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An American National Standard

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

This standard is issued under the fixed designation D 1224; 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:

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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:*

C 322 Practice for Sampling Ceramic Whiteware Clays[2]

D 585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Products[3]

D 644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying[3]

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).

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.

[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 Test Methods.

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[2] *Annual Book of ASTM Standards*, Vol 15.02.

[3] *Annual Book of ASTM Standards*, Vol 15.09.

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 D 585 (for paper) or Practice C 322 (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 D 644.

5.4 *Procedure*[4]:

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.

[4] 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.

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,
W = weight of specimen, g,

A_2 = increase in galvanometer deflection when the potential is increased from − 1.09 to − 1.40 V for the specimen,
B_2 = increase in galvanometer deflection when the potential is increased from − 1.09 to− 1.40 V for the blank, in accordance with the procedure, and
F_2 = factor in grams of zinc per galvanometer scale division at full sensitivity.

6. Test Method B—Gravimetric and Volumetric

6.1 *Apparatus*:

6.1.1 *For Cadmium by the Gravimetric Procedure*:

6.1.1.1 *Platinum Dish*, evaporating, about 50 cm^3.

6.1.1.2 *Other Apparatus*—Beakers, three 400-cm^3; graduated cylinders, 25 and 50-cm^3; filter funnel with fine filter paper.

6.1.2 *For Zinc by the Volumetric Procedure*—The same apparatus described in 6.1.1 and a 3 and 5-cm^3 pipet (or a small graduated cylinder); medium filter paper; 50-cm^3 buret.

6.2 *Reagents*:

6.2.1 *For Cadmium by the Gravimetric Procedure*:

6.2.1.1 *Hydrochloric Acid*, diluted HCl (3 + 7).

6.2.1.2 *Hydrogen Sulfide*, H_2S (generator or cylinder).

6.2.1.3 *Nitric Acid*, concentrated HNO_3.

6.2.1.4 *Sulfuric Acid*, —concentrated H_2SO_4, diluted (1 + 1).

6.2.2 *For Zinc by the Volumetric Procedure*:

6.2.2.1 The same apparatus described in 5.1.1 and the following:

6.2.2.2 *Ammonia*, diluted NH_4OH (1 + 1).

6.2.2.3 *Hydrochloric Acid*, concentrated HCl; also diluted (1 + 1).

6.2.2.4 *Litmus Paper*.

6.2.2.5 *Methyl Orange Indicator*.

6.2.2.6 *Potassium Ferrocyanide Standard Solution (1 cm^3 = 0.01 g Zn)*—Dissolve 42.3 g of potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) in water and dilute to 1000 cm^3. To standardize, transfer 0.3200 to 0.3400 g of zinc to a 400-cm^3 beaker then dissolve in 10 cm^3 of concentrated HCl and 20 cm^3 of water. Add NH_4OH until slightly alkaline to litmus paper; then add HCl until just acid, plus 3 cm^3 in excess. Dilute to about 250 cm^3 with hot water and heat nearly to boiling. Titrate with $K_4Fe(CN)_6$ solution, while stirring constantly, until a drop tested on a white porcelain plate with a drop of uranyl acetate indicator shows a brown tinge after standing 1 min. Make a blank determination following the same procedure and using the same amounts of reagents and water. Calculate the zinc factor of the $K_4Fe(CN)_6$ solution as follows:

$$F = \frac{C}{(A - B)} \tag{5}$$

where:
F = zinc equivalent of the $K_4Fe(CN)_6$ solution, g/cm^3,
A = $K_4Fe(CN)_6$ solution required to titrate the zinc solution, cm^3,
B = $K_4Fe(CN)_6$ solution required to titrate the blank, cm^3, and
C = zinc used, g.

6.2.2.7 *Sulfuric Acid*, diluted H_2SO_4(5 + 95).

6.2.2.8 *Uranyl Acetate Indicator*—Dissolve 5 g of $UO_2(CH_3COO)_2 \cdot 2H_2O$ in water, acidify with acetic acid, and dilute to 100 cm^3.

6.2.2.9 *Zinc*, metal, reagent grade.

6.3 *Sampling and Test Specimen*:

6.3.1 Obtain a sample as previously described for the polarographic procedure (4.3.1), except use a 4-g specimen for the analysis of zinc in zinc pigments.

6.3.2 Normally about 4 g or less of dry paper is sufficient for a single determination of zinc and cadmium in paper.

6.4 *Procedures*:

6.4.1 *For Cadmium by the Gravimetric Procedure*:

6.4.1.1 Place approximately 4 g of the specimen in a tared weighing bottle, dry to constant weight and weigh to the nearest 5 mg. Transfer to a 400-cm^3 beaker and add 20 cm^3 of concentrated H_2SO_4. Heat to char the paper and add sufficient concentrated HNO_3 to oxidize the mixture to a clear solution. Evaporate to dryness and add approximately 100 cm^3 of water and 10 cm^3 of H_2SO_4(1 + 1). Heat to dissolve, and filter if there is any insoluble residue. Dilute to approximately 200 cm^3, and pass a rapid stream of H_2S through the solution for 20 min. Filter through fine paper, but do not wash. Reserve the filtrate.

