



Standard Test Methods for Chemical Analysis of Refined Nickel¹

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 (ϵ) 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:

Element	Weight, %
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:

Test Methods	Sections
Antimony, Arsenic, Bismuth, Cadmium, Lead, Selenium, Silver, Tellurium, Tin, and Thallium by the Graphite Furnace Atomic Absorption Spectrometric Method	21-31
Bismuth, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Silver, and Zinc by the Flame Atomic Absorption Spectrometric Method	9-20
Carbon, Total, by the Combustion-Instrumental Method (Refer to Test Methods E1019)	32

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

Current edition approved Dec. 15, 2010. Published February 2011. Originally approved in 1994. Last previous edition approved in 2005 as E1587 – 05. DOI: 10.1520/E1587-10.

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

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:²

- D1193 Specification for Reagent Water
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- 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

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.

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 (Withdrawn 2004)³

E1601 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.⁴

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

Element	Concentration Range, %	
	Method A	Method B
Silver	0.0002 to 0.01	...
Bismuth	0.0010 to 0.01	...
Cadmium	0.0002 to 0.0025	...
Cobalt	0.0010 to 0.01	0.01 to 1.00
Copper	0.0005 to 0.01	0.01 to 1.00
Iron	0.0025 to 0.01	0.01 to 0.15
Manganese	0.0005 to 0.01	0.01 to 0.20
Lead	0.0006 to 0.01	...
Zinc	0.0005 to 0.0025	0.001 to 0.015

³ The last approved version of this historical standard is referenced on www.astm.org.

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

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 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 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 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 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 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_3 (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.

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) $\mu\text{g/mL}$ 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) $\mu\text{g/L}$ of zinc.

No.	Aliquot of Solution A, mL	Analyte Concentration μ g/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, 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) μ g/mL of cobalt, copper, iron, and manganese and (0, 0.25, 0.5, 1.0, 1.5, 2.0, and 2.5) μ g/mL of zinc.

No.	Aliquot of Mixed Analyte, Standard Solution B, mL	Analyte Concentration μ g/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, Standard 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 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 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 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 HNO_3 (1 + 1) and 100 mL of water. Heat to complete dissolution, cool, and filter,

if necessary, through either glass wool or a cellulose filter which have been washed with 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 HNO_3 should be increased in proportion. Even larger sample weights can be used, with greater amounts of 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 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 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 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 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 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 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 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 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 of the test sample, transfer to a 400-mL beaker and dissolve in 20 mL of 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 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 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 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

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)
Silver			
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
Bismuth			
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
Cadmium			
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
Cobalt			
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
Copper			
S65	0.00079	0.00012	0.00022
J62	0.00517	0.00009	0.00025
J61	0.01006	0.00009	0.00041
Iron			
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
Manganese			
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
Lead			
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
Zinc			
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

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, µg/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 HNO₃ and the solution is diluted to a known volume. An aliquot is introduced into a graphite furnace atomic absorption 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 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 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 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 µL to 25 µL.

24.3 *Glass Storage Bottles*—The glass bottles used to store mixed analyte standard solutions shall be of borosilicate glass,

SILVER, ARSENIC, BISMUTH, CADMIUM, LEAD, ANTIMONY, SELENIUM, TIN, TELLURIUM, AND THALLIUM BY THE 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,

thoroughly cleaned, then soaked for several days in 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 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 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 HNO_3 shall be used throughout the procedure. If high blanks are obtained, the 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 (Tl_2O_3) (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Add 10 mL of 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, 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 μg 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 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 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 μg of Silver and Cadmium)—Using a pipet, transfer 10.0 mL of the silver and the cadmium stock solutions to a 1-L volumetric flask containing 100 mL of HNO_3 (1 + 1). Dilute to volume with water and mix. Store in a glass container. Using a pipet, transfer 10.0 mL of this solution to a 1-L volumetric flask containing 100 mL of HNO_3 (1 + 1). Dilute to volume with water and mix. Prepare this solution immediately before use.

