Designation: E363 – 16

Standard Test Methods for Chemical Analysis of Chromium and Ferrochromium[1]

This standard is issued under the fixed designation E363; 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 the chemical analysis of chromium and ferrochromium having chemical compositions within the following limits:

Element	Composition, %
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 Spectrophotometric Test Method [0.001 % to 0.005 %]	10 – 20
Lead by the Dithizone Spectrophotometric Test Method [0.001 % to 0.05 %]	21 – 31
Chromium by the Sodium Peroxide Fusion-Titrimetric Test Method [50 % to 75 %]	32 – 38

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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 6 and in special "Warning" paragraphs throughout these test methods.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

A101 Specification for Ferrochromium

A481 Specification for Chromium Metal

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

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]

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

3. Terminology

3.1 For definition of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of chromium metal and ferrochromium alloy are primarily intended to test such materials for compliance with compositional specifications such as Specifications A101 and A481. It is assumed that all who use these test methods will be trained analysts

[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] 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.

capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Spectrophotometric Practice

5.1 Apparatus, standard solutions, and other reagents required for each determination are listed in separate sections preceding the procedure. Spectrophotometers shall conform to the requirements prescribed in Practice E60.(Note 1)

NOTE 1—In these methods, cells utilized to contain the reference material and sample solutions in spectrophotometers are referred to as "absorption cells." The radiant energy passed through the cells can be measured as absorbance or transmittance. These methods refer to absorbance measurements. Refer to Practices E60 for details.

5.2 Spectrophotometric practices prescribed in these test methods shall conform to Practice E60.

6. Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

6.2 Specific hazard statements are given in 27.1, 27.6, and 36.2.

7. Sampling

7.1 For procedures to sample the material, and particle size requirements of the sample, refer to Practices E32.

8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places as directed in the Rounding Procedure of Practice E29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice E173, unless otherwise noted in the precision and bias section. Practice E173 has been replaced by Practice E1601. The Reproducibility R_2 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability R_1 of Practice E173 corresponds to the Repeatability Index r of Practice E1601.

ARSENIC BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC TEST METHOD

10. Scope

10.1 This test method covers the determination of arsenic in chromium and ferrochromium in compositions from 0.001 % to 0.005 %.

11. Summary of Method

11.1 Arsenic is first separated by distillation as the trivalent chloride. Ammonium molybdate is added to form arsenomolybdate, which is then reduced by hydrazine sulfate to form the molybdenum blue complex. Spectrophotometric absorbance measurement is made at 850 nm.

12. Concentration Range

12.1 The recommended concentration range is 0.01 mg to 0.15 mg of arsenic per 50 mL of solution using a 1-cm cell.

NOTE 2—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amount of sample and reagents used.

13. Stability of Color

13.1 The color is stable for at least 2 h.

14. Interferences

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

15. Apparatus

15.1 Distillation Apparatus, Fig. 1.

15.2 Zirconium Crucibles, 30-mL capacity.

16. Reagents

16.1 *Ammonium Bromide* (NH_4Br).

16.2 *Ammonium Molybdate Solution* (10 g/L)—Dissolve 2.5 g of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in 40 mL of warm water. Add 128 mL of H_2SO_4 (1 + 3), dilute to 250 mL, and mix.

16.3 *Ammonium Molybdate-Hydrazine Sulfate Solution*—Dilute 100 mL of ammonium molybdate solution to 900 mL, add 10 mL of hydrazine sulfate solution, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 h.

16.4 *Arsenic, Standard Solution A* (1 mL = 0.10 mg As)—Transfer 0.1320 g of arsenic trioxide (As_2O_3) to a 1-L volumetric flask, dissolve in 100 mL of HCl, cool, dilute to volume, and mix.

16.5 *Arsenic, Standard Solution B* (1 mL = 0.01 mg As)—Using a pipet, transfer 100 mL of arsenic solution A (1 mL = 0.10 mg As) to a 1-L volumetric flask, dilute to volume, and mix.

16.6 *Hydrazine Sulfate* ($(NH_2)_2 \cdot H_2SO_4$).

16.7 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2 \cdot H_2SO_4$) in water, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 day.

