



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

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## 1. Scope

1.1 These test methods<sup>2</sup> 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 in the sections indicated below:

	Sections
Antimony, Arsenic, Bismuth, Cadmium, Lead, Selenium, Silver, Tellurium, Tin, and Thallium by the Electrothermal Atomic Absorption Method	20 to 30
Bismuth, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Silver, and Zinc by the Flame Atomic Absorption Method	8 to 19
Carbon, Total, by the Combustion-Instrumental Method <sup>3</sup>	31 to 42
Nickel by the Dimethylglyoxime Gravimetric Method <sup>4</sup>	91 to 99
Nitrogen by the Inert Gas Fusion Thermal Conductivity Method <sup>3</sup>	66 to 77
Oxygen by the Inert Gas Fusion Method <sup>3</sup>	78 to 90
Sulfur by the Infrared Absorption Method <sup>3</sup>	43 to 54

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E-1 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 Jan. 15, 1994. Published March 1994.

<sup>2</sup> These methods represent revisions of, and replacements for, methods covered by Methods E 39 and E 107.

Sulfur by the Methylene Blue Spectrophotometric Method After Generation of Hydrogen Sulfide 55 to 65

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautions, see Section 5.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 1193 Specification for Reagent Water<sup>5</sup>
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>6</sup>
- E 39 Methods for Chemical Analysis of Nickel<sup>7</sup>
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>7</sup>
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals<sup>7</sup>
- E 107 Test Methods for Chemical Analysis of Electronic Nickel<sup>7</sup>
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>7</sup>
- E 354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys<sup>8</sup>
- E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory<sup>8</sup>
- E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, Oxygen, and Hydrogen in Steel and in Iron, Nickel, and Cobalt Alloys<sup>8</sup>
- E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Absorption Spectrophotometry<sup>8</sup>

### 2.2 ISO Standard:

- ISO 5725 Precision of Test Methods—Determination of

<sup>3</sup> This method appears in Test Methods E 1019 – 88, in the 1992 *Annual Book of ASTM Standards*, Vol 03.05.

<sup>4</sup> Supporting data are available from ASTM Headquarters. Request RR:E03-1051.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>7</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>8</sup> *Annual Book of ASTM Standards*, Vol 03.06.

Repeatability and Reproducibility by Interlaboratory Tests<sup>9</sup>

### 3. Significance and Use

3.1 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 such as those described in Guide E 882.

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

4.1 *Apparatus*—Special apparatus and reagents required for each determination are listed in the Apparatus section of each test method. In some cases, reference is made to Practices E 50.

#### 4.2 Reagents:

4.2.1 *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.

4.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

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

4.2.4 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.

4.3 *Instrumental Practices*—Information on the use of some instrumental techniques employed in these test methods are described in Practice E 60 and in Guide E 1024.

### 5. Hazards

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

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

### 6. Sampling

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

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

6.3 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.

6.4 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.

### 7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method in Practice E 29.

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

### 8. Scope

8.1 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
Ag	0.0002 to 0.01	...
Bi	0.0010 to 0.01	...
Cd	0.0002 to 0.0025	...
Co	0.0010 to 0.01	0.01 to 1.00
Cu	0.0005 to 0.01	0.01 to 1.00
Fe	0.0025 to 0.01	0.01 to 0.15
Mn	0.0005 to 0.01	0.01 to 0.20
Pb	0.0006 to 0.01	...
Zn	0.0005 to 0.0025	0.001 to 0.015

8.2 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.

8.3 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 (12.8).

8.4 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.

### 9. Summary of Test Method

9.1 The sample is dissolved in dilute nitric acid, 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 spectrophotometer. 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.

### 10. Interferences

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

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

<sup>9</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

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

**11. Apparatus**

11.1 *Atomic Absorption Spectrophotometer:*

11.1.1 The atomic absorption spectrophotometer used in this test method shall meet the instrument performance parameters in accordance with Guide E 1024.

11.1.2 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.

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

**12. Reagents**

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

12.1.1 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.

12.1.2 Add 40 mL of HNO<sub>3</sub> (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<sub>3</sub> (1 + 1), dilute to volume with water, and mix. Store in a polyethylene bottle.

NOTE 1—Use the same batch of nitric acid throughout the entire procedure. Also see Note 4.

12.2 *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 12.1.2.

12.3 *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 12.1.2.

12.4 *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 12.1.2.

12.5 *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 12.1.2.

12.6 *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 12.1.2.

12.7 *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 12.1.2.

12.8 *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.

12.9 *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 12.1.2, except store in a glass bottle.

12.10 *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 12.1.2.

12.11 *Working Solutions:*

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

12.11.2 *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 bottle.

**13. Calibration Solutions**

13.1 *Set A:*

13.1.1 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 µg/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

13.1.2 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 14.2

13.1.3 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 14.3 and Note 5.

13.2 *Set B:*

13.2.1 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 µg/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

13.2.2 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 15.2.2.

13.2.3 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 Reference Solution B to the 200-mL volumetric flasks. Dilute to volume with water and mix. The solution with no analyte added is the blank. See Note 5.

NOTE 3—For convenience, 80 g of nickel/L stock nickel nitrate solution may be prepared by dissolving 20.0 g of nickel powder in water and 120 mL of HNO<sub>3</sub> (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 13.2 and 14.2.1.

### 14. Procedure A

14.1 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.

14.2 *Preparation of Test Solution*—Weigh, to the nearest 0.01 g, 4.9 to 5.1 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<sub>3</sub> (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<sub>3</sub> (1 + 1) and 100 mL of H<sub>2</sub>O. Heat to complete dissolution, cool, and filter, if necessary, through either glass wool or a cellulose filter which have been washed with HNO<sub>3</sub> (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<sub>3</sub> should be increased in proportion. Even larger sample weights can be used, with greater amounts of HNO<sub>3</sub> 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.

14.3 *Reagent Blank Solution*—The zero reference solution of the Calibration Solution Set A (13.1) serves as the reagent blank, since the same batch of nitric acid is used for dissolution of both the nickel reference and test samples.

NOTE 5—If it is impossible to use the same batch of nitric acid, 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.

#### 14.4 Instrumental Parameters:

14.4.1 Use the spectral lines specified in the following table are to be used in the analysis:

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

14.4.2 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

14.4.3 Set the required instrument parameters in accordance with the manufacturer's recommendations. Light the burner and aspirate diluted HNO<sub>3</sub> (1 + 19) until thermal equilibrium is reached. A fuel-lean air-acetylene flame shall be used.

14.4.4 Ensure that the instrument meets the performance requirements given in Practice E 60. Optimum settings for the operating parameters vary from instrument to instrument. Scale expansion may have to be used to obtain the required readability.

#### 14.5 Photometry:

14.5.1 Ensure that the test solution (14.2) and the calibration solutions, Set A (13.1) are within 1°C of the same temperature.

14.5.2 Aspirate diluted HNO<sub>3</sub> (1 + 19) and zero the instrument.

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

14.5.4 Aspirate diluted HNO<sub>3</sub> (1 + 19) until the initial reading is obtained. Zero the instrument if necessary.

14.5.5 Aspirate the Set A calibration solutions (13.1) 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<sub>3</sub> (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.

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

14.5.7 Proceed with the preparation of the calibration curves and calculations as directed in Sections 16 and 17.

### 15. Procedure B

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

#### 15.2 Preparation of Test Solution:

15.2.1 If a test solution has been prepared by Procedure A (14.2), using a pipet, transfer a 100.0-mL aliquot portion into a 250-mL volumetric flask, dilute to volume with diluted HNO<sub>3</sub> (1 + 19). Otherwise, proceed as directed in 15.2.2.

15.2.2 Weigh to the nearest 0.005 g, 1.9 to 2.1 g of the test sample, transfer to a 400-mL beaker and dissolve in 20 mL of HNO<sub>3</sub> (1 + 1). Complete the preparation as directed in 14.2.

15.3 *Reagent Blank Solution*—The zero reference solution of the calibration solution Set B (13.2) serves as the reagent blank. See Note 5.

#### 15.4 Instrumental Parameters:

15.4.1 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

15.4.2 Proceed as directed in 14.4.3 and 14.4.4.

15.5 *Photometry:*

15.5.1 Proceed as directed in 14.5.1 through 14.5.6, substituting the Set B calibration solution (13.2) for the Set A solutions.

15.5.2 Proceed with the preparation of the calibrations curves and calculations as directed in Sections 16 and 17.

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<sub>3</sub> (1 + 19) may be made. The nickel content of the calibration solutions should be matched with those of the test solutions.

16. Preparation of Calibration Curves

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

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<sub>3</sub> 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.

17. Calculations

17.1 Determine the concentration of analyte in the test solution from the corresponding calibration curves for each of the three sets of instrument readings. Average the resultant concentrations.

17.2 *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, µg/mL,

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

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

17.3 *Procedure B:*

17.3.1 For the procedure in 15.2.1, 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.

18. Precision and Bias

18.1 *Precision:*

18.1.1 Eighteen laboratories in nine countries participated in testing this test method under the auspices of ISO/TC-155/SC-3/WG-1 and obtained the data summarized in Table 1. Precision may be judged by examination of these data. All testing meets the requirements of Practice E 173.

18.1.2 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.

TABLE 1 Statistical Information—Flame AA Method, Procedure A

Test Material	Mean, %	Repeatability, R <sub>1</sub>	Reproducibility, R <sub>2</sub>
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

18.2 *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.

## 19. Keywords

19.1 bismuth; cadmium; cobalt; copper; flame atomic absorption; spectrophotometry; iron; lead; manganese; refined nickel; silver; zinc

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

## 20. Scope

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

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

20.2 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.

## 21. Summary of Test Method

21.1 The test sample is dissolved in nitric acid and the solution is diluted to a known volume. An aliquot is introduced into an electrothermal atomic absorption instrument 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.

## 22. Interferences

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

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

22.3 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.

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

22.5 Because of the high sensitivity of electrothermal atomic absorption, 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.

## 23. Apparatus

23.1 *Atomic Absorption Spectrophotometer and Electro-*

*thermal 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 manufacturer.

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

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

## 24. Reagents

24.1 *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.

24.2 *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.

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

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

24.3 *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 24.2.1.

24.4 *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 24.2.1.

24.5 *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 24.2.1.

24.6 *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.

24.7 *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 24.2.1.

24.8 *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 24.2.1, except store in an amber glass bottle.

24.9 *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 24.2.1.

24.10 *Thallium, Standard Stock Solution* (1 mL = 1 mg Thallium)—Transfer a 0.112-g sample of thallium (III) oxide (Tl<sub>2</sub>O<sub>3</sub>) (purity, 99.9 % minimum), weighed to the nearest 0.1 mg, to a 100-mL beaker. Add 10 mL of HNO<sub>3</sub> and heat to dissolve (Note 9). Cool and transfer to a 100-mL volumetric flask, dilute to volume, and mix. Store in a glass container.

24.11 *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<sub>3</sub> (Note 9), and water. Heat until dissolved. Boil gently to expel oxides of nitrogen. Cool and transfer to a 250-mL plastic volumetric flask. Dilute to volume and mix. Store in a plastic container.

24.12 *Working Solutions:*

24.12.1 *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<sub>3</sub> (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 100-mL volumetric flask containing 10 mL of HNO<sub>3</sub> (1 + 1). Dilute to volume with water and mix. Store in a glass container (Note 9).

24.12.2 *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<sub>3</sub> (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<sub>3</sub> (1 + 1). Dilute to volume with water and mix. Prepare this solution immediately before use.

24.12.3 *Nickel Nitrate Solution* (40 g Nickel/L)—Transfer a 4.00-g sample of nickel metal (24.6), weighed to the nearest 1 mg, to a 400-mL beaker. Add 50 mL of water and 28 mL of HNO<sub>3</sub> (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<sub>3</sub> (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.

25. Calibration Solutions

25.1 *Set A:*

25.1.1 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.

25.1.2 Using a buret, transfer 2.50 mL of the nickel nitrate solution (24.12.3) 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 (24.12.1). Dilute to volume with HNO<sub>3</sub> (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

25.2 *Set B:*

25.2.1 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 to 5.0 µg/g.

25.2.2 Using a buret, transfer 2.50 mL of nickel nitrate stock solution (23.12.3) 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 (24.12.2). Dilute to volume with HNO<sub>3</sub> (1 + 1) 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

26. Procedure

26.1 *Preparation of Test Solution*—Weigh, to the nearest 0.01 g, 0.9 to 1.1 g of the test sample and transfer to a clean unetched 100-mL beaker. Add 30 mL of H<sub>2</sub>O and 12 mL of HNO<sub>3</sub> and allow to dissolve. Heat the complete dissolution, boil gently to expel oxides of nitrogen, cool, and transfer to a 100-mL volumetric flask. Dilute to volume with H<sub>2</sub>O and mix.

NOTE 10—The life of the graphite furnace tubes may be extended by using 5 mL of HNO<sub>3</sub> 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<sub>3</sub> should be increased in proportion. Even larger sample weights can be used, with greater amounts of HNO<sub>3</sub>, 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.

26.2 *Reagent Blank Solution*—The zero reference solutions of the Sets A and B calibration solutions (25.1 and 25.2) serve as reagent blanks since the same batch of HNO<sub>3</sub> 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<sub>3</sub>, 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.

### 26.3 Instrumental Parameters:

26.3.1 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

26.3.2 Set the required instrument parameters and align the electrothermal 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 to 2700°C are preferable for a nickel matrix. The use of background compensation is essential.

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

### 26.4 Photometry:

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

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

26.4.3 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.

26.4.4 Inject, into the atomizer, the predetermined volume (5 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.

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

26.4.6 Inject and atomize the same predetermined volume (5 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.

26.4.7 Evaluate the analyte contents in each group of test solutions based on the applicable calibration solutions as directed in Sections 26 and 27.