25.12.3 *Nickel Nitrate Solution* (40 g Nickel/L)—Transfer a 4.00-g sample of nickel metal (25.6), weighed to the nearest 1 mg, to a 400-mL beaker. Add 50 mL of water and 28 mL of HNO_3 (Note 9). Do not stir or apply heat until the vigorous reaction has ceased. Heat to complete dissolution, then boil gently to expel oxides of nitrogen. Cool and filter through a low-porosity filter paper which has been pre-washed with HNO_3 (1 + 1). Recycle the filtrate through the filter paper to collect the fine carbon particles which may have escaped the first filtration. Collect the filtrate in a 100-mL volumetric flask. Wash the filter with water, also collecting the washings, and dilute to volume with water and mix.

26. Calibration Solutions

26.1 Set A:

26.1.1 This set corresponds to (0, 0.005, 0.010, 0.02, 0.05, 0.07, 0.1, 0.15, 0.20, 0.25, and 0.30) $\mu\text{g/mL}$ each of arsenic, bismuth, lead, antimony, selenium, tin, tellurium, and thallium, respectively, and is used for analyte levels from 0.5 $\mu\text{g/g}$ to 30.0 $\mu\text{g/g}$.

26.1.2 Using a buret, transfer 2.50 mL of the nickel nitrate solution (25.12.3) to each of eleven 10-mL volumetric flasks. Add, using a buret graduated in 0.01-mL divisions, (0, 0.05, 0.1, 0.2, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, and 3.0) mL, respectively,

of mixed analyte standard Solution A (25.12.1). Dilute to volume with HNO_3 (1 + 1) and mix. See the following table:

Aliquot, of Mixed Analyte Standard Solution A, mL	Analyte Concentration, $\mu\text{g/mL}$ Arsenic, Bismuth, Lead, Antimony, Selenium, Tin, Tellurium, and Thallium
0	Blank
0.05	0.005
0.1	0.010
0.2	0.02
0.5	0.05
0.7	0.07
1.0	0.10
1.5	0.15
2.0	0.20
2.5	0.25
3.0	0.30

26.2 Set B:

26.2.1 This set corresponds to (0, 0.0005, 0.001, 0.002, 0.005, 0.010, 0.02, and 0.05) $\mu\text{g/mL}$ each of Silver and Cadmium and is used for analyte levels from 0.01 $\mu\text{g/g}$ to 5.0 $\mu\text{g/g}$.

26.2.2 Using a buret, transfer 2.50 mL of nickel nitrate stock solution (25.12.3) to each of eight 10-mL volumetric flasks. Add, using a buret graduated in 0.01-mL divisions, (0, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0) mL respectively of the mixed analyte standard Solution B (25.12.2). Dilute to volume with HNO_3 (1 + 19) and mix.

Aliquot, of Mixed Analyte Standard Solution B, mL	Analyte Concentration, $\mu\text{g/mL}$ Silver and Cadmium
0	Blank
0.05	0.0005
0.10	0.0010
0.20	0.0020
0.50	0.0050
1.0	0.010
2.0	0.020
5.0	0.050

27. Procedure

27.1 *Preparation of Test Solution*—Weigh, to the nearest 0.01 g, 0.9 g to 1.1 g of the test sample and transfer to a clean unetched 100-mL beaker. Add 30 mL of water and 12 mL of HNO_3 and allow to dissolve. Heat to complete dissolution, boil gently to expel oxides of nitrogen, cool, and transfer to a 100-mL volumetric flask. Dilute to volume with water and mix.

NOTE 10—The life of the graphite furnace tubes may be extended by using 5 mL of HNO_3 rather than 12 mL.

NOTE 11—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 10 g in a final volume of 1000 mL is recommended. The amount of HNO_3 should be increased in proportion. Even larger sample weights can be used, with greater amounts of HNO_3 , to prepare a more concentrated nickel test solution. However, this must then be diluted to give a test portion containing 10 $\mu\text{g/L}$ nickel to match the calibration solutions.

27.2 *Reagent Blank Solution*—The zero reference solutions of the Sets A and B calibration solutions (26.1 and 26.2) serve as reagent blanks since the same batch of HNO_3 is used for dissolution of both the nickel reference and test samples.

NOTE 12—If it is impossible to use the same batch of HNO_3 , a second reagent blank must be prepared using the same high-purity nickel metal.

This blank is then compared with the standard zero calibration solution and an appropriate correction made, if significant.

