Designation: E1587 – 17

Standard Test Methods for Chemical Analysis of Refined Nickel[1]

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	Mass Fraction, %
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
Sulfur by the Methylene Blue Spectrophotometric Method After Generation of Hydrogen Sulfide	32 – 42

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.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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

2.2 *ISO Standard:*[4]

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

[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.

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

[3] 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.

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*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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 masses of substances of known composition so that the concentrations of the resulting standard stock 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 riffling 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 FLAME ATOMIC ABSORPTION SPECTROMETRY

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	Mass Fraction 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

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 calibration 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 calibration solutions.

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. 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.

9.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

[5] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

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 calibration solutions prepared from high-purity nickel metal. See Note 1.

NOTE 1—In this test method, any effect of nonspecific absorption and light scatter is compensated for by matching the matrix of the calibration solutions 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.

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) 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. Use the same batch of HNO_3 throughout the entire procedure.

13.1.3 If inhomogeneity is suspected in the test sample, or if the sample pieces are relatively large, a larger sample mass should be used to prepare the test solution. Under such circumstances, a sample mass 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 masses 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.

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). Use the same batch of HNO_3 throughout the entire procedure. 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 containing 80 mL of HNO_3 (1 + 1). 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.

		Analyte Concentration µ g/mL	
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, Standard Solution A to the 200-mL volumetric flasks. Dilute to volume with water and mix. 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.

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

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) µg⁄mL of cobalt, copper, iron, and manganese and (0, 0.25, 0.5, 1.0, 1.5, 2.0, and 2.5) µg⁄mL of zinc.

		Analyte Concentration µ g/mL	
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, 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. 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.

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 that has 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.

15.2.1 If inhomogeneity is suspected in the test sample, or if the sample pieces are relatively large, a larger sample mass should be used to prepare the test solution. Under such circumstances, a sample mass 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 masses 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.

15.3.1 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 1.

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. 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.

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.

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.

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 mass fraction 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, µg/mL,

B = volume of the test solution, mL, and

C = mass of the test sample, g.

18.3 *Procedure B:*

18.3.1 For the procedure in 16.2.1, calculate mass fraction 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 because of a

TABLE 1 Statistical Information—Flame AAS Method, Procedure A

Test Material	Mean, %	Repeatability Index, *r* (Practice E1601)	Reproducibility, Index *R* (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

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, because of 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 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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	Mass Fraction 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 calibration solutions.

21.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

22. Summary of Test Method

22.1 The test sample is dissolved in HNO_3 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 calibration solutions 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 standard stock solutions.

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 stock, 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 stock and calibration solutions shall be of borosilicate glass, 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 [$K(SbO)C_4H_4O_6 \cdot ½\ H_2O$] (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 4—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) 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.

25.2.2 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. 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.

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 µg/g of iron and less than 1 µg/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. 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. 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, and water. 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. 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 PTFE container. 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.

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. 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. 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 that 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) µg/mL each of arsenic, bismuth, lead, antimony, selenium, tin, tellurium, and thallium, respectively, and is used for analyte levels from 0.5 µg/g to 30.0 µg/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, µg/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) µg/mL each of Silver and Cadmium and is used for analyte levels from 0.01 µg/g to 5.0 µg/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, µg/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.

27.1.1 If inhomogeneity is suspected in the test sample, or if the sample pieces are relatively large, a larger sample mass should be used to prepare the test solution. Under such circumstances a sample mass 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 masses 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 g/L nickel to match the calibration solutions.

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

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. 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.

28.4 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.

NOTE 6—In this test method, any effect of nonspecific absorption and light scatter is compensated for by matching the matrix of the calibration solutions with the test solutions and by background correction. Also, since the same lot of HNO_3 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.

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

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

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 mass fraction of the analyte, in micrograms per gram, in the test sample as follows:

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

where:

A = analyte concentration found in the test solution, µg/mL,

B = volume of the test solution, mL, and

C = mass 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. 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

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

32. Scope

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

32.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

33. Summary of Test Method

33.1 The sample is dissolved in a nitric-chloric acid mixture and the sulfur oxidized to sulfate ion. After removal of nitrates by evaporation with HCl 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.

34. Interferences

34.1 Elements normally present do not interfere.

35. Hazards

35.1 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.

36. Apparatus

36.1 *Conventional Distillation Apparatus*—Equipped with a jacketed approximately 50-cm in length, Vigreux or packed reflux column for the purification of acids by distillation under atmospheric pressure, as shown in Fig. 1.

36.2 *Distillation Apparatus*—For purification of the reducing mixture (37.8), as shown in Fig. 2.

