



Standard Test Method for Determination of Zinc in Zinc Ores and Concentrates by Complexometric Titrimetry¹

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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	Concentration 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

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:

- D 1193 Specification for Reagent Water²
- 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 135 Terminology Relating to Analytical Chemistry for Metals, Ores and Related Materials⁴
- E 173 Practice for Conducting Interlaboratory Studies of

Methods for Chemical Analysis of Metals⁵

E 663 Practice for Flame Atomic Absorption Analysis⁶

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁷

E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry⁷

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method⁴

3. Terminology

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

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 E 882.

6. Interferences

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

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.

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, Refractories, Cement, and Related Metallurgical Materials.

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² *Annual Book of ASTM Standards*, Vol 11.01.

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

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

⁵ Discontinued 1997; Available from Global Engineering, 15 Iverness Way East, Englewood, Colorado 80112.

⁶ Discontinued; see 1997 *Annual Book of ASTM Standards*, Vol 03.06.

⁷ *Annual Book of ASTM Standards*, Vol 03.06.

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 Atomic absorption spectrophotometers shall conform to Practice E 663 or Guide E 1024.

7.2 *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.⁸ 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 of Specification D 1193.

8.3 *Ammonium Fluoride Solution (250 g/L)*—Dissolve 250 g of ammonium fluoride (NH₄F) 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 (NH₄Cl) in water and dilute to 1 L.

8.5 *Ammonium Thiocyanate (500 g/L)*—Dissolve 500 g of ammonium thiocyanate (NH₄SCN) in distilled water and dilute to 1 L.

8.6 *Buffer Solution (pH 5.5)*—Dissolve 250 g of hexamethylenetetramine (C₆H₁₂N₄) in 750 mL of water. Add 57 mL of acetic acid, dilute to 1 L, and mix.

8.7 *Chloroform (CHCl₃)*.

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 · 2H₂O to use.

NOTE 1—The use of varying concentrations of EDTA solution allows the volume of the titrant to be between 30 and 50 mL.

⁸ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

If the expected zinc is:	EDTA · 2H ₂ O Weight, 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 used, mL

8.9 *Ethanol (CH₃CH₂OH)*—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 (FeCl₃·6H₂O) in water and dilute to 100 mL.

8.11 *4-Methyl-2-Pentanone (MIBK)*—CH₃COCH₂CH(CH₃)₂.

8.12 *2-Nitroso-1-Naphthol Solution (10 g/L)*—Dissolve 0.5 g of 2-nitroso-1-naphthol (NOC₁₀H₆OH) 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 (NH₂CSNH₂) 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 HNO₃ 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 E 50.

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.

10.2 Pulverize the laboratory sample to pass a No. 100 (150-μm) sieve. The repeatability, R1, of Practice E 173 corresponds to the repeatability index, r, of Practice E 1601.

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 E 29.

12. Interlaboratory Studies

12.1 This test method has been evaluated in accordance with Practice E 173. For those methods tested according to Practice E 173, the reproducibility, R_2 , of Practice E 173 corresponds to the reproducibility index, R , of Practice E 1601.

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

13.2 Moisten the sample in the Erlenmeyer flask with approximately 5 mL of water and add 2 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 $\text{H}_2\text{SO}_4(1+1)$, mix, and heat gently to remove the brown bromine and nitric oxide fumes. Do not boil.

13.5 Remove from the heat, add 3 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 $\text{H}_2\text{SO}_4(1+1)$, 1 mL of $\text{HCl}(1+4)$, 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, 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.

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 and mix.

NOTE 2—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 and mix.

13.9.3 Add NH_4OH , dropwise, until a slight turbidity develops. Then add 5 mL of $\text{HCl}(1+4)$ 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 $\text{HCl}(1+1)$ or $\text{NH}_4\text{OH}(1+1)$ solution. Add 5 drops of $\text{H}_2\text{O}_2(30\%)$ and 2 mL of 2-nitroso-1-naphthol solution. 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 and repeat the extraction again discarding the lower phase.

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

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

13.9.7 Add 80 mL of MIBK 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 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 $\text{HCl}(1+4)$ 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, 10 mL of thiourea solution, and 20 mL of buffer solution.

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.

13.10.4 Add 10 drops of xylenol orange indicator solution and 0.25 to 0.30 g ascorbic acid, and continue to stir. Titrate with the appropriate EDTA solution chosen as prescribed in 8.8 to a yellow end point.

NOTE 3—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 4—If the end-point is inadvertently passed, add 1.00 mL of zinc standard solution 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 4).

15. Precision and Bias ⁹

15.1 *Precision*—The precision of this test method, calculated according to Practice E 173, 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 EDTA titration; extraction; zinc ores; concentrates

⁹ Supporting data available from ASTM International Headquarters. Request RR: E16-1007.

TABLE 1 Statistical Summary

Test Sample	Average	Repeat-ability (R ₁ , E 173)	Reproduc-ibility (R ₂ , E 173)	Number of Deter-minations	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

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