



Designation: E 54 – 80 (Reapproved 1996)

# Standard Test Methods for Chemical Analysis of Special Brasses and Bronzes<sup>1</sup>

This standard is issued under the fixed designation E 54; 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 procedures for the chemical analysis<sup>2</sup> of the commercial alloys known as copper-base alloy ingots for sand castings, forging rods, bars, and shapes; aluminum brass; manganese bronze; phosphor bronze; copper-silicon alloys; and similar alloys having chemical compositions within the following limits.<sup>2</sup>

Element	Concentration Range, %
Copper, %	50 and over
Lead, %	0.0 to 27
Tin, %	0.0 to 20
Silicon, %	0.0 to 5
Aluminum, %	0.0 to 12
Nickel, %	0.0 to 5
Iron, %	0.0 to 5
Manganese, %	0.0 to 6
Sulfur, %	0.0 to 0.1
Phosphorus, %	0.0 to 1.0
Arsenic, %	0.0 to 1.0
Antimony, %	0.0 to 1.0
Zinc <sup>A</sup>	0.0 to 50

<sup>A</sup> In the case of copper-base alloys containing 5.0 % and over of zinc, the zinc is usually calculated by difference.

Whenever possible the technique and procedures for analysis should be checked against a National Institute of Standards and Technology standard sample having a composition comparable to the material being analyzed.

1.2 The test methods appear in the following order:

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.07 on Cu and Cu Alloys.

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<sup>2</sup> For procedures for sampling wrought products, see ASTM Practice E 55, Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition (*Annual Book of ASTM Standards*, Vol 03.05). For procedures for sampling cast products, see ASTM Practice E 88, Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition (*Annual Book of ASTM Standards*, Vol 03.05). For procedures for the chemical analysis of other brasses, see ASTM Method E 36, for Chemical Analysis of Brasses (Discontinued; Replaced by Methods E 478, *Annual Book of ASTM Standards*, Vol 03.05). For photometric procedures applicable to special brasses and bronzes, see ASTM Method E 62, Photometric Methods for Chemical Analysis of Copper and Copper Alloys (*Annual Book of ASTM Standards*, Vol 03.05).

<sup>2a</sup> Discontinued as of June 30, 1975.

<sup>2b</sup> Discontinued as of Aug. 27, 1976.

<sup>2c</sup> Discontinued as of April 27, 1979.

<sup>2d</sup> Discontinued as of May 30, 1980.

	Sections
Copper, or Copper and Lead Simultaneously, by the Electrolytic Method	2 <sup>a</sup>
Lead:	
Electrolytic Method	2 <sup>c</sup>
Sulfate Method	2 <sup>b</sup>
Tin by the Iodometric Titration Method	2 <sup>b</sup>
Silicon:	
Sulfuric Acid Dehydration Method	18 to 19
Perchloric Acid Dehydration Method	20 to 22
Aluminum by the Gravimetric Method	23 to 26
Nickel by the Dimethylglyoxime Method	2 <sup>a</sup>
Iron by the Dichromate Method	30 to 33
Manganese:	
Bismuthate Method	2 <sup>b</sup>
Persulfate Method	2 <sup>b</sup>
Bromate Method	2 <sup>d</sup>
Phosphorus by the Alkalimetric Method	2 <sup>b</sup>
Arsenic by the Distillation-Bromate (Moffat) Method	46 to 49
Arsenic and Antimony by the Distillation - Iodometric Method	2 <sup>d</sup>
Antimony and Tin by the Manganese Coprecipitation Method	2 <sup>d</sup>
Sulfur:	
Direct Combustion - Iodate Method	56 to 59
Evolution Method	60 to 63
Tin by the Hypophosphite Reduction (Volumetric) Method	64 to 71
Zinc by the Ethylenediamine Tetraacetate (Titrimetric) Method	2 <sup>a</sup>
Lead by the Disodium (Ethylenedinitrilo) Tetraacetate Titrimetric Method	2 <sup>b</sup>

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.* For precautions to be observed in these methods, refer to Practices E 50.

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>3</sup>

## 3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications. 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.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.05.

