Designation: E945 – 12

Standard Test Method for Determination of Zinc in Zinc Ores and Concentrates by EDTA Complexometric Titrimetry[1]

This standard is issued under the fixed designation E945; 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 This test method covers the determination of zinc in ores, concentrates, and related materials having chemical composition within the following limits:

Element	Application Range, %
Zinc	5.0 to 70.0
Lead	0.5 to 50.0
Copper	0.1 to 3.0
Iron	0.5 to 16.0
Sulfur	4.0 to 30.0
Calcium	0.1 to 20.0
Magnesium	0.1 to 10.0
Cadmium	0.1 to 8.0
Arsenic	0.01 to 1.0
Antimony	0.01 to 0.005
Bismuth	0.001 to 0.1
Cobalt	0.1 to 0.5
Nickel	0.3 to 3.0
Silver	0.00 to 150 oz/ton
Gold	0.00 to 1.0 oz/ton

NOTE 1—As used in this test method, *percent* or "%" refers to a mass fraction.

1.2 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

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E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

E663 Practice for Flame Atomic Absorption Analysis (Withdrawn 1997)[3]

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample, after appropriate acid decomposition, is evaporated to near dryness. The salts are dissolved in acid, interfering elements are removed, and the zinc is extracted as thiocyanate complex into MIBK. Zinc is determined in the extract by titrating with EDTA, using an internal indicator.

5. Significance and Use

5.1 This test method is primarily intended to test materials for compliance with compositional specifications. It is assumed that all who use this test method will be trained analysts working in properly equipped laboratories.

5.2 Appropriate quality control practices shall be followed such as those described in Guide E882.

6. Interferences

6.1 With the exception of cadmium and cobalt, elements do not interfere if their compositional ranges are under the maximum limits shown in 1.1.

[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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

6.2 When the cadmium content is above 5.0 % in the material to be analyzed, some of the cadmium is extracted and will titrate as zinc. The addition of potassium iodide before the titration serves to prevent the interference of cadmium. The amount of potassium iodide solution to add in order to prevent the interference of cadmium is listed in 13.10.3.

6.3 Cobalt is extracted and titrated with the zinc. If the cobalt content of the material to be analyzed is less than 0.05 %, the interference is negligible. For cobalt contents greater than 0.05 %, the cobalt must be extracted as outlined in 13.9.5.

7. Apparatus

7.1 *Magnetic Stirrer,* with TFE-fluorocarbon covered magnetic stirring bar. A magnetic stirrer provided with illumination is preferred.

8. Reagents and Materials

8.1 *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 sufficient high purity to permit its use without lessening the accuracy of the determination.

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

8.3 *Ammonium Fluoride Solution* (250 g/L)—Dissolve 250 g of ammonium fluoride (NH_4F) in water and dilute to 1 L. Store in a polyethylene bottle.

8.4 *Ammonium Chloride Solution* (250 g/L)—Dissolve 250 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

8.5 *Ammonium Thiocyanate* (500 g/L)—Dissolve 500 g of ammonium thiocyanate (NH_4SCN) in distilled water and dilute to 1 L.

8.6 *Buffer Solution* (pH 5.5)—Dissolve 250 g of hexamethylenetetramine ($C_6H_{12}N_4$) in 750 mL of water. Add 57 mL of acetic acid, dilute to 1 L, and mix.

8.7 *Chloroform* ($CHCl_3$).

8.8 *Disodium Ethylenedinitrilo Tetraacetate Dihydrate (EDTA) Standard Solution*—Prepare a solution as follows:

8.8.1 *Preparation*—Dissolve disodium ethylenedinitrilo tetraacetate (EDTA) dihydrate in water, transfer to a 1–L volumetric flask, dilute to volume, and mix. The solution is stable for several months when stored in plastic or borosilicate glass bottles.

Use the following table as a guide for the specific weight of EDTA · $2H_2O$ to use.

NOTE 2—The use of varying concentrations of EDTA solution allows the volume of the titrant to be between 30 mL and 50 mL.

If the expected zinc is:	EDTA · $2H_2O$ Mass, g/L	EDTA Concentration	Amount of Standard Zinc Solution to Use
5 % to 20 %	6.642	6 g/L	10 mL
20 % to 40 %	13.29	12 g/L	30 mL
40 % to 56 %	17.71	16 g/L	40 mL
56 % to 70 %	22.14	20 g/L	50 mL

8.8.2 Standardize the EDTA solution by pipetting the suggested amount of standard zinc solution into a 250-mL separatory funnel. Add 10 drops of ferric chloride solution, add distilled water to adjust volume to 50 mL, mix, and proceed as directed in 13.9.2. It is recommended that replicate standardizations be made to ensure better accuracy.

8.8.3 Calculate the zinc equivalent of the EDTA solution as follows:

$$\text{Zinc Equivalent (mg/mL)} = \frac{A}{B} \quad (1)$$

where:

A = zinc in the chosen aliquot, mg and
B = EDTA solution (8.8) used, mL

8.9 *Ethanol* (CH_3CH_2OH)—Certain denatured ethanols interfere with the color of the indicator during the titration. Pure ethanol is recommended for this reason.

