



Designation: E 315 – 88 (Reapproved 1999)

Standard Test Methods for Chemical Analysis of Molybdenum¹

This standard is issued under the fixed designation E 315; 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 molybdenum and molybdenum alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Carbon	0.010 to 0.040
Iron	0.020 max
Molybdenum	99.25 to 99.99
Nickel	0.010 max
Nitrogen	0.0010 max
Oxygen	0.0030 max
Silicon	0.010 max
Titanium	0.005 to 0.55
Zirconium	0.06 to 0.12

1.2 The test methods in this standard are contained in the sections indicated below:

	Sections
Nickel by the Persulfate-Dimethylglyoxime Photometric Method	9-18
Iron by the 1,10-Phenanthroline Photometric Method	19-29
Silicon by the Molybdenum Blue-Extraction Photometric Method	30-40

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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary information is given in Section 5.

2. Referenced Documents

2.1 ASTM Standards:

- B 384** Specification for Molybdenum and Molybdenum Alloy Forgings²
- B 385** Specification for Molybdenum and Molybdenum Alloy Billets for Reforging²
- B 386** Specification for Molybdenum and Molybdenum Alloy Plate, Sheet, Strip, and Foil²
- B 387** Specification for Molybdenum and Molybdenum Alloy Bar, Rod, and Wire²
- E 29** Practice for Using Significant Digits in Test Data to

¹ These test methods are under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Titanium, Zirconium, Wolfram, Molybdenum, Tantalum, Niobium, Hafnium.

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² Annual Book of ASTM Standards, Vol 02.04.

Determine Conformance With Specifications³

- E 50** Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴
- E 60** Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴
- E 173** Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁴

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 sections, and other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50E 50, except the photometers shall conform to the requirements prescribed in Practice E 60E 60.

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

5. Hazards

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

6. Sampling

6.1 For procedures for sampling the material, refer to Specifications B 384, B 385, B 386, and B 387B 384B 385B 386B 387.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29E 29.

³ Annual Book of ASTM Standards, Vol 14.02.

⁴ Annual Book of ASTM Standards, Vol 03.05.

8. Interlaboratory Studies

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

NICKEL BY THE PERSULFATE-DIMETHYLGLYOXIME PHOTOMETRIC TEST METHOD

9. Scope

9.1 This test method covers the determination of nickel in concentrations from 1 to 400 ppm. The range may be extended by suitably varying the sample weight, aliquot size, amount of reagents, and cell depth.

10. Summary of Test Method

10.1 A red soluble salt of trivalent nickel and dimethylglyoxime is formed. Photometric measurement is made at approximately 445 nm.

11. Concentration Range

11.1 The recommended concentration ranges are from 1.0 to 2.0 μg and from 10 to 100 μg of nickel for each 50 mL of solution, using cell depths of 5 and 2 cm respectively.

NOTE 1—This test method has been written for cells having 5 and 2-cm light paths. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

12. Stability of Color

12.1 The color develops in 5 min and is stable for 30 min.

13. Interferences

13.1 Provision has been made for the correction of any interfering elements present.

14. Reagents

14.1 *Ammonium Persulfate Solution (150 g/L)*—Dissolve 15 g of ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ in water and dilute to 100 mL. Prepare fresh as needed.

14.2 *Citric Acid Solution (100 g/L)*—Dissolve 10 g of citric acid in water and dilute to 100 mL.

14.3 *Nickel, Standard Solution A (1 mL = 10 μg Ni)*—Dissolve 0.1000 g of nickel (purity 99.9 % min) in 10 mL of water and 5 mL of HNO_3 in a 150-mL beaker. When dissolution is complete boil to remove oxides of nitrogen. Cool to room temperature, transfer to a 1-L volumetric flask, dilute to volume, and mix. Transfer a 50-mL aliquot of this solution to a 500-mL volumetric flask, dilute to volume, and mix.

