Designation: D 6313 – 99

Test Method for
Total Sulfur in Aromatic Compounds by Hydrogenolysis and Sulfur Specific Difference Photometry[1]

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 Water[2]

D 3437 Practice for Sampling and Handling Liquid Cyclic Products[3]

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid[3]

D 4052 Test Method for Density and Relative Density of Liquids for Digital Density Meter[4]

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals[3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]

2.2 *Other Documents:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.12000[6]

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 *oxyhydropyrolysis, 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 H_2S. Analysis is by difference photometry of the colorimetric reaction of H_2S with lead acetate.

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

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[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. SO_2 and SO_3 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 SO_2 and SO_3 formed within the inner tube are then reduced to H_2S. Analysis is by difference photometry of the colorimetric reaction of H_2S 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 "oxyhydropyrolysis" configuration. The oxyhydropyrolysis 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 oxyhydropyrolysis 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 ½ 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 oxyhydropyrolysis 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.

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.

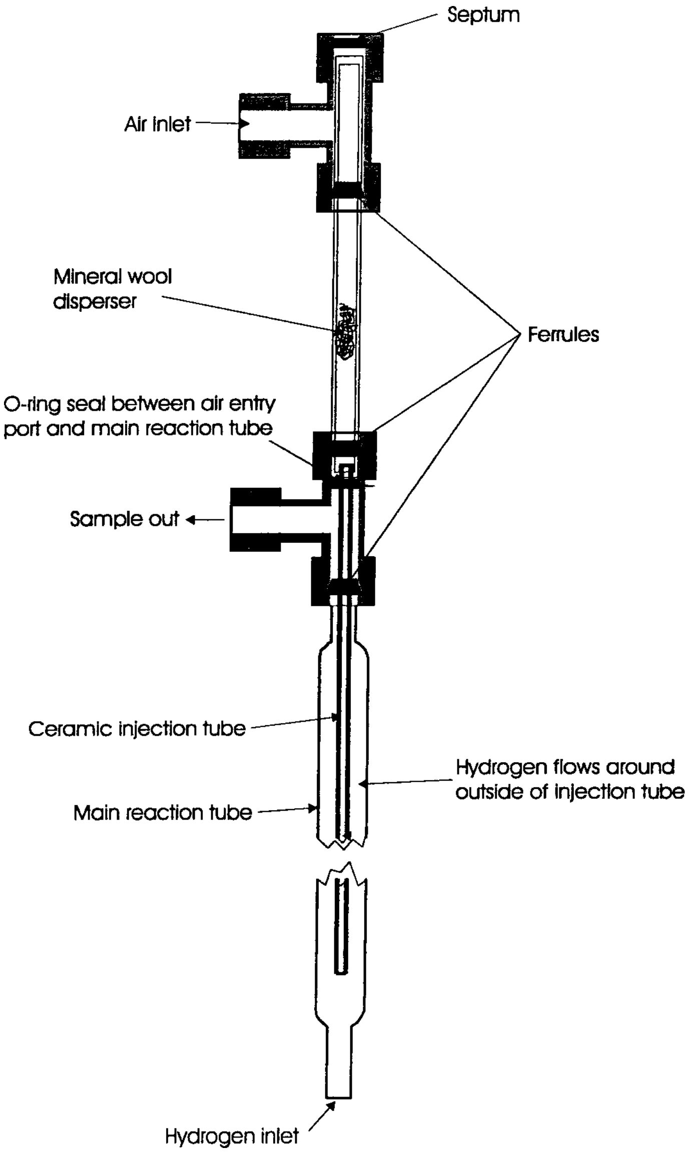

FIG. 1 Oxyhydrogen Furnace Adapter Detail

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 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 H_2S and other sulfur compounds. Gas

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[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.

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.

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:

$$A = \frac{B}{0.1C}D \tag{1}$$

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 the analyzer will make the appropriate density corrections between the standard samples and the unknowns being analyzed. The reported measurement units of the answer can be set by the operator.

11. Preparation of Apparatus

11.1 *Reductive Setup*—Connect all flow tubing between components and hydrogen (see Fig. 2). Make sure gas source

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[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.

