



Designation: ~~D3120~~—~~08~~ **D3120 – 08 (Reapproved 2014)**

## Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry<sup>1</sup>

This standard is issued under the fixed designation D3120; 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.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

### 1. Scope<sup>\*</sup>

1.1 This test method covers the determination of sulfur concentration in the range from 3.0 to ~~1000~~1000 mg ~~-mg/kg~~-kg in light liquid hydrocarbons and fuels with oxygenates boiling in the range from 26 to 274°C (80 to 525°F).

NOTE 1—Preliminary data has shown that this test method is also applicable to the determination of sulfur in denatured fuel ethanol (Specification **D4806**), automotive spark ignition engine fuel (Specification **D4814**), Ed75–Ed85 (Specification **D5798**) or gasoline-oxygenate fuel blends with greater than 10% ethanol. However, the precision for these materials has not been determined. Subcommittee D02.03 is undertaking activities to obtain precision statements for these materials.

1.2 Other materials falling within the distillation range specified in 1.1, but having sulfur concentrations above 1000 mg/kg, may be tested using appropriate dilutions to bring them within the specified limit. In addition, sample types that may be outside the specified distillation range, such as diesels and biodiesels, may be analyzed by this test method.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. The preferred units are milligrams per kilogram (mg/kg).

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 Sections 7 – 9.

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

**D1193** Specification for Reagent Water

**D1298** Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

**D4052** Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

**D4057** Practice for Manual Sampling of Petroleum and Petroleum Products

**D4177** Practice for Automatic Sampling of Petroleum and Petroleum Products

**D4806** Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel

**D4814** Specification for Automotive Spark-Ignition Engine Fuel

**D5798** Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines

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

#### 2.2 OSHA Regulations:

**OSHA Regulations** 29 CFR, paragraphs 1910.1000 and 1910.1200<sup>3</sup>

### 3. Summary of Test Method

3.1 A liquid sample is introduced into a pyrolysis tube maintained at a temperature between ~~900–1200°C~~, 900 to 1200°C, having a flowing stream of gas containing ~~50–80%~~ 50 to 80% oxygen and ~~20–50%~~ 20 to 50% inert gas (for example, argon, helium, etc.)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products—Products, Liquid Fuels, 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.

<sup>3</sup> Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

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

and so forth). 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 ion consumed is coulometrically replaced and the total current ( $I \times t$ ) required to replace it is a measure of the sulfur present in the sample.

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 ion (iodine) are equal to the number of microequivalents of titratable  $SO_2$  ion entering the titration cell.

#### 4. Significance and Use

4.1 This test method is used to determine the concentration of sulfur in light liquid hydrocarbons, gasoline, and diesels and their additives, where such concentrations of sulfur can be detrimental to their production, performance, and use. The measurement of sulfur in the production and final product of gasoline and diesel is required for both regulatory purposes and to ensure maximum life expectancy of catalytic converters used in the automotive industry.

#### 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 concentrations of up to 1000 times the sulfur level.

5.1.1 Stringent techniques shall be employed and all possible sources of sulfur contamination eliminated to attain the quantitative detectability capable with this test method.

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

#### 6. Apparatus

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

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

6.3 *Furnace*—Maintained at a temperature sufficient to completely pyrolyze the organic matrix, ~~900–1200°C~~, 900 to 1200°C, and completely oxidize the organically bound sulfur to  $SO_2$ . Independently controlled inlet and outlet temperature zones are optional. An electrical furnace has been found suitable to use.

6.4 *Pyrolysis Tube*—Fabricated from quartz and constructed so the sample is vaporized in a heated zone before the furnace and swept into the oxidation zone by an inert carrier gas, where the vaporized sample mixes with oxygen and is pyrolyzed. The inlet shall be constructed large enough to accommodate a sample boat completely into the oxidation zone of the pyrolysis tube or allow the direct injection of the sample into the heated zone before the furnace. The pyrolysis tube shall have side arms for the introduction of oxygen and inert carrier gas.