## 27. Preparation of Calibration Curve

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

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

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 HNO<sub>3</sub> 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.

## 28. Calculation

28.1 Use the average of the three instrument readings obtained for the test solution and the calibration curve prepared in 27.2 to obtain the concentration of the analyte in the test solution.

28.2 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, µg/mL,

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

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

## 29. Precision and Bias

29.1 *Precision*—Eleven laboratories in six countries participated in testing this test method under the auspices of ISO/TC-155/SC-3/WG-3 and obtained the data summarized in Table 3. Precision may be judged by examination of these data. All testing meets the requirements of Practice E 173. 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.

29.2 *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.

TABLE 2 Statistical Information—Flame AA Method, Procedure B

Test Material	Mean, %	Repeatability, <i>R</i> <sub>1</sub>	Reproducibility, <i>R</i> <sub>2</sub>
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—Electrothermal AA Method**

Test Material	Mean, %	Repeatability, $R_1$	Reproducibility, $R_2$
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

### 30. Keywords

30.1 antimony; arsenic; bismuth; cadmium; electrothermal atomic absorption spectrophotometry; lead; refined nickel; selenium; silver; tellurium; thallium; tin

### TOTAL CARBON BY THE COMBUSTION INSTRUMENTAL MEASUREMENT METHOD

#### 31. Scope

31.1 This test method covers the determination of carbon in concentrations from 0.005 to 4.5 %.

#### 32. Summary of Test Methods

32.1 The carbon is converted to carbon dioxide by combustion in a stream of oxygen.

32.1.1 *Thermal Conductivity Method*—The carbon dioxide is absorbed on a suitable grade of zeolite, released by heating the zeolite, and swept by helium or oxygen into a chromatographic column. Upon elution, the amount of carbon dioxide is measured in a thermistor-type conductivity cell. Refer to Fig. 1.

32.1.2 *Infrared (IR) Absorption, Method A*—The amount of carbon dioxide is measured by infrared (IR) absorption. Carbon dioxide (CO<sub>2</sub>) absorbs IR energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed

as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed to only CO<sub>2</sub> and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber. Total carbon, as CO<sub>2</sub>, is monitored and measured over a period of time. Refer to Fig. 2.

32.1.3 *Infrared (IR) Absorption, Method B*—The detector consists of an IR energy source, a separate measure chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor. During specimen combustion, the flow of CO<sub>2</sub> with its oxygen gas carrier is routed through the measure chamber while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the CO<sub>2</sub> present in the measure chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as CO<sub>2</sub>. Total carbon, as CO<sub>2</sub>, is monitored and measured over a period of time. Refer to Fig. 3.

32.1.4 *Infrared (IR) Absorption, Method C, Closed Loop*—The combustion is performed in a closed loop, where CO and CO<sub>2</sub> are detected in the same infrared cell. Each gas is measured with a solid-state energy detector. Filters are used to pass the appropriate IR wavelength to each detector. In the absence of CO and CO<sub>2</sub>, the energy received by each detector is maximum. During combustion, the IR absorption properties of CO and CO<sub>2</sub> gases in the chamber cause a loss of energy; therefore a loss in signal results which is proportional to concentrations of each gas in the closed loop. Total carbon, as CO<sub>2</sub> plus CO, is monitored and measured over a period of time. Refer to Fig. 4.

32.2 This test method is written for use with commercial analyzers, equipped to carry out the above operations automatically and calibrated using steels of known carbon content.

#### 33. Interferences

33.1 The elements ordinarily present do not interfere.

#### 34. Apparatus

34.1 *Combustion and Measurement Apparatus*—See Figs. 1-3, and Fig. 4.

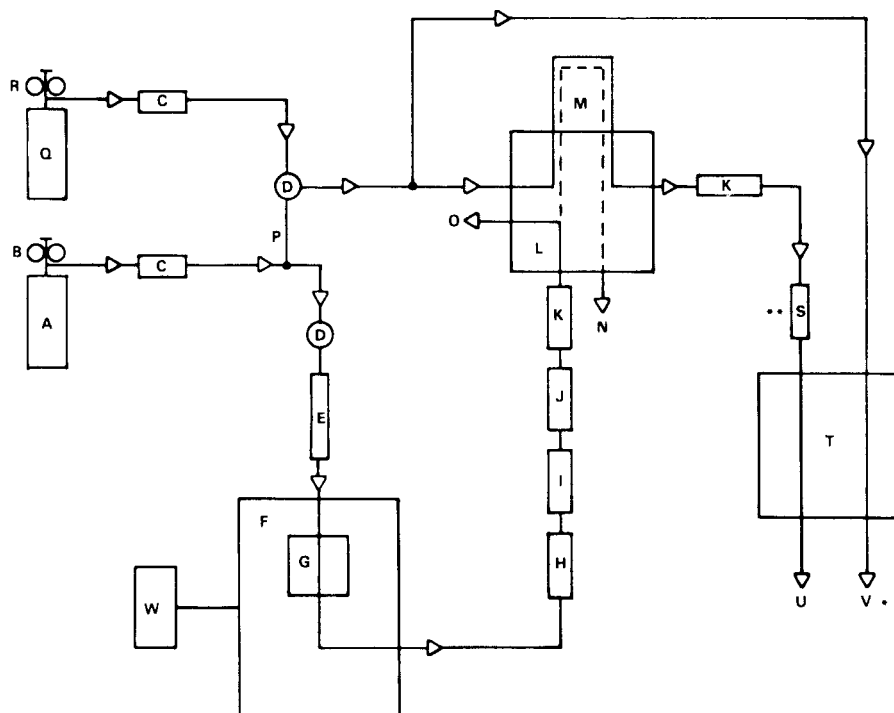
34.2 *Crucibles*—Use crucibles that meet or exceed the specifications of those recommended by the manufacturer of the instrument used and preheat in a suitable furnace for not less than 40 min at 1000°C. Remove from the furnace and cool in air for 90 ± 15 s before use. Crucibles may be placed in a desiccator for periods of 1 h prior to use.

34.3 *Crucible Tongs*—Capable of handling recommended crucibles.

#### 35. Reagents

35.1 *Acetone*—The residue after evaporation must be <0.0005 %.

35.2 *Copper (Low-Carbon)*, granular (10 to 30 mesh) (Note 15).



- |   |   |
|---|---|
| <p>A—High-Purity Oxygen<br/>         B—Oxygen Regulator (2 Stage)<br/>         C—Sodium Hydroxide Impregnated Clay/Magnesium Perchlorate<br/>         D—Secondary Pressure Regulator<br/>         E—Flowmeter<br/>         F—Induction Furnace<br/>         G—Combustion Tube<br/>         H—Dust Trap<br/>         I—Manganese Dioxide<br/>         J—Heated CO to CO<sub>2</sub> Converter<br/>         K—Magnesium Perchlorate<br/>         L—Valve Manifold</p> | <p>M—CO<sub>2</sub> Collection Trap<br/>         N—Furnace Combustion Exhaust<br/>         O—Furnace Purge Exhaust<br/>         P—Metal Connector To Use Oxygen As Carrier Gas<br/>         Q—High-Purity Helium<br/>         R—Helium Regulator (2 Stage)<br/>         S—Chromagraphic Column<br/>         T—TC Cell/Readout<br/>         U—Measure Flowmeter<br/>         V—Reference Flowmeter<br/>         W—Furnace Power Stat</p> |
|---|---|

\* May be sealed chamber if oxygen is carrier gas.

\*\* Not required if oxygen is carrier gas.

FIG. 1 Apparatus for Determination of Carbon by the Combustion Thermal Conductivity Method

35.3 *Oxygen, Ultra High Purity* (purity: 99.95 % minimum)—Other grades of oxygen may be used if low and consistent blank readings are obtained, or the oxygen may be purified as described in Practices E 50.

35.4 *Platinum or Platinized Silica*, heated to 350°C for the conversion of carbon monoxide to carbon dioxide.

35.5 *Tungsten (Low-Carbon)*, 12 to 20 mesh (Note 15).

35.6 *Tungsten-Tin (Low-Carbon)*, 20 to 40 mesh.

NOTE 15—The accelerator should contain no more than 0.001 % carbon. Wash three times with acetone by decantation to remove organic contaminants and dry at room temperature. The mesh size is critical to the inductive coupling which heats the sample.

### 36. Preparation of Apparatus

36.1 Assemble the apparatus as recommended by the manufacturer.

36.2 Test the furnace and analyzer to ensure the absence of leaks and make the required electrical power connections. Prepare the analyzer for operation in accordance with the manufacturer's instructions. Make a minimum of two determi-

nations using the specimen and accelerator in accordance with 39.1.2 and 39.1.3 before attempting to calibrate the system or determine the blank.

### 37. Sample Preparation

37.1 The sample should be uniform in size, but not finer than 40 mesh.

37.2 Wash in acetone and dry at 70 to 100°C.

### 38. Calibration

38.1 *Calibration Standards* (Note 16):

38.1.1 For Range I, 0.005 to 0.10 % carbon, select three primary standard reference materials containing approximately 0.005, 0.05, and 0.10 % carbon and designate them as Standards A, B, and C, respectively.

38.1.2 For Range II, 0.10 to 1.25 % carbon, select two primary standard reference materials containing approximately 0.12 and 1.00 % carbon and designate them as Standards BB and CC, respectively.

38.1.3 For Range III, 1.25 to 4.50 % carbon, select two

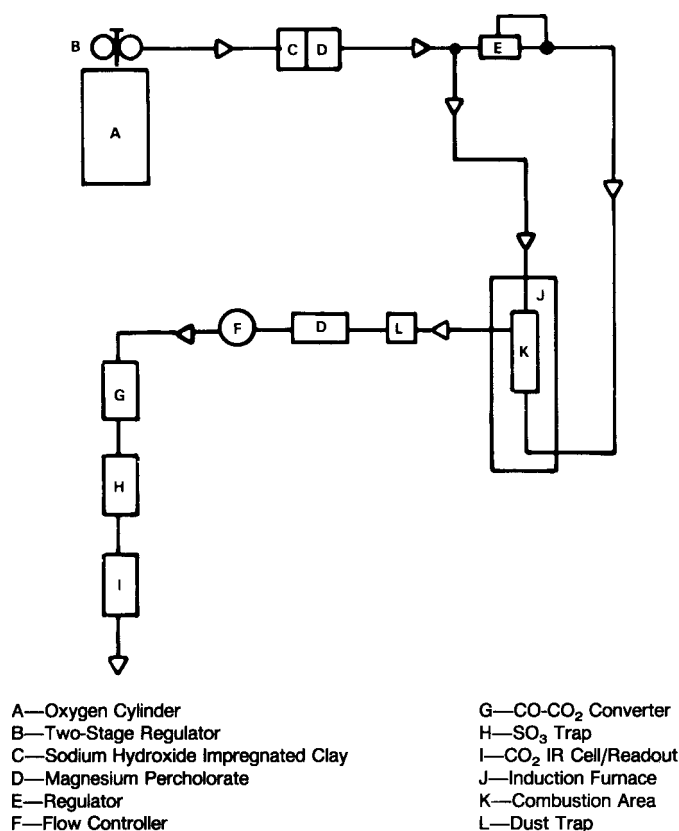


FIG. 2 Infrared Absorption Method A

primary standard reference materials containing approximately 1.25 and 4.00 % carbon and designate them as Standards BBB and CCC, respectively.

NOTE 16—The accuracy of this test method is dependent upon the accuracy of the test methods used to certify the carbon concentration in the calibration primary standard reference materials, as well as upon their homogeneity.

### 38.2 Adjustment of Response of Measurement System:

38.2.1 Transfer 1.0 g of Standard B, weighed to the nearest 1 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to a preburned crucible.

38.2.2 Proceed in accordance with 39.1.2 and 39.1.3.

38.2.3 Repeat 38.2.1 and 38.2.2 until the absence of drift is indicated. Adjust the signal to provide a reading within  $\pm 0.003$  of the certified percent carbon value for the primary standard reference material.

### 38.3 Determination of Blank Reading—Range I:

38.3.1 Transfer 1.0 g of Standard A, weighed to the nearest 1 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, into a preburned crucible.

38.3.2 Proceed in accordance with 39.1.2 and 39.1.3.

38.3.3 Repeat 38.3.1 and 38.3.2 a sufficient number of times to establish that low (less than 0.020 mg of carbon) and consistent ( $\pm 0.002$  mg of carbon) readings are obtained. Blank values are equal to the total result of the accelerator and Standard A minus the certified value for the primary standard reference material.

38.3.4 Record the average value of at least three blank determinations.

38.3.5 If the blank readings are too high or inconsistent, determine the cause, correct it, and repeat in accordance with 38.3.1 to 38.3.4.

38.3.6 Enter the average blank value in the analyzer (Note 17); refer to the manufacturer's instructions. This mechanism will electronically compensate for the blank value.

NOTE 17—If the unit does not have this function, the blank value must be subtracted from the total result prior to any calculation.

38.4 Determination of Blank Reading—Range II—Proceed in accordance with 38.3.

### 38.5 Determination of Blank Reading—Range III:

38.5.1 Transfer 0.5 g of Standard A, weighed to the nearest 1 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to a preburned crucible.

38.5.2 Proceed in accordance with 38.3.2-38.3.6.

### 38.6 Calibration—Range I (0.005 to 0.10 % Carbon):

38.6.1 Weigh four 1.0-g specimens of Standard C, to the nearest 1 mg, the place in preburned crucibles. To each, add 1.5 g of accelerator, weighed to the nearest 5 mg.

