



Standard Test Method for Trace Quantities of Sulfur in Liquid Aromatic Hydrocarbons by Oxidative Microcoulometry¹

This standard is issued under the fixed designation D 3961; 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 determines total sulfur content in aromatic hydrocarbons, their derivatives, and related chemicals.

1.2 This test method is applicable to samples with sulfur concentrations from 0.5 to 100 mg/kg.

1.3 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or a calculated value shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

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 Section 9.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products³

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

2.2 Other Document:

OSHA Regulations - 29 CFR paragraphs 1910.1000 and 1910.1200⁵

3. Terminology

3.1 Definitions:

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.04.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

3.1.1 *dehydration tube*—a chamber containing phosphoric acid 85 % that scrubs the effluent gases from combustion to remove water vapor.

3.1.2 *oxidative pyrolysis*—a process in which a sample is combusted in an oxygen-rich atmosphere at high temperature to break down the components of the sample into elemental oxides.

3.1.3 *recovery factor*—an indication of the efficiency of the measurement computed by dividing the measured value of a standard by its theoretical value.

3.1.4 *reference sensor pair*—detects changes in triiodide ion concentrations.

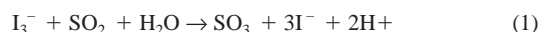
3.1.5 *titration parameters*—various instrumental conditions that can be changed for different types of analysis.

3.1.6 *working electrode (generator electrode)*—an electrode consisting of an anode and a cathode separated by a salt bridge or a liquid electrolyte bridge; maintains a constant triiodide ion concentrations.

4. Summary of Test Method

4.1 A liquid specimen is injected into a combustion tube that can be maintained between 900° to 1200° C and having a flowing stream of gas containing approximately 50 to 75 % oxygen and 25 to 50 % inert gas (for example helium, 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 electrical work required to replace it is a measure of the sulfur present in the sample injected.

4.2 The reaction is generated in the titration cell as sulfur dioxide as follows:



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



5. Significance and Use

5.1 Total sulfur concentrations are typically required for benzene, toluene, and xylenes used as chemical intermediates and in solvents. This test method may be used for both final product inspections and process control.

5.2 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.

6. Interferences

6.1 This test method is not applicable in the presence of total metal concentrations (for example, nickel, vanadium, and lead) in excess of 500 mg/kg.

NOTE 1—To ensure reliable results, all sources of sulfur contamination must be eliminated.

7. Apparatus

7.1 *Pyrolysis Furnace*, which can maintain a temperature sufficient to pyrolyze the organic matrix and convert sulfur present in the specimen to sulfur dioxide.

7.2 *Pyrolysis Tube*, made of quartz and constructed so that when a sample is volatilized in the front of the furnace, it is swept into the pyrolysis zone by an inert gas, where it combusts when in the presence of oxygen. The inlet end of the tube must have a sample inlet port with a septum through which a sample can be injected by a syringe. The inlet end must also have side arms for the introduction of oxygen and inert carrier gas. The pyrolysis tube must be of ample volume, so that complete pyrolysis of the sample is ensured.

7.3 *Titration Cell*, containing a reference electrode, a working electrode, and a sensor electrode, as well as a magnetic or gas stirrer, with an inlet from the pyrolysis tube, is also required.

7.4 *Microcoulometer*, capable of measuring the potential of the sensing-reference electrode pair, comparing this potential with a bias potential, and amplifying the difference to the working electrode pair to generate a current. The microcoulometer output voltage signal should be proportional to the generating current.

7.5 *Automatic Boat Drive*, having variable stops, such that the sample boat may be driven into the furnace, and stopped at various points as it enters the furnace.

7.6 *Constant Rate Injector*, capable of injecting 0.5 $\mu\text{L/s}$.

7.7 *Controller*, with connections for the reference, working, and sensor electrodes. The controller is used for setting of operating parameters and integration of data.

7.8 *Dehydration Tube*, if applicable, positioned at the end of the pyrolysis tube so that effluent gases are bubbled through a phosphoric acid solution, and water vapor is subsequently trapped, while other gases are allowed to flow into the titration cell.

7.9 *Gas-Tight Sampling Syringes*, having 10, 25, 50 and 250 μL capacity, capable of accurately delivering 10, 40 and 50 to 200 μL of sample.

7.10 *Quartz or Platinum Boats*.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests, unless otherwise indicated, it is intended that

all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

8.3 *Acetic Acid*, concentrated acetic acid.

8.4 *Dibenzothiophene*, ($\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{S}$) 98 % +.

8.5 *Argon, Helium*, see instrument manufacturer's specifications.

8.6 *Cell Electrolyte*, see instrument manufacturer's specifications.

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

8.8 *Oxygen*, high-purity grade (HP) (Note 2, used as the reactant gas).

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

8.10 *Sodium Azide*, (N_3N_3) fine granular.

8.11 *Phosphoric Acid*, 85 % free of sulfur.

8.12 *Toluene, p-Xylene, 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.

8.13 *Sulfur*, standard stock solution (approximately 1000 $\mu\text{g/mL}$ xylene) weigh accurately 0.58 g of dibenzothiophene into a tared 100-mL volumetric flask. Dilute to the mark with *p-xylene, isooctane* or toluene as follows:

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

where:

DBT = dibenzothiophene,

A = percent S in dibenzothiophene, and

B = purity of dibenzothiophene.

9. Hazards

9.1 Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations.

10. Sampling

10.1 Sample the material in accordance with Practice D 3437.

11. Preparation of Apparatus

11.1 Carefully insert the quartz pyrolysis tube into the pyrolysis furnace and connect the reactant and carrier gas lines.