6.5 *Titration Cell*—Consisting of a sensor/reference pair of electrodes to detect changes in triiodide ion concentration, a generator anode-cathode pair of electrodes to maintain a constant triiodide ion concentration, an inlet for gaseous sample from the pyrolysis tube, and an outlet to vent the exit gases from the titration cell. The reference electrode can be either an Ag/AgCl double junction reference electrode or a platinum wire in a saturated triiodide half-cell. The sensor electrode and both the anode and cathode electrodes of the generator are made of platinum. The titration cell shall require mixing, which can be accomplished with a magnetic stir bar, stream of gas, or other suitable means. Other sensor and reference electrodes may be used if they meet the performance criteria of this test method.

NOTE 2—Take care not to use excessive stirring and possibly damage the electrodes with the stir bar. The creation of a slight vortex is adequate.

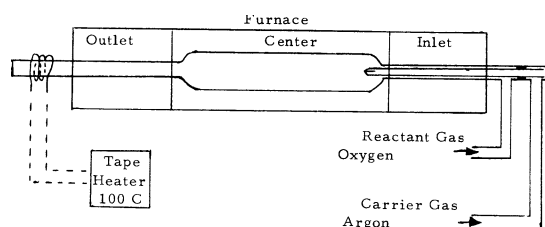


FIG. 1 Typical Pyrolysis Tube

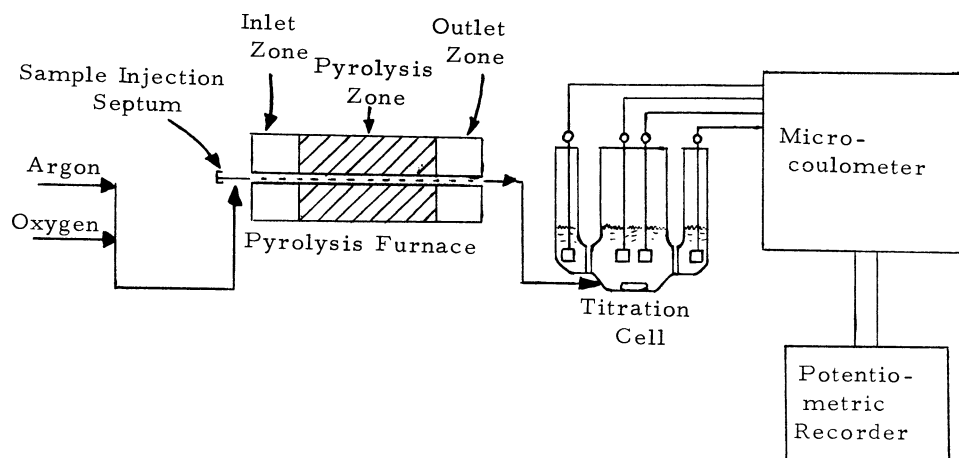


FIG. 2 Flow Diagram for Typical Coulometric Apparatus for Trace Sulfur Determination

6.6 *Microcoulometer*— The apparatus' microcoulometer, with variable attenuation and gain control, shall be capable of measuring the potential of the sensing-reference electrode pair and compare this potential to a bias potential. By amplifying this potential difference and applying the difference to a working-auxiliary pair of electrodes (the generator), a titrant is generated. The microcoulometer integrates the amount of current used, calculates the equivalent mass of sulfur titrated and calculates the concentration of sulfur in the sample.

6.7 *Strip Chart Recorder (Optional)* —To monitor and plot the mV potential of the titration cell during the analysis.

6.8 *Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant supply of oxygen and inert carrier gas.

6.9 *Dryer Tube*—The oxidation of samples produces water vapor which, if allowed to condense between the exit of the pyrolysis tube and the titration cell, will absorb the SO<sub>2</sub> formed and result in low recovery. Steps shall be taken to prevent such an occurrence. This is easily accomplished by placing a phosphoric acid dehydration tube between the titration cell and exit of the pyrolysis tube. Other approaches, such as heating tape or permeation tubes, can be used if precision and accuracy are not degraded.

6.10 *Sampling Syringes*—Microlitre syringes able to accurately deliver 5 to 80 mL of sample are required. The volume injected should not exceed 80% of a syringe's capacity.

6.11 *Sample Inlet System*—Either type of sample inlet system described can be used.