38.6.2 Follow the calibration procedure recommended by the manufacturer. Use Standard C as the primary calibration standard and analyze at least three specimens to determine the calibration slope. Treat each specimen, as directed in 39.1.2 and 39.1.3, before proceeding to the next one.

38.6.3 Confirm the calibration by analyzing Standard C following the calibration procedure. The value should be within the allowable limits of the certified value for the primary standard reference material. If not, repeat 38.6.1 and 38.6.2.

38.6.4 Weigh at least two 1.0-g specimens of Standard B, weighed to the nearest 1 mg, and transfer them to preburned crucibles. To each, add 1.5 g of accelerator, weighed to the nearest 5 mg.

38.6.5 Treat each specimen as directed in 39.1.2 and 39.1.3 before proceeding to the next one.

38.6.6 Record the results of 38.6.4 and 38.6.5 and compare them to the certified carbon value of Standard B. The results should be within the allowable limits of the primary standard reference material. If not, refer to the manufacturer's instructions for checking the linearity of the system.

NOTE 18—Repeat the calibration when: (1) a different lot of crucibles is used, (2) a different lot of accelerator is used, (3) the system has not been in use for 1 h, and (4) the oxygen supply has been changed.

### 38.7 Calibration—Range II (0.10 to 1.25 % Carbon):

38.7.1 Proceed in accordance with 38.6.1 to 38.6.3, using Standard CC.

38.7.2 Proceed in accordance with 38.6.4 to 38.6.6, using Standard BB.

### 38.8 Calibration—Range III (1.25 to 4.50 % Carbon):

38.8.1 Weigh four 0.5-g specimens of Standard CCC, to the nearest 1 mg, and place in preburned crucibles. To each, add 1.5 g of accelerator, weighed to the nearest 5 mg.

38.8.2 Follow the calibration procedure recommended by the manufacturer. Use Standard CCC as the primary calibration standard and analyze at least three specimens to determine the calibration slope. Treat each specimen, as directed in 39.1.2 and 39.1.3, before proceeding to the next one.

38.8.3 Confirm the calibration by analyzing Standard CCC following the calibration procedure. The value should be

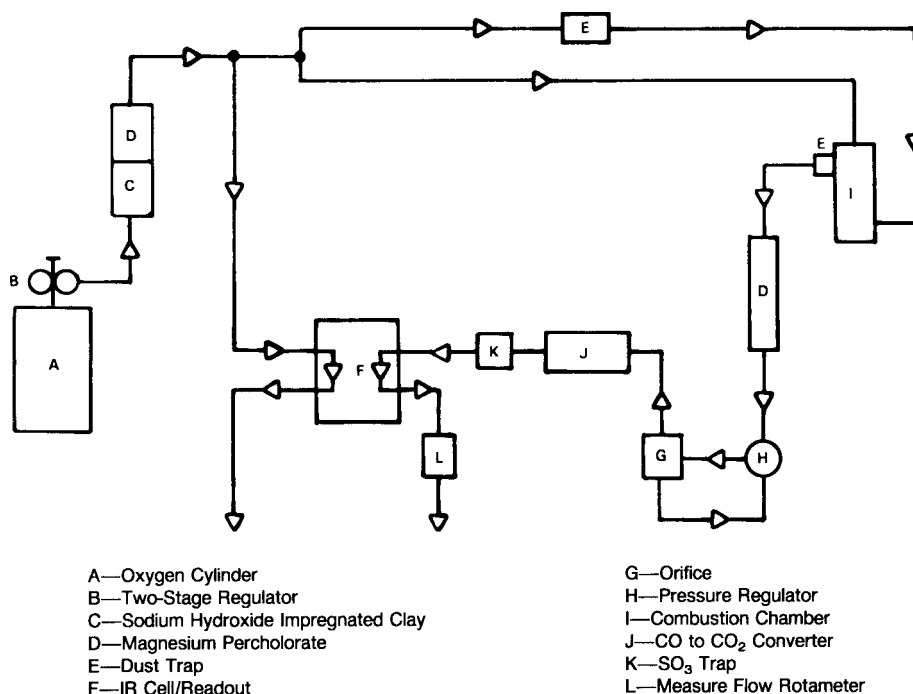


FIG. 3 Infrared Absorption Method B

within the allowable limits of the certified value for the primary standard reference material. If not, repeat 38.8.1 and 38.8.2.

38.8.4 Weigh at least two 0.5-g specimens of Standard BBB, weighed to the nearest 1 mg, and transfer to preburned crucibles. To each, add 1.5 g of accelerator, weighed to the nearest 5 mg.

38.8.5 Treat each specimen as described in 39.1.2 and 39.1.3 before proceeding to the next one.

38.8.6 Record the results of 38.8.4 and 38.8.5 and compare to the certified carbon value of the Standard BBB. The results should be within the allowable limits of the primary standard reference material. If not, refer to manufacturer's instructions for checking the linearity of the analyzer (Note 18).

### 39. Procedure

#### 39.1 Procedure—Range I:

39.1.1 Stabilize the furnace and analyzer as directed in Section 14. Transfer 1.0 g of specimen, weighed to the nearest 1 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to a preburned crucible. (See 34.2.)

39.1.2 Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs to handle the preburned crucibles.

39.1.3 Start the analysis cycle; refer to the manufacturer's recommended procedure regarding entry of specimen weight and blank value.

39.2 Procedure—Range II—Proceed in accordance with 39.1.

39.3 Procedure—Range III—Proceed in accordance with 39.1, using a 0.5-g specimen.

### 40. Calculation

40.1 Since most commercially available instruments calculate percent concentrations directly, including corrections for

blank and sample weight, calculations by the analyst are not required.

NOTE 19—If the analyzer does not compensate for blank and sample weight values, then use the following formula:

$$\text{Carbon, \%} = [(A - B) \times C/D] \quad (4)$$

where:

- A = DVM reading for specimen,
- B = DVM reading for blank,
- C = weight compensator setting, and
- D = specimen weight, g.

### 41. Precision and Bias<sup>10</sup>

41.1 Precision—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 4, Table 5, and Table 6. Testing was performed in compliance with Practice E 173.

41.2 Bias—No information on the accuracy of this test method is known. The accuracy of this test method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

### 42. Keywords

42.1 carbon; combustion/instrumental; refined nickel

### SULFUR BY THE COMBUSTION-INFRARED ABSORPTION METHOD

### 43. Scope

43.1 This test method covers the determination of sulfur in

<sup>10</sup> Supporting data are available from ASTM Headquarters. Request RR:E03-1038.



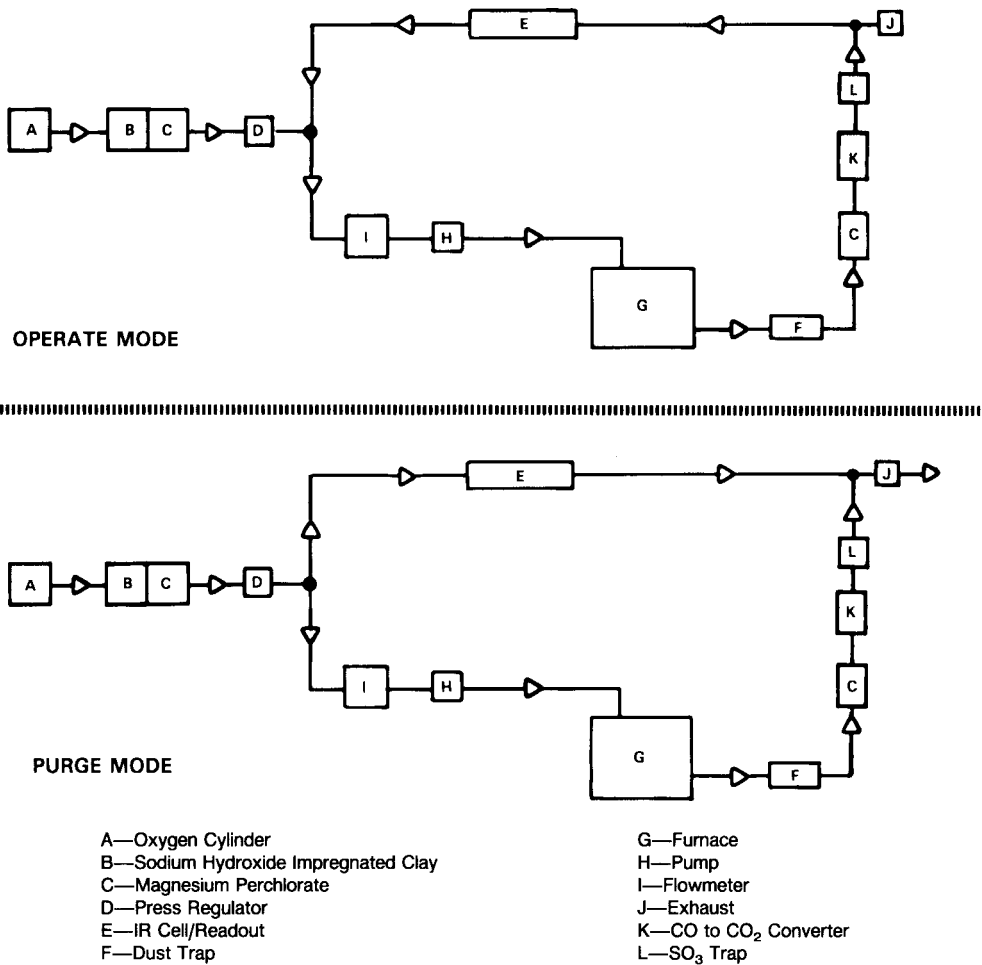


FIG. 4 Infrared Absorption Method C—Closed Loop

TABLE 4 Statistical Information—Carbon, Range I—Combustion/Instrumental Measurement Method

Test Material	Carbon Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. Electrolytic iron (NBS 365, 0.0068 C)	0.007	0.002	0.003
2. Bessemer carbon steel (NBS 8j, 0.081 C)	0.080	0.003	0.006
3. Type 304L stainless steel 18Cr-8Ni (NBS 101f, 0.014 C)	0.014	0.002	0.004
4. Type 446 stainless steel 26Cr (NBS 367, 0.093 C)	0.094	0.003	0.004
5. Nickel steel 36Ni (NBS 126b, 0.090 C)	0.092	0.003	0.004
6. Waspaloy 57Ni-20Cr-14Co-4Mo (NBS 349, 0.080 C)	0.078	0.003	0.004
7. Silicon steel (NBS 131a, 0.004 C)	0.004	0.002	0.002
8. High-temperature alloy A286 26Ni-15Cr (NBS 348, 0.044 C)	0.046	0.003	0.004

TABLE 5 Statistical Information—Carbon, Range II—Combustion/Instrumental Measurement Method

Test Material	Carbon Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. Basic open-hearth steel (NBS 11h, 0.200 C)	0.201	0.006	0.010
2. Basic open-hearth carbon steel (NBS 337, 1.07 C)	1.087	0.039	0.053
3. Low-alloy electric-furnace steel (NBS 51b, 1.21 C)	1.224	0.039	0.048
4. High-temperature nickel alloy (LE 105, 0.130 C)	0.130	0.005	0.008
5. Tool steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 0.902 C)	0.905	0.023	0.027
6. Type 416 stainless steel (NBS 133b, 0.128 C)	0.126	0.005	0.013
7. Low-alloy steel 1Cr (NBS 163, 0.933 C)	0.934	0.016	0.020

the range from 0.001 to 0.01 %.

#### 44. Summary of Test Methods

44.1 The sample is combusted in a stream of oxygen that

converts the sulfur in the sample to sulfur dioxide. The sulfur is then determined by infrared absorption.

44.1.1 *Infrared Absorption Method A*—Sulfur dioxide

TABLE 6 Statistical Information—Carbon, Range III—Combustion/Instrumental Measurement Method

Test Material	Carbon Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. Tool steel (CISRI 150, 1.56 C)	1.550	0.027	0.049
2. Low-alloy electric-furnace steel (NBS 51b, 1.21 C)	1.228	0.039	0.050
3. Cast iron (LECO 501-105, 2.20 C)	2.202	0.044	0.056
4. Ductile iron (LECO 501-083, 4.24 C)	4.244	0.083	0.091
5. White iron (LECO 501-024, 3.25 C)	3.274	0.064	0.074
6. Iron (BAM 035-1, 1.31 C)	1.314	0.034	0.048
7. Ferritic stainless steel (BAM 228-1, 2.05 C)	2.040	0.027	0.055

(SO<sub>2</sub>) absorbs infrared (IR) energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Therefore, the absorption of IR energy can be attributed to only SO<sub>2</sub> and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber. Total sulfur, as SO<sub>2</sub>, is monitored and measured over a period of time. Refer to Fig. 5.

44.1.2 *Infrared Absorption Method B*—The combustion is performed in a closed loop where SO<sub>2</sub> is detected in an infrared cell. The SO<sub>2</sub> is measured with a solid-state energy detector, and filters are used to pass the appropriate IR wavelength to the detector. During combustion, the IR absorption properties of the SO<sub>2</sub> gas in the chamber causes a loss of energy, therefore a loss in signal results which is proportional to the concentration of the gas in the closed loop. Total sulfur, as SO<sub>2</sub>, is monitored and measured over a period of time. Refer to Fig. 6.

44.1.3 *Infrared Absorption Method C*—The detector consists of an IR energy source, a separate measure chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor. During specimen combustion, the flow of SO<sub>2</sub> with its oxygen gas carrier is routed through the measure chamber while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the SO<sub>2</sub>

present in the measure chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as SO<sub>2</sub>. Total SO<sub>2</sub> is monitored and measured over a period of time. Refer to Fig. 7.

