



Standard Test Methods for Analysis of Metal Bearing Ores and Related Materials for Carbon, Sulfur, and Acid-Base Characteristics¹

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1. Scope

1.1 These test methods cover the determination of total carbon and sulfur and acid-base characteristics in metal bearing ores and related materials such as leach residues, tailings, and waste rock within the following ranges:

Analyte	Application Range, %	Quantitative Range, %
Total Carbon	0 to 10	0.08 to 10
Total Sulfur	0 to 8.8	0.023 to 8.8

NOTE 1—The test methods were tested over the following ranges:

Total Carbon	0.01 % to 5.87 %
Total Sulfur	0.0002 % to 4.70 %
Residual Carbon from Pyrolysis	0.002 % to 4.97 %
Residual Sulfur from Pyrolysis	0.014 % to 1.54 %
Pyrolysis Loss Sulfur	0 % to 4.42 %
Hydrochloric Acid Insoluble Carbon	0.025 % to 0.47 %
Hydrochloric Acid Loss Carbon	0 % to 5.78 %
Hydrochloric Acid Insoluble Sulfur	0.012 % to 4.20 %
Acid Neutralization Potential Acidity Titration	-1.0 % to 100 %
Acid Neutralization Potential Acidity Titration Low Range	-1.0 % to 2 % CaCO ₃
Nitric Acid Insoluble Sulfur	0.006 % to 0.924 %
Nitric Acid Loss Sulfur	-0.08 % to 4.19 %
Sodium Carbonate Insoluble Sulfur	0.007 % to 3.78 %

1.2 The quantitative ranges for the partial decomposition test methods are dependent on the mineralogy of the samples being tested. The user of these test methods is advised to conduct an interlaboratory study in accordance with Practice E1601 on the test methods selected for use at a particular mining site, in order to establish the quantitative ranges for these test methods on a site-specific basis.

1.3 The test methods appear in the following order:

	Sections
Carbon and Sulfur, Total	10.1-10.9
Carbon and Sulfur, Residual from Pyrolysis	10.10-10.18
Carbon and Sulfur, Hydrochloric Acid Insoluble	10.19-10.27
Acid Neutralization Potential Acidity Titration	10.28-10.36
Acid Neutralization Potential Acidity Titration Low Range	10.37-10.46
Sulfur, Nitric Acid Insoluble	10.47-10.55
Sulfur, Sodium Carbonate Insoluble	10.56-10.64

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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1.4 The values stated in SI units are to be regarded as standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in Section 6.

2. Referenced Documents

2.1 ASTM Standards:²

- D1067 Test Methods for Acidity or Alkalinity of Water
- D1193 Specification for Reagent Water
- D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy
- D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
- D5744 Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell
- D6234 Test Method for Shake Extraction of Mining Waste by the Synthetic Precipitation Leaching Procedure
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
- E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
- E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
- E1950 Practice for Reporting Results from Methods of Chemical Analysis

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

E2242 Test Method for Column Percolation Extraction of Mine Rock by the Meteoric Water Mobility Procedure

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *standardization, v*—analysis of samples with known values or known additions, prior to and within groups of test samples to assure accuracy.

3.2.2 *standardization sample, n*—calibration mixtures or samples with known values or known additions that are analyzed with test samples to assure accuracy of analysis.

4. Significance and Use

4.1 These test methods are primarily intended to test materials for compliance with compositional specifications and for monitoring.

4.1.1 The determination of carbon and sulfur and acid neutralization potential in ores and related materials is necessary to classify ores for metallurgical processing and to classify waste materials from the mining and processing of ores such as leach residues, waste rock, and tailings according to their potential to generate acid in the environment. This information is useful during mine development to assist in mining and mineral processing operations and for proper disposal of waste materials.

4.1.1.1 The use of the acid neutralization potential titration low range method is most useful where acidity is present in the samples and when acid potential by titration is desired in the uncertain content range below 2 % CaCO₃.

4.1.2 These test methods are also used to isolate minerals based on carbon and sulfur contents of metal-bearing ores and related materials so that acid-base accounting can be performed (that is, carbonate mineral acid neutralization potential (ANP) minus sulfide-sulfur mineral acid generation potential (AGP) = net calcium carbonate (NCC)).

4.1.3 Additionally, the carbon hydrochloric acid insoluble test method has utility to identify the amount of organic carbon contained in gold ores so that potential for preg robbing can be identified and rectified through established pretreatment methods prior to cyanidation. **Warning**—Pyrolysis pretreatment at 550 °C has a potential to thermally decompose some carbonate minerals: (1) transition metal carbonates (for example, siderite, FeCO₃, and rhodochrosite, MnCO₃) decompose, yielding carbon dioxide, CO₂, in the range of 220 °C to 520 °C; (2) calcite decomposes slightly between 300 °C and 500 °C, although most decomposition occurs above 550 °C; (3) dolomite decomposes at 800 °C to 900 °C (Hammack, 1994, p. 440).³

4.2 These test methods also may be used for the classification of rock to be used in construction, where the potential to generate acid under environmental conditions exists.

4.3 It is assumed that the users of these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices such as those described in Guide E882 must be followed.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Type I of Specification D1193.

6. Hazards

6.1 For hazards to be observed in the use of reagents and apparatus in these test methods, refer to Practices E50. Use care when handling hot crucibles or boats and when operating furnaces to avoid personal injury by either burn or electrical shock.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in the Rounding Method of Practice E29.

8. Interlaboratory Studies

8.1 These test methods have been evaluated in accordance with Practice E1601 unless otherwise noted in the precision and bias section. The lower limit in the scope of these test methods specifies the lowest analyte content that may be analyzed with an acceptable error. A warning statement is included in the scope for test methods not observing this convention.

8.2 *Site-Specific Quantitative Ranges*—An interlaboratory study may be conducted in accordance with Practice E1601 to establish quantitative ranges for the partial decomposition test methods selected for a particular site. Test samples shall be selected for each alteration or lithologic unit, or both, containing high and low contents of carbon and sulfur minerals. Each test sample must be analyzed in rapid succession for total carbon and sulfur followed by the different partial decomposition treatments selected in order to minimize the between-method variation.

³ Hammack, R. W., "Evolved-Gas Analysis: A Method for Determining Pyrite, Marcasite, and Alkaline-Earth Carbonates," *Environmental Geochemistry of Sulfide Oxidation*, Alpers, C., and Blowes, D., eds., Chapter 28, ACS Symposium Series 550, American Chemical Society, Washington, D.C., 1994, pp. 431–444.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

9. Sampling and Sample Preparation

9.1 *Materials Safety*—Samples must be prepared, stored, and disposed of in accordance with the materials and safety guidelines in Practices E50.

9.2 *Prepared Sample*—Dry a representative portion of the gross sample at 80 °C to constant mass in order to minimize sulfide mineral oxidation. Pulverize or grind the laboratory sample until 100 % passes a No. 100 (150- μ m) sieve.

NOTE 2—Results from the interlaboratory study suggest that it may be necessary to grind samples to pass a No. 200 (75- μ m) sieve in order to improve precision for samples containing low contents of carbon or sulfur.

9.3 *Diluted Sample*—If the content of sulfur in the test material exceeds 1.75 % for the minimum range instrument, prepare a diluted sample as in 9.3.1.

9.3.1 Weigh 10.0 g \pm 0.1 g prepared sample and combine with 40.0 g \pm 0.1 g dry silica (SiO₂). Grind the mixture in a ring and puck mill, or equivalent, until 100 % will pass through a No. 100 (150- μ m) sieve; mix, and store in a 250-mL glass bottle.

10. Procedures

TOTAL CARBON AND SULFUR

10.1 *Scope*—This test method covers the determination of total carbon in the content range between 0.1 % and 10 % and total sulfur contents in the range between 0.1 % and 8.8 %.

10.2 Summary of Test Method:

10.2.1 The carbon in the test sample is converted to carbon dioxide and the sulfur to sulfur dioxide by combustion in a stream of oxygen.

10.2.2 The amount of carbon dioxide and sulfur dioxide are measured by infrared absorption.

10.3 Apparatus:

10.3.1 *Combustion-Infrared Spectrophotometer*, equipped with a combustion chamber, oxygen carrier stream, and infrared absorption detector, suitable for analysis of sulfur in a minimum range instrument from 0.1 % to 1.75 % or in a maximum range instrument from 0.1 % to 8.8 % and carbon in the range of 0.1 % to 10 %, using 0.2-g test portions of ores and related materials. Instruments, such as those shown in Test Methods E1019 that can be shown to give equivalent results may also be used for these test methods.

10.4 Reagents and Materials:

10.4.1 Reagents:

10.4.1.1 *Barium Sulfate (BaSO₄)*, Anhydrous, contains 13.74 % sulfur (purity 99.9 % minimum). Dry 100 g at 120 °C for 2 h and store in a 250-mL glass bottle.

10.4.1.2 *Blank Reference Sample*—Prepare a blank reference sample by pulverizing or grinding 100 g of SiO₂ (see 10.4.1.6), to pass through a No. 100 (150- μ m) sieve, mix, and store in a 250-mL glass bottle. This blank contains 0.00 % carbon and 0.00 % sulfur.

10.4.1.3 *Calcium Carbonate (CaCO₃)*, Anhydrous, contains 12.00 % carbon (purity 99.9 % minimum). Dry 100 g for 2 h at 120 °C and store in a 250-mL glass bottle.

10.4.1.4 *Calibration Mixture A*—(1 g = 20 mg C and 20 mg S)—Combine 16.67 g CaCO₃, 14.56 g BaSO₄, and

68.77 g SiO₂ in a ring and puck grinding mill or equivalent device. Grind until 100 % passes through a No. 100 (150- μ m) sieve, pass the mixture through the screen to break up any lumps, mix, and store in a glass bottle. This mixture contains 2.00 % carbon and 2.00 % sulfur.

(1) Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.4.1.5 *Calibration Mixtures*—Transfer 4.00 g, 10.00 g, 20.00 g, and 30.00 g of Calibration Mixture A to ring and puck grinding mills or equivalent devices. Add the amount of dried SiO₂ needed to bring the total mass to 40.0 g in each mill, grind to 100 % passing a No. 100 (150- μ m) sieve, pass the mixture through the screen, mix, and store in 250-mL glass bottles. These mixtures contain: 0.2 %, 0.5 %, 1.0 %, and 1.5 % for both carbon and sulfur.

(1) Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

(2) Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.4.1.6 *Silica (SiO₂)* (purity 99.9 % minimum), Ottawa sand, washed and ignited, containing less than 0.01 % carbon and 0.01 % sulfur. Dry at 120 °C for 2 h and store in a 250-mL glass bottle.

10.4.1.7 *Tungstic Acid (H₂WO₄)* (purity 99 % minimum).

10.4.1.8 *Vanadium Pentoxide (V₂O₅)* (purity 99 % minimum).

10.4.2 Materials:

10.4.2.1 *Crucibles or boats*, suitable for combustion analyses.

10.5 Calibration and Standardization:

10.5.1 *Apparatus*—Operate and calibrate the instrument in accordance with the manufacturer's instructions. Resistance furnace instruments require the use of V₂O₅ or H₂WO₄ for the determination of sulfur in this test method. Use a 0.200 g \pm 0.01 g mass for all calibration mixtures, reference materials, blank reference materials, test samples, and diluted test samples in this test method.

10.5.1.1 Certain instruments may require different sample masses for certain content ranges, which is permissible as long as the precision and bias requirements of these test methods are fulfilled.

10.5.2 Ignite the crucibles or boats for test samples and standard samples in a muffle furnace for 1 h at 550 °C \pm 10 °C.

10.5.3 *Laboratory Test Method Performance Demonstration*—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified.

10.5.3.1 *Linearity Verification*—Measure total carbon and sulfur for the blank reference sample, calibration mixtures, BaSO₄, and CaCO₃ in increasing order using the same mass of calibration mixtures selected for test samples, in accordance with the manufacturer's instructions. Record the calibration mixture masses used and the carbon and sulfur results from the instrument. Check for linearity by linear regression or by a graphical method to meet a deviation less than 10 % relative

TABLE 1 Calibration Mixture 95 % Confidence Limits from Interlaboratory Testing

Mixture	Min., % Carbon	Max., % Carbon	Min., % Sulfur	Max., % Sulfur
0.0	-0.02	0.04	-0.01	0.01
0.2	0.16	0.25	0.12	0.26
0.5	0.44	0.55	0.42	0.55
1.0	0.92	1.08	0.85	1.14
1.5	1.42	1.59	1.34	1.62
2.0	1.87	2.13	1.78	2.16
BaSO ₄	12.4	14.5
CaCO ₃	10.9	12.8

for each of the calibration material results at or above a content of 0.2 % carbon and 0.2 % sulfur and a correlation coefficient of at least 0.99. Correct any problems with the instrument before proceeding with the analysis of test samples.

(1) Linearity may also be verified by the use of BaSO₄ and CaCO₃ masses equivalent to the content of the calibration mixtures.