16.8 *Sodium Carbonate* (Na_2CO_3).

16.9 *Sodium Peroxide* (Na_2O_2).

17. Preparation of Calibration Curve

17.1 *Calibration Solutions:*

17.1.1 Using pipets, transfer (1, 2, 5, 10, and 15) mL of arsenic Solution B (1 mL = 0.01 mg As) to 125-mL Erlenmeyer flasks.

17.1.2 Add 10 mL of HNO_3 and evaporate the solution to dryness on a hot plate. Bake for 30 min at 150 °C to 180 °C. Remove from the hot plate. Add 45 mL of ammonium molybdate-hydrazine sulfate solution to each flask, warm gently to dissolve the residue, and transfer the solution to a 50-mL volumetric flask. Proceed as directed in 17.3.

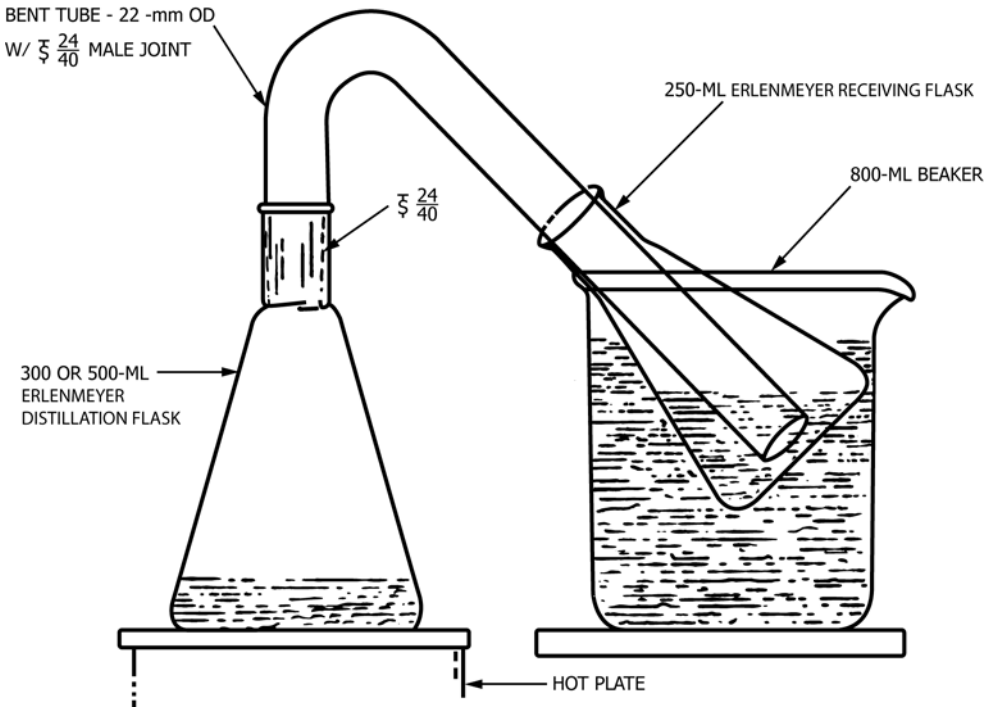

FIG. 1 Arsenic Distillation Apparatus

17.2 *Reference Solution*—Transfer 10 mL of HNO_3 to a 125-mL Erlenmeyer flask and proceed as directed in 17.1.2.

17.3 *Color Development*—Heat the flask in a boiling water bath for 15 min. Remove the flask, cool to room temperature, dilute to volume with ammonium molybdate-hydrazine sulfate solution, and mix.

17.4 *Spectrophotometry:*

17.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at 850 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions.

17.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at 850 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

17.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of arsenic per 50 mL of solution. Follow the instrument manufacturer's instructions for generating the calibration curve.

18. Procedure

18.1 *Test Solution:*

18.1.1 Select and weigh a sample to the nearest 0.2 mg as follows:

As, %	Sample Weight, g
0.001 to 0.015	0.500
0.01 to 0.04	0.250
0.035 to 0.10	0.125

18.1.1.1 Transfer the sample to a 30-mL zirconium crucible containing 10 g of Na_2O_2 and 1 g of Na_2CO_3 if ferrochromium, or 8 g of Na_2O_2 plus 2 g of Na_2CO_3 if chromium metal.

