



Standard Test Methods for Chemical Analysis of Chromium and Ferrochromium¹

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^{ε1} NOTE—Warnings were moved from notes to section text editorially December 2002

1. Scope

1.1 These test methods cover the chemical analysis of chromium and ferrochromium having chemical compositions within the following limits:

| Element | Concentration, % |
|------------|------------------|
| Aluminum | 0.25 max |
| Antimony | 0.005 max |
| Arsenic | 0.005 max |
| Bismuth | 0.005 max |
| Boron | 0.005 max |
| Carbon | 9.00 max |
| Chromium | 51.0 to 99.5 |
| Cobalt | 0.10 max |
| Columbium | 0.05 max |
| Copper | 0.05 max |
| Lead | 0.005 max |
| Manganese | 0.75 max |
| Molybdenum | 0.05 max |
| Nickel | 0.50 max |
| Nitrogen | 6.00 max |
| Phosphorus | 0.03 max |
| Silicon | 12.00 max |
| Silver | 0.005 max |
| Sulfur | 0.07 max |
| Tantalum | 0.05 max |
| Tin | 0.005 max |
| Titanium | 0.50 max |
| Vanadium | 0.50 max |
| Zinc | 0.005 max |
| Zirconium | 0.05 max |

1.2 The analytical procedures appear in the following order:

| | Sections |
|---|----------|
| Arsenic by the Molybdenum Blue Photometric Method | 9-19 |
| Lead by the Dithizone Photometric Method | 20-30 |
| Chromium by the Sodium Peroxide Fusion-Titrimetric Method | 31-37 |

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 whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 5.

2. Referenced Documents

2.1 ASTM Standards:

- A 101 Specification for Ferrochromium²
- A 481 Specification for Chromium Metal²
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³
- E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition⁴
- E 50 Practices for Apparatus, Reagents, and Safety Considerations of Metals, Ores, and Related Materials⁴
- E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry⁴
- E 173 Practice for Conducting Interlaboratory Studies of test methods for Chemical Analysis of Metals⁵
- E 360 Test Methods for Chemical Analysis of Silicon and Ferrosilicon⁴
- E 361 Test Methods for the Determination of Arsenic and Lead in Ferromanganese⁴

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, Reagents, and Photometric Practice

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

4.2 Photometric practices prescribed in these test methods shall conform to Practice E 60.

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 E01.01 on Iron, Steel, and Ferroalloys.

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² *Annual Book of ASTM Standards*, Vol 01.02.

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

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

⁵ Discontinued. See 1997 *Annual Book of ASTM Standards*, Vol 03.06.

5. Safety Hazards

5.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E 50.

6. Sampling

6.1 For procedures for sampling the material, and for particle size of the sample for chemical analysis, refer to Practices E 32.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in 6.4 to 6.6, Rounding Procedure, of Practice E 29.

8. Interlaboratory Studies

8.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision and bias section.

**ARSENIC BY THE MOLYBDENUM BLUE
PHOTOMETRIC METHOD**

9. Scope

9.1 This method covers the determination of arsenic in chromium and ferrochromium in concentrations from 0.001 to 0.005 %.

10. Summary of Method

10.1 See Section 10 of Test Methods E 360.

11. Concentration Range

11.1 See Section 11 of Test Methods E 360.

12. Stability of Color

12.1 See Section 12 of Test Methods E 360.

13. Interferences

13.1 See Section 13 of Test Methods E 360.

14. Apparatus

14.1 See Section 14 of Test Methods E 360.

15. Reagents

15.1 Proceed as directed in 15.1 through 15.9 of Test Methods E 360.

16. Preparation of Calibration Curve

16.1 Proceed as directed in 16.1 through 16.5 of Test Methods E 360.

17. Procedure

17.1 Proceed as directed in 17.1 through 17.4 of Test Methods E 360.

18. Calculation

18.1 Proceed as directed in Section 18 of Test Methods E 360.

19. Precision and Bias

19.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1. Samples with arsenic concentrations near the upper limit of the scope were not available for testing. The user is cautioned to verify, by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