11.2 Connect the boat drive or constant rate injector to the pyrolysis tube.

⁶ Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

11.3 Add the electrolyte solution to the titration cell according to manufacturer's specifications.

11.4 Add the proper solutions to the chamber of the working electrode and to the inner and outer chambers of the reference electrode or follow manufacturer's recommendation for preparation of electrodes.

11.5 Connect the titration cell to the microcoulometer according to manufacturer's instruction.

11.6 Adjust the flow of the gases, the pyrolysis furnace temperature, and titration parameters to the desired operating conditions, located in the Appendix X1.

11.7 Pre-bake the sample boats to be used for the determination. Follow manufacturer's recommendations for preparation of sample boats.

12. Calibration and Standardization

12.1 Using the sulfur standard stock solution (see 8.13) make a series of three calibration standards as follows: 1 µg S/mL, 50 µg S/mL, and 100 µg S/mL.

12.2 Adjust the operational parameter for a three-point calibration. If the instrument is not equipped for a three-point calibration, manually record the recovery factors and calculate or follow manufacturer's procedures and recommendations to standardize.

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

12.3.1 Volumetric measurement can be utilized by filling the syringe with standard, carefully eliminating all bubbles, and pushing the plunger to a calibrated mark on the syringe, and recording the volume of liquid in the syringe. After injecting the standard, read the volume remaining in the syringe. The difference between the two volume readings is the volume of standard injected. This method requires the known or measured density, to the third decimal place. Several densities of various hydrocarbons are listed in Table 1.

12.3.2 Alternatively, the syringe may be weighed before and after the injection to determine the weight of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of ±0.0001 g is used.

12.4 Insert the syringe needle through the septum into the quartz boat or combustion tube and inject the sample. Start the boat drive or constant rate injector, and insert the standard into the furnace. Check with instrument manufacturer's recommendations for rate of injection and boat speed.

TABLE 1 Densities of Common Hydrocarbons^A

Component	Density	Temperature° C
Benzene	0.879	20
Cyclohexane	0.779	20
Ethylbenzene	0.867	20
Isopropylbenzene	0.862	20
Toluene	0.867	20
<i>m</i> -Xylene	0.864	20
<i>o</i> -Xylene	0.880	20
<i>p</i> -Xylene	0.861	20

^AHandbook of Chemistry and Physics, 40th ed., "Table, Physical Constants of Organic Compounds," Chemical Rubber Co.

12.5 Repeat the measurement of a blank and each calibration standard at least three times.

12.6 If low recovery factor occurs, fresh standards should be prepared. If the recovery factor remains low, new electrolyte, or new electrode solution, or both, should be prepared. If the recovery factor still does not fall in the proper range, procedural details should be reviewed. Check with manufacturer's specifications for low recovery.

12.7 Calculate a three-point calibration curve. If the instrument is not equipped with a three-point calibration, then follow manufacturer's recommendations for standardization of instrument.

13. Procedure

13.1 Clean the syringe to be used for the sample. Flush it several times with the sample. Determine the sulfur concentration in accordance with 12.3-12.6.

13.2 Sulfur determination for the sample may require a change in titration parameters or adjustment in sample size, or both. Check with instrument manufacturer's recommendations.

14. Calculation

14.1 Measurement utilizing volume and known specific gravity in milligrams per kilograms is as follows:

$$\text{Sulfur, mg/kg} = \frac{(M - B)}{V \times D} \times \frac{1}{RF} \quad (4)$$

14.2 Measurement utilizing weight of sample, considering dilution's in milligrams per kilograms is as follows:

$$\text{Sulfur, mg/kg} = \frac{(M - B)}{W} \times \frac{1}{RF} \quad (5)$$

where:

M = measured sulfur value, µg,

B = blank sulfur value, µg,

V = sample injection volume, µL,

W = weight of sample, g,

D = density of sample, g/mL, and

RF = recovery factor = µg sulfur titrated/theoretical value.

15. Report

15.1 Report the sulfur results as (mg/kg) of the sample.

16. Precision and Bias

16.1 *Repeatability*:

16.1.1 Based on the data from one laboratory on seven different samples done in triplicate (7), the standard deviation of this revised method is as follows:

$$\text{Standard deviation} = 0.011 \times Y \quad (6)$$

where:

Y = the mean value of triplicate determination.

16.2 *Reproducibility*—To be determined.

16.3 *Bias*—To be determined.

17. Keywords

17.1 aromatic hydrocarbons; oxidative microcoulometry; sulfur

APPENDIX
(Nonmandatory Information)
X1. DESIRED OPERATING CONDITIONS

X1.1 Table X1.1 illustrates two instrument's parameters and settings.

TABLE X1.1 Desired Operating Conditions^{A,B}

INSTRUMENT 1		INSTRUMENT 2	
Instrument 1 Parameters	Instrument 1 Settings	Instrument 2 Parameters	Instrument 2 Setting
Endpoint	225 to 275 mV	Temperatures	800°C inlet 900°C outlet
Gain 1	1.5		
Gain 2	2.5	Cell bias	140
Gain 3	5.0	Gain	1
Sensitivity	0.1 to 10 mV	Integration time	4 min
Furnace temperature	900°C		
Oxygen flow	200 mL/min		
Carrier gas flow	250 mL/min		
Delay	180 s		

^AThe sole source of supply of the apparatus for Instrument 1, known to the committee at this time is Cosa Instrument Corporation, Norwood, NJ. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

^BThe sole source of supply of the apparatus for Instrument 2, known to the committee at this time is Tekmar-Dohrmann, Cincinnati, OH. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

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