



Designation: D 6313 – 99

Test Method for Total Sulfur in Aromatic Compounds by Hydrogenolysis and Sulfur Specific Difference Photometry¹

This standard is issued under the fixed designation D 6313; 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 the determination of sulfur in aromatic hydrocarbons, their derivatives and related chemicals having typical sulfur concentrations from 0.005 to 10 mg/kg.

1.2 This test method may be extended to higher concentrations by dilution.

1.3 This test method is applicable to aromatic hydrocarbons such as benzene, toluene, cumene, *p*-xylene, *o*-xylene, cyclohexane, phenol, cresols, xylenols, and other aromatic or oxygenated aromatic compounds.

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

1.5 *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.* Specific precautionary statements are given in 7.5, 7.6, 8, 11.4.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products³

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid³

D 4052 Test Method for Density and Relative Density of Liquids for Digital Density Meter⁴

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals³

E 29 Practice for Using Significant Digits in Test Data to

Determine Conformance with Specifications⁵

2.2 Other Documents:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.12000⁶

3. Terminology

3.1 Definitions:

3.1.1 *difference photometry, n*—an analytical method where a photometric property of a colorimetric reactant (such as reflectivity) is first measured as a baseline reading, the reactant exposed to the material in question, then a second reading taken.

3.1.1.1 *Discussion*—The difference between the post exposure reading and the baseline reading constitute the measurement of the reaction between the material in question and the reactant, that is, if the reactant changes its photometric property proportionally to the concentration of the material in question, the method could be used to measure concentration.

3.1.2 *oxyhydrolysis, v*—The act of first burning a material within an inner chamber in a pyrolysis furnace to change that material to combustion products, and then to release those products into a hydrogen rich atmosphere to then reduce those combustion products.

3.2 See Terminology D 4790 for definitions of other terms used in this test method.

4. Summary of Test Method

4.1 *Reductive Configuration*—A specific amount of sample is injected at a uniform rate into an air stream and introduced into a sample dispersing mechanism where the liquid sample is evaporated and thoroughly mixed with the hydrogen. This mixture is then introduced into a pyrolysis furnace. Within this apparatus the sample is pyrolyzed at temperatures of 1200° to 1300°C and in the presence of excess hydrogen. The sulfur compounds are broken down and reduced to H₂S. Analysis is by difference photometry of the colorimetric reaction of H₂S with lead acetate.

4.2 *OxyhydroPyrolysis Configuration*—A specific amount of sample is injected at a uniform rate into an air stream and

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 D016.04 on Instrumental Analysis.

Current edition approved April 10, 1999. Published June 1999. Originally published as D 6313 – 98. Last previous edition D 6313 – 98.

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 05.02.

⁵ Annual Book of ASTM Standards, Vol 14.02.

⁶ Available from Superintendent of Documents, U.S. Government Printing office, Washington, DC 20402.

introduced into a sample dispersing mechanism where the liquid sample is evaporated and thoroughly mixed with the air. This mixture is then introduced into a pyrolysis furnace. The sample flows through an inner tube within the furnace where it combusts with the oxygen in the air carrier. SO₂ and SO₃ are formed from the sulfur compounds in the sample. The sample then leaves the inner tube within the pyrolyzer and is mixed with hydrogen within the main reaction tube and is pyrolyzed at temperatures of 1200° to 1300°C. The SO₂ and SO₃ formed within the inner tube are then reduced to H₂S. Analysis is by difference photometry of the colorimetric reaction of H₂S with lead acetate.

5. Significance and Use

5.1 Sulfur can be a catalyst poison in the aromatic chemical manufacturing process. This test method can be used to monitor the amount of sulfur in aromatic hydrocarbons. This test method may also be used as a quality control tool and in setting specifications for sulfur determination in finished products.

6. Apparatus

6.1 The apparatus of this test method can be set up in two different configurations that will be described herein as the “reductive pyrolysis” configuration, and the “oxyhydrolysis” configuration. The oxyhydrolysis configuration is a modification of the reductive pyrolysis configuration, which minimizes the formation of coke within the pyrolysis furnace when running aromatic samples. Both setups can be used to measure sulfur in aromatic compounds as outlined in this test method.

6.2 *Pyrolysis Furnace*—A tube furnace that can provide an adjustable temperature of 900 to 1300° C. An 8-mm or larger inner diameter is required in the furnace to fit reaction tubes of sufficient size to pyrolyze the sample.

