



# Standard Test Method for Total Sulfur in Aromatic Compounds by Hydrogenolysis and Rateometric Colorimetry<sup>1</sup>

This standard is issued under the fixed designation D 6212; 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.

## 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 0.020 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 and related chemicals such as benzene, toluene, cumene, *p*-xylene, *o*-xylene, and to cyclohexane.

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 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 6.4, 7.5, 7.7, and 8.1.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 3437 Practice for Sampling and Handling Liquid Cyclic Products<sup>3</sup>

D 4045 Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry<sup>4</sup>

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>4</sup>

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals<sup>3</sup>

E 29 Practice for Using Significant Digits in Test Digits in

Test Data to Determine Conformance with Specifications<sup>5</sup>

### 2.2 Other Documents:

OSHA Regulations, 29 CFR paragraphs 1910.1 and 1910.1200<sup>6</sup>

## 3. Terminology

3.1 See Terminology D 4790 for definition of terms used in this test method.

## 4. Summary of Test Method

4.1 *Reductive Configuration*—The sample is injected at a constant rate into a hydrogenolysis apparatus. Within this apparatus the sample is pyrolyzed at temperatures in the range of 1200°C to 1300°C and in the presence of excess hydrogen. Sulfur compounds are reduced to hydrogen sulfide (H<sub>2</sub>S). Analysis is by rateometric detection of the colorimetric reaction of H<sub>2</sub>S with lead acetate. Hydrocarbon components are converted to gaseous such as methane during hydrogenolysis.

4.2 *OxyhydroPyrolysis Configuration*—Sample is injected at a constant rate into an air stream and 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<sub>2</sub> and SO<sub>3</sub> 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 in the range of 1200°C to 1300°C (see Fig. 1). The SO<sub>2</sub> and SO<sub>3</sub> formed within the inner tube are then reduced to H<sub>2</sub>S. Analysis is by rateometric detection of the colorimetric reaction of H<sub>2</sub>S 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 setup in two

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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>4</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>6</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