**LEAD BY THE DITHIZONE PHOTOMETRIC
METHOD**

20. Scope

20.1 This method covers the determination of lead in chromium and ferrochromium in concentrations from 0.001 to 0.05 %.

21. Summary of Method

21.1 See Section 21 of Test Methods E 361.

22. Concentration Range

22.1 See Section 22 of Test Methods E 361.

23. Stability of Color

23.1 See Section 23 of Test Methods E 361.

24. Interferences

24.1 See Section 24 of Test Methods E 361.

25. Apparatus

25.1 See Section 25 of Test Methods E 361.

26. Reagents

26.1 Proceed as directed in Section 26 of Test Methods E 361.

27. Preparation of Calibration Curve

27.1 Proceed as directed in 27.1 through 27.5 of Test Methods E 361.

28. Procedure

28.1 *Test Solution:*

28.1.1 Transfer a sample, selected in accordance with 28.1.1 of Test Methods E 361 and weighed to the nearest 0.1 mg, to a 250-mL beaker. Add 30 mL of HCl (1 + 1) and heat until dissolution is nearly complete. In the case of high-carbon ferrochromium (4.00 to 9.00 % C), add 30 mL of HCl (concentrated) and several drops of HF, and heat until the reaction has subsided.

28.1.2 Add several drops of HF (omit if added in preceding paragraph) plus 10 mL of HNO₃ and 10 mL of HClO₄. Evaporate to heavy fumes of HClO₄ and fume until the volume is reduced to approximately 5 mL. Add H₂O₂ solution (1 + 9)

TABLE 1 Statistical Information—Arsenic

| Ferroalloy Type | Arsenic Found, % | Repeatability (<i>R</i> ₁ , E 173) | Reproducibility (<i>R</i> ₂ , E 173) |
|-----------------|------------------|---|--|
| 1. 70Cr-1Si-5C | 0.0015 | 0.0001 | 0.0005 |

dropwise until any precipitated manganese dioxide is dissolved. Boil to remove excess H₂O₂ and cool.

28.1.3 Proceed as directed in 28.1.4 through 28.4 of Test test methods E 361.

29. Calculation

29.1 Proceed as directed in Section 29 of Test test methods E 361.

30. Precision and Bias

30.1 Four laboratories cooperated in testing this method and obtained the results shown in Table 2. Samples with lead concentrations near the upper limit of the scope were not available for testing. The user is cautioned to verify, by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

CHROMIUM BY THE SODIUM PEROXIDE FUSION-TITRIMETRIC METHOD

31. Scope

31.1 This method covers the determination of chromium in all carbon grades of ferrochromium in concentrations from 50 to 75 %.

32. Summary of Method

32.1 The sample is fused in sodium peroxide. After dissolution of the melt in dilute sulfuric acid, chromium and manganese are oxidized by ammonium peroxydisulfate with silver nitrate as a catalyst. The permanganate ions are reduced with hydrochloric acid and the chromate ions are reduced by adding an excess of standard ferrous ammonium sulfate salt. The excess ferrous ions are titrated with standard potassium permanganate solution.

33. Interferences

33.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

34. Reagents

34.1 *Ammonium Peroxydisulfate* ((NH₄)₂S₂O₈).