10.5.3.2 Blank Sample Precision Verification—Analyze ten replicates of the blank reference sample. If the standard deviation of the replicate analyses exceeds 0.02 % for carbon or 0.01 % for sulfur, correct any instrumental problems and repeat the blank sample precision verification before proceeding with test method implementation.

10.5.3.3 Low Calibration Mixture Precision Verification—Analyze four replicates of the 0.2 % calibration mixture. If any result for the 0.2 % calibration mixture exceeds the limits shown in **Table 1**, correct any instrumental problems and repeat the low calibration mixture precision verification before proceeding with test method implementation.

10.5.4 Method Quality Control:

10.5.4.1 Calibration Verification—Analyze a calibration mixture with a content greater than or equal to 0.5 % carbon and 0.5 % sulfur prior to and within each group of fifty test samples. If the calibration mixture result exceeds the limits in **Table 1**, correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.5.4.2 Blank Reference Sample—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the limits in **Table 1** for the 0.0 % calibration mixture, correct any instrumental problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.5.4.3 Reference Sample—Analyze a reference sample, certified for total carbon and total sulfur before analysis of test samples for total carbon and sulfur and within each group of fifty test samples. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in **Table 1** for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.5.4.4 Control Sample—Analyze the 0.2 % calibration mixture prior to and within each group of fifty test samples. If

the result for the control sample exceeds the limits shown in **Table 1** for the 0.2 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.5.4.5 Standard Addition Sample—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.5 % calibration mixture just prior to determination of carbon and sulfur. Calculate the reference values for the standard addition sample by adding 0.5 % to the carbon and sulfur results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in **Table 1** for materials of comparable content, correct any instrumental problems and repeat the standard addition sample analysis before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

10.6 Interferences—The elements normally present in ores and related materials do not interfere with this test method.

10.7 Procedure:

10.7.1 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at 550 °C ± 10 °C, unless it is demonstrated that omission of this step does not degrade the precision and bias of the analysis.

10.7.2 Test Samples—Transfer test samples, diluted test samples and standardization samples using 0.200 g ± 0.01 g into the crucible or boat used for instrumental analysis and record the mass. Use of a different sample mass may be required on some instruments for some samples (see **10.5.1.1**).

10.7.3 Duplicate Test Sample—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in **Table 1** for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems, and repeat the analyses from **10.7.2**.

10.7.4 Analysis:

10.7.4.1 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in **10.5.4**. Measure the carbon and sulfur contents for quality control samples, test samples, and diluted test samples in percent in accordance with the instrument manufacturer's instructions, and record the measurements.

10.7.4.2 Continue analysis until the batch of test samples is completed, or until a quality control sample or duplicate test sample result deviates more than the limits shown in **Table 1**, for a material of comparable content. If the difference of the results exceeds the limits shown in **Table 1** for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from **10.7.4.2**.

10.8 Calculation:

TABLE 2 Statistical Information—Total Carbon

Test Material	Number of Laboratories	Carbon Found, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R, Practice E1601)	R_{rel} %
Blank	7	0.012	0.004	0.034	300
Ottawa Sand (D)	10	0.021	0.011	0.0477	230
Inert Diorite (K)	7	0.050	0.005	0.037	74
Inert Andesite (J)	7	0.090	0.004	0.054	59
Autoclave Feed Ore (A)	10	0.086	0.016	0.115	133
Calibration Mixture 0.1	7	0.117	0.007	0.049	42
Duluth Waste Rock (B)	10	0.142	0.017	0.112	79
Spiked Andesite	6	0.292	0.008	0.051	17
Reclamation Tailings (C)	10	0.462	0.025	0.223	48
Vinini Waste Rock (E)	10	0.771	0.024	0.180	23
Pit Rock (G)	10	0.800	0.025	0.117	15
Diorite Gneiss (F)	10	1.04	0.032	0.170	16
Zinc Plant Tailings (H)	10	5.87	0.055	0.494	8
Refractory Gold Ore (I)	10	5.70	0.038	0.478	8

TABLE 3 Statistical Information—Total Sulfur

Test Material	Number of Laboratories	Sulfur Found, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R, Practice E1601)	R_{rel} %
Blank	7	0.0002	0.002	0.010	5000
Ottawa Sand (D)	11	0.004	0.003	0.0133	312
Diorite Gneiss (F)	11	0.014	0.007	0.039	283
Calibration Mixture 0.1	7	0.095	0.004	0.024	25
Inert Andesite (J)	7	0.176	0.005	0.095	54
Inert Diorite (K)	7	0.190	0.004	0.081	43
Pit Rock (G)	11	0.285	0.014	0.068	24
Spiked Andesite	6	0.336	0.005	0.055	16
Vinini Waste Rock (E)	11	0.761	0.019	0.269	35
Refractory Gold Ore (I)	11	1.50	0.052	0.326	22
Duluth Waste Rock (B)	11	1.57	0.024	0.186	12
Zinc Plant Tailings (H)	11	3.79	0.072	0.423	11
Reclamation Tailings (C)	11	4.04	0.053	0.462	11
Autoclave Feed Ore (A)	11	4.70	0.067	0.648	14

10.8.1 Calculate the total carbon and sulfur contents for the test samples in accordance with the manufacturer’s instructions.

10.8.2 Round the results above 0.1 % to the nearest 0.01 % and record as total carbon or sulfur. Enclose results from 0.03 % to 0.1 % in parentheses and below 0.03 % in parentheses followed by an asterisk in accordance with Practice E1950.

10.8.3 *Over-Range Results*—If the sulfur result exceeds 1.75 % for the minimum range instrument, discard the result and repeat the procedure from with the diluted sample. Multiply the diluted test sample result by five and round to the nearest 0.1 %.

10.8.3.1 Alternatively, use a lower sample mass for the analysis as specified in 10.5.1.1.

10.9 Precision and Bias:^{5,6}

10.9.1 *Precision*—Eleven laboratories cooperated in testing this test method, providing ten sets of data for carbon and eleven sets of data for sulfur, and obtained the precision data summarized in Tables 2 and 3.

10.9.2 *Bias*—The accuracy of this test method for carbon and sulfur is deemed satisfactory based on the values in Tables 4 and 5. Users are encouraged to employ these or similar reference materials to verify that this test method is performing accurately in their laboratory.

NOTE 3—The user of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of 50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1023.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1040.

TABLE 4 Bias Information—Total Carbon

Test Material	Reference Carbon, %	Difference Carbon, %	Source	Description
Diorite Gneiss (F)	1.0 ± 0.1 Provisional	0.040	CANMET	SY-4 Diorite gneiss

TABLE 5 Bias Information—Total Sulfur

Test Material	Reference Sulfur, %	Difference Sulfur, %	Source	Description
Diorite Gneiss (F)	0.015 ± 0.004 Provisional	−0.001	CANMET	SY-4 Diorite gneiss
Pit Rock (G)	0.298 ± 0.015 Recommended	−0.013	CANMET	NBM-1 pit rock
Refractory Gold Ore (I)	1.466 ± 0.044 Certified	0.034	NIST	SRM-886 refractory gold ore

RESIDUAL CARBON AND SULFUR FROM PYROLYSIS

10.10 *Scope*—This test method covers the determination of residual carbon from pyrolysis in the content range between 0.1 % and 10 % and residual sulfur from pyrolysis contents in the range between 0.1 % and 8.8 %.

10.11 Summary of Test Method:

10.11.1 The test sample is ignited in a muffle furnace prior to instrumental analysis where the carbon in the test sample is converted to carbon dioxide and the sulfur to sulfur dioxide by combustion in a stream of oxygen.

10.11.2 The amount of carbon dioxide and sulfur dioxide are measured by infrared absorption.

10.12 Apparatus:

10.12.1 *Combustion-Infrared Spectrophotometer*, equipped with a combustion chamber, oxygen carrier stream and infrared

absorption detector, suitable for analysis of sulfur in a minimum range instrument from 0.1 % to 1.75 % or in a maximum range instrument from 0.1 % to 8.8 % and carbon in the range of 0.1 % to 10 %, using 0.2-g test portions of ores and related materials. Instruments, such as those shown in Test Methods E1019 that can be shown to give equivalent results may also be used for these test methods.

10.13 Reagents and Materials:

10.13.1 Reagents:

10.13.1.1 Barium Sulfate (see 10.4.1.1).

10.13.1.2 Blank Reference Sample (see 10.4.1.2).

10.13.1.3 Calcium Carbonate (see 10.4.1.3).

10.13.1.4 Calibration Mixture A (see 10.4.1.4).

10.13.1.5 Calibration Mixtures (see 10.4.1.5).

10.13.1.6 Silica (see 10.4.1.6).

10.13.1.7 Tungstic Acid (see 10.4.1.7).

10.13.1.8 Vanadium Pentoxide (see 10.4.1.8).

10.13.2 Materials:

10.13.2.1 Crucibles or boats, suitable for combustion analyses.

10.14 Calibration and Standardization:

10.14.1 Apparatus: Operate and calibrate the instrument in accordance with the manufacturer's instructions. Resistance furnace instruments require the use of vanadium pentoxide or H_2WO_4 for the determination of sulfur in this test method. Use a $0.200 \text{ g} \pm 0.01 \text{ g}$ mass for all calibration mixtures, reference materials, blank reference materials, test samples, and diluted test samples in this test method.

10.14.1.1 Certain instruments may require different sample masses for certain content ranges, which is permissible as long as the precision and bias requirements of these test methods are fulfilled.

10.14.2 Ignite the crucibles or boats for test samples and standard samples in a muffle furnace for 1 h at $550 \text{ }^\circ\text{C} \pm 10 \text{ }^\circ\text{C}$.

10.14.3 Laboratory Test Method Performance Demonstration—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified. Carry out the performance demonstration as described in 10.5.3.

10.14.4 Method Quality Control:

10.14.4.1 Calibration Verification—Analyze a calibration mixture with a content greater than or equal to 0.5 % carbon and 0.5 % sulfur prior to and within each group of fifty test samples. If the calibration mixture result exceeds the limits in Table 1, correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.14.4.2 Blank Reference Sample—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the limits in Table 1 for the 0.0 % calibration mixture, correct any instrumental problems and repeat the analysis of the blank reference sample before proceeding with

analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.14.4.3 Reference Sample—Analyze a reference sample, certified for total carbon and total sulfur before analysis of test samples for and within each group of fifty test samples and a reference sample certified for pyrolysis residual carbon or sulfur from pyrolysis, if available. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in Table 1 for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.14.4.4 Control Sample—Analyze the 0.2 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in Table 1 for the 0.2 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.14.4.5 Standard Addition Sample—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.5 % calibration mixture just prior to determination of carbon and sulfur. Calculate the reference values for the standard addition sample by adding 0.5 % to the carbon and sulfur results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in Table 1 for materials of comparable content, correct any instrumental problems and repeat the standard addition sample analysis before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

NOTE 4—Add the 0.5 % calibration mixture after the pyrolysis procedure but before the analysis step.

10.15 Interferences—The elements normally present in ores and related materials do not interfere with this test method. Use of adequate draft in the muffle furnace is necessary to avoid excessive adsorption of sulfur gasses on the solid phase of the test samples, leading to low sulfur loss by pyrolysis.

NOTE 5— $\text{SO}_2(\text{g})$ can be adsorbed by carbonate minerals within a sample and from other samples in a batch, resulting in low pyrolysis loss estimates for sulfide. Pyrolysis pretreatment at $550 \text{ }^\circ\text{C}$ has a potential to thermally decompose some carbonate minerals:

- (1) Transition metal carbonates (for example, FeCO_3 and MnCO_3) decompose, yielding CO_2 , in the range of $220 \text{ }^\circ\text{C}$ to $520 \text{ }^\circ\text{C}$;
- (2) calcite decomposes slightly between $300 \text{ }^\circ\text{C}$ and $500 \text{ }^\circ\text{C}$, although most decomposition occurs above $550 \text{ }^\circ\text{C}$;
- (3) dolomite decomposes at $800 \text{ }^\circ\text{C}$ to $900 \text{ }^\circ\text{C}$.

10.16 Procedure:

10.16.1 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at $550 \text{ }^\circ\text{C} \pm 10 \text{ }^\circ\text{C}$ (see 10.7.1).

10.16.2 Test Samples—Transfer test samples, diluted test samples, and standardization samples using $0.200 \text{ g} \pm 0.01 \text{ g}$ into the crucible or boat used for instrumental analysis and

record the mass. Use of a different sample mass may be required on some instruments for some samples (see 10.14.1.1).

10.16.3 *Ignition*—Ignite the crucibles or boats containing the test samples, blank, reference samples for pyrolysis residual carbon and sulfur from pyrolysis and standard addition samples in a muffle furnace for 1 h at 550 °C ± 10 °C. Add the calibration mixture portion for the standard addition sample after pyrolysis and cooling, then mix.

10.16.4 *Duplicate Test Sample*—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in Table 1 for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from 10.16.2.

