



Designation: ~~E1587-05~~ Designation: E1587 - 10

## Standard Test Methods for Chemical Analysis of Refined Nickel<sup>1</sup>

This standard is issued under the fixed designation E1587; 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 apply to the chemical analysis of refined nickel and other forms of metallic nickel having chemical compositions within the following limits:

<u>Element</u>	<u>Weight %</u>
Antimony, less than	0.005
Arsenic, less than	0.005
Bismuth, less than	0.01
Cadmium, less than	0.0025
Carbon, max	0.03
Cobalt, max	1.00
Copper, max	1.00
Hydrogen, max	0.003
Iron, max	0.15
Lead, less than	0.01
Manganese, less than	0.20
Nickel, min	98.0
Nitrogen, less than	0.50
Oxygen, less than	0.03
Phosphorus, less than	0.005
Selenium, less than	0.0010
Silicon, less than	0.005
Silver, less than	0.01
Sulfur, max	0.01
Tellurium, less than	0.0010
Thallium, less than	0.0010
Tin, less than	0.005
Zinc, less than	0.015

1.2 These test methods may be used to determine the following elements by the methods indicated below:

- ~~Antimony, Arsenic, Bismuth, Cadmium, Lead, Selenium, Silver, Tellurium, Tin, and Thallium by the Electrothermal Atomic Absorption Method~~
- ~~Bismuth, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Silver, and Zinc by the Flame Atomic Absorption Method~~
- ~~Carbon, Total, by the Combustion-Instrumental Method~~
- ~~Nickel by the Dimethylglyoxime Gravimetric Method~~
- ~~Nitrogen by the Inert Gas Fusion Thermal Conductivity Method~~
- ~~Oxygen by the Inert Gas Fusion Method~~
- ~~Sulfur by the Infrared Absorption Method~~

<u>Test Methods</u>	<u>Sections</u>
<u>Antimony, Arsenic, Bismuth, Cadmium, Lead, Selenium, Silver, Tellurium, Tin, and Thallium by the Graphite Furnace Atomic Absorption Spectrometric Method</u>	<u>21-31</u>
<u>Bismuth, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Silver, and Zinc by the Flame Atomic Absorption Spectrometric Method</u>	<u>9-20</u>

<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 E01.08 on Ni and Co and High Temperature Alloys.

Current edition approved May/Dec. 15, 2005-2010. Published June 2005-February 2011. Originally approved in 1994. Last previous edition approved in 1998 as E1587-94(1998):E1587 - 05. DOI: 10.1520/E1587-105.

<u>Carbon, Total, by the Combustion-Instrumental Method (Refer to Test Methods E1019)</u>	<u>32</u>
<u>Test Methods</u>	<u>Sections</u>
<u>Nitrogen by the Inert Gas Fusion Thermal Conductivity Method (Refer to Test Methods E1019)</u>	<u>45</u>
<u>Oxygen by the Inert Gas Fusion Method (Refer to Test Methods E1019)</u>	<u>46</u>
<u>Phosphorus by the Phosphovanadomolybdate Molecular Absorption Spectrometric Method (Refer to Test Methods E1019)</u>	<u>47</u>
<u>Sulfur by the Combustion-Infrared Absorption Method (Refer to Test Methods E1019)</u>	<u>33</u>
<u>Sulfur by the Methylene Blue Spectrophotometric Method After Generation of Hydrogen Sulfide</u>	<u>34-44</u>

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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautions, see Section 6.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D1193 [Specification for Reagent Water](#)

E29 [Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications](#) E39 [Methods for Chemical Analysis of Nickel](#)

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](#) [bbf93a3/astm-e1587-10](#)

E1019 [Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques](#)

E1024 [Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry](#)

E1601 [Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method](#)

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method  
 E1917 Test Method for Determination of Phosphorus in Nickel, Ferronickel, and Nickel Alloys by Phosphovanadomolybdate  
 Molecular Absorption Spectrometry

2.2 *ISO Standard*:<sup>3</sup>

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility by Interlaboratory Tests

### 3. Terminology

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

### 4. Significance and Use

4.1 These test methods are primarily intended to test refined nickel metal 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 the analytical work will be performed in a properly equipped laboratory under appropriate quality control practices.

### 5. Apparatus, Reagents, and Instrumental Practices

#### 5.1 Apparatus:

5.1.1 Special apparatus and reagents required for each determination are listed in the Apparatus section of each test method.