#### 4. Apparatus and Reagents

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50.

#### COPPER, OR COPPER AND LEAD SIMULTANEOUSLY, BY THE ELECTROLYTIC TEST METHOD

(This test method, which consisted of Sections 5 through 8 of this standard, was discontinued in 1975.)

#### LEAD BY THE ELECTROLYTIC TEST METHOD

(This test method, which consisted of Sections 9 and 10 of this standard, was discontinued in 1979.)

#### LEAD BY THE SULFATE TEST METHOD

(This test method, which consisted of Sections 11 and 12 of this standard was discontinued in 1976.)

#### TIN BY THE IODIMETRIC TITRATION TEST METHOD

(This test method, which consisted of Sections 13 through 15, was discontinued in 1976.)

#### ZINC BY THE OXIDE OR FERROCYANIDE TEST METHOD

(This test method, which consisted of Sections 16 and 17 of this standard, was discontinued in 1975.)

#### SILICON BY THE SULFURIC ACID DEHYDRATION TEST METHOD

##### 18. Procedure

18.1 *Solution of Samples Containing Under 1.0 % of Silicon*—Transfer 5.0 g of the sample to a 340-mL porcelain casserole, cover, and dissolve in 10 mL of HCl and 20 mL of HNO<sub>3</sub>. When solution of the sample is complete, add 30 mL of H<sub>2</sub>SO<sub>4</sub>.

18.2 *Solution of Samples Containing 1.0 to 5.0 % of Silicon*—Transfer 1.00 g of the sample to a 340-mL porcelain casserole, cover, and dissolve in 5 mL of HCl and 10 mL of HNO<sub>3</sub>. When solution of the sample is complete, add 15 mL of H<sub>2</sub>SO<sub>4</sub>.

18.3 Place the casserole on a hot plate and, with a cover glass placed slightly to one side, evaporate until the HCl and HNO<sub>3</sub> have been expelled. Then, with the casserole well covered, heat strongly for several minutes while dense white fumes are being driven off. Allow to cool, add carefully 100 mL of HCl (1 + 5), and bring to a boil. If lead is present in the alloy, add 5 g of NH<sub>4</sub>Cl and continue the boiling until all PbSO<sub>4</sub> is in solution. Filter the solution immediately through an 11-cm close-texture, ashless paper, scrubbing the casserole with a policeman and washing with HCl (1 + 99) to completely transfer the residue to the paper. Wash the paper and residue (Note 1) thoroughly with HCl (1 + 99) and reserve.

NOTE 1—If black silicides, such as those of manganese or iron, are present in the residue, ignite in accordance with 18.3. Fuse the residue

with Na<sub>2</sub>CO<sub>3</sub> and a crystal of NaNO<sub>3</sub> or KNO<sub>3</sub>. Dissolve the melt in water and H<sub>2</sub>SO<sub>4</sub> and continue in accordance with 18.3. Combine the filtrate with the original filtrate from 18.3, and complete the determination in accordance with 18.4 to 18.8.

18.4 Return the filtrate to the casserole and treat in accordance with 18.3.

18.5 Transfer the two papers and residues to a platinum crucible. Ignite at a low temperature until the paper has been consumed, and then at 1100 to 1150°C to constant weight (see Note 1). Cool in a desiccator and weigh.

18.6 Add 1 or 2 drops of H<sub>2</sub>SO<sub>4</sub>(1 + 1) and sufficient HF (2 to 5 mL) to dissolve the residue, and evaporate the solution slowly to dense white fumes. Continue to heat the crucible until all of the free H<sub>2</sub>SO<sub>4</sub> has been expelled, and then ignite at 1000°C for 5 min. Cool in a desiccator and weigh. The loss in weight represents SiO<sub>2</sub>.

18.7 *Blank*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

18.8 *Calculation*—Calculate the percentage of silicon as follows:<sup>4</sup>

$$\text{Silicon, \%} = [(A - B) \times 0.4675] / C \times 100$$

where:

*A* = grams of SiO<sub>2</sub>,

*B* = correction for blank, g, and

*C* = grams of sample used.