18.1.2 Mix thoroughly with a metal spatula. Fuse carefully over a free flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have completely melted; raise the temperature gradually to avoid spattering. When the contents are molten, give the crucible a rotary motion to stir up any unattacked particles of the alloy adhering to the bottom or sides. Finally, increase the temperature until the crucible is bright red for 1 min. Cool the crucible to room temperature. Transfer the crucible to an 800-mL beaker containing 60 mL of H_2SO_4 (1 + 1) and 200 mL of water. Dissolve the melt; remove and rinse the crucible.

18.1.3 If manganese dioxide is present, add H_2SO_4 dropwise until the solution clears.

18.1.4 Heat to boiling, and cool. While stirring vigorously, add NH_4OH until the solution is alkaline to litmus, and then add 3 mL to 5 mL in excess. Heat to boiling, remove from the heat, and allow the precipitate to settle. Filter on a coarse filter paper and wash five times with hot water. Discard the filtrate. Remove the filter paper, carefully open it, and place it on the inside wall of the original 800-mL beaker. Wash the precipitate from the paper using a fine stream of water. Pass 25 mL of HNO_3 (1 + 1) over the paper, and wash well with water but do not exceed a total volume of 40 mL. Discard the paper. Warm gently until the precipitate dissolves.

18.1.5 Transfer the solution to the distillation flask, add 1 g of NH_4Br and 0.75 g of hydrazine sulfate. Add 20 mL of HNO_3 (1 + 1) to the receiving flask, and place the flask in an 800-mL

TABLE 1 Statistical Information—Arsenic

Ferroalloy Type	As Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. 70Cr-1Si-5C	0.0015	0.0001	0.0005

beaker containing cold water. Assemble the apparatus (Fig. 1), heat the distillation flask, and distill into the receiving flask.

18.1.6 Distill until the volume is reduced to 10 mL or until oxides of nitrogen are noted in the distillation flask. Remove the distillation flask from the heat source. Place the receiving flask on a hot plate and evaporate the solution to dryness. Bake for 30 min at 150 °C to 180 °C. Add 45 mL of ammonium molybdate-hydrazine sulfate solution to the flask, warm gently to dissolve the residue, and transfer the solution to a 50-mL volumetric flask. Proceed as directed in 18.3.

18.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted. Proceed as directed in 18.3.

18.3 *Color Development*—Proceed as directed in 17.3.

18.4 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 17.4.

19. Calculation

19.1 Convert the net spectrophotometric absorbance reading of the test solution to milligrams of arsenic by means of the calibration curve. Calculate the percentage of arsenic as follows:

$$\text{Arsenic , \%} = A/(B \times 10) \quad (1)$$

where:

A = milligrams of arsenic found in 50 mL of final test solution, and

B = grams of sample represented in 50 mL of final test solution.

20. Precision and Bias

20.1 Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 1. Samples with arsenic compositions 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 test method is adequate for the contemplated use.

LEAD BY THE DITHIZONE SPECTROPHOTOMETRIC TEST METHOD

21. Scope

21.1 This test method covers the determination of lead in chromium and ferrochromium in compositions from 0.001 % to 0.05 %.

22. Summary of Test Method

22.1 After dissolution of the sample, lead is precipitated with NH_4OH. Interfering metals are complexed with sodium citrate and sodium cyanide, and the lead dithizone complex is extracted with chloroform. Spectrophotometric absorbance measurement is made at 520 nm.

23. Concentration Range

23.1 The recommended concentration range is from 0.001 mg to 0.025 mg of lead per 10 mL of solution, using a 1-cm cell.

NOTE 3—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

24. Stability of Color

24.1 The color is quite stable if the solution is protected against evaporation and decomposition of chloroform. Because of the volatility of the solvent, it is advisable to make all readings promptly. The color develops almost immediately.

25. Interferences

25.1 The elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1. If more than 0.005 % bismuth is present, it must be removed as directed in 28.3.3 to avoid high results for lead.