5.1.2 Glass storage containers shall be of borosilicate glass.

5.1.3 Plastic containers shall be polyethylene or preferably polytetrafluoroethylene (PTFE).

#### 5.2 Reagents:

5.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in each Precision and Bias section.

5.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

5.2.3 Reagents and their preparation are described in the Reagents section in each test method.

5.2.4 Instructions for the preparation of standard solutions used in these test methods frequently call for measuring exact weights of substances of known composition so that the concentrations of the resulting standard solutions can be expressed using simple numbers. Small variations from these specified quantities are acceptable, provided that the true weighed masses are used to calculate the concentration of the prepared solutions and then these calculated values are used throughout the test methods.

5.3 *Instrumental Practices*—Information on the use of some instrumental techniques employed in these test methods are described in Practice E60 and in Guide E1024.

### 6. Hazards

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

6.2 Where appropriate, specific precautionary information is given in the Hazards sections and in special warning paragraphs.

### 7. Sampling

7.1 Sampling shall be carried out by a mutually acceptable method.

7.2 The laboratory sample normally is in the form of a powder, granules, millings, or drillings and no further preparation is necessary.

7.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it may be cleaned by washing with high-purity acetone and drying in air.

7.4 If the laboratory sample contains particles or pieces of widely varying sizes, the test sample should be obtained by riffing or coning and quartering techniques.

### 8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method in Practice E29.

## SILVER, BISMUTH, CADMIUM, COBALT, COPPER, IRON, MANGANESE, LEAD, AND ZINC BY THE FLAME ATOMIC ABSORPTION SPECTROMETRIC METHOD

### 9. Scope

9.1 This test method applies to the determination of the silver, bismuth, cadmium, cobalt, copper, iron, manganese, lead, and

<sup>3</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

zinc contents of refined, wrought, and cast nickel metal within the following ranges.

Element	Concentration Range, %	
	Method A	Method B Ag
Silver	0.0002 to 0.01	...Bi
Silver	0.0002 to 0.01	...
Bismuth	0.0010 to 0.01	...Cd
Bismuth	0.0010 to 0.01	...
<del>Cadmium</del>	<del>0.0002 to 0.0025</del>	...Ce
Cadmium	0.0002 to 0.0025	...
<del>Cobalt</del>	<del>0.0010 to 0.01</del>	0.01 to 1.00 Cu
Cobalt	0.0010 to 0.01	0.01 to 1.00
<del>Copper</del>	<del>0.0005 to 0.01</del>	0.01 to 1.00 Fe
Copper	0.0005 to 0.01	0.01 to 1.00
<del>Iron</del>	<del>0.0025 to 0.01</del>	0.01 to 0.15 Mn
Iron	0.0025 to 0.01	0.01 to 0.15
<del>Manganese</del>	<del>0.0005 to 0.01</del>	0.01 to 0.20 Pb
Manganese	0.0005 to 0.01	0.01 to 0.20
<del>Lead</del>	<del>0.0006 to 0.01</del>	...Zn
Lead	0.0006 to 0.01	...
Zinc	0.0005 to 0.0025	0.001 to 0.015

9.2 This test method is applicable to the independent determination of any one or more of the elements listed without including all the elements specified in the standard solutions.

9.3 The lower level for iron can be extended to less than 0.0025 % provided nickel metal containing less than 0.0001 % iron is used for preparation of standards.

9.4 The upper limit for the determination of cobalt and copper can be raised to 2 % by a minor modification to the test method. See Note 6.

## 10. Summary of Test Method

10.1 The sample is dissolved in dilute nitric acid,  $\text{HNO}_3$ , excess acid is evaporated, and the solution diluted to a known volume. The test solution is aspirated into the air/acetylene flame of an atomic absorption spectrometer. The absorption of the resonance line energy from the spectrum of each element is measured and compared with that from a set of calibration solutions of the same element in a matched nickel matrix.

## 11. Interferences

11.1 Elements ordinarily present in nickel metal do not present spectral interferences in the atomic absorption analysis.

11.2 For the determination of silver, take care to avoid contamination of the sample and calibration solutions with chloride.

11.3 Potential background absorption interference is eliminated by use of matched matrix standards prepared from high-purity nickel metal. See Note 7.

## 12. Apparatus

12.1 *Atomic Absorption Spectrometer* :

12.1.1 The atomic absorption spectrometer used in this test method ~~shall~~should meet the instrument performance parameters in accordance with Guide E1024.

12.1.2 The instrument shall be equipped with a burner head capable of accepting a solution containing 25 g/L of nickel, as nitrate, and suitable for an air/acetylene flame.

