

GAS CHROMATOGRAPHIC ANALYSIS
OF COMBUSTION GASES

by 4589

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INTRODUCTION

Elemental analysis has long been the task of the analytical chemist. The work described in this thesis now permits us to determine carbon, hydrogen and sulfur simultaneously in 15 minutes. In the early attempts to obtain information pertaining to the elemental composition of a substance, a sample was simply oxidized in a stream of oxygen in the presence of copper oxide heated to 680°C to yield carbon dioxide and water. Any extraneous combustion products were absorbed out of the system by various materials (1). To measure the carbon dioxide and water, these two gaseous materials were absorbed by Ascarite and Anhydrone, respectively. Having weighed the tubes containing these two absorbents both before and after a combustion; it was possible, in about two hours, to determine how much carbon and hydrogen had been present in the original sample.

In addition to carbon and hydrogen, it became possible to determine the nitrogen content of organic compounds with the advent of the Dumas method (2). The gaseous combustion products in this case would contain nitrogen and some nitrogen oxides in addition to carbon dioxide and water. Hot copper was found to reduce the oxides of nitrogen to elemental nitrogen and this nitrogen could be determined volumetrically after absorption of the other combustion products. This method required about $\frac{1}{2}$ hours for a single determination. An alternate method for the determination of nitrogen was the Kjeldahl method (1), requiring from 4 to 5 hours for a complete analysis. In this instance, an

organic compound containing nitrogen was heated in the presence of sulfuric acid. Again, carbon dioxide and water were formed. Ammonium bisulfate was also formed. The bisulfate was allowed to react with sodium hydroxide to yield ammonia. The ammonia could then be titrated with standard acid.

Two methods were also introduced for the determination of sulfur in organic compounds. The first of these procedures, the Carius method (1), consisted of a sealed tube combustion which usually required 7 to 8 hours for a single analysis. In the presence of nitric acid and an alkali salt other than a sulfate, the alkali sulfate would be formed and could be measured either gravimetrically or titrimetrically. The second procedure, the Pregl method (2), involved the conversion of the oxides of sulfur to sulfuric acid by reaction with hydrogen peroxide. The resulting sulfuric acid could then be either titrated with standard base or allowed to react with barium chloride to yield the insoluble sulfate. The technique employed in this determination made use of a combustion tube containing a platinum catalyst heated to a temperature of 650°C .

The Pregl method for sulfur could be slightly modified to allow for the determination of halogens in organic compounds (2) with an analysis time of 2 to 3 hours. In the case of halogens, a combustion tube containing a platinum catalyst heated to 650°C was again used. The elemental halogen formed by the combustion procedure was allowed to react with sodium carbonate in the presence of hydrazine. The resulting sodium halide could then

be reacted with silver nitrate and the precipitated silver halide measured gravimetrically.

The common denominator relating each of these procedures was the rather long period of time required to obtain a single determination; usually 2 to 3 hours or more. A faster method of elemental analysis was definitely needed. With the introduction of the gas chromatograph, rapid elemental analysis became a definite possibility. Analysis times could be reduced from several hours to a few minutes.

The work of Duswalt and Brandt (3) and that of Sundberg and Maresh (4) appeared simultaneously. Both teams of researchers working independently applied the technique of gas chromatography to the problem of elemental analysis. Duswalt and Brandt combusted an organic sample in a dry, carbon dioxide-free stream of oxygen in the presence of a platinum catalyst heated to 750°C. The resulting water vapor and carbon dioxide were passed through a calcium carbide tube where the water was converted to acetylene. The mixture of carbon dioxide and acetylene was collected in a liquid nitrogen cooled trap. The trapping procedure was necessary in order to facilitate a "plug" injection of the combustion products onto the chromatographic column. In this case, the gas chromatograph was equipped with an activated silica gel column and a thermal conductivity detector. A helium carrier gas was employed. For organic nitrogen compounds, the combustion products resulting from the nitrogen constituent appeared as peaks well separated from the carbon dioxide and

acetylene peaks. In the case of sulfur and halogen containing organic compounds, a section of silver needles was sufficient to remove any sulfur oxides or halogen compounds from the gaseous products. Analysis time for this procedure was about 35 minutes.

Sundberg and Maresh combusted organic samples in a tube containing copper oxide heated to 750°C in a helium atmosphere. They also passed the resulting combustion products through a calcium carbide tube to convert the water vapor to acetylene. As with the work of Duswalt and Brandt, the carbon dioxide and acetylene were concentrated in a liquid nitrogen cooled trap before introduction onto the silica gel column. Once again, a helium carrier gas was employed along with a thermal conductivity detector. The usual analysis time was about 40 minutes.