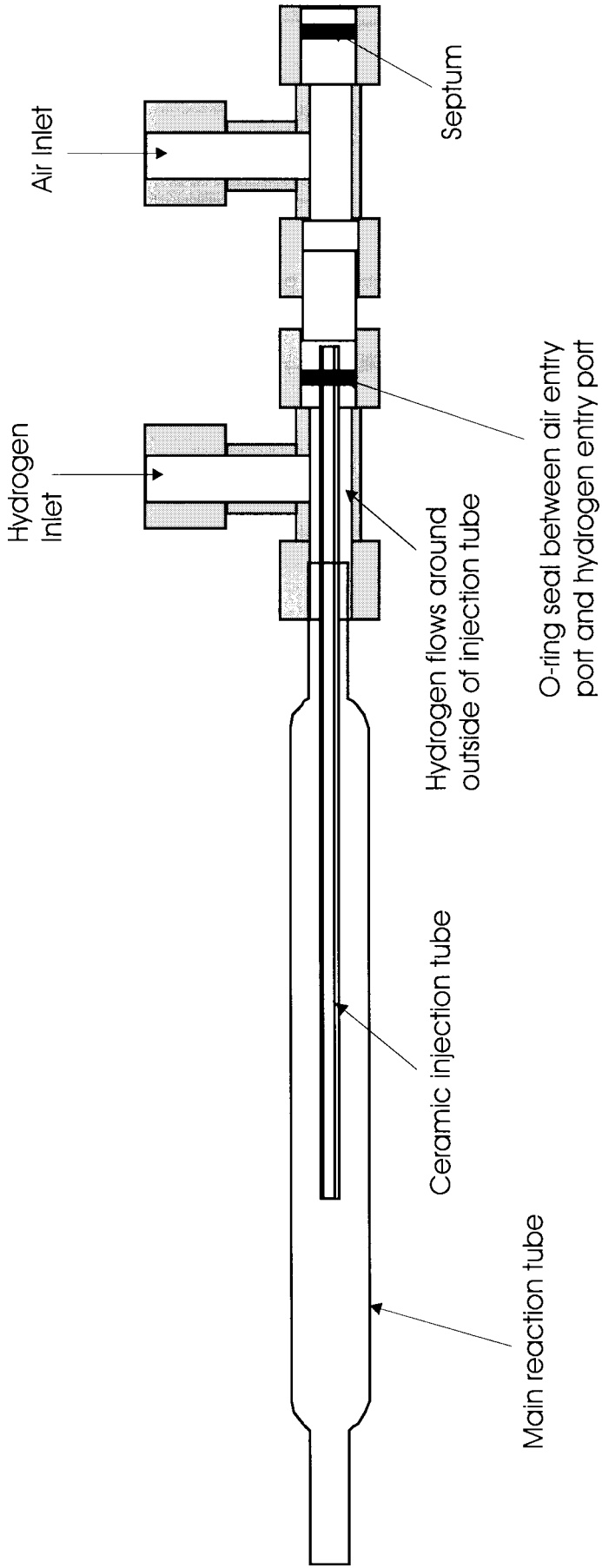


FIG. 1 Oxyhydrogen Furnace Adapter

different configurations, which will be described herein as the “reductive pyrolysis” configuration, and the “oxyhydropyrolysis” configuration. The reductive pyrolysis configuration is the one referenced in Test Method D 4045. The oxyhydropyrolysis configuration is a modification of the reductive pyrolysis configuration that 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 1400°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 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 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 Rateometric H<sub>2</sub>S Detector**—Hydrogenolysis products contain H<sub>2</sub>S in proportion to sulfur in the sample. The H<sub>2</sub>S is measured by measuring rate of change of reflectance caused by darkening when lead sulfide is formed. Rateometric electronics, adapted to provide a first derivative output, allows sufficient sensitivity to measure below 0.01 mg/L.

**6.4 Hypodermic Syringe**—A hypodermic having a needle long enough to reach into the pyrolyzer reaction tube to the 550°C zone is required. Usually a 75-mm long needle is sufficient for the straight reductive setup. The oxyhydropyrolysis setup requires a needle length of 150 mm. A side port is convenient for vacuum filling and for flushing the syringe. A 100-μL syringe is satisfactory for injection rates down to 3 μL/min. and a 25-μL syringe for lower rates.

**NOTE 1—Warning:** Exercise caution as hypodermics can cause accidental injury.

**6.5 Syringe Injection Drive**—The drive must provide uniform, continuous sample injections. Variation in drive injection rate caused by mechanical irregularities of gears will cause noise in the reading of the detector. The adjustable drive must be capable of injection rates from 6 μL/min. to 0.06 μL/min. over a 6-min interval.

**6.6 Recorder**—A chart recorder with 10-V full scale and 10 kΩ input impedance or greater is required, having a chart speed of 0.5 to 3 cm/min. An attenuator may be used for more sensitive recorders.

**6.7 Pyrometer**—A pyrometer with a 25-cm long thermocouple suitable for use at 500 to 1400°C. Diameter must be small enough to fit through the injection tube of the oxyhydrogen furnace adapter. Type K with a 316 stainless steel sheath is suitable.

## 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.<sup>7</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, 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.

**NOTE 2—Warning:** Hydrogen has wide explosive limits when mixed with air.

**7.6 Purge Gas**—Sulfur-free purge gas, nitrogen, CO<sub>2</sub>, or other inert gas. Commercial grade cylinder gas is satisfactory.

