Designation: ~~E396 – 12ε1~~ E396 – 17

Standard Test Methods for Chemical Analysis of Cadmium[1]

This standard is issued under the fixed designation E396; 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.

~~ε[1] NOTE—Editorial corrections were made throughout in August 2012.~~

1. Scope

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

Element	Composition, 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 Spectrophotometric Method [0.0002 % to 0.0010 %]	62 – 72
Arsenic by the Molybdenum Blue Spectrophotometric Method [0.001 % to 0.005 %]	40 – 50
Copper by the Neocuproine Spectrophotometric Method [0.002 % to 0.030 %]	10 – 19
Copper, Lead, Silver, and Zinc by the Atomic Absorption Spectrometry 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 Spectrophotometric Method [0.001 % to 0.05 %]~~	~~20 – 29~~
Lead by the Dithizone Spectrophotometric Method [0.001 % to 0.05 %]	20 – 29
~~Thallium by the Rhodamine B Spectrophotometric Method [0.0003 % to 0.005%]~~	~~30 – 39~~
Thallium by the Rhodamine B Spectrophotometric Method [0.0003 % to 0.005 %]	30 – 39
Tin by the 8-Quinolinol Spectrophotometric 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary information is given in Section 6, , , and .

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

B440 Specification for Cadmium

[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, Precious Metals, 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.

D1193 Specification for Reagent Water
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]
E1601 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 E135.

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 B440. 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 Spectrophotometric 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 E50. Spectrophotometers shall conform to the requirements prescribed in Practice E60.

5.2 Spectrophotometric practice prescribed in these methods shall conform to Practice E60.

5.3 *Reagents*—

5.3.1 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193. Type III or Type IV may be used if they effect no measurable change in the blank or sample.

5.3.2 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

7. Sampling

7.1 Wrought products shall be sampled in accordance with Practice E55. Cast products shall be sampled in accordance with Practice E88. 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~~Rounding of test results obtained using this test method shall be performed in accordance with Practice E29~~of places as directed in Practice~~, Rounding Method, unless an alternative ~~E29.~~rounding method is specified by the customer or applicable material specification.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practices E173, unless otherwise noted in the precision section.

9.2 Practice E173 has been replaced by Practice E1601. The reproducibility index, R_2, of Practice E173 corresponds to the reproducibility index, R, of Practice E1601. The repeatability index, R_1 , of Practice E173, corresponds to the repeatability index, r, of Practice E1601.

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

~~10. Scope~~

~~10.1 This test method covers the determination of copper content from 0.002 % to 0.030 %.~~

[3] The last approved version of this historical standard is referenced on www.astm.org.

[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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD

10. Scope

10.1 This test method covers the determination of copper content 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. Spectrophotometric absorbance measurement is made at ~~approximately~~ 455 nm.

12. Concentration Range

12.1 The recommended concentration range is from 0.01 mg 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 spectrophotometric readings promptly.

14. Interferences

14.1 The elements ordinarily present do not interfere if their contents 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_2~~OH · HCl~~OH·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)~~ 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 D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.~~

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_2~~OH · HCl~~OH·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 *Spectrophotometry:*

16.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at ~~approximately~~ 455 ~~nm~~ (nm. ~~Note 3~~). Using the test cell, take the spectrophotometric absorbance 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.~~

16.4.1.1 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 Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at ~~approximately~~ 455 nm (Note 1). While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

16.5 *Calibration Curve*—Plot the net spectrophotometric absorbance 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 *Spectrophotometry*—Proceed as directed in 16.4.

18. Calculation

18.1 Convert the net spectrophotometric absorbance 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*~~—*Bias*—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 E173 has been replaced by Practice E1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.~~

LEAD BY THE DITHIZONE SPECTROPHOTOMETRIC METHOD

~~**20. Scope**~~

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

20. Scope

20.1 This test method covers the determination of lead in content 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. ~~spectrophotometric~~ Spectrophotometric absorbance measurement is made at ~~approximately~~ 515 nm.

TABLE 1 Statistical Information

Specimen	Copper Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
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 mg 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 spectrophotometric readings promptly.

24. Interferences

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

25. Reagents

25.1 *Ascorbic ~~Acid.~~Acid* ($C_6H_8O_6$).

25.2 *Bromine Water,* ~~(~~saturated.~~Saturated).~~

25.3 *Chloroform* ($CHCl_3$).