12.1.3 The instrument should be capable of using single-element hollow cathode or electrodeless discharge lamps operated at currents recommended by the instrument manufacturer.

## 13. Reagents

13.1 *Bismuth, Standard Stock Solution* (1 mL = 1 mg Bismuth):

13.1.1 Transfer a 1.00-g sample of bismuth metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker.

13.1.2 Add 40 mL of  $\text{HNO}_3$  (1 + 1) (Note 1) and heat gently until dissolution is complete. Boil gently to expel oxides of nitrogen and cool. Transfer to a 1-L volumetric flask containing 160 mL of  $\text{HNO}_3$  (1 + 1), dilute to volume with water, and mix. Store in a polyethylene or PTFE bottle.

NOTE 1—Use the same batch of nitric acid,  $\text{HNO}_3$ , throughout the entire procedure. Also see Note 4.

13.2 *Cadmium, Standard Stock Solution* (1 mL = 1 mg Cadmium)—Transfer a 1.00-g sample of cadmium metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.3 *Cobalt, Standard Stock Solution* (1 mL = 1 mg Cobalt)—Transfer a 1.00-g sample of cobalt metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.4 *Copper, Standard Stock Solution* (1 mL = 1 mg Copper)—Transfer a 1.00-g sample of copper metal (purity, 99.9 %

minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.5 *Iron, Standard Stock Solution (1 mL = 1 mg Iron)*—Transfer a 1.00-g sample of iron metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.6 *Lead, Standard Stock Solution (1 mg = 1 mg Lead)*—Transfer a 1.00-g sample of lead metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.7 *Manganese, Standard Stock Solution (1 mL = 1 mg Manganese)*—Transfer a 1.00-g sample of manganese metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

13.8 *Nickel Powder*—High-purity, containing less than 0.0005 % Iron and less than 0.0001 % each of silver, bismuth, cadmium, cobalt, copper, manganese, lead, and zinc.

13.9 *Silver, Standard Stock Solution (1 mL = 1 mg Silver)*—Transfer a 1.00-g sample of silver metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2, except store in an amber glass container.

13.10 *Zinc, Standard Stock Solution (1 mL = 1 mg Zinc)*—Transfer a 1.00-g sample of zinc metal (purity, 99.9 % minimum), weighed to the nearest 0.001 g, to a 600-mL beaker. Proceed as directed in 13.1.2.

#### 13.11 Working Solutions:

13.11.1 *Mixed Analyte Standard Solution A (1 mL = 20 µg of Silver, Bismuth, Cadmium, Cobalt, Copper, Iron, Manganese, and Lead and 10 µg of Zinc)*—Using pipets, transfer 20.0 mL of each of the standard stock solutions for Silver, Bismuth, Cadmium, Cobalt, Copper, Iron, Manganese, and Lead and 10 mL of the standard stock solution for Zinc to a 1-L volumetric flask containing 160 mL of HNO<sub>3</sub>. Mixed Analyte Standard Solution A (1 mL = 20 µg of silver, bismuth, cadmium, cobalt, copper, iron, manganese, and lead and 10 µg of zinc)—Using pipets, transfer 20.0 mL of each of the standard stock solutions for silver, bismuth, cadmium, cobalt, copper, iron, manganese, and lead and 10 mL of the standard stock solution for zinc to a 1-L volumetric flask containing 160 mL of HNO<sub>3</sub> (1 + 1) (Note 1). Dilute to volume with water and mix. Store in a glass container.

13.11.2 *Mixed Analyte Standard Solution B (1 mL = 100 µg of Cobalt, Copper, Iron, and Manganese and 10 µg of Zinc)*—Using pipets, transfer 50.0 mL of the Cobalt, Copper, Iron, and Manganese standard stock solutions and 5.0 mL of the Zinc standard stock solution to a 500-mL volumetric flask. Dilute to volume and mix. Store in a polyethylene or PTFE container. (1 mL = 100 µg of cobalt, copper, iron, and manganese and 10 µg of zinc)—Using pipets, transfer 50.0 mL of the cobalt, copper, iron, and manganese standard stock solutions and 5.0 mL of the zinc standard stock solution to a 500-mL volumetric flask. Dilute to volume and mix. Store in a polyethylene or PTFE container.

## 14. Calibration Solutions

### 14.1 Set A:

14.1.1 This set corresponds to (0, 0.2, 0.5, 1.0, 1.5, 2.0, and 2.5) µg/mL each of silver, bismuth, cadmium, cobalt, copper, iron, manganese, and lead and (0, 0.1, 0.25, 0.5, 0.75, 1.0, and 1.25) µg/L of Zinc. zinc.