#### 19. Precision and Bias

19.1 This test method was originally approved for publication before the inclusion of precision and accuracy statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and accuracy of this test method is adequate for the contemplated use.

#### SILICON BY THE PERCHLORIC ACID DEHYDRATION TEST METHOD

##### 20. Reagents

20.1 *Hydrogen Peroxide (3 %)*.

##### 21. Procedure

21.1 *Solution of Samples Containing Under 1.0 % of Silicon*—Transfer 5.0 g of the sample to a 340-mL porcelain casserole, cover, and dissolve in 10 mL of HCl and 20 mL of HNO<sub>3</sub>. When solution of the sample is complete, add 40 mL of HClO<sub>4</sub>.

21.2 *Solution of Samples Containing 1.0 to 5.0 % of Silicon*—Transfer 1.00 g of the sample to a 340-mL porcelain casserole, cover, and dissolve in 5 mL of HCl and 10 mL of HNO<sub>3</sub>. When solution of the sample is complete, add 25 mL of HClO<sub>4</sub>.

21.3 If appreciable amounts of tin or antimony, or both, are present, add, while stirring, 15 to 30 mL of HBr to volatilize these constituents. Place the casserole on a hot plate and evaporate to white fumes. Heat the covered casserole strongly

<sup>4</sup> For the recommended procedure for rounding calculated values, see 3.4 and 3.5 of ASTM Recommended Practice E 29, Indicating Which Places of Figures Are to Be Considered Significant in Specified Limiting Values, *Annual Book of ASTM Standards*, Vol 14.02.

for 15 min while copious white fumes are being driven off. Allow to cool, but not to become cold, add 100 to 150 mL of hot water, stir well, and heat until the salts are dissolved. If manganese dioxide is present, bring it into solution with a few drops of  $\text{H}_2\text{O}_2$  (3 %). Filter the solution immediately through an 11-cm, close-texture, ashless paper, scrubbing the casserole with a policeman and washing with HCl (1 + 99) to completely transfer the residue to the paper. Wash the paper and residue (see Note 1) thoroughly with HCl (1 + 99) and reserve.

21.4 Return the filtrate to the casserole and treat in accordance with 21.3.

21.5 Complete the determination of silicon as described in 21.5–21.8.

## 22. Precision and Bias

22.1 This test method was originally approved for publication before the inclusion of precision and accuracy statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and accuracy of this test method is adequate for the contemplated use.

## ALUMINUM BY THE GRAVIMETRIC TEST METHOD

(Aluminum Content 0.10 % and Over)

### 23. Apparatus

23.1 *Mercury Cathode Cell*—Apparatus No. 10B.

23.2 *Filtering Crucible*—A 35-mL fritted-glass crucible of fine porosity (Apparatus No. 2).

### 24. Reagents

24.1 *Ferric Chloride Solution* (100 g/L)—Dissolve 100 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water and dilute to 1 L.

24.2 *Methyl Red Indicator Solution* (0.2 g/L)—Dissolve 0.02 g of methyl red indicator in 100 mL of hot water, cool, and filter.

24.3 *Bromcresol Purple Indicator Solution* (0.4 g/L)—Dissolve 0.04 g of bromcresol purple indicator in 100 mL of hot water, cool, and filter.

24.4 *8-Hydroxyquinoline Solution* (25 g/L)—Add 50 mL of acetic acid to 25 g of 8-hydroxyquinoline and warm gently to effect solution. Pour the resulting solution into 900 mL of water at 60°C. Cool, filter if necessary, and dilute to 1 L.

### 25. Procedure

25.1 For samples containing 0.5 % and over of aluminum, the electrolyte reserved from the determination of copper on a 2-g sample may be used, or a separate sample may be taken. If the electrolyte is used, continue in accordance with 25.10. If a separate sample (Note 2) is taken, proceed in accordance with 25.2 or 25.3.