6.11.1 *Boat Inlet System*—The inlet of the pyrolysis tube is sealed to the boat inlet system. The system provides a cooled area before the furnace for the sample boat prior to quantitative introduction of sample into the boat and is purged with the inert carrier gas. The boat driving mechanism then fully inserts the boat into the oxidation zone of the furnace. The drive mechanism shall advance and retract the sample boat into and out of the oxidation zone of the furnace at a controlled and repeatable rate (see Note 3).

6.11.1.1 *Boat Inlet Cooler (Optional)*—Sample volatility and injection volume may require an apparatus capable of cooling the sample boat prior to sample introduction. Thermoelectric coolers (peltier) or recirculating refrigerated liquid devices are strongly recommended. Switching sample boats between each analysis may prove effective, provided sample size is not too large.

6.11.1.2 *Sample Boats*—Quartz or other suitable material which will not react with the sample or sulfur compounds being analyzed and able to withstand the temperatures extremes of the test method.

6.11.2 *Syringe Inlet System*—The system shall deliver a quantitative amount of sample from a microlitre syringe into a heated area before the oxidation zone of the pyrolysis tube at a controlled and repeatable rate. There the sample is volatilized and the inert carrier gas stream purging the heated area transports the volatilized sample into the oxidation zone of the pyrolysis furnace. An adjustable drive mechanism capable of injecting the sample from a microlitre syringe at a constant rate between 0.5 to 1.0 mL/s is required (see Note 3).

NOTE 3—Take care not to introduce the sample too fast into the oxidation zone of the furnace and overload the combustion capacity of the pyrolysis tube. Program the sample inlet system to deliver the sample at a sufficiently controlled and repeatable rate to prevent any incomplete combustion by-products (coke or soot) from forming at the exit of the pyrolysis tube.

6.12 *Balance*—With a weighing precision of ±0.01 mg.

## 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>4</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*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**, Type II and III.

7.3 *Quartz Wool*—Grade fine.

7.4 *Acetic Acid* (CH<sub>3</sub>COOH)—Glacial acetic acid with specific gravity = 1.05. (**Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

7.5 *Phosphoric Acid (85 % w/w)*—Orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>). (**Warning**—Poison. Corrosive. May be fatal if swallowed. Causes severe burns.)

7.6 *Inert Gas*—Argon or helium, high purity grade (HP),<sup>5</sup> used as carrier gas. (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.)

7.7 *Oxygen*—High purity grade (HP),<sup>5</sup> used as the reactant gas. (**Warning**—Oxygen vigorously accelerates combustion.)

7.8 *Gas Regulators*—Two-stage gas regulators shall be used for the oxygen and inert carrier gas.

7.9 *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 6 mL of glacial acetic acid (CH<sub>3</sub>COOH), and dilute to 1000 mL or follow the manufacturer's specifications.

NOTE 4—Take care to store bulk quantities of the electrolyte in a dark place. It is recommended to prepare fresh electrolyte at least every three months.

7.10 *Sodium Azide* (NaN<sub>3</sub>), fine granular. (**Warning**—Toxic. Causes eye and skin irritation. Explosive.)

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

7.12 *Potassium Chloride* (KCl), fine granular. Used for the 1M Ag/AgCl double junction reference electrode.

7.13 *Potassium Nitrate* (KNO<sub>3</sub>), fine granular. Used for the 1M Ag/AgCl double junction reference electrode.

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

7.15 *Toluene, Xylenes, Isooctane*—Reagent grade. (Other solvents similar to those occurring in the samples being analyzed are acceptable.) A solvent blank correction is required due to the inherent sulfur present in the solvents used for standard preparation and sample dilution. (**Warning**—Flammable solvents. Harmful if inhaled. Vapors may cause flash fire.)

NOTE 5—The use of solvents with non-detectable levels of sulfur relative to the sulfur content in the sample can make the solvent blank correction unnecessary.

7.16 *Dibenzothiophene*—FW 184.26, 17.399 % (mass/mass) S (see **Note 5**).

7.17 *n-Butyl Sulfide*—FW 146.29, 21.92 % (mass/mass) S (see **Note 5**).