26. Apparatus

26.1 *Glassware*—Use only borosilicate beakers, covers, and funnels. Wash all glassware with hot HNO_3 (1 + 1) and reserve for this determination only. Before using separatory funnels, rinse them with dithizone solution and then with water. Store all reagents in glass-stoppered borosilicate bottles which have been previously washed with hot HNO_3 (1 + 1) and rinsed with distilled water.

26.2 *pH Meter*—A pH meter for measurements to within ±0.10 pH units is required.

27. Reagents

27.1 *Chloroform* ($CHCl_3$)—(**Warning—**Chloroform is highly toxic and must be used in a well-ventilated hood. Consult the Safety Data Sheet or other source of data prior to use. Refer to the Hazards Section of Practices E50.)

27.2 *Dithizone Solution* (0.04 g/L in chloroform)—Dissolve 0.02 g of dithizone (diphenylthiocarbazone) in 80 mL of $CHCl_3$ in a 500-mL conical separatory funnel, add 100 mL of cold water and 10 mL of NH_4OH, stopper, and shake vigorously for 1 min to 2 min. Draw off the $CHCl_3$ layer and discard. Wash the aqueous layer with 5 mL of $CHCl_3$ and discard the latter. Add HCl (1 + 9) to the aqueous layer until it is just acidic to litmus paper, cool, and extract with three 50-mL portions of $CHCl_3$. Combine the $CHCl_3$ extracts, wash several times with water until the aqueous phase does not give an acid test with pH paper, and discard the aqueous layer. Dilute the $CHCl_3$ layer to 500 mL with $CHCl_3$ and store in an amber glass bottle preferably in a refrigerator.

27.3 *Hydroxylamine Hydrochloride Solution (10 g/L)*—Dissolve 0.5 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 50 ml of water. Prepare fresh as needed.

27.4 *Lead Standard Solution* (1 mL = 0.001 mg Pb)—Dissolve 0.2000 g of lead (purity 99.9 % minimum) in 20 mL

of HNO_3 (1 + 1), and heat moderately to expel oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 5 mL of this solution to a 1-L volumetric flask, dilute to volume, and mix.

27.5 *Sodium Citrate Solution*—Dissolve 30 g of sodium citrate dihydrate in 100 mL of distilled water. Add NH_4OH until the pH is between 9.5 and 10.0. Add 10 mL of $CHCl_3$ and 1 mL of dithizone solution, and shake. If the $CHCl_3$ solution is red or gray, add a few drops more of the dithizone solution and shake again. Repeat until the color becomes green. Discard the organic layer and re-extract with a 10 mL portion of fresh $CHCl_3$. If the color becomes green, draw off the organic phase and then extract several times more with $CHCl_3$ until the aqueous phase is colorless and the $CHCl_3$ phase is almost colorless or very light green.

27.6 *Sodium Cyanide Solution* (300 g/L)—Dissolve 60 g of sodium cyanide (NaCN) in 200 mL of water. Store in a polyethylene bottle. (**Warning—**The preparation, storage, use and disposal of NaCN solutions requires special care and attention. Avoid any possibility of inhalation, ingestion, or skin contact with the compound, its solutions, or its vapors. Work only in a well-ventilated hood. Refer to the Hazards Section of Practices E50.)

NOTE 4—Because of the strongly alkaline properties of NaCN solutions, contact with borosilicate glass may result in contamination of the reagent.

27.7 *Sodium Sulfite Solution* (Saturated)—Prepare a saturated solution of sodium sulfite (Na_2SO_3).

27.8 *Wash Solution*—Add 10 mL of NH_4OH, 40 mL of Na_2SO_3 solution, and 20 mL of NaCN solution (**Warning—** See 27.6.) to 100 mL of water, and dilute to 1 L with water (Note 4).

27.9 *Water*—Distilled water should be free of any lead salts. Low-quality water may be passed through a laboratory-type mixed-bed demineralizer prior to use.

28. Preparation of Calibration Curve

28.1 *Calibration Solutions*—Using pipets, transfer (1, 5, 10, 15, 20, and 25) mL of Standard Lead Solution (1 mL = 0.001 mg Pb) to 250-mL beakers and add enough water to make a total volume of approximately 25 mL. Proceed as directed in 28.3.