14.4 *Nickel, Standard Solution B (1 mL = 1 μg Ni)*—Transfer a 10-mL aliquot of nickel solution A (1 mL = 10 μg Ni) to a 100-mL volumetric flask, dilute to volume, and mix.

14.5 *Sodium Dimethylglyoximate Solution (30 g/L)*—Dissolve 30 g of sodium dimethylglyoximate in water and dilute to 1 L.

15. Preparation of Calibration Curves

15.1 *Calibration Solutions:*

15.1.1 Transfer 1.00, 3.00, 4.00, 7.00, and 10.00 mL of nickel solution A (1 mL = 10 μg Ni) to five 50-mL volumetric flasks, dilute to 20 mL, and proceed as directed in 15.3.

15.1.2 Transfer 1.00, 5.00, 10.00, 15.00, and 20.00 mL of nickel solution B (1 mL = 1 μg Ni) to five 50-mL volumetric flasks, dilute to 20 mL, and proceed as directed in 15.3.

15.2 *Reference Solution*—Transfer 20 mL of water to a 50-mL volumetric flask and proceed as directed in 15.3.

15.3 *Color Development*—Add 4 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, 5 mL of citric acid solution, and 10 mL of NH_4OH , and cool to room temperature. Add 1 mL of sodium dimethylglyoximate solution, dilute to volume, and mix.

15.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 2 or a 5-cm light path, as appropriate (see 11.1), and adjust the photometer to the initial setting, using a light band centered at approximately 445 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

15.5 *Calibration Curves*—Plot the photometric readings of the calibration solutions against micrograms of nickel per 50 mL of solution.

16. Procedure

16.1 *Test Solution:*

16.1.1 Select a sample weight in accordance with the following table:

Nickel, ppm	Sample Weight, g
1 to 50	1.00
45 to 120	0.50
115 to 400	0.25

16.1.2 Weigh duplicate samples of the size selected to the nearest 1 mg (Note 2), and transfer to 100-mL beakers. Add 10 mL of HCl and heat. Add HNO_3 dropwise until all the metal has decomposed (Note 3). Remove from the hot plate and cool.

NOTE 2—Duplicate samples are taken in order to have one available to determine the sample blank. For the higher concentrations of nickel, a larger sample may be dissolved and diluted to volume; duplicate aliquots may then be taken from a single sample.

NOTE 3—If any molybdic oxide precipitates, add more HCl dropwise and boil gently until the molybdenum is completely in solution.

16.1.3 Transfer the solutions to 50-mL volumetric flasks and dilute to about 20 mL.

16.2 *Reference Solution*—Distilled water.

16.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amount of all reagents.

16.4 *Sample Blank Solution*—Treat the duplicate as directed in 15.3 but omit the addition of the sodium dimethylglyoximate solution.

16.5 *Color Development*—Proceed as directed in 15.3.

16.6 *Photometry*—Take the photometric readings of the reagent blank solution, the sample blank solution, and the test solution as directed in 15.4.

17. Calculation

17.1 Convert the photometric readings of the test solution to micrograms of nickel, and of the reagent blank and sample

blank solutions to the equivalent micrograms of nickel from the appropriate calibration curve. Calculate the parts per million of nickel as follows:

$$\text{Nickel, ppm} = [A - (B + C)]/D \quad (1)$$

where:

A = micrograms of nickel found in 50 mL of the final solution,

B = reagent blank correction, in equivalent micrograms of nickel,

C = sample blank correction, in equivalent micrograms of nickel, and

D = grams of sample represented in 50 mL of the final solution.

18. Precision and Bias

18.1 *Precision*—Data on this test method were obtained by nine cooperators. Repeatability, standard deviation, and coefficient of reproducibility were graphically calculated as directed in Practices E 173E 173, and were found to be as listed in Table 1.

18.2 *Bias*—Data on bias is not available because of the lack of standard samples. However, one cooperator prepared synthetic samples containing the equivalent of 53.9 ppm of nickel and recoveries within 0.8 ppm were obtained. Another cooperator added 25 µg of nickel, equivalent to 25 ppm, to four 1-g samples of Material A. Nickel recoveries (25 ppm plus 4 ppm present) ranged between 28 and 30 ppm.

