

SULFUR IN HYDROCARBONS BY OXY - HYDROGEN COMBUSTION

UOP Method 586-71

SCOPE

This is a method for determining sulfur concentrations ranging from 1 ppm to greater than 500 ppm in hydrocarbons, including aromatics and olefins. The method is applicable to styrene. The higher concentrations of sulfur are handled through appropriate dilution of the samples. Although there are no limitations as to the state of chemical combination of the sulfur, the material analyzed must be a liquid or gas; or, a solid that will dissolve in a suitable combustible solvent.

OUTLINE OF METHOD

A sample is burned by means of a stainless steel burner in a Wickbold quartz oxy - hydrogen combustion apparatus¹. The oxides of sulfur produced by the combustion are absorbed in a hydrogen peroxide solution. The solution is evaporated to a concentrate and then diluted with isopropyl alcohol. The sulfur, now present in the solution as sulfate, is titrated with a standardized barium perchlorate solution using Arsenazo III indicator to detect the endpoint.

APPARATUS

Alcohol lamp, Type used in ASTM Method D 1266²

Column, silica gel, having a 2000-mL reservoir with ball and socket joint between column and reservoir.

Provide a 2-mm bore Teflon plug stopcock at the bottom of the column; make the column 24 inches long and 50 mm in diameter. Place a plug of glass wool just above the stopcock and fill the column with about 1200 mL of silica gel. Process only 1 gal of isooctane before replacing silica gel.

Crocus cloth, or emery paper, 0 grade or finer

Cylinders, graduated, 5-mL

Flasks, Erlenmeyer, 50- and 500-mL

Flasks, volumetric, 25-mL

Funnel, separatory, 2000-mL

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Magnetic stirrer

Microburets, calibrated, 5-mL, two required

Oxy-hydrogen burner, obtainable from Fisher Scientific Co., Cat. No. 13-559-300, stainless steel (fits Wickbold combustion apparatus)

Pipets, 1-, 2-, and 3-mL

Shim stock, for separating the last 2 sections of the burner, 0.002-, 0.003-, 0.005-, 0.007-, 0.008- and 0.010-inch thick

Stirring bar, magnetic, 17-mm length, 3-mm diameter, glass- or Teflon - coated

Titration vessels, cylindrical, flat-bottomed vials, 2.5-cm diameter and 9.5-cm height

Vacuum loss warning device. See Fig. 3.

Vacuum pump, oil-less with minimum capacity of 1500 liters/hr. (Caution: Do *not* use a conventional rotary oil vacuum pump – the oxygen used in this method would create a hazard.)

Wickbold combustion apparatus. The complete apparatus, ready for use with modification but without the burner, can be obtained from the Atlas Instrument Co., Tulsa, Okla. For the United States and Canada the apparatus requiring specific alterations described here and without the burner can be obtained from Engelhard Industries, Inc., Amersil Quartz Division, 685 Ramsey Avenue, Hillside, N. J. For delivery outside the United States or Canada, the apparatus can be obtained directly from the manufacturing firm of Heraeus Quarzschmelze G.m.b.H., Hanau, Germany, and requires the same specific alterations as that obtainable from Engelhard. The specific alterations are (see Figs. 1 and 2) :

1. Replace the existing flowmeters for the air and oxygen with Fischer & Porter glass-ball flowmeters, Cat. No. 449-306, or equivalent instruments. Calibrate the oxygen flowmeter by passing oxygen through the flowmeter and then into a wet-test meter.
2. Replace all stopcocks used for regulating air, oxygen and hydrogen with 1/8-inch stainless steel needle valves.
3. Replace all rubber tubing connections underneath the base with copper tubing. Test all connections for leaks by putting 10-psi air pressure on the lines and checking for pressure drop.
4. Incorporate a vacuum loss warning device in the Wickbold exhaust stream as a safety precaution (see Fig. 3).

A complete Wickbold apparatus setup is available from the Koehler Instrument Co., Inc., Jamaica, New York 11433. The apparatus has not been tried in this laboratory, however.

REAGENTS AND MATERIALS

All reagents shall conform to specifications established by the Committee on Analytical Reagents of the American Chemical Society where such specifications exist, unless specifically stated otherwise. References to water mean distilled water subsequently deionized.

