Designation: D3624 – 85a (Reapproved 2015)

# 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 U.S. 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)

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[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.

Current edition approved June 1, 2015. Published June 2015. Originally approved in 1977. Last previous edition approved in 2010 as D3624 – 85a (2010). DOI: 10.1520/D3624-85AR15.

[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.

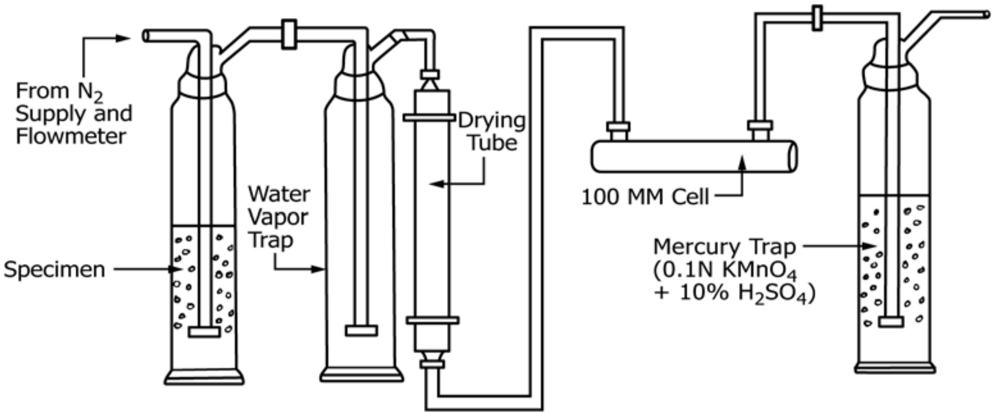

FIG. 1 Apparatus

5.9 *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.

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.

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[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.

## 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.

8.4 Transfer 0, 5, 10, 15, and 20-mL aliquots of the working mercury standard (containing 0 to 2 µg of mercury) to a series of 250-mL gas washing bottles. Add enough water to each bottle to make a total volume of 100 mL. Add 5 mL of $H_2SO_4$ and 3 mL of $HNO_3$ to each bottle and mix thoroughly. Make dropwise additions of 0.1 *N* $KMnO_4$ solution to each bottle in turn until a pink color persists for at least 30 s (1 mL is usually sufficient). Add exactly 1 mL of $NH_2OH{\cdot}HCl$ solution dropwise to each bottle and swirl until the pink color is discharged.

8.5 Add 10 mL of $SnCl_2$ solution to the bottle containing no added working mercury standard. Immediately insert the fritted glass inlet tube, making sure that the stopper provides a good seal. Adjust the nitrogen flow rate to a previously determined optimum setting (see Note 3) and take a reading. A blank value greater than 5 % of full scale indicates either reagent or apparatus contamination. When the recorder, meter, or other readout device reaches a maximum value, it should be immediately zeroed. Repeat this blank determination until a steady, repeatable zero value is obtained at the maximum response.

NOTE 3—Optimum nitrogen flow rate may be determined by analyzing 1-µg quantities of mercury (10 mL of working mercury standard diluted to 100 mL) by this procedure, varying the flow rate to determine the optimum mercury signal and time required for analysis. Then use this optimum flow rate for all analyses, unless a change is made in the volume or geometry of the apparatus.

8.6 Similarly treat each standard solution made up in 8.4, recording the maximum peak height for each. When the recorder pen begins dropping, remove the fritted glass inlet tube from the gas washing bottle and insert it into another bottle containing only water. Continue nitrogen flow until the absorbance reaches zero, when the apparatus is ready for the next solution.

NOTE 4—Because mercury vapor is very toxic, take precautions to avoid its inhalation. Bubble the exhaust from the absorption cell through an absorbing solution consisting of equal volumes of 0.1 *N* $KMnO_4$ solution and 10 % $H_2SO_4$ (see Fig. 1). Do not discharge the absorbing solution into a sewer system.

8.7 Construct a standard curve by plotting peak heights versus micrograms of mercury. Peak heights used should be the mean of duplicate determinations on each solution.