10.16.5 *Analysis:*

10.16.5.1 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in 10.14.4. Measure the carbon and sulfur contents for quality control samples, test samples and diluted test samples in percent in accordance with the instrument manufacturer’s instructions and record the measurements.

10.16.5.2 Continue analysis until the batch of test samples is completed, or until a quality control sample or duplicate test sample result deviates more than the limits shown in Table 1 for a material of comparable content. If the difference of the results exceeds the limits shown in Table 1 for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems, and repeat the analyses from 10.16.2.

10.17 *Calculation:*

10.17.1 Calculate the residual carbon and sulfur from pyrolysis contents for the test samples in accordance with the manufacturer’s instructions.

10.17.2 Calculate the pyrolysis loss sulfur, % A, as follows:

$$A = B - C \tag{1}$$

where:

- B = total sulfur result, %, and
- C = residual sulfur from pyrolysis result, %.

10.17.3 Round the results to the nearest 0.01 % and record as residual carbon from pyrolysis, residual sulfur from pyrolysis, or pyrolysis loss sulfur, at or above the lower scope limit established during interlaboratory testing. Report results below the lower scope limits enclosed in parentheses and below the null limit followed by an asterisk in accordance with Practice E1950.

10.17.4 *Over-Range Results*—If the sulfur result exceeds 1.75 % for the minimum range instrument, discard the result and repeat the procedure from with the diluted sample. Multiply the diluted test sample result by five and round to the nearest 0.1 %.

10.17.4.1 Alternatively, use a lower sample mass for the analysis as specified in 10.14.1.1.

TABLE 6 Residual Carbon From Pyrolysis

Test Material	Number of Laboratories	Carbon Found, %	Min, SD (S _M , Practice E1601)	Reproducibility Index (R, Practice E1601)	R _{rel} , %
Ottawa Sand (D)	7	0.002	0.014	0.053	2449
Inert Diorite (K)	7	0.011	0.006	0.061	530
Autoclave Feed Ore (A)	7	0.024	0.009	0.051	210
Inert Andesite (J)	7	0.030	0.009	0.061	204
Duluth Waste Rock (B)	7	0.107	0.009	0.071	66
Vinini Waste Rock (E)	7	0.131	0.009	0.087	67
Reclamation Tailings (C)	7	0.216	0.011	0.101	47
Pit Rock (G)	7	0.359	0.010	0.261	73
Diorite Gneiss (F)	7	0.931	0.015	0.125	13
Refractory Gold Ore (I)	7	4.84	0.076	0.752	16
Zinc Plant Tailings (H)	7	4.97	0.047	1.82	37

10.18 *Precision and Bias:*⁷

10.18.1 *Precision*—Nine laboratories cooperated in testing this test method, providing seven sets of data for carbon and nine sets of data for sulfur, and obtained the precision data summarized in Tables 6-8.

10.18.2 *Bias*—No information on the bias of this test method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

NOTE 6—The user of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of 50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

HYDROCHLORIC ACID INSOLUBLE CARBON AND SULFUR

10.19 *Scope*—This test method covers the determination of HCl insoluble carbon in the content range of 0.1 % to 10 % and hydrochloric acid insoluble sulfur contents in the range of 0.1 % to 8.8 %.

10.20 *Summary of Test Method:*

10.20.1 The test sample is partially decomposed with HCl prior to instrumental analysis, where the carbon in the test sample is converted to carbon dioxide and the sulfur to sulfur dioxide by combustion in a stream of oxygen.

10.20.2 The amount of carbon dioxide and sulfur dioxide are measured by infrared absorption.

10.21 *Apparatus:*

10.21.1 *Combustion-Infrared Spectrophotometer*, equipped with a combustion chamber, oxygen carrier stream, and infrared absorption detector, suitable for analysis of sulfur in a

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1026.

TABLE 7 Residual Sulfur From Pyrolysis

Test Material	Number of Laboratories	Sulfur Found, %	Min. SD ($S_{M, Practice}$ E1601)	Reproducibility Index ($R, Practice$ E1601)	R_{reb} %
Ottawa Sand (D)	9	0.014	0.009	0.029	204
Diorite Gneiss (F)	9	0.107	0.038	0.164	153
Inert Andesite (J)	8	0.196	0.019	0.176	90
Pit Rock (G)	9	0.229	0.037	0.187	82
Inert Diorite (K)	9	0.244	0.016	0.187	77
Autoclave Feed Ore (A)	9	0.288	0.022	0.323	112
Vinini Waste Rock (E)	9	0.425	0.015	0.162	38
Refractory Gold Ore (I)	9	0.710	0.032	0.244	34
Duluth Waste Rock (B)	9	0.714	0.056	0.275	38
Zinc Plant Tailings (H)	9	1.24	0.042	1.45	117
Reclamation Tailings (C)	9	1.54	0.025	0.435	28

TABLE 8 Pyrolysis Loss Sulfur

Test Material	Number of Laboratories	Sulfur Loss, %	Min. SD ($S_{M, Practice}$ E1601)	Reproducibility Index ($R, Practice$ E1601)	R_{reb} %
Diorite Gneiss (F)	9	- 0.106	0.038	0.197	-186
Inert Diorite (K)	9	- 0.063	0.015	0.143	-224
Inert Andesite (J)	8	- 0.041	0.018	0.165	-406
Ottawa Sand (D)	9	- 0.017	0.009	0.070	-420
Pit Rock (G)	9	0.042	0.035	0.225	536
Vinini Waste Rock (E)	9	0.322	0.024	0.248	77
Refractory Gold Ore (I)	9	0.763	0.059	0.373	49
Duluth Waste Rock (B)	9	0.863	0.058	0.384	44
Reclamation Tailings (C)	9	2.50	0.062	0.599	24
Zinc Plant Tailings (H)	9	2.53	0.082	1.21	48
Autoclave Feed Ore (A)	9	4.42	0.076	0.696	16

minimum range instrument from 0.1 % to 1.75 % or in a maximum range instrument from 0.1 % to 8.8 % and carbon in the range of 0.1 % to 10 %, using 0.2-g test portions of ores and related materials. Instruments, such as those shown in Test Methods E1019 that can be shown to give equivalent results may also be used for these test methods.

10.22 Reagents and Materials:

10.22.1 Reagents:

10.22.1.1 Barium Sulfate (see 10.4.1.1).

10.22.1.2 Blank Reference Sample (see 10.4.1.2).

10.22.1.3 Calcium Carbonate (see 10.4.1.3).

10.22.1.4 Calibration Mixture A (see 10.4.1.4).

10.22.1.5 Calibration Mixtures (see 10.4.1.5).

10.22.1.6 Silica (see 10.4.1.6).

10.22.1.7 Tungstic Acid (see 10.4.1.7).

10.22.1.8 Vanadium Pentoxide (see 10.4.1.8).

10.22.2 Materials:

10.22.2.1 Crucibles or boats, suitable for combustion analyses.

10.22.2.2 Glass Filters—Fine-porosity glass micro filters, carbon content must be less than 0.15 %, sulfur content must be less than 0.05 % and the filter mass must be less than 0.2 g.

10.23 Calibration and Standardization:

10.23.1 Apparatus—Operate and calibrate the instrument in accordance with the manufacturer’s instructions. Resistance furnace instruments require the use of V_2O_5 or H_2WO_4 for the determination of sulfur in this test method. Use a $0.200\text{ g} \pm 0.01\text{ g}$ mass for all calibration mixtures, reference materials, blank reference materials, test samples and diluted test samples in this test method.

10.23.1.1 Certain instruments may require different sample masses for certain content ranges, which is permissible as long as the precision and bias requirements of these test methods are fulfilled.

10.23.2 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at $550\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$.

10.23.3 Laboratory Test Method Performance Demonstration—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified. Carry out the performance demonstration as described in 10.5.3.

10.23.4 Method Quality Control:

10.23.4.1 Calibration Verification—Analyze a calibration mixture with a content greater than or equal to 0.5 % carbon and 0.5 % sulfur prior to and within each group of fifty test samples. If the calibration mixture result exceeds the limits in Table 1, correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.23.4.2 Blank Reference Sample—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the limits in Table 1 for the 0.0 % calibration mixture, correct any instrumental problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.23.4.3 Reference Sample—Analyze a reference sample, certified for total carbon and total sulfur before analysis of test samples for total carbon and sulfur and within each group of fifty test samples and a reference sample certified for hydrochloric acid insoluble carbon or sulfur, if available. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in Table 1 for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.23.4.4 *Control Sample*—Analyze the 0.2 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in **Table 1** for the 0.2 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.23.4.5 *Standard Addition Sample*—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.5 % calibration mixture just prior to determination of carbon and sulfur. Calculate the reference values for the standard addition sample by adding 0.5 % to the carbon and sulfur results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in **Table 1** for materials of comparable content, correct any instrumental problems and repeat the standard addition sample analysis before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

NOTE 7—Add the 0.5 % calibration mixture after the hydrochloric acid decomposition procedure but before the analysis step.

10.24 Interferences:

10.24.1 The elements normally present in ores and related materials do not interfere with this test method. Use of a halogen trap may be necessary for some commercially available instruments.

10.25 Procedure:

10.25.1 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at 550 °C ± 10 °C (see 10.7.1).

10.25.2 *Test Samples*—Transfer test samples, diluted test samples, blank samples, reference samples for HCl insoluble carbon or sulfur and standard addition samples using 0.200 g ± 0.01 g into a 150-mL beaker and record the mass.

10.25.3 *Decomposition*—Add 25 mL of HCl (1 + 4) to the beaker and let stand at room temperature for 30 min. Cover with a watch glass and place the beaker on a hot plate and gently boil for 10 min. Cool.

10.25.4 *Filtration*—Filter through a glass filter, wash with water at least three times and discard filtrate, and dry.

10.25.5 Transfer filter and solids to the crucible or boat used for instrumental analysis. Use of a different sample mass may be required on some instruments for some samples (see 10.23.1.1). Add the calibration mixture portion for the standard addition sample after digestion, and mix.

10.25.6 *Duplicate Test Sample*—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in **Table 1**, for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from 10.25.2.

10.25.7 Analysis:

10.25.7.1 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in 10.23.4. Measure the carbon and sulfur contents for quality control samples, test samples and diluted test samples in percent in accordance with the instrument manufacturer's instructions and record the measurements.

10.25.7.2 Continue analysis until the batch of test samples is completed, or a quality control sample or duplicate test sample result deviates more than the limits shown in **Table 1**, for a material of comparable content. If the difference of the results exceeds the limits shown in **Table 1** for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems, and repeat the analyses from 10.25.2.

10.26 Calculation:

10.26.1 Calculate the HCl insoluble carbon and sulfur contents for the test samples in accordance with the manufacturer's instructions.

10.26.2 Calculate the HCl loss carbon, % *D*, as follows:

$$D = E - F \quad (2)$$

where:

E = total carbon result, %, and

F = hydrochloric acid insoluble carbon result, %.

10.26.3 Round the results to the nearest 0.01 % and record as HCl insoluble carbon and sulfur, or hydrochloric acid loss carbon, at or above the lower scope limit established during interlaboratory testing. Enclose results below the lower scope limits in parentheses and below the null limit followed by an asterisk, in accordance with Practice E1950.

10.26.4 *Over-Range Results*—If the sulfur result exceeds 1.75 % for the minimum range instrument, discard the result and repeat the procedure from with the diluted sample. Multiply the diluted test sample result by five and round to the nearest 0.1 %.

10.26.4.1 Alternatively, use a lower sample mass for the analysis as specified in 10.23.1.1.

10.27 Precision and Bias:

10.27.1 *Precision*—Eight laboratories cooperated in testing this test method, providing eight sets of data for carbon and eight sets of data for sulfur, and obtained the precision data summarized in **Table 9**, **Table 10**, and **Table 11**.

10.27.2 *Bias*—No information on the bias of this test method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

NOTE 8—The user of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of 50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

ACID NEUTRALIZATION POTENTIAL ACIDITY TITRATION

10.28 Scope:

TABLE 9 Statistical Information Hydrochloric Acid Insoluble Carbon

Test Material	Number of Laboratories	Carbon Found, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{rel} %
Ottawa Sand (D)	8	0.025	0.010	0.053	209
Pit Rock (G)	8	0.054	0.009	0.092	169
Inert Diorite (K)	8	0.056	0.009	0.095	169
Reclamation Tailings (C)	8	0.068	0.011	0.067	99
Autoclave Feed Ore (A)	8	0.078	0.009	0.060	77
Zinc Plant Tails (H)	8	0.082	0.010	0.186	229
Diorite Gneiss (F)	8	0.122	0.013	0.103	85
Duluth Waste Rock (B)	8	0.133	0.014	0.094	70
Vinini Waste Rock (E)	8	0.222	0.021	0.131	59
Refractory Gold Ore (I)	8	0.470	0.009	0.389	83

TABLE 10 Statistical Information Hydrochloric Acid Insoluble Sulfur

Test Material	Number of Laboratories	Sulfur Found, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{rel} %
Ottawa Sand (D)	8	0.012	0.004	0.044	358
Diorite Gneiss (F)	8	0.021	0.003	0.064	308
Inert Diorite (K)	8	0.164	0.008	0.080	49
Pit Rock (G)	8	0.252	0.039	0.136	54
Vinini Waste Rock (E)	8	0.653	0.033	0.392	60
Duluth Waste Rock (B)	8	0.863	0.089	0.709	82
Refractory Gold Ore (I)	8	1.22	0.067	1.21	99
Reclamation Tails (C)	8	2.96	0.166	1.70	58
Zinc Plant Tails (H)	8	3.12	0.185	4.28	137
Autoclave Feed Ore (A)	8	4.20	0.114	0.994	24

10.28.1 This test method covers the determination of acid neutralization potential with acidity correction in metal-bearing ores and related materials such as tailings and waste rock within the range of -1.0 % to 100 % expressed as CaCO_3 .

