Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry

This standard is issued under the fixed designation D 3246; 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.

Nors 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 the 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:
D 1265 Practice for Sampling Liquified Petroleum (LP) Gases—Manual Method
D 1193 Specification for Reagent Water
D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
F 307 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. 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.

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

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:

<table>
<thead>
<tr>
<th>Zone Description</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet zone</td>
<td>up to at least 700°C</td>
</tr>
<tr>
<td>Center pyrolysis zone</td>
<td>up to at least 1000°C</td>
</tr>
<tr>
<td>Outlet zone (optional)</td>
<td>up to at least 800°C</td>
</tr>
</tbody>
</table>

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 Titrination 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.

Notes:

3. Caution—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 4—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 cm³ 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. 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 D 1193 for reagent water.

Note 5—Distilled water obtained from an all borosilicate glass still, freed from a demineralizer, has proven very satisfactory.

7.3 Acetic Acid (rel dens 1.05)—Concentrated acetic acid (CH₃COOH).


7.4 Argon, Helium, or Nitrogen, high-purity grade (HP), used as the carrier gas.


7.5 Cell Electrolyte Solution—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN₃) in approximately 500 mL of high-purity water, add 5 mL of acetic acid (CH₃COOH) and dilute to 1000 mL.

Note 8—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 (I₂), 20 mesh or less, for saturated reference electrode.

Note 9: Warning—Toxic fumes. See A1.3.

7.8 Isooctane¹¹ (2,2,4-trimethyl pentane).


Note 11—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)], isooctane (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 (CH₃CH₂CH₂CH₂S).

7.10 Oxygen, high-purity grade (HP), used as the reactant gas.


7.11 Potassium Iodide (KI), fine granular.

7.12 Sodium Azide (NaN₃), fine granular.


7.13 Sulfur, Standard Solution (approximately 30 ppm)

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¹¹ 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 Analytical 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.

¹² High-purity grade gas has a minimum purity of 99.995%.

¹¹ A high purity isooctane of pesticide quality has been found satisfactory.
mg/kg)—Pipet 10 mL of sulfur stock solution (reagent 7.14) into a 100-mL volumetric flask and dilute to volume with isoctane.

Notes 14—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 isoctane and reweigh.

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

8. Sampling
8.1 Supply samples to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice D 1265 and Practice F 307.
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 ¼ to ¾ 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. Figure 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 isoctane.
10.2 Adjust the operational parameters (9.5).

Notes 15—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 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 16—Not all of the sulfur in the sample comes through the furnace as titratable SO₂. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to SO₃ which does not react with the titrant. Accordingly, sulfur standards of n-butyl sulfide in isoctane 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:

\[
\text{Sulfur recovered, } \% = \frac{[(A \times 1.99) / (R \times S_o \times V_L/1000)] \times 100}{(5)}
\]

where:
\(A\) = area, cm²,
\(R\) = 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:

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

where:

![Table 1: Typical Operational Conditions](image-url)
\( C = 100 \times \text{number of integrator pen full scale excursions.} \)

Derivation of equations is given in Appendix X1.

10.6.2 For an electronic integrator:

\[
\text{Sulfur Recovered, \%} = \frac{A}{B} \times 100
\]

(using consistent sample sizes) \( (6) \)

where:

\( A \) = integrator result, mg/kg, and

\( B \) = known concentration of sulfur in standard blend, mg/kg.

Note 17—For further explanation of the derivation of the calculation, see Test Method D 3120.

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, \( F, \mu g S/cm^2 \), as follows:

\[
F = \frac{(S_o \times V_L/1000)}{A}
\]

(7)

11. Procedure

11.1 Place a silicone rubber septum in a bushing and connect to the valve on the sample cylinder containing the gaseous sample (for liquefied gas samples, see Note 5). 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.

Note 18: Warning—Samples are extremely flammable. See Annex A1.7.

11.2 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.


11.3 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.

11.4 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 to 10.7.

11.5 Sulfur concentration can require adjustment of sample volume.

11.6 Report a needle blank with test results.

12. Calculation

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

\[
\text{Sulfur, mg/kg} = \frac{(A \times F)}{W}
\]

(8)

where:

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

\( W \) = weight of sample, g, and

\( F \) = calibration factor, \( \mu g S/cm^2 \)

For gases:

\[
W = \frac{V_g \times 273 \times P \times M}{(273 + C) \times 760 \times 22410}
\]

(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:

\[
W = V_g \times 0.001154
\]

(10)

For liquid:

\[
W = \frac{V_L \times 1000 \times d}{1000}
\]

(11)

where:

\( V_L \) = volume, \( \mu L \), and

\( d \) = density, g/mL.