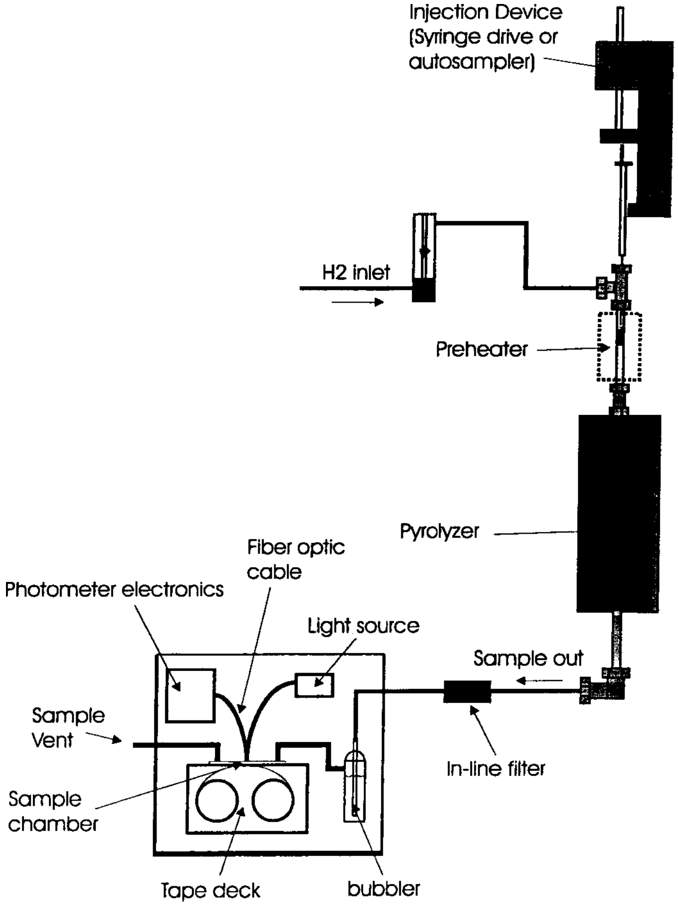

FIG. 2 Reductive Setup

is closed before connecting it to the apparatus. Turn on hydrogen gas and check all connections for leaks with soap solution and repair any leaks. Turn off carrier gas when leak check is complete.

11.2 *Oxyhydropyrolysis Setup*—Connect all flow tubing between components and carrier gases (hydrogen and air) (see Fig. 3). Make sure gas sources are closed before connecting it to the apparatus. Turn on each carrier gas in turn and check all connections for leaks with soap solution and repair any leaks. Turn off carrier gases when leak check is complete.

11.3 Turn on the furnace and allow temperature to stabilize at 1200°C. If monoaromatics of C_{10} or lower are to be run, make final pyrolyzer temperature adjustment to 1215 ± 15°C. For all other aromatic compounds make final pyrolyzer temperature adjustment to 1315 ± 15°C.

11.4 Install sensing tape into difference photometer. Fill the humidifier with a 5 % by volume acetic acid solution. Take care to not spill the acetic acid on the apparatus. Turn difference photometer on. **Warning:** Use adequate safety precautions in handling lead acetate tape.

11.5 Adjust the zero of the difference photometer (and recorder if used) to its desired position with no flow. This should be performed with span at maximum. Skip this step if the difference photometer is computerized and automatically sets its own zero level.

11.6 Test hydrogen purity. Set photometer on its most sensitive scale. Set hydrogen flow to 200mL/min. Pull a new piece of tape into the sample chamber window. Allow tape to humidify for 30 s. Take an initial reading on the photometer. Allow the run time of the measurement to elapse and take reading and record. Subtract the initial reading from the final reading. If the difference greater than 10 % of the full scale of the photometer, then the hydrogen source should be suspect as not being sulfur free and should be changed or scrubbed.

11.7 For apparatus configured in the oxyhydropyrolysis setup, also test air purity. This is done by maintaining the hydrogen flow at 200 mL/min. and setting the air flow to 250 mL/min. Pull an new piece of tape into the sample chamber window. Allow tape to humidify for 30 s. Take an initial reading on the photometer. Allow the run time of the measurement to elapse and take reading and record. Subtract the initial reading from the final reading. If the difference is greater than 10 % of the full scale of the photometer, then the air source should be suspect as not being sulfur free and should be changed or scrubbed.

