

DETERMINATION OF SULFUR IN ORGANIC
COMPOUNDS UTILIZING GAS CHROMATOGRAPHY

by

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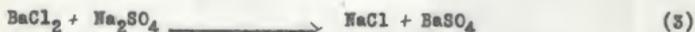
INTRODUCTION

There are at present, two predominant methods for determining the sulfur content of organic compounds. These are the Carius and Pregl methods with their many variations.

The Carius method consists of combusting the organic compound in a sealed tube in the presence of nitric acid and an alkali salt other than a sulfate. These reactions are shown as follows:



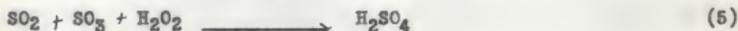
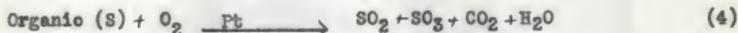
The sodium hydrogen sulfate is converted to sodium sulfate by the action of NaOH and titrated with a standard solution of barium chloride in the presence of tetrahydroquinone indicator. (11)



This method can also be modified by determining the barium sulfate by gravimetric techniques.

However, the Carius method lends itself to the introduction of personal errors. It necessitates the technique of sealing the tube and breaking it after the combustion. The combustion products must be quantitatively washed from the tube, evaporated to dryness, redissolved, transferred to a cuvette, made alkaline, and titrated. There are therefore many opportunities for error.

The Pregl method consists of combusting the compound in a combustion tube at 650° C. using platinum stars as catalysts. The resulting oxides of sulfur are then converted to sulfuric acid by their reaction with hydrogen peroxide. These reactions are shown as follows:



If nitrogen or halogens are absent, the sulfuric acid may be quantitatively transferred to a flask and titrated with a standard base using phenolphthalein as an indicator. If nitrogen or halogens are present, the sulfate must be precipitated as barium sulfate and determined by gravimetric techniques. The gravimetric method requires more time and care than the titrimetric method.

Other methods have been described in the literature but most of them are adapted to specific types of analysis. Huffman (3) adopted Pregl's method to the simultaneous determination of carbon, hydrogen and sulfur. He trapped the sulfur on silver and subjected the silver sulfate formed to electrolysis. The sulfur in organic sulfur compounds has been hydrogenated to hydrogen sulfide and determined by various techniques (10). Sulfur has been determined manometrically by Hoagland (2). These methods have not been as universally accepted as those of Carius and Pregl. However, they do show attempts to develop methods that are more versatile and faster than those of Carius and Pregl.

Duswalt and Brandt (1) and Sunderberg and Maresh (5,12) in 1960 developed a method for determining carbon and hydrogen in organic compounds by utilizing the principles of gas chromatography. The sample was combusted to carbon dioxide and water by a method similar to that of Pregl (11). The combustion gases were passed over calcium carbide to convert the water to acetylene, and subsequently trapped in a cold trap immersed in a liquid nitrogen bath. Afterwards the gases were vaporized and injected into a gas chromatographic column of silica gel for separation. The components were detected as they emerged from the column by their action on ceramic thermistors.

This technique enabled a carbon-hydrogen determination to be completed in about twenty minutes which is about one-sixth the time required by the standard method of Pregl (11). Scott et al. (9,10) have modified this technique to adapt it to the determination of oxygen and nitrogen. Maresh (5) has adapted it to the simultaneous determination of carbon, hydrogen, and nitrogen.

This paper encompasses the work of modifying the techniques described previously using gas chromatography, to adapt them to the determination of sulfur in organic compounds. Further work should reveal that carbon and sulfur, and perhaps carbon hydrogen, sulfur, and nitrogen can be determined simultaneously by using gas chromatography.

EXPERIMENTAL

Apparatus

The apparatus used in this work consisted of a combustion train (Figure 1), trapping system (Figure 1 and 2), and a gas chromatograph (Figure 3 - 6).

The combustion train consisted of an oxygen source, furnace, combustion tube and drying cartridge as shown in Figure 1 and Table 1.

The source of oxygen was a cylinder of oxygen prepared from the distillation of air. This was equipped with a two stage pressure regulator and needle valve. The oxygen was passed through a bubble counter and U shaped absorption tube into the side arm of the combustion tube. Since the combustion products of any organic material contain carbon dioxide and water, it was necessary to use oxygen that was void of these compounds. The U shaped absorption tube was filled with ascarite and anhydron to insure that the oxygen was free of carbon dioxide and water.

The combustion furnace was a Sargent Micro Combustion furnace capable of obtaining temperatures of 900° C. The combustion tube was a pyrex combustion tube with side arm inlet. The drying cartridge was a Pregl absorption tube filled with a desiccant. This cartridge was used to remove the water from the combustion gases to prevent its reaction with sulfur trioxide and sulfur dioxide as follows



All of the gas lines were constructed of one sixteenth inch stainless steel tubing of type 304. They were connected to the glass joints by inserting them into a silicone rubber seal connected to the glassware with rubber tubing as shown in Figure 2.

The cold trap was constructed from seven millimeter glass tubing as shown in Figure 2. Silicone stopcock grease was used as a stopcock lubricant.

The stopcocks were held in place by Todd tension clips. These were necessary to prevent the loss of material from the trap due to the increase in pressure upon vaporization of the trapped material. The trap was immersed in a one quart Dewar flask filled with a refrigerant.

The gas chromatograph consisted of a constant temperature cabinet, helium supply, chromatographic column, control box, detector, and a Sargent SR Recorder.

A cylinder of helium was used as a source of the carrier gas. This cylinder was equipped with a two stage pressure regulator and a Vee type brass needle valve. The helium was passed through a laboratory flow meter into a U shaped absorption tube filled with anhydrous and ascarite to remove any traces of moisture or carbon dioxide that may be in the system. The helium then entered the reference side of the detector block and proceeded to sweep through the sample trap into the column. When it emerged from the column it was directed to the sample side of the detector block and into a soap bubble type of flow meter.

The control was constructed according to the circuit diagram shown in Figure 4 and housed in a convenient cabinet. This circuit provided a source of direct current to the thermistors with proper sensitivity control and attenuation to send the correct signal to the recorder.

The detector block was machined from a brass block to the specifications shown in Figure 5 (5). It was equipped with a matched pair of No. All, 2000 ohm bead thermistors with B-4 type mounting obtained from the Victory Engineering Corporation (catalog no. 32 A48).