36.3 *Distillation Apparatus*—For the generation and volatilization of hydrogen sulfide from the test solution, as shown

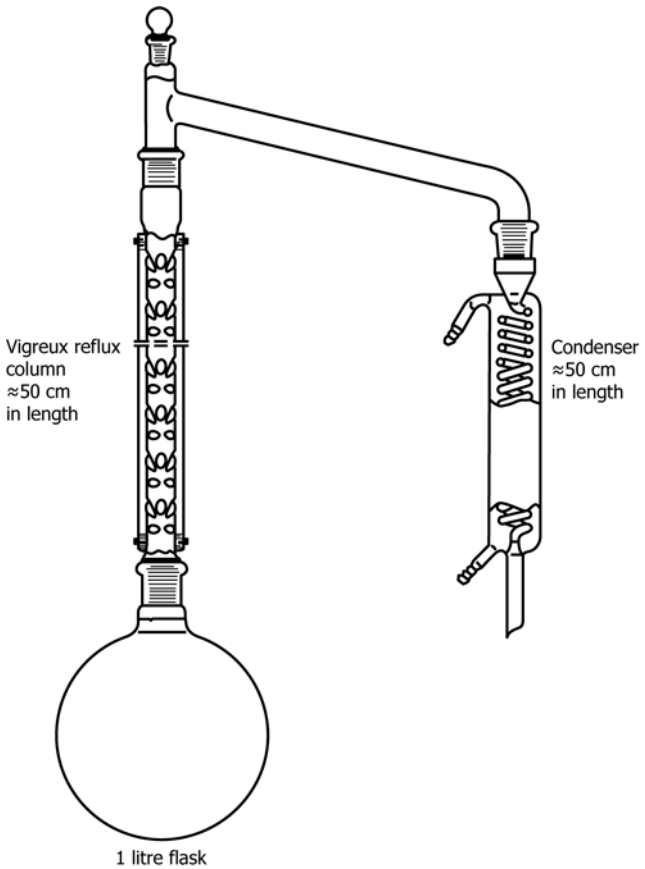

FIG. 1 Apparatus for Purification of Acids

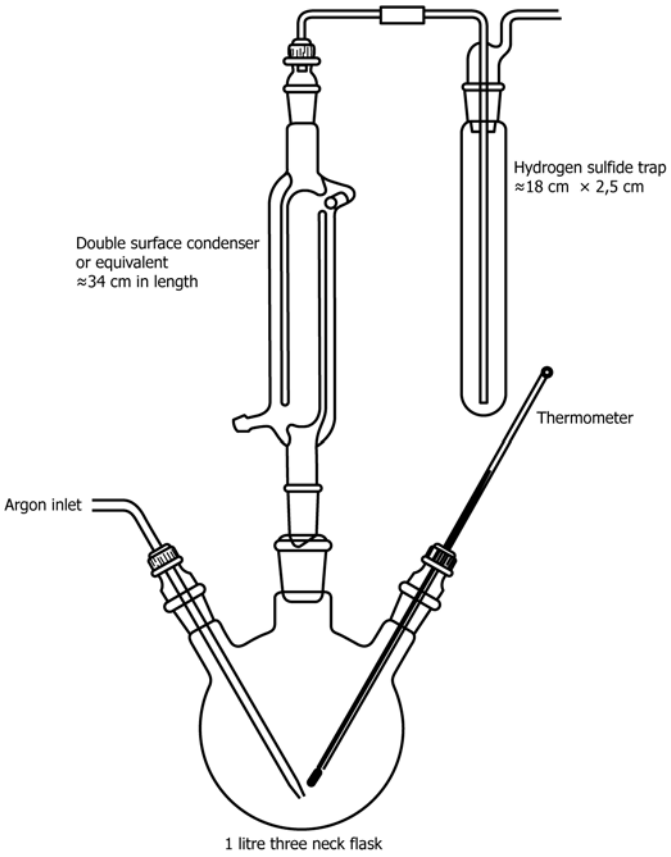

FIG. 2 Apparatus for Purification of Reducing Mixture

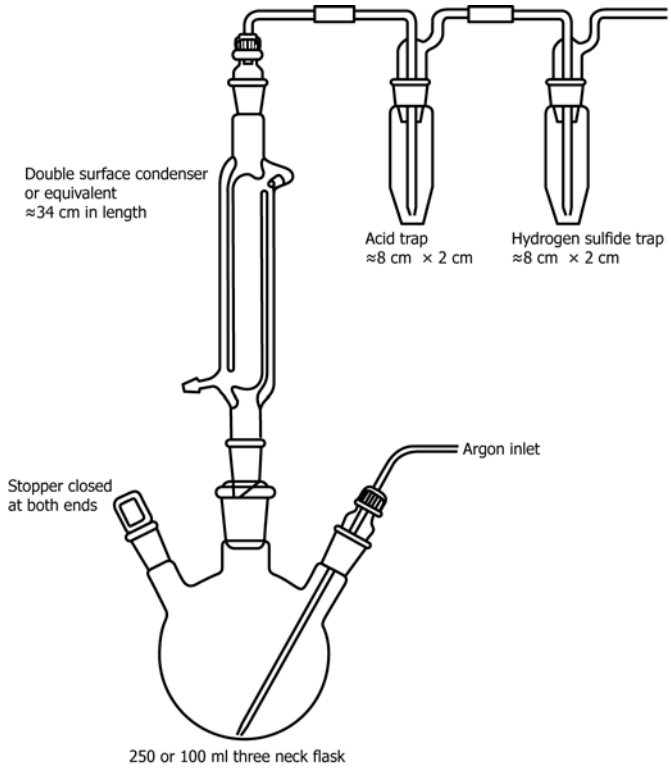

FIG. 3 Apparatus for Distillation of Hydrogen Sulfide

in Fig. 3. The double-surface condenser is preferred because of its superior cooling efficiency.

36.4 *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.

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

36.6 Glass storage containers shall be of borosilicate glass.

37. Reagents

37.1 *Argon Gas*—(purity, 99.998 % min).

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

37.3 *Ferric Chloride Solution*—Dissolve 1.0 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 10 mL of HCl and 40 mL of water. Dilute to 100 mL with water and store in a glass bottle.

37.4 *Purified Formic Acid*—Distill reagent grade formic acid using the apparatus in 36.1 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.

37.5 *Purified HCl*—Distill HCl (3 + 2) using the apparatus in 36.1 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.

37.6 *Purified HNO_3*—Distill HNO_3 using the apparatus in 36.1 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.

37.7 *Nitric-Chloric Acid Mixture*—Dissolve 3 g of potassium chlorate ($KClO_3$) in 30 mL of water and 100 mL of purified HNO_3 (37.6). Store in a glass bottle.

37.8 *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 (36.2). Attach the hydrogen sulfide trap containing 50 mL of the zinc acetate absorbing solution (37.10). 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. During the purification of the reducing mixture, take care to ensure that the solution does not become overheated. Temperature monitoring with a thermometer is recommended. 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.

37.9 *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.

37.10 *Zinc Acetate Absorbing Solution*—Dissolve 5 g of zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and 70 g of ammonium chloride (NH_4Cl) in about 350 mL of water. Add 7.5 g of NaOH, stir to dissolve, and dilute to 500 mL with water. Store in a glass bottle.

38. Calibration

38.1 *Evolution of Hydrogen Sulfide:*

38.1.1 To the cold, sulfur-free reducing mixture in a three-neck flask from the blank (39.4), add, from a micro-pipette, 10 µL (1 µg S) of standard sulfur solution (37.9). Proceed as directed in 39.2 and 39.3.

38.1.2 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 (37.9), to the same sulfur-free reducing mixture as in 38.1.1. Proceed after each addition as directed in 39.2 and 39.3. 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.