45. Interferences

45.1 The elements ordinarily present do not interfere.

46. Apparatus

46.1 *Combustion and Measurement Apparatus*—See Figs. 5 and 6, and Fig. 7.

46.2 *Crucibles*—Use crucibles recommended by the manufacturer of the instrument, or equivalent, and preheat in a suitable furnace for not less than 1 h at 1100°C. Remove from furnace and cool in air for 90 ± 15 s before use. Preheated crucibles may also be stored in a desiccator prior to use.

46.3 *Micropipet*, (50 µL).

46.4 *Crucible Tongs*—Capable of handling recommended crucibles.

46.5 *Tin Capsules*—Approximate dimensions: diameter 6 mm, length 20 mm. Wash twice with acetone and dry at 90°C for 4 h prior to use.

47. Reagents

47.1 *Acetone*—The residue after evaporation must be <0.0005 %.

47.2 *Iron* (purity, 99.8 % minimum)—Must be free of sulfur or of low known sulfur content.

47.3 *Oxygen, Ultra High Purity* (purity: 99.95 % min)—Other grades of oxygen may be used if low and consistent blank readings are obtained, or the oxygen may be purified as described in Practices E 50.

47.4 *Potassium Sulfate* (K<sub>2</sub>SO<sub>4</sub>)—Dry 20 g of K<sub>2</sub>SO<sub>4</sub> at 105 to 110°C for 1 h to a constant weight. Cool in a desiccator.

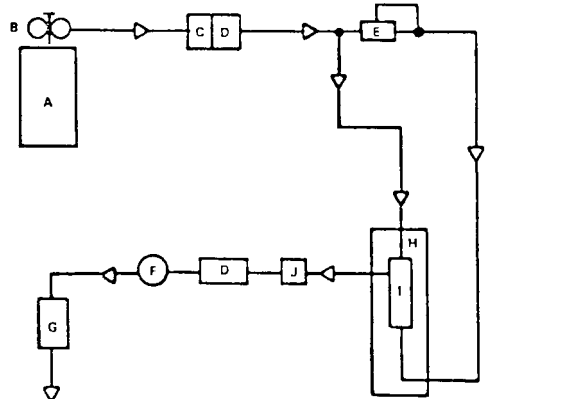
47.5 *Tungsten Accelerator (Low Sulfur)*, 12 to 20-mesh.

NOTE 20—The accelerator should contain no more than 0.001 % sulfur. Wash three times with acetone by decantation to remove organic contaminants and dry at room temperature. The mesh size is critical to the inductive coupling that heats the sample.

48. Preparation of Apparatus

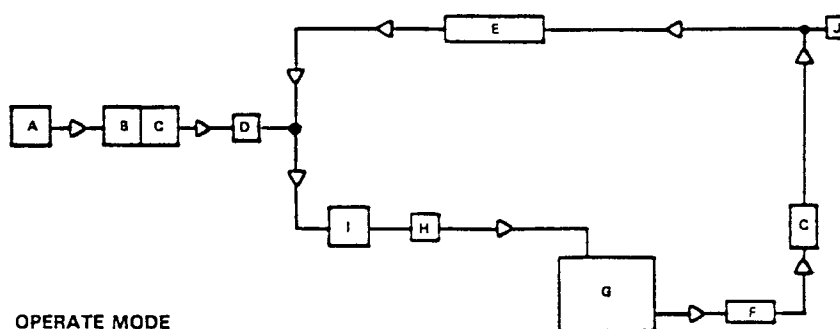
48.1 Assemble the apparatus as recommended by the manufacturer.

48.2 Test the furnace and analyzer to ensure the absence of leaks, and make the required electrical power connections. Prepare the analyzer for operation in accordance with the manufacturer’s instructions. Make a minimum of two determinations using the specimen and accelerator as directed in 51.2

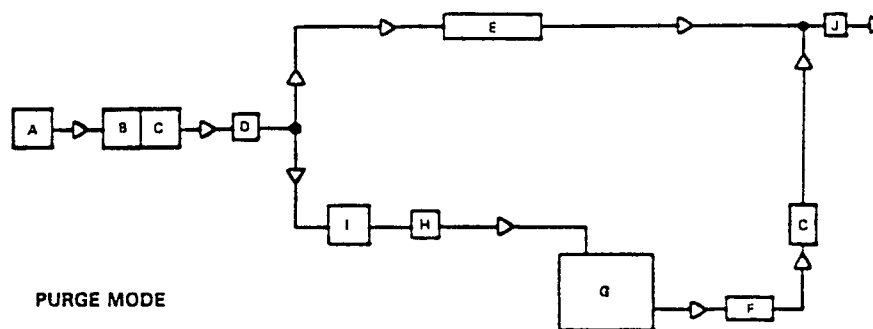


- A—Oxygen Cylinder
- B—Two-Stage Regulator
- C—Sodium Hydroxide Impregnated Clay
- D—Magnesium Perchlorate
- E—Regulator
- F—Flow Controller
- G—IR Cell/Readout
- H—Induction Furnace
- I—Combustion Area
- J—Dust Trap

FIG. 5 Infrared Absorption Method A



OPERATE MODE



PURGE MODE

- A — Oxygen Cylinder
- B — Sodium Hydroxide Impregnated Clay
- C — Magnesium Perchlorate
- D — Press Regulator
- E — IR Cell/Readout
- F — Dust Trap
- G — Furnace
- H — Pump
- I — Flowmeter
- J — Exhaust
- K — CO to CO<sub>2</sub> Converter
- L — SO<sub>3</sub> Trap

FIG. 6 Infrared Absorption Method B

and 51.3 before attempting to calibrate the system or determine the blank.

**49. Sample Preparation**

49.1 The sample should be uniform in size but not finer than 40 mesh.

49.2 Wash in acetone and dry at 70 to 100°C.

**50. Calibration**

50.1 *Calibration Standards:*

50.1.1 Weigh to the nearest 0.0001 g the following masses of K<sub>2</sub>SO<sub>4</sub>:

Sulfur Solution	K <sub>2</sub> SO <sub>4</sub> , g	Sulfur Concentration, mg/mL
A	0.1087	0.2
B	0.2718	0.5
C	0.5435	1.0
D	1.0870	2.0
H	0.0000	0.0

50.1.2 Dissolve each mass of K<sub>2</sub>SO<sub>4</sub> with 50 mL of water in five 100-mL beakers.

50.1.3 Transfer quantitatively each solution to five 100-mL volumetric flasks. Dilute to volume and mix.

50.1.4 Using a pipet, transfer 50 μL of the following sulfur solutions to individual tin capsules. Prepare the number of replicates indicated and then proceed as directed in 50.1.5.

Sulfur Solution	S, μg	S, % in the Test Portion	Number of Replicates
H	0	0.0000	5
A	10	0.0010	2
B	25	0.0025	5
C	50	0.0050	2
D	100	0.0100	5

50.1.5 Dry the tin capsules slowly at about 90°C to full dryness, and cool in a desiccator. Compress the top part of the tin capsule before use.

50.2 *Adjustment of Response of Measurement System:*

50.2.1 Transfer one dried capsule of sulfur Solution B to a preburned crucible. Add 1.0 g of pure iron, weighed to the nearest 5 mg, and 1.5 g of tungsten, weighed to the nearest 5 mg, to the crucible. Proceed as directed in 51.2 and 51.3.

50.2.2 Repeat 50.2.1 until the absence of drift is indicated. (Prepare more capsules of sulfur Solution B if necessary.) Adjust the signal to provide a reading of 0.0025 ± 0.0003 % sulfur.

50.3 *Determination of Blank Reading:*

50.3.1 Transfer one dried capsule of sulfur Solution H to a preburned crucible. Add 1.0 g of pure iron, weighed to the nearest 5 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to the crucible. Proceed as directed in 51.2 and 51.3.

50.3.2 Repeat 50.3.1 a sufficient number of times to establish that low (less than 5 μg of sulfur) and consistent (±2 μg of

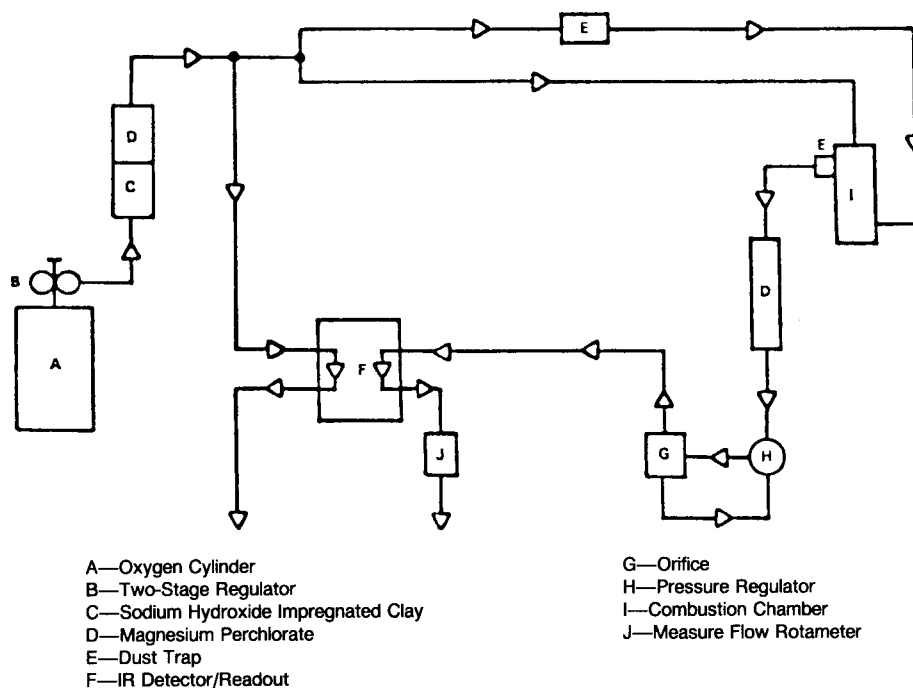


FIG. 7 Infrared Absorption Method C

sulfur) readings are obtained. Blank values are equal to the total result of accelerator, iron, and capsule of solution H minus the sulfur contained in 1.0 g of iron.

50.3.3 Record the average value of at least three blank determinations.

50.3.4 If the blank readings are too high or inconsistent, determine the cause, correct it, and repeat 50.3.1 to 50.3.3. Prepare more capsules of sulfur Solution H if necessary.

50.3.5 Enter the average blank value in the analyzer (Note 21). Refer to the manufacturer's instructions. This mechanism will electronically compensate for the blank value.

NOTE 21—If the unit does not have this function, the blank value must be subtracted from the total result prior to any calculation.

50.4 Calibration:

50.4.1 Transfer four dried capsules of sulfur Solution D to preburned crucibles. Add 1.0 g of pure iron, weighed to the nearest 5 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to each crucible.

50.4.2 Follow the calibration procedure recommended by the manufacturer using dried capsules of sulfur Solution D as the primary standard, analyzing at least three specimens to determine the calibration slope. Treat each capsule as directed in 51.2 and 51.3 before proceeding to the next one.

50.4.3 Confirm the calibration by analyzing a capsule of sulfur Solution D after the calibration procedure. The value should be  $0.0100 \pm 0.0005$  % sulfur. If not, repeat 50.4.1 and 50.4.2.

50.4.4 Transfer two dried capsules of sulfur Solution A, B, and C to preburned crucibles. Add 1.0 g of pure iron, weighed to the nearest 5 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to each crucible.

50.4.5 Treat each capsule in accordance with 51.2 and 51.3 before proceeding to the next one.

50.4.6 Record the results of 50.4.5 and compare them to the

theoretical sulfur values of Solution A, B, and C. If they are not within 0.0003 % of the theoretical concentrations of sulfur in the test portions, refer to the manufacturer's instructions for checking the linearity of the system.

NOTE 22—Repeat the calibration when:

- (1) a different lot of crucibles is used,
- (2) a different lot of accelerator is used,
- (3) the system has not been in use for 1 h, and
- (4) the oxygen supply has been changed.

51. Procedure

51.1 Stabilize the furnace and analyzer as directed in Section 25. Transfer 1.0 g of specimen, weighed to the nearest 1 mg, and 1.5 g of accelerator, weighed to the nearest 5 mg, to a preburned crucible. (See 46.2.)

51.2 Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs to handle the preburned crucibles.

51.3 Start the analysis cycle; refer to manufacturer's recommended procedure regarding entry of specimen weight and blank value.

52. Calculation

52.1 Since most commercially available instruments calculate percent concentrations directly, including corrections for blank and sample weight, calculations by the analyst are not required.

NOTE 23—If the analyzer does not compensate for blank and sample weight values, then use the following formula:

$$\text{Sulfur, \%} = \frac{(A - B) \times C}{D} \quad (5)$$

where:

A = DVM reading for the specimen,



- B* = DVM reading for the blank,  
*C* = weight compensator setting, and  
*D* = specimen weight, g.

### 53. Precision and Bias <sup>11</sup>

53.1 *Precision*—Twenty-five laboratories participated in testing this test method under the auspices of WG-3 of ISO Committee TC 17/SC 1 and obtained the data summarized in Table 7. All testing meets the requirements of Practice E 173.

53.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

### 54. Keywords

54.1 combustion; infrared absorption; refined nickel; sulfur

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

### 55. Scope

55.1 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 %.

### 56. Summary of Test Method

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

### 57. Interferences

57.1 Elements normally present do not interfere.

### 58. Hazards

58.1 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 the tightness of joints checked.

### 59. Apparatus

59.1 *Conventional Distillation Apparatus*—Equipped with a jacketed 40-cm Vigreux<sup>12</sup> or packed reflux column for the purification of acids by distillation under atmospheric pressure, as shown in Fig. 8.

