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Zinc and cadmium in paper

1. Scope and significance

1.1 This method may be used for the determination of cadmium and zinc either in paper or in highly opaque pigments. Zinc is usually present in zinc oxide, zinc sulfide, or as lithopone (a combination of zinc sulfide and barium sulfate), which is occasionally used in filled paper, in paper coatings and in high-pressure laminates and wallpaper. Some forms of zinc oxide have photoelectric properties and are found in certain papers used for photo reproduction. 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.

1.2 Three procedures 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% Zn 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 procedure for each material is based on its concentration.

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

1.4 In the atomic absorption procedure, sensitivities for 1% absorption are 0.02 mg/mL Zn and 0.03 mg/mL Cd, respectively. The repeatability of this procedure is questionable at present for Zn and Cd concentrations of greater than 5%.

2. Polarographic procedure

2.1 Apparatus.

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

2.1.2 *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 is 15 x 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.

2.1.3 *Nitrogen cylinder and tubing.*

2.1.4 *Other apparatus:* pipets, 5, 15, 20, and 50 mL; three 200 mL volumetric flasks.

2.2 *Reagents.*

2.2.1 *Standard zinc solution* (1 mL = 0.0010 g of Zn): Dissolve 1.245 g of freshly ignited ZnO in 50 mL of hot HCl (1:10). Cool, dilute with water to 1000 mL in a volumetric flask, and mix.

2.2.2 *Standard cadmium solution* (1 mL = 0.0010 g of Cd): Dissolve 1.631 g of anhydrous CdCl₂ in 100 mL of hot water. Cool, dilute to 100 mL in a volumetric flask and mix.

2.2.3 *Gelatin solution* (2 g/1000 mL): Dissolve 2.00 g of gelatin in boiling water and dilute the clear solution to 1000 mL.

2.2.4 *Nitrogen* (with minimum oxygen content).

2.2.5 *NH₄Cl* (crystalline).

2.2.6 *HCl* (12 N).

2.2.7 *NH₄OH* (14.8 N).

2.2.8 *HNO₃* (15.7 N).

2.3 *Sampling and test specimen.*

2.3.1 From each test unit obtained in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product" (for paper) or TAPPI T 657 "Sampling of Fillers and Pigments" (for pigments), prepare a specimen sufficient to contain at least 10 mg of zinc or 10 mg of cadmium if present.

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

2.3.3 If the moisture content is unknown, determine it in accordance with TAPPI T 412 "Moisture in Paper and Paperboard."

2.4 *Procedure.*

2.4.1 Detailed information regarding the polarographic procedure may be found in the literature (1-3).

2.4.2 *Zinc and cadmium factors.*

2.4.2.1 Transfer 20.0 and 50 mL aliquots of the standard zinc and cadmium solutions, respectively, to each of two 200 mL 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 NH₄Cl and 5 mL of HCl, and dilute to approximately 150 mL with water. Add 15 mL of NH₄OH and 10 mL of gelatin solution. Cool, dilute to the mark with water, and mix.

2.4.2.2 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 specimens 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.

2.4.2.3 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.

2.4.2.4 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 amount of cadmium in grams. 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 settings used and plot these values against the amount of zinc in grams. The three points must fall approximately on a straight line for both metals.

2.4.2.5 Calculate the cadmium and zinc factors as follows:

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

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

where

- F_1 = cadmium per galvanometer scale division at full sensitivity, gx.
 C_1 = cadmium in the standard, g.
 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 = zinc per galvanometer scale division at full sensitivity, g.
 C_2 = zinc in the standard, g.
 R_2 = increase in galvanometer deflection when the potential is increased from -1.09 to -1.40 V for the standard.
 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.

2.4.3 Analysis of specimen. Transfer about 0.5 g of the dried specimen, weighed to the nearest 0.001 g, to a 400 mL beaker. Add 10 mL 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 mL of HCl , and 50 mL of water. Heat until solution is complete. Cool, transfer to a 200 mL volumetric flask, and dilute to approximately 150 mL with water. Add 15 mL of NH_4OH and 1 mL of gelatin solution. Cool, dilute to 200 mL, and continue in accordance with the procedure for determining the zinc and cadmium factors.

2.4.4 Calculation. Calculate the percentage of cadmium and zinc as follows:

$$\text{Cadmium, \%} = \frac{(A_1 - B_1) F_1}{W} \times 100$$

$$\text{Zinc, \%} = \frac{(A_2 - B_2) F_2}{W} \times 100$$

where

- A_1 = increase 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 = cadmium per galvanometer scale division at full sensitivity, g.
 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.
 F_2 = zinc per galvanometer scale division at full sensitivity, g.

3. Gravimetric and volumetric procedures

3.1 Apparatus.

3.1.1 For cadmium by the gravimetric procedure.

3.1.1.1 Platinum dish, evaporating about 50 mL.

3.1.1.2 Other apparatus: three 400 mL beakers; 25 and 50 mL graduated cylinders; filter funnel with fine filter paper.

3.1.2 For zinc by the volumetric procedure. As for cadmium and in addition: a 3 and a 5 mL pipet (or small graduated cylinder); medium filter paper; 50 mL buret.

3.2 Reagents.