8.10 *Ferric Chloride Solution* (140 g/L)—Dissolve 14 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) in water and dilute to 100 mL.

8.11 *4-Methyl-2-Pentanone* (MIBK) —$CH_3COCH_2CH(CH_3)_2$.

8.12 *2-Nitroso-1-Naphthol Solution* (10 g/L)—Dissolve 0.5 g of 2-nitroso-1-naphthol ($NOC_{10}H_6OH$) in 50 mL of acetic acid. Prepare fresh as needed.

8.13 *Potassium Iodide* (1000 g/L)—Dissolve 100 g of potassium iodide (KI) in distilled water and dilute to 100 mL.

8.14 *Sodium Fluoride Solution* (20 g/L)—Dissolve 10 g of sodium fluoride (NaF) in water and dilute to 500 mL. Store in a polyethylene bottle.

8.15 *Thiourea Solution* (100 g/L)—Dissolve 50 g of thiourea (NH_2CSNH_2) in water and dilute to 500 mL.

8.16 *Xylenol Orange Tetrasodium Salt Indicator Solution* (2 g/L)—Dissolve 100 mg of xylenol orange tetrasodium salt in water and dilute to 50 mL.

8.17 *Zinc, Standard Solution* (1 mL–3.50 mg)—Dissolve 3.50 g of zinc (minimum purity 99.99 %) in 10 mL of HNO_3 and 25 mL of water. Heat gently; when dissolution is complete, boil. Cool. Transfer to a 1-L flask. Dilute to the mark and mix thoroughly.

9. Hazards

9.1 For precautions to be observed in the use of certain reagents in this test method, refer to Practices E50.

10. Sampling and Sample Preparation

10.1 The gross sample shall be collected and prepared so as to be representative of the material to be analyzed.

[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.

10.2 Pulverize the laboratory sample to pass a No. 100 (150-µm) sieve. The repeatability, R1, of Practice E173 corresponds to the repeatability index, r, of Practice E1601.

11. Rounding Calculated Values

11.1 Calculated values shall be rounded to the desired number of places as directed in the Rounding-Off Procedure section of Practice E29.

12. Interlaboratory Studies

12.1 This test method has been evaluated in accordance with Practice E173. For those methods tested according to Practice E173, the reproducibility, R2, of Practice E173 corresponds to the reproducibility index, R, of Practice E1601.

13. Procedure

13.1 Weigh approximately 2.5 g of sample into a weighing bottle. Dry the bottle and contents at least 1 h at 105 °C, but not more than 3 h. Cap the bottle and cool to room temperature in a desiccator.

13.1.1 Momentarily release the cap to equalize the pressure and weigh the capped bottle and sample to the nearest 0.1 mg.

13.1.2 Transfer all of the sample into a 250-mL to 300-mL Erlenmeyer flask or Phillips beaker. Reweigh the capped bottle to the nearest 0.1 mg. The difference between the mass recorded in 13.1.1 and the mass recorded in 13.1.2 is the mass of the sample.

13.2 Moisten the sample in the Erlenmeyer flask with approximately 5 mL of water and add 2 mL to 3 mL bromine. Allow to stand for 15 min with occasional stirring.

13.3 Add 10 mL of HNO_3 cautiously and allow to stand for 5 min with occasional stirring.

13.4 Cautiously add 15 mL of H_2SO_4 (1 + 1), mix, and heat gently to remove the brown bromine and nitric oxide fumes. Do not boil.

13.5 Remove from the heat, add 3 drops to 5 drops of HF, 5 mL of $HClO_4$, replace on the hotplate, and evaporate the solution until the volume is reduced to approximately 5 mL.

13.6 Remove from the heat, wash down the sides with water, add 5 mL of H_2SO_4 (1 + 1), add 1 mL of HCl (1 + 4), and dilute to 40 mL. Mix and bring to a boil.

13.6.1 For samples containing more than 10 % SiO_2, proceed as directed in 13.7. For samples containing less than 10 % SiO_2, proceed as directed in 13.8.

13.7 Filter the solution into a 500-mL volumetric flask, using a Whatman #1 or equivalent paper. Wash the residue thoroughly to remove soluble precipitate.

13.7.1 Transfer the paper plus residue into a platinum crucible. Char the paper at a low temperature and then ignite in a muffle furnace at 800 °C. Remove from the furnace and cool.

13.7.2 Add 5 mL of HF, add 5 mL of $HClO_4$, mix, and heat until dense fumes are being given off. Remove from the heat and cool.

13.7.3 Dilute with water and transfer to the 500-mL volumetric flask, which contains the filtrate from 13.7. Dilute to volume and mix. Allow any remaining residue to settle. Proceed to 13.9.