Acetone

2-Amino-2-(hydroxymethyl)-1,3-propanediol, acidimetric standard, sometimes designated by a trade name, "THAM", or "Tris buffer".

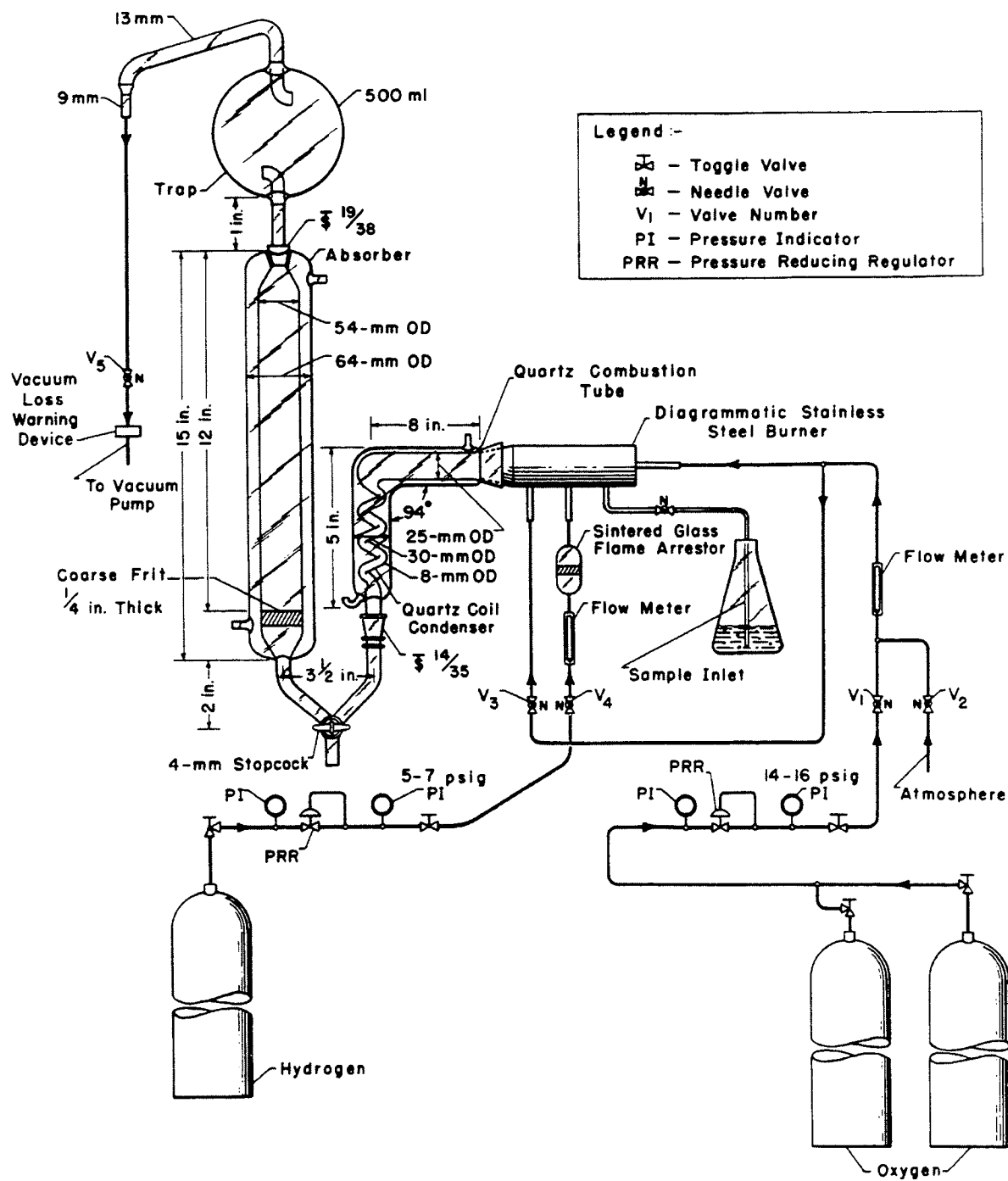


Figure 1
Wickbold Oxy-Hydrogen Apparatus

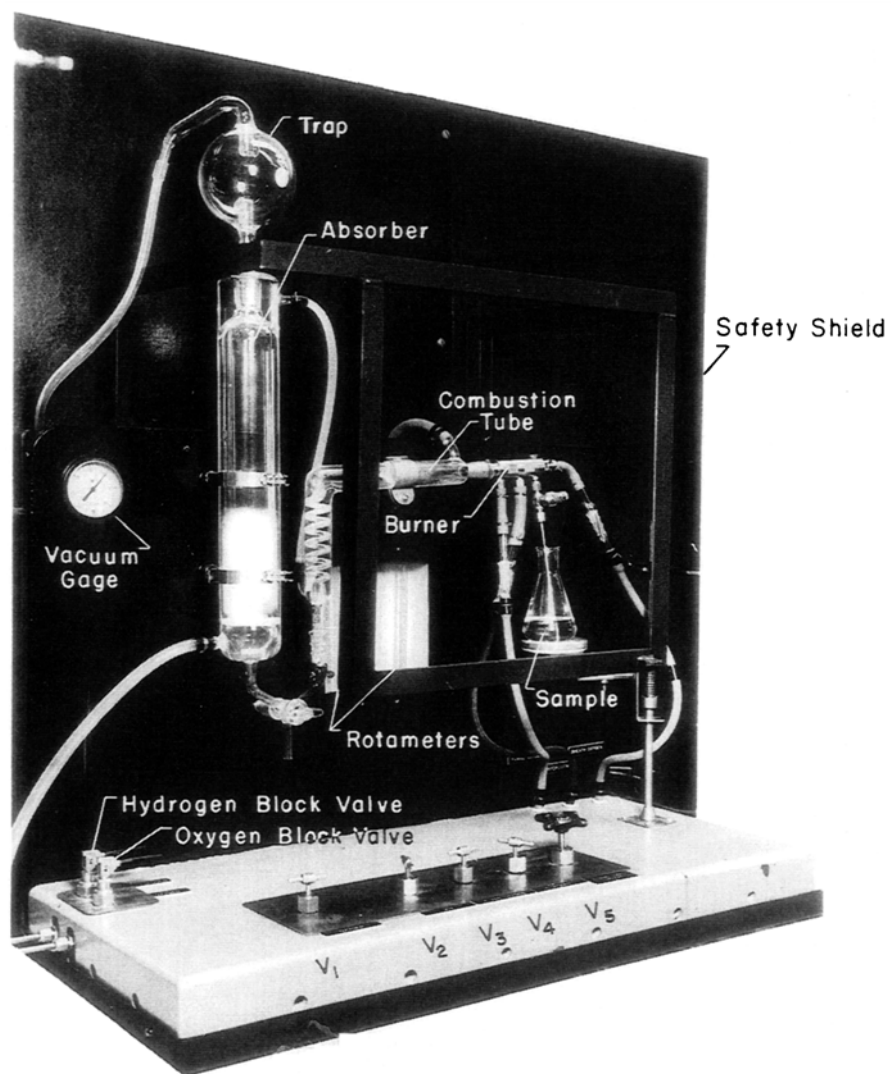


Figure 2

Wickbold Oxy – Hydrogen Combustion Apparatus

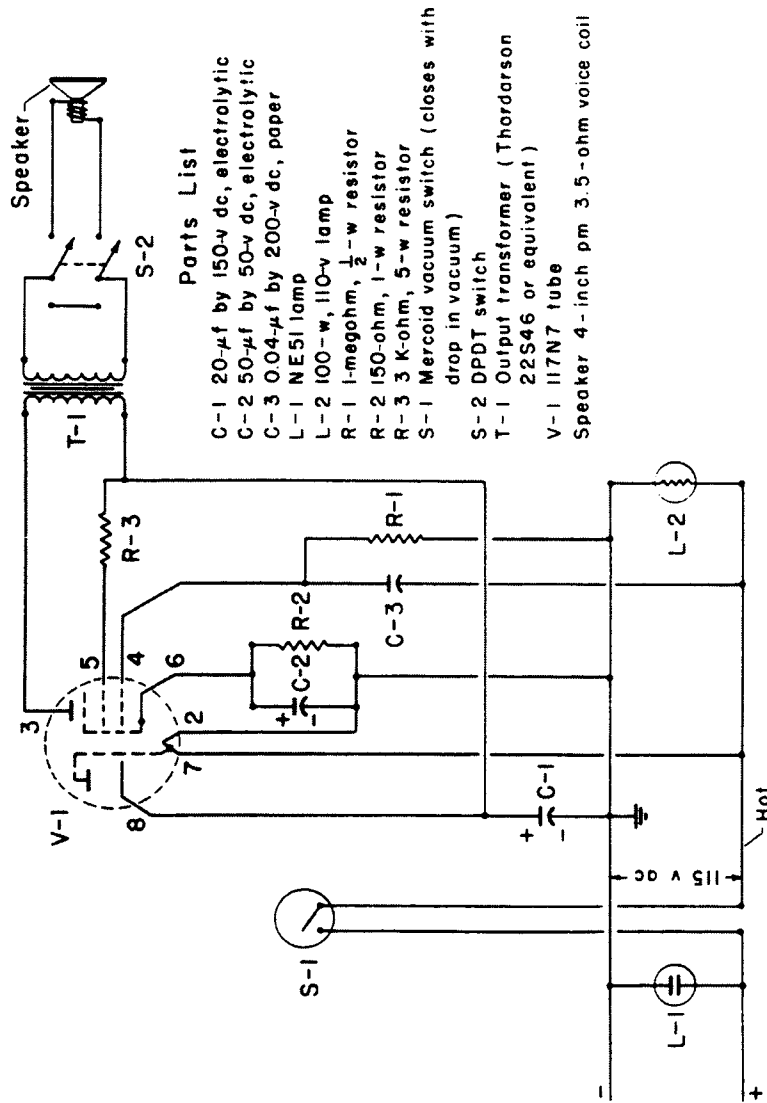


Figure 3

Vacuum Loss Warning Device

Arsenazo III indicator solution. Dissolve 0.1 g of Arsenazo III (available from J. T. Baker Chemical Company) in 100 mL of water.

Barium perchlorate, 0.005-M. Dissolve 2.0 g of barium perchlorate trihydrate in 200 mL of water and add 800 mL of isopropyl alcohol. Adjust the apparent pH of the solution to 4 with perchloric acid using pH paper. Standardize the barium perchlorate solution in the following manner:

A calibration curve is required since this method is somewhat empirical in nature. To obtain this curve, prepare “synthetic absorber solutions” in respective 500-mL Erlenmeyer flasks by adding known amounts of 0.006-*N* sulfuric acid to 50 mL of 1.5% hydrogen peroxide to contain 0, 50, 100, 200 and 300 γ of sulfur. Dilute each standard to 100 mL with water, add 2 drops of methyl purple and titrate with 0.03 *N* sodium hydroxide until the color changes to a faint green. Add 1 mL excess of sodium hydroxide and concentrate each of the solutions to 2 to 3 mL by gentle boiling.

Cool each concentrate to room temperature and measure it to 3 mL in a 5-mL graduated cylinder. Bring volume to 3 mL with water if less than 3 mL and transfer each solution to a titration vial. Rinse the cylinder and the 500-mL Erlenmeyer flask thoroughly with one 2-mL and two 5-mL portions of isopropyl alcohol. Transfer the rinsings to the titration vials and add 0.200 mL of 0.006 *N* sulfuric acid, hereafter referred to as a “spike”. If the volume of the concentrated “absorber solution” is greater than 3 mL, add isopropyl alcohol until the final alcoholic concentration of the solution is 80%.

Add 3 drops of the Arsenazo III indicator for each 15 mL of solution titrated. Titrate with 0.1 *N* perchloric acid, using magnetic stirring, until the color of the solution changes from blue to reddish purple. Titrate the resulting solution with the barium perchlorate until the solution changes to a bluish purple color, again using magnetic stirring. Record the volume of barium perchlorate titrant used after the endpoint is reached.

Add another spike of sulfuric acid and again titrate with barium perchlorate to the same endpoint. Determine the incremental volume required to titrate the additional spike of sulfuric acid and subtract this from the first titration volume to determine the micrograms of sulfur per milliliter of 0.005-*M* barium perchlorate for each standard.