At this stage in the development of the use of gas chromatography in elemental analysis, carbon and hydrogen could be determined. Nitrogen was added to the list by the work of Nightingale and Walker (5). The method used by these workers employed a high frequency induction furnace to cause rapid combustion of the sample and reduced analysis time to 15 minutes. Use of this type of furnace eliminated the need for a liquid nitrogen cooled trap. A mixture of silver permanganate and copper oxide was employed as the oxidant. The combustion was performed in a helium atmosphere. The water vapor is converted to acetylene on passage through a calcium carbide tube while the oxides of nitrogen are reduced to elemental nitrogen after being passed over hot copper. The resulting

carbon dioxide, acetylene and nitrogen are separated on a four foot column of 5Å molecular sieves. Temperature programming is necessary in this method and the combustion products are measured by means of a thermal conductivity detector equipped with thermistors.

Parsons, Pennington and Walker (6) made use of the system developed by Nightingale and Walker to arrive at a gas chromatographic method for the determination of nitrogen having an analysis time of 10 minutes. The procedure was identical to that of Nightingale and Walker except that the carbon dioxide and water were absorbed out of the system on Ascarite and Anhydrone, respectively. Since the carbon dioxide and water never reached the molecular sieve column, a temperature programmed procedure was not required. This factor allowed for the substantial reduction in analysis time.

Beuerman and Meloan (7) made use of a chromatographic separation in the determination of sulfur in organic compounds. Their procedure called for a combustion in an oxygen stream over a platinum catalyst heated to 850°C. In the initial investigation, the water formed during the combustion was absorbed out of the system by a calcium sulfate tube. A liquid nitrogen cooled trap was necessary as a concentration step before sweeping the combustion products onto the separation column of 30% dinonylphthalate. No attempt was made to quantitate the carbon dioxide produced during the analysis. Only the sulfur dioxide peak was considered. This method

usually required about 20 minutes for a determination. In a later paper by the same authors (8), a successful separation of oxygen, carbon dioxide and sulfur dioxide was reported and the results were quantitative. Beuerman and Meloan employed a thermal conductivity detector equipped with thermistors.

Pennington and Meloan (9) were able to determine carbon, nitrogen and sulfur in organic compounds in about 3.5 minutes by combustion of the sample over copper oxide heated to 850°C. This temperature was the minimum temperature that would result in complete conversion of sulfur to sulfur dioxide. A second furnace was needed to heat a section of copper wire to 500°C. This lower temperature was found to be necessary in order to insure quantitative data for a sulfur analysis. A column of 33% silicon oil 550 on Chromasorb P was used for the separation of the gaseous combustion products. Water was not intentionally absorbed from the system but did not appear to influence the chromatograms.

Mamaril and Meloan (10) were able to obtain quantitative information concerning the halogen composition of organic compounds by making use of the apparatus developed by Beuerman and Meloan. Their work did not concern itself with sulfur or nitrogen in the organic compounds studied. Any water formed during the combustion had to be removed from the system by anhydrous calcium sulfate. Failure to remove the water caused erratic results due to the reaction of water with the other combustion gases. In any work that involves halogens, special

precautions must be taken. One of these precautions is the careful construction of the apparatus itself. Nickel tubing was found to be well suited for work with such reactive materials as the halogens. The thermal conductivity detector used in halogen analysis is usually fitted with thermistors rather than with the more common tungsten filaments, due to the extremely corrosive nature of the gases being detected.

Recently, Dugan and Aluise (11) were able to determine carbon, hydrogen, sulfur and nitrogen in 16 minutes with a gas chromatographic method. The authors used a dynamic, flash-combustion of an organic sample at 1060-1080⁰C in an atmosphere of 40% oxygen in helium. The carbon dioxide, sulfur dioxide and water formed during the combustion were trapped on a column of 20% Carbowax 20M on Haloport F at liquid nitrogen temperatures. The nitrogen oxides were converted to elemental nitrogen by reduction over hot copper and the resulting nitrogen was trapped on 5⁰Å molecular sieves at liquid nitrogen temperatures. Any excess oxygen remaining after the combustion was removed from the system after passing the reaction products through the section of hot copper used to reduce the nitrogen oxides. The combustion products were once more measured with a thermal conductivity cell employing thermistors.

Given this basic review of elemental analysis procedures, the next step would logically appear to be a combination of techniques to prove the possibility of a total analysis for carbon, hydrogen, and sulfur. It was the author's intent to

develop such a combination of techniques.

EXPERIMENTAL

Apparatus: A Varian Aerograph Model A-90-P gas chromatograph equipped with nickel filaments was used for this study. The percentage of carbon, hydrogen and sulfur in organic compounds was determined using a 6 foot, $\frac{1}{4}$ inch O.D. stainless steel column packed with Porapak Q, 50-80 mesh. With the idea in mind to extend this work at a later date to include nitrogen and halogen analysis, a section of hot copper was added to the system to reduce the oxides of nitrogen to elemental nitrogen. Samples were introduced into the combustion system (Figure 1) with 10 microliter syringes from Precision Sampling Corporation. In every instance the sample size used was 2 microliters.