13.8 Transfer the solution obtained in 13.6 to a 500-mL volumetric flask. Dilute to volume and mix. Allow any remaining residue to settle.

13.9 *Extraction:*

13.9.1 Pipet 50 mL of the clear solution obtained in 13.7.3 or 13.8 into a 250-mL separatory funnel. Add 10 drops of ferric chloride solution (8.10) and mix.

NOTE 3—Ferric chloride is added to aid the analyst in setting the pH of the solution. If iron is present in the sample already, the addition of the ferric chloride solution can be eliminated.

13.9.2 Add 20 mL of NH_4Cl solution (8.4) and mix.

13.9.3 Add NH_4OH, dropwise, until a slight turbidity develops. Then add 5 mL of HCl (1 + 4) and mix.

13.9.4 Add 20 mL of NH_4F solution and mix.

13.9.4.1 If the cobalt content of the sample is known to be less than 0.05 %, proceed as directed in 13.9.6. When the cobalt content is higher than 0.05 %, the cobalt must be removed. Proceed as directed in 13.9.5.

13.9.5 Adjust the pH using pH paper to between 3 and 4 by the dropwise additions of HCl (1 + 1) or NH_4OH (1 + 1) solution. Add 5 drops of H_2O_2 (30 %) and 2 mL of 2-nitroso-1-napthol solution (8.12). Allow to stand 30 min with occasional stirring.

13.9.5.1 Add 20 mL of $CHCl_3$, shake for 30 s, and allow the phases to separate. Discard the lower phase.

13.9.5.2 Add another 20 mL of $CHCl_3$ (8.7) and repeat the extraction again discarding the lower phase.

13.9.5.3 Extract a third time using 10 mL of $CHCl_3$ (8.7) and discard the lower phase. Proceed as directed in 13.9.6.

13.9.6 Add 5 mL of thiourea (8.15) solution and 25 mL NH_4SCN solution (8.5), mixing after each addition.

13.9.7 Add 80 mL of MIBK (8.11) and shake vigorously for 1 min. Allow the phases to separate, and then draw off the lower aqueous phase into a second separatory funnel. Retain the upper organic phase.

13.9.8 Add 20 mL of MIBK (8.11) to the second separatory funnel and shake for 1 min. Allow the phases to separate and discard the lower aqueous phase. Retain the upper organic phase.

13.9.9 Transfer the portions from both separatory funnels to a 400-mL beaker. To each separatory funnel add 1 mL of HCl (1 + 4) and 50 mL of ethanol and shake for 5 s. Transfer both of these solutions to the 400-mL beaker. Cover the beaker until the titration is to begin.

13.10 *Titration:*

13.10.1 Place a stirring bar into the solution in the 400-mL beaker and place the beaker on a magnetic stirrer. Begin to stir at a moderate rate.

13.10.2 While stirring, add 10 mL of NaF solution (8.14), 10 mL of thiourea solution (8.15), and 20 mL of buffer solution (8.6).

13.10.3 If the cadmium content of the original sample is believed to be from 5 % to 10 % add 10 mL of KI solution (8.13).

13.10.4 Add 10 drops of xylenol orange indicator solution (8.16) and 0.25 g to 0.30 g ascorbic acid, and continue to stir.

TABLE 1 Statistical Summary

Test Sample	Mean	Repeatability (R_1, E173)	Reproducibility (R_2, E173)	Number of Determinations	Number of Participating Laboratories
1	11.76	0.177	0.244	20	5
2	15.94	0.124	0.224	19	5
3	44.78	0.591	0.543	19	5
4	54.26	0.683	0.803	20	5

Titrate with the appropriate EDTA solution (8.8) chosen as prescribed in 8.8 to a yellow end point.

NOTE 4—The reaction between EDTA and zinc is slowed down in the presence of organic solvents. On approaching the equivalence point, it is necessary to work more slowly than usual. Wait 10 s after each addition of EDTA. Should a phase separation occur or the sample become cloudy, add 20 mL of ethanol and proceed with the titration.

NOTE 5—If the end-point is inadvertently passed, add 1.00 mL of zinc standard solution (8.17) by means of a microburet. Complete the titration as usual. Correct the final result for the quantity of zinc added.

14. Calculation

14.1 Calculate the percentage of zinc as follows:

$$\text{Zinc, } \% = \frac{(C \times D) - F}{E \times 10} \quad (2)$$

where:

C = EDTA used, mL,
D = zinc equivalent, (mg/mL) EDTA solution,
E = sample in aliquot extracted, g and
F = zinc added, mL (Note 5).

15. Precision and Bias[5]

15.1 *Precision*—The precision of this test method, calculated according to Practice E173, appears in Table 1.

15.2 *Bias*—No information on the accuracy of this test method is available. However, the accuracy may be judged by comparing accepted reference values with the corresponding arithmetic averages obtained by interlaboratory testing.

16. Keywords

16.1 concentrates; EDTA titration; extraction; zinc ores

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: RR:E16-1007.