



Standard Test Methods for Chemical Analysis of Copper-Nickel and Copper-Nickel-Zinc Alloys¹

This standard is issued under the fixed designation E 75; 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 of copper-nickel and copper-nickel-zinc alloys having chemical compositions within the following limits:²

Element	Concentration Range, %
Copper	40 and over
Nickel ^A	10 to 50
Zinc ^B	0 to 40
Lead	0 to 15
Tin	0 to 10
Iron	0.00 to 2
Manganese	0.00 to 2
Cobalt	0.00 to 0.5

^A Includes cobalt.

^B In the case of copper-base alloys containing 5 % 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:

	Sections
Cobalt:	
Alpha-Nitroso-Beta-Naphthol Method	26 to 28
Nitroso-R-Salt (Photometric) Method	29 to 37
Copper, or Copper and Lead Simultaneously, by the Electrolytic Method	2 ^a
Iron:	
Dichromate Method	38 to 40
Thiocyanate (Photometric) Method	2 ^a
Salicylate (Photometric) Method	2 ^a
Lead:	
Electrolytic Method	12 to 15
Sulfate Method	2 ^b
Manganese:	
Persulfate Method	2 ^b
Periodate (Photometric) Method	59 to 66

¹ 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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² For procedures for the chemical analysis of nickel-copper alloys containing 50 % and over of nickel, see ASTM Methods E 76, for Chemical Analysis of Nickel-Copper Alloys, *Annual Book of ASTM Standards*, Vol 03.05.

^{2a} Discontinued as of June 30, 1975.

^{2b} Discontinued Aug. 27, 1976.

Nickel by the Dimethylglyoxime Method
Tin by the Iodimetric Titration Method
Zinc by the Oxide or Ferrocyanide Method

Sections

2^a

2^b

2^a

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 test methods, refer to Practices E 50E 50.

2. Referenced Documents

2.1 ASTM Standards:

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance With Specifications³

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition⁴

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition⁴

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.

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 50E 50, except that photometers shall conform to the requirements prescribed in Practice E 60E 60.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

5. Photometric Practice

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

6. Sampling

6.1 Wrought products shall be sampled in accordance with Practice E 55E 55. Cast products shall be sampled in accordance with Practice E 88E 88.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method given in 3.4 and 3.5 of Practice E 29E 29.

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

(This test method, which consisted of Sections 8-11 of this standard, was discontinued in 1975.)

NOTE 1—Sections 8-11 of this standard were removed as a part of the revision of E75 approved June 30, 1975. Since they are no longer an approved part of this standard, the sections are included here for reference purposes only. Subcommittee E03.05 is in the process of updating these methods.

8. Apparatus

8.1 *Electrodes for Electroanalysis*—Apparatus No. 9.

9. Reagents

- 9.1 *Sodium Hydroxide Solution* (250 g NaOH/L).
- 9.2 *Sodium Sulfide Solution* (250 g Na₂S/L).
- 9.3 *Sodium Sulfide Solution* (20 g Na₂S/L).
- 9.4 *Sulfamic Acid Solution* (100 g/L).

10. Procedure for Alloys Containing Under 6 % of Lead

NOTE 2—If more than 6 % of lead is present, the copper only shall be determined by this procedure as the anode deposit is not sufficiently adherent for safe handling. The lead shall then be determined on a separate sample as described in the sulfate method, Sections 16 and 17.

10.1 Transfer 2.0000 g of the sample to a 250-mL beaker, cover, and dissolve in 25 mL of HNO₃(1 + 1). When dissolution is complete, boil gently to expel brown fumes. Add 50 mL of hot water and observe the clarity of the solution. If the solution is clear, proceed as described in 10.5. If enough tin is present at this point to form a cloud, proceed as described in 10.2 and 10.3 or 10.2 and 10.4.