**7.7 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.

**NOTE 3—Warning:** Do not use pure oxygen as a substitute for instrument air.

**7.8 Toluene**, (sulfur free).

**7.9 Thiophene**, 99+ % purity.

## 8. Hazards

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

## 9. Sampling

**9.1** Use the practices in accordance with Practice D 3437.

## 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 0.2625 g (250 μL) of

<sup>7</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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeial and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

thiophene directly into the flask and record the exact weight added to a precision of  $\pm 0.1$  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: 32.06,

$C$  = molecular weight of thiophene: 84.14, and

$D$  = exact weight of the sulfur compound used in milligrams.

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). Keep containers closed as much as possible. Do not open containers of pure sulfur compounds in the vicinity of low level calibration standards.

NOTE 4—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 of 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.

## 11. Set-Up Apparatus

11.1 *Straight Reductive Setup*—Connect apparatus as shown in Fig. 2. Fill humidifier bubbler inside the cabinet with 5 % by volume acetic acid solution. Install sensing tape and turn on detector. Connect the recorder. Set pyrolysis furnace temperature to 1200°C and allow system to come to temperature. Purge system with inert gas, and check all connections for leaks with soap solution. Stop flow of inert gas and allow temperature to stabilize. *If monoaromatics of  $C_{10}$  or lower are to be run, make final pyrolyzer temperature adjustment to  $1215 \pm 15^\circ\text{C}$ . For all other aromatic compounds, make final pyrolyzer temperature adjustment to  $1315 \pm 15^\circ\text{C}$ .* Use a standard thermocouple to verify temperature by inserting through a septum with the hydrogen flowing at the rate used for analysis. Determine depth of insertion required with the pyrometer (measure temperature with gases flowing) and always insert the needle tip to a depth corresponding to the 550°C point.

11.2 *Oxyhydrolysis Setup*—Connect apparatus as shown in Fig. 3. Fill humidifier inside the cabinet with 5 % by volume acetic acid solution. Set pyrolysis furnace temperature to 1200°C and allow system to come to temperature. Purge system with inert gas and check all connections for leaks with soap solution. Stop flow of inert gas and allow temperature to stabilize. *If monoaromatics of  $C_{10}$  or lower are to be run, make final pyrolyzer temperature adjustment to  $1215 \pm 15^\circ\text{C}$ . For all other aromatic compounds make final pyrolyzer temperature adjustment to  $1315 \pm 15^\circ\text{C}$ .* Use a standard thermocouple to verify temperature by inserting through a septum with the hydrogen flowing at the rate used for analysis. Determine depth of insertion required with the pyrometer (measure temperature

with gases flowing) and always insert the needle tip to a depth corresponding to the 550°C point.

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

11.4 *Test Hydrogen Purity*—Set the hydrogen flow to 200 mL/min. Advance tape to a new spot. If the reading is upscale from the zero set point by greater than 4 % full scale, then the hydrogen source should be suspect as not being sulfur free and should be changed or scrubbed.

11.5 If the change in the reading is less than 4 %, reset analyzer zero with the hydrogen flowing. This will compensate for the small amount of sulfur in the hydrogen.

11.6 For apparatus configured in the oxyhydrolysis 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. If the reading is upscale from the zero set point by greater than 4 %, then the air source should be suspect as not being sulfur free and should be changed or scrubbed.

11.7 If the changes in the reading is less than 4 %, reset analyzer zero with the hydrogen and air flowing. This will compensate for the small amount of sulfur in the hydrogen and air.

## 12. Calibration

12.1 Advance tape and inject a working standard solution with a sulfur concentration similar to the highest expected value of the unknown samples. Set the plateau of the response curve (see Fig. 4) to approximately 90 % of the recorder's span. This working standard should be analyzed in triplicate to ensure the analyzer has stabilized. Replicate analyses should not differ by more than 5 % relative. Record the average reading as  $R_{\text{std}}$  in 14.1. If the analyzer is computerized, follow calibration steps as indicated in manufacturer's instruction.

12.2 Analyze a working standard that has a concentration 100 times less than the standard used in 12.1. This will be the lower limit of detection for the instrumental conditions used in the testing and should produce a barely discernible response from the recorder.

