Standard Test Method for
Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[1]

1. Scope

1.1 This test method covers the determination of sulfur in the range from 3.0 to 100 ppm (µg/g) in light liquid hydrocarbons boiling in the range from 26 to 274°C (80 to 525°F).

1.2 This test method may be extended to liquid materials with higher sulfur concentrations by appropriate dilution.

1.3 The preferred units are micrograms per grams. Values stated in SI units are to be regarded as the standard. Values in inch-pound units are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.3, 6.4, 6.8, and 6.10.

2. Summary of Test Method

2.1 A liquid 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.

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

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+ \qquad (1)$$
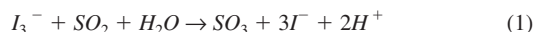
The triiodide ion consumed in the above reaction is generated coulometrically thus:

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

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

3. Significance and Use

3.1 This test method is used to determine trace quantities of sulfur in reformer charge stocks and similar petroleum fractions where such trace concentrations of sulfur are deleterious to the performance and life of the catalyst used in the process. Higher concentrations of sulfur in products analyzed by this test method after appropriate dilution are often detrimental to the use of the product.

4. Interferences

4.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen concentrations of up to 1000 times the sulfur level.

4.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 µg/g (ppm).

NOTE 1—To attain the quantitative detectability that the method is capable of, stringent techniques must be employed and all possible sources of sulfur contamination must be eliminated.

5. Apparatus [2]

5.1 *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.

[1] 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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[2] The apparatus described in Sections 5.1 to 5.5 inclusive, is similar in specifications to equipment available from Dohrmann Div. of Rosemount, 3240 Scott Blvd., Santa Clara, CA 95050. 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.

5.1.1 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	800 to 1000°C
Outlet zone (optional)	up to at least 800°C

5.2 *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 ensure complete pyrolysis of the sample.

5.3 *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 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.)

5.4 *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.

5.5 *Recorder*, having a sensitivity of at least 0.1 mV/in. with chart speeds of ½ to 1 in./min. Use of a suitable electronic or mechanical integrator is recommended but optional.

5.6 *Sampling Syringe*—A microlitre syringe of 10-µL capacity capable of accurately delivering 1 to 10 µL of sample into the pyrolysis tube. 3-in. by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

Note 2—Since care must 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. Reagents and Materials

6.1 *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.[3] 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.

6.2 *Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential.

Note 3—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

6.3 *Acetic Acid* (rel dens 1.05)—Glacial acetic acid (CH_3COOH). (**Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

6.4 *Argon, Helium, or Nitrogen*, high purity grade (HP),[4] used as carrier gas. (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.)

6.5 *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 4—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.

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

6.7 *Iodine* (I), 20 mesh or less, for saturated reference electrode.

6.8 *Iso octane*[5] (2,2,4-trimethylpentane). (**Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.)

Note 5—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)].

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

6.10 Oxygen, high purity grade (HP),[4] used as the reactant gas. (**Warning**—Oxygen vigorously accelerates combustion.)

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

6.12 *Sodium Azide* (NaN_3), fine granular. (**Warning**—Toxic, causes eye and skin irritation; explosive.)

6.13 *Sulfur, Standard Solution* (*approximately 30 µg/g (ppm)*)—Pipet 10 mL of sulfur stock solution (reagent 6.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

Note 6—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.

6.14 *Sulfur, Standard Stock Solution* (*approximately 300 µg/g (ppm)*)—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.

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

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[3] *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.

[4] High-purity grade gas has a minimum purity of 99.995 %.
[5] Pesticide test grade such as Mallinckrodt "Nano-grade" *iso*octane has been found satisfactory.

7. Preparation of Apparatus

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

7.2 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.

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

7.4 Position the platinum foil electrodes (mounted on the moveable 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.

7.4.1 Turn the heating tape on.

7.5 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.

8. Calibration and Standardization

8.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 6.13, 6.14, or dilute to appropriate level with *iso*octane.

8.2 Adjust the operational parameters (7.5).

NOTE 7—See Fig. 1 for the variance of percent recoveries with gas ratios and temperature.

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

8.3.1 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.

8.3.2 Alternatively, the sample injection device may be weighed before and after the injection to determine the amount of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of ±0.00001 g is used.

8.4 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. If 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.

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

NOTE 8—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. Satisfactory standard materials[6] are given in Table 2.

8.6 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.

9. Procedure

9.1 Flush the 10-μL syringe several times with the unknown sample. Determine the sulfur concentration in accordance with 8.2 to 8.6.

9.2 Sulfur concentration may require adjustment of sensitivity settings or sample volume or both.

10. Calculation

10.1 Calculate the sulfur content of the sample in parts per million, ppm μg/g, by mass as follows:

$$\text{Sulfur, ppm μg/g} = (A \times 1.99)/(R \times M \times F) \qquad (4)$$

$$\text{Sulfur, ppm} = (A \times 1.99 \times 10^3)/(R \times V \times D \times F) \qquad (5)$$

where:
A = area under curve, in.^{2},
1.99 = derivation will be found in X1.3,
R = coulometer range switch setting, Ω,
M = mass of sample, g (volume × density),
V = volume of sample, μL,
D = density of sample, g/mL, and
F = recovery factor, fraction of sulfur in standard that is titrated, ratio of ppm sulfur determined in standard divided by the known ppm sulfur in standard.
$F = (A \times 1.99)/(R \times M \times C_{std})$

where:
C_{std} = concentration of standard, ppm.

10.2 Derivation of the calculation equation will be found in X1.3.

NOTE 9—The calculation equation is valid only when the chart speed is 0.5 in./min and a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. is used.

NOTE 10—If a disk integrator is used, see X1.3 for calculations, derivations, and equations.

NOTE 11—A more general form of the equation in 10.1 which is not

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TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), cm³/min	160
Carrier gas flow (Ar, He, N) cm³/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)

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[6] Wallace, L. D., "Comparison of Oxidative and Reductive Methods for the Microcoulometric Determinations of Sulfur in Hydrocarbons," *Analytical Chemistry*, Vol 42, March 1970, p. 393.