Plot the net volume of the barium perchlorate vs. the micrograms of sulfur titrated for each standard. Obtain the micrograms of sulfur per milliliter of the 0.005-*M* barium perchlorate from the calibration curve by reading the micrograms of sulfur for 0.5 mL and for 1.5 mL of barium perchlorate and determine the difference between these sulfur values, which will be the sulfur concentration per milliliter of titrant.

A typical calibration curve for 0.005-*M* barium perchlorate is shown in Fig. 4. Note that the calibration curve contains corrections for indicator, sodium hydroxide and peroxide blank. Recalibration is required when any of these solutions is changed.

Ethyl alcohol

Hydrogen, cylinder, high-purity, dry. The quality should be such that the burning blank with oxygen will not exceed 20 γ of sulfur for 20 minutes of burning time.

Hydrogen peroxide, 1.5%. Prepare by diluting a 30% solution each time gas cylinders are changed or every 6 weeks.

Isooctane, ASTM knock test grade washed with water and percolated through silica gel as follows: Fill the column reservoir with isooctane. Rotate the stopcock to fully open. Collect the purified effluent in a

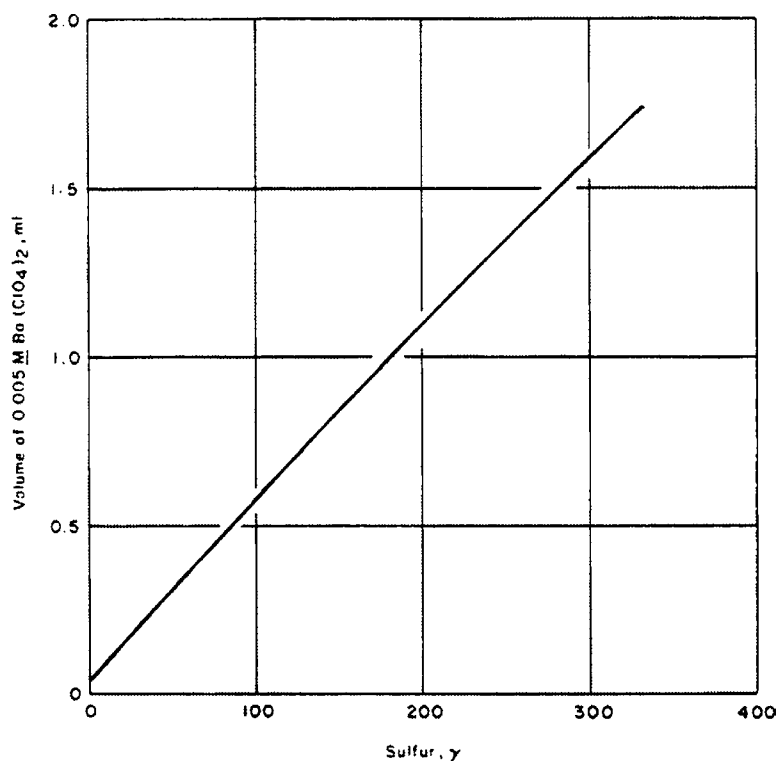


Figure 4

Typical Calibration Curve For 0.005-M Barium Perchlorate

clean glass stoppered storage bottle. Discard the silica gel and recharge the column with fresh gel after purifying each gallon of isooctane.

Isopropyl alcohol

Methyl purple, indicator solution, Fleisher's, available from Fisher Scientific Co.

Oxygen, cylinder, dry. The quality should be such that the burning blank with hydrogen will not exceed 20 γ of sulfur for 20 minutes of burning time.

Perchloric acid, 0.1-N. Prepare by diluting 40 mL of aqueous 0.5 N perchloric acid with 160 mL of isopropyl alcohol.

Rinse solution, for sample burning. Mix acetone 1:1 by volume with isopropyl alcohol.

Silica gel, 60-200 mesh, code 950, available from W. R. Grace & Co., Davison Chemical Division, P. O. Box 188, Pompton Plains, N. J. 07444

Sodium hydroxide, 0.03-N. To determine that this solution is sufficiently pure for the purposes of this method concentrate 400 mL to 30 mL. Determine the sulfate content by ASTM Method D 1266, Turbidimetric Finish. If more than 10 γ of sulfur are found, prepare a new sodium hydroxide solution.