10.29 Summary of Test Method:

10.29.1 A finely ground sample is reacted with a known amount of H_2SO_4 , filtered, treated with hydrogen peroxide (H_2O_2) to oxidize the metals present in filtrate, boiled to expel the excess peroxide, and the potential of the sample to neutralize acid is determined by automatic or manual titration of the acid remaining in the filtrate, using standard sodium hydroxide (NaOH).

10.30 Apparatus:

10.30.1 *Automatic Titrator*—Capable of determination of the equivalence point for a strong acid neutralization titration

TABLE 11 Statistical Information Hydrochloric Acid Loss Carbon

Test Material	Number of Laboratories	Carbon Loss, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{rel} %
Ottawa Sand (D)	7	-0.009	0.010	0.047	- 536
Duluth Waste Rock (B)	7	0.021	0.015	0.100	478
Autoclave Feed Ore (A)	7	0.023	0.009	0.094	412
Reclamation Tails (C)	7	0.413	0.014	0.103	25
Vinini Waste Rock (E)	7	0.573	0.020	0.128	22
Pit Rock (G)	7	0.740	0.014	0.128	17
Diorite Gneiss (F)	7	0.933	0.016	0.142	15
Refractory Gold Ore (I)	7	5.30	0.042	0.335	6
Zinc Plant Tails (H)	7	5.78	0.046	0.406	7

within the parameters measured during the interlaboratory testing of this method.

10.31 Reagents and Materials:

10.31.1 *Blank Reference Sample* (see 10.4.1.2).

10.31.2 *Calcium Carbonate* (see 10.4.1.3).

10.31.3 *Calcium Carbonate Calibration Mixtures*—Transfer 5.00 g and 50.00 g of Calibration Mixture B to ring and puck grinding mills or equivalent devices. Add the amount of dried SiO_2 needed to bring the total mass to 100.0 g in each mill, grind to 100 % passing a No. 100 (150- μm) sieve, pass the mixture through the screen, mix, and store in 250-mL glass bottles. These mixtures contain: 1.00 % and 10.0 % CaCO_3 .

10.31.3.1 Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.31.3.2 Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.31.4 *Calibration Mixture B*—(1 g = 200 mg CaCO_3)—Combine 20.0 g CaCO_3 and 80.0 g SiO_2 in a ring and puck grinding mill or equivalent device. Grind until 100 % passes through a No. 100 (150- μm) sieve, pass the mixture through the screen to break up any lumps, mix, and store in a glass bottle. This mixture contains 20.0 % CaCO_3 .

10.31.4.1 Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.31.4.2 Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.31.5 *Calibration Mixture C*—(1 g = 184 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)—Combine 18.37 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 81.63 g SiO_2 in a ring and puck grinding mill or equivalent device. Grind until 100 % passes through a No. 100 (150- μm) sieve, pass the mixture through the screen to break up any lumps, mix, and store in a glass bottle.

10.31.5.1 Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.31.5.2 Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.31.6 *Acidic Calibration Mixture*—Transfer 10.00 g of Calibration Mixture C to ring and puck grinding mill or equivalent device. Add the amount of dried SiO_2 needed to

bring the total mass to 100.0 g in the mill, grind to 100 % passing a No. 100 (150- μ m) sieve, pass the mixture through the screen, mix, and store in 250-mL glass bottles.

10.31.6.1 Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.31.6.2 Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.31.7 *Ferrous Sulfate, 7 hydrate (FeSO₄·7H₂O)* (99.5 % minimum purity).

10.31.8 *Hydrogen Peroxide (H₂O₂)* (30 %).

10.31.9 *Potassium Hydrogen Phthalate*—Primary standard.

10.31.10 *Phenolphthalein Indicator Solution*—Dissolve 0.2 g of phenolphthalein in 100 mL of ethanol.

10.31.11 *Silica* (see 10.4.1.6).

10.31.12 *Sodium Hydroxide, Standard Solution (NaOH)* (0.500 M).

10.31.12.1 *Preparation*—Dissolve 50 g of NaOH in 50 mL of water and transfer to a large test tube; avoid wetting the top. Stopper tightly and let stand in a vertical position until the supernatant liquid is clear. Carefully withdraw and transfer 20.0 mL of the clear solution to a 1-L volumetric flask containing about 750 mL of freshly boiled and cooled water, dilute to volume with more of the freshly prepared water, and mix. Protect the NaOH solution from CO₂ by means of a soda-lime or soda-mica mineral tube (Ascarite II).

10.31.12.2 *Calibration*—Transfer 2.000 g of primary standard sample of potassium hydrogen phthalate to a 250-mL Erlenmeyer flask. Dissolve in 100 mL of freshly boiled and cooled water. Add 3 drops of phenolphthalein indicator solution and titrate to a faint pink color with the NaOH solution.

10.31.12.3 *Calculation*—Calculate the molarity of the NaOH solution as follows:

$$G = 9.793/H \quad (3)$$

where:

G = concentration of NaOH, M, and

H = volume of titrant, mL.

10.31.12.4 Commercially-produced titrant solutions, which meet these specifications, may also be used.

NOTE 9—The concentration of the titrant must be maintained between 0.495 M–0.505 M NaOH and should be checked weekly.

10.31.13 *Sulfuric Acid High NP Solution (1.00 M H₂SO₄)*—Transfer 53.3 mL of concentrated H₂SO₄ to a 1-L flask, dilute to the mark, and mix. Transfer by pipet, 5-mL of this solution into a 250-mL beaker and standardize against the standard 0.500 M NaOH solution using phenolphthalein as indicator.

10.31.13.1 Commercially-produced standard solutions, which meet these specifications, may also be used.

10.31.14 *Sulfuric Acid Low NP Solution (0.0100 M H₂SO₄)*—Transfer 10-mL of 1.00 M H₂SO₄ to a 1-L volumetric flask, dilute to the mark, and mix.

10.31.14.1 Commercially-produced standard solutions, which meet these specifications, may also be used.

NOTE 10—Use of 0.0100 N H₂SO₄ will result in low results using this method, since the molarity is 0.0050 M H₂SO₄.

10.32 *Preparation of Apparatus:*

TABLE 12 Calibration Mixture 95 % Confidence Limits from Interlaboratory Testing

Mixture	Min, % CaCO ₃	Max, % CaCO ₃
-1.0	-1.28	-0.01
1.0	0.64	1.38
10.0	8.62	12.4
20.0	18.0	23.3
CaCO ₃	92.9	103

10.32.1 Prepare the automatic titrator according to the manufacturer's instructions or use a buret readable to at least ± 0.01 mL in conjunction with a pH meter.

10.33 *Calibration:*

10.33.1 *Apparatus*—Operate and calibrate the automatic titrator or pH meter according to the manufacturer's instructions.

10.33.2 *Laboratory Test Method Performance Demonstration*—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified or method quality control requirements cannot be met using other corrective actions.

10.33.2.1 *Linearity Verification*—Measure acid neutralization potential for the blank reference sample, calibration mixtures, and CaCO₃ in increasing order using the same mass used for test samples following instructions in the Procedure section (10.34) and in accordance with the manufacturer's instructions. Measure the 10.0 % calibration mixture using both the 100-mL addition of 0.0100 M H₂SO₄ and the combined 100-mL addition of 0.0100 M H₂SO₄ and 10-mL of 1.00 M H₂SO₄. Record the calibration mixture masses used, the acid additions and the titration results measured by the instrument or manually. Check for linearity by linear regression of the automatic titrator or manual titration response versus the percent CaCO₃ in the calibration mixtures or by a graphical method. Calibration must meet a deviation less than 10 % relative for each of the calibration material results at or above a content of 1.00 % CaCO₃ and a correlation coefficient of at least 0.99 for both sets of acid additions. Correct any problems with the instrument or manual titration before proceeding with the analysis of test samples.

(1) Linearity may also be verified by the use of FeSO₄ and CaCO₃ masses equivalent to the content of the calibration mixtures.

10.33.2.2 *Blank Sample Precision Verification*—Analyze ten replicates of the blank reference sample. If the standard deviation of the replicate analyses exceeds 0.01 % CaCO₃, correct any instrumental problems and repeat the blank sample precision verification before proceeding with test method implementation.

10.33.2.3 *Low Calibration Mixture Precision Verification*—Analyze four replicates of the 1.00 % calibration mixture. If any result for the 1.00 % calibration mixture exceeds the limits shown in Table 12, correct any instrumental problems and

TABLE 13 Statistical Information—Acid Neutralization Potential, Acidity Corrected (ANPA)

Test Material	Number of Laboratories	ANPA Measured, % CaCO ₃	Min, SD (S _M , Practice E1601)	Reproducibility Index (R, Practice E1601)	R _{rel} %
Hard Rock Mine Waste (A) SRM-2780	8	0.3	0.10	0.89	369
Ottawa Sand (I)	8	0.3	0.01	0.91	291
Disseminated Gold Ore (D) DGPM-1	8	0.5	0.16	0.90	175
Copper Mill Tails (J) SRM-331a	8	2.15	0.11	1.1	51
Refractory Gold Ore (H) SRM-886	8	45.5	0.97	6.83	15
Limestone Waste Rock (C) 502-372	8	57.2	1.5	9.45	17

repeat the low calibration mixture precision verification before proceeding with test method implementation.

10.33.3 Method Quality Control:

10.33.3.1 *Calibration Verification*—Analyze a calibration mixture within each group of fifty test samples. If the calibration mixture result exceeds the limits in **Table 12**, correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.33.3.2 *Blank Reference Sample*—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the range of -1.5 % CaCO₃ to 2.1 % CaCO₃, correct any instrumental or manual titration problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.33.4 *Reference Sample*—Analyze a reference sample, certified for CaCO₃ or neutralization potential, before analysis of test samples and within each group of fifty test samples. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in **Table 13** for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.33.5 *Control Sample*—Analyze the 1.00 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in **Table 12** for the 1.00 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.33.6 *Standard Addition Sample*—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 1.00 % calibration mixture just after weighing the test sample. Calculate the reference values for the standard addition sample by adding 1.00 % to the acid neutralization potential results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in **Table 13** for materials of comparable content, correct any instrumental or manual titration problems and repeat the standard addition sample analysis before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.34 Procedure:

10.34.1 *Test Samples*—Transfer test samples, 1.00 g ± 0.01 g into a 250-mL beaker.

10.34.2 *Duplicate Test Sample*—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in **Table 13** for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from **10.34.1**.

10.34.3 *Digestion*—Add 100 mL of 0.0100 M H₂SO₄, mix, and record the volume and concentration of acid added.

10.34.4 Measure the pH and if the pH > 4, add 10 mL of 1.00 M H₂SO₄, mix, and record the volume and concentration of acid added.

10.34.4.1 Some difficult to digest carbonate minerals may not consume enough acid under the conditions of the first acid addition and digestion and may result in a pH below 4. The user of the method should use the second acid addition whenever the HCl loss carbon exceeds 1 % C for the sample, to assure that all of the carbonate is reacted prior to titration.

10.34.5 Cover the beaker with a watch glass and heat on a water bath at 80 °C for 1 h.

10.34.6 If only 100 mL of 0.0100 M H₂SO₄ has been added, measure the pH, and if the pH > 4, add 10 mL of 1.00 M H₂SO₄, mix, record the volume and concentration of acid added, cover the beaker with a watch glass and heat on a water bath, again, at 80 °C for 1 h.

10.34.7 Filter through a fine porosity filter paper and wash into a 250-mL beaker.

10.34.8 Add 5 mL of 30 % H₂O₂, cover with watch glass and boil for at least 5 min or until the peroxide has been expelled and the final volume can be transferred to a 100-mL volumetric flask, removing the watch glass if necessary to reduce the volume.

10.34.9 Cool to room temperature, transfer to a 100-mL volumetric flask, dilute to mark, and mix.

10.34.10 Analysis:

10.34.10.1 Automatically titrate the solution to the equivalence point for a strong acid titration using the 0.500 M NaOH, in accordance with the automatic titrator manufacturer's instructions and record the results.

