

Standard Method of Test for
LOW CONCENTRATIONS OF LEAD IN PAINT BY ATOMIC ABSORPTION SPECTROSCOPY
ASTM D3335 - 74

1. Scope

1.1 This method covers the determination of lead contents between 0.01 and 5% present in the solids of liquid coatings or contained in dry films.

1.2 Only pigmented coatings were used for evaluating this method, but there is no reason to believe that varnishes and lacquers could not be analyzed successfully, provided that appropriate precautions are taken.

2. Applicable Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water

D 2832 Recommended Practices for Determining Nonvolatile Content of Paint and Paint Materials

3. Summary of Method

3.1 The sample of liquid paint or dried film is prepared for analysis by dry ashing. The lead content of an acid extract of the ash is determined by atomic absorption spectroscopy.

4. Apparatus

4.1 Atomic Absorption Spectrophotometer, consisting of an atomizer and either a single or three-slot burner; gas pressure regulating and metering devices for air and acetylene; a lead hollow cathode tube with a regulated constant current supply; a monochromator and associated optics; a photosensitive detector connected to an electronic amplifier; and a red-out device.

4.2 Muffle Furnace, capable of maintaining $500 \pm 5^\circ \text{C}$.

4.3 Crucibles, wide form, porcelain, glazed inside and out except for the outside bottom surface, approximately 30-ml capacity, 50-mm rim diameter, and a 31-mm height.

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

4.5 High-Silica Glass Beakers, 100 and 250-ml

4.6 Volumetric Flasks, 50, 100, and 1000 ml.

4.7 Dropping Bottles, $\frac{1}{2}$ or $\frac{1}{4}$ oz. capacity

4.8 Glass or Disposable Syringes, 5 or 10-ml capacity

4.9 Pipets, 1, 2, 5, and 10-ml capacity

5. Reagents

5.1 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. 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.

5.2 Purity of Water - Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specifications D1193.

5.3 Ammonium Acetate Diluting Solution - Add 50 ml of HNO_3 (sp. gr. 1.42) to 150 ml of 50% weight by volume ammonium acetate solution and dilute to 1 litre.

5.4 Ammonium Acetate Solution (50% weight by volume) - Dissolve 500 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) in water and dilute to 1 litre.

5.5 Lead Standard Solution (1000 ppm.) - Dissolve 1.5980 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in 10 ml of water, add 10 ml of HNO_3 (sp. gr. 1.42) and dilute to 1 litre.

5.6 Nitric Acid (sp. gr. 1.42) Concentrated Nitric Acid (HNO_3)

5.7 Nitric Acid (1+1) - Add 1 volume of HNO_3 to 1 volume water.

6. Calibration and Standardization

6.1 Prepare 100ml quantities of at least four standard solutions bracketing the expected lead concentration in the sample to be tested. To suitable aliquots of the 1000-ppm standard lead solution, add 5ml of the HNO_3 and 15 ml of the 50% ammonium acetate solution. Dilute to 100 ml with water.

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

6.3 Turn the instrument on and set the wavelength to the 2833A line for lead. Apply the current recommended by the manufacturer to the hollow cathode lamp. Allow the instrument to warm-up at least 15 minutes and set the slit width. Adjust the air pressures and ignite the burner according to the manufacturer's instructions.

6.4 Aspirate water to rinse the atomizer chamber. Aspirate a standard solution and make any necessary readjustment in instrument parameters to obtain maximum absorption.

6.5 Atomize each of the appropriate standard solutions and record the corresponding instrument readings. Atomize water between each standard.

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

7. Procedure

7.1 If the sample is a liquid coating, mix it until homogeneous, preferably on a mechanical shaker. Determine the nonvolatile content in accordance with Method D 2832.

7.2 Prepare at least two replicate samples by weighing by difference from a dropping bottle or syringe approximately 2 to 3 g of the mixed paint, or by directly weighing approximately 1 to 2 g of dried paint film, into a 30 ml porcelain crucible. Weigh to the nearest 0.1 mg. See Note 1, and 2.