FIGURE 1
FLOW DIAGRAM OF COMBUSTION TRAIN

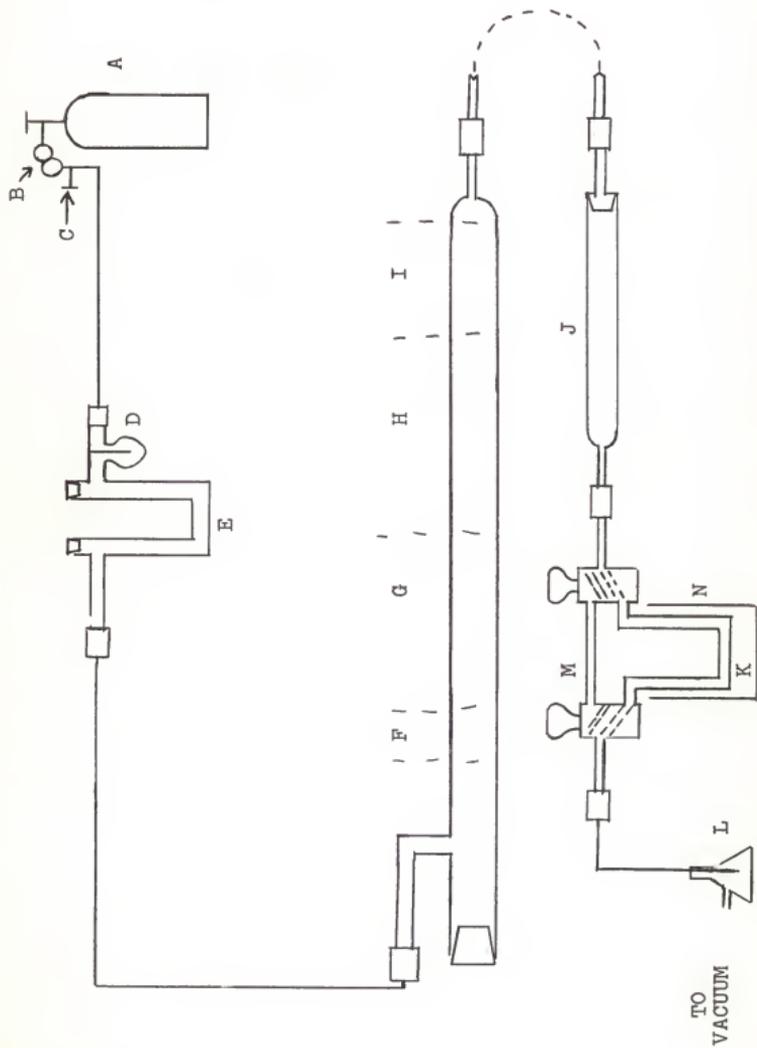
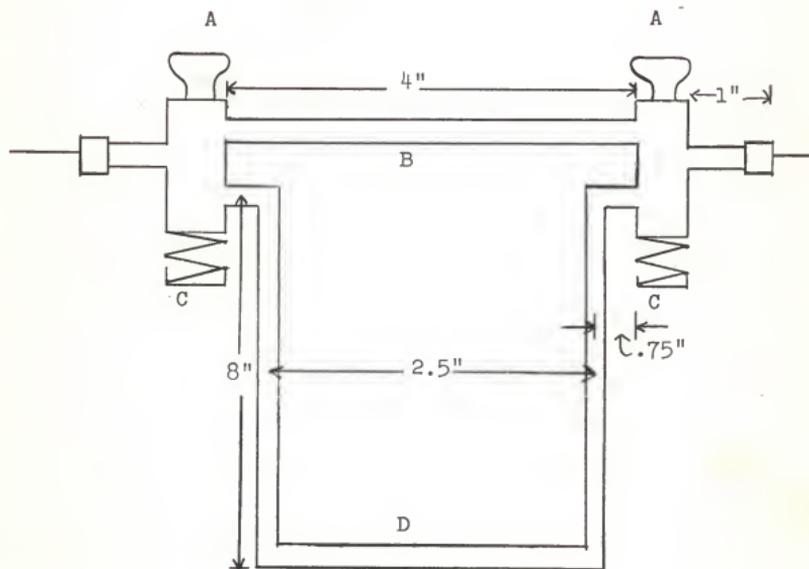


TABLE 1

Components of Figure 1.

- A. Cylinder of oxygen
- B. Two stage pressure regulator
- C. Vee point type needle valve
- D. Bubble counter filled with mineral oil
- E. Absorption tube - Fisher catalog no. 20-228
- F. Area of small movable heater of combustion furnace
- G. Pyrex combustion tube - Fisher catalog no. 20-235
- H. Area of long heater of combustion furnace
- I. Area of heating mortar of combustion furnace
- J. Pregl absorption tube filled with a desiccant
- K. Cold trap
- L. Trap used with vacuum system when liquid nitrogen is used as a coolant
- M. Bypass on trap
- N. Dewar flask

FIGURE 2
COLD TRAP



DETAILS OF CONNECTIONS

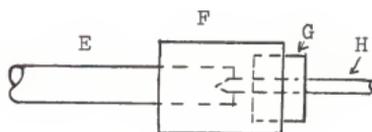


TABLE 2

Components of Figure 2

- A. Stopcocks, Pyrex brand, 3 way - Fisher catalog no. 14-587
- B. Bypass constructed of 7 mm. glass tubing
- C. Todd tension clips - Fisher catalog no. 14-631-50
- D. Trap constructed of 7 mm. glass tubing
- E. 7 mm. glass tubing
- F. Rubber tubing
- G. Burrell seals, one hole, silicone rubber - Burrell catalog no. 261-9
- H. 1/16 inch stainless steel tubing or drawn out glass tubing depending upon the type of connection used

FIGURE 3
FLOW DIAGRAM OF GAS CHROMATOGRAPH

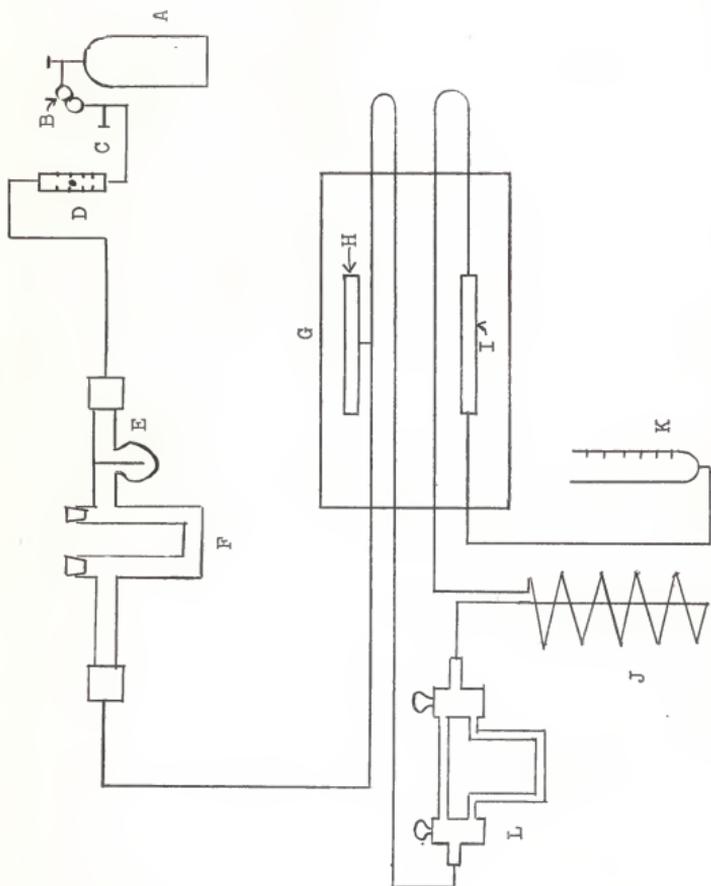


TABLE 3

Components of Figure 3

- A. Helium cylinder
- B. Two stage pressure regulator
- C. Vee point, brass needle valve
- D. Flow meter
- E. Bubble counter - not used
- F. Absorption tube - Fisher catalog no. 20-228
- G. Detector block
- H. Reference side of detector block
- I. Sample side of detector block
- J. Chromatographic column from 1/4" stainless steel or copper tubing
- K. Soap bubble flow meter
- L. Sample trap