34.2 *Ferrous Ammonium Sulfate Salt*—Fine, well mixed, free flowing crystals of Fe (NH₄)₂(SO₄)₂·6H₂O will be required. Standardize as follows: Transfer 0.9806 g of NBS K₂Cr₂O₇ (equivalent to 200 mL of 0.1 N solution) to a 600-mL beaker. Add 300 mL of water, 30 mL of H₂SO₄(1 + 1), and 8.00 g of the ferrous ammonium sulfate. Stir until completely dissolved. Add 6 drops of 1,10-phenanthroline indicator solu-

tion, and using a 50-mL buret, titrate with 0.1 N KMnO₄ solution to the color change from red to green. Record the buret reading to the nearest 0.05 mL. Calculate the volume of 0.1 N K₂Cr₂O₇ solution equivalent to 1 g of ferrous ammonium sulfate as follows:

$$A = (200 + B)/8 \quad (1)$$

where:

A = millilitres of 0.1 N K₂Cr₂O₇ solution equivalent to 1 g of ferrous ammonium sulfate, and

B = millilitres of 0.1 N KMnO₄ solution used.

The salt has proved to be stable for at least 1 week.

34.3 *Ferrous Ammonium Sulfate, Standard Solution* (0.25 N) (Note 1)—Dissolve 89.6 g of Fe (NH₄)₂(SO₄)₂·6H₂O in 500 mL of cold H₂SO₄(5 + 95) and dilute to 1 litre with H₂SO₄(5 + 95). Use a solution that has been standardized within the previous 8 h as follows: Transfer 0.9806 g of NBS K₂Cr₂O₇(equivalent to 200 mL of 0.1 N solution) to an 800-mL beaker. Add 300 mL of water, 30 mL of H₂SO₄(1 + 1). Stir until completely dissolved, and add a slight excess of the ferrous ammonium sulfate solution. Add 6 drops of 1,10-phenanthroline indicator solution and titrate with 0.1 N KMnO₄ solution to the color change from red to green. Calculate the volume of 0.1 N K₂Cr₂O₇ solution equivalent to 1 mL of ferrous ammonium sulfate solution as follows:

$$A = (200 + B)/C \quad (2)$$

where:

A = millilitres of 0.1 N K₂Cr₂O₇ solution equivalent to 1 mL of ferrous ammonium sulfate solution,

B = millilitres of 0.1 N KMnO₄ solution used, and

C = millilitres of 0.25 N ferrous ammonium sulfate used.

NOTE 1—Ferrous ammonium sulfate salt is preferred to the standard ferrous ammonium sulfate solution. If the ferrous ammonium sulfate solution is used, it is necessary to add it by means of a calibrated 100-mL buret.

34.4 *1,10-Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Reagent No. 122.

34.5 *Potassium Permanganate Standard Solution* (0.1 N)—Reagent No. 13.

34.6 *Potassium Permanganate Solution* (20 g/L)—Reagent No. 134.

34.7 *Silver Nitrate Solution* (8 g/L)—Reagent No. 133.

35. Procedure

35.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 30-mL iron crucible (Note 2). Add 8 g of dry sodium peroxide (Na₂O₂) and mix thoroughly with a small stainless steel spatula. Clean the spatula after mixing by scraping on the inside edge of the crucible. Cover the mixture with an additional 1 to 2 g of Na₂O₂.

NOTE 2—Crucibles made of ingot iron have a negligible blank and resist attack by the molten peroxide.

35.2 Place the crucible on a wire gauze supported on a tripod and heat with a Meker burner until the fusion has been initiated. Grasp the crucible with long handled tongs and fuse carefully by moving it around the edge of a free flame with a gyratory motion while raising the temperature gradually to

TABLE 2 Statistical Information—Lead

| Ferroalloy Type | Lead Found, % |
|--------------------------|-----------------------|
| 1. Electrolytic Cr Metal | Lab A: 0.0020, 0.0020 |
| | 0.0019, 0.0020 |
| | Lab B: 0.0025, 0.0023 |
| | 0.0020, 0.0011 |
| | Lab C: 0.0020, 0.0021 |
| | 0.0020, 0.0020 |
| | Lab D: 0.0011, 0.0009 |
| | Average: 0.0019 |

avoid spattering. When the contents are molten, swirl the crucible to dissolve any unattached particles of sample adhering to the bottom or sides. Finally, increase the temperature until the crucible is bright red for 1 min. Cool the crucible to almost room temperature. (**Warning**—Use proper safety practices and equipment when performing sodium peroxide fusions.)

