Designation: D3246 – 15

Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry[1]

This standard is issued under the fixed designation D3246; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers determination of sulfur in the range from 1.5 to 100 mg/kg (ppm by mass) by weight in hydrocarbon products that are gaseous at normal room temperature and pressure.

NOTE 1—The test method has been tested cooperatively only on high-purity ethylene gas. Precision data have not been developed for other products.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D1193 Specification for Reagent Water

D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

F307 Practice for Sampling Pressurized Gas for Gas Analysis

2.2 *Other Standards:*

Compressed Gas Association Booklets G-4 and G-4-1 on the Use of Oxygen[3]

3. Summary of Test Method

3.1 A sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

3.2 The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+ \quad (1)$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^- \quad (2)$$

3.3 These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.4 A liquid blend containing a known amount of sulfur is used for calibration.

4. Significance and Use

4.1 Trace quantities of sulfur compounds in hydrocarbon products can be harmful to many catalytic chemical processes in which these products are used. Maximum permissible levels of total sulfur are normally included in specifications for such hydrocarbons. It is recommended that this test method be used to provide a basis for agreement between two laboratories when the determination of sulfur in hydrocarbon gases is important.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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

[3] Available from Compressed Gas Association, 1235 Jefferson Davis Hwy., Arlington, VA 22202.

***A Summary of Changes section appears at the end of this standard**

4.2 On liquefied petroleum gas, total volatile sulfur is measured on an injected gas sample. For such material a liquid sample must be used to measure total sulfur.

5. Interferences

5.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen content of up to 1.0 %. Free nitrogen does not interfere.

5.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 mg/kg.

NOTE 2—To attain the quantitative detectability that the method is capable of, stringent techniques should be employed and all possible sources of sulfur contamination must be eliminated.

6. Apparatus[4,5]

6.1 *Pyrolysis Furnace*—The sample should be pyrolyzed in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

6.1.1 Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

Inlet zone	up to at least 700°C
Center pyrolysis zone	up to at least 1000°C
Outlet zone (optional)	up to at least 800°C

6.2 *Pyrolysis Tube,* fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to assure complete pyrolysis of the sample.

6.3 *Titration Cell,* containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and the reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means. (**Warning—**Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.)

6.4 *Microcoulometer,* having variable attenuation gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

6.5 *Recorder,* having a sensitivity of at least 0.1 mV/25 mm with chart speeds of 12 to 25 mm/min. Use of a suitable electronic or mechanical integrator is recommended but optional.

6.6 *Sampling Syringe for Liquid*—A microlitre syringe of 10-µL capacity capable of accurately delivering 1 to 10 µL of liquid blend into the pyrolysis tube 75 mm by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

NOTE 3—Since care should be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2 µL/s).

6.7 *Sampling Syringe for Gas*—A gas syringe capable of delivering up to 5 cm^3 of gas sample into the pyrolysis furnace. A 25-mm by 28-gage needle should be attached to the syringe.

6.8 *Exit Tube Insert,* with quartz wool.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] 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.

7.2 *Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential. See Specification D1193 for reagent water.

NOTE 4—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

7.3 *Acetic Acid* (rel dens 1.05)—Concentrated acetic acid (CH_3COOH). (**Warning—**May cause burns. See A1.1.)

7.4 *Argon, Helium, or Nitrogen* , high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995 %. (**Warning—**Hazardous pressure. See A1.2.)

[4] The apparatus described in 6.1 to 6.5 inclusive, is similar in specifications to equipment available from Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 524549. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7–12, 1969, p. B232 "Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry," by Harry V. Drushel.

[5] Tekmar-Dohrmann is the sole source of supply of the apparatus known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN_3) in approximately 500 mL of high-purity water, add 5 mL of acetic acid (CH_3COOH) and dilute to 1000 mL.

NOTE 5—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

7.6 *Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

7.7 *Iodine*—(I_2), 20 mesh or less, for saturated reference electrode. (**Warning—**Toxic fumes. See A1.3.)

7.8 *Isooctane (2,2,4-trimethyl pentane)*—A high purity *iso*octane of pesticide quality has been found satisfactory. (**Warning—**Combustible, very harmful. See A1.4.)

NOTE 6—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], *iso*octane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

7.9 *n-Butyl Sulfide* $(CH_3CH_2CH_2CH_2)_2S$.

7.10 *Oxygen,* high-purity grade (HP),[6] used as the reactant gas. (**Warning—**Oxygen accelerates combustion. See A1.5.)

7.11 *Potassium Iodide* (KI), fine granular.

7.12 *Sodium Azide* (NaN_3), fine granular. (**Warning—**Highly toxic. Can react violently with shock, friction or heat.)