59.2 *Distillation Apparatus*—For purification of the reducing mixture (60.8), as shown in Fig. 9.

59.3 *Distillation Apparatus*—For the generation and volatilization of hydrogen sulfide from the test solution, as shown in Fig. 10. The double-surface condenser is preferred because of its superior cooling efficiency.

59.4 *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.

59.5 *Micropipettes*—10, 20, 50, and 100 µL.

### 60. Reagents

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

60.2 *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 24—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.

60.3 *Ferric Chloride Solution*—Dissolve 1.0 g of ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) in 10 mL of concentrated HCl and 40 mL of water. Dilute to 100 mL with water and store in a glass bottle.

60.4 *Purified Formic Acid*—Distill reagent grade formic acid using the apparatus in 59.1 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.

60.5 *Purified Hydrochloric Acid*—Distill HCl (3 + 2) using the apparatus in 59.1 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.

60.6 *Purified Nitric Acid*—Distill HNO<sub>3</sub> using the apparatus in 59.1 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.

60.7 *Nitric-Chloric Acid Mixture*—Dissolve 3 g of potassium chlorate (KClO<sub>3</sub>) in 30 mL of water and 100 mL of purified HNO<sub>3</sub> (60.6). Store in a glass bottle.

<sup>11</sup> Supporting data are available from ASTM Headquarters. Request RR:E03-1041.

<sup>12</sup> Available from Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219.

**TABLE 7 Statistical Information—Sulfur—Combustion/Infrared Absorption Method**

Test Material	Sulfur Found, %	Repeatability ( <i>R</i> <sub>1</sub> , E 173)	Reproducibility ( <i>R</i> <sub>2</sub> , E 173)
Low-alloy steel (JK 24, 0.0010 S)	0.0010	0.00045	0.00051
Stainless steel (NBS 348, 0.0020 S)	0.00198	0.0005	0.00064
Silicon steel (IRSID 114-1, 0.0037 S)	0.00322	0.00051	0.0007
Plain carbon steel (JSS 240-8, 0.0060 S)	0.00549	0.00055	0.00099
Stainless steel (JSS 652-7, 0.0064 S)	0.00615	0.00084	0.00087

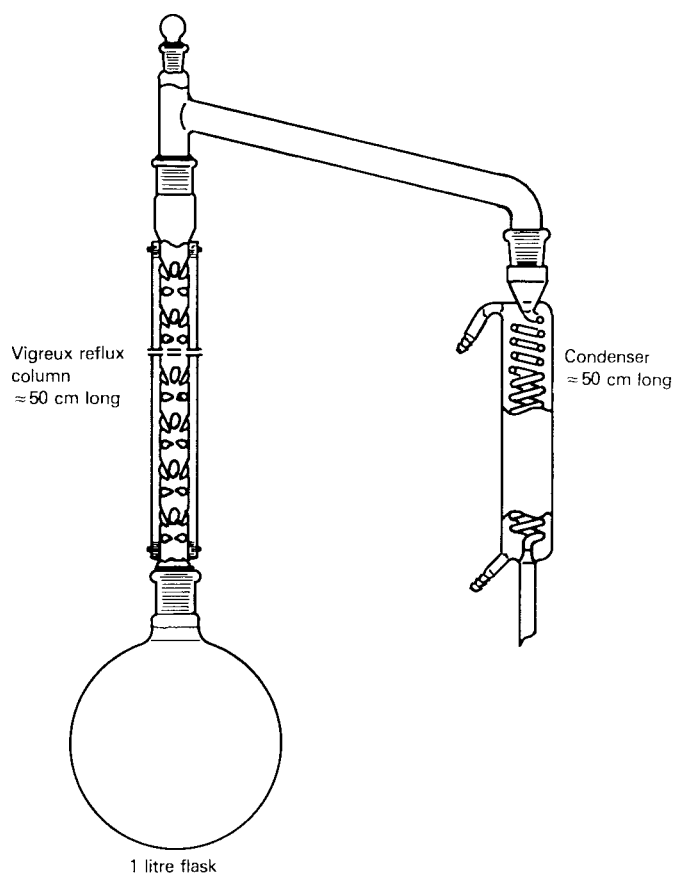


FIG. 8 Apparatus for Purification of Acids

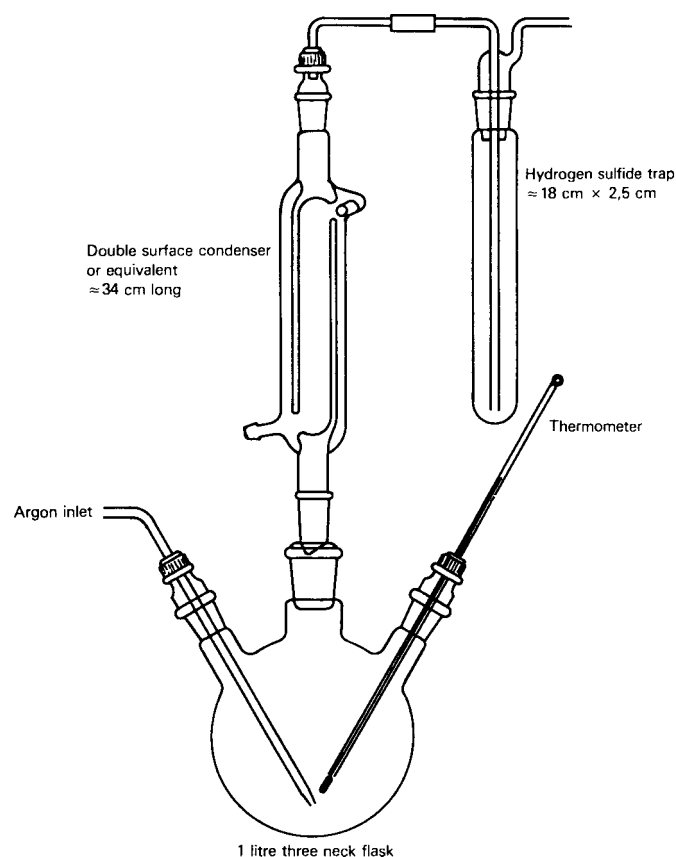


FIG. 9 Apparatus for Purification of the Reducing Mixture

60.8 *Reducing Mixture*—Transfer 420 mL of hydriodic acid (HI, 55 % minimum), 80 mL of hypophosphorous acid ( $\text{H}_3\text{PO}_2$ , 50 % minimum) and 70 g of sodium iodide (NaI) to the purifying apparatus (59.2). Attach the hydrogen sulfide trap containing 50 mL of the zinc acetate absorbing solution (60.10). Purge with argon at a flow rate of 200 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 to 115°C for 4 h in a continuous flow of argon (Note 25). 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 25—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.

60.9 *Standard Sulfur Solution* (10 mL = 1 mg Sulfur)—Dissolve exactly 0.5435 g of potassium sulfate ( $\text{K}_2\text{SO}_4$ ), previously dried at 105°C for 1 h, in water in a 1000-mL volumetric flask. Dilute to volume with water and mix.

60.10 *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 ( $\text{NH}_4\text{Cl}$ ) 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.

## 61. Calibration

### 61.1 *Evolution of Hydrogen Sulfide:*

61.1.1 To the cold, sulfur-free reducing mixture in a three-

neck flask from the blank (62.4), add, from a micro-pipette, 10  $\mu\text{L}$  (1  $\mu\text{g}$  S) of standard sulfur solution (60.9). Proceed in accordance with 62.2 and 62.3.

61.1.2 Continue with additions, in order, of 20, 50, and 100  $\mu\text{L}$  (2, 5, and 10  $\mu\text{g}$  S) of standard sulfur solution (60.9), to the same sulfur-free reducing mixture as in 61.1.1. Proceed after each addition as directed in 62.2 and 62.3. 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.

61.2 *Methylene Blue Development*—Introduce 3.0 mL of the diamine salt solution (60.2) into the sulfide trap by means of the gas inlet. Immediately follow with the addition of 0.5 mL of ferric chloride solution (60.3) 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.

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

61.4 *Calibration Curve*—Plot the absorbance readings of the solutions obtained in 61.1.1 and 61.1.2 against micrograms of sulfur present in the solutions. The line need not pass through the origin as the absorbing solution usually shows a

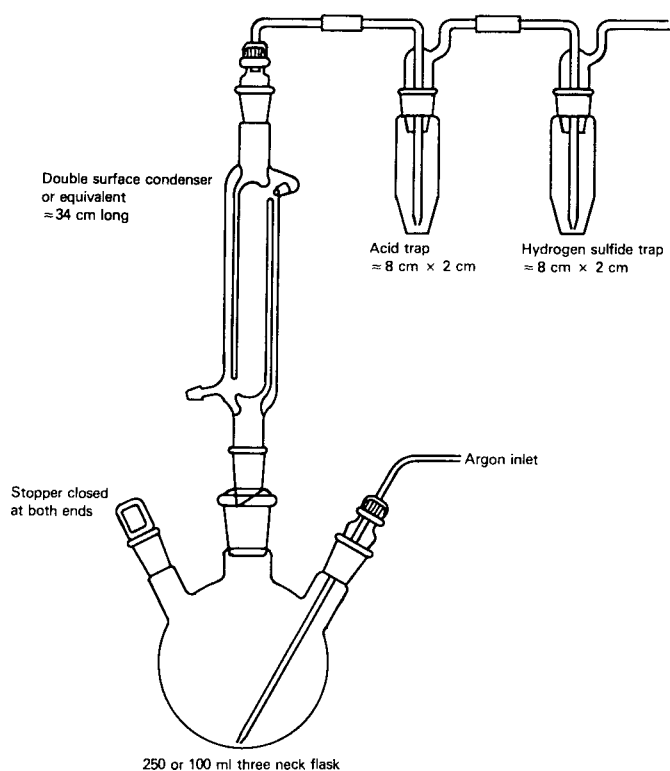


FIG. 10 Apparatus for Distillation of Hydrogen Sulfide

slight background absorption upon addition of the diamine salt and ferric chloride.

## 62. Procedure

### 62.1 Dissolution of Sample:

62.1.1 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.

62.1.2 Weigh 1.0 g of the test sample to the nearest 0.01 g, and transfer to a 100 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.

62.1.3 Add 10 mL of purified HCl (60.5) and heat to dissolve the residue. Add 2 mL of purified formic acid (60.4) 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 26—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.

62.2 *Hydrogen Sulfide Evolution*—Attach the three-neck flask to the distillation apparatus (59.3). Place 3 mL of purified HCl (1 + 4) into the acid trap, and 5.0 mL of zinc acetate

solution (60.10) into the hydrogen sulfide trap. Add 30 mL of the reducing mixture (60.8) 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 27—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 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 62.1.2 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.

62.3 *Methylene Blue Development and Spectrophotometry*—Proceed in accordance with 61.2 and 61.3.

62.4 *Reagent Blank*—Proceed in accordance with 62.1 to 62.3 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 (61.1).

## 63. Calculation

63.1 Convert the absorbance reading obtained for the samples and blank into micrograms of sulfur using the calibration graph (61.4).

63.2 Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, \%} = \frac{A - B}{C} \times 10\,000 \quad (6)$$

where:

$A$  = weight of sulfur in the test sample,  $\mu\text{g}$ ,

$B$  = weight of sulfur in the blank,  $\mu\text{g}$ , and

$C$  = weight of the test portion, g.

63.3 For a meaningful result,  $A$  must be equal to or be greater than two times  $B$ . If  $A$  is less than  $2B$ , 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  $\mu\text{g}$  of sulfur has been found to be attainable and is acceptable.

## 64. Precision and Bias

64.1 *Precision*—This test method was subjected to a limited interlaboratory test program under the auspices of WG-1 of ISO Committee TC-155/SC-4 involving three laboratories in three countries. Three samples were analyzed. The data were analyzed in accordance with ISO 5725 with results given in Table 8. The precision of this test method may be judged by examination of these results.

TABLE 8 Statistical Information—Sulfur by Distillation/Methylene Blue Method

Test Material	Mean, $\mu\text{g/g}$	Repeatability, $R_1$	Reproducibility, $R_2$
C-21	0.77	0.19	0.26
C-22	3.30	0.33	0.67
C-23	13.10	0.68	3.90

64.2 *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.

**65. Keywords**

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

**NITROGEN BY THE INERT GAS FUSION THERMAL CONDUCTIVITY METHOD<sup>9</sup>**

**66. Scope**

66.1 This test method covers the determination of nitrogen (N) in concentrations from 0.001 to 0.2 % (Note 28).

NOTE 28—The upper limit of the scope has been set at 0.2 % because sufficient numbers of test materials containing higher nitrogen contents were unavailable for testing in accordance with Practice E 173. However, recognizing that commercial nitrogen determinators are capable of handling higher concentrations, this test method provides a calibration procedure up to 0.5 %. Users of this test method are cautioned that use of it above 0.2 % is not supported by interlaboratory testing.

**67. Summary of Test Method**

67.1 The specimen, contained in a small, single-use graphite crucible, is fused under a flowing helium atmosphere at a

minimum temperature of 1900°C. Nitrogen present in the sample is released as molecular nitrogen into the flowing helium stream. The nitrogen is separated from other liberated gases such as hydrogen and carbon monoxide and is finally measured in a thermal conductivity cell. Refer to Figs. 11-13, and Fig. 14.

67.2 This test method is written for use with commercial analyzers equipped to carry out the above operations automatically and calibrated using standard samples of known nitrogen content.

**68. Interferences**

68.1 The elements ordinarily present do not interfere.

**69. Apparatus**

69.1 *Fusion and Measurement Apparatus*—See Fig. 11.

69.2 *Graphite Crucibles*—Use the size crucibles recommended by the manufacturer of the instrument. Crucibles must be composed of high-purity graphite.