28.2 *Reference Solution*—Add 25 mL of water to a 250-mL beaker. Proceed as directed in 28.3.

28.3 *Color Development:*

28.3.1 In a well-ventilated hood, add 10 mL of sodium citrate solution, 10 mL of Na_2SO_3 solution, and 10 mL of NaCN solution (**Warning—**See 27.6.), heat at 80 °C for 3 min, and cool. Using a pH meter, adjust the pH to 10.5 ± 0.2 with NH_4OH (1 + 1) or HCl (1 + 1) as required. Cool to 10 °C and transfer to a 125-mL conical separatory funnel with a minimum of washing.

28.3.2 Using a pipet, transfer 10 mL of dithizone solution to the funnel, shake vigorously for 1 min, and allow the layers to separate. Draw off the lower $CHCl_3$ layer into a second 125-mL separatory funnel containing 50 mL of wash solution. Shake for 30 s, allow the layers to separate, and drain off the lower $CHCl_3$ layer into a third 125-mL separatory funnel containing 50 mL of wash solution. Shake for 30 s and allow the layers to separate thoroughly. Eliminate water droplets in the $CHCl_3$ solution by transferring this solution to a clean, dry test tube before transferring to the absorption cell.

28.3.3 If more than 0.005 % bismuth is present in the sample, the $CHCl_3$ layer should be back-washed with a solution of hydroxylamine hydrochloride (10 g/L) adjusted to a pH of 3.0.

28.4 *Spectrophotometry:*

28.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the reference solution (28.2) in absorption cells with a 1-cm light path and using a light band centered at 520 nm. Using the test cell, take spectrophotometric absorbance readings of the calibration solutions versus the reference solution (28.2).

28.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (28.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at 520 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

28.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of lead per 10 mL of solution. Follow the instrument manufacturer's instructions for generating the calibration curve.

29. Procedure

29.1 *Test Solution:*

29.1.1 Select a sample as follows:

Pb, %	Sample Weight, g	Dilution, mL	Aliquot Volume, mL
0.001 to 0.01	1.000	100	25
0.01 to 0.025	1.000	250	25
0.025 to 0.05	0.500	250	10

29.1.1.1 Weigh the sample to the nearest 0.1 mg and transfer it to a 250-mL beaker. Add 30 mL of HCl (1 + 1) and heat until dissolution is nearly complete. For high-carbon ferrochromium (4.00 % C to 9.00 % C), add 30 mL of HCl and several drops of HF, and heat until the reaction has subsided.

29.1.2 Add several drops of HF (omit if added in preceding paragraph) plus 10 mL of HNO_3 and 10 mL of $HClO_4$. Evaporate to heavy fumes of $HClO_4$ and fume until the volume is reduced to approximately 5 mL. Add H_2O_2 solution (1 + 9) dropwise until any precipitated manganese dioxide is dissolved. Boil to remove excess H_2O_2 and cool.

29.1.3 Dilute to approximately 100 mL, add NH_4OH (1 + 1) until the solution is neutral to litmus paper, and add 10 mL in excess. Boil for approximately 1 min, and cool.

29.1.4 If the sample does not contain sufficient iron, add a volume of iron solution equivalent to about 100 mg of iron to act as a carrier, and then adjust the pH again. Prepare the iron solution as follows: Dissolve 1 g of iron (lead content 0.001 %

TABLE 2 Statistical Information—Lead

Ferroalloy Type		Pb 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

maximum) in 10 mL of HCl (1 + 1) and 10 mL of HNO_3. Add 10 mL of $HClO_4$, heat to strong fumes, cool, and dilute to 100 mL.

29.1.5 Filter using a medium paper and wash 3 times or 4 times with NH_4OH (1 + 9). Discard the filtrate. Dissolve the precipitate with 30 mL of HCl (1 + 9) into the original 250-mL beaker, and wash the paper 6 times to 8 times with hot HCl (2 + 98). Add 10 mL of HNO_3 and 10 mL of $HClO_4$ to the beaker and evaporate to approximately 5 mL, and cool.