TABLE 14 Bias Information—Acid Neutralization Potential, Acidity Corrected (ANPA)

Test Material	Number of Measurements	Reference Acid Neutralization Potential, %, CaCO ₃	ANPA Measured, %, CaCO ₃	Source	Description
NBM-1	8	4.66	4.72	CANMET	Acid Base Accounting Material
KZK-1	8	5.89	5.68	CANMET	Acid Base Accounting Material

NOTE 11—The automatic acidity titration is based on Test Method C of Test Methods **D1067**.

10.34.10.2 Alternatively, titrate the solution manually to obtain an equivalence point of pH 8.3 that remains stable within ± 0.1 pH units for a minimum of 30 s.

10.34.10.3 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in method quality control (**10.33.3**). Measure the acid neutralization potential contents for quality control samples and test samples in reference to the calibrations for the same number of acid additions determined during Linearity Verification (**10.33.2.1**) in percent CaCO₃, according to the automatic titrator manufacturer's instructions or manually in accordance with and record the measurements.

10.34.10.4 Continue analysis until the batch of test samples is completed or a quality control sample or duplicate test sample result deviates more than the limits shown in **Table 13**, for a material of comparable content, taking corrective actions as necessary.

10.35 Calculation:

10.35.1 Calculate the acid to react with the test sample in grams CaCO₃, as follows:

$$I = 100.1 (JK + LM) / 1000 \quad (4)$$

where:

- I* = acid added, g CaCO₃,
- J* = volume (100) dilute acid (0.0100 M) added, mL,
- K* = molarity of dilute acid added, moles/L,
- L* = volume (10.0) of concentrated (1.00 M) acid added, mL, and
- M* = molarity of concentrated acid added.

10.35.1.1 The nominal acid to react is 0.100 g CaCO₃ for the first stage addition and 1.10 g CaCO₃ for the combined addition.

10.35.2 Calculate the residual acid titrated in grams of CaCO₃ as follows:

$$N = -100.1 OP / 2000 \quad (5)$$

where:

- N* = residual acid titrated, g CaCO₃,
- O* = volume NaOH titrant (0.500 M) added, mL, and
- P* = molarity of NaOH titrant added, moles/L.

10.35.3 Calculate the net neutralization potential in grams CaCO₃ in the sample as follows:

$$Q = I + N \quad (6)$$

where:

- Q* = net neutralization potential, g CaCO₃,
- I* = acid added, g CaCO₃, and
- N* = residual acid titrated, g CaCO₃.

10.35.4 Calculate the acid neutralization potential, acidity corrected, in percent CaCO₃ as follows:

$$R = 100Q/S \quad (7)$$

where:

- R* = acid neutralization potential acidity corrected, % CaCO₃,
- Q* = net neutralization potential, grams CaCO₃, and
- S* = test sample mass, g.

10.35.5 Round to the nearest 0.1 % CaCO₃.

NOTE 12—Acidity present detected using this test method should be confirmed using a method performed without acid addition on a larger sample mass (that is, 20 g).

10.35.6 Negative results should be reported and interpreted as acidity present in the samples.

10.36 Precision and Bias:⁸

10.36.1 *Precision*—Eight laboratories cooperated in testing this test method, providing eight sets of data for acid neutralization potential, and obtained the precision data summarized in **Table 13**.

10.36.2 *Bias*—The accuracy of this test method for acid neutralization potential is deemed satisfactory based on the values in **Table 14**. Users are encouraged to employ these or similar reference materials to verify that this test method is performing accurately in their laboratory.

NOTE 13—The user of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of 50 % relative, in accordance with Practice **E1601**. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

ACID NEUTRALIZATION POTENTIAL ACIDITY TITRATION LOW RANGE

10.37 Scope:

10.37.1 This test method covers the determination of acid neutralization potential with acidity correction in metal-bearing ores and related materials such as tailings and waste rock within the range of -1.0 % to 2 % expressed as CaCO₃.

10.38 Summary of Test Method:

10.38.1 A finely ground sample is reacted with a known amount of H₂SO₄, filtered, treated with hydrogen peroxide (H₂O₂) to oxidize the metals present in filtrate, boiled to expel the excess peroxide, and the potential of the sample to neutralize acid is determined by automatic or manual titration of the acid remaining in the filtrate, using standard sodium hydroxide (NaOH).

10.39 Apparatus:

10.39.1 *Automatic Titrator*—Capable of determination of the equivalence point for a strong acid neutralization titration

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1111.

within the parameters measured during the interlaboratory testing of this method.

10.40 *Reagents and Materials:*

10.40.1 *Blank Reference Sample* (see 10.4.1.2).

10.40.2 *Calcium Carbonate* (see 10.4.1.3).

10.40.3 *Calcium Carbonate Calibration Mixtures, Low Range*—Transfer 1.00 g, 5.00 g and 10.0 g of Calibration Mixture A to ring and puck grinding mills or equivalent devices. Add the amount of dried SiO₂ needed to bring the total mass to 100.0 g in each mill, grind to 100 % passing a 150-μm sieve, pass the mixture through the screen, mix and store in 250-mL glass bottles. These mixtures contain: 0.200 %, 1.00 % and 2.00 % CaCO₃.

10.40.3.1 Alternatively, grind the reagents separately, mix, and pass through the screen prior to final mixing.

10.40.3.2 Commercially-produced calibration mixtures, which meet these specifications, may also be used.

10.40.4 *Calibration Mixture B* (see 10.31.4).

10.40.5 *Calibration Mixture C* (see 10.31.5).

10.40.6 *Acidic Calibration Mixture* (see 10.31.6).

10.40.7 *Ferrous Sulfate, 7 hydrate* (see 10.31.7).

10.40.8 *Hydrogen Peroxide* (see 10.31.8).

10.40.9 *Potassium Hydrogen Phthalate* (see 10.31.9).

10.40.10 *Phenolphthalein Indicator Solution* (see 10.31.10).

10.40.11 *Silica* (see 10.4.1.6).

10.40.12 *Sodium Hydroxide, Titrant Solution (NaOH)* (0.100 M).

10.40.12.1 *Preparation*—Dissolve 10 g of NaOH in 50 mL of water and transfer to a large test tube; avoid wetting the top. Stopper tightly and let stand in a vertical position until the supernatant liquid is clear. Carefully withdraw and transfer 20.0 mL of the clear solution to a 1-L volumetric flask containing about 750 mL of freshly boiled and cooled water, dilute to volume with more of the freshly prepared water, and mix. Protect the NaOH solution from CO₂ by means of a soda-lime or soda-mica mineral tube (Ascarite II).

10.40.12.2 *Calibration*—Transfer 2.000 g of primary standard sample of potassium hydrogen phthalate to a 250-mL Erlenmeyer flask. Dissolve in 100 mL of freshly boiled and cooled water. Add 3 drops of phenolphthalein indicator solution and titrate to a faint pink color with the NaOH solution.

10.40.12.3 *Calculation*—Calculate the molarity of the NaOH titrant solution as follows:

$$G = 9.793/H \quad (8)$$

where:

G = concentration of NaOH, M, and

H = volume of titrant, mL.

10.40.12.4 Commercially-produced titrant solutions, which meet these specifications, may also be used.

NOTE 14—The concentration of the titrant must be maintained between 0.095 M–0.105 M NaOH and should be checked weekly.

10.40.13 *Sulfuric Acid Low NP Solution* (see 10.31.14).

NOTE 15—Use of 0.0100 N H₂SO₄ will result in low results using this method, since the molarity is 0.0050 M H₂SO₄.

10.41 *Preparation of Apparatus:*

TABLE 15 Calibration Mixture 95 % Confidence Limits from Interlaboratory Testing

Material	Min., % CaCO ₃	Max., % CaCO ₃
-1.0 % Calibration Mixture	-0.50	-0.04
Blank Reference	-0.01	0.27
0.200 % Calibration Mixture	0.15	0.65
1.00 Calibration Mixture	0.84	1.20
2.00 Calibration Mixture	1.52	2.22

10.41.1 Prepare the automatic titrator according to the manufacturer's instructions or use a buret readable to at least + 0.01 mL in conjunction with a pH meter.

10.42 *Calibration:*

10.42.1 *Apparatus*—Operate and calibrate the automatic titrator or pH meter according to the manufacturer's instructions.

10.43 *Laboratory Test Method Performance Demonstration*—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified or method quality control requirements cannot be met using other corrective actions.

10.43.1 *Linearity Verification*—Measure acid neutralization potential for the blank reference sample, calibration mixtures 0.200 %, 1.00 % and 2.00 % in increasing order using the same mass used for test samples following instructions in the Procedure section (10.44.1) and in accordance with the manufacturer's instructions. Record the reference and calibration mixture masses used, the acid addition and the titration results measured by the instrument or manually. Check for linearity by linear regression of the automatic titrator or manual titration response versus the percent CaCO₃ in the calibration mixtures or by a graphical method. Calibration must meet a deviation less than 30 % relative for each of the calibration material results at a content of 0.200 % CaCO₃, and 10 % relative at a content of 1.00 % and 2.00 % and a correlation coefficient of at least 0.99. Correct any problems with the instrument or manual titration before proceeding with the analysis of test samples.

NOTE 16—Linearity may also be verified by the use of CaCO₃ masses equivalent to the content of the calibration mixtures.

10.43.2 *Blank Sample Precision Verification*—Analyze ten replicates of the blank reference sample. If the standard deviation of the replicate analyses exceeds 0.015 % CaCO₃, correct any instrumental problems and repeat the blank sample precision verification before proceeding with test method implementation.

10.43.3 *Low Calibration Mixture Precision Verification*—Analyze four replicates of the 0.200 % calibration mixture. If any result for the 0.200 % calibration mixture exceeds the limits shown in Table 15, correct any instrumental problems and repeat the low calibration mixture precision verification before proceeding with test method implementation.

10.43.4 *Method Quality Control:*

TABLE 16 Statistical Information—Acid Neutralization Potential, Acidity Corrected Low Range (ANPA)

Test Material	Number of Laboratories	ANPA Measured, % CaCO ₃	Min, SD (S _M , Practice E1601)	Reproducibility Index (R, Practice E1601)	R _{reb} %
Highly Acidic Waste Rock (P)	6	-0.543	0.0162	0.575	-105
Ottawa Sand (D)	6	0.140	0.0161	0.297	212
SRM-2780 Hard Rock Mine Waste (L)	6	0.202	0.0303	0.284	141
DGPM-1 Pinson Gold Ore (N)	6	0.432	0.0185	0.218	51
SRM 330a Copper Leach Head (O)	6	0.605	0.0384	0.344	57
SRM-331a Copper Mill Tails (M)	7	1.09	0.030	0.220	20

10.43.4.1 *Calibration Verification*—Analyze a calibration mixture within each group of fifty test samples. If the calibration mixture result exceeds the limits in [Table 15](#), correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.43.4.2 *Blank Reference Sample*—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the range shown in [Table 15](#), correct any instrumental or manual titration problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.43.4.3 *Reference Sample*—Analyze a reference sample, certified for CaCO₃ or neutralization potential, before analysis of test samples and within each group of fifty test samples. If the difference of the reference sample and the reference value for the reference sample exceeds the reproducibility limits shown in [Table 16](#) for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.43.4.4 *Control Sample*—Analyze the 0.200 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in [Table 15](#), correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.43.4.5 *Standard Addition Sample*—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.200 % calibration mixture just after weighing the test sample. Calculate the reference values for the standard addition sample by adding 0.200 % to the acid neutralization potential results for the test

sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the reproducibility limits shown in [Table 16](#) for materials of comparable content, correct any instrumental or manual titration problems and repeat the standard addition sample analysis before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.44 Procedure:

10.44.1 *Test Samples*—Transfer test samples, 5.00 g + 0.01 g into a 250-mL beaker.

10.44.2 *Duplicate Test Sample*—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the reproducibility limits shown in [Table 16](#) for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from [10.44.1](#).

10.44.3 *Digestion*—Add 100 mL of 0.0100 M H₂SO₄, mix, and record the volume and concentration of acid added.

10.44.4 Measure the pH and if the pH > 4, discard the sample and proceed from [10.34.1](#) using the 1.00 g sample mass.

10.44.5 Cover the beaker with a watch glass and heat on a water bath at 80 °C for 1 h.

10.44.6 Measure the pH and if the pH > 4, discard the sample and proceed from [10.34.1](#) using the 1.00 g sample mass.

10.44.7 Filter through a fine porosity filter paper and wash into a 250-mL beaker.

10.44.8 Add 5 mL of 30 % H₂O₂, cover with watch glass and boil for at least 5 min or until the peroxide has been expelled and the final volume can be transferred to a 100-mL volumetric flask, removing the watch glass if necessary to reduce the volume.

10.44.9 Cool to room temperature, transfer to a 100-mL volumetric flask, dilute to mark, and mix.

10.44.10 Analysis:

10.44.10.1 Automatically titrate the solution to the equivalence point for a strong acid titration using the 0.100 M NaOH, in accordance with the automatic titrator manufacturer's instructions and record the results.

NOTE 17—The automatic acidity titration is based on Test Method C of Test Methods [D1067](#).