10.2 Allow to stand on a steam bath for 1 h or until the precipitate has coagulated. Add paper pulp and filter off the metastannic acid through a fine paper into a 250-mL beaker. Wash several times with hot HNO₃ (1 + 99) and reserve the filtrate and washings.

10.3 Transfer the filter paper and contents to the original beaker and add 15 mL of H₂SO₄ and 15 mL of HNO₃. Heat until all organic matter is decomposed, adding additional HNO₃ as necessary, and finally evaporate to fumes. Transfer the digested solution to a 400-mL beaker and dilute to 250 mL. Add NaOH solution until the solution is alkaline and the tin hydroxide has dissolved. Add 20 mL of Na₂S solution (250 g

Na₂S/L), stir thoroughly, and digest on the steam bath for several hours, or until the supernatant liquid is clear. Cool to room temperature, filter through a fine paper, and wash the precipitate with Na₂S solution (20 g Na₂S/L). Dissolve the residue in a few millilitres of HNO₃ (1 + 1), neutralize with NH₄OH, and redissolve any precipitate with a minimum of HNO₃ (1 + 1). Combine with the reserved filtrate (10.2) and continue in accordance with 10.5.

10.4 An alternative method for recovering copper and lead is to return the metastannic acid and paper obtained as described in 10.2 to the original beaker, add 15 to 20 mL of HNO₃ and 10 to 15 mL of HClO₄, heat to copious white fumes, and boil to destroy organic matter. Cool, wash the cover glass and sides of the beaker, and add 15 to 25 mL of HBr. Heat to copious white fumes to volatilize the tin. If the solution is not clear, repeat the treatment with HBr. Evaporate the solution to near dryness, cool, and dissolve the residue in a few millilitres of water. Combine with the reserved filtrate (10.2) and continue in accordance with 10.5.

10.5 Add 1 drop of HCl (1 + 99) and 5 mL of sulfamic acid solution and dilute to 150 mL. Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze overnight at a current density of 0.5 A/dm² or for a short period at a current density of 4 A/dm²(Note 3). The more rapid procedure requires the use of gauze cathodes. After the blue color of the copper has disappeared, wash down the cover glasses, electrodes, and sides of the beaker, and continue the electrolysis until deposition of the copper is complete, as indicated by failure to plate on a new surface when the level of the solution is raised. When no copper appears, it can be assumed that all the lead also has been deposited (Note 4). Reserve the electrolyte.

NOTE 3—When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes generally available may be employed.

NOTE 4—If the electrolyte is not to be used for subsequent determinations, remove a few drops of the solution, place on a porcelain spot plate, and treat with saturated H₂S solution. Continue electrolysis until no CuS precipitate is observed.

10.6 When deposition of the copper is complete, with the current still on, lower the beaker slowly, while washing the cathode with water. Remove the cathode, rinse it in water, and dip it in two successive baths of ethanol or methanol. Dry in an oven at 110°C for 3 to 5 min, cool, and weigh the deposit as metallic copper.

10.7 If lead is being determined, remove the anode, rinse thoroughly with water, and dry at 110 to 120°C for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit.

10.8 Correction must be made for manganese, which is frequently present in these alloys and some of which may codeposit with the lead. Place the anode in a 150-mL beaker and dissolve the deposit in 20 mL of HNO₃ (1 + 1) and 1 mL of H₂O₂ (3 %). Remove the anode and wash with water. Add 5 mL of H₃PO₄ and boil for 5 to 10 min. Determine manganese either photometrically by the periodate method (Sections 31–38) or volumetrically by the persulfate method (Sections 56 to 58).

10.9 *Calculation*—Calculate the percentages of copper and lead as follows:

$$\text{Copper, \%} = (A/B) \times 100$$

$$\text{Lead, \%} = [(C - 1.58 D) \times 0.866]/B \times 100$$

where:

A = grams of copper,

B = grams of sample used,

C = grams of combined deposit of PbO₂ plus MnO₂, and

D = grams of manganese.