25.4 *Dithizone Solution (0.01 g/L ~~of~~in $CHCl_3$)*—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) 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 8 of Practices E50.)

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.

~~25.11 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.~~

26. Preparation of Calibration Curve

26.1 *Calibration Solutions*—Using pipets, transfer (1, 2, 3, 5, and 10)-mL volumes of lead solution (1 mL = 0.005 mg Pb) to 125-mL separatory funnels (set No. 1). Dilute to 15 mL with water and add 1 drop of metacresol purple indicator ~~solution.~~solution (Note 3).

26.2 *Reference Solution*—Transfer 15 mL of water to a 125-mL separatory funnel (one of set No. 1), and add 1 drop of metacresol purple indicator solution.

26.3 *Color Development:*

26.3.1 Add NH_4OH (1 + 1) dropwise, with swirling, until the indicator color begins to change from red to yellow. Add 2 drops of HNO_3. Extract with successive 10-mL portions of dithizone solution until the color of the dithizone remains unchanged. Discard all extracts.

26.3.2 Add 2 mL of sodium tartrate solution, about 20 mg of ascorbic acid, and 2 drops of thioglycolic acid solution (1 + 99). Add NH_4OH (1 + 1), while mixing, until the solution turns yellow. Add 20 mL of KCN solution **(Warning**—see) and mix. Add 10 mL of acetic acid (1 + 4), and mix.

NOTE 3—The indicator color should be purple and the pH approximately 8.5. Some lots of KCN may give a pH lower than 8.0 or higher than 9.0. Should this occur, use NH_4OH (1 + 1) or acetic acid (1 + 4) to adjust the pH to 8.5 ± 0.5.

26.3.3 Dilute to 60 mL with water, add 15.0 mL of dithizone solution, and shake vigorously for 1 min. Allow the layers to separate for 1 min. Transfer the lower layer to another 125-mL separatory funnel (set No. 2) containing 50 mL of the sodium sulfite

wash solution. Add an additional 10.0 mL of dithizone solution to the original separatory funnel (set No. 1) and shake for 1 min. Again allow the layers to separate for 1 min and add this second portion to the No. 2 separatory funnel.

26.3.4 Shake the combined organic layers in the No. 2 funnel for 1 min and allow the layers to separate for 1 min. Draw off and discard a few millilitres of the lower layer to rinse out the stem of the funnel.

26.4 *Spectrophotometry:*

26.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at ~~approximately~~ 515 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions.

26.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at ~~approximately~~ 515 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

26.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of lead per 25 mL of solution.

27. Procedure

27.1 *Test Solution*—Transfer a 5-g sample, weighed to the nearest 10 mg, to a 125-mL beaker. Add 25 mL of HNO_3 (1 + 1). When dissolution is complete, add several drops of HCl and 1 mL of saturated bromine water. Boil gently to eliminate the oxides of nitrogen and to remove excess bromine. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer a 2-mL to 10-mL portion (containing between 0.005 mg and 0.050 mg of Pb) to a 125-mL separatory funnel. Dilute to 15 mL with water, and add 1 drop of metacresol purple indicator solution. Proceed as directed in 27.3.

27.2 *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.

27.3 *Color Development*—Proceed as directed in 26.3.

27.4 *Spectrophotometry*—Proceed as directed in 26.4.

28. Calculation

28.1 Convert the net spectrophotometric absorbance reading of the test solution to milligrams of lead by means of the calibration curve. Calculate the percentage of lead as follows:

$$\text{Lead, \%} = A/(B \times 10) \quad (2)$$

where:

A = lead in the 25 mL of final test solution, mg, and
B = sample represented in 25 mL of final test solution, g.

29. Precision and Bias

29.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 2.

29.2 ~~*Accuracy*—~~*Bias*—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.

~~29.3 E173 has been replaced by Practice E1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.~~

THALLIUM BY THE RHODAMINE B SPECTROPHOTOMETRIC METHOD

~~30. Scope~~

~~30.1 This test method covers the determination of thallium in concentrations from 0.0003 % to 0.005 %. Higher and lower amounts can be determined by varying the sample size or the dilution within reasonable limits. However, the standard solutions used to establish the calibration curve must contain about the same amount of cadmium as the test solution.~~

TABLE 2 Statistical Information

Specimen	Lead Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1	0.0066	0.0009	0.0020
2	0.0236	0.0025	0.0053