11.8 If the change in the reading is less than 10 % then the air and hydrogen are usable.

12. Calibration and Standardization

12.1 This analytical method is ratiometric in nature. The response of an unknown sample is compared with a calibration curve made from the readings of a series of standard samples. Four samples spaced in concentration throughout the anticipated range of the unknown samples, including a zero value, is

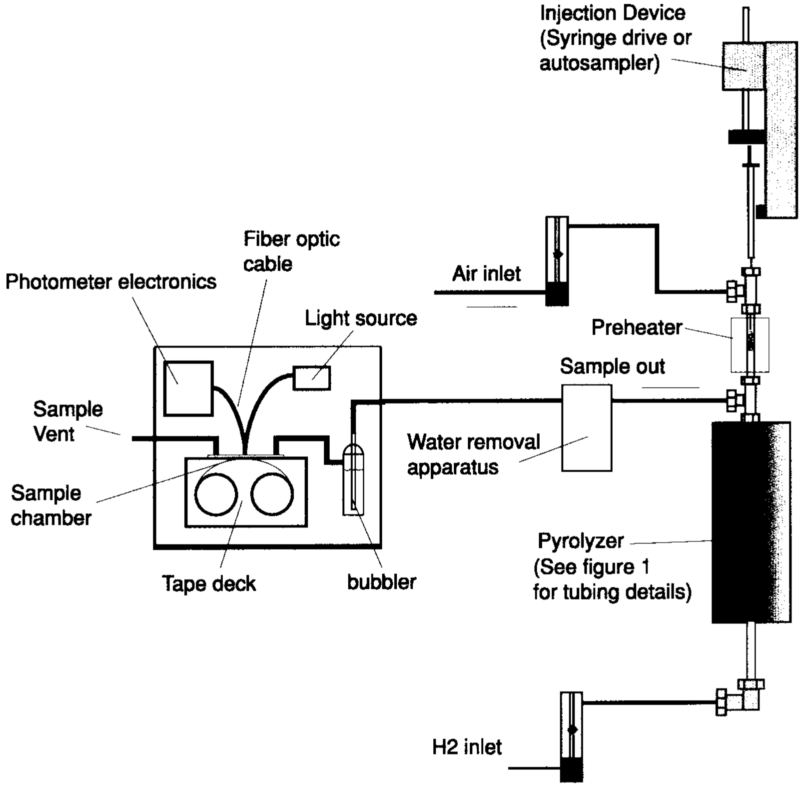

FIG. 3 Oxyhydropyrolysis Setup

sufficient to establish a curve of suitable accuracy.

12.2 *Non-computerized Analyzers:* Do an initial run with the highest anticipated standard sample to season the tubing of the apparatus.

12.3 Move tape to a clean spot within the sample chamber window. Allow the tape to become humidified for 30 s.

12.4 Take a reading of the reflectivity of the clean piece of tape and record.

12.5 Start introducing with a sample injector a predetermined amount of sample into the inlet of the pyrolysis furnace. Also start timing the run. It has been found that 50 µL of sample is sufficient for analyses of samples containing from 0.005 mg/kg to 1 mg/kg of sulfur. Lessen the amount of sample delivered when running higher concentrations to keep from exceeding the response window of the photometer. Multiple injections during a run can be used to increase the sensitivity of the method.

NOTE 3—Multiple injections of a smaller syringe create less carboning in the pyrolysis furnace than injecting the same amount of sample from a larger syringe.

12.6 Note the photometer readings during the analysis. The readings should change most rapidly during sample injection and then should level off to a final value towards the end of the run. The reading might continues to slowly change towards the end of the run; this can be due to small concentrations of sulfur compounds in the carrier gas. When the reading seems fairly stable, note the time of the run and take a reading from the photometer.

12.7 Allow the system to idle with gas flowing for ½ h. then repeat 12.3-12.5 but this time do not inject any sample. Allow the analysis to run for the length of time noted for the run in 12.6. When the run time has elapsed take a reading. Subtract the initial reading from the final one. This reading difference represents the concentration of sulfur impurities in the hydrogen and air carrier gases. Record this reading difference because it will be used later to correct sample runs for sulfur impurities in the carrier gases. Repeat actions in 12.7 every time a carrier gas bottle is changed. It does not have to be reported unless a carrier gas change has occurred.

12.8 Repeat the procedure outlined in 12.3-12.6, but using the run time determined in the first run to time run, with each of the standard samples needed to build the desired calibration curve. For best accuracy, it is recommended that the calibration procedure be repeated three times for each standard value and the calibration curve be constructed using the average of the replicates for each calibration point.

12.9 Note density of the calibration standard. If the density of the calibration standard is not known, it may be determined using Test Method D 4052.