7.3 Place the crucible (or beaker) containing the liquid coating on a 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.

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

7.5 After charring is complete, place the material in a preheated muffle furnace and ash at 475 to 500° C. See Note 3.

7.6 When the ashing appears to be complete (approximately 1 to 2 h), remove the crucible or beaker from the muffle furnace and allow it to cool to room temperature. Break up the ash into fine particles with a glass stirring rod, leaving the rod with the container through the filtering step.

7.7 Add 10 ml of HNO_3 (1+1) acid, taking care to avoid losses due to spattering in case the ash reacts violently with the acid. Heat carefully on hot plate until 2 to 3 ml of the solution remain. Add an additional 10 ml of HNO_3 (1+1) acid and continue heating on the hot plate until less than 5 ml of the solution remains.

7.8 Filter the solution through medium porosity filter paper into a 50-ml volumetric flask. If the filtrate is not clear, refilter through fine porosity filter paper. Wash the container 3 times with 2.5 ml hot ammonium acetate solution (5.4), each time transferring the washings to the filter paper. Wash the filter paper several times with water. Adjust the volume to 50-ml with water.

7.9 Aspirate the specimen solution and determine the absorbance in the same manner in which the instrument was calibrated. Determine the concentration of lead in micrograms/ millilitre from the calibration curve. If the absorbance is above the range covered by the calibration curve, dilute an aliquot of the sample solution to a suitable volume with ammonium acetate diluting solution. See Note 4.

8. Calculation

8.1 Calculate lead in the nonvolatile portion of the sample as follows:

$$\text{Lead, \% of nonvolatile} = (C \times F \times 0.5) / (NV \times S)$$

where:

C = micrograms per millilitre concentration of lead in the aspirated sample solution.

F = dilution factor from 7.9 (Volume diluted to/volume of aliquot)

NV = percent nonvolatile of paint sample (use 100 if sample was a dried film), and

S = grams of specimen

9. Report

9.1 Report the percent lead of the nonvolatile content of the paint and whether the analysis was done on a liquid sample or dried film.

10. Precision

10.1 The following criteria should be used for accepting the results.

10.1.1 Repeatability (Single Analyst) - The coefficient of variation of results (each the average of duplicate determinations) obtained by the same analyst on different days was estimated to be 3.4% relative at 24 degrees freedom. Two such values should be considered suspect (95% confidence level) if they differ by more than 10% relative.

10.1.2 Reproducibility

(Multilaboratory) - The coefficient of variation of results (each the average of duplicate determinations) obtained by analysts in different laboratories, has been estimated to be 9.3% relative at 20 degrees of freedom. To such values should be considered suspect (95% confidence level) if they differ by more than 27% relative.

NOTES

1. The specimen size specified will give a concentration of approximately 10 to 20 ppm lead in the final diluted solutions for materials containing approximately 500 ppm lead based on the solids. If the sample is estimated to contain more or less than 500 ppm lead, the specimen size should be adjusted accordingly. In the event that significantly less than 500 ppm lead is expected, a 250-ml high-silica glass beaker may be used instead of the crucible accomadating sample weights up to 10 g.
2. Recover dried paint films from previously coated substrates or prepare in the laboratory from liquid samples. For the laboratory preparation, flow the well-mixed sample onto a clean glass plate and allow to dry in an oven at 105° C. Scrape the dried film off the glass plate with a single-edge razor blade.
3. Ashing at temperatures in excess of 500° C. may result in the loss of some of the lead by volitization.
4. The method of standard additions may be used to improve the accuracy of the analysis. This 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 instrument manual provided by the instruemnt manufacturer.



Designation: D 3335 - 78²

An American National Standard

Standard Test Method for LOW CONCENTRATIONS OF LEAD, CADMIUM, AND COBALT IN PAINT BY ATOMIC ABSORPTION SPECTROSCOPY¹

This standard is issued under the fixed designation D 3335; 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.

