



Designation: D3246 – 05

## Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry<sup>1</sup>

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 ( $\epsilon$ ) 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:<sup>2</sup>

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:

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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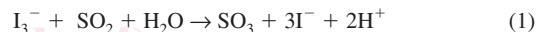
<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Compressed Gas Association Booklets G-4 and G-4-1 on the Use of Oxygen<sup>3</sup>

### 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:



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



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.

<sup>3</sup> Available from Compressed Gas Association, 1235 Jefferson Davis Hwy., Arlington, VA 22202.

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

## 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<sup>4,5</sup>

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- $\mu$ L capacity capable of accurately delivering 1 to 10  $\mu$ L 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  $\mu$ L/s).

6.7 *Sampling Syringe for Gas*—A gas syringe capable of delivering up to 5 cm<sup>3</sup> 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.<sup>6</sup> 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<sub>3</sub>COOH). (**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**.)

7.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN<sub>3</sub>) in approximately 500 mL of high-purity water, add 5 mL of acetic acid (CH<sub>3</sub>COOH) 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.

<sup>4</sup> 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.

<sup>5</sup> 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,<sup>1</sup> which you may attend.

<sup>6</sup> *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.

7.7 *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 isooctane 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)], 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* ( $CH_3CH_2CH_2CH_2)_2S$ .

7.10 *Oxygen*, high-purity grade (HP),<sup>6</sup> 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 isooctane.

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 isooctane and reweigh.

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

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 1/8 to 1/4 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 isooctane.

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 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

TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), cm <sup>3</sup> /min	160
Carrier gas flow (Ar, He, N), cm <sup>3</sup> /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)

rate not to exceed 0.1 to 0.2  $\mu\text{L/s}$ . 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  $\mu\text{L/s}$ .

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  $\text{SO}_2$ . In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to  $\text{SO}_3$  which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *isooctane* 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:

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

where:

- $A$  = area,  $\text{cm}^2$ ,
- $R$  = coulometer range setting,  $\Omega$ ,
- $S_o$  = known concentration of sulfur in the standard blend,  $\mu\text{g/mL}$ , and
- $V_L$  = volume standard blend charged,  $\mu\text{L}$ .

10.6.1 For a disk integrator:

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

where:

- $C$  = 100  $\times$  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,  $\text{mg/kg}$ , and
- $B$  = known concentration of sulfur in standard blend,  $\text{mg/kg}$ .

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

10.7 If the fraction of sulfur converted to  $\text{SO}_2$  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,  $F$ ,  $\mu\text{g S/cm}^2$ , as follows:

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

## 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  $\text{cm}^3$  of gas.

12.4 Insert the tip of the needle barely through the septum. Inject 5.0  $\text{cm}^3$  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 ( $\Omega$ ) as calibration,
- $W$  = weight of sample, g, and
- $F$  = calibration factor,  $\mu\text{g S/cm}^2$

For gases:

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

where:

- $V_g$  = gas,  $\text{cm}^3$
- $P$  = barometric pressure, mm Hg
- $M$  = molecular weight of gas,  $\text{g/mol}$ , and
- $C$  = temperature, gas,  $^\circ\text{C}$ .

For ethylene at 23 $^\circ\text{C}$  and 760 mm Hg:

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

For liquid:

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