FIGURE 4
WIRING DIAGRAM OF GAS CHROMATOGRAPH

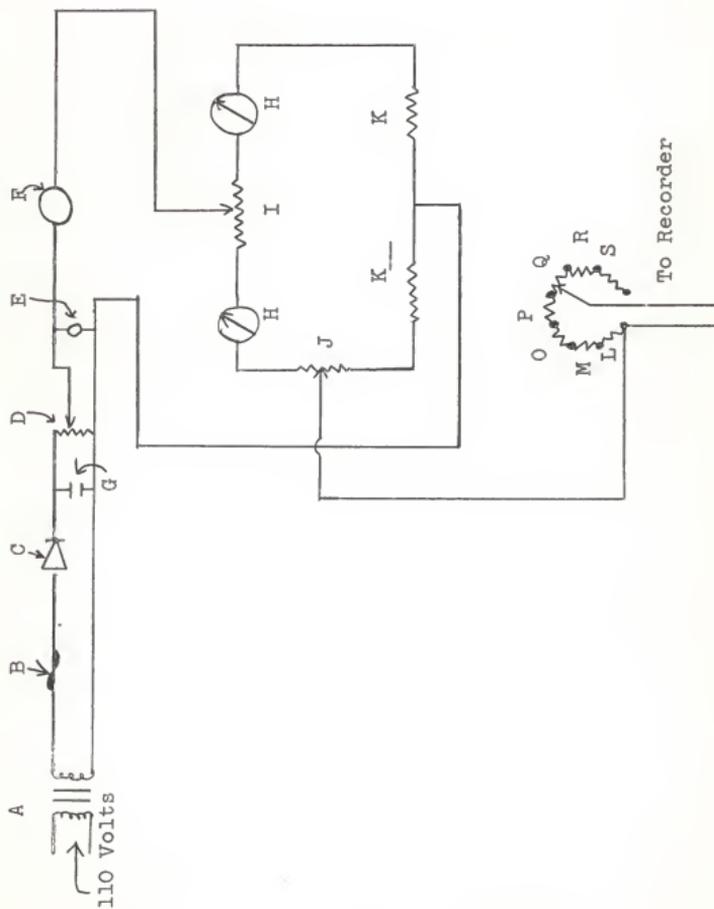


TABLE 4

Components of Figure 4

- A. Step down transformer, 110 V to 25 V
- B. Fuse box for 1 ampere fuse
- C. 500 mil selenium rectifier
- D. 5 K potentiometer, 1 turn
- E. Voltmeter, 0-10 volts
- F. Milliammeter, 0-50 milliamperes
- G. 200 mfd condenser
- H. 2000 ohm thermistors - Victory Engineering Corp Cat. no. 32A48
- I. 25 ohm, 10 turn, Helipot with microdial
- J. 5 ohm, 10 turn, Helipot with microdial
- K. Matched 200 ohm, 1 watt resistors
- L. 0.25 ohm resistor, 1%
- M. 0.47 ohm resistor, 1%
- N. 0.90 ohm resistor, 1%
- O. 1.8 ohm resistor, 1%
- P. 3.5 ohm resistor, 1%
- Q. 7.0 ohm resistor, 1%
- R. 14.0 ohm resistor, 1%
- S. 25.0 ohm resistor, 1%

Resistors L to S are mounted on a 3 gang selector switch.

The constant temperature cabinet was constructed from 16 gauge galvanized metal, insulated on the outside with one-fourth inch of asbestos and covered with heavy duty aluminum foil as shown in Figure 6. It was equipped with a four inch fan, powered by a 1/100 horsepower motor. This forced the air over a 500 watt heating tape that was installed in front of the fan. The cabinet consisted of an inner and outer chamber to provide a definite pattern for the circulation of air.

A separate heating cabinet was constructed for the detector block. This was an open end box made from 16 gauge galvanized metal, wrapped with a 500 watt heating tape and insulated with one-fourth inch of asbestos covered with heavy duty aluminum foil as shown in Figure 6. The temperature in the two cabinets was held constant by a constant flow of current to each heating element. The temperatures were monitored by thermometers.

All of the gas lines except the column were of 1/16" stainless steel, type 304 and connected to the glassware as shown in Figure 2. The tubing was connected to the detector block and column as shown in Figure 6.

The recorder was a Sargent SR Recorder equipped with a 1 millivolt sensitivity plug.

The column packing was prepared by dissolving a weighed amount of the liquid phase in diethyl ether and mixing it thoroughly with a weighed amount of the solid phase that had been acid washed and dried. The ether was then evaporated from the mixture. After drying, the prepared packing material was put into a desired length of 1/4 inch tubing that was plugged on the end with glass wool. The tubing was well agitated by vibration while it was being filled to insure its uniform packing. When the column was full, the other end was plugged with glass wool and the column bent into a coil and fitted with the proper swagelock fittings.