27.3 Instrumental Parameters:

27.3.1 The spectral lines specified in the following table are to be used in the analysis. An alternate line for bismuth is 306.8 nm.

Spectral Lines					
Element	Silver	Arsenic	Bismuth	Cadmium	Lead
Wavelength, nm	328.1	193.7	223.1	228.8	283.3
Element	Antimony	Selenium	Tin	Tellurium	Thallium
Wavelength, nm	217.6	196.0	286.3	214.3	276.8

27.3.2 Set the required instrument parameters and align the graphite furnace atomizer in accordance with the manufacturer's recommendations. Optimum settings for the operating parameters vary from instrument to instrument. Scale expansion may have to be used to obtain the required readability. Atomization temperatures of 2600 °C to 2700 °C are preferable for a nickel matrix. The use of background compensation is essential.

27.3.3 Determine the optimum graphite furnace atomizer parameters for the particular type of atomizer and sample size (5 μL to 25 μL) as recommended by the instrument manufacturer or normal laboratory practice for each element to be determined.

27.4 Spectrometry:

27.4.1 Ensure that the test solution and the Set A and Set B calibration solutions are within 1 °C of the same temperature.

27.4.2 Zero the instrument and set the base line on the recorder.

27.4.3 Check the zero stability and lack of spectral interference within the atomization system by running the preset heating program for blank firing of the graphite atomizer. Repeat to ensure base line stability.

27.4.4 Inject, into the atomizer, the predetermined volume (5 μL to 25 μL) of each of the test solutions for the element being determined. Atomize, and note the instrument response. Sort the test solutions into groups of three or four with similar concentration levels of the analyte, starting with the lowest level.

27.4.5 Select the appropriate calibration solutions, from Set A or Set B, to cover the range and bracket the concentration levels in the test solutions.

27.4.6 Inject and atomize the same predetermined volume (5 μL to 25 μL) of the calibration and test solutions in order of increasing instrument response. Atomize each solution three times and, if the replication is good, record the readings for averaging. Check the instrument for memory effects, especially at high-analyte levels, by running the blank firing program. Reset the zero base line if necessary.

27.4.7 Evaluate the analyte contents in each group of test solutions based on the applicable calibration solutions as directed in Sections 28 and 29.

28. Preparation of Calibration Curve

28.1 Calculate the average of the three instrument readings for each of the applicable calibration solutions.

28.2 Plot the average instrument readings versus the concentrations of the analyte in the calibration solutions.

28.3 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 13—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 and by background correction. Also, since the same lot of HNO₃ is used for both sample and test solutions, the reagent blank is incorporated into the calibration curve. Thus, the calibration curve may not pass through the origin.

NOTE 14—If the high-purity nickel metal used to prepare the calibration solution is contaminated by the element being determined, graphic, or arithmetic methods must be used to take this into account.

29. Calculation

29.1 Use the average of the three instrument readings obtained for the test solution and the calibration curve prepared in 28.2 to obtain the concentration of the analyte in the test solution.

29.2 Calculate the concentration of the analyte, in micrograms per gram, in the test sample as follows:

$$\text{Analyte, } \mu\text{g/g} = \frac{A \times B}{C} \quad (3)$$

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 portion, g.

30. Precision and Bias

30.1 *Precision*—Eleven laboratories in six countries participated in testing this method under the auspices of ISO/TC-155/SC-3/WG-3 in the early 1980s and obtained the statistical data summarized in Table 3 as evaluated by ISO 5725 and equivalent to Practice E1601.