6.4.1.2 Dissolve the precipitate on the paper with cold HCl (3 + 7) and wash the paper well with water, catching the solution in the same 400-cm^3 beaker. Add 15 cm^3 of H_2SO_4(1 + 1) and evaporate to dense white fumes. Cool, dilute to 200 cm^3, and reprecipitate as above.

6.4.1.3 Filter, using a fine paper. Combine the filtrate with that reserved in 5.4.1.1 and reserve the combined filtrates for the determination of zinc. Dissolve the precipitate with cold HCl (3 + 7) followed by washing with water, receiving the solution in a weighed platinum dish. Add 10 cm^3 of H_2SO_4(1 + 1) and evaporate to dense white fumes. Remove the excess H_2SO_4 by cautiously heating the dish, and finally heat to 500 to 600°C. Cool, and weigh as $CdSO_4$.

6.4.1.4 *Calculation*—Calculate the percentage of cadmium as follows:

$$\text{Cadmium, \%} = \frac{(A = 0.5392)}{B} \times 100 \tag{6}$$

where:
A = weight of $CdSO_4$, and
B = dry weight of specimen, g.

6.4.2 *For Zinc by the Volumetric Procedure*:

6.4.2.1 Evaporate the combined filtrates, obtained in accordance with the gravimetric procedure for cadmium, to dryness. Add 5 cm^3 of H_2SO_4(1 + 1) to 100 cm^3 of water, and heat to dissolve. Cool, and add NH_4OH (1 + 4) until just alkaline. Add H_2SO_4(1 + 4) until neutral to methyl orange, and then add 3 cm^3 of H_2SO_4(5 + 95). Dilute to 200 cm^3. Using a short glass tube, pass a rapid stream of H_2S through the solution for 40 min. Leave the tube in the beaker and allow the precipitate to settle for 10 min.

6.4.2.2 Filter, using a medium paper, and wash twice with cold water. Discard filtrate. Place the original beaker and gassing tube under the funnel and punch a hole in the paper. Wash the bulk of the ZnS into the beaker using hot water. Wash the paper with 40 cm^3 of hot HCl (1 + 4) and again with hot

water. Dissolve the ZnS still adhering to the gassing tube with a minimum quantity of hot HCl (1 + 4).

6.4.2.3 Boil to expel H_2S. Cool, and add NH_4OH, until slightly alkaline, to litmus paper; then add HCl until just acid, plus 3 cm^3 in excess. Dilute to 250 cm^3 with hot water and heat nearly to boiling. Titrate as described previously.

6.4.2.4 *Calculation*—Calculate the percentage of zinc in the specimen as follows:

$$\text{Zinc, \%} = \frac{(A - B)F}{C} \times 100 \quad (7)$$

where:

A = $K_4Fe\ (CN)_6$ solution required to titrate the specimen, cm^3,
B = $K_4Fe\ (CN)_6$ solution required to titrate the blank as described under reagents-standardization of potassium ferrocyanide, cm^3,
F = zinc equivalent of the $K_4Fe\ (CN)_6$ solution, g/cm^3, and
C = weight of specimen, g.

7. Test Method C—Atomic Absorption

7.1 *Summary of Method*—A paper specimen is reacted with H_2SO_4 and H_2O_2. The resulting solution is diluted, and the concentrations of zinc or cadmium, or both, are measured with an atomic absorption spectrophotometer. A calculation of the weight percents of zinc or cadmium, or both, is then made.

NOTE 4—The atomic absorption procedure can be applied to many other metal ions. In the atomic absorption method the extent of interferences from other ions has not been examined fully; however, the absorbances of zinc and cadmium are not significantly affected by 10-fold excesses of each other. Calcium in a 10-fold excess slightly depresses zinc absorbance. Titanium in a 10-fold excess seems to have no effect on zinc absorbance. Sulfuric acid enhances both absorbances.

7.2 *Definition*:

7.2.1 *linear working range*—the concentration range over which instrument response is proportional to concentration by a constant factor.

7.3 *Apparatus*:

7.3.1 *Atomic Absorption Spectrophotometer*, preferably equipped with deuterium arc background corrector and direct concentration readout mode.[4] A graphite tube furnace is an accessory part for many atomic absorption spectrophotometers. It atomizes materials by the use of an electrically heated graphite tube.

NOTE 5—Detection limits can be improved significantly by the use of a graphite tube furnace in the atomic absorption procedure.

7.3.2 *Erlenmeyer Flask*, 250-cm^3, with 24/40 ground-glass opening.

7.3.3 *Parallel Side Arm Connector*, 3-way, with 24/40 ground-glass joint.

7.3.4 *Graduated Cylindrical Funnel*, 50-cm^3, with 24/40 ground-glass joint.

7.3.5 *Hot Plate*.

7.3.6 *Ring Stand*.

7.3.7 *Analytical Balance*, capable of reading to ± 0.001 g.