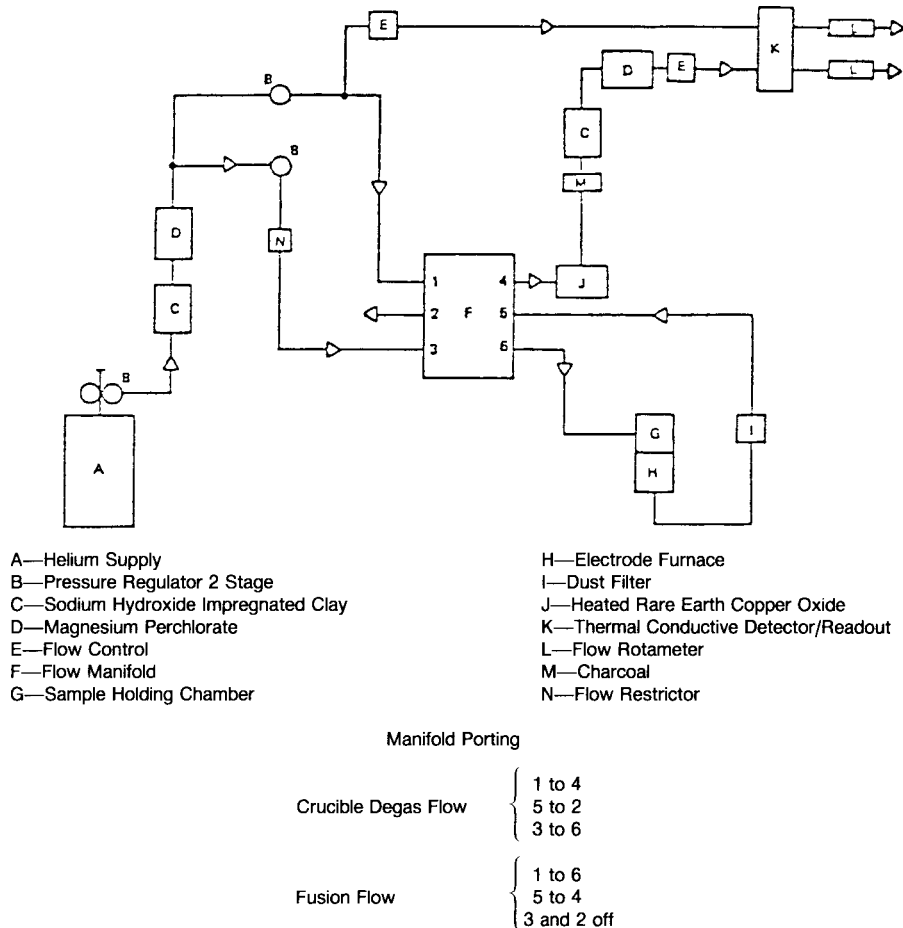
69.3 *Crucible Tongs*—Capable of handling the recommended crucibles.

**70. Reagents**

70.1 *Acetone*, low-residue.

70.2 *Helium*, high-purity (99.99 %).

70.3 *Magnesium Perchlorate*, (known commercially as *Anhydron*).



**FIG. 11 Nitrogen Method A Flow Diagram**



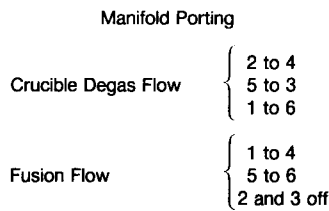
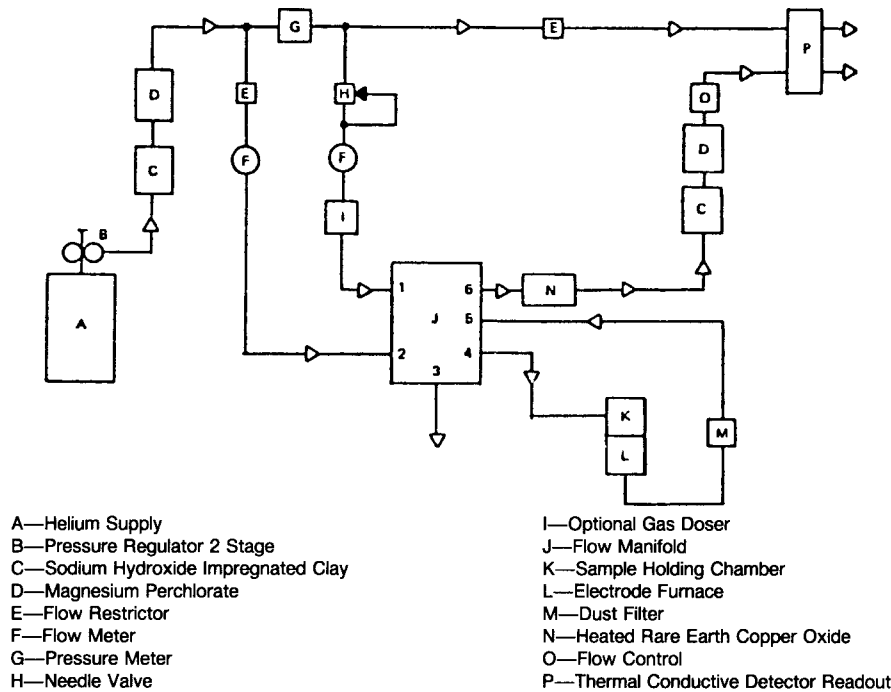


FIG. 12 Nitrogen Method B Flow Diagram

70.4 Sodium Hydroxide, on clay, (known commercially as Ascarite II).

**71. Preparation of Apparatus**

71.1 Assemble the apparatus as recommended by the manufacturer.

71.2 Test the furnace and analyzer to ensure the absence of leaks, and make the required electrical power and water connections. Prepare the apparatus for operation in accordance with the manufacturer's instructions. Make a minimum of two determinations using a specimen as directed in 74.2.1 or 74.2.2 before attempting to calibrate the system or to determine the blank.

**72. Sample Preparation**

72.1 Use chips, drillings, or solid-form specimens prepared in accordance with 72.2 or 72.3 (Note 29).

NOTE 29—Size all specimens to permit free introduction through the loading device of the equipment or directly into the graphite crucible.

72.2 If a solid specimen is used, cut it with a water-cooled abrasive cut-off wheel or by another means that will prevent overheating. Using a file, abrade the surface of the specimen to be used for analysis to remove oxides and other impurities, rinse in acetone, air dry, and weigh.

72.3 If drillings or chips are used, prepare in accordance with Method E 59.

**73. Calibration**

73.1 Calibration Standards:

73.1.1 For Range I, 0.0005 to 0.10 % nitrogen, select five certified reference materials containing approximately 0.002, 0.01, 0.03, 0.05, and 0.10 % nitrogen and designate them as Standards, A, B, C, D, and E, respectively (Note 30).

73.1.2 For Range II, 0.10 to 0.50 % nitrogen, select three certified reference materials containing approximately 0.10, 0.30, and 0.50 % nitrogen and designate them as Standards AA, BB, and CC, respectively (Note 30).

NOTE 30—The accuracy of this test method is largely dependent upon the accuracy of the methods used to certify the nitrogen concentration in the calibration of certified reference materials, as well as upon their homogeneity. Thus, calibration specimens should be NBS Standard Reference Materials (SRM) or other certified reference materials.

73.2 Adjustment of Response of Measurement System:

73.2.1 Prepare a 1.0-g specimen of Standard C weighed to the nearest 1 mg as directed in 72.2 or 72.3.

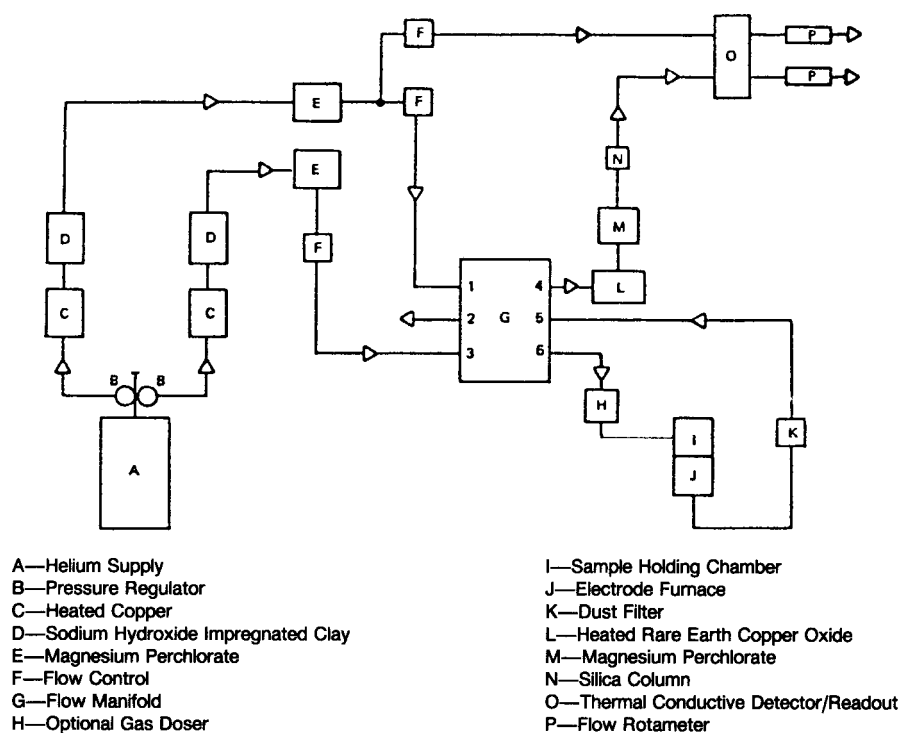
73.2.2 Proceed as directed in 74.2.1 or 74.2.2.

73.2.3 Repeat 73.2.1 and 73.2.2 and adjust as recommended by the manufacturer until the absence of drift is indicated.

73.3 Determination of Blank Reading—Ranges I and II:

73.3.1 If the instrument is equipped with an electronic blank compensator, adjust to zero, and proceed with the determination of the blank value.

73.3.2 Make three blank determinations in accordance with



Manifold Porting

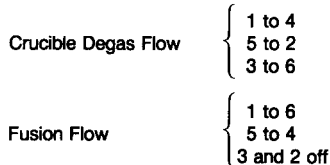


FIG. 13 Nitrogen/Oxygen Method A Flow Diagram

74.2.1 or 74.2.2 with the sample omitted. Use a fresh crucible each time (Note 31).

NOTE 31—If the loading device is used to analyze the unknown or standard sample, see Note 29.

73.3.3 If the blank values exceed 0.0003 % or a spread of three consecutive values exceeds 0.0003 %, then determine the cause, make necessary corrections, and repeat 73.3.1 and 73.3.2.

73.3.4 Record the average value of at least three blank readings.

73.3.5 Enter the average blank value in the appropriate mechanism of the analyzer (Note 32); refer to manufacturer's instructions. This mechanism will electronically compensate for the blank value.

NOTE 32—If the unit does not have this function, the average blank value must be subtracted from the DVM readings for standards and specimens (Note 36).

73.4 Calibration Procedure—Range I:

73.4.1 Prepare four 1.0-g specimens of Calibration Standard D weighed to the nearest 1 mg, as directed in 72.2 or 72.3.

73.4.2 Follow the calibration procedure recommended by the manufacturer using Standard D as the primary standard. Analyze at least three standard specimens to determine the calibration slope. Treat each specimen in accordance with 74.2.1 or 74.2.2 before proceeding to the next one.

73.4.3 Confirm the calibration by analyzing Standard D after calibration. The value should be within the allowable limits of the certified value. If not, repeat 73.4.1 and 73.4.2.

73.4.4 Prepare two 1.0-g specimens each of Standards A, B, C, and E weighed to the nearest 1 mg, in accordance with 72.2 or 72.3.

73.4.5 Treat each specimen in accordance with 74.2.1 or 74.2.2 before proceeding to the next one.

73.4.6 Record the results and compare them to the actual certified nitrogen values of the certified reference material. They should be within the allowable limits of the respective certified reference material. If not, refer to the manufacturer's instructions for checking the linearity of the analyzer.

NOTE 33—Repeat the calibration when: (1) a different lot of crucibles is used, (2) the system has not been in use for 1 h, or (3) the carrier gas supply has been changed.

73.5 Calibration Procedure—Range II:

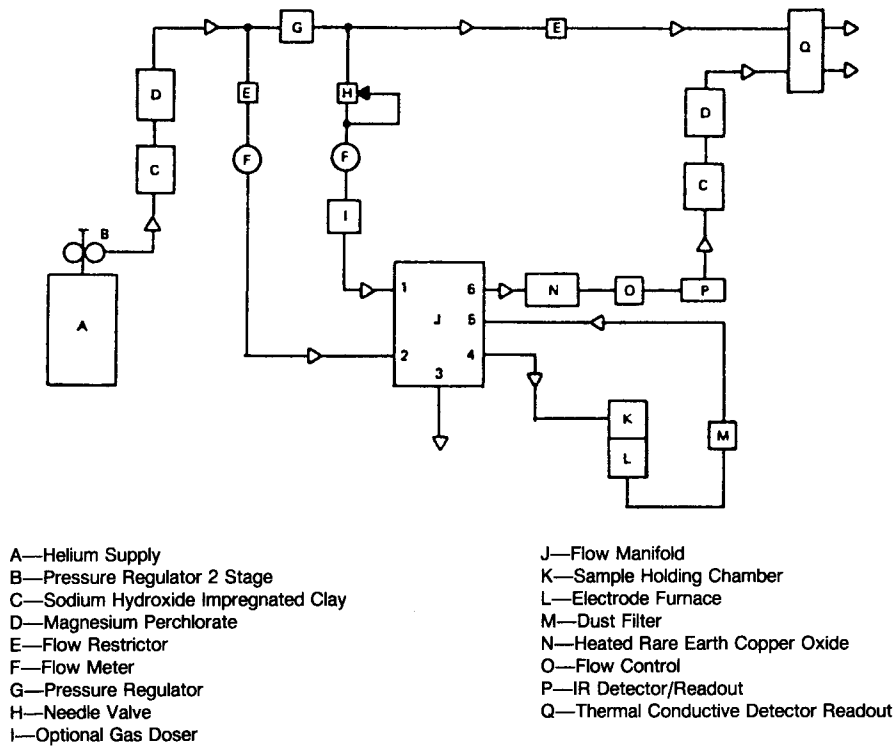
73.5.1 Proceed in accordance with 73.4.1-73.4.3 using Standard CC.

