maximum absorption.

7.7 Aspirate each standard solution and record the corresponding instrument readings. Aspirate 1 + 3 HNO_3 , then water between each standard.

7.8 Construct a calibration curve for lead on linear graph paper by plotting the absorbance versus concentration (micrograms per millilitre) for each standard solution.

7.9 Replace the lead source lamp with the chromium source lamp, adjust the applied current to that recommended and allow to warm up for 10 min. Adjust the wavelength to 357.9 nm, set the slit to 0.7-nm bandpass, and maximize transmitted energy by fine wavelength adjustment.

7.10 Prepare fresh standard solutions each day containing 0.1, 0.2, 0.5, 1.0 and 2.0 ppm chromium by appropriate dilutions of the 1000 µg/mL stock standard. Add 20 mL of concentrated HNO_3 and 2 mL of 50 % ammonium acetate in each case per 100 mL of final dilution.

7.11 Turn on air and acetylene, adjust the flow rates and ignite according to the instruction manual. Adjust the acetylene to give a rich flame. Allow a few minutes to equilibrate. (**Note 1**).

NOTE 1—The National Institute for Occupational Safety and Health (NIOSH) recommends the use of a nitrous oxide-acetylene flame, which reduces iron and nickel interference in the chromium determination. However, chromium sensitivity in the nitrous oxide flame is also much lower, so that air/acetylene is specified here. Iron, aluminum, titanium as well as SO_4 = interference may be reduced by adding 10 % of W/V KHSO_4 to both standard and sample solution, employing an air/acetylene flame. The comparison of the experimental lead to chromium ratio noted can be of some use here. (See Section 11.)

7.12 Aspirate water into the flame. Then aspirate the 2.0 ppm standard and adjust burner position and flame composition to give maximum absorption.

7.13 Aspirate all standards into the flame, aspirating water between each standard and the next. Construct a calibration curve for chromium on linear graph paper by plotting the absorbance versus concentration (micrograms per millilitre) for each standard solution.

8. Procedure

8.1 With each batch of samples a filter blank (minimum of 1 filter blank for every 10 filter samples) from the same membrane lot must be analyzed. The filter blank is carried through all steps of the analysis along with the sample(s).

8.2 Carefully open the filter cassette containing the air particulate sample. Remove the filter using forceps and deposit it in a 50-mL beaker.

8.3 Add 6 mL of 1 + 3 HNO_3 , cover the beaker with a watch glass, and keep just under boiling by placing on a hot water bath. Heat for 10 min. Add 2 mL of 50 % ammonium acetate solution and continue to heat, adding water as needed to keep the volume at about 5 to 6 mL. The solution *must not* be allowed to go to dryness. When analyzing lead silicochromate-type pigment dusts, add 0.5 mL of 30 % hydrogen peroxide (H_2O_2) after the 2 mL of 50 % ammonium acetate solution and continue heating until cellulose filter completely dissolves.

8.4 Continue heating for 1 h. If the cellulose filter is not dissolved, continue the digestion until the solution is clear. Cool and transfer to a 10.0-mL volumetric flask. Dilute to volume with water and determine lead and chromium.

8.5 Prepare the atomic absorption instrument for lead as noted in 7.3, 7.5, and 7.6.

8.6 Aspirate the test solution into the flame. Record the reading. Aspirate 1 + 3 HNO_3 , then water between test solutions.

8.7 Aspirate the appropriate standards, usually one above and below the test solution concentration. Aspirate 1 + 3 HNO_3 , then water between each standard and the next. Record readings.

8.8 If the absorption of any test solution is greater than that of the 10 ppm lead standard, make an appropriate dilution (matching the standard matrix), aspirate and measure the absorbance of the diluted solution. It is important that the diluted test solution be aspirated with the flame not being shut off or altered following aspiration of the standards.

8.9 Prepare the atomic absorption instrument for chromium as noted in 7.9, 7.11, and 7.12.

8.10 Repeat steps 8.6-8.8, in this case for chromium except that, between each standard or sample and the next, aspirate only water.

8.11 From the calibration curves determine the lead and chromium concentrations in the aspirated solutions.

9. Calculation

9.1 Calculate the micrograms of lead, *A*, on the filter as follows:

$$A = (L)(V_1)(F) \quad (1)$$

where:

L = lead read from calibration curve (8.11), µg/mL,

*V*₁ = final volume of lead solution which is measured (8.8 or if no dilution is necessary, 8.4), and

F = [volume to which originally diluted (8.4) divided by millilitres of aliquot of original dilution taken for final dilution].

9.2 Calculate the micrograms of chromium, *B*, on the filter as follows:

$$B = (C)(V_2)(F) \quad (2)$$

where:

C = chromium read from calibration curve (8.11), µg/mL,

*V*₂ = final volume of chromium solution which is measured (8.10 or if no dilution is necessary, 8.4), and

F = [volume to which originally diluted (8.4) divided by millilitres of aliquot of original dilution taken for final dilution].

10. Lead to Chromium Ratio

10.1 If the workplace dust involves a single, known lead chromate or lead silicochromate type pigment, the determined lead to chromium ratio found (9.1 and 9.2) may be compared with the theoretical ratio (or actual ratio) of the bulk pigment as an internal check.

11. Report

11.1 Report the micrograms of lead and the micrograms of chromium present on the filter.

12. Precision for Lead Chromate Type Pigment Dust

12.1 *Lead Determination*—On the basis of an interlaboratory study of the test method in which operators in eight laboratories analyzed sixteen air particulate samples containing from 16 to 80 µg of lead and from 3 to 15 µg of chromium, the within-laboratory coefficient of variation of the lead determination was found to be 9 % relative at 21 df and the between-laboratory coefficient of variation was 15 % relative at 18 df. 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 26 % relative for lead.

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 40.4 % relative for lead.

12.2 *Chromium Determination*—In the same interlaboratory study of the test method, the within-laboratory coefficient of variation of the chromium determination was found to be 11 % relative at 20 df and the between-laboratory coefficient of variation was 19 % relative at 18 df. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

12.2.1 *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 33 % relative for chromium.

12.2.2 *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 54 % relative for chromium.

13. Bias

13.1 Bias cannot be determined because there are no accepted standards for lead and chromium content of lead chromate type pigment dust.

14. Precision for Lead Silicochromate Type Pigment Dust

14.1 *Lead Determination*—On the basis of an interlaboratory study of the test method in which operators in five laboratories analyzed sixteen air particulate samples containing from 37 to 116 µg of lead and 2 to 8 µg of chromium, the within-laboratory coefficient of variation of the lead determination was found to be 2.7 % relative at 15 df and the between-laboratory coefficient of variation was 9.4 % relative at 12 df. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

14.1.1 *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 8.2 % relative for lead.

14.1.2 *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 28.4 % relative for lead.

14.2 *Chromium Determination*—In the same interlaboratory study of the test method, the within-laboratory coefficient of variation of the chromium determination was found to be 2.3 % relative at 12 df and the between-laboratory coefficient of variation was 23.6 % relative at 9 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

14.2.1 *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 6.8 % relative for chromium.

14.2.2 *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 68.8 % relative (Note 2) for chromium.

NOTE 2—Error appears large due to the low range of chromium studied (2 to 8 μm per filter) leading to poor reproducibility.

15. Bias

15.1 Bias cannot be determined because there are no accepted standards for lead and chromium content in lead silicochromate type pigment dust.

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16. Keywords

16.1 air particulates; air sampling; atomic absorption spectroscopy; chromium; lead; pigment dust