12.3 Analyze the solvent used to make the working standards, or run analysis without injecting any sample in order to obtain a blank reading. Record this reading as  $R_b$  in 14.1.

## 13. Procedure

13.1 Advance the tape and inject the unknown sample. After a stable reading is obtained, determine the plateau of the response curve (see Fig. 4). Record this value as  $R_S$ . If analyzer is computerized, read analysis answer from readout, and record.

13.2 Proceed with additional samples, advancing the tape each time.

13.3 Every 2 h, or as needed, verify blank and span values.

13.4 To measure samples below 1 mg/kg, inject the sample at the fastest rate that does not cause coking in the reaction tube. Higher injection rates will aid in obtaining the best signal to noise ratio.

13.5 Samples above 1 mg/kg require proportionally lower inject rates, span adjustment, or a smaller syringe. A sharp fall

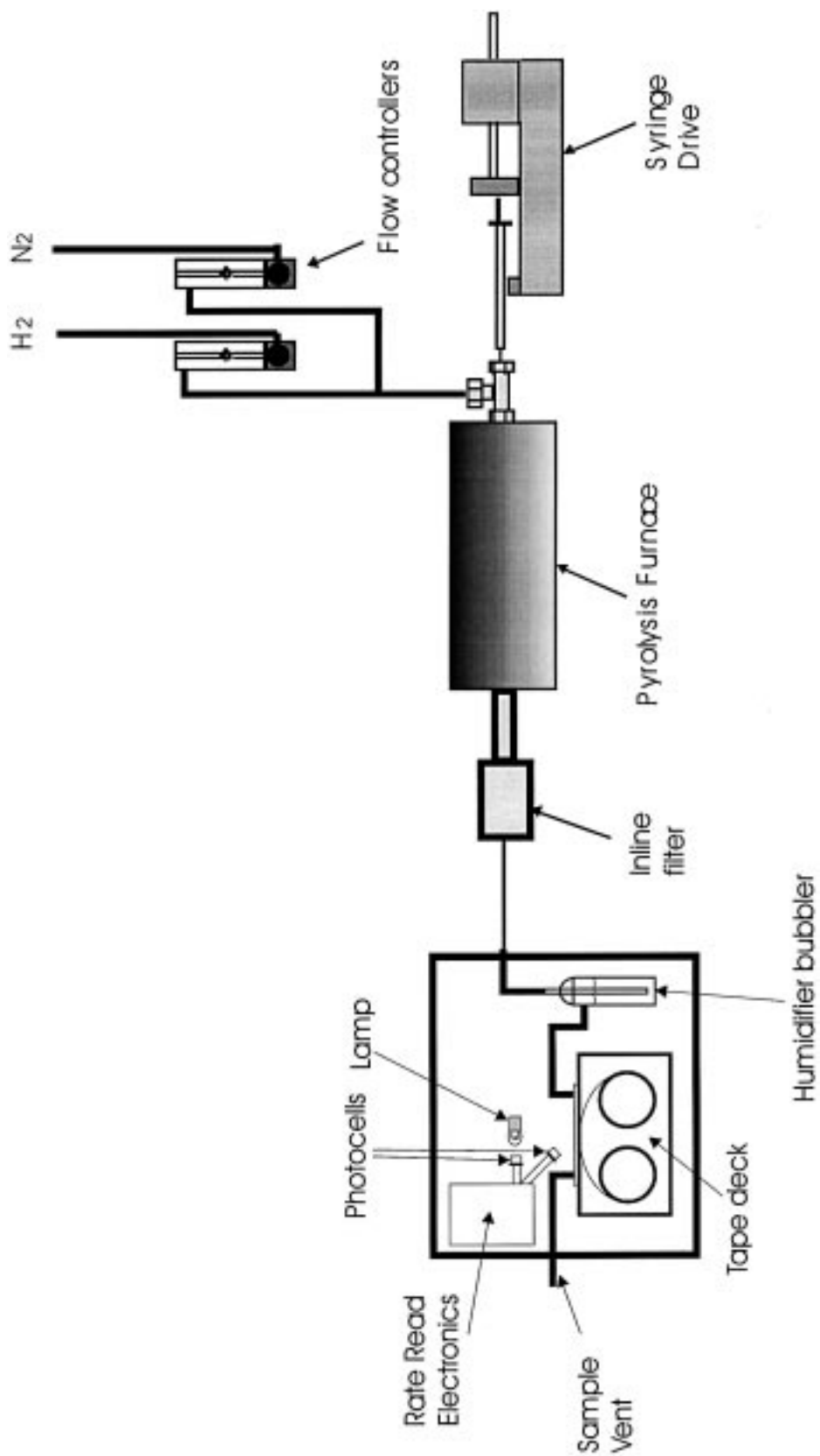


FIG. 2 Reductive Setup

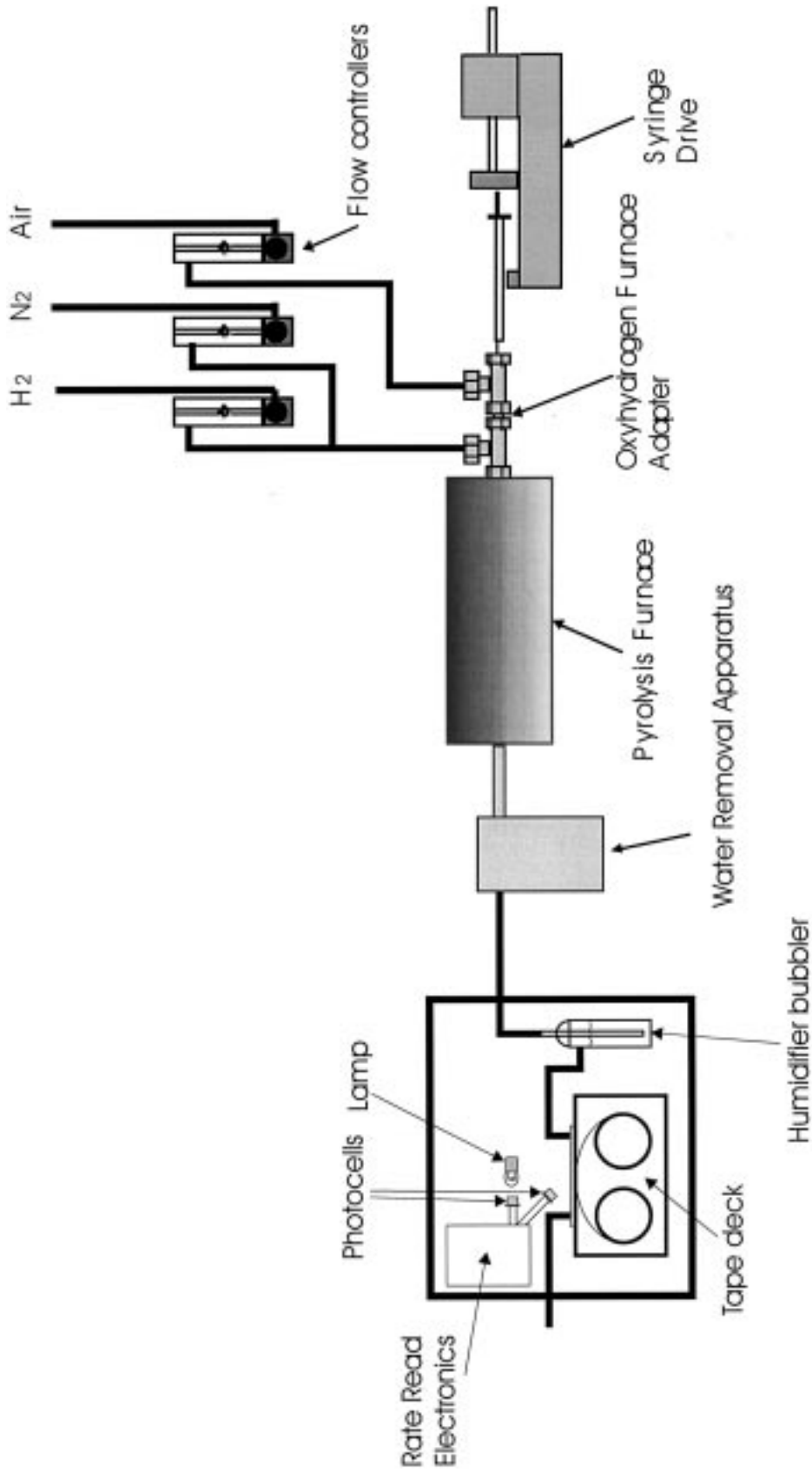
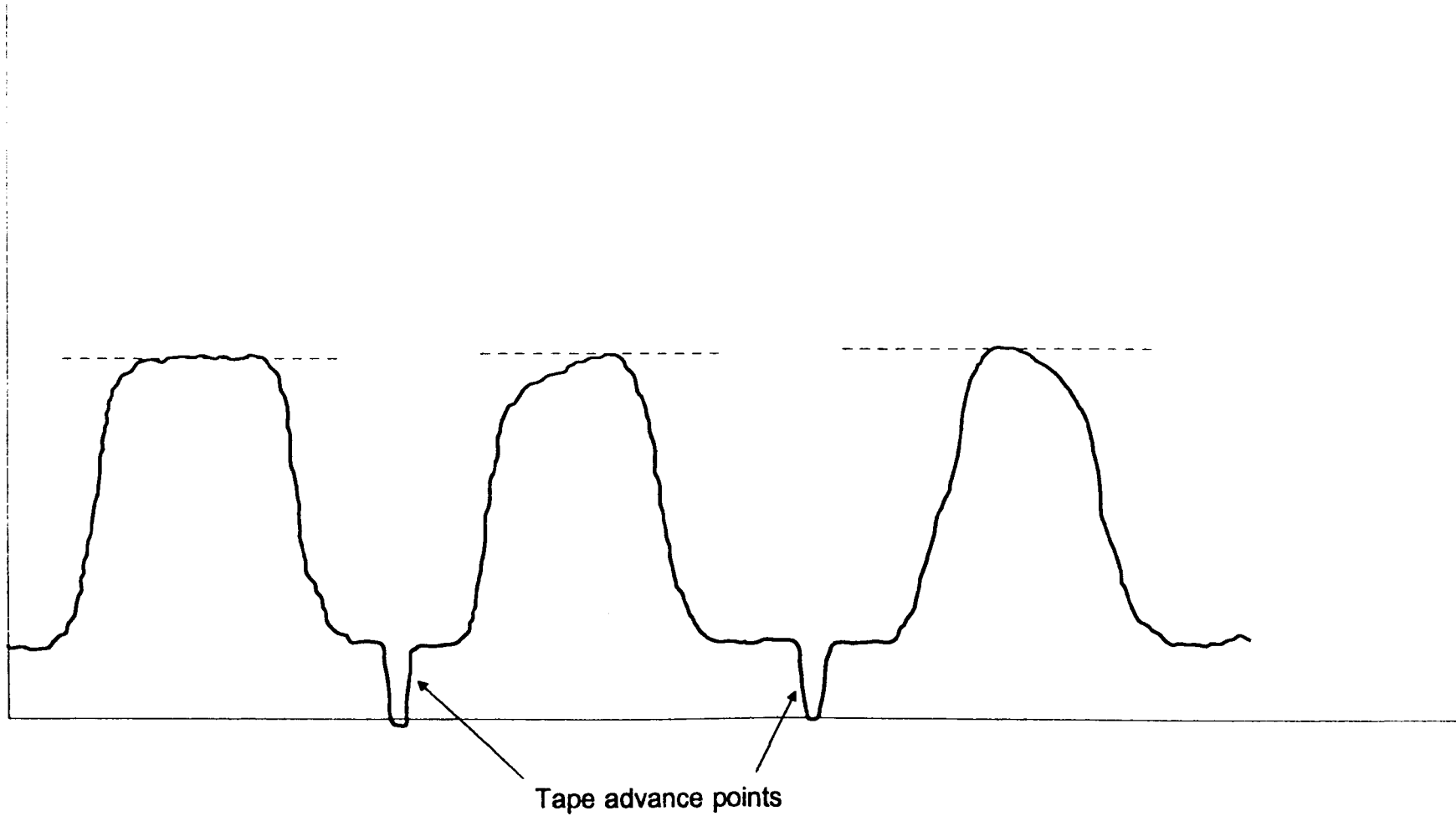