6.2.1 *Oxyhydrogen Furnace Adapter*—An apparatus, used in the oxyhydrolysis set up, that fits to the front of the reaction tube and adds an injection tube that extends partially within the main reaction tube to about 1/2 way into the furnace (see Fig. 1). The oxidative process occurs in the injection tube, then the combustion products of the sample are injected into the flow of hydrogen at the hot zone.

6.2.2 *Water Removal Apparatus*—A device that attaches close to the outlet of the pyrolysis furnace, used in the oxyhydrolysis set up to remove excess moisture from the sample stream. Both membrane counter flow driers or coalescing filters held at sub-ambient temperatures have been found to be suitable.

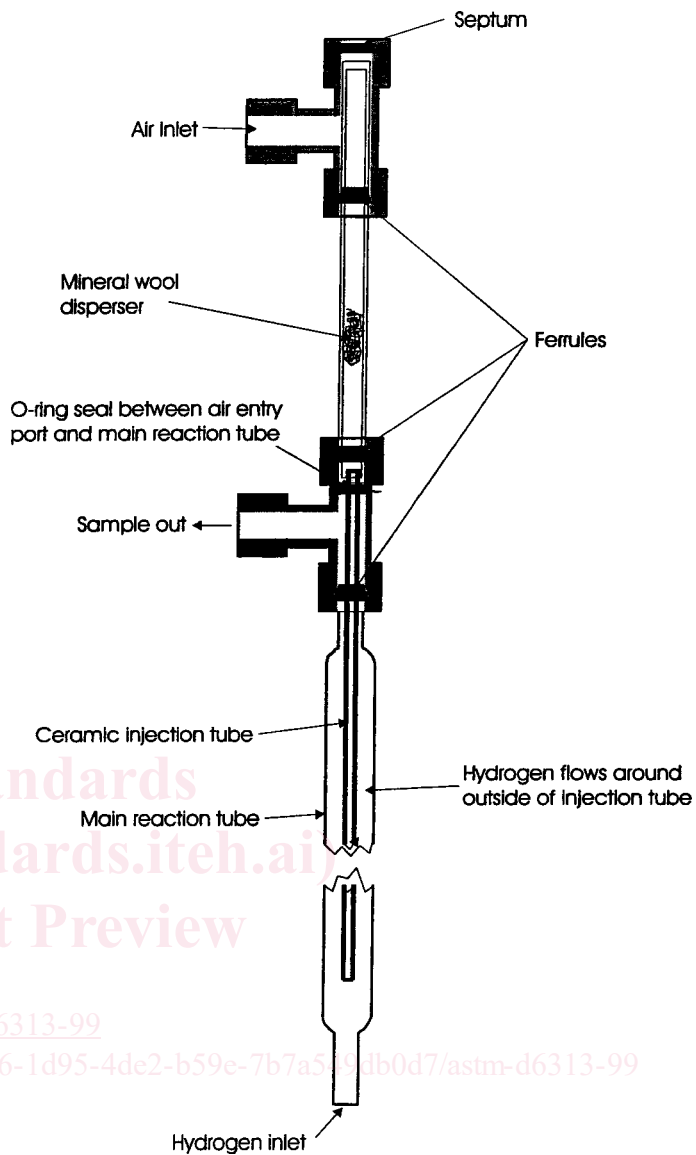


FIG. 1 Oxyhydrogen Furnace Adapter Detail

6.3 *Sample Injector*—A syringe drive, autosampler or other suitable injection system that can inject the sample into the pyrolysis furnace at a uniform injection rate adjustable between 1 to 50 µL/min.

6.4 *Sample Dispersion Apparatus*⁷—A tube filled with quartz wool or other porous material is placed at the inlet of the pyrolysis furnace to disperse and mix liquid samples into the gas carrier before entry into the pyrolyzer. This tube is surrounded by a small heater for the purpose of controlling the

⁷ The sample dispersion apparatus is covered by a patent held by Houston Atlas Inc. Interested parties are invited to submit information regarding the identification of acceptable alternatives to this patented item to the Committee on Standards, ASTM International Headquarters, 100 Barr Harbor Dr., West Conshohocken, Pa. 19428-2959 USA. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

evaporation rate of the liquid sample being injected. Higher boiling point liquids require higher inlet temperatures to ensure proper evaporation and dispersion. The inlet heater should be able to be set from room temperature to 350° C.

6.5 Flow System—The flow system to and from the pyrolysis furnace is to be a fluorocarbon, 316 stainless steel, nylon or other material inert to H₂S and other sulfur compounds. Gas flow should be controlled by mass flow or pressure differential-type flow controllers that have a range of 0 to 500 mL/min.