Detector Block

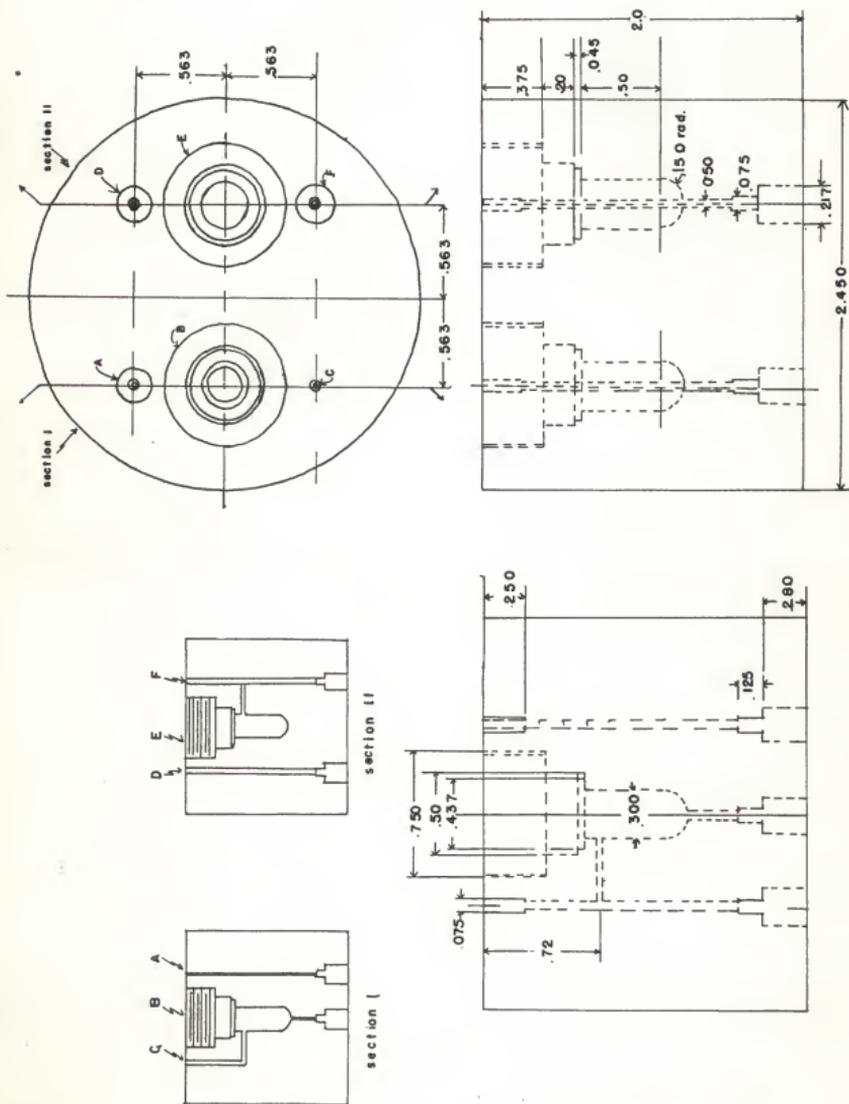
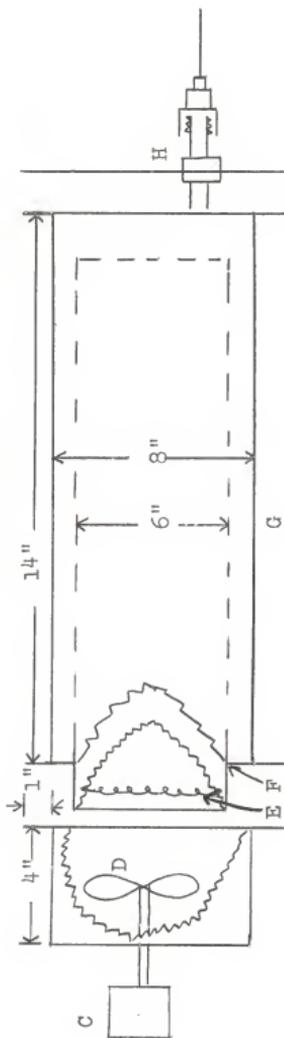


FIGURE 6
CONSTANT TEMPERATURE CABINET

FOR DETECTOR BLOCK



FOR COLUMN



CONNECTIONS



TABLE 5

Components of Figure 6

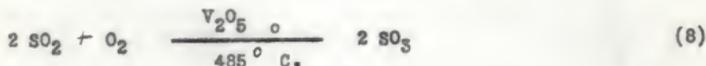
- A. 500 watt heating tape
- B. Detector block
- C. 1/100 horsepower motor
- D. 4 inch fan
- E. 500 watt heating coil
- F. Inner chamber
- G. Outer chamber
- H. Connection to column
- I. 1/16" tubing
- J. Burrell seals, 1 hole, silicone rubber - catalog no. 261-9
- K. Burrell brass connectors - catalog no. 270-2
- L. Swagelock fittings

Combustion

Conversion of Sulfur Dioxide to Sulfur Trioxide.

It was noted in equation 4 that the oxidation of organic sulfur compounds yields a mixture of sulfur dioxide and sulfur trioxide. It was desirable to convert all of this mixture to one form, namely sulfur trioxide. This method was tried and discontinued because of incomplete combustion.

The sulfur dioxide can be oxidized to sulfur trioxide by molecular oxygen in the presence of a catalyst such as Vanadium pentoxide (7) as follows:



The optimum temperature for this conversion is reported to be between 400 and 500° C. (7).

A combustion tube was packed with 3-5 cm. of magnesium perchlorate (hereafter referred to as anhydron). This was followed with 100 cm. of Vanadium pentoxide and another 3-5 cm. of anhydron as shown in Figure 7. The purpose of the anhydron was to remove the water vapor from the system and prevent the hydration of the oxides of sulfur.

The combustion tube was placed in the combustion furnace and the outlet connected to the cold trap which was immersed in a salt ice bath. A source of anhydrous oxygen was connected to the inlet.

After the tube was conditioned, sulfur dioxide was introduced into it at the rate of 2 mls. per minute for a period of five minutes. The vapors were trapped at -6° C. in the cold trap. At this temperature, the sulfur trioxide formed in the reaction would be trapped while the unconverted sulfur dioxide

would pass through the trap. A six foot column of 20 percent "Halowax", a chlorinated naphthalene supported on fire brick, was used at 55° C. to separate the components in the trap. Helium was used as a carrier gas at a flow rate of 31 mls. per minute.

Two peaks were observed on the chromatogram. One was at 2.25 minutes and the other at 15 minutes. The retention times of oxygen and sulfur dioxide with this column were 2.25 and 3.4 minutes respectively. It was assumed that the peak at 15 minutes was sulfur trioxide. No attempt was made to prove that the peak at 15 minutes was sulfur trioxide since the quantitative conversion was doubtful when using organic compounds. This is described later.

In an attempt to hasten the evolution of the questionable peak, another experiment was made using a column temperature of 85° C. The evolution of this substance did not materialize at this temperature. When the temperature was lowered to 52° C., the peak at 15 minutes was not noticed. It is believed that the sample gases reacted with the liquid phase at the higher temperature, thus changing the characteristics of the column.

Columns of the following materials were constructed and used:

<i>a</i> - chloronaphthalene	15 percent
Trioresyl phosphate	12 percent
Trioresyl phosphate	15 percent
Adiponitrile	20 percent

The *a* - chloronaphthalene column was the only one that gave good results. The retention times for oxygen and sulfur dioxide were 0.4 and 1.7 minutes respectively. When the above experiment converting sulfur dioxide to sulfur

trioxide was repeated, the α - chloronaphthalene column showed a peak at 9.8 minutes. It is believed that this peak was due to sulfur trioxide. This was not proven for reasons state previously.

Samples of phenyl sulfone and phenyl sulfoxide in platinum boats, were placed individually in the combustion tube. Each sample was combusted at 700° C. by the movable burner. All other conditions of this experiment, were the same as the above experiment using a column of α - chloronaphthalene. The injection of sulfur dioxide into the combustion tube was deleted.

The sample was vaporized as the small heater approached it. These vapors moved forward to the anhydrous plug and were oxidized at a very rapid rate which caused flashing and an occasional mild explosion. These explosions never broke the combustion tubes or caused any damage to the equipment since the resulting force was relieved by blowing the sealed joint in the end of the tube.