35.3 Cover the crucible with a crucible cover, hold upright, and rap the bottom sharply on a piece of heavy metal to loosen the cake. Transfer the cake to a dry, 800-mL beaker, add 300 mL of water all at once, and cover. Rinse and police the crucible and cover and add the rinsings to the beaker. Add 60 mL of H₂SO₄(1 + 1), 5 mL of H₃PO₄ and 5 mL of HNO₃, heat to boiling and boil for several minutes. Cool to 70–80°C, add 5 mL of AgNO₃ solution, 5 g of (NH₄)₂S₂O₈, and 3 or 4 drops of KMnO₄ solution (20 g/L). Boil for 10 min, add 5 mL of HCl (1 + 3), and boil for an additional 5 min after the KMnO₄ and any MnO₂ have completely disappeared. Cool to room temperature.

35.4 Select and weigh a portion of the standard ferrous ammonium sulfate salt (Note 3) to the nearest 0.1 mg in accordance with the following:

| Chromium, % | Ferrous Ammonium Sulfate, g |
|-------------|-----------------------------|
| 50 to 55 | 6.500 |
| 55 to 60 | 7.000 |
| 60 to 65 | 7.500 |
| 65 to 70 | 8.000 |
| 70 to 75 | 8.500 |

Add the salt to the test solution and stir until it has completely dissolved. Add 6 drops of 1,10-phenanthroline indicator solution and titrate with the KMnO₄ standard solution to the color change from red to green.

NOTE 3—A measured amount of the ferrous ammonium sulfate solution, in excess of that required for the reduction, may be used instead of the salt, if desired (see Note 1).

36. Calculation

36.1 When ferrous ammonium sulfate salt is used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = \frac{(A \times B) - C}{D} \times 0.1734 \quad (3)$$

where:

- A = millilitres of 0.1 N K₂Cr₂O₇ solution equivalent to 1 g of ferrous ammonium sulfate (see 34.2),
- B = grams of ferrous ammonium sulfate used,
- C = millilitres of 0.1 N KMnO₄ solution required to titrate the excess ferrous ammonium sulfate, and
- D = grams of sample used.

36.2 When ferrous ammonium sulfate solution is used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = \frac{(A \times B) - C}{D} \times 0.1734 \quad (4)$$

where:

- A = millilitres of 0.1 N K₂Cr₂O₇ solution equivalent to 1 mL of ferrous ammonium sulfate solution (see 34.3),
- B = millilitres of ferrous ammonium sulfate solution used,
- C = millilitres of 0.1 N KMnO₄ solution required to titrate the excess ferrous ammonium sulfate, and
- D = grams of sample used.

37. Precision and Bias

37.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 3. Samples with chromium concentrations near the upper limit of the scope were not available for testing. The user is cautioned to verify, by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

38. Keywords

38.1 arsenic; chemical analysis; chromium; ferrochromium; lead

TABLE 3 Statistical Information^A—Chromium

| Test Specimens | Chromium Found, % | Repeatability (R ₁ , E 173) | Reproducibility (R ₂ , E 173) |
|---|-------------------|--|--|
| Low-carbon ferrochromium | 70.16 | 0.12 | 0.64 |
| High-carbon ferrochromium | 52.03 | 0.38 | 0.83 |
| High-carbon ferrochromium (NBS 64b, 68.03 Cr) | 68.09 | 0.25 | 0.59 |

^A The reagent described in 34.2 was used to obtain these data.

APPENDIX


(Nonmandatory Information)

X1. TYPICAL SPECIFICATIONS

X1.1 Typical specifications⁶ covered by the methods in Test

Methods E 363 (Ferrochromium) ASTM Specifications are A 101 and A 481.

⁶ To determine whether a specification that is not listed falls into this category, compare the range of concentrations specified for each element with the range indicated in 1.1 of Test test methods E 363.

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