TABLE 3 Statistical Information—Graphite Furnace AAS Method

Test Material	Mean, %	Repeatability Index, r (Practice E1601)	Reproducibility Index, R (Practice E1601)
Silver (Ag)			
H79	0.00002	0.000010	0.000017
P45	0.00044	0.00004	0.00011
P44	0.00076	0.00006	0.00024
Arsenic (As)			
P45	0.00031	0.00005	0.000063
P44	0.00068	0.00005	0.00012
P46	0.00082	0.00016	0.00040
H79	0.00164	0.00015	0.00026
Bismuth (Bi)			
P45	0.00080	0.00011	0.00018
P46	0.00086	0.00012	0.00023
P44	0.00115	0.00013	0.00019
Cadmium (Cd)			
P44	0.00006	0.000015	0.000017
P45	0.00014	0.00003	0.00007
P46	0.00018	0.00002	0.000028
Lead (Pb)			
P42	0.000026	0.000011	0.000036
S65	0.00015	0.00004	0.00005
P45	0.00039	0.00005	0.00009
P46	0.00085	0.00009	0.00017
Antimony (Sb)			
P44	0.00028	0.000036	0.00009
P46	0.00085	0.00020	0.00059
S65	0.00120	0.00017	0.00031
Selenium (Se)			
H79	0.00013	0.00003	0.00009
P46	0.00063	0.00016	0.00018
P45	0.00083	0.00015	0.00026
Tin (Sn)			
H79	0.00025	0.00007	0.000112
Tellurium (Te)			
H79	0.00048	0.000010	0.000027
P44	0.00020	0.00005	0.00010
P46	0.00084	0.00016	0.00029
Thallium (Tl)			
S65	0.000065	0.000017	0.000023
P44	0.00020	0.00003	0.00008
P46	0.00086	0.00004	0.00019

lent to Practice E1601. Precision may be judged by examination of these data. Six samples were analyzed to cover the scope of this test method and of these, four were specially prepared by melting and granulation, and two were commercial products.

30.2 *Bias*—No information is currently available on the accuracy of this test method due to the lack of appropriate certified reference materials. The accuracy of a 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 this test method and appropriate corrections are not made.

31. Keywords

31.1 antimony; arsenic; bismuth; cadmium; graphite furnace atomic absorption spectrometry; lead; refined nickel; selenium; silver; tellurium; thallium; tin

TABLE 2 Statistical Information—Flame AAS Method, Procedure B

Test Material	Mean, %	Repeatability Index, r (Practice E1601)	Reproducibility Index, R (Practice E1601)
Cobalt			
J61	0.010	0.0012	0.0017
H79	0.106	0.0027	0.0076
S65	0.076	0.0047	0.0060
Copper			
J61	0.010	0.0006	0.0014
H79	0.113	0.0008	0.0089
C1A	0.467	0.016	0.056
Iron			
J61	0.012	0.0013	0.0036
H79	0.137	0.0024	0.010
Manganese			
J61	0.010	0.0005	0.0015
H79	0.164	0.0016	0.013
Zinc			
J62	0.0026	0.0002	0.0004
J61	0.0068	0.0004	0.0009

TOTAL CARBON BY THE COMBUSTION INSTRUMENTAL MEASUREMENT METHOD

32. Scope

32.1 Refer to Test Methods E1019 for this test method that covers the determination of carbon in concentrations from 0.005 % to 4.5 %.

SULFUR BY THE COMBUSTION-INFRARED ABSORPTION METHOD

33. Scope

33.1 Refer to Test Methods E1019 for this test method that covers the determination of sulfur in the range from 0.001 % to 0.01 %.

SULFUR BY THE METHYLENE BLUE SPECTROPHOTOMETRIC METHOD AFTER GENERATION OF HYDROGEN SULFIDE

34. Scope

34.1 This test method covers the determination of the sulfur content of refined, wrought and cast nickel metal in the concentration range from 0.0001 % to 0.002 %.

35. Summary of Test Method

35.1 The sample is dissolved in a nitric-chloric acid mixture and the sulfur oxidized to sulfate ion. After removal of nitrates