In other experiments where the anhydrous plug was deleted from the combustion tube, there was no explosion but considerable flashing in the tube. This flashing was due to the incomplete combustion of the sample by the small heater and its oxidation by the vanadium pentoxide. Work on the conversion of sulfur dioxide to sulfur trioxide was discontinued.

Quantitative Combustion of Organic Sulfur Compounds to Sulfur Dioxide.

It has been reported that the conversion of sulfur dioxide to sulfur trioxide over a catalyst is negligible at temperatures of 750° C. (6). If the rate of the above conversion is small, it is possible that the rate of formation of sulfur trioxide from the oxidation of organic sulfur compounds is also negligible.

Phenyl sulfoxide was combusted at different temperatures in a combustion tube packed with platinum asbestos and platinum stars. This is shown in Figure 7. Oxygen was fed into the tube at a rate of 6 mls. per minute. The combustion gases were bubbled through 25 mls. of 1.0 M barium chloride solution. The barium chloride solution was made acidic with hydrochloric acid to prevent the formation of barium carbonate and barium sulfite. The sulfur trioxide present in the combustion gases would form a precipitate of barium sulfate according to the following reaction:



The solubility of barium sulfate in the above solution was equivalent to 2×10^{-11} gms. of sulfur trioxide.

The barium chloride solution was analyzed for turbidity using a Leitz Photrometer. The percent transmittance of radiation at 520 mμ was measured and compared to a blank (untreated solution) set at 100 percent transmittance. The results of this experiment are shown in Table 6.

In this experiment, a white precipitate formed on the interior of the combustion tube. It is possible that this formation was a sulfide (6). The precipitate was removed and analyzed by infra-red and emission spectroscopy. Neither of these analysis revealed the identity of the material. In later work at 850° C., the formation of this material was negligible.

Table 6. Relation between combustion temperature and the Formation of SO_3 .

Temperature ° C.	Percent Transmittance	
	Trial 1	Trial 2
Blank	100	100
650	39.8	35.1
700	63.1	59.7
750	88.7	85.9
800	99.1	99.3
825	100	
850	100	100

Desiccants

The hydrogen in the organic compounds will undergo oxidation to water. This water must be removed to prevent its reaction with the sulfur dioxide. This would prevent the trapping of the sulfur dioxide in the cold trap.

Two types of desiccants were tried. One type, such as calcium carbide and barium oxide, reacts with the water to form a new compound.

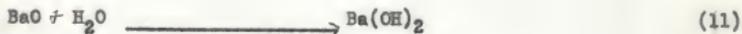
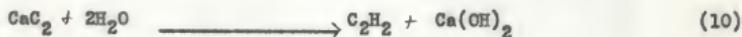
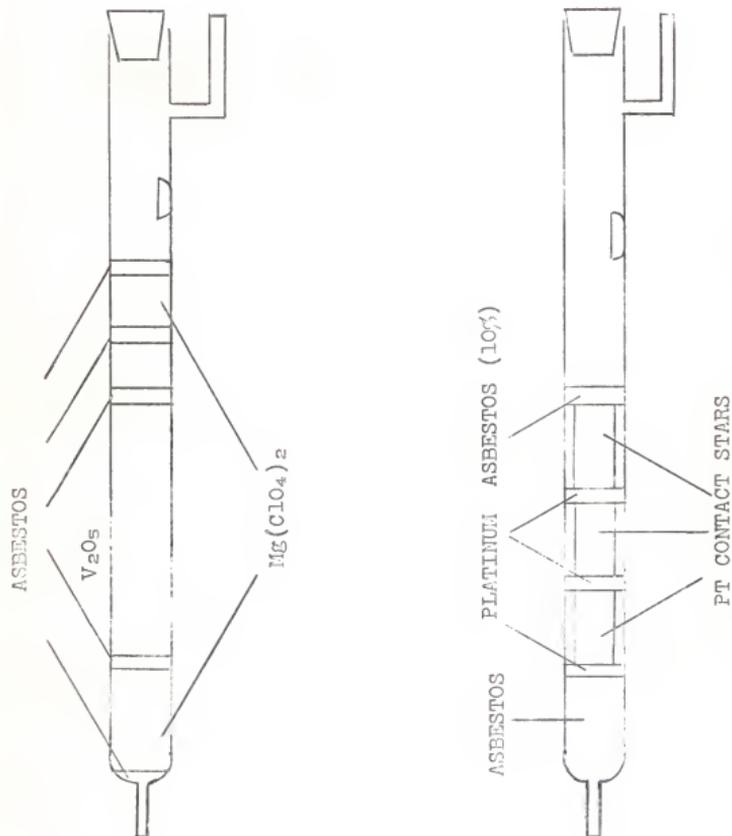


FIGURE 7
COMBUSTION TUBES



Sundenberg and Maresh (12) report that the calcium hydroxide formed in equation 10, does not attract the carbon dioxide and interfere with its determination. This same principle was tested to determine if it would apply to the sulfur dioxide.

A Pregl absorption tube was filled with barium oxide and placed at the exit end of the combustion tube as in Figure 1. A sample of phenylsulfoxide was combusted and the combustion tube flushed for five minutes after the completion of the reaction. The combustion gases were trapped at -61° C. in a dry ice-chloroform slush bath. Analysis of these gases on the gas chromatograph did not reveal the presence of sulfur dioxide. It was assumed that the sulfur dioxide was held by the barium hydroxide and failed to move beyond the drying tube.

A similar experiment was conducted using calcium carbide as the drying agent. Some sulfur dioxide passed through the first trap and was caught in the second trap. This was determined by analysis of the material in the second trap. However, the peak was small and not sharp. The calcium carbide was dissolved in water, filtered and treated with hydrogen peroxide and barium chloride. A precipitate was formed that did not redissolve upon acidification. The presence of this precipitate, barium sulfate, showed that some sulfur dioxide was held by the calcium hydroxide.

The other type of desiccant was compounds that combine with water to form hydrates. Such compounds as anhydrous calcium sulfate were used. The use of anhydrous calcium sulfate was discussed earlier. The above experiment was repeated using anhydrous calcium sulfate in the drying tube. There was no evidence of any absorption of the sulfur dioxide by the calcium sulfate. This is shown later by the quantitative results in the determination of sulfur in organic compounds.

Chromatographic Column

Various chromatographic columns were made and installed in the gas chromatograph. They were purged with the desired flow rate and at the desired temperature until the recorder charted a stable base line for one hour. Samples of oxygen, carbon dioxide, and sulfur dioxide were injected into the gas chromatograph, and the emerging gases were monitored by the recorder. If the longest retention time for the individual gases was less than 15 minutes, a sample of the mixed gases was used to determine the resolution.

The various columns, operating conditions and retention times are listed in Table 7. Dinonylphthalate gave the best results and was chosen as the liquid phase for further work. The resolution of the above gases on a 20 ft. column of 30 percent dinonylphthalate is shown in Figure 8.

