



Designation: E363 – 16

# Standard Test Methods for Chemical Analysis of Chromium and Ferrochromium<sup>1</sup>

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 ( $\epsilon$ ) 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*

<sup>1</sup> 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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*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:<sup>2</sup>

- 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)<sup>3</sup>
- 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

<sup>2</sup> 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.

<sup>3</sup> 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* ( $\text{NH}_4\text{Br}$ ).

16.2 *Ammonium Molybdate Solution* (10 g/L)—Dissolve 2.5 g of ammonium heptamolybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) in 40 mL of warm water. Add 128 mL of  $\text{H}_2\text{SO}_4$  (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 ( $\text{As}_2\text{O}_3$ ) 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* ( $(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ ).

16.7 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ( $(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ ) in water, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 day.

16.8 *Sodium Carbonate* ( $\text{Na}_2\text{CO}_3$ ).

16.9 *Sodium Peroxide* ( $\text{Na}_2\text{O}_2$ ).

## 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  $\text{HNO}_3$  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.

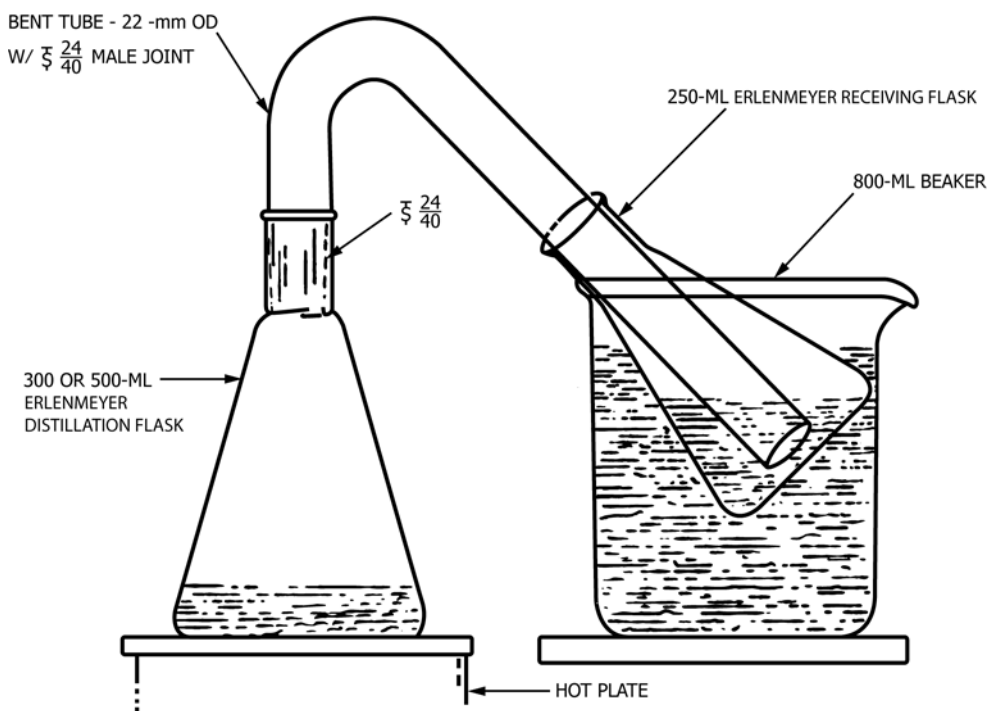


FIG. 1 Arsenic Distillation Apparatus

17.2 *Reference Solution*—Transfer 10 mL of HNO<sub>3</sub> 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<sub>2</sub>O<sub>2</sub> and 1 g of Na<sub>2</sub>CO<sub>3</sub> if ferrochromium, or 8 g of Na<sub>2</sub>O<sub>2</sub> plus 2 g of Na<sub>2</sub>CO<sub>3</sub> 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 unattached 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<sub>2</sub>SO<sub>4</sub> (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<sub>2</sub>SO<sub>4</sub> dropwise until the solution clears.

18.1.4 Heat to boiling, and cool. While stirring vigorously, add NH<sub>4</sub>OH 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<sub>3</sub> (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<sub>4</sub>Br and 0.75 g of hydrazine sulfate. Add 20 mL of HNO<sub>3</sub> (1 + 1) to the receiving flask, and place the flask in an 800-mL

**TABLE 1 Statistical Information—Arsenic**

Ferrous Alloy Type	As Found, %	Repeatability	Reproducibility
		( <i>R</i> <sub>1</sub> , Practice E173)	( <i>R</i> <sub>2</sub> , 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<sub>4</sub>OH. 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<sub>3</sub> (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<sub>3</sub> (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<sub>3</sub>)—(**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 (diphenylthiocarbazon) in 80 mL of CHCl<sub>3</sub> in a 500-mL conical separatory funnel, add 100 mL of cold water and 10 mL of NH<sub>4</sub>OH, stopper, and shake vigorously for 1 min to 2 min. Draw off the CHCl<sub>3</sub> layer and discard. Wash the aqueous layer with 5 mL of CHCl<sub>3</sub> 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<sub>3</sub>. Combine the CHCl<sub>3</sub> 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<sub>3</sub> layer to 500 mL with CHCl<sub>3</sub> 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<sub>2</sub>OH·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