Analyte Concentration  $\mu\text{g/mL}$

No.	Aliquot of Solution A, mL	Silver, Bismuth, Cadmium, Cobalt, Copper, Iron, Manganese and Lead	Zinc
No.	Aliquot of Solution A, mL	Silver, Bismuth, Cadmium, Cobalt, Copper, Iron, Manganese, and Lead	Zinc
1	0	0	0
2	2.0	0.2	0.1
3	5.0	0.5	0.25
4	10.0	1.0	0.5
5	15.0	1.5	0.75
6	20.0	2.0	1.0
7	25.0	2.5	1.25

14.1.2 Weigh, to the nearest 0.01 g, seven separate 5.0-g portions of high-purity nickel powder and transfer to 600-mL beakers. Treat as directed in 15.2 to the point of dilution.

14.1.3 Add, using a buret graduated in 0.05-mL divisions, (0, 2.0, 5.0, 10.0, 15.0, 20.0, and 25.0) mL respectively of the mixed Analyte<sub>2</sub> Standard Solution A to the 200-mL volumetric flasks. Dilute to volume with water and mix.

NOTE 2—The solution with zero addition is the reagent blank. See 15.3 and Note 5.

14.2 Set B:

14.2.1 This set corresponds to (0, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0)  $\mu\text{g/mL}$  of cobalt, copper, iron, and manganese; and (0, 0.25, 0.5, 1.0, 1.5, 2.0, and 2.5)  $\mu\text{g/mL}$  of ~~Zinc~~-zinc.

No.	Aliquot of Mixed Analyte Standard Solution B, mL	Cobalt, Copper, Iron, and Manganese	Zinc
No.	Aliquot of Mixed Analyte, Standard Solution B, mL	Cobalt, Copper, Iron, and Manganese	Zinc
1	0	0	0
2	5.0	2.5	0.25
3	10.0	5.0	0.5
4	20.0	10.0	1.0
5	30.0	15.0	1.5
6	40.0	20.0	2.0
7	50.0	25.0	2.5

14.2.2 Weigh, to the nearest 0.005 g, seven separate 2.00-g portions of high-purity nickel powder and transfer to 400-mL beakers. Dissolve as directed in 16.2.2.

14.2.3 Using a buret, add (0, 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0) mL respectively of the mixed Analyte<sub>2</sub> Standard Reference Solution B to the 200-mL volumetric flasks. Dilute to volume with water and mix. The solution with no analyte added is the blank. See Note 5.

NOTE 3—For convenience, 80 g of nickel/L stock nickel nitrate solution may be prepared by dissolving 20.0 g of nickel powder in water and 120 mL of  $\text{HNO}_3$  (1 + 1) in an 800-mL beaker and filtering through acid-washed glass wool or a cellulose filter into a 250-mL volumetric flask. Aliquots (25.0 mL) of this solution are then evaporated and processed as directed in 14.2 and 15.2.

15. Procedure A

15.1 This procedure is applicable to 0.0005 % to 0.01 % of silver, bismuth, cadmium, cobalt, copper, iron, manganese, and lead and 0.0005 % to 0.005 % zinc.

15.2 Preparation of Test Solution—Weigh, to the nearest 0.01 g, 4.9 g, to ~~6.1 g~~ 6.1 g of the test sample and transfer to a clean, unetched 600-mL beaker. Add sufficient water to cover the sample and dissolve by adding 60 mL of  $\text{HNO}_3$  (1 + 1) in small portions. Heat to complete dissolution, boil gently to expel oxides of nitrogen, and evaporate to a viscous syrup. Redissolve the salts by adding 20 mL  $\text{HNO}_3$  (1 + 1) and 100 mL of  $\text{H}_2\text{O}$ -water. Heat to complete dissolution, cool, and filter, if necessary, through either glass wool or a cellulose filter which have been washed with  $\text{HNO}_3$  (1 + 1). Collect the filtrate in a 200-mL volumetric flask. Wash the filter with water, collecting the washings, and dilute to volume with water and mix.