6.6 Lead Acetate Difference Photometer—A device that consists of a paper tape transport mechanism, a sample chamber with a window opening to the surface of lead acetate treated paper tape, a photometer to read the reflectivity of the lead acetate treated tape, and sufficient electronics to control the transport of tape, to do system timing, to take the photometric readings, and to control the sample injector. The photometer should have sufficient sensitivity to detect 0.005 mg/kg.

NOTE 1—The difference photometer works as follows: The paper tape is advanced to a new spot. The paper tape is exposed to carrier gas for a predetermined amount of time (usually 60 s). A zero reading is taken and then sample injection is started and the photometer starts timing its run. (The run time has been predetermined by trial runs of a specific sample. The time is set so that all of the sulfur in the sample has had the chance to flow through the system and no more change in reflectivity is seen.) A final reading is then taken. The zero reading and final reading in conjunction with a calibration curve is used to determine the sulfur concentration in the sample. Some computerized difference photometers can generate the calibration curve internally during calibration.

6.7 Recorder—A suitable chart recorder may be used for a permanent record of analysis. A suitable printer may be used by computerized photometric analyzers, or data can be read to magnetic media for storage or further analysis.

7. Reagents and Materials

7.1 Purity of Chemicals—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.⁸ 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, reference to water shall be understood to mean Type IV, reagent grade water, conforming to Specification D 1193.

7.3 Sensing Tape—Lead-acetate-impregnated analytical-quality filter paper shall be used.

7.4 Acetic Acid, 5 %—Mix 1 part by volume reagent grade glacial acetic acid with 19 parts water to prepare 5 % acetic acid solution.

7.5 Hydrogen Gas—Use sulfur-free hydrogen of laboratory grade. **Warning:** Hydrogen has wide explosive limits when mixed with air.

⁸ *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 *Analar 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.

7.6 Instrument Air—Use dry, sulfur free air. Nitrogen/oxygen, or helium/oxygen bottled gas blends containing no more than 30 % oxygen by volume can be used where air utilities are not available. **Warning:** Do not use pure oxygen as a substitute for instrument air.

7.7 Toluene, sulfur free.

7.8 Thiophene—99 + % purity.

8. Hazards

8.1 Consult current OSHA regulations, suppliers Material Safety Date Sheets, and local regulations for all materials used in this test method.

9. Sampling

9.1 Sample the material in accordance with Practice D 3437.

9.2 Sample phenol and cresylic acid in accordance with Practice D 3852.

10. Calibration Standards

10.1 Prepare a reference standard solution or solutions of strength greater than that expected in the unknown, by first preparing a stock solution of thiophene in toluene and volumetrically diluting the stock to prepare low level standards.

10.2 Preparation of the Stock Standard Solution: To prepare a sulfur standard with a sulfur concentration of 1000 mg/L, obtain a clean 100-mL volumetric flask. Pour approximately 90 mL of toluene (sulfur free), kept at a room temperature of 25°C. into the flask. Weigh approximately 0.2625g (250 µL) of thiophene directly into the flask and record the exact weight added to a precision of ±0.1 mg. Add additional toluene to make 100.0 mL.

10.3 Calculate the sulfur concentration of the stock solution as follows:

$$A = \frac{B}{0.1C}D \quad (1)$$

where:

A = concentration of sulfur in mg/L,

B = molecular weight of sulfur: 32.6,

C = molecular weight of thiophene: 84.14,

D = exact weight of the sulfur compound used in milligrams, and

0.1 = volume of standard in litres.

10.4 Preparation of Working Standards: The preparation of working standards is accomplished by volumetric dilution of the stock solution. As an example, to prepare a 1.00-mg/L standard, dilute 0.10 mL of the 1000-mg/L stock solution into 100 mL of toluene (sulfur free). Note: keep containers closed as much as possible. Do not open containers of pure sulfur compounds in the vicinity of low level calibration standards.

NOTE 2—The use of standard samples made to mg/L units have the advantage of delivering a specific number of milligrams of sulfur into the analyzer for a specific sample size regardless of the sample compound used. A standard of one type of compound could be used to calibrate the analyzer, with an unknown of another type sample compound run. To determine the sulfur content of the unknown in mg/kg simply divide the mg/L answer by the density (expressed in g/mL) of the unknown sample. Some analyzers complying with this method have provision to enter the densities of both the calibration standard and the unknown. In these cases