Designation: E 396 – 05

Standard Test Methods for Chemical Analysis of Cadmium[1]

This standard is issued under the fixed designation E 396; 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.

Note—Corrections were made throughout and the year date changed on July 25, 2005.

1. Scope

1.1 These test methods cover the chemical analysis of cadmium having chemical compositions with the following limits:

Element	Concentration, max, %
Antimony	0.001
Arsenic	0.003
Copper	0.015
Lead	0.025
Silver	0.010
Thallium	0.003
Tin	0.010
Zinc	0.035

1.2 The test methods appear in the following order:

	Sections
Antimony by the Rhodamine B Photometric Method [0.0002 to 0.0010%]	62-72
Arsenic by the Molybdenum Blue Photometric Method [0.001 to 0.005%]	40-50
Copper by the Neocuproine Photometric Method [0.002 to 0.030%]	10-19
Copper, Lead, Silver, and Zinc by the Atomic Absorption Method [0.004 to 0.02% Cu, 0.01 to 0.05% Pb, 0.004 to 0.02 % Ag and 0.01 to 0.05% Zn]	51-61
Lead by the Dithizone Photometric Method [0.001 to 0.05%]	20-29
Thallium by the Rhodamine B Photometric Method [0.0003 to 0.005%]	30-39
Tin by the 8-Quinolinol Photometric Method [0.0025 to 0.0150%]	73-82

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.* Specific precautionary information is given in Section 6 and 25.8.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

B 440 Specification for Cadmium

D 1193 Specification for Reagent Water

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 173 Practices for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E 135.

4. Significance and Use

4.1 These test methods for the chemical analysis of cadmium are primarily intended to test such material for compliance with compositional specifications in Specification B 440. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Photometric Practice

5.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and reagents shall conform to the requirements prescribed in Practices E 50. Photometers shall conform to the requirements prescribed in Practice E 60.

5.2 Photometric practice prescribed in these methods shall conform to Practice E 60.

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Cu, Pb, Zn, Cd, Sn, Be, their Alloys and Related Metals.

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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.

[3] Withdrawn.

6. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E 50.

7. Sampling

7.1 Wrought products shall be sampled in accordance with Practice E 55. Cast products shall be sampled in accordance with Practice E 88. However, these test methods do not supersede any sampling requirements specified in a specific ASTM material specification.

8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places as directed in Practice E 29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practices E 173, unless otherwise noted in the precision section.

COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

10. Scope

10.1 This test method covers the determination of copper in concentrations from 0.002 to 0.030 %.

11. Summary of Test Method

11.1 Copper is separated as cuprous copper from other metals by extraction of the copper-neocuproine complex with chloroform. Photometric measurement is made at approximately 455 nm.

12. Concentration Range

12.1 The recommended concentration range is from 0.01 to 0.15 mg of copper for each 25 mL of solution, using a 1-cm cell.

NOTE 1—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

13. Stability of Color

13.1 The color develops within 5 min and the extracted complex is stable. However, because of the volatile nature of the solvent, it is advisable to take photometric readings promptly.

14. Interferences

14.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

15. Reagents

15.1 *Chloroform* ($CHCl_3$).

15.2 *Copper, Standard Solution* (1 mL = 0.01 mg Cu)—Dissolve 0.1000 g of copper (purity: 99.9 % min) in 10 mL of HNO_3(1 + 1). Add 25 mL of water, heat to boiling, and boil gently for 2 min to eliminate oxides of nitrogen. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 5.00 mL to a 500-mL volumetric flask. Add 1 mL of HNO_3(1 + 1), dilute to volume, and mix.

15.3 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 50 mL of water. Prepare fresh as needed.

15.4 *Metacresol Purple Indicator Solution (1 g/L)*—Dissolve 0.100 g of metacresol purple together with 1 pellet of sodium hydroxide (NaOH) in about 10 mL of water by warming. Dilute to 100 mL, and mix.

15.5 *Neocuproine Solution (1 g/L)*—Dissolve 0.10 g of neocuproine (2,9-dimethyl-1,10-phenanthroline hemihydrate) in 100 mL of either methanol or 95 % ethanol.

15.6 *Sodium Citrate Solution (300 g/L)*—Dissolve 300 g of sodium citrate dihydrate in water, dilute to 1 L, and mix.

15.7 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

16. Preparation of Calibration Curve

16.1 *Calibration Solution*:

16.1.1 Using pipets, transfer 2, 5, 10, 15, and 20 mL of copper solution (1 mL = 0.01 mg Cu) to five 150-mL beakers, and dilute to about 40 mL.

16.1.2 Add 2 drops of metacresol purple indicator solution, and then add HNO_3(1 + 1) dropwise to the red color change of the indicator. Proceed as directed in 16.3.

16.2 *Reference Solution*—Add 40 mL of water to a 150- mL beaker. Proceed as directed in 16.1.2.

16.3 *Color Development*:

16.3.1 Add 10 mL of $NH_2OH \cdot HCl$ solution, and stir. Add 10 mL of sodium citrate solution, and stir. Add NH_4OH to the purple color of the indicator (pH about 8.5). Add 5.0 mL of neocuproine solution, stir, and allow to stand for 5 min.

NOTE 2—The precipitate that may form upon addition of sodium citrate solution will redissolve when the pH is raised to 8.5 with NH_4OH.