NOTE 4—If inhomogeneity is suspected in the test sample, or if the sample pieces are relatively large, a larger sample weight should be used to prepare the test solution. Under such circumstances, a sample weight of 25 g in a final volume of 1000-mL may be used. The amount of  $\text{HNO}_3$  should be increased in proportion. Even larger sample weights can be used, with greater amounts of  $\text{HNO}_3$  to prepare a more concentrated nickel test solution. However, an aliquot portion to correspond to a 5-g sample must be taken from such a solution and processed in accordance with the procedure given to give a test solution containing 25 g/L of nickel to match the calibration solutions.

15.3 Reagent Blank Solution—The zero reference solution of the Calibration Solution Set A (14.1) serves as the reagent blank, since the same batch of nitric acid  $\text{HNO}_3$  is used for dissolution of both the nickel reference and test samples.

NOTE 5—If it is impossible to use the same batch of nitric acid  $\text{HNO}_3$ , a second reagent blank shall be prepared using the same high-purity nickel powder. This blank is then compared with the standard zero calibration solution and an appropriate correction made.



**15.4 Instrumental Parameters:**

15.4.1 Use the spectral lines specified in the following table:

Spectral Lines—Procedure A

Element	Silver	Bismuth	Cadmium	Cobalt	Copper
Wavelength, nm	328.1	223.1	228.8	240.7	324.7
Element	Iron	Manganese	Lead	Zinc	
Wavelength, nm	248.3	279.5	217.0	213.9	

15.4.2 The alternative, less-sensitive spectral lines specified in the following table may be used:

Alternate Spectral Lines—Procedure A

Element	Cobalt	Copper	Iron	Manganese	Lead
Wavelength, nm	241.2	327.4	252.3	403.1	283.3

 15.4.3 Set the required instrument parameters in accordance with the manufacturer's recommendations. Light the burner and aspirate diluted  $\text{HNO}_3$  (1 + 19) until thermal equilibrium is reached. A fuel-lean air-acetylene flame shall be used.

15.4.4 Ensure that the instrument meets the performance requirements given in Practice E60. Optimum settings for the operating parameters vary from instrument to instrument.

**15.5 Spectrometry:**

15.5.1 Ensure that the test solution (15.2) and the calibration solutions, Set A (14.1) are within 1 °C of the same temperature.

 15.5.2 Aspirate diluted  $\text{HNO}_3$  (1 + 19) and zero the instrument.

15.5.3 Aspirate the test solution(s) and note the reading to determine its place within the set of calibration solutions.

 15.5.4 Aspirate diluted  $\text{HNO}_3$  (1 + 19) until the initial reading is obtained. Zero the instrument if necessary.

 15.5.5 Aspirate the Set A calibration solutions (14.1) and the test solution(s) in order of increasing instrument response, starting with the zero reference solution. When a stable response is obtained, record the reading. Flush the system by aspirating diluted  $\text{HNO}_3$  (1 + 19) between each test or calibration solution. Avoid aspirating the high-nickel solutions for long periods without flushing; otherwise, the burner may tend to clog.

15.5.6 Repeat the measurement of the full set of the calibration and test solutions twice more and record the data. See Note 7.

15.5.7 Proceed with the preparation of the calibration curves and calculations as directed in Sections 17 and 18.

**16. Procedure B**

~~16.1 This procedure is applicable to 0.01 to 0.25% of Co, Cu, Fe, and Mn and 0.005 to 0.025% of Zn.~~

16.1 This procedure is applicable to 0.01 % to 0.25 % of cobalt, copper, iron, and manganese and 0.005 % to 0.025 % of zinc.

**16.2 Preparation of Test Solution:**

 16.2.1 If a test solution has been prepared by Procedure A (15.2), using a pipet, transfer a 100.0-mL aliquot portion into a 250-mL volumetric flask, dilute to volume with diluted  $\text{HNO}_3$  (1 + 19). Otherwise, proceed as directed in 16.2.2.

 16.2.2 Weigh to the nearest 0.005 g, 1.9 g to ~~2.1 g~~ 2.1 g of the test sample, transfer to a 400-mL beaker and dissolve in 20 mL of  $\text{HNO}_3$  (1 + 1). Complete the preparation as directed in 15.2.

 16.3 *Reagent Blank Solution*—The zero reference solution of the calibration solution Set B (14.2) serves as the reagent blank. See Note 5.

**16.4 Instrumental Parameters:**

16.4.1 The spectral lines specified in the following table are to be used in the analysis:

Spectral Lines—Procedure B

Element	Cobalt	Copper	Iron	Manganese	Zinc
Wavelength, nm	241.2	327.4	252.3	403.1	213.9

16.4.2 Proceed as directed in 15.4.3 and 15.4.4.

**16.5 Spectrometry:**

16.5.1 Proceed as directed in 15.5.1 through 15.5.6, substituting the Set B calibration solution (14.2) for the Set A solutions.