11. Precision and Bias

11.1 This 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 method is adequate for the contemplated use.

LEAD BY THE ELECTROLYTIC TEST METHOD

12. Apparatus

12.1 *Electrodes for Electroanalysis*—Apparatus No. 9. Use the larger electrode as the anode.

13. Procedure for Alloys Containing Under 0.05 % of Tin

13.1 *Solution of Samples Containing Under 0.1 % of Lead*—Transfer 10 g of the sample to a 400-mL beaker, cover, and dissolve in 60 mL of HNO₃ (1 + 1). When dissolution is complete, boil gently to expel brown fumes. Wash down the cover glass and the sides of the beaker and dilute to 250 mL.

13.2 *Solution of Samples Containing 0.1 to 6 % of Lead (see Note 2)*—Transfer 1.000 g of the sample to a 250-mL beaker, cover, and dissolve in 20 mL of HNO₃ (1 + 1). When dissolution is complete, boil gently to expel brown fumes. Wash down the cover glass and the sides of the beaker and dilute to 150 mL.

13.3 Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze for 2 h at a current density of 1.25 to 1.50 A/dm². It is preferable to agitate the electrolyte. Electrolysis may take place overnight without agitation and using a lower current density. Wash down the cover glasses, electrodes, and sides of the beaker, and continue the electrolysis until no darkening of the newly exposed surface of the platinum anode can be detected when the current has been continued for 15 min after the level of the liquid was raised.

13.4 When deposition of the lead is complete, without interrupting the current, siphon off the electrolyte, at the same time filling the beaker with water. Remove the anode quickly, rinse thoroughly with water, and dry at 110 to 120°C for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit.

13.5 Correct for manganese and calculate the percentage of lead in accordance with 10.8 and 10.9.

14. Procedure for Alloys Containing 0.05 % and Over of Tin

14.1 Proceed in accordance with 13.1 or 13.2. Remove tin in accordance with 10.2 and 10.3 or 10.2 and 10.4. Electrolyze and determine lead as directed in 13.3-13.5.

15. Precision and Bias

15.1 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 method is adequate for the contemplated use.

LEAD BY THE SULFATE TEST METHOD

(This test method, which consisted of Sections 16 and 17, was discontinued in 1976.)

TIN BY THE IODOMETRIC TITRATION TEST METHOD

(This test method, which consisted of Sections 18 through 20, was discontinued in 1976.)

ZINC BY THE OXIDE OR FERROCYANIDE TEST METHOD

(This test method, which consisted of Sections 21 and 22 of this standard, was discontinued in 1975.)

NICKEL BY THE DIMETHYLGLYOXIME TEST METHOD

(This test method, which consisted of Sections 23 through 25 of this standard, was discontinued in 1975.)

COBALT BY THE ALPHA-NITROSO-BETA-NAPHTHOL TEST METHOD

26. Reagents

26.1 *Alpha-Nitroso-Beta-Naphthol Solution* (70 g/L)—Dissolve 7 g of alpha-nitroso-beta-naphthol in 100 mL of glacial acetic acid and filter the solution. Prepare this reagent as required just before using.

26.2 *Zinc Oxide Suspension*—Transfer 300 mL of water and 50 g of finely powdered ZnO to a 500-mL flask. Stopper the flask and shake the mixture vigorously each time before using.

27. Procedure

27.1 Transfer 5 g of the sample to a 250-mL beaker and dissolve in 40 mL of HNO₃ (1 + 1). When dissolution is complete, boil gently to expel brown fumes. If a precipitate of tin is present, add 50 mL of hot water, heat on the steam bath for 1 h, and filter off the metastannic acid through a fine paper, washing thoroughly with hot HNO₃ (1 + 99).

27.2 Remove the copper and lead in accordance with 10.5.

27.3 Evaporate the electrolyte to a thick syrup, and convert the nitrates to chlorides by two evaporations to dryness with 25-mL portions of HCl. Cool, add 100 mL of HCl (1 + 19), and