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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Low Concentrations of Antimony in Paint by Atomic Absorption Spectroscopy[1]

This standard is issued under the fixed designation D 3717; 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 determination of the content of antimony in the range between 50 and 200 ppm (mg/kg) 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 *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.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 2832 Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings[3]

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 refluxing with hydrochloric acid and stannous chloride. The antimony content of the acid extract 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 antimony 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 air and acetylene; an antimony source 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 *Oven*, maintained at 105 ± 2°C.

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

5.5 *Reflux Condenser*, water-cooled, and fitted with a standard-taper joint.

5.6 *Erlenmeyer Flask*, 125-mL, with standard-taper joint to fit condenser.

5.7 *Volumetric Flasks*, 100 and 1000-mL.

5.8 *Dropping Bottles*, ¼ or ½-oz (8 or 15-mL) capacity.

5.9 *Glass or Disposable Syringes*, 10-mL capacity.

5.10 *Pipets*, 1, 5, 10, and 15-mL capacity.

5.11 *Filter Paper*, ashless, medium or slow filtering.

5.12 *Paint Shaker*.

5.13 *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.[4] 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 grade water conforming to Type II of Specification D 1193.

6.3 *Antimony Standard Stock Solution* (0.1 mg/mL)—Dissolve 0.1000 g of antimony metal in 40 mL of sulfuric acid (H_2SO_4, sp gr 1.84) by heating. Cool, carefully transfer quantitatively to a 1-L volumetric flask already approximately

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[1] This test method is under the jurisdiction of ASTM Committee D-1 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] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] *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.

half full with water, allow to cool to room temperature, and dilute to 1 L.

6.4 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

6.5 *Stannous Chloride Solution* (400 g/L in HCl)—Dissolve 40 g of tin (II) chloride ($SnCl_2$) in 50 mL of HCl (sp gr 1.19). Transfer to a 100-mL volumetric flask and fill to the mark with concentrated HCl.

7. Hazards

7.1 Use care in handling concentrated HCl because it is corrosive and may cause burns to the skin and eyes and its vapor is irritating to mucous membranes. Refer to suppliers' Material Safety Data Sheet.

7.2 Use only a rubber bulb aspirator for pipetting liquids.

8. Calibration and Standardization

8.1 Prepare 100-mL quantities of at least four standard solutions bracketing the expected antimony concentration in the sample to be tested. To suitable aliquots of the 0.1 mg/mL standard antimony solution, add 40 mL of concentrated HCl and 8 drops of $SnCl_2$ solution. Dilute to 100 mL with water. Prepare a blank solution by diluting 40 mL of concentrated HCl and 8 drops of $SnCl_2$ solution to 100 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 217.6-nm antimony line. Apply the recommended current to the antimony source lamp. Allow the instrument to warm up for about 15 min and set the slit width. Adjust the air and acetylene pressures and ignite the burner in accordance with 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.

8.5 Aspirate the blank solution. When the recorder, meter, or other readout device reaches a constant value, it should be immediately zeroed. Repeat this blank determination until a steady, repeatable zero value is obtained at the maximum response.

8.6 Aspirate each of the appropriate standard solutions in ascending antimony concentrations and record the corresponding instrument readings. Aspirate water between each standard.

NOTE 1—A deuterium background corrector, if available, should be used to correct for background absorption. If not available, it is necessary to reaspirate each standard solution and measure the background at a nearby nonabsorbing region of the spectrum.

NOTE 2—Because of the high concentration and corrosive nature of the acids used for the analysis, it is essential that the burner assembly be disassembled and thoroughly cleaned out immediately after the analyses are completed. Consult the instrument manual for cleaning instructions.

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

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 D 2832.

9.2 Prepare at least two replicate samples by weighing by difference from a dropping bottle or syringe, 5 to 10 g of the mixed liquid coating, or by directly weighing approximately 2 to 6 g of dried film, into 125-mL Erlenmeyer flasks. Weigh to the nearest 0.1 mg.

NOTE 3—The specimen size called for will have a concentration of approximately 4 to 12 µg/mL antimony in the final diluted solution for paints containing approximately 200 ppm (mg/kg) antimony based on the nonvolatile content, and 1 to 3 µg/mL for paints containing approximately 50 ppm antimony, based on the nonvolatile content.

NOTE 4—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 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.

9.3 Place the flasks containing the liquid coating on the hot plate and slowly increase the temperature until the material is dried.

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

9.5 After charring appears complete, place the flasks in the muffle furnace and ash at 500°C. When the ashing appears to be complete (approximately 1 to 2 h), remove the flasks from the muffle furnace and allow to cool to room temperature.

9.6 Carefully add 40 mL of concentrated HCl and 8 drops of $SnCl_2$ solution to each flask. Connect the flasks to water-cooled condensers and reflux for 1 h.

9.7 Filter each digested specimen through medium-porosity filter paper into a 100-mL volumetric flask. If the filtrate is not clear, refilter through fine-porosity filter paper. Rinse each flask several times with water, adding the rinsings to the filter paper. Wash the filter paper several times with water. Adjust the volume to 100 mL with water and mix.

9.8 Aspirate each test solution and determine the absorbance in the same manner in which the instrument was calibrated (see Note 1 and Note 2). Determine the concentration of antimony 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 test solution to a suitable volume with water containing 40 mL of HCl and 8 drops of $SnCl_2$ solution per 100 mL. If the absorbance is below the range covered by the calibration curve, repeat the analysis using a larger specimen size.

NOTE 5—Increased sensitivity may be obtained with instruments possessing scale expansion and concentration readout capability.

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.

10. Calculation

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

$$\text{Antimony, ppm (mg/kg) in nonvolatile} = (C \times F \times 10^{4})/(NV \times S) \quad (1)$$

where:

C = concentration of antimony in the aspirated test solution, µg/mL,

F = dilution factor from 9.8 (volume diluted to/volume of aliquot),

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

S = grams of sample.

11. Report

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

12. Precision and Bias [5]

12.1 The precision estimates are based on an interlaboratory study in which eight different laboratories analyzed in duplicate, on two different days, three samples of water-reducible paints and three samples of solvent-reducible paints containing from 50 to 200 ppm (mg/kg) antimony. The within-laboratory coefficient of variation was found to be 4.8 % relative at 31 degrees of freedom and the between-laboratory coefficient of variation was 8.8 % relative at 25 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 26 % relative.

12.2 *Bias*—The mean of duplicate determinations within any laboratory should be within 18 % relative of true value.

13. Keywords

13.1 AAS, antimony; low concentration of antimony in paints

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[5] Supporting data are available from ASTM Headquarters. Request RR: D01-1011.