73.5.2 Proceed in accordance with 73.4.4-73.4.6 using Standards AA and BB (Note 33).

74. Procedure

74.1 Assemble the apparatus and condition it in accordance with Section 71.

74.2 Procedure—Ranges I and II:



Manifold Porting

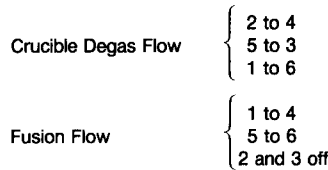


FIG. 14 Nitrogen/Oxygen Method B Flow Diagram

74.2.1 Manual Operation:

74.2.1.1 Set the analyzer to operate in the manual mode.

74.2.1.2 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

74.2.1.3 Weigh a 1.0-g specimen to the nearest 1 mg and refer to the manufacturer's recommended procedure, including entry of sample weight.

74.2.1.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Note 34).

74.2.2 Automatic Operation:

74.2.2.1 Set the analyzer to operate in the automatic mode.

74.2.2.2 Place a 1.0-g specimen weighed to the nearest 1 mg in the loading device. Refer to the manufacturer's recommended procedure, including entry of sample weight.

74.2.2.3 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

74.2.2.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Note 34 and Note 35).

NOTE 34—If the samples are to be analyzed in the automatic mode, blank determination and calibration should also be performed in the automatic mode. If samples are to be analyzed in the manual mode, blank determination and calibration should be performed in the manual mode. Solid samples may be analyzed in either automatic or manual mode, but drillings or chips should be analyzed in the manual mode.

NOTE 35—The presence of nitrogen as refractory nitrides in the matrix may affect sample fusion and nitrogen evolution under standard operating

conditions of the analyzer. It is therefore recommended that calibration standards be of the same or similar composition as the samples to be analyzed.

75. Calculation

75.1 With most commercially available instruments the readings will be given directly in concentration (Note 36).

NOTE 36—If the analyzer does not compensate for blank and sample weight values, then the equation is as follows:

$$\text{Nitrogen, \%} = \frac{(A - B) \times C}{D} \quad (7)$$

where:

- A = DVM reading for the specimen,
- B = DVM reading for the blank,
- C = weight compensator setting, and
- D = specimen weight, g.

76. Precision and Bias <sup>4</sup>

76.1 Precision—Nine laboratories cooperated in testing this test method and obtained the precision data summarized in Tables 9 and 10, and Table 11.

76.2 Bias—The accuracy of this test method can be inferred from the data in Tables 9 and 10, and Table 11 by comparing the certified values for nitrogen with the average values obtained (Note 37).

**TABLE 9 Statistical Information—Nitrogen, Range I (chip)—Inert Gas Fusion/Thermal Conductivity Method**

Test Material	Nitrogen Found, %	Repeatability ( $R_1$ , E 173)	Reproducibility ( $R_2$ , E 173)
No. 1 High-purity iron (Eurostandard 088.1, 0.0009 % N)	0.0010	0.0005	0.0008
No. 2 High-purity iron (JSS-001, 0.0017 % N)	0.0016	0.0004	0.0010
No. 3 Carbon steel (BAM 028/1, 0.0029 % N)	0.0033	0.0007	0.0012
No. 4 Carbon steel (JK NR3B, 0.0054 % N)	0.0051	0.0005	0.0010
No. 5 Carbon steel (JK 2D, 0.0085 % N)	0.0099	0.0013	0.0015
No. 6 Tool steel (NBS 50 C, 0.012 % N)	0.012	0.0008	0.0010
No. 7 Tool steel (NBS 153a, 0.024 % N)	0.026	0.001	0.002
No. 8 Stainless steel (NBS 73c, 0.037 % N)	0.037	0.003	0.003
No. 9 Cast iron (NBS 890, 0.089 % N)	0.088	0.004	0.008

**TABLE 10 Statistical Information—Nitrogen, Range II (chip)—Inert Gas Fusion/Thermal Conductivity Method**

Test Material	Nitrogen Found, %	Repeatability ( $R_1$ , E 173)	Reproducibility ( $R_2$ , E 173)
No. 1 High-temperature alloy A661 (Car Tech, 0.1598 % N)	0.115	0.005	0.015
No. 2 Stainless steel (NBS 367, 0.168 % N)	0.158	0.005	0.017
No. 3 Valve steel (Leco 502-016, 0.218 % N)	0.203	0.009	0.020

**TABLE 11 Statistical Information—Nitrogen, Range I (solid)—Inert Gas Fusion/Thermal Conductivity Method**

Test Material	Nitrogen Found, %	Repeatability ( $R_1$ , E 173)	Reproducibility ( $R_2$ , E 173)
No. 1 Low-alloy steel (NBS 1098, 0.0032 % N)	0.0041	0.0006	0.0014
No. 2 Low-alloy steel (NBS 1096, 0.0040 % N)	0.0043	0.0006	0.0011
No. 3 Cast iron (ACIPCO ~0.01 % N)	0.0076	0.0011	0.0014
No. 4 Low-alloy steel 4320 (TC, 0.0080 % N)	0.0083	0.0011	0.0015
No. 5 Tool steel (LSC, 0.064 % N)	0.067	0.004	0.006
No. 6 High-temperature alloy Inco 600 (LTV, 0.1 % N)	0.088	0.008	0.015
No. 7 Stainless steel, Type 316 (LTV, 0.09 % N)	0.096	0.004	0.007

NOTE 37—Although this test method was tested to only 0.22 %, most commercial instruments are believed to be capable of analyzing samples containing nitrogen up to 0.5 %.

## 77. Keywords

77.1 inert gas fusion; nitrogen; refined nickel

## OXYGEN BY THE INERT GAS FUSION METHOD<sup>10</sup>

## 78. Scope

78.1 This test method covers the determination of oxygen in the range from 0.001 to 0.005 % in nickel having chemical compositions within the limits shown in 1.1.

## 79. Summary of Test Method

79.1 This test method is written for use with automated, commercially available analyzers which are based on the inert gas fusion principle and use a variety of gas conditioning and measuring techniques. All use calibration methods traceable to primary Standard Reference Materials (SRM).

79.2 The sample, contained in a small, single-use graphite crucible, is fused under a flowing inert gas stream at a temperature sufficient to release oxygen, nitrogen, and hydrogen. The oxygen combines with carbon from the crucible to form carbon monoxide (CO) and is carried by the flowing inert gas stream to either a thermal conductivity or an infrared detector. The detector output is compared to that obtained from similar Standard Reference Materials and is displayed as oxygen content of the sample.

79.3 In a typical instrument based on thermal conductivity detection (Fig. 12), the sample is fused in a stream of helium which carries the released gases over copper oxide which oxidizes CO to CO<sub>2</sub> and hydrogen to water. The water is then absorbed by magnesium perchlorate and the remaining nitrogen and carbon dioxide are separated chromatographically. The nitrogen is eluted from the chromatographic column within seconds and is either measured or disregarded. The oxygen (as CO<sub>2</sub>) then elutes from the column and enters the measuring cell of the thermistor bridge. Bridge output is integrated and the data are processed and displayed directly as percent oxygen.

79.4 In a typical instrument based on infrared detection (Fig. 13), the sample is fused in a stream of nitrogen or argon and the evolved gases are passed directly into a cell through which infrared energy is transmitted. The absorption of infrared energy by the CO in the gas stream causes a reduction in the energy received at an infrared detector. The detector response data are processed and displayed directly as percent oxygen.

## 80. Interferences

80.1 The elements usually present in these alloys do not interfere.

## 81. Hazards

81.1 For precautions to be observed in the use of certain reagents in this test method, refer to Practices E 50.

81.2 Use care when handling hot crucibles and operating furnaces to avoid personal injury by either burn or electrical shock.



**82. Apparatus**

82.1 *Instrument*—The general features of the instruments used in developing the test data accompanying this test method are shown schematically in Figs. 15 and 16. These units are commercially available.

82.2 *Graphite Crucibles*—The crucibles must be made of high-purity graphite and should be those recommended by the manufacturer or their equivalent.

**83. Reagents**

83.1 *Acetone*—Residue after evaporation must be <0.0005 %.

83.2 *Sodium Hydroxide*, on clay, (known commercially as *Ascarite II*).

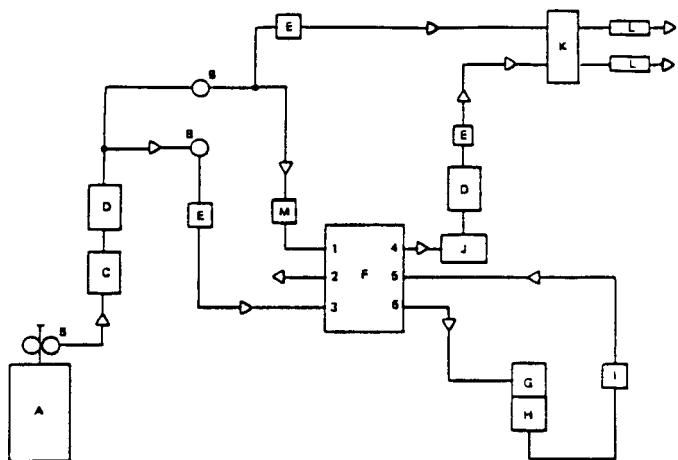
83.3 *Inert Gas (Helium, Argon, or Nitrogen as Specified for the Instrument Being Used)*—Use the purity specified by the manufacturer.

83.4 *Magnesium Perchlorate*, (known commercially as *Anhydron*).

**84. Preparation of Apparatus**

84.1 Assemble the apparatus as recommended by the manufacturer. Make the required power, gas, and water connections. Turn on the instrument and allow sufficient warm-up time to stabilize the system.

84.2 Change the chemical traps and filters as required. Test the furnace and the analyzer to ensure the absence of leaks.

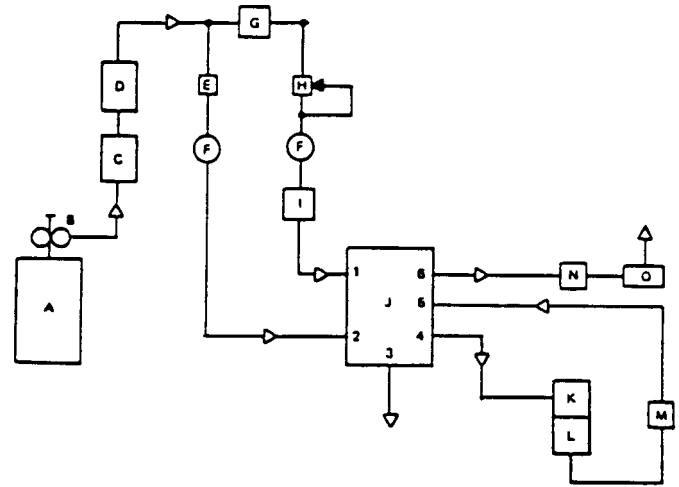


- A—Helium Supply
- B—Pressure Regulator
- C—Sodium Hydroxide Impregnated Clay
- D—Magnesium Perchlorate
- E—Flow Control
- F—Flow Manifold
- G—Sample Holding Chamber
- H—Electrode Furnace
- I—Dust Filter
- J—Heated Rare Earth Copper Oxide
- K—Thermal Conductive Detector/Readout
- L—Flow Rotameter
- M—Optional Gas Doser

**Manifold Porting**

Crucible Degas Flow	$\left\{ \begin{array}{l} 1 \text{ to } 4 \\ 5 \text{ to } 2 \\ 3 \text{ to } 6 \end{array} \right.$
Fusion Flow	$\left\{ \begin{array}{l} 1 \text{ to } 6 \\ 5 \text{ to } 4 \\ 3 \text{ and } 2 \text{ off} \end{array} \right.$

**FIG. 15 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Thermal Conductivity Method**



- A—Argon or Nitrogen Supply
- B—Pressure Regulator 2 Stage
- C—Sodium Hydroxide Impregnated Clay
- D—Magnesium Perchlorate
- E—Flow Restrictor
- F—Flowmeter
- G—Pressure Regulator
- H—Needle Valve
- I—Optional Gas Doser
- J—Flow Manifold
- K—Sample Holding Chamber
- L—Electrode Furnace
- M—Dust Filter
- N—Flow Control
- O—IR Detector/Readout

**Manifold Porting**

Crucible Degas Flow	$\left\{ \begin{array}{l} 2 \text{ to } 4 \\ 5 \text{ to } 3 \\ 1 \text{ to } 6 \end{array} \right.$
Fusion Flow	$\left\{ \begin{array}{l} 1 \text{ to } 4 \\ 5 \text{ to } 6 \\ 2 \ \& \ 3 \ \text{off} \end{array} \right.$

**FIG. 16 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Infrared Absorption Method**

Make a minimum of two determinations using a sample in accordance with Section 87 to condition the instrument before attempting to calibrate the system or to determine the value of the blank.