7.3.8 *Volumetric Glassware*, to include at least one of each of the following: flasks, 500 cm^3, 250 cm^3, and 100 cm^3; pipets, 50 cm^3, 25 cm^3, 10 cm^3, and 1 cm^3.

7.4 *Reagents and Materials*:

7.4.1 *Stock Zinc Solution*, 500 µg/cm^3. Prepare by dissolving 0.500 g of zinc metal in a minimum volume of HCl (1 + 1) and diluting to 1000 cm^3 with 1 % (V/V) HCl.

7.4.2 *Stock Cadimum Solution*, 500 µg/ cm^3. Prepare by dissolving 0.500 g of cadmium metal in a minimum volume of HCl (1 + 1) and diluting to 1000 cm^3 with 1 % (V/V) HCl.

7.4.3 *Sulfuric Acid (H_2SO_4 98 % weight/weight)*.

7.4.4 *Hydrogen Peroxide (H_2O_2, 30 %, weight/weight)*.

7.5 *Sampling and Test Specimen*:

7.5.1 Obtain a sample in accordance with Method D 585.

7.5.2 Obtain 1 to 2 g of specimen from various positions on each test unit in the form of small strips.

7.5.3 Dry the test specimens for 1 h at 105°C. Place in a desiccator at least 0.5 h before analyzing.

7.6 *Procedure*:

7.6.1 Weigh to the third decimal place, a specimen between 1 and 2 g. Add the test specimen to a 250-cm^3 Erlenmeyer flask containing 10 cm^3 of concentrated H_2SO_4. Attach a 3-way parallel side arm connector and a 50-cm^3 cylindrical funnel containing approximately 40 cm^3 of 30 % H_2O_2 to the flask. Support the glassware with a ring stand and place the flask on a hot plate. Heat the mixture until the specimen is charred completely and dense white fumes appear. Add H_2O_2 at a rate of approximately 1 drop per second until a clear solution results. Transfer contents of the flask to a 1000-cm^3 volumetric flask, allow to cool, and dilute to the mark with water.

7.6.2 Prepare calibration standards by diluting stock zinc and cadmium solutions to 0.1, 0.5, and 1.0 µg/cm^3 with 1 % (V/V) H_2SO_4. Set instrumental conditions in accordance with the manufacturer's specifications. Adjust the flame in accordance with the manufacturer's specifications. Instrument operating conditions are given in 7.6.3. Use either absorbance or concentration readout mode, depending on how the instrument is equipped. Zero the instrument with deionized water. Measure calibration standards or set concentration readout. Measure the specimens in the following sequence: specimen, standard, specimen. Make three readings on each specimen. If a specimen concentration readout or absorbance falls outside of the linear range suggested by the manufacturer or established by experimentation, dilute the solution to get the response in linear working range.

7.6.3 *Instrument Operating Conditions*:

Element	Slit, nm	Analytical Wavelength, nm	Light Source	Flame Type
Zinc	0.7	213.9	hollow cathode lamp	air-acetylene (lean)
Cadmium	0.7	228.8	hollow cathode lamp	air-acetylene (lean)

7.6.4 *Calculation*—Calculate the percentages of zinc or cadmium, or both, as follows:

$$\text{Cadmium or Zinc, \%} = \left(\frac{(A\ B)}{C}\right)(10^4) \quad (8)$$

where:

A = concentration of zinc or cadmium, µg/cm^3,

B = dilution factor (for example, a 10-cm^3 aliquot of solution is diluted to 100 cm^3; then dilution factor equals 10), and
C = weight of test specimen, µg.

8. Report

8.1 Report the following information:

8.1.1 Amount of zinc or cadmium as a percentage of the moisture-free material, to the nearest 0.1 %, and state the procedure used.

8.2 For the atomic absorption procedure, report the following:

8.2.1 Measured absorbances or concentrations,

8.2.2 Graph on which the concentrations of zinc and cadmium standards are plotted against their absorbances,

8.2.3 Statement of instrumental conditions to include lamp current, wavelength of measurement, type of flame, type of burner, and any special equipment used for the improvement of instrument performance,

8.2.4 Calculation of percent zinc or cadmium, or both, and

8.2.5 Notes on any observations of unusual behavior of either the instrument or the reaction.

9. Precision and Bias

9.1 *Precision*

9.1.1 *Repeatability*—All repeatability values are based on the amount present:

Material, %	Method	Repeatability, %
Zn (0 to 25)	Polarographic	±1
Cd (0 to 25)	Polarographic	±1
Zn (>25)	Volumetric	±1
Cd	Gravimetric	±0.5
Zn (0 to 5)	Atomic absorption	±2
Cd (0 to 5)	Atomic absorption	±2

9.1.2 *Reproducibility*—Not known.

9.2 *Bias*

9.2.1 Since there is no accepted reference material for determining the bias for the procedure in Test Method D 1224 for measuring zinc and cadmium in paper, bias has not been determined.

10. Keywords

10.1 paper; pigments; zinc cadmium