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Designation: D1224 – 92 (Reapproved 2006)

An American National Standard

Standard Test Methods for Zinc and Cadmium in Paper[1]

This standard is issued under the fixed designation D1224; 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 These test methods cover the determination of cadmium and zinc either in paper or in highly opaque pigments.

1.2 The test methods appear as follows:

	Section
Method A—Polarographic	5
Method B—Gravimetric and Volumetric	6
Method C—Atomic Absorption	7

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]

C322 Practice for Sampling Ceramic Whiteware Clays

D585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, and Related Product

D644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying

3. Summary of Test Methods

3.1 Three test methods for each element are described: polarographic, either gravimetric or volumetric, and atomic absorption. The gravimetric procedure is suitable if a polarograph is not available. For the determination of zinc in a zinc-bearing pigment, the volumetric procedure is recommended, because the polarographic procedure is insensitive over 25 % in levels. The polarographic procedure can be used for the determination of zinc and cadmium in paper and for cadmium in cadmium-bearing pigments. The preferred method for each material is based on its concentration and on the availability of equipment.

3.2 When zinc is to be determined volumetrically (cadmium absent) one precipitation of heavy metals with washing is sufficient.

3.3 In the atomic absorption procedure sensitivities for 1 % absorption are 0.02 mg/cm^3 Zn and 0.03 mg/cm^{3}Cd, respectively. The repeatability of this method is questionable at present for zinc and cadmium concentrations of greater than 5 %.

4. Significance and Use

4.1 Zinc is usually present as zinc oxide, zinc sulfide, or as lithopone (a combination of zinc sulfide and barium sulfate), which is occasionally used in filled paper, paper coatings, and high pressure laminates and wallpaper. Some forms of zinc oxide have photoelectric properties and are found in certain papers used for photoreproduction. Zinc or cadmium pigments are sometimes added to papers to cause fluorescence, and zinc oxide has been used to enhance the cohesive strength of some types of paper coatings.

5. Test Method A—Polarographic

5.1 *Apparatus*:

5.1.1 *Polarograph*, of the manually operated type. A recording polarograph may be used, although this method is written specifically for a manually operated instrument.

5.1.2 *Electrolysis Equipment*, including a cell, a dropping mercury electrode, an arrangement for maintaining a constant head of mercury above the capillary, and a constant-temperature bath. The cell may be of simple design (for example, a test tube 15 by 85 mm). This cell is fitted with a three-hole notched rubber stopper that will hold the dropping mercury electrode, the contact electrode for the anode (a pool of mercury), and a tube for flushing the solution with nitrogen.

5.1.3 *Nitrogen Cylinder and Tubing*.

5.1.4 *Other Apparatus*—Pipets, 5, 15, 20, and 50-cm^3; volumetric flasks, three 200 cm^3.

5.2 *Reagents*:

5.2.1 *Ammonium Chloride*—Crystalline NH_4Cl.

5.2.2 *Ammonium Hydroxide (NH_4OH, 14.8 N)*.

5.2.3 *Gelatin Solution*—Dissolve 2 g of gelatin in boiling water and dilute the clear solution to 1000 cm^3.

5.2.4 *Hydrochloric Acid (HCl, 12 N)*.

5.2.5 *Nitrogen* (with minimum oxygen content).

[1] These test methods are under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and are the direct responsibility of Subcommittee D06.92 on Standard Documents Relating to Paper and Paper Products.

Current edition approved Nov. 1, 2006. Published November 2006. Originally approved in 1952. Last previous edition approved in 2001 as D1224 – 92 (2001). DOI: 10.1520/D1224-92R06.

[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.

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5.2.6 *Standard Cadmium Solution (1 cm^3 = 0.0010 g Cd)*—Dissolve 1.631 g of anhydrous cadmium chloride ($CdCl_2$) in 100 cm^3 of hot water. Cool, dilute to 1000 cm^3 in a volumetric flask, and mix.

5.2.7 *Standard Zinc Solution (1 cm^3 = 0.0010 g Zn)*—Dissolve 1.245 g of freshly ignited zinc oxide (ZnO) in 50 cm^3 of hot HCl (1 + 10). Cool, dilute with water to 1000 cm^3 in a volumetric flask, and mix.

5.3 *Sampling and Test Specimen*:

5.3.1 From each test unit obtained in accordance with Method D585 (for paper) or Practice C322 (for pigments), prepare a specimen sufficient to contain at least 10 mg of zinc or 10 mg of cadmium if present.

5.3.2 Normally about 1 g or less of dry paper is sufficient for a single determination. More is needed if its moisture content is unknown.