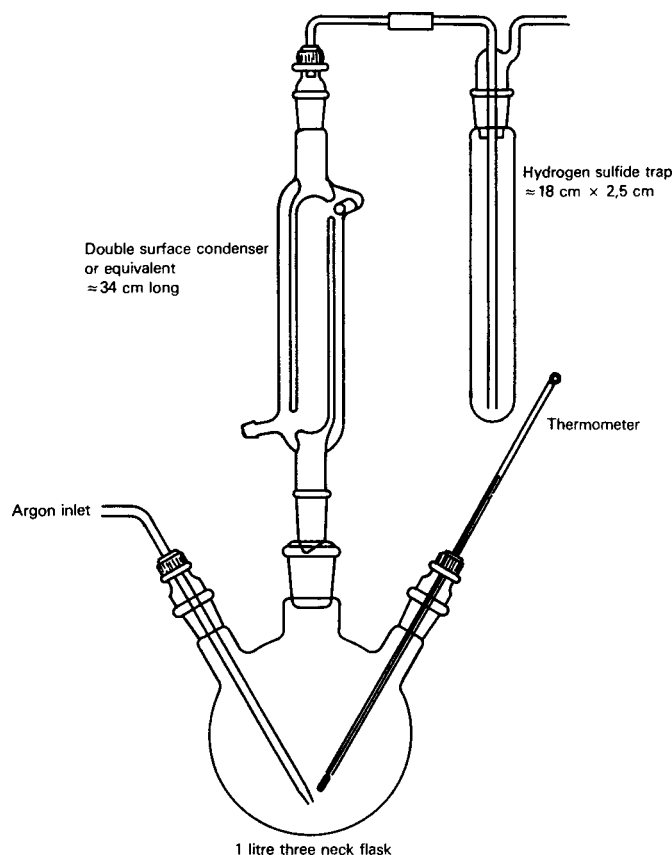


FIG. 2 Apparatus for Purification of the Reducing Mixture

by evaporation with hydrochloric and formic acids, the sulfate is reduced to hydrogen sulfide by hydriodic and hypophosphorous acids, evolved from the solution in an argon atmosphere, and absorbed by a zinc amine complex solution. The absorbed sulfide sulfur is converted to methylene blue and the absorbance of the solution is measured at 665 nm and converted to micrograms of sulfur.

36. Interferences

36.1 Elements normally present do not interfere.

37. Hazards

37.1 There are toxicity risks related to the chemicals used in the procedure and reasonable precautions must be taken. Examine the glassware used in the distillation apparatus carefully for cracks and check the tightness of joints.

38. Apparatus

38.1 *Conventional Distillation Apparatus*—Equipped with a jacketed 40-cm Vigreux⁵ or packed reflux column for the purification of acids by distillation under atmospheric pressure, as shown in Fig. 1.

38.2 *Distillation Apparatus*—For purification of the reducing mixture (39.8), as shown in Fig. 2.

⁵ Available from Fisher Scientific Co., 2000 Park Lane Dr., Pittsburgh, PA 15275, www.fishersci.com.