**85. Sample Preparation**

85.1 Use only solid samples to minimize the potential for errors due to surface oxidation. Samples must be of the proper size to permit free introduction into the sample loading device, if required, and to fit in the graphite crucible.

85.2 Cut the sample to an appropriate size using a silicon carbide, water-cooled cut-off wheel or by other means that will avoid overheating. Avoid oxide cutting or oxide abrading materials. Thin, flat samples may be stamped using a punch and die. Using a clean file, abrade all surfaces of the sample to remove all traces of surface oxidation oxides or other impurities, rinse in acetone, air-dry, and weigh. Be sure that all pores in the surface of the sample are free of acetone.

85.3 Do not touch the sample with fingers during and following the final stages of cleaning. Store the prepared samples in a desiccator. If they are not analyzed within four hours of preparation, repeat the filing step prior to analysis. For some material, such as plain carbon sheet steel, a rimmed or semi-killed deoxidation practice is used and the oxygen may not be uniformly distributed throughout the thickness of the sample. In these cases, the removal of too much surface material may cause erroneous results.

NOTE 38—Careful adherence to the sample preparation procedures described above is critical to obtaining accurate and precise results. The use of small and irregular-shaped samples requires a diligent effort to ensure that all surface contamination has been removed.

## 86. Calibration

86.1 *Calibration Standards*—Select three standards containing approximately 0.0005, 0.002, and 0.005 % oxygen and designate them as Standards A, B, and C, respectively.

NOTE 39—The accuracy of this test method is dependent to a large extent upon the accuracy of the methods used to certify the oxygen concentration in the calibration standards as well as upon their homogeneity.

86.2 *Gas Dosing*—Automated and manual gas dosing (recommended by some instrument manufacturers) can be used to set up the instrument, but instrument response must be confirmed as described below using the standards described in 86.1.

86.3 *Adjustment of Response of Measurement System*—Using Standard B as the sample, proceed in accordance with 87.2-87.4. Repeat 87.2-87.4 until the absence of drift is indicated; continue running a series of samples until the last four readings have a maximum variation range of 0.0005 % oxygen, making appropriate adjustments to the calibration potentiometer, if applicable. Record potentiometer settings. Adjust the instrument calibration to provide a reading within  $\pm 0.0003$  % absolute of the certified value for the standard using the average of the last four readings. Refer to the manufacturer's instructions.

86.4 *Determination of Blank Reading*—Using Standard A as the sample, proceed in accordance with 87.2-87.4. Repeat a sufficient number of times to establish that a low average blank value (0.0002 % oxygen or less) and consistent individual blank values ( $\pm 0.0001$  % oxygen) are obtained. Blank values are equal to the total result from the crucible and Standard A minus the certified oxygen content of Standard A. Record the average value of four successive blank determinations which meet the above requirements for maximum and consistent values. If the blank readings are too high or inconsistent, determine the cause, correct it, and repeat 87.2-87.4. Enter the average blank value in the appropriate mechanism of the analyzer; refer to manufacturer's instructions. This mechanism will electronically compensate for the blank value (Note 40).

NOTE 40—If the unit does not have this function, the blank value must be subtracted from the total result prior to any calculation.

86.5 *Calibration*—Weigh an appropriate sample size of Standard C, (refer to the manufacturer's instructions) to the nearest 1 mg, and place it in the instrument sample loading device or directly in the outgassed crucible, following the manufacturer's directions. Follow the calibration procedure recommended by the manufacturer using Standard C as the primary standard, analyzing samples of Standard C to determine the calibration slope. Run samples until the maximum variation range of four successive samples does not exceed 0.0005 % oxygen. Treat each sample of the standard in accordance with 87.2-87.4 before proceeding to the next one. Confirm the calibration by analyzing an additional Standard C after the calibration procedure is completed. The value should be within the allowable limits of the certified oxygen content of

the standard. If not, repeat the calibration procedure. Next, weigh at least two appropriate-sized samples of Standard B, weighed to the nearest 1 mg, and transfer to the instrument sample loading device. Treat each sample of the standard as directed in 87.2-87.4 before proceeding to the next one. Record the results and compare them to the actual certified oxygen value of Standard B; they should be within the allowable limit of the standard. If not, refer to the manufacturer's instructions for checking linearity of the system.

NOTE 41—Repeat the calibration when (1) a different lot of crucibles is used, (2) the system has not been in use for 1 h, or (3) the carrier gas supply has been changed.

## 87. Procedure

87.1 Assemble the apparatus, calibrate, set the blank, and test the performance in accordance with Section 84 and 86.

87.2 Transfer an appropriate-sized sample, weighed to the nearest 1 mg to the instrument sample loading device. (Alternatively, the weighed sample may be manually introduced into the outgassed crucible in accordance with 87.5. Refer to the manufacturer's directions.)

87.3 Place a crucible on the furnace pedestal and raise the pedestal into position.

87.4 Start the crucible degassing cycle (Note 42); refer to the manufacturer's recommended procedure regarding entry of sample weight.

NOTE 42—For some instruments this procedure automatically precedes the analysis cycle.

87.5 Transfer the sample to the crucible and start the analysis cycle.

87.6 Repeat 87.1-87.5 two additional times and report the average of the three determinations.

## 88. Calculation

88.1 Follow the manufacturer's directions to ensure that all essential variables in the calculation of analysis results have been accounted for, including the blank, weight of sample, and calibration data. Since the output of most modern instruments is given directly in percent concentration, post-analysis calculations may not be required.

## 89. Precision and Bias

89.1 *Precision*—Sixteen laboratories cooperated in testing this test method and obtained the data summarized in Table 12. Note that the values for  $R_1$  and  $R_2$  are based on  $M = 3$  (see Practice E 173), this means that similar values for  $R_1$  and  $R_2$  may be expected from the averages of triplicate determinations.

89.2 *Bias*—Information on the accuracy of this test method is incomplete at this time. The user is cautioned to verify by the use of certified reference materials, if available, that the accuracy of this test method is adequate for the contemplated use.

## 90. Keywords

90.1 inert gas fusion; oxygen; refined nickel

**TABLE 12 Statistical Information—Oxygen (Weight, %)—Inert Gas Fusion Method**

Test Material	Oxygen Found	Repeatability <sup>A</sup> ( <i>R</i> <sub>1</sub> , Practice E 173)	Reproducibility <sup>A</sup> ( <i>R</i> <sub>2</sub> , Practice E 173)
Ni-Cr-Mo Alloy (AISI 4330)	0.00048	0.00018	0.00040
Tool Steel (M-50)	0.00056	0.00015	0.00061
Cr-Alloy Steel (52100)	0.00080	0.00022	0.00088
Carbon Steel (1070)	0.00118	0.00026	0.00065
Carbon Steel (1570)	0.00126	0.00024	0.00071
Alloy Steel (33100)	0.00139	0.00023	0.00048
Cr-Alloy Steel (52100)	0.00218	0.00034	0.00091
Ni-Cr-Mo Alloy (8622)	0.00237	0.00034	0.00076
Carbon Steel (1026)	0.00357	0.00023	0.00092
Cr-Stainless (440C)	0.00437	0.00032	0.00108
Ingot Iron (NBS SRM-466, 0.0050 weight % oxygen)	0.00538	0.00031	0.00081

<sup>A</sup>M = 3, see Practice E 173, paragraphs 4.11 and 4.12 and Note 1.

**TABLE 13 Statistical Information—Carbon by Combustion Infrared Method**

Test Material	Mean, %	Repeatability, <i>R</i> <sub>1</sub>	Reproducibility, <i>R</i> <sub>2</sub>
Nickel Metal			
S	0.025	0.0018	0.0020
Nickel Alloys <sup>A</sup>			
02	0.010	0.0021	0.0041
49	0.093	0.0018	0.0033
13	0.223	0.0041	0.0120
Ferronickel			
A-22 (25 % Ni)	0.014	0.0017	0.0024
B-31 (35 % Ni)	0.061	0.0045	0.0046
A-28 (22 % Ni)	1.840	0.0330	0.1900

<sup>A</sup>The approximate composition of the nickel alloys are as follows:

02—Cu 30 %, Fe 2 %, Mn 2 %, Ni balance

13—Co 17 %, Cr 20 %, Ti 2.5 %, Ni balance

49—Cr 15 %, Fe 7 %, Nb 1.0 %, Ti 2.3 %, Al 1.0 %, Ni balance

**TABLE 14 Statistical Information—Sulfur by Combustion Infrared Method**

Test Material	Mean, %	Repeatability, <i>R</i> <sub>1</sub>	Reproducibility, <i>R</i> <sub>2</sub>
Nickel Metal			
G	0.0063	0.0005	0.0016
F	0.013	0.0007	0.0038
Nickel Alloys <sup>A</sup>			
AK	0.0025	0.0006	0.0019
AO	0.016	0.0010	0.0033
Ferronickel			
A-22 (25 % Ni)	0.020	0.0018	0.0040
A-28 (22 % Ni)	0.023	0.0009	0.0050
C-1 (25 % Ni)	0.024	0.0014	0.0032
C-2 (33 % Ni)	0.048	0.0021	0.0089
C-3 (25 % Ni)	0.074	0.0025	0.0091
C-4 (23 % Ni)	0.20	0.009	0.038

<sup>A</sup>The approximate analyses of the nickel alloys used are as follows:

AK—20 % Cr, 15 % Fe, 5 % Mo, 4.5 % Al, Ni balance

AO—10 % Cr, 7 % Fe, 0.3 % Ti, Ni balance

## NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD<sup>13</sup>

### 91. Scope

91.1 This test method covers the determination of nickel in concentrations from 8.50 to 99.9 %.

### 92. Summary of Test Method

92.1 Nickel, in an ammoniacal solution, is precipitated with

<sup>13</sup> This test method was originally published in E39, in the *Annual Book of ASTM Standards*, Vol 03.05. Ammonium Citrate solution replaced Tartaric Acid solution.

dimethylglyoxime. The precipitate is separated by filtration, dried, and weighed.

### 93. Interferences

93.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits in accordance with 1.1.

### 94. Apparatus

94.1 *Filtering Crucible*, 30 or 50-mL capacity, medium porosity, fritted glass, Apparatus No. 2.

### 95. Reagents

95.1 *Ammonium Citrate Solution* (200 g/L)—Dissolve 200 g of diammonium hydrogen citrate [(NH<sub>4</sub>)<sub>2</sub>HC<sub>6</sub>H<sub>5</sub>O<sub>7</sub>] in 600 mL of water. Filter and dilute to 1 L.

95.2 *Dimethylglyoxime Solution in Alcohol* (10 g/L)—Dissolve 10 g of dimethylglyoxime in 100 mL of warm ethanol or methanol. Prepare fresh as needed.

### 96. Procedure

96.1 Transfer 0.100 to 0.200 g of sample, weighed to the nearest 0.1 mg, to a 400-mL beaker. Cover the beaker, add 10 mL of HNO<sub>3</sub> (2 + 1), and heat gently until dissolution is complete. Add 10 mL of HClO<sub>4</sub>, and evaporate to dense white fumes. Continue to heat for 10 to 15 min. Cool, add 100 mL of hot water, and heat to dissolve the soluble salts. Filter through a medium-porosity filter paper, containing paper pulp, into to 600-mL beaker. Police the beaker and transfer the residue to the filter paper. Wash the paper and residue with hot HCl (1 + 19), and then with hot water. Reserve the filtrate and washings.

96.2 Transfer the paper and residue to a 35-mL platinum crucible, ignite at 100°C for 1 h and allow to cool (Note 43). Add 5 mL of HClO<sub>4</sub>, 5 mL of water, and 5 mL of HF, and evaporate to 2 to 3 mL. Cool and add 15 mL of water and filter through a medium-porosity filter paper into the main nickel solution reserved in 96.1. Wash the filter paper with at least 50 mL of hot water.

NOTE 43—Small residues, such as those obtained from wrought alloys containing 0.10 % or less of silicon may be discarded.

96.3 Add 10 mL of ammonium citrate solution, neutralize to litmus with NH<sub>4</sub>OH. Add 3 mL of NH<sub>4</sub>OH in excess. Dilute to approximately 400 mL, and heat to 60 to 70°C.

96.4 Add 0.4 mL of dimethylglyoxime solution for each 1

mg of nickel estimated to be present, and add 5 to 10 mL in excess. Stir the mixture vigorously, place in a cold-water bath, and let stand for 1 h, stirring occasionally. Filter with suction using a tared fritted-glass crucible of medium porosity, and wash with cool water. Do not allow the filter to run dry until after the last wash.

96.5 Dry the precipitate for 30 min at 110°C, then at 150 to 160°C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

## 97. Calculation

97.1 Calculate the percent of nickel as follows:

$$\text{Nickel, \% } [(A \times 0.2032)/B] \times 100 \quad (8)$$

where:

*A* = nickel dimethylglyoxime, g, and

*B* = sample used, g.

## 98. Precision and Bias

98.1 *Precision*—Due to the limited number of laboratories participating in the cooperative testing of this test method, a

precision statement conforming to the requirements of Practice E 173 cannot be furnished. However, in a cooperative program conducted by four laboratories, the between laboratory range of individual values was from 99.05 to 99.53 % on a sample averaging 99.36 % nickel, and from 90.91 to 91.10 % on a sample averaging 91.02 % nickel.

98.2 *Bias*—No information is available on the accuracy of this test method due to the lack of appropriate certified reference materials. The user of this test method is cautioned to verify the performance of the test method by use of reference materials, if available.

98.3 This test method was adapted for use with nickel alloys in accordance with Test Method E 354. The user is encouraged to review the performance data presented in Test Method E 354.

## 99. Keywords

99.1 dimethylglyoxime; gravimetry; nickel; refined nickel

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