16.5.2 Proceed with the preparation of the calibrations curves and calculations as directed in Sections 17 and 18.

NOTE 6—For test samples containing greater than 0.25 % and less than 2 % of cobalt or copper, further dilutions of the test solution with  $\text{HNO}_3$  (1 + 19) may be made. The nickel content of the calibration solutions should be matched with those of the test solutions.

**17. Preparation of Calibration Curves**

17.1 Plot the average instrument reading against the concentration of the analyte for the calibration solutions for each set of measurements.

17.2 For instruments that have automated calibration features and direct read-out in concentration plotting of calibration curves is not required. Follow the instrument operating instructions for calibration and curvature correction procedures.

NOTE 7—In this test method, any effect of nonspecific absorption and light scatter is compensated for by matching the matrix of the calibration standards with the test solutions. Also, since the same lot of  $\text{HNO}_3$  is used for both calibration and test solutions, the reagent blank is incorporated in

the calibration curve. Thus, the calibration curve may not pass through the origin.

## 18. Calculations

18.1 Determine the concentration of analyte in the test solution from the corresponding calibration curves or instrument read-out for each of the three sets of instrument readings. Average the resultant concentrations.

18.2 *Procedure A*—Calculate the concentration of the analyte in the test sample as follows:

$$\text{Analyte, \%} = \frac{A \times B}{C} \times 10^{-4} \quad (1)$$

where:

*A* = analyte concentration found in the test solution,  $\mu\text{g/mL}$ ,

*B* = volume of the test solution, mL, and

*C* = weight of the test sample, g.

18.3 *Procedure B*:

18.3.1 For the procedure in 16.2.1, calculate concentration of the analyte in the test sample as follows:

$$\text{Analyte, \%} = \frac{A \times B}{C} \times 2.5 \times 10^{-4} \quad (2)$$

where 2.5 = correction factor for the dilution made.

## 19. Precision and Bias

19.1 *Precision*:

19.1.1 Eighteen laboratories in nine countries participated in testing this method under the auspices of ISO/TC-155/SC-3/WG-1 in the early 1980's-1980s and obtained the statistical data summarized in Table 1 as evaluated by ISO 5725 and equivalent to Practice E1601. Precision may be judged by examination of these data. Twelve sample were analyzed to cover the scope of this test method. Of these, ten were specially prepared as no materials containing the impurity levels were available commercially.

19.1.2 The laboratory test program was designed so that the statistics on repeatability would include variations due to a change in the atomic absorption instrument or operator, or both, while maintaining the same test solution.

19.2 *Bias*—No information is currently available on the bias of this test method, due to the lack of appropriate certified reference materials. The bias of a test method may be judged, however, by comparing accepted reference values with the arithmetic average obtained by interlaboratory testing. The user is cautioned that the results will be biased to the low side if the nickel metal used for the preparation of the calibration solutions does not meet the purity specifications given in the test method and appropriate corrections are not made.

## 20. Keywords

20.1 bismuth; cadmium; cobalt; copper; flame atomic absorption spectrometry; iron; lead; manganese; refined nickel; silver; spectrometry; zinc

## SILVER, ARSENIC, BISMUTH, CADMIUM, LEAD, ANTIMONY, SELENIUM, TIN, TELLURIUM, AND THALLIUM BY THE ELECTROTHERMAL-GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRIC METHOD

## 21. Scope

21.1 This test method applies to the determination of the silver, arsenic, bismuth, cadmium, lead, antimony, selenium, tin, tellurium, and thallium contents of high-purity, refined, wrought, and cast nickel metal within the ranges specified in the following table:

Element	Concentration Range, $\mu\text{g/g}$
Silver	0.3 to 10
Arsenic	1.3 to 20
Bismuth	4.0 to 15
Cadmium	0.3 to 2
Lead	0.7 to 10
Antimony	1.8 to 10
Selenium	1.8 to 10
Tin	2.2 to 5
Tellurium	1.5 to 10
Thallium	0.5 to 10

21.2 This test method is applicable to the independent determination of any one or more of the elements listed without including all elements specified in the standard solutions.