7.18 *Thionaphthene (Benzothiophene)*—FW 134.20, 23.90% (mass/mass) S (see **Note 5**).

NOTE 6—A correction for chemical impurity can be applied if deemed necessary.

7.19 *Sulfur, Standard Solution* (approximately 1000 mg-S/mL)—Prepare a stock solution by accurately weighing approximately 0.5748 g of dibenzothiophene or 0.4652 g of n-butyl sulfide or 0.4184 g of thionaphthene into a tared 100 mL, type A volumetric flask. Dilute to volume with a selected solvent. This stock can then be further diluted to prepare sulfur working and calibration standards as outlined in **Tables 1-3** (see **Notes 7-9**).

$$\mu\text{g-S/mL} = \frac{A \times B \times C \times 10^6}{100 \text{ mL}} \quad (3)$$

where:

<sup>4</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.

<sup>5</sup> High-purity grade gas has a minimum purity of 99.995 %.

**TABLE 1 Recommended Preparation of Working Standards**

Working Standard Concentration, μg-S/mL	Stock Standard Concentration, μg-S/mL	Volume Stock Standard, mL	Total Volume Working Standard, mL
500	1000	25	50
50	1000	5	100
10	500 <sup>A</sup>	2	100

<sup>A</sup> Working standard.

**TABLE 2 Recommended Calibration Standards versus Desired Calibration Range**

Calibration Range, mg-S/kg	Calibration Standards Concentration		
	Concentration 1, mg-S/mL	Concentration 2, mg-S/mL	Concentration 3, mg-S/mL
Trace–2.5	0.2	1.0	2.5
0.5–50	0.2	5	50
1.0–250	0.5	10	250
2.5–500	1.0	25	500
5.0–1000	2.5	50	1000

**TABLE 3 Recommended Preparation of Calibration Standards**

Concentration Working Standard, µg-S/mL	Volume of Working Standard, mL	Total Volume Calibration Standard, mL	Concentration Calibration Standard, µg-S/mL
10	2	100	0.2
10	5	100	0.5
50	2	100	1.0
50	5	100	2.5
50	10	100	5.0
500	5	100	25
500	10	100	50
1000 <sup>A</sup>	25	100	250
500	...	...	500
1000 <sup>A</sup>	...	...	1000 <sup>A</sup>

<sup>A</sup> Standard stock solution.

A = grams of standard.

B = weight of fraction sulfur (S) in standard.

C = weight of fraction standard purity.

7.20 *Sulfur, Standard Working Solution*—Prepare the working standards using standard type A volumetric pipet as outlined in **Table 1**.

NOTE 7—Working and calibration standards prepared on a regular basis recommended, depending upon frequency of use and age. Stock solutions typically have a useful life of about 3 months.

NOTE 8—Calibration standards can be prepared and diluted on a mass/mass basis, when calculation results are adjusted to accommodate them.

NOTE 9—Stock, working and calibration standards from commercial sources can be used if checked for accuracy and can meet the performance criteria of this test method.

7.21 *Quality Assurance (QA) Samples*—Samples that are liquid petroleum materials or standards products of known sulfur content that were not used in the generation of the apparatus' calibration curve. These (QA) samples are to be used to check the validity of the testing process as described in Section 11. An ample supply of QA sample material should be available for the intended period of use and shall also be homogenous and stable under the anticipated storage time and conditions.

## 8. Hazards

8.1 High temperature is employed in this test method. Extra care shall be exercised when using flammable materials near the furnace.

8.2 Consult current OSHA regulations and supplier's Material Safety Data Sheets (MSDS) for materials used in this test method.

## 9. Sampling

9.1 Obtain a test sample in accordance with Practice **D4057** or Practice **D4177**. To preserve volatile components which are in some samples, do not uncover samples any longer than necessary. Samples should be analyzed as soon as possible after collection from bulk supplies to prevent loss of sulfur, or contamination due to exposure or contact with sample container.

9.1.1 (**Warning**—Samples collected at temperatures below room temperature can undergo expansion and rupture the container. For such samples, do not fill the container to the top; leave sufficient air space above the sample to allow room for expansion.)