¹NOTE 1—An editorial change was made by adding Section 1.4 in December 1978.

²NOTE 2—An editorial change was made in Section 9.1 in June 1980.

1. Scope

1.1 This method covers the determination of lead² contents between 0.01 and 5 %, cadmium contents between 50 and 150 ppm (mg/kg), and cobalt contents between 50 and 2000 ppm (mg/kg) present in the nonvolatile portion of liquid coatings or contained in dried films. There is no reason to believe that higher levels of all three elements could not be determined by this method, provided that appropriate dilutions and adjustments in specimen size and reagent quantities are made.

NOTE 1—ASTM Method D 2088, Determination of Low Concentrations of Lead in Paint,³ describes an alternative method of analysis for lead, using an electrolytic analyzer.

1.2 Only pigmented coatings were used for evaluating this method, but there is no reason to believe that varnishes and lacquers could not be analyzed successfully, provided that appropriate precautions are taken.

1.3 This method is not applicable to the determination of lead in samples containing antimony pigments (low recoveries are obtained).

1.4 If lead is present in the sample to be analyzed in the form of an organic lead compound at a concentration greater than 0.1 %, small losses of lead may occur, resulting in slightly poorer precision than shown in Section 11.

2. Applicable Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

D 2832 Recommended Practices for Determining Nonvolatile Content of Paint and Paint Materials⁴

3. Summary of Method

3.1 The specimen of liquid coating or dried film is prepared for analysis by dry ashing. The content of lead, cadmium, or cobalt of an acid extract of the ash is determined by atomic absorption spectroscopy.

4. Apparatus

4.1 *Atomic Absorption Spectrophotometer*, consisting of an atomizer and either a single- or three-slot burner; gas pressure regulating and metering devices for air and acetylene; lead, cadmium, and cobalt source lamps⁵ with a regulated constant-current supply; a monochromator and associated optics; a photosensitive detector connected to an electronic amplifier, and a read-out device.

4.2 *Muffle Furnace*, capable of maintaining $500 \pm 10^\circ\text{C}$.

4.3 *Crucibles*, wide-form, porcelain, glazed

¹ This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Material.

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² Vandenberg, J. T., Swafford, H. D., and Scott, R. W., "Determination of Low Concentrations of Lead in Paint," *Journals of Paint Technology*, JPTYA, Vol 47, No. 604, May 1975.

³ 1983 Annual Book of ASTM Standards, Vol 06.03.

⁴ 1983 Annual Book of ASTM Standards, Vol 06.01.

⁵ Both hollow cathode lamps and electrodeless discharge lamps have been found satisfactory for this purpose.

inside and outside except for the outside bottom surface, approximately 30-ml capacity, 50-mm rim diameter and 31 mm height.⁶

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

4.5 *High-Silica Glass Beakers*,⁷ 100 and 250-ml.

4.6 *Volumetric Flasks*, 50, 100, and 1000-ml.

4.7 *Dropping Bottles*, $\frac{1}{4}$ or $\frac{1}{2}$ -oz (7 or 15-ml) capacity.

4.8 *Glass or Disposable Syringes*, 5 or 10-ml capacity.

4.9 *Pipets*, 1, 2, 5, and 10-ml capacity.

4.10 *Paint Shaker*.

4.11 *Paint Draw-Down Bar*.

5. Reagents

5.1 *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.⁸ 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water conforming to Specification D 1193.

5.3 *Ammonium Acetate Solution (50 % weight/volume)*—Dissolve 500 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) in water and dilute to 1 litre.

5.4 *Ammonium Acetate Diluting Solution*—Add 50 ml of HNO_3 (sp gr 1.42) to 150 ml of 50 % weight/volume ammonium acetate solution and dilute to 1 litre.

5.5 *Cadmium Standard Stock Solution (1000 $\mu\text{g}/\text{ml}$)*—Dissolve 2.1032 g of cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) in 10 ml of water, add 10 ml of HNO_3 (sp gr 1.42), and dilute to 1 litre.