## 22. Summary of Test Method

22.1 The test sample is dissolved in nitric acid- $\text{HNO}_3$  and the solution is diluted to a known volume. An aliquot is introduced



**TABLE 1 Statistical Information—Flame AAS Method,  
Procedure A**

Test Material	Mean, %	Repeatability Index, <i>r</i> (Practice E1601)	Reproducibility, Index <i>R</i> (Practice E1601)
<b>Silver</b>			
P45	0.00043	0.00003	0.00012
P44	0.00077	0.00005	0.00007
P46	0.00095	0.00012	0.00015
P41	0.00191	0.00008	0.00017
J63	0.00232	0.00010	0.00022
P43	0.00282	0.00017	0.00022
J61	0.00970	0.00025	0.00142
<b>Bismuth</b>			
P44	0.00133	0.00027	0.00076
P41	0.00171	0.00028	0.00047
P43	0.00245	0.00031	0.00049
J61	0.01037	0.00044	0.00057
<b>Cadmium</b>			
P46	0.00019	0.00003	0.00008
J63	0.00025	0.00002	0.00009
J61	0.00135	0.00007	0.00025
S65	0.00225	0.00007	0.00025
<b>Cobalt</b>			
P43	0.00105	0.00007	0.00016
P44	0.00155	0.00007	0.00040
P41	0.00185	0.00011	0.00014
J62	0.00508	0.00023	0.00030
J61	0.01002	0.00038	0.00060
<b>Copper</b>			
S65	0.00079	0.00012	0.00022
J62	0.00517	0.00009	0.00025
J61	0.01006	0.00009	0.00041
<b>Iron</b>			
P46	0.00241	0.00020	0.00059
P45	0.00298	0.00033	0.00060
P44	0.00311	0.00013	0.00058
P41	0.00437	0.00018	0.00103
S65	0.00474	0.00026	0.00058
<b>Manganese</b>			
P41	0.00054	0.00003	0.00020
P46	0.00070	0.00005	0.00020
P45	0.00107	0.00008	0.00020
P43	0.00200	0.00005	0.00014
J62	0.00536	0.00013	0.00037
J61	0.01028	0.00027	0.00052
<b>Lead</b>			
H79	0.00078	0.00003	0.00017
P46	0.00090	0.00030	0.00036
P41	0.00202	0.00032	0.00048
P44	0.00252	0.00024	0.00026
J62	0.00350	0.00011	0.00041
J63	0.00365	0.00017	0.00017
J61	0.00777	0.00020	0.00046
<b>Zinc</b>			
H79	0.00029	0.00004	0.00015
P44	0.00041	0.00004	0.00020
P41	0.00050	0.00007	0.00016
P46	0.00062	0.00008	0.00010
S65	0.00101	0.00009	0.00017
P43	0.00117	0.00009	0.00028
P45	0.00128	0.00023	0.00040
J62	0.00269	0.00014	0.00024

into an electrothermal graphite furnace atomic absorption instrument spectrometer (GF-AAS) and the absorption of the resonance line energy from the spectrum of each element is measured and compared with that from a set of calibration solutions of the same element in a matched nickel matrix. All readings are background-corrected.

### 23. Interferences

23.1 Elements ordinarily present in nickel metal do not present spectral interferences in the electrothermal graphite furnace atomic absorption analysis.

23.2 Potential background absorption interference is eliminated by instrumental background correction and by the use of matched-matrix standards prepared from high-purity nickel metal.

23.3 The lower limit for the determination of the elements is affected by the residual level of each element in the high-purity nickel metal used to prepare the matched matrix standards.

23.4 For the determination of silver and tin, care must be taken to avoid contamination of the sample and calibration solutions with chloride ion.

23.5 Because of the high sensitivity of ~~electrothermal atomic absorption~~ GF-AAS, stringent precautions must be taken to clean all glassware and avoid contamination of sample, standard, and calibration solutions from foreign material and dust from the laboratory atmosphere.

## 24. Apparatus

24.1 *Atomic Absorption Spectrometer and Electrothermal Graphite Furnace Analyzer*—The instrument shall be equipped with a background corrector and high-speed read-out electronics or a high-speed recorder, or both. The instrument should also be capable of using single element hollow cathode or electrodeless discharge lamps operated at currents recommended by the lamp and instrument manufacturers.

24.2 *Micropipets*, 5 to 25  $\mu\text{L}$ , 5  $\mu\text{L}$  to 25  $\mu\text{L}$ .

24.3 *Glass Storage Bottles*—The glass bottles used to store mixed analyte standard solutions shall be of borosilicate glass, thoroughly cleaned, then soaked for several days in  $\text{HNO}_3$  (1 + 19), and rinsed thoroughly with water.