NOTE 2—The preliminary separation of aluminum from interfering elements avoids too great contamination of mercury during the subsequent electrolysis. In certain cases, this may not be objectionable if the sample is not larger than 1 g, and a direct separation may be carried out in the mercury cathode cell as follows: Dissolve 1.000 g of the sample as described in 25.3. Continue as described in 25.4, 25.5, or 25.6 except that before dilution the sample shall twice be taken to dense white fumes to remove the last traces of  $\text{HNO}_3$ , and the final volume shall be kept below 75 mL. Transfer the solution to the mercury cell and electrolyze in accordance with 25.10. Continue in accordance with 25.11–25.14.

25.2 For samples containing 0.1 to 1.0 % of aluminum, transfer 5.00 g of the sample to a 400-mL beaker and decompose with 5 mL of HCl and 20 mL of  $\text{HNO}_3$ , adding more HCl if necessary. Continue in accordance with 25.4, 25.5, or 25.6.

25.3 For samples containing 1.0 % and over of aluminum, transfer 1.000 g of the sample to a 250-mL beaker and decompose with 5 mL of HCl and 5 mL of  $\text{HNO}_3$ . Continue in accordance with 25.4, 25.5, or 25.6.

25.4 If an appreciable amount of silicon is present, add 5 to 15 mL of  $\text{H}_2\text{SO}_4$  and evaporate until the HCl and  $\text{HNO}_3$  have been expelled. Heat strongly for several minutes while dense white fumes are being driven off. Allow to cool and dissolve soluble salts in a small amount of water. Transfer to a platinum dish, add sufficient HF to volatilize the silicon, and heat slowly to dense white fumes. Cool and transfer the contents of the dish to the original beaker and dilute to 50 mL with  $\text{H}_2\text{SO}_4$  (1 + 19). Heat to boiling, allow to settle, and filter if a precipitate is present. Filter through an 11-cm fine paper, wash, and discard any residue. Continue in accordance with 25.7 if 5 g of the sample were used, or electrolyze in accordance with 25.8 if 1 g of the sample was used.

25.5 In the absence of an appreciable amount of silicon and in the presence of an appreciable amount of lead, add 5 to 10 mL of  $\text{H}_2\text{SO}_4$  and evaporate to dense white fumes. Cool and dilute to 150 mL. Filter off the  $\text{PbSO}_4$ . Continue in accordance with 25.7 if 5 g of the sample were used, or electrolyze in accordance with 25.8 if 1 g of the sample was used.

25.6 In the absence of appreciable amounts of silicon and lead, add 20 mL of water and heat gently until brown fumes have been expelled. Wash down the cover glass and sides of the beaker and dilute to approximately 150 mL. Continue in accordance with 25.7 if 5 g of the sample were used, or electrolyze in accordance with 25.8 if 1 g of the sample was used.

25.7 If there is insufficient iron in the alloy to gather the aluminum, add 2 mL of  $\text{FeCl}_3$  solution (100 g/L). Add  $\text{NH}_4\text{OH}$  until the solution is slightly but distinctly ammoniacal, and bring to a boil. Allow the precipitate to settle on the steam bath for 5 min, filter on a loose-texture paper, and wash the beaker and precipitate with hot  $\text{NH}_4\text{Cl}$  solution (10 g/L) until most of the blue copper salts have been washed out. Place the paper and precipitate in the original beaker, and add 5 mL of  $\text{H}_2\text{SO}_4$  and 20 mL of  $\text{HNO}_3$ . Heat until all organic matter is destroyed, adding small quantities of  $\text{HNO}_3$  as required. Evaporate to dense white fumes. Cool, wash down the cover glass and sides of the beaker with water, and evaporate to dense white fumes again to remove the last traces of  $\text{HNO}_3$ . Continue in accordance with 25.10.

25.8 Add 2 mL of  $\text{HNO}_3$ , and remove the copper by electrolysis. Reserve the electrolyte.

25.9 To the electrolyte or a suitable aliquot of it, reserved in accordance with 25.8, add sufficient  $\text{H}_2\text{SO}_4$  to bring the total content of  $\text{H}_2\text{SO}_4$  to 5 mL and evaporate to dense white fumes. Allow the solution to cool, wash down the sides of the beaker with water, and evaporate again to dense white fumes to remove the last traces of  $\text{HNO}_3$ .

25.10 Cool the solution obtained in accordance with 25.7 or