INTERNATIONAL

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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.

ε[1]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
Arsenic by the Molybdenum Blue Photometric Test Method [0.001 % to 0.005 %]	10-20
Lead by the Dithizone Photometric Method	20-30
Lead by the Dithizone Photometric Test Method [0.001 % to 0.05 %]	21-31
Chromium by the Sodium Peroxide Fusion-Titrimetric Method	31-37
Chromium by the Sodium Peroxide Fusion-Titrimetric Test Method [50 % to 75 %]	32-38

1.3

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 56.

[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. 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 Molecular Absorption Spectrometry
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E173 Practice for Conducting Interlaboratory Studies of ~~Test~~ Methods for Chemical Analysis of Metals[3] ~~E360Test Methods for Chemical Analysis of Silicon and Ferrosilicon~~
E~~361Test Methods for the Determination of Arsenic and Lead in Ferromanganese~~ 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. ~~Significance and Use~~

~~3.1These 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.~~ 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 metals and alloys are primarily intended to test such materials for compliance with compositional specifications such as Specification A101 and A481. 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.

5. Apparatus, Reagents, and Photometric Practice

~~4.1Apparatus 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 E50, except that photometers shall conform to the requirements prescribed in Practice~~

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

~~4~~5.2 Photometric practices prescribed in these test methods shall conform to Practice E60.

~~5.~~6. ~~Safety~~ Hazards

~~5.1For~~6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

~~6.~~

6.2 Specific hazard statements are given in 27.1, 27.5, and 36.2.

7. Sampling

~~6.1For~~7.1 For procedures for sampling the material, and for particle size of the sample for chemical analysis, refer to Practices E32.

~~7.~~

8. Rounding Calculated Values

~~7~~8.1 Calculated values shall be rounded to the desired number of places as directed in ~~6.4 to 6.6,~~ the Rounding Procedure~~,~~ of Practice E29.

~~8.Interlaboratory Studies~~

~~8.1These test methods have been evaluated in accordance with Practice E173, unless otherwise noted in the precision and bias section.~~

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

ARSENIC BY THE MOLYBDENUM BLUE PHOTOMETRIC METHOD

9. Scope

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

10.Summary of Method

10.1See Section 10 of Test Methods E360Interlaboratory 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 PHOTOMETRIC TEST METHOD

10. Scope

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

11. Concentration Range

11.1See Section 11 of Test Methods E360. 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. Photometric measurement is made at approximately 850 nm.

12. Stability of Color

12.1See Section 12 of Test Methods E360. 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 1—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

13.1See Section 13 of Test Methods E360

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

14.

15. Apparatus

14.1See Section 14 of Test Methods E360

15.1 Distillation Apparatus, Fig. 1.

15.Reagents

15.1Proceed as directed in 15.1 through 15.9 of Test Methods E360.

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 ($(NH_4)_6$-Mo_7O_{24}•$4H_2O$) 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 fl ask, dilute to volume, and mix.

16.6 *Hydrazine Sulfate* ($(NH_2)_2$•H_2SO_4).