Trapping of Sulfur Dioxide

The liquification temperature of sulfur dioxide is -10° C. However, the flow rate through the trap and the surface area of the trap affect the rate of condensing these vapors. It is necessary to have a trapping system that will quantitatively trap the sulfur dioxide vapors. A reduction of the flow rate of oxygen through the combustion train and cold trap resulted in incomplete combustion. This was evidenced by the carbon residue deposited in the exit of the combustion tube. Therefore the flow rate of oxygen was stabilized between 10-12 mls. per minute.

Table 7. Retention times on various column packings.

Column Liquid Phase	Stationary Phase	Length	Conditions		Retention Time		
			Temp	Flow Rate ml/min	O ₂	CO ₂	SO ₂
10% Halowax	Fire Brick	8'	52°C	32	2.25	3.1	3.4
10% Halowax	Fire Brick	8'	52°C	32	*	*	**
15% A Chloro Naphthalene	Fire Brick	6'	52°C	43	.4	.9	1.7
Halo carbon grease (S)	Fire Brick	6'	52°C	63	***	***	***
Halo carbon grease (S)	Fire Brick	6'	92°C	63	***	***	***
12% TCP	Chromosorb W	6'	52°C	63	.3	.7	2.6
10% Adipo Nitrile	Chromosorb W	6'	52°C	63	2.5	*	**
20% Adipo Nitrile	Chromosorb W	6'	52°C	63	3.0	*	**
Di-nonylphthalate (30%)	Fire Brick	6'	52°C	45	2.9	3.7	4.3
Di-nonylphthalate (30%)	Fire Brick	6'	92°C	45	2.1	3.0	3.7
Di-nonylphthalate (30%)	Fire Brick	20'	92°C	45	3.0	4.1	7.9
Di-octylphthalate	Fire Brick	15'	92°C	45	*	*	**

* Poor peaks

** No peaks within 1 hour

*** Unreliable data

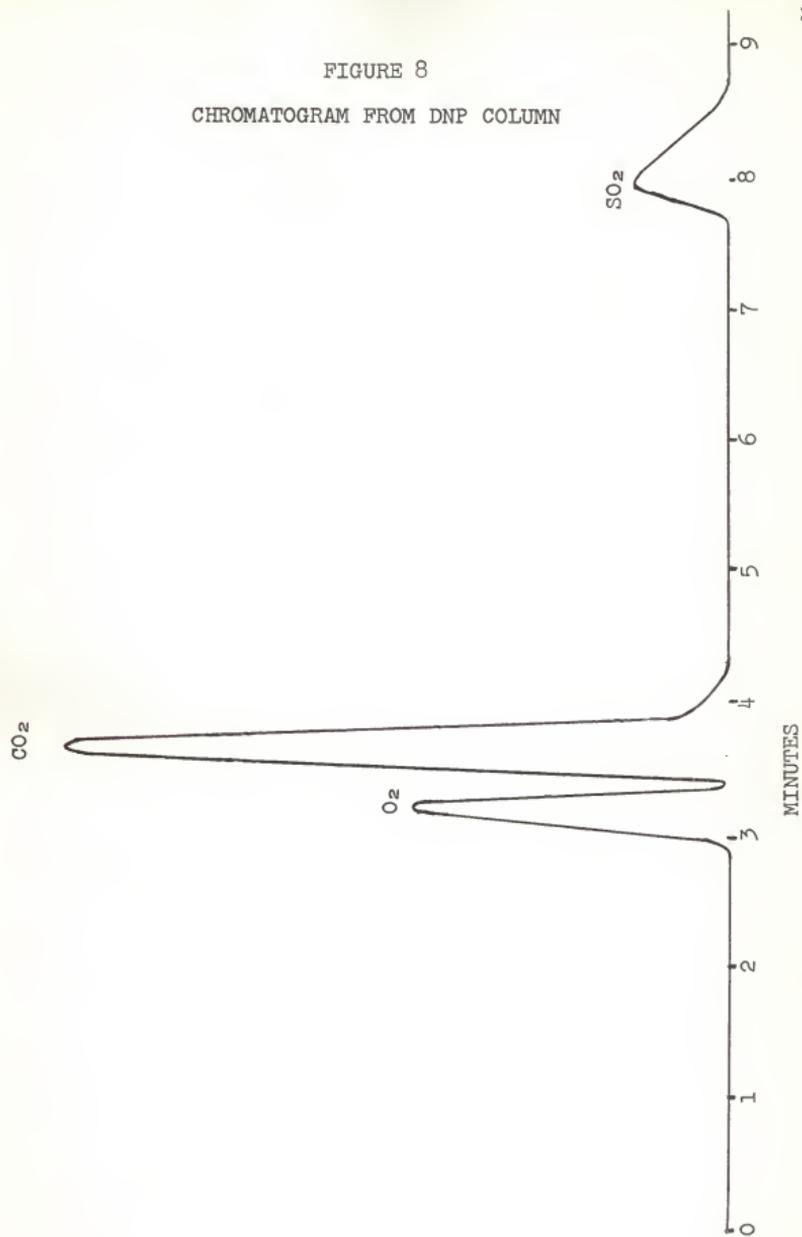
The combustion train was assembled as shown in Figure 1, except that the cold traps were connected in series to the exit of the combustion tube. The refrigerant in the first trap was altered with each experiment while the second trap was immersed in an acetone slush bath at -94.8° C. Any material not caught in the first trap would be held in the second trap. The presence of sulfur dioxide in the second trap was determined by a gas chromatographic column of dinonylphthalate. A list of the coolants that were used and the results of this work are shown in Table 8.

Table 8. Effect of temperature upon trapping of SO_2 .

Coolant	Temperature	SO_2 present in second trap
Salt-ice	-15° C	Yes
Chloroform slush	-61.2° C	Yes
Acetone slush	-94.8° C	Yes
Mixed slush	-131.0° C	Yes
Liquid nitrogen *	-195.6° C	No

* The pressure of the system was slightly reduced to prevent the condensation of oxygen.

FIGURE 8
CHROMATOGRAM FROM DNP COLUMN



CONCLUSIONS

Combustion

It is possible to quantitatively combust organic sulfur compounds to sulfur dioxide in an atmosphere of oxygen by using platinum asbestos and platinum stars as catalysts and a combustion temperature of 850° C. The work describing the combustion of the sample with the small heater and converting the mixed oxides of sulfur to sulfur trioxide over vanadium pentoxide catalyst was abandoned because of the difficulties described previously. It may be possible to use this approach to the determination of sulfur by further exploration.

Desiccants

Anhydrous calcium sulfate was a satisfactory desiccant to remove the moisture from the combustion gases. Anhydron was not used because of its strong oxidative property which was discussed previously. Barium oxide and calcium carbide were not used since there was some evidence of attraction between them and the sulfur dioxide. If a means can be found to use calcium carbide as a drying agent, it should be possible to adapt this method to include the determination of hydrogen with other elements.

Chromatographic Column

Halowax and *a*-chloronaphthalene did not give good resolution in the separation of oxygen, carbon dioxide and sulfur dioxide. Halocarbon grease produced blunt bumps instead of sharp peaks. A 20 ft. column of 30 percent dinonylphthalate resolved the above gases in a reasonable length of time.