5.6 *Cobalt Standard Stock Solution (1000 $\mu\text{g}/\text{ml}$)*—Dissolve 4.9387 g of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 10 ml of water, add 10 ml of HNO_3 (sp gr 1.42), and dilute to 1 litre.

5.7 *Lead Standard Stock Solution (1000 $\mu\text{g}/\text{ml}$)*—Dissolve 1.5980 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in 10 ml of water, add 10 ml of

HNO_3 (sp gr 1.42), and dilute to 1 litre.

5.8 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

5.9 *Nitric Acid (1+1)*—Add 1 volume of HNO_3 (sp gr 1.42) to 1 volume of water.

6. Safety Precautions

6.1 Concentrated nitric acid is corrosive and may cause severe burns of the skin or eyes; the vapor is irritating to mucous membranes. Use care in handling this acidic substance. In case of contact, flush skin or eyes with plenty of water, while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse. See MCA Chemical Safety Data Sheet SD-5.

6.2 Use only a rubber bulb aspirator for pipeting liquids.

7. Calibration and Standardization

7.1 Prepare 100-ml quantities of at least four standard solutions bracketing the expected lead, cadmium, or cobalt concentration in the sample to be tested. To suitable aliquots of the 1000 $\mu\text{g}/\text{ml}$ standard lead, cadmium, or cobalt solution, add 5 ml of HNO_3 (sp gr 1.42) and 15 ml of 50 % ammonium acetate solution. Dilute to 100 ml with water.

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 Turn the instrument on and set the wavelength to the 283.3-nm lead line, the 228.8-nm cadmium line, or the 240.7-nm cobalt line. Apply the current recommended by the manufacturer to the lead, cadmium, or cobalt source lamp. Allow the instrument to warm up for about 15 min and set the slit width. Adjust the air and acetylene pressure or flow rates and ignite the burner in accordance with the manufacturer's instructions.

7.4 Aspirate water to rinse the atomizer

⁶ Coors No. 25007 crucibles, or equivalent, have been found satisfactory for this purpose.

⁷ Vycor beakers manufactured by the Corning Glass Co. have been found satisfactory for this purpose.

⁸ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."



chamber. Aspirate a standard solution and make any necessary readjustment in instrument parameters to obtain maximum absorption.

7.5 Aspirate each of the appropriate standard solutions and record the corresponding instrument readings. Aspirate water between each standard.

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

8. Procedure

8.1 If the sample is a liquid coating, mix it until homogeneous, preferably on a mechanical shaker. Determine the nonvolatile content in accordance with Method D 2832.

8.2 Prepare at least two replicate specimens by weighing by difference from a dropping bottle or syringe approximately 2 to 3 g of the mixed liquid coating, or by directly weighing approximately 1 to 2 g of dried paint film, into a 30-ml porcelain crucible. Weigh to the nearest 0.1 mg.

NOTE 2—The specimen size called for will give a concentration of approximately 10 to 20 $\mu\text{g/ml}$ lead in the final diluted solution for paints containing approximately 500 ppm (mg/kg) lead, based on the solids. If the material is estimated to contain more or less than 500 ppm (mg/kg) lead, the quantity taken should be adjusted accordingly. In the event that significantly less than 500 ppm (mg/kg) lead is expected, a 250-ml high-silica beaker may be used in place of the crucible to accommodate specimen weights up to 10 g. The size specified will give a concentration of approximately 2 to 4 $\mu\text{g/ml}$ cadmium in the final diluted solution for paints containing approximately 100 ppm (mg/kg) cadmium, based on the solids. The size specified will give a concentration of approximately 10 to 20 $\mu\text{g/ml}$ cobalt in the final diluted solution for paints containing approximately 500 ppm (mg/kg) cobalt, based on the solids.

NOTE 3—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 wet film thickness not exceeding 2 mils (50 μm). 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.

8.3 Place the crucible (or beaker) containing the liquid coating on a 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.