FIG. 3 Oxyhydrolysis Setup



NOTE 1—These example curves show the common responses that can be gotten from an analog-based rate-reading (rateometric) tape based analyzer. The dotted lines show where the plateau of the response curve would be determined for the common types of response encountered.

**FIG. 4 Response Curve Examples**

**TABLE 1 Densities of Aromatics<sup>A</sup>**

Benzene	0.8765
Cumene	0.8618
Cyclohexane	0.7785
<i>p</i> -Xylene	0.8611
Toluene	0.8669

<sup>A</sup>Densities are at 20°C relative to water at 4°C. From *CRC Handbook of Chemistry and Physics* 72<sup>nd</sup> Edition, CRC Press, Inc.

**TABLE 2 Results Based on Using a 1 ppm<sub>wt</sub> Standard of Thiophene in Benzene**

Analysis No.	Peak height, mm	Value, (ppm)
1	105	0.98
2	104	0.97
3	107	1.00
4	105	0.98
5	106	0.99
6	107	1.00
7	109	1.02
8	108	1.01
9	109	1.02
10	108	1.01
11	110	1.03
Average	107	1.00
Standard Deviation	1.9	0.02

in response at high sulfur levels indicates color saturation of the tape. Use a smaller syringe or a slower injection rate, or both, to lessen color saturation.

#### 14. Calculation

NOTE 5—Computerized analyzers may do the following calculations internally as part of their analysis procedure and output their answers already presented in appropriate reporting units.

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14.1 Calculate the concentration of sulfur as follows:

$$S_{mgL} = C_{std} \frac{(R_s - R_b)}{(R_{std} - R_b)} \quad (2)$$

where:

$C_{std}$  = concentration of sulfur in standard sample, mg/L,  
 $R_s$  = response of unknown sample,  
 $R_b$  = response of blank run using no sample or solvent known to be sulfur free,  
 $R_{std}$  = response of standard reference sample, and  
 $S_{mgL}$  = concentration of sulfur in the sample, mg/L.

14.2 Report reading in mg/kg of sulfur as follows:

$$S_{mgkg} = \frac{Concentration_{mgL}}{Density_{g/mL}} \quad (3)$$

where density is the appropriate value obtained from Table 1. Alternatively, density may be determined by using Test Method D 4052 at 25°C.

14.3 Report the sample value to the nearest 0.01 for a sample analysis indicating no sulfur, report the sulfur content as less than the value of the lower calibration standard used in 12.2.

#### 15. Precision and Bias

15.1 *Intermediate Precision*—Intermediate precision has been determined as shown in Table 2.

15.2 *Reproducibility*—The reproducibility of this test method is being determined.

#### 16. Keywords

16.1 aromatic; aromatic compounds; benzene; colorimetry; cumene; cyclohexane; pyrolysis; rateometry; sulfur; toluene; trace total sulfur