29.1.6 Transfer the solution to the appropriate volumetric flask, selected as directed in 29.1.1, dilute to volume, and mix. As directed in 29.1.1, use a pipet and transfer a suitable aliquot to a 250-mL beaker. Proceed as directed in 29.3.

29.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents but with the sample omitted. Proceed as directed in 29.3.

29.3 *Color Development*—Proceed as directed in 28.3.

29.4 *Spectrophotometry*—Proceed as directed in 28.4.

30. Calculation

30.1 Convert the net spectrophotometric absorbance reading of the test solution to milligrams of lead by means of the calibration curve. Calculate the percentage of lead as follows:

$$\text{Lead}, \% = A/(B \times 10) \quad (2)$$

where:

A = lead found in 10 mL of the final test solution, mg, and

B = sample represented in 10 mL of the final test solution, g.

31. Precision and Bias

31.1 Four laboratories cooperated in testing this test method and obtained the results shown in Table 2. Samples with lead compositions 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 test method is adequate for the contemplated use.

CHROMIUM BY THE SODIUM PEROXIDE FUSION-TITRIMETRIC TEST METHOD

32. Scope

32.1 This test method covers the determination of chromium in all carbon grades of ferrochromium in compositions from 50 % to 75 %.

33. Summary of Test Method

33.1 The sample is fused in sodium peroxide. After dissolution of the melt in dilute H_2SO_4, chromium and manganese are oxidized by ammonium peroxydisulfate with silver nitrate as a catalyst. The permanganate ions are reduced with HCl 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.

34. Interferences

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

35. Reagents

35.1 *Ammonium Peroxydisulfate* ($(NH_4)_2S_2O_8$).

35.2 *Ferrous Ammonium Sulfate Salt*—Fine, well mixed, free flowing crystals of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ will be required. Standardize as follows: Transfer 0.9806 g of NIST $K_2Cr_2O_7$ (equivalent to 200 mL of 0.1 *N* solution) to a 600-mL beaker. Add 300 mL of water, 30 mL of H_2SO_4 (1 + 1), and 8.00 g of the ferrous ammonium sulfate. Stir until completely dissolved. Add 6 drops of 1,10-phenanthroline indicator solution, and using a 50-mL buret, titrate with 0.1 *N* $KMnO_4$ 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* $K_2Cr_2O_7$ solution equivalent to 1 g of ferrous ammonium sulfate as follows:

$$A = (200 + B)/8 \quad (3)$$

where:

A = millilitres of 0.1 *N* $K_2Cr_2O_7$ solution equivalent to 1 g of ferrous ammonium sulfate, and

B = millilitres of 0.1 *N* $KMnO_4$ solution used.

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

35.3 *Ferrous Ammonium Sulfate, Standard Solution* (0.25 *N*) (Note 5)—Dissolve 89.6 g of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ in 500 mL of cold H_2SO_4 (5 + 95) and dilute to 1 L with H_2SO_4 (5 + 95). Use a solution that has been standardized within the previous 8 h as follows: Transfer 0.9806 g of NIST $K_2Cr_2O_7$ (equivalent to 200 mL of 0.1 *N* solution) to an 800-mL beaker. Add 300 mL of water, 30 mL of H_2SO_4 (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* $KMnO_4$ solution to the color change from red to green. Calculate the volume of 0.1 *N* $K_2Cr_2O_7$ solution equivalent to 1 mL of ferrous ammonium sulfate solution as follows:

$$A = (200 + B)/C \quad (4)$$

where:

A = millilitres of 0.1 *N* $K_2Cr_2O_7$ solution equivalent to 1 mL of ferrous ammonium sulfate solution,

B = millilitres of 0.1 *N* $KMnO_4$ solution used, and

C = millilitres of 0.25 *N* ferrous ammonium sulfate used.

NOTE 5—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.

35.4 *1,10-Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$).

35.5 *Ferrous Sulfate Solution* (0.025 M)—Dissolve 6.95 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in 500 mL of water and dilute to 1 L.

35.6 *Potassium Permanganate, Standard Solution* (0.1 *N*).