## 9. Procedure

9.1 If the sample is a liquid coating, mix it until homogeneous, preferably on a mechanical paint shaker. Prepare at least two replicate specimens by weighing to 0.1 mg by difference from a dropping bottle or syringe, 100 to 200 mg of the mixed paint into the PTFE insert of the acid decomposition vessel. Place the insert in an oven set at 60°C (140°F) for 1 h to remove all volatiles.

9.1.1 **Caution**—If the solvent present in a sample is not removed prior to the digestion step as recommended, potentially dangerous pressures may result when the vessel is heated at 140°C.

9.2 If the sample consists of dried film, coarsely grind it and weigh 50 to 100 mg by difference from a weighing bottle into the digestion vessel.

NOTE 5—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 60°C for a minimum of 1 h. Scrape the dried film off the glass plate, preferably with a single-edge razor blade.

9.3 Pipet 5 mL of concentrated $H_2SO_4$ and 3 mL of concentrated $HNO_3$ into the decomposition vessel insert, using a fume hood for the operation. Seal the vessel tightly and place in the circulating oven at 140°C for 1½ h. Remove the vessel from the oven and allow it to cool slowly to room temperature.

NOTE 6—Do not assist cooling by putting the vessel in a refrigerator or freezer, or by submerging it in a cooling liquid; otherwise mercury losses may occur due to leakage of pressurized gases resulting from uneven contraction of the bomb parts and PTFE seal.

NOTE 7—Analysis of the digested specimen (9.4 – 9.7) should be completed within 1 h after the digestion step.

9.4 When completely cooled, carefully unseal the vessel in a fume hood, add approximately 5 mL of cold water and swirl gently. Quantitatively transfer the contents to a 100-mL beaker, using several small quantities of water. Dilute to a volume of 30 to 40 mL and filter through filter paper directly into a 100-mL volumetric flask. Wash the residue on the filter paper several times with small volumes of water. Dilute to volume with water and mix thoroughly.

9.5 Transfer an aliquot of each digested specimen containing not over 2 µg of mercury to a 250-mL gas washing bottle. Add enough water to make a total volume of 100 mL. To each bottle, add 5 mL of concentrated $H_2SO_4$ and 3 mL of concentrated $HNO_3$ and mix thoroughly.

NOTE 8—If large aliquots are taken for analysis, reduce the amount of added $H_2SO_4$ and $HNO_3$ proportionately to compensate for the amounts present in the digested solutions.

9.6 Proceed with the addition of $KMnO_4$, $NH_2OH{\cdot}HCl$, and $SnCl_2$ solutions as described in 8.4 and 8.5. Record the maximum peak height for each solution.

9.7 If the response obtained is above or below the response obtained for the standards (8.7), repeat 9.5 and 9.6 using an appropriate aliquot size. Determine the concentration of mercury present in microgram per millilitre from the calibration curve.

## 10. Calculation

10.1 Calculate the mean concentration of mercury in the sample as follows:

$$\text{mercury in sample, ppm (mg/kg)} = (100 \times C)/(F \times S) \quad (1)$$

where:

$C$ = concentration of mercury in aliquot used, µg/mL,
$F$ = dilution factor from 9.5 (aliquot volume used), and
$S$ = grams of sample.

## 11. Report

11.1 Report the mercury content in the material being tested and whether the analysis was conducted on a liquid coating or a dried film.

## 12. Precision and Bias[5]

12.1 *Precision*—The precision estimates are based on an interlaboratory study in which seven different laboratories analyzed in duplicate, on two different days, four samples of waterborne paints and four samples of solvent-reducible paints containing from 1 to 1000 ppm mercury. The within-laboratory coefficient of variation was found to be 6.4 % relative at 42 df, and the between-laboratory coefficient of variation 10 % relative at 36 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 18 % 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 30 % relative.

12.2 *Bias*—The true value for the amount of mercury present in a coating should be between 79 and 121 % of the experimental value.

## 13. Keywords

13.1 AAS; low concentration of mercury in paints; mercury

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1006. Contact ASTM Customer Service at service@astm.org.