Designation: D3624 – 85a (Reapproved 2005)

Standard Test Method for Low Concentrations of Mercury in Paint by Atomic Absorption Spectroscopy[1]

This standard is issued under the fixed designation D3624; 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.

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

1. Scope

1.1 This test method covers the determination of the content of mercury in the range between 10 and 1000 ppm (mg/kg) present in liquid coatings, coatings vehicles, 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 and 9.1.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 The sample of liquid coating or dried film is weighed into a polytetrafluoroethylene (PTFE)-lined acid decomposition vessel and digested at an elevated temperature using sulfuric and nitric acids. Use of a sealed acid decomposition vessel prevents loss of mercury during the digestion. The digested sample is diluted to a known volume with water and the concentration of mercury is determined using a cold-vapor, atomic absorption technique.

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 mercury present in both water and solvent-reducible coatings to determine compliance.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*—Any commercial instrument having an open sample presentation area in which to mount the absorption cell or an instrument designed specifically for the measurement of mercury using the cold vapor technique.

5.2 *Recorder*, 0 to 10 mV.

5.3 *Mercury Source Lamp*.

5.4 *Absorption Cell*—Standard spectrophotometer cells 100 mm long, having quartz end windows may be used. Prior to use, the cell must be positioned in the optical path of the spectrophotometer and held in place by suitable clamps or straps. The cell should be carefully aligned both vertically and horizontally to give the maximum transmittance.

5.5 *Reduction Vessel*—Cylindrical gas washing bottle, 250-mL, equipped with a coarse (40 to 60-μm) fritted glass inlet tube and a standard-taper glass stopper. Polyethylene or poly(vinyl chloride) tubing may be used for connecting the reduction vessel to the absorption cell.

5.6 *Flowmeter*, capable of measuring a gas flow of 1 L/min.

5.7 *Drying Tube*—Approximately 150 by 20-mm (6 by ¾-in.) glass tube filled with magnesium perchlorate. The tube should be filled each day that it is in use, and the $Mg(ClO_4)_2$ should be replaced whenever it becomes saturated (carefully observe after each analysis).

NOTE 1—Use of an indicator desiccant at the exit end of the tube will make this observation easier.

5.8 *Water Vapor Trap*—A second 250-mL gas washing bottle (the same as used for the reduction vessel). If preferred, a 250-mL Erlenmeyer vacuum flask fitted with a one-hole stopper and 200 mm of 5-mm outside diameter glass tubing, may be substituted. (Fig. 1)

5.9 *Mercury Trap*—A 250-mL Erlenmeyer vacuum flask containing 75 mL of 10 % sulfuric acid and 75 mL of 0.1 *N* potassium permanganate solution to absorb the mercury vapor after analysis.

5.10 *Circulating Oven*, maintained at 140 ± 5°C.

[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.

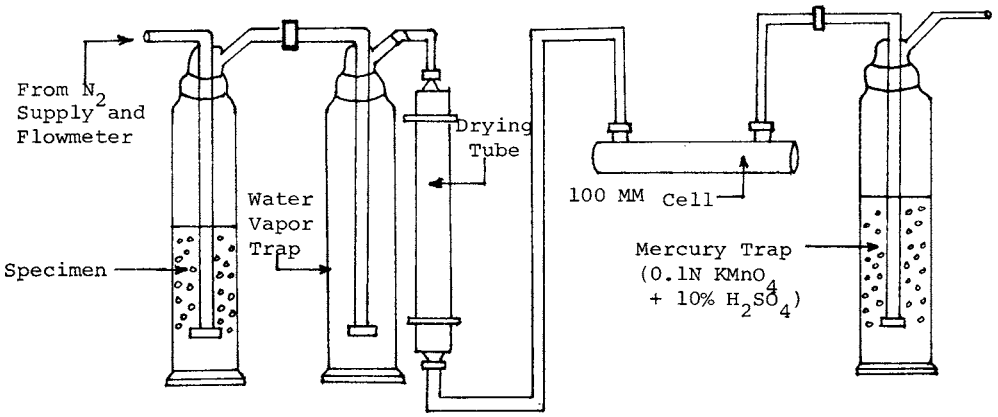

FIG. 1 Apparatus

5.11 *Acid Decomposition Vessel*, with 25-mL PTFE digestion cup.[3]

5.12 *Volumetric Flasks*, 100, 250, and 1000-mL.

5.13 *Paint Shaker*.

5.14 *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 water conforming to Type II of Specification D1193.

6.3 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 10 g of $NH_2OH{\cdot}HCl$ in 100 mL of water. Transfer a portion of this solution to a small dropping bottle.

6.4 *Mercury Solution, Stock (1 mg/mL)*—Dissolve 0.1354 g of $HgCl_2$ in 50 mL of water. Carefully add 5 mL of concentrated H_2SO_4 and 3 mL of concentrated HNO_3 and dilute to 100 mL. This solution contains 1000 µg/mL of mercury.

6.5 *Mercury Standard, Working (0.1 µg/mL)*—Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 mg/L (0.1 µg/mL), maintaining a concentration of 5 % H_2SO_4 and 3 % HNO_3 by volume, in the diluted solutions. The working mercury standard and the dilutions of the stock mercury solution should be prepared fresh each day that it is used.

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

6.7 *Nitrogen*.

6.8 *Potassium Permanganate Solution* (0.1 *N*)—Dissolve 15.8 g of $KMnO_4$ in water and dilute to 1 L.

6.9 *Stannous Chloride Solution (100 g/L)* Dissolve 25 g of tin (II) chloride ($SnCl_2$) by adding it to 60 mL of concentrated HCl (sp gr 1.19) and warming on a hotplate. When all of the $SnCl_2$ has dissolved, transfer to a 250-mL volumetric flask and dilute to volume with water. Mix well. This solution should be prepared fresh each week that it is used.

6.10 *Sulfuric Acid (sp gr 1.84)* Concentrated sulfuric acid (H_2SO_4).

6.11 *Sulfuric Acid (1+9)* Carefully mix 1 volume of H_2SO_4(sp gr 1.84) into 9 volumes of water.

7. Hazards

7.1 Concentrated nitric and sulfuric acids are corrosive and may cause severe burns of the skin or eyes. The vapor from concentrated nitric acid is irritating to mucous membranes. Use care in handling these acidic substances. Refer to suppliers' Material Safety Data Sheet.

7.2 Mercury and its compounds are harmful and accumulate in the aquatic environment. Mixtures containing mercury 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 Assemble the various components, as illustrated in Fig. 1 if an atomic absorption spectrophotometer is used, or prepare the instrument for operation if a commercial mercury analyzer is being used.

NOTE 2—Be sure that all glassware has been thoroughly cleaned and rinsed with reagent water prior to use.

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

8.3 With the apparatus empty, stabilize the recorder base line while maintaining a flowrate of 250 mL of nitrogen per minute.

[3] The sole source of supply of an acid decomposition vessel, Catalog No. 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, [1] which you may attend

[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.