Sulfuric acid, 0.006-*N*, standardized. Dilute 0.1-*N* sulfuric acid with a sulfate-free solution consisting of 80% isopropyl alcohol and 20% water. Standardize the 0.006-*N* solution by titrating against weighed quantities of 2-amino-2-(hydroxymethyl)-1, 3-propanediol dissolved in 80% isopropyl alcohol.

PROCEDURE

Combustion of Sample

Weigh the sample to be burned into a 50-mL Erlenmeyer flask, using the following tabulation as a guide.

<u>Sulfur Content, ppm</u>	<u>Sample Size, mL</u>
1	20
5	15
10	10

Stopper the flasks until the samples are to be burned.

Refer to Figs. 1 and 2. Turn on the cold water so that a rapid flow circulates through the water jackets of both the absorber and the quartz combustion tube. Close the stopcock located at the base of the absorber and charge the absorber with 50 mL of 1.5% hydrogen peroxide.

Make sure that the rear shim in the burner is of such a thickness that a non-pulsating flame, which indicates a steady flow, is attained. Dilute aromatic or high boiling samples with equal volumes of purified isooctane, or other suitable sulfur-free solvent, which will tend to reduce deposit formations on the burner tip. This will also aid in combustion of the sample. If a styrene sample is being analyzed, use pure ethyl alcohol as the diluent.

Turn on the vacuum pump. Turn on the vacuum loss warning device. The alarm will sound until the vacuum gage reads more than 15 inches. If the alarm does not sound, repair the device and then continue. Close all valves including the sample needle valve on the burner. Insert the burner into the combustion tube and open valves V_2 and V_3 . Open the stopcock at the base of the absorber so that the absorber is open to the combustion tube. Simultaneously, adjust valve V_5 with the burner in place in the combustion tube, so that an air flow of 1200 liters per hour is indicated on the flowmeter. From this point on do not change the setting of valve V_5 (see Note 1).

Remove the burner from the combustion tube. Close valves V_2 and V_3 and open valve V_1 . Open the reducing valve on the oxygen cylinder source to 14 to 16 psig and then open the block valve. Open valve V_3 until an oxygen flow of 1100 liters per hour is registered on the flowmeter. Open the reducing valve on the hydrogen source to 5 to 7 psig and then open the hydrogen block valve. Open valve V_4 and light the burner with an alcohol lamp. Adjust the length of the flame to 2 to 3 cm by adjusting valve V_4 . Note the hydrogen flow rate and continue to use this setting. In this laboratory the hydrogen flowmeter is set at about 90 liters per hour.

Insert the burner into the combustion tube. Place the sample flask in position under the sample inlet tube. Open the sample valve $\frac{1}{2}$ to $1\frac{1}{4}$ turns. Note the time of the beginning of the sample combustion. Adjust the sample valve until the flame extends approximately 2.5 inches from the end of the burner. If a slight pulsation of the flame occurs, open the oxygen valve, V_3 , a little more and then readjust the flame length to

2.5 inches by opening the sample valve further. Burn the sample until the sample flask is empty. As the last of the sample enters the sample inlet tube, close the sample needle valve $\frac{1}{4}$ to $\frac{1}{2}$ turn. This will eliminate any sudden surging of the sample into the combustion tube. Rinse the sample flask once with 5 mL or rinse solution, isooctane or other suitable sulfur-free solvent. Burn the rinse solution in the same manner used for the sample. As the last of the rinse solution leaves the burner, gradually open the sample valve until it is wide open. At the same time gradually reduce the oxygen flow through valve V_3 to 1000 liters per hour. Continue burning until the length of the flame decreases to the original size of the hydrogen pilot flame. Return the oxygen flow with valve V_3 to 1100 liters per hour.

Close the sample needle valve after the rinse solution has been burned. Turn off the hydrogen valve, V_4 , and then remove the burner from the combustion tube. Close valve V_1 and then valve V_3 . Rinse the combustion tube with a spray of water for about 10 seconds, making an effort during each analysis to maintain a constant wash volume and time period. Turn off the vacuum valve, V_5 , and close the stopcock at the base of the absorber simultaneously.

Record the total time required to burn the sample and the rinse solution. Transfer the absorber solution to a 500-mL Erlenmeyer flask. Maintain a constant absorber wash operation by washing the absorber trap 4 times and the absorber 3 times with successive 10-mL portions of water. Using a rubber bulb aspirator, blow each wash through the absorber frit.