8.4 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.

8.5 After charring is complete, place the container in a preheated muffle furnace and ash at 475 to 500°C.

NOTE 4—Ashing at temperatures in excess of 500°C may result in the loss of some lead by volatilization.

8.6 When the ashing appears to be complete (do not exceed 1 to 2 h), remove the crucible or beaker from the muffle furnace and allow it to cool to room temperature. Break up the ash into fine particles with a glass stirring rod, leaving the rod with the container through the filtering step.

8.7 Add 10 ml of HNO_3 (1+1), taking care to avoid losses due to spattering in case the ash reacts vigorously with the acid. Heat carefully on a hot plate until 2 to 3 ml of solution remain. Add an additional 10 ml of HNO_3 (1+1) and continue heating on the hot plate until less than 5 ml of the solution remains.

8.8 Filter the solution through medium-porosity filter paper into a 50-ml volumetric flask. If the filtrate is not clear, refilter through fine-porosity filter paper. Wash the container three times with 2.5 ml of hot ammonium acetate solution (5.3), each time transferring the washings to the filter paper. Wash the filter paper several times with water. Adjust the volume to 50 ml with water and mix.

8.9 Aspirate the test solution and determine the absorbance in the same manner in which the instrument was calibrated. Determine the concentration of lead, cadmium, or cobalt in micrograms per millilitre from the calibration curve. If the absorbance is above the range covered by the calibration curve, dilute an aliquot of the sample solution to a suitable volume with ammonium acetate diluting solution.

NOTE 5—For maximum accuracy, calibration and standardization (Section 6) should be completed just prior to aspirating the sample solution.

NOTE 6—The method of standard additions may be used to improve the accuracy of the analysis. This 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.

9. Calculation

9.1 Calculate the mean concentration of lead, cadmium, or cobalt in the nonvolatile portion of the sample as follows:

$$\text{lead, cadmium or cobalt, ppm (mg/kg) in nonvolatile} = (C \times F \times 5000) / (NV \times S)$$

where:

C = concentration of lead, cadmium, or cobalt in the aspirated specimen solution, ($\mu\text{g}/\text{ml}$)

F = dilution factor from 8.9 (volume diluted to/volume of aliquot),

5000 = factor derived from multiplying the 50 mL volume obtained in Par. 8.8 by 100 (to convert NV used to a whole number) and 10^6 (to obtain PPM), then dividing by 10^6 (to convert grams of sample to μg).

NV = percent nonvolatile of paint sample (use 100 if sample was a dried film), and

S = grams of sample.

10. Report

10.1 Report the lead, cadmium, or cobalt content of the nonvolatile content of the sample and whether the analysis was conducted on a liquid coating or a dried film.

11. Precision and Accuracy⁹

11.1 In an interlaboratory study of the method the within-laboratory coefficient of variation was found to be 3.4 % relative at 24 degrees of freedom for lead, 3.7 % relative at 15 degrees of freedom for cadmium, and 3.3 %

relative at 21 degrees of freedom for cobalt. The between-laboratory coefficient of variation was 9.3 % relative at 20 degrees of freedom for lead, 8.9 % relative at 11 degrees of freedom for cadmium, and 5.5 % relative at 17 degrees of freedom for cobalt. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.1 *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 11 % relative for all three metals.

11.1.2 *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 % relative for lead or cadmium and if they differ by more than 17 % relative for cobalt.

11.2 Accuracy:

11.2.1 The true value for the amount of lead present in the solids of a coating should be between 97 and 111 % of the experimental value.

11.2.2 The true value for the amount of cadmium present in the solids of a coating should be between 77 and 143 % of the experimental value.

11.2.3 The true value for the amount of cobalt present in the solids of a coating should be between 96 and 120 % of the experimental value.

⁹ Results of the interlaboratory studies of this method, which were used to calculate precision, are available from ASTM, 1916 Race St., Philadelphia, Pa. 19103, as RR: D01-1005.

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