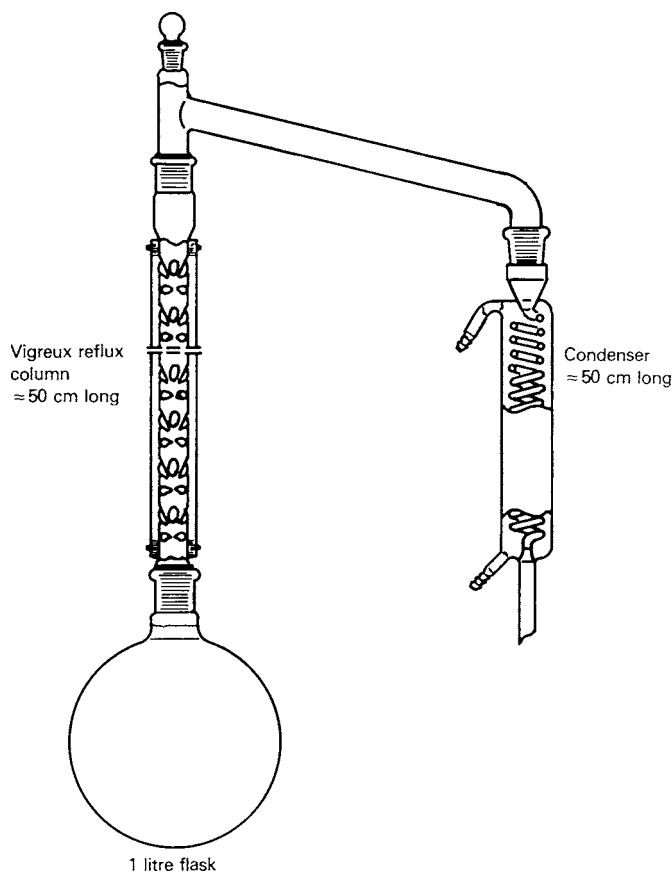


FIG. 1 Apparatus for Purification of Acids

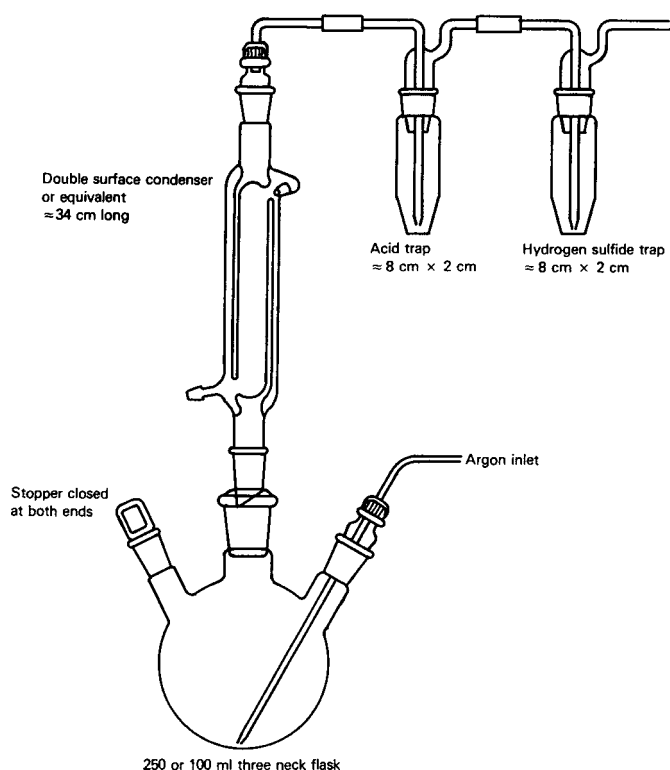


FIG. 3 Apparatus for Distillation of Hydrogen Sulfide

38.3 Distillation Apparatus—For the generation and volatilization of hydrogen sulfide from the test solution, as shown in Fig. 3. The double-surface condenser is preferred because of its superior cooling efficiency.

38.4 Heating Mantle—The heating mantle should have a variable power setting such that the optimum temperature of 114 °C for the rapid reduction of sulfate to hydrogen sulfide can be maintained.

38.5 Micropipettes—(0, 20, 50, and 100) μL .

38.6 Glass storage containers shall be of borosilicate glass.

39. Reagents

39.1 Argon Gas—(purity, 99.998 % min).

39.2 Diamine Salt Solution—Dissolve 0.1 g of *N,N*-dimethyl-*p*-phenylenediamine hydrochloride or sulfate in 26 mL of concentrated HCl and dilute to 100 mL with water. Store in a cool dark place. Prepare fresh weekly.

NOTE 15—All acids used in the sample dissolution and the nitrate removal steps shall be purified by distillation to remove sulfur-containing species. Each reagent shall contain less than 1 mg/L of sulfur. To keep the reagent blank low, hydrochloric acid should contain less than 0.05 mg/L of sulfur.

39.3 Ferric Chloride Solution—Dissolve 1.0 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 10 mL of concentrated HCl and 40 mL of water. Dilute to 100 mL with water and store in a glass bottle.

39.4 Purified Formic Acid—Distill reagent grade formic acid using the apparatus in 38.1 and discard the first 10 % (v/v)

of the distillate. Collect the remaining distillate (except the last few millilitres) in a thoroughly cleaned glass bottle.

39.5 Purified Hydrochloric Acid—Distill HCl (3 + 2) using the apparatus in 38.1 and discard the first 10 % (v/v) of the distillate. Collect the remaining distillate (except the last few millilitres) in a thoroughly cleaned glass bottle.

39.6 Purified HNO_3 —Distill HNO_3 using the apparatus in 38.1 and discard the first 10 % (v/v) of the distillate. Collect the remaining distillate (except for the last few millilitres) in a thoroughly cleaned glass bottle.

39.7 Nitric-Chloric Acid Mixture—Dissolve 3 g of potassium chlorate (KClO_3) in 30 mL of water and 100 mL of purified HNO_3 (39.6). Store in a glass bottle.