(1) Alternatively, titrate the solution manually to obtain an equivalence point of pH 8.3 that remains stable within + 0.1 pH units for a minimum of 30 s.

10.44.10.2 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in method quality control ([10.43.4](#)). Measure the acid neutralization potential contents for quality control samples and test samples in reference to the calibrations for the same number of acid additions determined during Linearity Verification ([10.43.1](#)) in percent CaCO₃, according to the

automatic titrator manufacturer's instructions or manually in accordance with 10.44.10.1(*I*) and record the measurements.

10.44.10.3 Continue analysis until the batch of test samples is completed or a quality control sample or duplicate test sample result deviates more than the limits shown in Table 15, for a material of comparable content, taking corrective actions as necessary.

10.45 Calculation:

10.45.1 Calculate the acid to react with the test sample in grams CaCO₃, *I*, as follows:

$$I = 100.1(JK)/1000 \quad (9)$$

where:

J = volume (100) dilute acid (0.0100 M) added, mL, and

K = molarity of dilute acid added, moles/L.

10.45.2 Calculate the residual acid titrated in grams of CaCO₃, *N*, as follows:

$$N = -100.1(OP)/2000 \quad (10)$$

where:

O = volume NaOH titrant (0.100 M) added, mL, and

P = molarity of NaOH titrant added, moles/L.

10.45.3 Calculate the net neutralization potential in grams CaCO₃, *Q*, in the sample as follows:

$$Q = 1 + N \quad (11)$$

where:

I = acid added, g CaCO₃, and

N = residual acid titrated, g CaCO₃.

10.45.4 Calculate the acid neutralization potential, acidity corrected, in percent CaCO₃, *R*, as follows:

$$R = 100Q/S \quad (12)$$

where:

Q = net neutralization potential, g CaCO₃, and

S = test sample mass, g.

10.45.5 Round to the nearest 0.1 % CaCO₃.

NOTE 18—Acidity present detected using this test method should be confirmed using a method performed without acid addition on a larger sample mass (that is, 20 g). Negative results should be reported and interpreted as acidity present in the samples.

10.46 Precision and Bias:⁹

10.46.1 *Precision*—Seven laboratories cooperated in testing this test method, providing seven sets of data for acid neutralization potential for SRM-331a Copper Mill Tails and six sets of data for the other materials, and obtained the precision data summarized in Table 16.

10.46.2 *Bias*—No suitable certified reference materials were available to cover the test range when the interlaboratory study was undertaken. Users are encouraged to employ these or similar reference materials to verify that this test method is performing accurately in their laboratory.

NOTE 19—The user of this test method is cautioned that the method

may not be quantitative for reporting above a reproducibility index (*R*) of 50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

NITRIC ACID INSOLUBLE SULFUR

10.47 *Scope*—This test method covers the determination of HNO₃ insoluble sulfur contents in the range of 0.006 % to 0.924 %.

10.48 Summary of Test Method:

10.48.1 The test sample is partially decomposed with HNO₃ prior to instrumental analysis, where the sulfur in the test sample is converted to sulfur dioxide by combustion in a stream of oxygen.

10.48.2 The amount of sulfur dioxide is measured by infrared absorption.

10.49 Apparatus:

10.49.1 *Combustion-Infrared Spectrophotometer*, equipped with a combustion chamber, oxygen carrier stream, and infrared absorption detector, suitable for analysis of sulfur in a minimum range instrument from 0.1 % to 1.75 % or in a maximum range instrument from 0.1 % to 8.8 %, using 0.2-g test portions of ores and related materials. Instruments, such as those shown in Test Methods E1019 that can be shown to give equivalent results may also be used for these test methods.

10.50 Reagents and Materials:

10.50.1 Reagents:

10.50.1.1 *Barium Sulfate* (see 10.4.1.1).

10.50.1.2 *Blank Reference Sample* (see 10.4.1.2).

10.50.1.3 *Calcium Carbonate* (see 10.4.1.3).

10.50.1.4 *Calibration Mixture A* (see 10.4.1.4).

10.50.1.5 *Calibration Mixtures* (see 10.4.1.5).

10.50.1.6 *Silica* (see 10.4.1.6).

10.50.1.7 *Tungstic Acid* (see 10.4.1.7).

10.50.1.8 *Vanadium Pentoxide* (see 10.4.1.8).

10.50.2 Materials:

10.50.2.1 *Crucibles or boats*, suitable for combustion analyses.

10.50.2.2 *Glass Filters*—Fine-porosity glass micro filters, carbon content must be less than 0.15 %, sulfur content must be less than 0.05 % and the filter mass must be less than 0.2 g.

10.50.2.3 Filtering crucibles may also be used if they are shown to provide equivalent results.

10.51 Calibration and Standardization:

10.51.1 *Apparatus*—Operate and calibrate the instrument in accordance with the manufacturer's instructions. Resistance furnace instruments require the use of V₂O₅ or H₂WO₄ for the determination of sulfur in this test method. Use a 0.200 g ± 0.01 g mass for all calibration mixtures, reference materials, blank reference materials, test samples, and diluted test samples in this test method.

10.51.1.1 Certain instruments may require different sample masses for certain content ranges, which is permissible as long as the precision and bias requirements of these test methods are fulfilled.

10.51.2 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at 550 °C ± 10 °C.

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1119.

10.51.3 Laboratory Test Method Performance Demonstration—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified. Carry out the performance demonstration as described in [10.5.3](#).

10.51.4 Method Quality Control:

10.51.4.1 Calibration Verification—Analyze a calibration mixture with a content greater than or equal to 0.5 % sulfur prior to and within each group of fifty test samples. If the calibration mixture result exceeds the limits in [Table 1](#), correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

10.51.4.2 Blank Reference Sample—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the limits in [Table 1](#) for the 0.0 % calibration mixture, correct any instrumental problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.51.4.3 Reference Sample—Analyze a reference sample, certified for total sulfur, before analysis of test samples for and within each group of fifty test samples and a reference sample certified for HNO₃ insoluble sulfur, if available. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in [Table 1](#) for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.51.4.4 Control Sample—Analyze the 0.2 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in [Table 1](#) for the 0.2 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.51.4.5 Standard Addition Sample—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.5 % calibration mixture just prior to determination of carbon and sulfur. Calculate the reference values for the standard addition sample by adding 0.5 % to the carbon and sulfur results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in [Table 1](#) for materials of comparable content, correct any instrumental problems and repeat the standard addition sample analysis before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

NOTE 20—Add the 0.5 % calibration mixture after the HNO₃ decomposition procedure but before the analysis step.

10.52 Interferences:

10.52.1 The elements normally present in ores and related materials do not interfere with this test method.

10.53 Procedure:

10.53.1 Ignite the crucibles or boats for test samples and standard samples in a muffle furnace for 1 h at 550 °C ± 10 °C (see [10.7.1](#)).

10.53.2 Test Samples—Transfer test samples, diluted test samples, reference samples for HNO₃ insoluble sulfur, and standard addition samples using 0.200 g ± 0.01 g into a 150-mL beaker and record the mass.

10.53.3 Decomposition—Add 25 mL of HNO₃ (1 + 4) to the beaker and let stand at room temperature for 30 min Cover with a watch glass and place the beaker on a hot plate and gently boil for 10 min Cool.

10.53.4 Filtration—Filter through a glass filter, wash with water at least three times and discard filtrate, and dry.

10.53.5 Transfer filter and solids to the crucible or boat used for instrumental analysis. Use of a different sample mass may be required on some instruments for some samples (see [10.51.1.1](#)). Add the calibration mixture portion for the standard addition sample after digestion, mix.

10.53.6 Duplicate Test Sample—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in [Table 1](#), for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analysis from [10.53.2](#).

10.53.7 Analysis:

10.53.7.1 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in [10.53.2](#). Measure the sulfur contents for quality control samples, test samples and diluted test samples in percent in accordance with the instrument manufacturer's instructions and record the measurements.

10.53.7.2 Continue analysis until the batch of test samples is completed, or a quality control sample or duplicate test sample result deviates more than the limits shown in [Table 1](#), for a material of comparable content. If the difference of the results exceeds the limits shown in [Table 1](#) for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems, and repeat the analyses from [10.53.2](#).

10.54 Calculation:

10.54.1 Calculate the HNO₃ insoluble sulfur contents for the test samples in accordance with the manufacturer's instructions.

10.54.2 Calculate the HNO₃ loss sulfur, % *T*, as follows:

$$T = U - V \quad (13)$$

where:

U = HCl insoluble sulfur result, %

V = HNO₃ insoluble sulfur result, %

TABLE 17 Statistical Information Nitric Acid Insoluble Sulfur

Test Material	Number of Laboratories	Sulfur Found, %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{reb} %
Ottawa Sand (D)	6	0.0064	0.005	0.027	91
Diorite Gneiss (F)	6	0.011	0.007	0.032	303
Reclamation Tails (C)	6	0.069	0.007	0.281	407
Refractory Gold Ore (I)	6	0.079	0.007	0.289	367
Pit Rock (G)	6	0.104	0.013	0.242	234
Autoclave Feed Ore	6	0.105	0.016	0.318	303
Vinini Waste Rock (E)	6	0.109	0.024	0.417	381
Inert Diorite (K)	5	0.120	0.013	0.073	61
Zinc Plant Tails (H)	6	0.212	0.038	1.19	560
Duluth Waste Rock	6	0.924	0.050	1.20	129

TABLE 18 Statistical Information Nitric Acid Loss Sulfur

Test Material	Number of Laboratories	Sulfur Found %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{reb} %
Duluth Waste Rock (B)	6	-0.080	0.091	0.904	-1137
Ottawa Sand (D)	6	-0.003	0.005	0.003	-106
Diorite Gneiss (F)	6	-0.001	0.007	0.004	-301
Inert Diorite (K)	5	0.031	0.015	0.107	344
Pit Rock (G)	6	0.150	0.044	0.183	122
Vinini Waste Rock (E)	6	0.534	0.036	0.560	105
Refractory Gold Ore (I)	6	1.19	0.035	1.33	112
Zinc Plant Tails (H)	6	2.93	0.208	4.99	170
Reclamation Tails (C)	6	2.91	0.200	1.85	64
Autoclave Feed Ore (A)	6	4.19	0.116	0.828	20

10.54.3 Round the results to the nearest 0.01 % and record as HNO₃ insoluble sulfur, or HNO₃ loss sulfur, at or above the lower scope limit established during interlaboratory testing. Enclose results below the lower scope limits in parentheses and below the null limit followed by an asterisk, in accordance with Practice E1950.

10.54.4 *Over-Range Results*—If the sulfur result exceeds 1.75 % for the minimum range instrument, discard the result and repeat the procedure from with the diluted sample. Multiply the diluted test sample result by five and round to the nearest 0.1 %.

10.54.4.1 Alternatively, use a lower sample mass for the analysis as specified in 10.51.1.1.

10.55 *Precision and Bias*:¹⁰

10.55.1 *Precision*—Six laboratories cooperated in testing this test method providing ten sets of data for sulfur and obtained the precision data summarized in Table 17 and Table 18.

10.55.2 *Bias*—No information on the bias of this test method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

NOTE 21—The use of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of 50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

SODIUM CARBONATE INSOLUBLE SULFUR

10.56 *Scope*—This test method covers the determination of sodium carbonate insoluble sulfur contents in the range of 0.007 % to 3.78 %.

10.57 *Summary of Test Method*:

¹⁰ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1040.

10.57.1 The test sample is partially decomposed with sodium carbonate prior to instrumental analysis, where the sulfur in the test sample is converted to sulfur dioxide by combustion in a stream of oxygen.

10.57.2 The amount of sulfur dioxide is measured by infrared absorption.

10.58 *Apparatus*:

10.58.1 *Combustion-Infrared Spectrophotometer*; equipped with a combustion chamber, oxygen carrier stream and infrared absorption detector, suitable for analysis of sulfur in a minimum range instrument from 0.1 % to 1.75 % or in a maximum range instrument from 0.1 % to 8.8 %, using 0.2-g test portions of ores and related materials. Instruments, such as those shown in Test Methods E1019 that can be shown to give equivalent results may also be used for these test methods.

10.59 *Reagents and Materials*:

10.59.1 *Reagents*:

10.59.1.1 *Barium Sulfate* (see 10.4.1.1).

10.59.1.2 *Blank Reference Sample* (see 10.4.1.2).

10.59.1.3 *Calcium Carbonate* (see 10.4.1.3).

10.59.1.4 *Calibration Mixture A* (see 10.4.1.4).

10.59.1.5 *Calibration Mixtures* (see 10.4.1.5).

10.59.1.6 *Silica* (see 10.4.1.6).

10.59.1.7 *Sodium Carbonate Solution (10 %)*—Transfer 100 g of sodium carbonate (purity 99.0 % minimum) to 500 mL of water in a 1-L volumetric flask. Dilute to the mark and mix.

10.59.1.8 *Tungstic Acid* (see 10.4.1.7).