Trapping of Sulfur Dioxide

It was necessary to use liquid nitrogen as the refrigerant, to insure the quantitative trapping of the sulfur dioxide. At this temperature, the carbon dioxide and sulfur dioxide were trapped as solids and the vapor pressure of these oxides was lowered sufficiently to prevent any loss beyond the first trap. The oxygen present was also liquified at this temperature. It was necessary to reduce the pressure of the system to equal the vapor pressure of the oxygen and prevent its condensation.

METHOD

The results of the previous studies were incorporated into a single method to determine the sulfur content in organic sulfur compounds.

Procedure for Combustion of Sample

1. A combustion tube was cleaned and packed with 10% platinum asbestos and platinum stars as shown in Figure 7. Eight cm. of asbestos was packed in the tube and each platinum asbestos plug was 2 cm. thick.
2. After placing the combustion tube in the Sargent micro furnace, the inlet was attached to the supply of oxygen. A Pregl absorption tube, previously filled with 4-5 cm. of anhydrous calcium sulfate and the unused space filled with glass wool, was attached to the exit end of the combustion tube by rubber tubing covering a glass to glass joint.
3. The absorption tube was joined to the trap by pushing the drawn out end of the tube through the one hole silicone rubber stopper attached to the trap as shown in Figure 2. The bypass on the trap was opened.
4. The open end of the combustion tube was sealed with a cork, and oxygen allowed to flow through the system at the rate of 10-12 ml. per minute. The system was purged for 30 minutes.
5. During this time, the long burner was heated to 850° C. and the mortar to about 180° C. to prevent condensation in the exit end of the tube.
6. The trap was immersed in a Dewar flask containing liquid nitrogen and the trap opened to the system.
7. A vacuum system was attached to the exit of the trap and the pressure regulated by adjusting the screw clamp on the trap until the oxygen would flow through the trap without condensings.
8. The stopcocks were set to deadhead the system and the cork removed from the end of the combustion tube. This allowed a positive pressure in the tube during the introduction of the sample.

9. A 5-10 mg sample, previously weighed in a platinum boat to the nearest 0.001 mg, was introduced into the combustion tube and positioned 1-2 inches from the long burner.

10. After replacing the cork in the end of the tube, the stopcocks were set to allow the gases to pass through the trap.

11. The short burner was heated to 850° C. and allowed to traverse toward the sample at a slow speed. When the combustion was completed, the small burner was allowed to traverse the tube the second time to insure a complete oxidation. To speed up the combustion process, the sample can be initially vaporized with a flame, and the small burner used to sweep the system of any remaining sample. This requires only one sweep of the small burner.

12. After the sample was combusted the system was flushed with oxygen for three minutes.

13. The trap was closed by adjusting the stopcocks and removed from the system.

Procedure for Analysis of Combustion Gases

1. A 20 foot column of 30 percent dinonylphthalate which had been previously installed and conditioned was heated to 92° C. The detector block was heated to 92° C.

2. After removing the cold trap from the Dewar flask, it was connected to the gas chromatograph by pushing the gas tubing through the Burrell seals as shown in Figure 2.

3. The bypass was opened and helium was passed through the instrument at a rate of 45 ml per minute. The pressure of the gas will vary with the individual column.

4. The potential to the thermistors was set at 8 volts, and the recorder, which had a sensitivity of 1 millivolt full scale deflection, was turned on.

5. While the gas trap was allowed to warm to room temperature, about 4-5 minutes, the flow of helium was purging any foreign gases which may have been present in the inlet and outlet of the trap.

6. When the trap had reached room temperature as evidenced by touching it or the absence of any condensed material inside it, the stopcocks were opened. The stopcock farthest downstream was opened first to allow the release of the pressure in the trap into the column. The other stopcock was then opened to flush the entire sample into the column.

7. A second combustion was started as soon as the first trap was removed from the combustion train. Therefore the combustion of one sample can be carried out while the trapped gases of the previous combustion are being determined.

Evaluation of the Method

A series of different compounds were analyzed according to the above procedure. Table 9 lists the results of these determinations. Compounds containing fluorine, chlorine, nitrogen and oxygen were successfully analyzed. Quinine sulfate did not give a sulfur dioxide peak. This compound contained the sulfur as a sulfate ion. D.L. -methionine did not produce satisfactory results. No explanation is available for its behavior. *p*-nitrophenylmethyl

sulfide produced some stray peaks that were not identified. This suggested that the combustion was incomplete.

A factor was obtained from the analysis of the phenyl sulfone samples by dividing the actual amount of sulfur in the sample by the area in square inches under the sulfur dioxide peak of the chromatogram.

$$\frac{0.608 \text{ mg sulfur in sample}}{1 \text{ square inch}} = 0.608 \text{ mg sulfur per square inch}$$

$$\frac{0.915 \text{ mg sulfur in sample}}{1.5 \text{ square inches}} = 0.610 \text{ mg sulfur per square inch}$$

$$\text{average} = 0.609 \text{ mg sulfur per square inch}$$

The weight percent of sulfur in each determination was calculated as follows:

$$\frac{\text{Square inches} \times 0.609 \text{ mg sulfur per square inch} \times 100}{\text{mg sample}} = \%$$

The average deviation between the actual and the determined percent of sulfur was calculated.

$$\text{Average deviation} = \frac{\sum \text{deviations}}{n} = \frac{4.25}{17} = 0.25 \%$$

Figure 9 shows that there is a straight line relationship between the area under the sulfur dioxide peak and the weight of sulfur in the sample.