39.8 Reducing Mixture—Transfer 420 mL of hydriodic acid (HI, 55 % minimum), 80 mL of hypophosphorous acid (H_3PO_2 , 50 % minimum) and 70 g of sodium iodide (NaI) to the purifying apparatus (38.2). Attach the hydrogen sulfide trap containing 50 mL of the zinc acetate absorbing solution (39.10). Purge with argon at a flow rate of 200 mL/min to 300 mL/min for 10 min to expel air from the system. Switch on the electric heating mantle and heat the mixture at 113 °C to 115 °C for 4 h in a continuous flow of argon (Note 16). Allow the mixture to cool while maintaining the argon flow. Transfer the cold reducing mixture, without delay, to a brown glass bottle. Stopper and store in a cool dark place.

NOTE 16—During the purification of the reducing mixture, care must be taken to ensure that the solution does not become overheated. Temperature monitoring with a thermometer is recommended.

39.9 Standard Sulfur Solution (10 mL = 1 mg Sulfur)—Dissolve exactly 0.5435 g of potassium sulfate (K_2SO_4), previously dried at 105 °C for 1 h, in water in a 1000-mL volumetric flask. Dilute to volume with water and mix.

39.10 Zinc Acetate Absorbing Solution—Dissolve 5 g of zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and 70 g of ammonium chloride (NH_4Cl) in about 350 mL of water. Add 7.5 g of sodium hydroxide (NaOH), stir to dissolve, and dilute to 500 mL with water. Store in a glass bottle.

40. Calibration

40.1 Evolution of Hydrogen Sulfide:

40.1.1 To the cold, sulfur-free reducing mixture in a three-neck flask from the blank (41.4), add, from a micro-pipette, 10 μL (1 μg S) of standard sulfur solution (39.9). Proceed in accordance with 41.2 and 41.3.

40.1.2 Continue with additions, in order, of 20 μL , 50 μL , and 100 μL (2 μg , 5 μg , and 10 μg S) of standard sulfur solution (39.9), to the same sulfur-free reducing mixture as in 40.1.1. Proceed after each addition as directed in 41.2 and 41.3. Throughout the hydrogen sulfide evolution sequence for the calibration points there is no need to replace either the reducing mixture or the acid trap solution.

40.2 Methylene Blue Development—Introduce 3.0 mL of the diamine salt solution (39.2) into the sulfide trap by means of the gas inlet. Immediately follow with the addition of 0.5 mL of ferric chloride solution (39.3) and mix gently. Rinse the inside and outside of the gas inlet tube with a small quantity of

water. Mix the solution and transfer it to a 25-mL volumetric flask. Wash the trap with water and add the washings to the flask. Dilute to volume with water, mix, and allow the solution to stand for at least 30 min before measurement. Once fully developed, the methylene blue coloration is stable for at least 24 h.

40.3 Spectrophotometric Measurement—Measure the absorbance of the solution in 1-cm or 2-cm cells, using water as the reference, at a wavelength of 665 nm with a spectrophotometer.

40.4 Calibration Curve—Plot the absorbance readings of the solutions obtained in 40.1.1 and 40.1.2 against micrograms of sulfur present in the solutions. The line need not pass through the origin as the absorbing solution usually shows a slight background absorption upon addition of the diamine salt and ferric chloride.

41. Procedure

41.1 Dissolution of Sample:

41.1.1 It is essential that all sample treatment be carried out in a scrupulously clean laboratory atmosphere, that is, free from sulfuric acid fumes and any vapors or dust containing sulfur species. Dissolution of the test sample in the three-neck flask, rather than a beaker, reduces the chance of contamination.

41.1.2 Weigh 1.0 g of the test sample to the nearest 0.01 g, and transfer to a 100-mL or 250-mL three-neck round-bottom flask. Add 10 mL of nitric/chloric acid mixture and allow the reaction to subside. Using low heat, carefully evaporate the solution to a viscous syrup.

41.1.3 Add 10 mL of purified HCl (39.5) and heat to dissolve the residue. Add 2 mL of purified formic acid (39.4) and evaporate to dryness. Dissolve the dry residue in 10 mL of purified HCl and 0.5 mL of purified formic acid. Heat and digest for a few minutes on the hot plate to complete dissolution, and cool. If brown fumes appear during the final dissolution, evaporate to dryness again and dissolve the residue in purified HCl and formic acids.