7.13 *Sulfur, Standard Solution (approximately 30 mg/kg)*—Pipet 10 mL of sulfur stock solution (reagent 7.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

NOTE 7—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

7.14 *Sulfur, Standard Stock Solution (approximately 300 ppm (µg/g))*—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with *iso*octane and reweigh.

$$\text{S, mg/kg} = \frac{\text{g of } n-\text{butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n-\text{butyl sulfide} + \text{solvent})} \quad (3)$$

7.15 *Calibration Check Sample(s)*—portions of one or more liquid petroleum or product standards of known sulfur content and not used in the generation of the calibration curve. A calibration check sample or samples shall be used to verify the validity of the calibration curve as described in Section 10.

7.16 *Quality Control (QC) Sample(s)*—preferably portions of one or more gaseous petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to verify that the testing process is in statistical control as described in Section 12.

8. Sampling

8.1 Supply samples to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice D1265 and Practice F307.

8.2 Because of the reactivity of most sulfur compounds, it has been found desirable to use TFE-fluorocarbon-coated cylinders or other specially treated sample containers. Test samples as soon as possible after receipt.

9. Preparation of Apparatus

9.1 Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

9.2 Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of ⅛ to ¼ in. (3.2 to 6.4 mm) above the platinum electrodes.

9.3 Place the heating tape on the inlet of the titration cell.

9.4 Place an exit tube insert packed loosely with about 1 in. (25 mm) of quartz wool into the exit end of the pyrolysis tube. The quartz wool end of the exit tube should be in the hot zone of the pyrolysis tube.

9.5 Depending upon the instrumentation used, set up the titration cell to allow for adequate mixing of its contents and connect the cell inlet to the outlet end of the pyrolysis tube. Position the platinum foil electrodes (mounted on the movable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Fig. X1.2 illustrates the typical assembly and gas flow through a coulometric apparatus.

9.5.1 Turn the heating tape on.

9.6 Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

10. Calibration and Standardization

10.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 7.13, 7.14, or dilute to appropriate level with *iso*octane.

10.2 Adjust the operational parameters (9.5).

NOTE 8—A ratio of 80 % oxygen to 20 % inert gas gives an acceptable recovery, and permits the use of a larger sample and a more rapid-charging rate.

10.3 The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

10.3.1 Volumetric measurement can be obtained by filling the syringe with about 8 µL or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1-µL mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1-µL mark, and record the volume of

TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), cm^3/min	160
Carrier gas flow (Ar, He, N), cm^3/min	40
Furnace temperature, °C:	
Inlet zone	700
Pyrolysis zone	800
Outlet zone	800
Titration cell	set to produce adequate mixing
Coulometer:	
Bias voltage, mV	160
Gain	low (approximately 200)

liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

10.3.2 Alternatively, the sample injection device can be weighed before and after the injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ±0.01 g is used.

10.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2 µL/s. When a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2 µL/s.

10.5 Repeat the measurement of each calibration standard at least three times.

NOTE 9—Not all of the sulfur in the sample comes through the furnace as titratable SO_2. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to SO_3 which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *iso*octane or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected.

10.6 Calculate the percent sulfur found by the coulometer. For a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. and a speed of 0.5 in./min:

$$\text{Sulfur recovered, \%} = \left[(A \times 1.99)/\left(R \times S_o \times V_L/1000\right)\right] \times 100 \quad (4)$$

where:

A = area, cm^2,
R = coulometer range setting, Ω,
S_o = known concentration of sulfur in the standard blend, µg/mL, and
V_L = volume standard blend charged, µL.

10.6.1 *For a disk integrator:*

$$\text{Sulfur recovered, \%} = \left[(C \times 1.99 \times 10^{-3})/\left(R \times S_o \times V_L/1000\right)\right] \times 100 \quad (5)$$

where:

C = 100 × number of integrator pen full scale excursions.

Derivation of equations is given in Appendix X1.

10.6.2 *For an electronic integrator:*

$$\text{Sulfur Recovered, \%} = \frac{A}{B} \times 100 \quad (6)$$

(using consistent sample sizes)

where:

A = integrator result, mg/kg, and
B = known concentration of sulfur in standard blend, mg/kg.

NOTE 10—For further explanation of the derivation of the calculation, see Test Method D3120.

10.6.3 *For Instruments Equipped with a Microprocessor or Computer*—Associated instrument software may be used to do the calculations automatically.