13. Precision and Bias

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

13.1.1 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:

<table>
<thead>
<tr>
<th>Range or Sample Type</th>
<th>Repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 10 mg/kg</td>
<td>0.4 mg/kg</td>
</tr>
</tbody>
</table>

13.1.2 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:

<table>
<thead>
<tr>
<th>Range or Sample Type</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 10 mg/kg</td>
<td>5 mg/kg</td>
</tr>
</tbody>
</table>

13.2 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.

14. Keywords

14.1 microcoulometer; oxidate microcoulometry; petroleum gas; pyrolysis furnace; sulfur; sulfur dioxide
ANNEX
(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Acetic Acid

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

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. 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. For technical use only. Do not use for inhalation purposes. See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A1.3 Iodine

Warning—Fumes highly toxic. Can cause irritation and burning of eyes, nose, and throat. Avoid breathing and prolonged breathing of vapors. Avoid contact with skin.

A1.4 Isooctane

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

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

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


A1.8 Flammable Gas

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.
APPENDIX

(Nonmandatory Information)

X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN PARAGRAPH 12.1

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

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 micro-
coulometric titration cell reaction \( \text{I}_3^- \rightarrow 3\text{I}^- + \text{H}^+ \). 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,
\( Q \).

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 \( \frac{Q}{F} \), where \( F \) is the
Faraday constant, 96,500 C per equivalent.

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

\[
\mu g S = A \left( \frac{0.1 \text{ mV/cm} \times 2 \text{ min/cm} \times 60 \frac{s}{\text{min}} \times 10^{-3} \text{ V/mV} \times 16 \frac{g}{\text{eq}} \times 10^6 \frac{\mu g}{g}}{R (\Omega) \times 96 \, 500 \frac{\text{C}}{\text{eq}} \times \frac{\text{A} \cdot \text{s}}{C} \times f} \right)
\]

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

substituting \( V/R = I(\text{amps}) \)

\[
\frac{Q(A \cdot s)}{R(\Omega)} = \frac{96 \, 500 \text{C/eq} \times \frac{\text{A} \cdot \text{s}}{C} \times f}{R(\Omega) \times 96 \, 500 \frac{\text{C}}{\text{eq}} \times \frac{\text{A} \cdot \text{s}}{C} \times f}
\]

\[ F = 96 \, 500 \text{C/eq} \]

\[ A \cdot \text{s/}^\circ \text{C} = \text{Faraday's constant}^8 \text{ (electrical equivalence of}
  \text{one gram-equivalent mass of any substance)} \]

\[ A = 1.99 \]

\[ \text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume} \times \text{density}} \]

Since ppm = \( \mu g/g \):

\[ \text{ppm S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \]

Therefore,

\[ \mu g S = A \times 1.99 \times 10^3 \times 16 \times 10^6 \frac{\mu g}{g} \]

Therefore,

\[ \mu g S = A \times 1.99 \times 10^3 \times 16 \times 10^6 \frac{\mu g}{g} \]

Therefore,

\[ \mu g S = (A \times 1.99)/(R \times f) \]

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Therefore,

\[ \mu g S = (A \times 1.99)/(R \times f) \]

Since ppm = \( \mu g/g \):

\[ \text{ppm S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \]

Therefore,

\[ \mu g S = (A \times 1.99)/(R \times f) \]

Thus, the expression to be solved to find the
mass of reactant is:

\[
\mu g S = A \left( \frac{0.1 \text{ mV/cm} \times 2 \text{ min/cm} \times 60 \frac{s}{\text{min}} \times 10^{-3} \text{ V/mV} \times 16 \frac{g}{\text{eq}} \times 10^6 \frac{\mu g}{g}}{R (\Omega) \times 96 \, 500 \frac{\text{C}}{\text{eq}} \times \frac{\text{A} \cdot \text{s}}{C} \times f} \right)
\]
Since mass = volume × density

\[ \text{ppm S} = \frac{(A \times 1.99)}{(R \times F \times \text{mass, g})} \] (X1.8)

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

\[ \mu\text{g S} = \frac{\text{counts} \times 1.99 \times 10^{-3}}{(R \times f)} \] (X1.9)

Then:

\[ \text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, } \mu\text{L} \times \text{density, } \frac{\text{g}}{\text{mL}} \times f} \] (X1.10)

\[ \text{ppm S} = \frac{(\text{counts} \times 1.99 \times 10^{-3})}{(R \times \text{mass, g} \times f)} \]

\[ \text{NOTE X1.1—Counts} = 100 \times \text{number of integrator per full-scale excursions.} \]