35.6.1 *Preparation*—Dissolve 3.2 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for 2 weeks. Filter, without washing, through a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

35.6.2 *Standardization*—Dry a portion of the NIST standard sample of sodium oxalate at 105 °C. Transfer 0.3000 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of $H2SO_4$ (5 + 95), previously boiled for 10 min to 15 min and then cooled to 27 °C ± 3 °C, and stir until the oxalate has dissolved. Add 39 mL to 40 mL (Note 6) of the $KMnO_4$ solution, at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s) (Note 7). Heat to 55 °C to 60 °C and complete the titration by adding $KMnO_4$ solution until a faint pink color persists for 30 s. Add the last 0.5 mL to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of H_2SO_4 (5 + 95), treated as above, with $KMnO_4$ solution to a faint pink color. The blank correction is usually equivalent to 0.30 mL ± 0.05 mL.

NOTE 6—A 0.3000-g portion of sodium oxalate requires 44.77 mL of $KMnO_4$ solution (0.1 *N*).

NOTE 7—If the $KMnO_4$ solution is too strong, the pink color will not fade at this point; begin again, adding a few millilitres less of the $KMnO_4$ solution.

35.7 *Potassium Permanganate Solution* (20 g/L)—Dissolve 20 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

35.8 *Silver Nitrate Solution* (8 g/L)—Dissolve 8 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

36. Procedure

36.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 30-mL iron crucible (Note 8). Add 8 g of dry sodium peroxide (Na_2O_2) 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 g to 2 g of Na_2O_2.

NOTE 8—Crucibles made of ingot iron have a negligible blank and resist attack by the molten peroxide.

36.2 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 avoid spattering. When the contents are molten, swirl the crucible to dissolve any unattacked 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.)

TABLE 3 Statistical Information[A] —Chromium

Test Specimens	Cr Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
Low-carbon ferrochromium	70.16	0.12	0.64
High-carbon ferrochromium	52.03	0.38	0.83
High-carbon ferrochromium (NIST 64b, 68.03 Cr)	68.09	0.25	0.59

[A] The reagent described in 35.2 was used to obtain these data.

36.3 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 H_2SO_4 (1 + 1), 5 mL of H_3PO_4 and 5 mL of HNO_3, heat to boiling and boil for several minutes. Cool to 70 °C to 80 °C, add 5 mL of $AgNO_3$ solution, 5 g of $(NH_4)_2S_2O_8$, and 3 drops or 4 drops of $KMnO_4$ solution (20 g/L). Boil for 10 min, add 5 mL of HCl (1 + 3), and boil for an additional 5 min after the $KMnO_4$ and any MnO_2 have completely disappeared. Cool to room temperature.

36.4 Select and weigh a portion of the standard ferrous ammonium sulfate salt (Note 9) to the nearest 0.1 mg as follows:

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 $KMnO_4$ standard solution to the color change from red to green.

NOTE 9—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 5).

37. Calculation

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

$$\text{Chromium, \%} = \frac{(A \times B) - C}{D} \times 0.1734 \qquad (5)$$

where:

A = millilitres of 0.1 *N* $K_2Cr_2O_7$ solution equivalent to 1 g of ferrous ammonium sulfate (see 35.2),
B = grams of ferrous ammonium sulfate used,
C = millilitres of 0.1 *N* $KMnO_4$ solution required to titrate the excess ferrous ammonium sulfate, and
D = grams of sample used.

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

$$\text{Chromium, \%} = \frac{(A \times B) - C}{D} \times 0.1734 \quad (6)$$

where:

A = millilitres of 0.1 N $K_2Cr_2O_7$ solution equivalent to 1 mL of ferrous ammonium sulfate solution (see 35.3),
B = millilitres of ferrous ammonium sulfate solution used,
C = millilitres of 0.1 N $KMnO_4$ solution required to titrate the excess ferrous ammonium sulfate, and
D = grams of sample used.

38. Precision and Bias

38.1 *Precision*—Nine laboratories cooperated in testing this test 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 of this test method is adequate for the contemplated use.

38.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference material in Table 3. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

39. Keywords

39.1 arsenic; chemical analysis; chromium; ferrochromium; lead