10.59.1.9 *Vanadium Pentoxide* (see 10.4.1.8).

10.59.2 *Materials*:

10.59.2.1 *Crucibles or boats*, suitable for combustion analyses.

10.59.2.2 *Glass Filters*—Fine-porosity glass micro filters, carbon content must be less than 0.15 %, sulfur content must be less than 0.05 % and the filter mass must be less than 0.2 g.

10.59.2.3 Filtering crucibles may also be used if they are shown to provide equivalent results.

10.60 *Calibration and Standardization*:

10.60.1 *Apparatus*—Operate and calibrate the instrument in accordance with the manufacturer's instructions. Resistance furnace instruments require the use of V_2O_5 or H_2WO_4 for the determination of sulfur in this test method. Use a $0.200\text{ g} \pm 0.01\text{ g}$ mass for all calibration mixtures, reference materials, blank reference materials, test samples, and diluted test samples in this test method.

10.60.1.1 Certain instruments may require different sample masses for certain content ranges, which is permissible as long as the precision and bias requirements of these test methods are fulfilled.

10.60.2 Ignite the crucibles or boats for test samples and standardization samples in a muffle furnace for 1 h at $550\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$.

10.60.3 *Laboratory Test Method Performance Demonstration*—A demonstration of laboratory test method performance must be performed before this test method may be used in a laboratory for the first time. This demonstration is particularly important if the laboratory needs to modify the test method in any way. The demonstration must be repeated whenever the test method is significantly modified. Carry out the performance demonstration as described in 10.5.3.

10.60.4 *Method Quality Control*:

10.60.4.1 *Calibration Verification*—Analyze a calibration mixture with a content greater than or equal to 0.5 % sulfur prior to and within each group of fifty test samples. If the calibration mixture result exceeds the limits in Table 1, correct any instrumental problems and repeat the linearity verification before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

10.60.4.2 *Blank Reference Sample*—Analyze a blank reference sample before analysis of test samples and within each group of fifty test samples. If the result for the blank reference sample exceeds the limits in Table 1 for the 0.0 % calibration mixture, correct any instrumental problems and repeat the analysis of the blank reference sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.60.4.3 *Reference Sample*—Analyze a reference sample, certified for total sulfur, before analysis of test samples for and within each group of fifty test samples and a reference sample certified for sodium carbonate insoluble sulfur, if available. If the difference of the reference sample and the reference value for the reference sample exceeds the limits shown in Table 1 for materials of comparable content, correct any instrumental problems and repeat the analysis of the reference material and discard the results since the last acceptable quality control sample result had been obtained.

10.60.4.4 *Control Sample*—Analyze the 0.2 % calibration mixture prior to and within each group of fifty test samples. If the result for the control sample exceeds the limits shown in Table 1 for the 0.2 % calibration mixture, correct any instrumental problems and repeat the analysis of the control sample before proceeding with analysis of test samples and discard the results since the last acceptable quality control sample result had been obtained.

10.60.4.5 *Standard Addition Sample*—Analyze a standard addition sample prior to analysis of each group of fifty test samples by preparing a duplicate of the first test sample in the group and adding an equal mass of the 0.5 % calibration mixture just prior to determination of carbon and sulfur. Calculate the reference values for the standard addition sample by adding 0.5 % to the carbon and sulfur results for the test sample performed without the standard addition and divide the sum by two. If the difference of any result for the standard addition sample and the reference value exceeds the limits shown in Table 1 for materials of comparable content, correct any instrumental problems and repeat the standard addition sample analysis before proceeding with analysis of test samples, and discard the results since the last acceptable quality control sample result had been obtained.

NOTE 22—Add the 0.5 % calibration mixture after the sodium carbonate decomposition procedure but before the analysis step.

10.61 *Interferences*:

10.61.1 The elements normally present in ores and related materials do not interfere with this test method.

10.62 *Procedure*:

10.62.1 Ignite the crucibles or boats for test samples and standard samples in a muffle furnace for 1 h at $550\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$ (see 10.7.1).

10.62.2 *Test Samples*—Transfer test samples, diluted test samples, reference samples for sodium carbonate insoluble sulfur, and standard addition samples using $0.200\text{ g} \pm 0.01\text{ g}$ into a 150-mL beaker and record the mass.

10.62.3 *Decomposition*—Add 25 mL of sodium carbonate solution (10.59.1.7) to the beaker, place the beaker on a hot plate, and gently boil for 30 min. Cool.

10.62.4 *Filtration*—Filter through a glass filter, wash with water at least three times and discard filtrate, and dry.

10.62.5 Transfer filter and solids to the crucible or boat used for instrumental analysis. Use of a different sample mass may be required on some instruments for some samples (see 10.60.1.1). Add the calibration mixture portion for the standard addition sample after digestion, mix.

10.62.6 *Duplicate Test Sample*—Analyze a duplicate test sample within each group of fifty test samples. If the difference of the duplicate results exceeds the limits shown in Table 1, for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problem and repeat the analyses from 10.62.2.

10.62.7 *Analysis*:

10.62.7.1 Analyze quality control samples before each batch of test samples and within each group of ten test samples as directed in 10.60.4. Measure the sulfur contents for quality control samples, test samples and diluted test samples in percent in accordance with the instrument manufacturer's instructions and record the measurements.

10.62.7.2 Continue analysis until the batch of test samples is completed, or a quality control sample or duplicate test sample result deviates more than the limits shown in Table 1, for a material of comparable content. If the difference of the results

TABLE 19 Statistical Information Sodium Carbonate Insoluble Sulfur

Test Material	Number of Laboratories	Sulfur Found %	Min, SD (S_M , Practice E1601)	Reproducibility Index (R , Practice E1601)	R_{reb} %
Ottawa Sand (D)	6	0.004	0.001	0.012	343
Diorite Gneiss (F)	6	0.013	0.006	0.037	284
Inert Diorite (K)	5	0.099	0.018	0.062	63
Pit Rock (G)	6	0.233	0.007	0.201	86
Vinini Waste Rock (E)	6	0.594	0.037	0.210	35
Refractory Gold Ore (I)	6	0.878	0.077	0.291	33
Duluth Waste Rock (B)	6	0.134	0.047	0.43	32
Zinc Plant Tails (H)	6	2.18	0.092	2.77	127
Reclamation Tails (C)	6	3.06	0.076	1.11	36
Autoclave Feed Ore (A)	6	3.78	0.11	0.99	26

exceeds the limits shown in Table 1 for a material of comparable content, discard the results since the last acceptable quality control sample result had been obtained, correct any sample preparation or instrumental problems and repeat the analyses from 10.62.2.

10.63 Calculation:

10.63.1 Calculate the sodium carbonate insoluble sulfur contents for the test samples in accordance with the manufacturer’s instructions.

10.63.2 Round the results to the nearest 0.01 % and record as sodium carbonate insoluble sulfur, at or above the lower scope limit established during interlaboratory testing. Enclose results below the lower scope limits in parentheses and below the null limit followed by an asterisk, in accordance with Practice E1950.

10.63.3 Over-Range Results—If the sulfur result exceeds 1.75 % for the minimum range instrument, discard the result and repeat the procedure from 10.62.2 with the diluted sample. Multiply the diluted test sample result by five and round to the nearest 0.1 %.

10.63.3.1 Alternatively, use a lower sample mass for the analysis as specified in 10.60.1.1.

10.64 Precision and Bias:¹¹

10.64.1 Precision—Six laboratories cooperated in testing this test method, providing ten sets of data for sulfur, and obtained the precision data summarized in Table 19.

10.64.2 Bias—No information on the bias of this test method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

NOTE 23—The user of this test method is cautioned that the method may not be quantitative for reporting above a reproducibility index (R) of

¹¹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1040.

TABLE 20 Semi-Quantitative Mineralogical Analysis of Carbon Minerals in Test Materials, %

Test Material	Calcite	Dolomite	Siderite
Autoclave Feed Ore (A)	1
Duluth Waste Rock (B)	2
Reclamation Tails (C)	2	1	...
Ottawa Sand (D)
Vinini Waste Rock (E)	10
Diorite Gneiss (F)	7
Pit Rock (G)	2	1	2
Zinc Plant Tails (H)	16	44	...
Refractory Gold Ore (I)	24	26	...
Inert Andesite (J)
Inert Diorite (K)

50 % relative, in accordance with Practice E1601. The user is advised to take this into account, in addition to the mineralogy of the sample, when interpreting the results for this test method.

11. Interpretation of Results

11.1 Carbon and Sulfur Mineral Phase Estimation—The mineralogy of the samples must be known in order to properly select the methods needed to estimate the carbon and sulfur mineral phase contents. Mineralogical methods may include X-ray diffraction combined with chemical characterization, petrography and microprobe methods. Semi-quantitative mineralogical compositions of the test materials determined by X-ray diffraction combined with chemical characterization are presented in Table 20 for the carbon minerals and Table 21 for the sulfur minerals.

11.1.1 Carbonate Carbon—In the absence of organic forms of carbon, the total carbon may be used to estimate the content of carbonate carbon. Samples obtained by drilling, however, are typically contaminated with oils from drilling and the HCl loss carbon normally will provide the best carbonate carbon estimate for these samples. The HCl loss should be used for estimating carbonate carbon in samples containing naturally occurring organic carbon. Pyrolysis residual carbon may be used to estimate carbonate carbon in the absence of naturally occurring organic carbon, but the results may be biased low, due to losses of carbonate minerals during pyrolysis.

11.1.2 Organic Carbon—In the absence of carbonate forms of carbon, total carbon may be used to estimate organic carbon. The HCl residual carbon is normally the best estimate of organic carbon content in ores and related materials. The content of organic carbon in gold ores may be a very important metallurgical parameter for gold ore control, as some organic carbon forms may result in gold losses by activated adsorption of gold cyanide complexes during ore processing operations.

11.1.3 Sulfate Sulfur—In the absence of sulfide forms of sulfur, the total sulfur may be used to estimate the content of sulfate sulfur. The pyrolysis residual sulfur may be the best estimate of sulfate sulfur in the presence of barite, alunite, jarosite, since these sulfate forms are not readily dissolved by sodium carbonate and in the presence of orpiment and realgar, since these sulfide minerals are soluble in sodium carbonate. The sodium carbonate sulfur loss may be the best estimate of sulfate sulfur in the presence of metal sulfide minerals other than iron sulfides, which may not be lost by pyrolysis and the absence of barite, alunite, orpiment, and realgar.

TABLE 21 Semi-Quantitative Mineralogical Analysis of Sulfur Minerals in Test Materials, %

Test Material	Gypsum	Pyrite
Autoclave Feed Ore (A)	...	9
Duluth Waste Rock (B)	...	2
Reclamation Tails (C)	1	7
Ottawa Sand (D)
Vini ni Waste Rock (E)	...	1
Diorite Gneiss (F)
Pit Rock (G)
Zinc Plant Tails (H)	...	5
Refractory Gold Ore (I)	...	3
Inert Andesite (J)
Inert Diorite (K)

11.1.4 *Sulfide Sulfur*—In the absence of sulfate forms of sulfur, total sulfur may be used to estimate the sulfide sulfur content. The pyrolysis loss sulfur may be the best estimate of sulfide sulfur, particularly where the acid generation potential due to iron sulfides is desired. The HNO₃ loss method may be appropriate where the sulfide forms are primarily pyrite and marcasite and pyrrhotite is absent, since pyrrhotite may react with acid. The sodium carbonate insoluble sulfur method is most appropriate where the content of metal sulfide minerals in addition to iron are desired in the absence of barite, alunite, jarosites, orpiment, and realgar.

NOTE 24—Classical acid-base accounting is based on the use of total sulfur to estimate acid generating potential, and it is not appropriate in the presence of sulfate minerals because it results in a higher bias in acid generation estimation. Where sulfate minerals and non-carbonate acid neutralizing minerals are present, use of the acid-base classification method presented in 11.2 is preferred.

11.2 *Acid Base Classification*—Ores and related materials may be classified according to their acid-base characteristics by estimating the ANP from the carbonate carbon content or acid neutralization potential acidity titration result and AGP from the sulfide sulfur content, which may be balanced in units of NCC percentage. Although there is imprecision in the individual estimates, the classifications provide a method to control materials according to their relative acid-base classification during active mining. Traditional acid-base accounting uses only three classifications, acid producing (normally includes slightly acidic to highly acidic NCC classifications), non acid producing (normally includes some basic and highly basic NCC classifications) and uncertain (generally includes inert, neutral, slightly basic and some basic NCC classifications).

11.2.1 *Acid Neutralization Potential*—Calculate the ANP in CaCO₃ percentage by multiplying the carbonate carbon percentage as carbon by 8.33 or use the acid neutralization potential acidity titration result. The acid neutralization potential low range method (ANPAL) may be useful where the content of carbonate carbon is less than 2% CaCO₃, uncertainty of NP estimation is of concern, neutralization potential ratios are not providing meaningful values, potentially acidic minerals are present, or where there is a potential for acid consumption by aluminosilicate minerals. Correct any negative values to zero. In classical acid base accounting, this is referred to neutralization potential (NP) and is expressed in tons of calcium carbonate per thousand tons of material. Convert ANP to NP by multiplying ANP by 10.