9.2 If the test sample is not used immediately, thoroughly mix the container prior to taking a test specimen.

## 10. Preparation of Apparatus

10.1 Carefully insert the quartz pyrolysis tube into the furnace, and connect the oxygen and inert carrier gas lines.

10.2 Connect the boat drive system or syringe drive system to the pyrolysis tube.

10.3 Perform a leak check according to the manufacturer's instructions.

10.4 Assemble the titration cell, and add all required solutions, including cell electrolyte, according to the manufacturer's instructions.

10.5 Connect the titration cell to the apparatus according to the manufacturer's instructions.

10.6 Adjust the flow of gases and set the furnace temperatures and instrumental parameters according to the manufacturer's instructions.

10.7 If using a boat inlet system, pre-bake the sample boats used for the analysis per the manufacturer's instructions.

## 11. Calibration and Standardization

11.1 Following the manufacturer's recommended procedures, set the operational parameters of the apparatus for internal calibration. If the apparatus is not so equipped, analyze the solvent blank and calibration standards, record their values as  $\mu\text{g}$  or  $\text{ng}$  of sulfur, and manually generate a calibration curve.

11.2 *Calibration Standards*—Select the desired calibration range from **Table 2**. Prepare the appropriate calibration standards for the range selected as outlined in **Table 3**. The calibration standards concentrations are calculated based on the formula below:

$$\text{Calibration Standard Concentration: } \mu\text{g-S/mL} = \frac{A \times B}{100 \text{ mL}} \quad (4)$$

where:

$A$  =  $\mu\text{g-S/mL}$  of working or stock solution.

$B$  = mL of working or stock solution.

NOTE 10—A calibration curve with three standards is recommended. It is recommended to use standards covering the range of sulfur concentrations expected in the samples being analyzed. Calibration curves with one or two standards can be used if it can be shown the calibration curve is linear over the concentration range being measured and the standards meet the performance criteria of this test method. Larger series of standards can also be used if it can be shown the calibration curve is linear over the concentration range being measured and the standards meet the performance criteria of this test method.

NOTE 11—The use of calibration standards with different concentrations is possible provided they cover the expected concentration range for the samples being analyzed and meet the performance criteria of this test method.

11.3 Select the appropriate syringe based on the recommended sample size in **Table 4** for the concentration of standards used to calibrate the apparatus.

11.4 Flush the microlitre syringe several times with the sample prior to analysis. If bubbles are present in the liquid column, flush the syringe and withdraw a new sample.

11.5 The sample size can be determined volumetrically or by mass with a syringe. The sample size should be 80% or less of the syringe's capacity.

11.5.1 *Volumetric Measurement*—Obtain the volume of injected material by filling the syringe to the selected level, retracting the plunger so the lower meniscus falls on the 10% scale mark, and recording the volume of liquid in the syringe. After the sample has been injected, retract the plunger again so the lower liquid meniscus falls on the 10% scale mark, and record the volume of liquid in the syringe. The difference between the two readings is the volume of sample injected.

NOTE 12—An automatic sampling and injection device can be used in place of the procedure described for the manual syringe injection.

11.5.2 *Mass Measurement*—The sample syringe 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  $\pm 0.01 \text{ mg}$  is used.

11.5.3 Once the appropriate sample size has been measured into the microlitre syringe, promptly and quantitatively deliver the sample into the apparatus. Again, there are two alternative techniques available.

11.5.4 *Boat Inlet System*—Add the sample by slowly discharging quantitatively the contents of the syringe into a sample boat containing quartz wool, being careful to include the last drop from the tip of the syringe needle. Remove the syringe and immediately start the analysis. The apparatus' baseline should remain stable until the boat approaches the furnace and volatilization of sample begins (see **Note 13**). The program of the inlet system should keep the boat completely in the oxidation zone of the

**TABLE 4 Recommended Sample Size for Expected Sample Concentrations**

Sample Concentrations, mg-S/kg	Injected Volume, $\mu\text{L}$	Mass Sulfur, $\mu\text{g-S}$
Trace–5.0	80	Trace–0.25
0.5–50	60	0.03–1.5
1.0–250	30	0.03–5.0
2.5–500	20	0.05–5.0
5.0–1000	10	0.05–10