24.4 *Plastic Containers*—Plastic storage containers shall be of polytetrafluoroethylene (PTFE).

## 25. Reagents

25.1 *Antimony, Standard Stock Solution (1 mL = 1 mg Antimony)*—Transfer 0.274 g of potassium antimonyl tartrate [ $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ ] (purity, 99.9 % minimum), weighed exactly, to a 100-mL volumetric flask, dissolve in water, dilute to volume, and mix. Do not use a solution that has stood for more than one day.

NOTE 8—The antimony concentrations in the more dilute, acidified solutions prepared from this solution are stable.

25.2 *Arsenic, Standard Stock Solution (1 mL = 1 mg Arsenic)*—Transfer a 0.100-g sample of arsenic metal (purity, 99.9 % min), weighed to the nearest 0.1 mg, to a 100-mL beaker.

25.2.1 Add 10 mL of  $\text{HNO}_3$  (1 + 1) (Note 9) and heat until dissolution is complete. Boil gently to expel oxides of nitrogen and cool. Transfer to a 100-mL volumetric flask containing 10 mL of  $\text{HNO}_3$  (1 + 1), dilute to volume with water, and mix. Store in a glass or PTFE container.

NOTE 9—The same reagent lot of  $\text{HNO}_3$  shall be used throughout the procedure. If high blanks are obtained, the  $\text{HNO}_3$  must be redistilled and the entire procedure repeated. See Note 12.

25.3 *Bismuth, Standard Stock Solution (1 mL = 1 mg Bismuth)*—Transfer a 0.100-g sample of bismuth metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1.

25.4 *Cadmium, Standard Stock Solution (1 mL = 1 mg Cadmium)*—Transfer a 0.100-g sample of cadmium metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1.

25.5 *Lead, Standard Stock Solution (1 mL = 1 mg Lead)*—Transfer a 0.100-g sample of lead metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1.

25.6 *Nickel Metal*, high-purity, containing less than 5  $\mu\text{g/g}$  of iron and less than 1  $\mu\text{g/g}$  of silver, arsenic, bismuth, cadmium, lead, antimony, selenium, tin, tellurium, and thallium.

25.7 *Selenium, Standard Stock Solution (1 mL = 1 mg Selenium)*—Transfer a 0.100-g sample of selenium metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1.

25.8 *Silver, Standard Stock Solution (1 mL = 1 mg Silver)*—Transfer a 0.100-g sample of silver metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1, except store in an amber glass bottle.

25.9 *Tellurium, Standard Stock Solution (1 mL = 1 mg Tellurium)*—Transfer a 0.100 g sample of tellurium metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Proceed as directed in 25.2.1.

25.10 *Thallium, Standard Stock Solution (1 mL = 1 mg Thallium)*—Transfer a 0.112-g sample of thallium (III) oxide ( $\text{Tl}_2\text{O}_3$ ) (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Add 10 mL of  $\text{HNO}_3$  and heat to dissolve (Note 9). Cool and transfer to a 100-mL volumetric flask, dilute to volume, and mix. Store in a glass or PTFE container.

25.11 *Tin, Standard Stock Solution (1 mL = 1 mg Tin)*—Transfer a 0.250-g sample of tin metal (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL poly(tetrafluoroethylene) beaker. Add 7.5 mL of a mixture of equal parts of HF,  $\text{HNO}_3$  (Note 9), and water. Heat until dissolved. Boil gently to expel oxides of nitrogen. Cool and transfer to a 250-mL PTFE volumetric flask. Dilute to volume and mix. Store in a PTFE container.

25.12 *Working Solutions:*

25.12.1 *Mixed Analyte Standard Solution A (1 mL = 1  $\mu\text{g}$  of Arsenic, Bismuth, Lead, Antimony, Selenium, Tin, Tellurium, and Thallium)*—Using a pipet, transfer 10.0 mL of each of the standard stock solutions (arsenic, bismuth, lead, antimony, selenium, tin, tellurium, and thallium) to a 1-L volumetric flask containing 100 mL of  $\text{HNO}_3$  (1 + 1). Dilute to volume with water and mix. Using a pipet, transfer 10.0 mL of this solution to a 100-mL volumetric flask containing 10 mL of  $\text{HNO}_3$  (1 + 1). Dilute to volume with water and mix. Store in a glass or PTFE container (Note 9).

25.12.2 *Mixed Analyte Standard Solution B (1 mL = 0.1  $\mu\text{g}$  of Silver and Cadmium)*—Using a pipet, transfer 10.0 mL of the