10.7 If the fraction of sulfur converted to SO_2 drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

10.8 Calculate the average calibration factor, F, µg S/cm^2, as follows:

$$F = \left(S_o \times V_L/1000\right)/A \quad (7)$$

11. Quality Assurance (QA)

11.1 *Calibration Check Sample(s)*—A sample of known sulfur content shall be run after each calibration. The sample can also be analyzed periodically throughout a series of analyses to check the functioning of the instrument and the validity of the calibration curve.

11.2 *Quality Control (QC) Sample(s)*—Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 7.16).

11.2.1 When QC/QA protocols are already established in the testing facility, they may be used when confirming the reliability of the test result.

11.2.2 When there is no QC/QA protocol established in the testing facility, Appendix X2 can be used as the QC/QA system.

12. Procedure

12.1 Place a silicone rubber septum in a bushing and connect to the valve on the sample cylinder containing the gaseous sample (liquefied gas samples are extremely flammable; see A1.7). Crack the cylinder valve so as to flush the air from all connections and then turn the bushing down to hold slight back pressure on the septum. Close the cylinder valve until the gas syringe is ready for filling.

12.2 Crack the valve on the sample cylinder until slight flow of gas is detected around the septum. Insert the gas syringe in the septum carefully. (**Warning—**High pressure. See A1.8.)

12.3 Withdraw the plunger and allow the gas to flow through the syringe. After sufficient time to flush the syringe with sample, withdraw the plunger so as to contain no less than 5 cm^3 of gas.

12.4 Insert the tip of the needle barely through the septum. Inject 5.0 cm^3 of gas into the instrument at a constant rate so that 15 s is required for the injection. Determine the sulfur concentration by the procedure described in 10.2 – 10.7.

12.5 Sulfur concentration can require adjustment of sample volume.

12.6 Report a needle blank with test results.

13. Calculation

13.1 Calculate the sulfur content of the sample in parts per million (ppm) by weight as follows:

$$\text{Sulfur, mg/kg} = (A \times F)/W \quad (8)$$

where:

A = area under curve, taking into account the area of the needle blank, in square centimetres using same range (Ω) as calibration,

W = weight of sample, g, and
F = calibration factor, µg S/cm^2

For gases:

$$W = \frac{V_g \times 273 \times P \times M}{(273+C) \times 760 \times 22410} \quad (9)$$

where:

V_g = gas, cm^3
P = barometric pressure, mm Hg
M = molecular weight of gas, g/mol, and
C = temperature, gas, °C.

For ethylene at 23°C and 760 mm Hg:

$$W = V_g \times 0.001154 \quad (10)$$

For liquid:

$$W = V_L/1000 \times d \quad (11)$$

where:

V_L = volume, µL, and
d = density, g/mL.

13.2 For instruments equipped with a microprocessor or computer, associated instrument software may be used to calculate the sulfur content of the sample in milligrams per kilogram (mg/kg) automatically.

14. Reporting

14.1 Report the results to the nearest 0.1 mg/kg, and indicate that they were obtained using Test Method D3246.

15. Precision and Bias

15.1 The following criteria should be used for judging the acceptability of results:

15.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range or Sample Type	Repeatability
0 to 10 mg/kg	0.4 mg/kg

15.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range or Sample Type	Reproducibility
0 to 10 mg/kg	5 mg/kg

15.2 *Bias*—The bias of the procedure of this test method cannot be determined since an appropriate standard reference material containing trace sulfur level in ethylene is not available.

16. Keywords

16.1 microcoulometer; oxidate microcoulometry; petroleum gas; pyrolysis furnace; sulfur; sulfur dioxide

ANNEX

(Mandatory Information)

A1. WARNING STATEMENTS

A1.1 Acetic Acid

A1.1.1 **Warning—**May produce severe burns to skin and eyes.

Prolonged breathing of concentrated vapor may be harmful.

Avoid contact with skin, eyes, and clothing.

Use with adequate ventilation.

A1.2 Compressed Gases Argon, Helium, Nitrogen

A1.2.1 **Warning—**Compressed gas under high pressure.

Gas reduces oxygen available for breathing.

Keep container closed.

Use with adequate ventilation.

Do not enter storage areas unless adequately ventilated.

Always use a pressure regulator.

Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Do not drop cylinder.

Make sure cylinder is supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For Technical Use only.

Do not use for inhalation purposes.

A1.3 Iodine

A1.3.1 **Warning—**Fumes highly toxic.

Can cause irritation and burning of eyes, nose, and throat.

Avoid heating and prolonged breathing of vapors.

Avoid contact with skin.

A1.4 *Iso*octane

A1.4.1 **Warning—**Extremely flammable.

Harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flame.