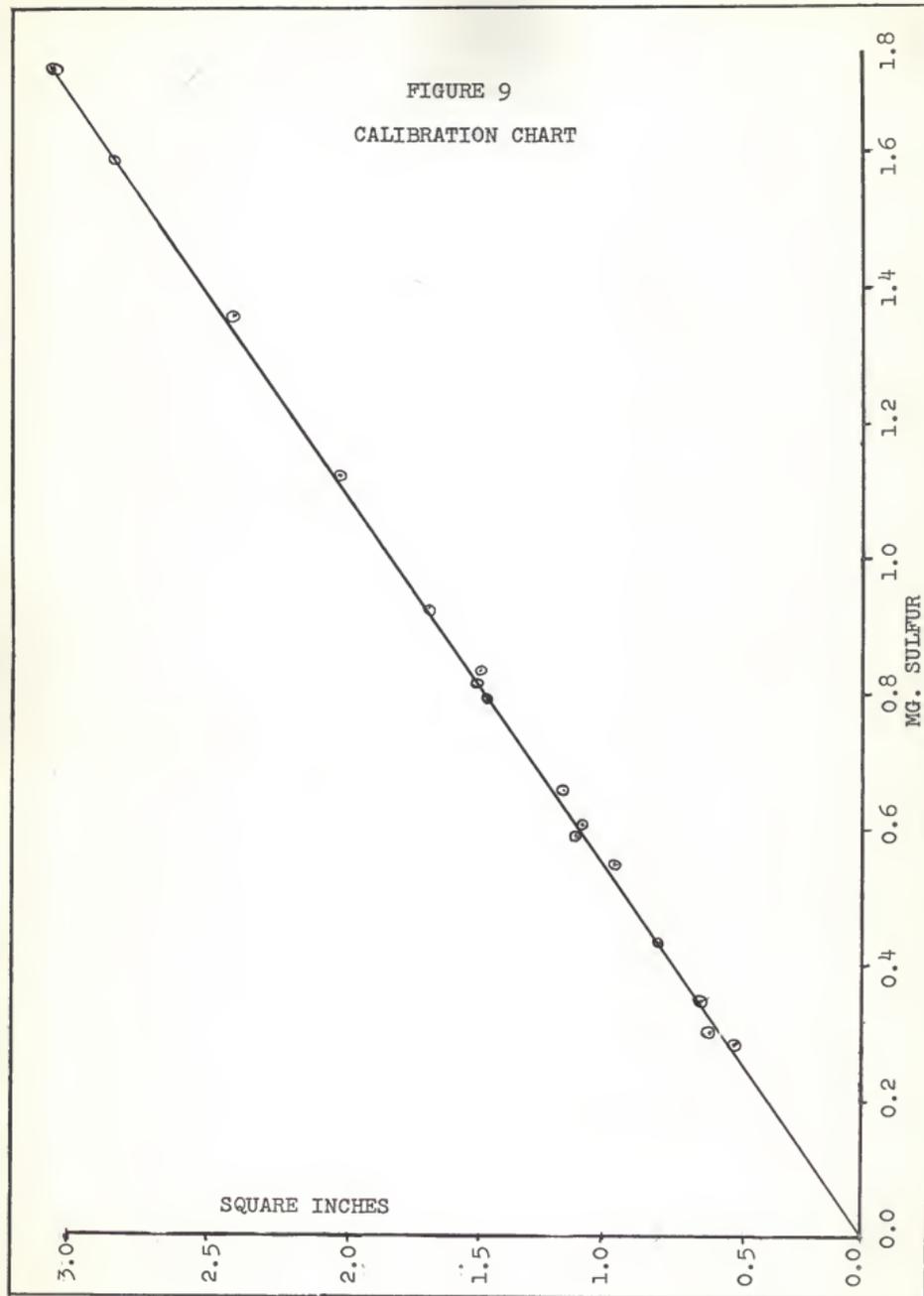
Further exploration should reveal that carbon and sulfur can be determined simultaneously. It is believed that this method can be modified to include the simultaneous determination of other elements such as hydrogen, nitrogen, oxygen, halogens, etc.

Table 9. Evaluation of method.

Compound	Weight sample	mg sulfur		Area inch ²	Percent	
		theory	found		actual	theory
phenyl sulfoxide	3.767	.608	.608	1.0	16.14	16.14
phenyl sulfoxide	5.668	.915	.915	1.54	16.14	16.14
phenyl sulfone	11.746	1.723	1.702	2.72	14.49	14.67
phenyl sulfone	2.503	.367	.363	.64	14.50	14.67
thianthrene	6.240	1.848	1.824	3.11	29.23	29.62
thianthrene	3.111	.921	.909	1.57	29.22	29.62
phenyl sulfone	2.916	.427	.423	.70	14.51	14.67
phenyl sulfone	4.627	.678	.670	1.08	14.48	14.67
phenyl sulfone	10.231	1.501	1.482	2.37	14.48	14.67
sulfanilic acid	4.042	.677	.669	1.10	16.54	16.74
thiourea *	4.441	1.867	1.824	3.00	41.06	42.04
thiourea *	5.069	2.131	2.087	3.40	41.17	42.04
4,4,4-trifluoro 1-(2 thienyl) 1,3-butadione	5.077	.731	.729	1.21	14.36	14.40
2,2 thio bis-4 chlorophenol	5.719	.641	.608	1.00	10.63	11.20
2,2 thio bis-4 chlorophenol	4.496	.504	.486	.80	10.81	11.20
n-butyl sulfone	5.939	1.068	1.034	1.72	17.41	17.98
mercaptoacetamide carbamate	8.042	1.223	1.216	2.02	15.12	15.21
thiocarbamilide	5.575	.866	.863	1.42	15.48	15.53
3,3 dibenzyl thio-tane	2.500	.331	.322	.53	12.88	13.22
quinine sulfate	No sulfur dioxide peak formed.					
d,l-methionine	Unreliable data.					
p-nitrophenylmethyl sulfide	Stray peaks.					

* The melting point of thiourea was 176-179° C. indicating an impure sample. The results were not used in further treatment.

FIGURE 9
CALIBRATION CHART



LITERATURE CITED

1. Duswalt, A. D., and Brandt, W. W., *Anal. Chem.* 32:272 (1960).
2. Hoegland, C. L., *J. Biol. Chem.* 136:543 (1940).
3. Huffman, E. W. D., *Ind. Eng. Chem. Anal. Ed.* 12:53 (1940).
4. Lee, J. K., University of Kansas, Private communication.
5. Maresh, Charles, American Cyanamid Co., Private communication.
6. Melan, C. E., Kansas State University, Private communication.
7. Moeller, T., "Inorganic Chemistry". John Wiley and Sons, New York (1956).
8. Scott, R. L., Phillips Petroleum Co., Private communication.
9. Scott, R. L., Smith, D. E., Puckett, J. E., and Heinrich, E. J., "Determination of Nitrogen and Oxygen in Organic Materials Utilizing Gas Chromatography", Presented at the American Petroleum Institute, May 1960.
10. Scott, W. W., "Standard Methods of Analysis", 5th Edition, Van Nostrand Co., New York (1939).
11. Steymark, Al, "Quantitative Organic Microanalysis", 1st Edition Blakiston Co., New York.
12. Sundenberg, O. E. and Maresh, Charles, *Anal. Chem.* 32:274 (1960).

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THE DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS
UTILIZING GAS CHROMATOGRAPHY

by

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Organic sulfur compounds were combusted at 850° C. to sulfur dioxide, carbon dioxide and water by a method similar to Pregl's. The combustion gases were dried over anhydrous calcium sulfate and trapped in a cold trap which was immersed in liquid nitrogen. After vaporization of the contents of the trap, the components were determined by gas chromatography. A twenty foot column of dinonylphthalate supported on firebrick was used at a temperature of 92° C. Helium was used as a carrier gas and passed through the system at a rate of 45 mls. per minute. Retention times for oxygen, carbon dioxide, and sulfur dioxide were 3.0, 4.1, and 7.9 minutes respectively. The percent sulfur by weight was determined by measuring the area in square inches, under the sulfur dioxide peak of the chromatogram, multiplying by a factor of 0.609 milligrams sulfur per square inch, dividing by the sample weight and multiplying by 100. The average deviation of nineteen determinations was 0.25 percent. This method has enabled a sulfur determination to be completed in twenty minutes with a minimum amount of special techniques. This compares with the 2 - 4 hours required by the Carius or Pregl method. Fluorine, chlorine, nitrogen, and oxygen do not interfere in this method. However, sulfur, when present as a sulfate ion could not be determined.