Add 2 drops of methyl purple indicator to the absorber solution. Titrate the pink solution with 0.03-N sodium hydroxide to a faint green color. Note the volume of sodium hydroxide solution needed to reach the endpoint. (If more than 2 mL of sodium hydroxide solution are required for 10 mL of sample burned there is either a leak in the system or the sulfur or halogen content in the sample is high. In the latter case the analyst can use the acid-base titration as a guide in selecting the proper size aliquot for the barium perchlorate titration.) Add 1 mL excess of the sodium hydroxide solution to the absorber solution. Concentrate the absorber solution to 2-3 mL by gently boiling it, taking care not to boil to dryness. Cool the solution to room temperature and bring the volume to 3 mL with water in a 5-mL graduated cylinder.

Preparation of Burning Blank Graph

Prepare a burning blank graph for the oxygen, hydrogen and 3 mL of rinse solution by burning the rinse solution in the manner described in the following paragraph at approximately the same conditions used for burning the samples.

Obtain burning blanks for 3, 6, and 12 minutes on new hydrogen and oxygen cylinders. (Note that the blank also includes sulfur in the oxygen, hydrogen and the hydrogen peroxide absorber solution.) Treat the absorber solutions from the burning blanks in the same manner as the samples. Obtain a reagent blank to establish the sulfur level at zero burn time. Plot milliliters of barium perchlorate titrated against burning time in minutes to the nearest $\frac{1}{4}$ minute (See Fig. 5). Determine new blanks whenever either of the gases or any of the reagents is changed and replot the graph.

Titration

Transfer the concentrated absorber solution to a titration vial. Rinse the graduated cylinder and the 500-mL Erlenmeyer flask thoroughly with one 2-mL and two 5-mL portions of isopropyl alcohol. Transfer the rinsings to the titration vial. If the volume of concentrated absorber solution is greater than 3 mL, add enough alcohol so that the final alcoholic concentration of the solution is 80%.

Add a spike of 0.200 ± 0.001 mL of the 0.006-*N* sulfuric acid to the vial. Add 3 drops of the Arsenazo III indicator for each 15 mL of the solution titrated. Titrate with 0.1-*N* perchloric acid until the color of the solution changes from blue to reddish purple to achieve a pH of 4. Now titrate with the barium perchlorate, using a 5-mL microburet, until the solution changes to a bluish purple color. Record the volume of barium perchlorate after the endpoint is reached. This titration includes the sulfur from the sample plus that from the first addition of 0.200 mL of 0.006-*N* sulfuric acid. Add an additional spike of 0.200 mL of the 0.006-*N* sulfuric acid and titrate to the same bluish purple endpoint. Obtain the volume of barium perchlorate required to titrate the sample by difference.

When the approximate sulfur content of the sample is suspected to be greater than 100 ppm, transfer the concentrated absorber solution to a 25-mL volumetric flask and dilute to the mark with water. Transfer a 3-mL aliquot to the titration vial. The dilution factor (*D*) in this case is 25/3. Add 12 mL of isopropyl alcohol and 3 drops of the Arsenazo III indicator. Titrate the solution as previously described in the second paragraph of this section.

CALCULATIONS

$$\text{Sulfur, ppm} = \frac{[D(V - S) - M]C}{W}$$

where:

- C** = amount of sulfur equivalent to 1 mL of the 0.005-*M* barium perchlorate solution, *y* (titer)
- D** = dilution factor = the volume, mL, to which the concentrated absorber solution was diluted, divided by the volume, mL, of aliquot taken
- M** = volume of 0.005-*M* barium perchlorate corresponding to the sample burning time in minutes from the burning blank graph, mL
- S** = volume of 0.005-*M* barium perchlorate required to titrate the spike, mL
- V** = volume of 0.005-*M* barium perchlorate required to titrate the sample plus the spike, mL
- W** = weight of sample, g

NOTES AND PRECAUTIONS

1. Incorporate a vacuum loss warning device (Fig. 3) in the exhaust stream as a safety measure. During the burning of a sample, if the vacuum is lost, a rapid accumulation of hydrogen is imminent, and the operator must immediately:

- a. Close both the hydrogen and oxygen block valves.
- b. Open valve V_2 (air vent).
- c. Remove the burner from the combustion tube.
- d. Correct the cause of vacuum loss.
- e. Purge the combustion train and absorber with water.
- f. Disassemble the burner and flush it with appropriate solvents.
- g. Start the determination again with a fresh portion of sample and absorber solution.