11.2.1.1 *Modal Mineralogy*—Use of modal mineralogy determined by the technique of mineral liberation analysis may be useful to identify trace minerals in test materials. Please see Table 22 for the results of modal mineralogy on the materials used in the interlaboratory testing of the acid neutralization potential low range method.

11.2.2 *Acid Generation Potential*—Calculate the AGP in CaCO₃ percentage by multiplying the sulfide sulfur percentage as sulfur by -3.10. Correct any positive values to zero. In classical acid base accounting this is referred to acid potential (AP) and is expressed in tons of CaCO₃ per thousand tons of material. Convert AGP to AP by multiplying AGP by 10.

11.2.3 *Net Calcium Carbonate*—Calculate the NCC percentage by adding the acid generation potential to the acid neutralization potential. In classical acid base accounting this is referred to net neutralization potential (NNP) and is expressed in tons of CaCO₃ per thousand tons of material. Convert NCC to NNP by multiplying NCC by 10.

11.2.4 Classify the materials by acid-base classification as follows:

Classification	Specifications
Highly Acidic	NCC ≤ -10
Acidic	-10 < NCC ≤ -2
Slightly Acidic	-2 < NCC ≤ -0.2
Neutral	-0.2 < NCC < 0.2 and AGP ≤ -0.2 or ANP ≥ 0.2
Inert	-0.2 < NCC < 0.2 and AGP > -0.2 and ANP < 0.2
Slightly Basic	0.2 ≥ NCC < 2.0
Basic	2.0 ≥ NCC < 10
Highly Basic	NCC ≥ 10

11.2.4.1 The inert classification represents materials that are near the quantitation limits for both ANP (~0.2 % CaCO₃) and AGP (-0.2 CaCO₃). The neutral classification differs in that either ANP or AGP, or both, have significant contents and offset each other within the ability to quantify their contents.

11.3 *Acid-Base Classification Confirmation and Testing*—It is recommended that each acid-base classification be confirmed for each geological (lithology and alteration) or metallurgical (ore, leach residue, and tailings type) classification in the ore deposit, where the geological or metallurgical and acid-base classification constitute a significant (> 5 %) proportion of the ore deposit to be mined and also for minor classifications which may have a significant environmental impact. Confirmation testing should be conducted on composites prepared from the analytical samples within the geological or metallurgical acid-base classification limits or from re-sampling of zones defined by the geological or metallurgical and acid-base classification. Confirmation testing should include:

11.3.1 Mineralogical analysis for identification of carbonate and sulfide minerals and their morphology;

11.3.2 Alternate carbonate carbon, sulfide sulfur and acid neutralization potential test methods to select the optimum method for routine use;

11.3.3 An interlaboratory study of the test methods selected for routine use in accordance with Practice E1601;

11.3.4 Kinetic test methods such as the biological acid production potential (Appendix X1), net acid generation (NAG), humidity cells in accordance with Test Method D5744, and site weathering columns or piles, or both;

TABLE 22 Modal Mineralogy of Interlaboratory Test Materials

Material	Highly Acidic Waste Rock (P)	Ottawa Sand (D)	SRM-2780 Hard Rock Mine Waste (L)	DGPM-1 Pinson Gold Ore (N)	SRM 330a Copper Leach Head (O)	SRM-331a Copper Mill Tails (M)
Carbonate Minerals						
Calcite, %	0.4		<0.01			0.1
Potentially Acid Containing Sulfate Minerals						
Jarosite, %	0.03	<0.01	0.4	3	<0.01	
Potentially Acid Consuming Aluminosilicate Minerals						
Biotite, %	0.7		1	0.04	4.4	7.7
Chlorite, %	0.7	0.03	2.1	1.1	2.2	3.6
Illite, %	4.2	0.01	37.7	14.9	6	2.2
Kaolinite, %			<0.01	0.1	<0.001	
Magnesiohornblende, %				0.1		0.1
Orthoclase, %	0.2	0.1	0.7	5.2	36.5	0.1
Plagioclase, %	0.2	<0.001	0.1	0.1	5	47.2
Pyrophyllite, %	3.5		1.1	1.2	0.5	0.02
Spessartine, %			0.1			

11.3.5 Meteoric water mobility procedure (MWMP) in accordance with Test Method E2242 or synthetic precipitation leaching procedure (SPLP) Test Method D6234; and

11.3.6 Elemental characterization of the composites for toxic release inventory (TRI) elements including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, and zinc, using methods that provide the lowest limits of detection.

11.4 *Use of Acid-Base Classification Confirmation and Testing Results*—The results of the testing program should be used on a site specific basis to develop economic criteria for engineering design of the ore and waste management facilities. Site specific criteria need to be developed to segregate the ore and waste for routing to the proper facilities during active mining and processing based on the acid-base classification confirmation and testing results, which is outside the scope of

these methods. Use of the classification system to select materials for testing assures that materials being tested covers the range of acid-base characteristics for each of the geological units for ore and waste. It is recommended that the methods used for routing ore and waste during active mining and processing be selected from these methods based on the material mineralogy and any additional methods which are necessary to account for any acidic salts and other ore and waste characteristics necessary to support efficient operations and environmental compliance.

12. Keywords

12.1 acid neutralization potential; carbonate carbon content; carbon content; net calcium carbonate content; ores; organic carbon content; related materials; sulfate sulfur content; sulfide sulfur content; sulfur content; tailings; leach residue; waste rock

APPENDIXES

(Nonmandatory Information)

X1. BIOLOGICAL ACID PRODUCTION POTENTIAL TESTING

X1.1 The biological acid production potential testing is based on the BC Research Confirmation Testing Method.¹² The method has been modified to use the same analytical samples used in the acid-base classification testing.

X1.2 Procedure

X1.2.1 Pulverize (shatterbox) the ore or waste sample.

X1.2.2 Dry the pulverized sample overnight at 105 °C or less.

X1.2.3 Place duplicate 30 g portions, or smaller amounts if the sulfide content exceeds 2 %, in 250-mL Erlenmeyer flasks

with 70 mL of BAPP nutrient medium¹³ containing 3 g/L ammonium sulphate ((NH₄)₂SO₄), 0.10 g/L potassium chloride (KCl), 0.5 g/L potassium hydrogen phosphate (K₂HPO₄), 0.50 g/L magnesium sulfate heptahydrate (MgSO₄ · 7H₂O), and 0.1 g/L calcium nitrate (Ca(NO₃)₂).

X1.2.4 Add sufficient H₂SO₄ to bring the pH to 2.5.

X1.2.5 Place flask on shaker for 4 h and recheck pH. If necessary, add additional acid until the pH remains about 2.5.

X1.2.6 Inoculate each flask with 5 mL of an active culture of *T. ferrooxidans*.

¹² BC Research Report Project 1499 for the Department of Environment, July 24, 1972.

¹³ Bruynesteyn, A., and Duncan, D.W., *Determination of acid production potential of waste materials*, Paper No. A-79-29, the Metallurgical Society of the American Institute of Mining Engineers, New York, 1979.

X1.2.7 Record the mass of each flask and its contents.

X1.2.8 Cap each flask with aluminum foil.

X1.2.9 Incubate at 35 °C on a gyratory shaker.

X1.2.10 Monitor the pH, ferrous iron and total iron for the first three days to ensure that the pH remains below 2.5. Prior to sampling, return the experimental flask to its original mass by adding distilled or deionized water.

X1.2.11 After the pH has stabilized below 2.5, monitor every second day until microbial activity ceases (that is, the pH no longer drops or the total iron concentration remains constant, or both.)

X1.2.12 When microbial activity ceases, add half the mass of feed sample used originally, shake for 24 h, and record the pH.

X1.2.13 If the pH is greater than 3.5, terminate the test. If the pH is 3.5 or less, again add half the mass of the feed and shake for 24 h.

X1.2.14 After 24 h, if the pH is less than 3.5 or greater than 4.0, terminate the experiment. If the pH is between 3.5 and 4.0, shake the sample an additional 48 h and record the final pH.

X1.2.15 Filter the final solution at 0.45 microns and preserve with HNO₃ to pH < 2 and submit for metals analyses.

X1.3 Interpretation

X1.3.1 The object of this test is to determine if the sulfide oxidizing bacteria can generate enough H₂SO₄ from the sulfides present in the sample to satisfy its acid demand. If they can, microbial action will continue on a self sustaining basis and acid mine water will result. In this test the acid demand is satisfied initially by adding H₂SO₄. This permits the bacteria to generate the maximum amount of H₂SO₄ from the sample concerned.

X1.3.2 Once bacterial action has ceased, half the original sample mass is added. If there has not been sufficient acid production, the pH will approach the natural pH of the sample and the sample is reported as not being a potential source of acid mine water.

X1.3.3 If the pH remains at 3.5 or below, the remainder of the sample is added and the sample is shaken for up to 72 h before measuring the final pH. If the pH is still in the leaching range, that is, pH 3.5 or lower, there is a strong possibility that natural leaching will occur and the acid mine drainage will be produced. If the pH is above 3.5, there is almost no possibility of acid mine drainage occurring in finely ground materials.

X1.3.4 Compare the metals analyses results with those obtained by other methods, such as meteoric water leaching to determine which metals need to be monitored and controlled in the drainage during waste disposal operations.

X2. PEROXIDE ACID GENERATION METHOD

X2.1 The Peroxide Acid Generation Method is based on the net acid generation (NAG) method.¹⁴ The method is useful in eliminating false positive results from the biological acid producing potential test for materials that do not contain significant amounts of neutralizing minerals that are able to raise the final pH significantly in that method. The method should be applied whenever there is a need to confirm that there are reactive sulfides in excess of neutralizing minerals in the sample. This is an optional method that is useful in confirming the acid-base behavior of a material classified using the carbon-sulfur methods and when it is desirable to measure the metals and sulfur dissolved, under the conditions of the test.

X2.2 Reagents

X2.2.1 *Hydrogen Peroxide*, 30 %.

X2.2.2 *Hydrogen Peroxide Solution*, (15 %)—Carefully add 500 mL of H₂O₂ to 500 mL of water.

X2.3 Procedure

X2.3.1 Weigh 0.250 g ± 0.001 g of test sample into a 50-mL flat bottom polypropylene disposable test tube and record the mass. Carry a sand blank (10.4.2) and reference-sample with known net sulfide reactivity, if available, through the entire procedure.

X2.3.2 Carefully add 25 mL of 15 % H₂O₂ solution to the tube.

NOTE X2.1—The amount of peroxide used in this test may be inadequate to react with all of the sulfide minerals in the sample, sequential NAG testing may be desirable in those cases, if the total amount of reactive sulfides is being estimated by this method.

X2.3.3 Place the open top tube in a rack. Place the rack on an orbital shaker and mix at moderate speed overnight, taking care that the mixing action does not eject slurry from the tube.

X2.3.4 Place the tubes in a water bath or heating block set to 90 °C and boil gently until effervescence ceases (approximately 1 h) to destroy any excess H₂O₂.

X2.3.5 Cool and add DI H₂O to regain original volume.

X2.3.6 Mix and centrifuge.

X2.3.7 Determine the pH of the solution and record.

X2.3.8 *Filtration*—Filter through a glass filter, save filtrate, wash with water at least three times and discard washings.

X2.3.9 Transfer filter and solids to the crucible or boat used for instrumental analysis.

X2.3.10 Measure the sulfur in percent in accordance with the instrument manufacturer's instructions (Section 10) and record the measurement.

X2.3.11 Filter the final solution at 0.45 microns and preserve with HNO₃ to pH < 2 and submit for metals and sulfur

¹⁴ Stewart, W., and Michaelsen, D., "Management of Potentially Acid Forming Overburden at Kaltim Prima Coal, Indonesia," Analytical Technologies in the Mineral Industries, pp. 237–252, TMS, Warrendale, PA.

analyses in accordance with Test Method **D1976** for major elements and Test Method **D5673** for trace elements.

X2.4 Interpreting Data

X2.4.1 If $\text{pH} < 4.5$ sample is characterized as “Potentially Acid Generating.”

X2.4.2 If $\text{pH} > 4.5$ sample is characterized as “Non Acid Forming.”

X2.4.3 Samples that have biological acid production potential final $\text{pH} < 3.5$ and peroxide acid generation $\text{pH} < 4.5$ are confirmed to be potentially acid generating.

X2.4.4 H_2O_2 treatment may remove soluble sulfates and react with sulfide minerals in the sample reducing the sulfur content of the solids and increasing the concentration of sulfur in solution.

X2.4.5 Results from metals and sulfur analyses of the filtrate should be compared with the solution analyses from the biological acid production potential and meteoric water mobility (Test Method **E2242**) or synthetic precipitation leaching procedure (Test Method **D6234**) results in order to rate the risks of environmental impact resulting from storage or disposal of the material under site specific conditions.

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