Keep container closed.
Use with adequate ventilation.
Avoid build-up of vapors and eliminate all sources of ignition, especially nonexplosion proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

A1.5 Oxygen

A1.5.1 **Warning—**Oxygen vigorously accelerates combustion.
Keep oil and grease away.
Do not use oil or grease on regulators, gauges, or control equipment.
Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.
Keep combustibles away from oxygen and eliminate ignition sources.
Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.
Always use a pressure regulator.
Release regulator tension before opening cylinder valve.
All equipment and containers used must be suitable and recommended for oxygen service.
Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.
Do not mix gases in cylinders.
Do not drop cylinder.
Make sure cylinder is secured at all times.
Keep cylinder valve closed when not in use.
Stand away from outlet when opening cylinder valve.
For technical use only.
Do not use for inhalation purposes.
Keep cylinder out of sun and away from heat.
Keep cylinders from corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A1.6 Sodium Azide

A1.6.1 **Warning—**Highly toxic.
Inhalation may cause nausea, shortness of breath, dizziness, and headaches.
Contact with dust may cause eye irritation.
Avoid breathing dust or vapors from acidified solutions.
Avoid contact with skin, eyes, and clothing.
Wash thoroughly after handling.

A1.7 Flammable Gas

A1.7.1 **Warning—**Extremely flammable (liquified) gas under pressure.
Keep away from heat, sparks, and open flame.
Use with adequate ventilation.
Never drop cylinder.
Make sure cylinder is supported at all times.
Keep cylinder out of sun and away from heat.
Always use a pressure regulator.
Release regulator tension before opening cylinder.
Do not transfer cylinder contents to another cylinder.
Do not mix gases in cylinder.

A1.8 Flammable Gas

A1.8.1 **Warning—**Keep cylinder valve closed when not in use.
Do not inhale.
Do not enter storage areas unless adequately ventilated.
Stand away from cylinder outlet when opening cylinder valve.
Keep cylinder from corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
For technical use only.
Do not inhale.

APPENDIXES

(Nonmandatory Information)

X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN PARAGRAPH 13.1

X1.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Fig. X1.1 is typical of apparatus currently in use.

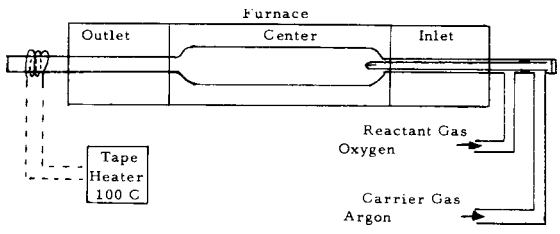

FIG. X1.1 Pyrolysis Tube

X1.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

X1.3 *Derivation of Equations:*

X1.3.1 The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the microcoulometric titration cell reaction ($I_3^- \rightarrow 3I^- + H^+$). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, Q.

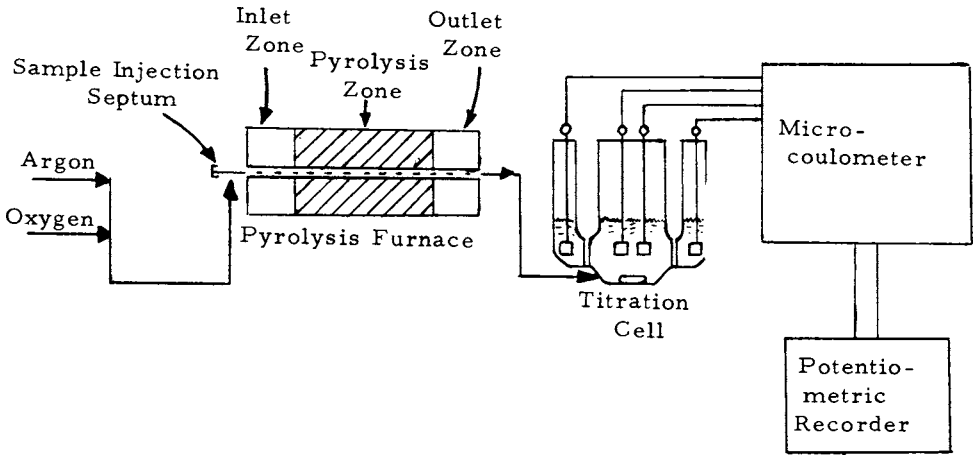

FIG. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

X1.3.2 In most applications a constant current is used so that the product of current, i, in amperes (coulombs per second), multiplied by the time, T (seconds), required to reach the end point provides a measure of the charge, Q (coulombs), necessary to generate the iodine equivalent to the reactant; that is, $Q = it$. Therefore, the number of equivalents of reactant is equal to Q/F, where F is the Faraday constant, 95 500°C per equivalent.