38.2 *Methylene Blue Development*—Introduce 3.0 mL of the diamine salt solution (37.2) into the sulfide trap by means of the gas inlet. Immediately follow with the addition of 0.5 mL of ferric chloride solution (37.3) 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.

38.3 *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.

38.4 *Calibration Curve*—Plot the absorbance readings of the solutions obtained in 38.1.1 and 38.1.2 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.

39. Procedure

39.1 *Dissolution of Sample:*

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

Test Material	Mean, µg/g	Repeatability Index, *r* (Practice E1601)	Reproducibility Index, *R* (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

39.1.1 It is essential that all sample treatment be performed 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.

39.1.2 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.

39.1.3 Add 10 mL of purified HCl (37.5) and heat to dissolve the residue. Add 2 mL of purified formic acid (37.4) 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 7—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.

39.2 *Hydrogen Sulfide Evolution*—Attach the three-neck flask to the distillation apparatus (36.3). Place 3 mL of purified HCl (1 + 4) into the acid trap, and 5.0 mL of zinc acetate solution (37.10) into the hydrogen sulfide trap. Add 30 mL of the reducing mixture (37.8) to the sample solution by means of the stoppered neck. 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.

39.2.1 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, take care in 39.1.2 to ensure 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.

39.3 *Methylene Blue Development and Spectrophotometry*—Proceed as directed in 38.2 and 38.3.

39.4 *Reagent Blank*—Proceed as directed in 39.1 to 39.3 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 (38.1).

40. Calculation

40.1 Convert the absorbance reading obtained for the samples and blank into micrograms of sulfur using the calibration graph (38.4).

40.2 Calculate the sulfur content of the sample as follows:

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

where:

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

40.3 For a meaningful result, A must be greater than or equal to two times B. If A is less than $2B$, the reagent blank must 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.

41. Precision and Bias

41.1 *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.

41.2 *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.

42. Keywords

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