16.3.2 Transfer to a 125-mL separatory funnel marked at 80 mL, and dilute to the mark with water. Add 25.0 mL of $CHCl_3$. Shake vigorously for 45 s, and allow the layers to separate. Draw off and discard about 1 mL of the $CHCl_3$ layer to rinse the stem of the separatory funnel.

16.4 *Photometry*:

16.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 455 nm (Note 3). Using the test cell, take the photometric readings of the calibration solutions.

NOTE 3—Avoid transfer of water to the absorption cell in the following manner. Insert a loose plug of sterilized absorbent cotton into the stem of each separatory funnel. Just prior to filling the absorption cell with the solution in the separatory funnel, discard about 1 mL of the $CHCl_3$ layer through the cotton plug and immediately transfer a suitable portion of the $CHCl_3$ layer into the dry absorption cell.

16.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 455 nm (Note 1). While maintaining this adjustment, take the photometric readings of the calibration solutions.

16.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of copper per 25 mL of solution.

17. Procedure

17.1 *Test Solution*—Transfer a 0.5-g sample, weighed to the nearest 1 mg, to a 150-mL beaker. Add 5 mL of HNO_3(1 + 1). When dissolution is complete, add 20 mL of water and boil gently to eliminate oxides of nitrogen. Cool, dilute to about 40 mL, and add 2 drops of metacresol purple indicator solution. Proceed as directed in 17.3.

17.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amount of all reagents with the sample omitted, for use as the reference solution.

17.3 *Color Development*—Proceed as directed in 16.3.

17.4 *Photometry*—Proceed as directed in 16.4.

18. Calculation

18.1 Convert the net photometric reading of the test solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, \%} = A/(B \times 10) \quad (1)$$

where:

A = copper found in the 25 mL of final test solution, mg, and

B = sample represented in 25 mL of final test solution, g.

19. Precision and Bias

19.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 1.

19.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

19.3 E 173 has been replaced by Practice E 1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E 1601.

LEAD BY THE DITHIZONE PHOTOMETRIC METHOD

20. Scope

20.1 This test method covers the determination of lead in concentrations from 0.001 to 0.05 %.

21. Summary of Test Method

21.1 Lead dithizonate is extracted with chloroform from a buffered cyanide solution at a pH of 8.5. The excess dithizone in the chloroform is then removed by extraction with an ammoniacal sulfite solution. Photometric measurement is made at approximately 515 nm.

TABLE 1 Statistical Information

Specimen	Copper Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.0074	0.003	0.0013
2	0.0173	0.0018	0.0031

22. Concentration Range

22.1 The recommended concentration range is from 0.005 to 0.050 mg of lead for each 25 mL of solution, using a 1-cm cell (Note 1).

23. Stability of Color

23.1 The color is stable for at least 2 h if protected from direct sunlight; however, because of the volatile nature of the solvent, it is advisable to take photometric readings promptly.

24. Interferences

24.1 The elements ordinarily present in cadmium do not interfere if their concentrations are under the maximum limits shown in 1.1.

25. Reagents

25.1 *Ascorbic Acid*.

25.2 *Bromine Water* (*Saturated*).

25.3 *Chloroform* ($CHCl_3$).

25.4 *Dithizone Solution (0.01 g/L of $CHCl_3$)*—Dissolve 0.05 g of dithizone (diphenylthiocarbazone) in a freshly opened 700-g bottle of $CHCl_3$. Mix several times over a period of several hours. Store in a cool, dark place. Just before use, dilute 50 mL of this solution to 500 mL with $CHCl_3$ in a dry borosilicate bottle or flask, and mix.

25.5 *Lead, Standard Solution (1 mL = 0.005 mg Pb)*—Dissolve 0.1000 g of lead (purity: 99.9 % min) in 20 mL of HNO_3(1 + 1), and boil gently to eliminate oxides of nitrogen. Cool, transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 5.00 mL to a 500-mL volumetric flask, dilute to volume, and mix. Prepare the final solution fresh as needed.

25.6 *Metacresol Purple Indicator Solution (1 g/L)*—Proceed as directed in 15.4.

25.7 *Potassium Cyanide Solution (200 g/L)*—Dissolve 200 g of potassium cyanide (KCN) (low in lead and sulfide) (**Warning** —See 25.8) in water, and dilute to 1 L. Bring to a boil and boil for 2 min. Cool, and store in a polyethylene bottle.

25.8 *Sodium Sulfite Wash Solution*—Dissolve 1 g of sodium sulfite (Na_2SO_3) in about 300 mL of water in a 1-L volumetric flask. Add 20 mL of the KCN solution and 475 mL of NH_4OH (1 + 1) which has been prepared from a freshly opened bottle. Dilute to volume, and mix. Store in a polyethylene bottle. (**Warning**—The preparation, storage, and use of KCN solutions require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical and its solutions. Do not allow solutions containing cyanide to come in contact with strongly acidic solutions. Work in a well-ventilated hood. Refer to Section 6 of Practices E 50.)

25.9 *Sodium Tartrate Solution (250 g/L)*—Dissolve 50 g of sodium tartrate dihydrate in water, and dilute to 200 mL.

25.10 *Thioglycolic Acid Solution (1 + 99)*—Dilute 1.0 mL of thioglycolic acid (mercaptoacetic acid) to 100 mL with water. Refrigerate both the concentrated and diluted acid solutions. Do not use concentrated acid that is more than 1 year old, nor diluted acid that has stood for more than 1 week.