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

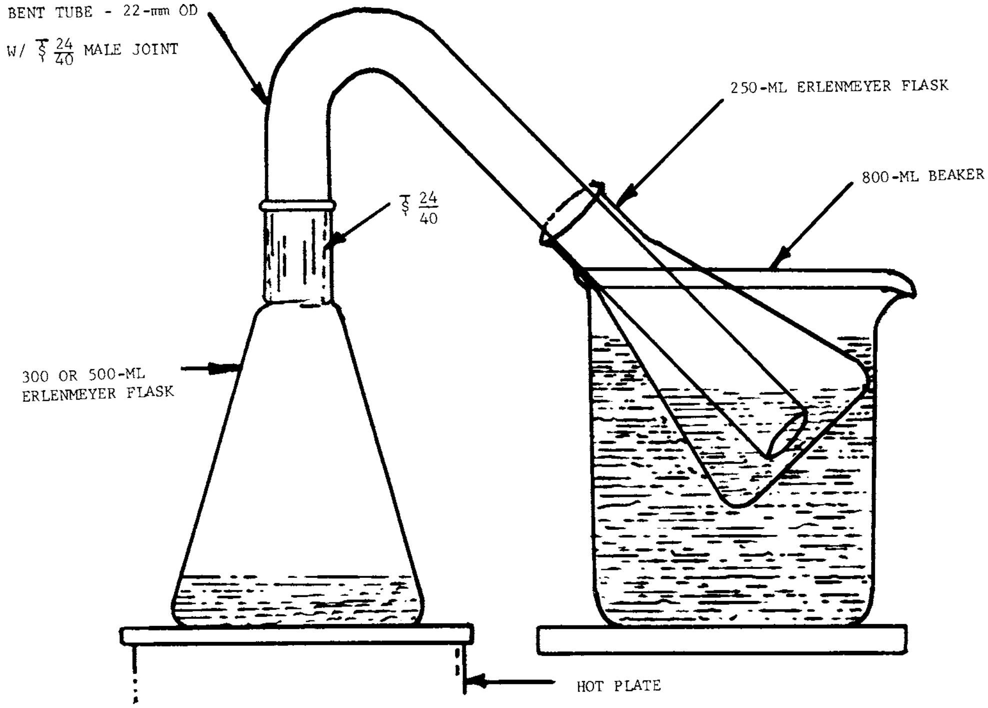

FIG. 1 Arsenic Distillation Apparatus

16.8 *Sodium Carbonate* (Na_2CO_3).

16.9 *Sodium Peroxide* (Na_2O_2).

17. Preparation of Calibration Curve

~~16.1Proceed as directed in 16.1 through 16.5 of Test Methods E360~~

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.

~~**17.Procedure**~~

~~17.1Proceed as directed in 17.1 through 17.4 of Test Methods E360~~

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 *Photometry*:

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

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

17.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of arsenic per 50 mL of solution.

18. ~~Calculation~~

~~18.1Proceed as directed in Section 18 of Test Methods E360~~Procedure

18.1 *Test Solution*:

18.1.1 Select and weigh a sample to the nearest 0.2 mg in accordance with the following:

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 ferrosilicon, or 8 g of Na_2O_2 plus 2 g of Na_2CO_3 if silicon 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 melted down quietly; 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_3 drop-wise 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 fi lter 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 fl ask, 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 beaker containing cold water. Assemble the apparatus (Fig. 1), heat the distillation fl ask, 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 fl ask, 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, for use as a reference solution.

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

18.4 *Photometry*—Take the photometric reading of the test solution as directed in 17.4.

19. Calculation

19.1 Convert the net photometric 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

19.1Nine20.1 Nine laboratories cooperated in testing this test 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 test method is adequate for the contemplated use.

LEAD BY THE DITHIZONE PHOTOMETRIC METHOD

20.Scope

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

21. Summary of Method

21.1See Section 21 of Test Methods E361. Scope

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

22. Concentration Range

22.1See Section 22 of Test Methods E361. Summary of Test Method

TABLE 1 Statistical Information—Arsenic

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

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

23. ~~Stability of Color~~

~~23.1See Section 23 of Test Methods E361.~~ 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 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 amounts of sample and reagents used.

24. ~~Interferences~~

~~24.1See Section 24 of Test Methods E361.~~ 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. ~~Apparatus~~

~~25.1See Section 25 of Test Methods E361.~~ Interferences

25.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1. If more than 0.005 % bismuth is present, it must be removed as directed in Note 4 in order to avoid high results for lead.

26. ~~Reagents~~

~~26.1Proceed as directed in Section 26 of Test Methods E361.~~ 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 is to be used in a well-ventilated hood. Consult the Material 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 *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.

27.4 *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.

27.5 *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 3—Because of the strongly alkaline properties of NaCN solutions, contact with borosilicate glass may result in contamination of the reagent.

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

27.7 *Wash Solution*—Add 10 mL of NH_4OH, 40 mL of Na_2SO_3 solution, and 20 mL of NaCN solution (**Warning—**See 27.5.) to 100 mL of water, and dilute to 1 L with water (Note 3).

27.8 *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

~~27.1Proceed as directed in 27.1 through 27.5 of Test Methods E361~~

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.