NOTE 17—The three-neck flask may be held in a cylindrical metal holder for heating on a hot plate. A sand bath on a hot plate may also be used. Alternatively, the flask may be suspended in a low-form beaker of suitable size.

41.2 Hydrogen Sulfide Evolution—Attach the three-neck flask to the distillation apparatus (38.3). Place 3 mL of purified HCl (1 + 4) into the acid trap, and 5.0 mL of zinc acetate solution (39.10) into the hydrogen sulfide trap. Add 30 mL of the reducing mixture (39.8) to the sample solution by means of the side arm. Replace the stopper. Ensure that all joints are secure and pass a flow of argon through the apparatus at a rate

of 30 mL/min. After approximately 2 min, switch on the heating mantle and continue heating at 114 °C for 30 min. Remove the sulfide trap and switch off the heating mantle. Continue the flow of argon until the apparatus is cool.

NOTE 18—Chemically, the reduction of sulfate sulfur to hydrogen sulfide is a difficult reaction, and to ensure complete sulfur recovery the reaction conditions must be closely controlled. The optimum reducing temperature is 114 °C to 116 °C. If the reducing solution is diluted excessively by the sample solution, the boiling point is decreased and the reduction kinetics are slowed appreciably. For this reason care must be taken in 41.1.2 that the final sample solution is approximately 10 mL. At temperatures above 120 °C the acid mixture shows signs of decomposition of hypophosphorous acid and formation of phosphine.

41.3 Methylene Blue Development and Spectrophotometry—Proceed in accordance with 40.2 and 40.3.

41.4 Reagent Blank—Proceed in accordance with 41.1 to 41.3 but omit the test sample. Allow the now sulfur-free reducing solution to cool in a flow of argon and use it in the calibration (40.1).

42. Calculation

42.1 Convert the absorbance reading obtained for the samples and blank into micrograms of sulfur using the calibration graph (40.4).

42.2 Calculate the sulfur content of the sample as follows:

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

where:

A = weight of sulfur in the test sample, µg,
B = weight of sulfur in the blank, µg, and
C = weight of the test portion, g.

42.3 For a meaningful result, *A* must be equal to or be greater than two times *B*. If *A* is less than 2*B*, the reagent blank has to be improved by additional purification of the reagents used. Another possible source for high blanks can be the laboratory environment. A blank value of 0.5 µg of sulfur has been found to be attainable and is acceptable.

43. Precision and Bias

43.1 Precision—This test method was subjected to a very limited interlaboratory test program in the early 1980s under the auspices of ISO/TC-155/SC-4/WG-1 involving three laboratories in three countries. Three samples were analyzed. The statistical data obtained as evaluated by ISO 5725 and equivalent to Practice E1601 are summarized in Table 4. The precision of this test method may be judged by examination of these results.

43.2 Bias—The bias of this test method could not be evaluated because adequate certified reference materials were unavailable at the time of testing. The user is cautioned to verify by the use of certified reference materials, if available, that the bias of this test method is adequate for the contemplated use.

44. Keywords

44.1 hydrogen sulfide; methylene blue; refined nickel; spectrophotometry; sulfur

TABLE 4 Statistical Information—Sulfur by Distillation/Methylene Blue Method

Test Material	Mean, µg/g	Repeatability Index, <i>r</i> (Practice E1601)	Reproducibility Index, <i>R</i> (Practice E1601)
C-21	0.77	0.19	0.26
C-22	3.30	0.33	0.67
C-23	13.10	0.68	3.90

**NITROGEN BY THE INERT GAS FUSION THERMAL
CONDUCTIVITY METHOD****45. Scope**

45.1 Refer to Test Methods **E1019** for this test method that covers the determination of nitrogen (*N*) in concentrations from 0.001 % to 0.2 %.

OXYGEN BY THE INERT GAS FUSION METHOD**46. Scope**

46.1 Refer to Test Methods **E1019** for this test method that covers the determination of oxygen (*O*) in concentrations from 0.001 % to 0.005 %.

**PHOSPHORUS BY THE
PHOSPHOVANADOMOLYBDATE MOLECULAR
ABSORPTION SPECTROMETRIC METHOD****47. Scope**

47.1 Refer to Test Method **E1917** for the determination of phosphorus in the concentration range 0.0007 % to 0.05 %.

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