5.3.3 If the moisture content is unknown, determine it in accordance with Test Method D644.

5.4 *Procedure*[3]:

5.4.1 *Zinc and Cadmium Factors*:

5.4.1.1 Transfer 20.0 and 50.0-cm^3 aliquots of the standard zinc and cadmium solutions, respectively, to each of two 200-cm^3 volumetric flasks. To each of these flasks, and to a third flask to be carried through the entire procedure as a blank, add 16.6 g of NH_4Cl and 5 cm^3 of HCl, and dilute to approximately 150 cm^3 with water. Add 15 cm^3 of NH_4OH and 10 cm^3 of gelatin solution. Cool, dilute to the mark with water, and mix.

5.4.1.2 Transfer suitable portions of the resulting solutions to electrolysis cells and remove oxygen by bubbling nitrogen through the solutions for 10 min.

NOTE 1—Since the diffusion current increases with increasing temperature, arrangement must be made to control standards and samples at a uniform temperature during electrolysis or to make corrections for temperature fluctuations. Other conditions such as drop time and height of the mercury column must also be constant.

5.4.1.3 Determine the increase in the galvanometer deflection in divisions when changing from an applied potential of – 0.58 to – 0.83 V, and again when changing from – 1.09 to – 1.40 V for each solution. Adjust the sensitivity of the polarograph circuit so as to obtain optimum increases in galvanometer deflection.

NOTE 2—These voltage settings must be on the residual current plateaus and the diffusion current plateaus, respectively. Since the wave form may be affected by the sensitivity of the galvanometer, a complete polarogram should be plotted and the above settings checked for the particular instrument being used.

5.4.1.4 Multiply the increase in galvanometer deflection obtained by increasing the potential from – 0.58 to – 0.83 V, for each solution by the shunt setting used and plot these values against the grams of cadmium. Next, multiply the increase in galvanometer deflection obtained by increasing the potential from – 1.09 to – 1.40 V for each solution by the shunt setting used and plot these values against the grams of zinc. The three points must fall approximately on a straight line for both metals.

5.4.2 *Calculation*—Calculate the cadmium and zinc factors as follows:

$$F_1 = \frac{C_1}{(R_1 - B_1)} \quad (1)$$

$$F_2 = \frac{C_2}{(R_2 - B_2)} \quad (2)$$

where:

F_1 = factor in grams of cadmium per galvanometer scale division at full sensitivity,
C_1 = grams of cadmium in the standard,
R_1 = increase in galvanometer deflection when the potential is increased from – 0.58 to – 0.83 V for the standard,
B_1 = increase in galvanometer deflection when the potential is increased from – 0.58 to – 0.83 V for the blank,
F_2 = factor in grams of zinc per galvanometer scale division at full sensitivity,
C_2 = grams of zinc in the standard,
R_2 = increase in galvanometer deflection when the potential is increased from – 1.09 to – 1.40 V for the standard, and
B_2 = increase in galvanometer deflection when the potential is increased from – 1.09 to – 1.40 V for the blank.

NOTE 3—If conditions are kept constant, there is no need to redetermine the cadmium and zinc factors until a new capillary is used.

5.5 *Analysis of Specimen*:

5.5.1 Transfer approximately 0.5 g of the dried specimen, weighed to the nearest 0.001 g, to a 400-cm^3 beaker. Add 10 cm^3 of concentrated H_2SO_4, and heat to char the paper. Oxidize with HNO_3 and, when the solution is clear, evaporate to dryness. Add 16.6 g of NH_4Cl, 5 cm^3 of HCl, and 50 cm^3 of water. Heat until solution is complete. Cool, transfer to a 200-cm^3 volumetric flask, and dilute to approximately 150 cm^3 with water. Add 15 cm^3 of NH_4OH and 10 cm^3 of gelatin solution. Cool, dilute to 200 cm^3, and continue in accordance with the procedure for determining the zinc and cadmium factors.

5.5.2 *Calculation*—Calculate the percentage of cadmium and zinc as follows:

$$\text{Cadmium, \%} = \left(\frac{[(A_1 - B_1)\,F_1]}{W}\right) \times 100 \quad (3)$$

$$\text{Zinc, \%} = \left(\frac{[(A_2 - B_2)\,F_2]}{W}\right) \times 100 \quad (4)$$

where:

A_1 = increase in galvanometer deflection when the potential is increased from – 0.58 to – 0.83 V for the specimen,
B_1 = increase in galvanometer deflection when the potential is increased from – 0.58 to – 0.83 V for the blank, in accordance with the procedure,
F_1 = factor in grams of cadmium per galvanometer scale division at full sensitivity,

[3] For detailed information, see the following references: Kolthoff, I. M., and Lingane J. J., *Polarography,* Interscience Publishers, Inc., New York, NY 1941; Muller, Otto H., "The Polarographic Method of Analysis," *Journal of Chemical Education,* JCEDA, 1941.

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