12.10 Build the calibration curve as follows:

12.10.1 Obtain a raw difference reading for each replicate of the calibration run. This is done by subtracting the initial reading obtained before each sample run from the reading that was obtained after the tape had been exposed to sample. From this number subtract the value calculated from executing 12.7. Average the raw difference readings for each calibration point. Construct a calibration curve by graphing the average of each raw difference count with respect to the value of the standard sample.

12.11 *Analyzers With Computer Controlled Calibration and*

Autosampler: Prepare sample vials for three replicates of the three values of the desired standard samples plus three blanks (can be air blanks). Load the autosampler and run as directed by the computerized analyzer. After the standards have run, key in the raw readings into the calibration routine of the analyzer. The analyzer will calculate the calibration curve and place it in memory for future use.

13. Sample Measurement Procedure (Non-Computerized Analyzers)

13.1 Move a clean spot of tape into the sample chamber window. Allow it to humidify for 30 s, Note photometer response and record it.

13.2 Inject a sample into the pyrolysis furnace using the same sample volume and sample delivery speed used to run the calibration standards. Allow analysis to run for the time determined during calibration. When the run time has elapsed, take a photometer reading and record it.

13.3 Determine the concentration of an unknown sample in mg/kg as follows:

$$X = (A - B - C) \tag{2}$$

where:

A = photometer reading for the unknown sample at after run has completed,
B = photometer reading from unexposed tape,
C = correction for impurities in the carrier gases, (see 12.7), and
X = raw difference from sample run.

13.4 Compare raw difference reading X with the calibration curve developed during the standardization procedure to ascertain correct concentration.

13.5 Use the following calculation to correct result obtained in 13.4 for differences in density between the sample and the calibration standard:

$$V_{corr} = \frac{D_{cal}}{D_{samp}} \cdot V_{raw} \tag{3}$$

where:

V_{corr} = value corrected for density, mg/kg,
D_{cal} = density of calibration standard, g/mL,
D_{samp} = density of sample, g/mL, and
V_{raw} = value of result determined in 13.4 mg/kg.

The density of the sample can be determined using Test Method D 4052 if not already known.

13.6 A partial list of the densities of aromatic compounds is given in Table X1.1 of Appendix X1.

14. Sample Measurement Procedure (Computerized Analyzers With Autosampler)

14.1 Prepare unknown samples for insertion into autosampler. After the autosampler has been loaded, enter the appropriate sample information into the analyzer and start the analysis procedure.

14.2 Computerized analyzers calculate the result from information entered during the calibration procedure, and display an answer in the appropriate engineering units.

15. Report

15.1 Report the following information:

15.1.1 Total sulfur concentration in mg/kg.

15.1.2 Full scale calibrations greater than 0.250 mg/kg, report sample concentrations to the nearest 2 % of full scale calibration. (For example for a full scale calibration of 10 mg/kg, report the result to the nearest 0.2 mg/kg.)

15.1.3 Full scale calibrations of 0.250 mg/kg or less, report sample concentrations to the nearest 0.005 mg/kg.

16. Precision and Bias

16.1 *Intermediate Precision*—Intermediate precision has been determined as shown in Table 1.

16.2 *Reproducibility*— Reproducibility has not been determined at this time.

16.3 *Bias*—Since there is not accepted reference material for determining the bias in this test method for measuring total sulfur in aromatic compounds, bias has not been determined.

17. Keywords

17.1 aromatic; aromatic compounds; benzene; cresol; cumene; cyclohexane; difference photometry; on-line; oxygenated aromatics; oxyhydropyrolysis; phenol; pyrolysis; sulfur; toluene; trace total sulfur; xylenol

TABLE 1 Intermediate Precision[A]

Value	Result 1	Result 2	Result 3	Result 4	Mean	Standard Deviation
1.08	0.99	1.09	1.11	1.11	1.08	0.04
0.205	0.22	0.23	0.23	0.22	0.22	0.01
0.05	0.06	0.08	0.07	0.02	0.06	0.02

[A] Results are ug/g. sulfur. Standards whose values are designated are made with thiophene in toluene. These results are from one operator in one laboratory.

APPENDIX

(Nonmandatory Information)

X1. DENSITIES OF AROMATICS

X1.1 Table X1.1 illustrates aromatic densities.

TABLE X1.1 Densities of Aromatics[A]

Benzene	0.8765
Cumene	0.8618
Cyclohexane	0.7785
p-Xylene	0.8611
Toluene	0.8669

[A] Densities are at 20° C relative to water at 4° C. From *CRC Handbook of Chemistry and Physics*, 72nd ed., CRC Press, Inc., 1991–1992.

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