IRON BY THE 1,10-PHENANTHROLINE PHOTOMETRIC TEST METHOD

19. Scope

19.1 This test method covers the determination of iron in concentrations from 50 to 750 ppm.

20. Summary of Test Method

20.1 The iron is reduced with hydroxylamine hydrochloride and converted to the 1,10-phenanthroline complex. Photometric measurement is made at approximately 510 nm.

21. Concentration Range

21.1 The recommended concentration range is from 50 to 300 µg of iron for each 100 mL of solution, using a 2-cm cell.

NOTE 4—This test method has been written for cells having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

22. Stability of Color

22.1 The color develops fully after heating at 60 to 70°C for 30 min and is stable for 15 to 20 h.

23. Interferences

23.1 Nickel, copper, and cobalt interfere if present in the final test solution in amounts greater than 800 µg, 1600 µg, and 800 µg, respectively. Reduced molybdenum produces a positive error and provision has been made in the method to eliminate this interference.

24. Apparatus

24.1 *Plastic (TFE-Fluorocarbon) Beakers and Covers*, 50-mL capacity.

NOTE 5—Platinum beakers and covers may be used.

25. Reagents

25.1 *Ammonium Citrate-Sodium Borate Solution*—Dissolve 200 g of ammonium citrate in 800 mL of water, and dilute to 1 L. Dissolve 85 g of sodium tetraborate, (Na₂B₄O₇·10H₂O) in 900 mL of hot water, cool, and dilute to 1 L. Transfer the two solutions to a 2-L bottle, and mix.

25.2 *Hydroxylamine Hydrochloride (10 g/L)*—Dissolve 1 g of hydroxylamine hydrochloride (NH₂OH·HCl) in water and dilute to 100 mL. Do not use a solution that has stood longer than 8 h.

25.3 *Iron, Standard Solution (1 mL = 100 µg Fe)*—Dissolve 0.1000 g of iron (purity: 99.8 % min)⁵ in 60 mL of HCl (1 + 1). Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

25.4 *1,10-Phenanthroline Solution (2 g/L)*—Dissolve 0.4 g of 1,10-phenanthroline monohydrate in 150 mL of warm water and dilute to 200 mL.

25.5 *Reagent Mixture*—Transfer 10 mL of HF and 8 mL of HNO₃ to a 50-mL plastic beaker (Note 5) and evaporate to about 10 mL. Add about 30 mL of water and transfer to a 500-mL volumetric flask containing 360 mL of ammonium citrate-sodium borate solution. Cool, dilute to volume, and mix.

26. Preparation of Calibration Curve

26.1 *Calibration Solution*—Using pipets, transfer 0.5, 1, 2, and 3 mL of iron solution (1 mL = 100 µg Fe) to 100-mL volumetric flasks containing 50 mL of reagent mixture, and dilute to about 75 mL. Proceed as directed in 26.3.

26.2 *Reference Solution*—Transfer 50 mL of reagent mixture to a 100-mL volumetric flask and dilute to about 75 mL.

26.3 *Color Development*—Using pipets, transfer 5 mL of NH₂OH·HCl solution and 10 mL of 1,10-phenanthroline solution. Dilute to about 90 mL and heat in a water bath at 60 to 70°C for 30 min. Cool, dilute to volume, and mix.

26.4 *Photometry*:

26.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 2-cm light path (see Note 4) and a light band centered at approximately 510 nm. Using the test cell, take the photometric readings of the calibration solutions.

26.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light

TABLE 1 Statistical Information

Test Material	Mean, ppm Ni	Repeatability, ppm Ni	Standard Deviation, ppm Ni	Coefficient of Reproducibility, %
A	3.9	0.737	0.226	18.9
B	114	11.04	3.45	9.7

⁵ National Institute of Standards and Technology Sample 55 has been found satisfactory for this purpose.