2. The laboratory air must be free from all forms of sulfur-rich gases during the burning operation.

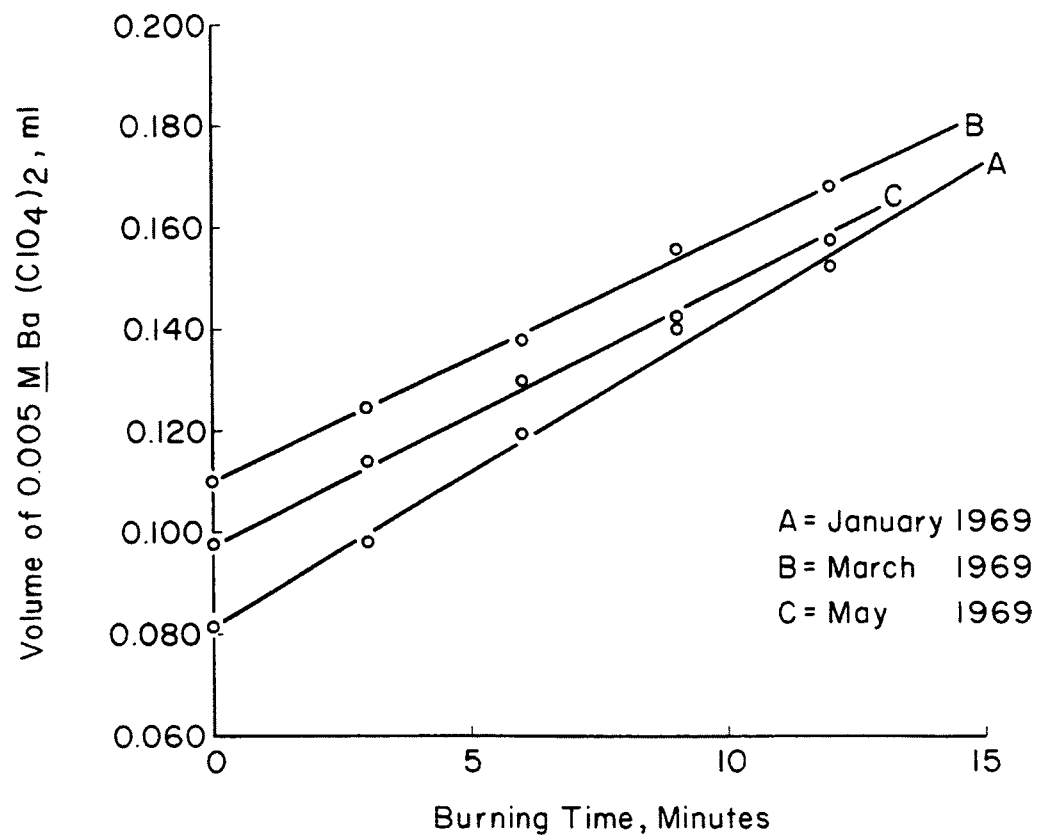


Figure 5
Burning Blank Graph

3. If the annular space through which the sample enters the burner should plug with a residue during a burning, remove the last section of the burner and clean the tip with fine crocus cloth. Start a new sample again from the beginning.

PRECISION

Based on 2 sets of 4 replicates for the 2- to 5-ppm level, the estimated standard deviation (esd) was calculated to be 0.2 ppm sulfur; at the 20- to 60-ppm level, based on 2 sets of 4 replicates, the esd was 0.5 ppm sulfur. Duplicate analyses should not differ by more than 0.4 ppm sulfur at the 1- to 5-ppm level; and by no more than 1 ppm sulfur at the 20- to 60-ppm sulfur level.

TIME FOR ANALYSIS

On a full time weekly basis, one man-day per week is required for the burning blank calibration and solution preparation with a daily apparatus preparation of 45 minutes. The average labor required per determination, including these prorated preliminary operations, is 1.7 man-hours. Starting with the system in calibration, the elapsed time required for the analysis of a sample is about 5 hours.

REFERENCES

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