X1.3.3 Therefore, the expression to be solved to find the mass of reactant is:

$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\dfrac{Q(C)}{FC} \times \dfrac{16\ \text{g}}{\text{eq}}}{\text{mass of sample, g}} \tag{X1.1}$$

$$\mu\text{g S} = A\ \text{cm}^2 \times \frac{\dfrac{0.1\ \text{mV}}{\text{cm}} \times \dfrac{2\text{min}}{\text{cm}} \times \dfrac{60\ \text{s}}{\text{min}} \times \dfrac{10^{-3}\ \text{V}}{\text{mV}} \times \dfrac{16\ \text{g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{g}}{R\ (\Omega) \times \dfrac{96\,500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f} \tag{X1.2}$$

where:

A cm^2 = peak area measured in square inches,
0.1 mV/cm = millivolt span of upscale deflection for the recorder,
2 min/cm = chart speed in minutes per inch,
60 s/min = conversion of time in minutes to seconds,
10^{-3} V/mV = conversion of volts to millivolts,
16 g/eq = gram-equivalent of sulfur,
10^6 µg/g = micrograms per gram conversion factor,
R (Ω) = microcoulometer range switch setting in ohms,

substituting $V/R = I$(amps)

$$A\ \text{cm}^2 \times \frac{0.1\ \text{mV}}{\text{cm}} \times \frac{2\text{min}}{\text{cm}} \tag{X1.3}$$

$$Q(A\cdot s) = \frac{\times \dfrac{60s}{min} \times \dfrac{10^{-3}\ V}{mV}}{R(\Omega)} \tag{X1.4}$$

F = 96 500°C/eq
= Faraday's constant[8] (electrical equivalence of one gram-equivalent mass of any substance)
A·s/°C = conversion of coulombs to ampere-seconds, and
f = recovery factor (ratio of ppm S determined in standard versus known ppm S in standard).

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3}\ \text{A}\cdot\text{s} \times \dfrac{16\text{g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{R \times \dfrac{96\,500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f} \tag{X1.5}$$

Therefore,

$$\mu\text{gS} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^{6}\ \mu\text{g}}{R \times 96\,500 \times f} \tag{X1.6}$$

Therefore,

$$\mu\text{g S} = (A \times 1.99)/(R \times f) \tag{X1.7}$$

Since ppm = µg/g:

$$\text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume, µL} \times 10^{-3} \dfrac{\text{mL}}{\mu\text{L}} \times \text{density, } \dfrac{\text{g}}{\text{mL}}} \tag{X1.8}$$

$$\text{ppm S} = \frac{\text{A} \times 1.99 \times 10^{3}}{\text{R} \times \text{f} \times \text{volume} \times \text{density}} \tag{X1.9}$$

Since mass = volume × density

$$\text{ppm S} = (A \times 1.99)/(R \times F \times \text{mass, g}) \tag{X1.10}$$

X1.3.4 *Derivation with Disk Integrator—A* in Eq X1.7 is expressed as in.^{2} However, it may also be expressed as counts. Therefore, A in.^{2} = counts × 10^{-3} since 1 in.^{2} = 1000 counts. Therefore, substituting counts × 10^{-3} for A in Eq 5 gives

$$\mu\text{g S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times f) \tag{X1.11}$$

Then:

$$\text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, µL} \times \text{density, } \dfrac{\text{g}}{\text{mL}} \times f} \tag{X1.12}$$

ppm S = (counts × 1.99 × 10^{-3})/(R × mass, g × f)

NOTE X1.1—Counts = 100 × number of integrator per full-scale excursions.

X2. QUALITY CONTROL MONITORING

X2.1 Confirm the performance of the instrument or the test procedure by analyzing QC sample(s).

X2.2 Prior to monitoring the measurement process, the user of this test method needs to determine the average value and control limits of the QC sample. See Practice D6299 and MNL 7.[7]

X2.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency. See Practice D6299 and MNL 7.[7] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X2.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against this ASTM test method precision to ensure data quality. See Practice D6299 and MNL 7.[7]

X2.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and it shall be homogenous and stable under the anticipated storage conditions.

X2.6 See Practice D6299 and MNL 7[7] for further guidance on QC and Control Charting techniques.

[7] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., Section 3, ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D3246 – 14) that may impact the use of this standard. (Approved Jan. 1, 2015.)

(1) Revised subsection 13.2 to use SI units.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D3246 – 11) that may impact the use of this standard. (Approved May 1, 2014.)

(1) Added new subsections 10.6.3 and 13.2.