The combustion tube, $\frac{1}{4}$ inch O.D. stainless steel, was heated to a temperature of 850°C by a Multiple Unit Electric Furnace type 123-3 (Hevi-Duty Electric Company, Milwaukee, Wisconsin) with current maintained by a Powerstat type 216 (Superior Electric Company, Bristol, Connecticut). The trapping and separation arrangement shown in Figure 2 is constructed of glass tubing and, where necessary, metal to glass connections are made with Cajon Ultra-Torr fittings (Kaw Valve and Fitting Company, Kansas City, Kansas).

To avoid water condensation in parts of the system diagrammed in Figure 2, a beaded, flexible heating element (Matheson Scientific Company) was coiled around the tubing and then covered with a shield of asbestos paper. The current

FIG. 1

- A Helium carrier gas cylinder.
- B Oxygen cylinder
- C Copper tubing, $\frac{1}{2}$ inch O.D.,
containing activated 5A molecular sieves.
- D S.S. injection port, 850°C.
- E S.S. combustion tube, 850°C.
- F Helium by-pass
- G To trap C (Fig. 2).

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

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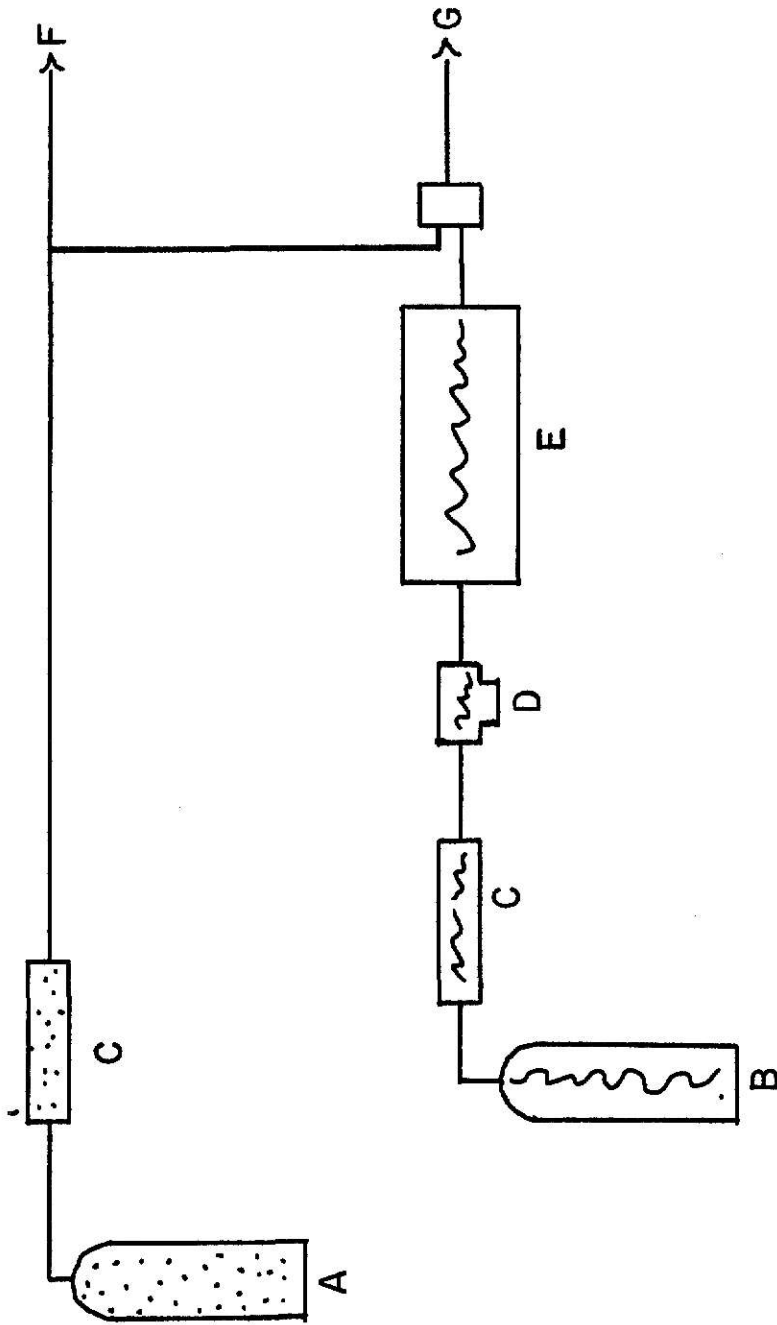


FIG. I

TABLE 1

Operating Conditions of Gas Chromatograph

Detector - 135°C 400 milliamps

Injection port - 840°C (actual)

Column - 6 feet, $\frac{1}{4}$ inch O.D. S.S. packed with Porapak Q,
50-80 mesh.

Carrier gas - Helium

Helium flow rate - 40 ml./min.

Oxygen flow rate - 14 ml./min.

Chart speed - 1 inch per minute

supplied to the heating element was controlled by a Variac type 2160 voltage regulator. To record the chromatograms of the combustion products, a Sargean Model SR recorder with a one millivolt range was used. The recorder was equipped with a Model 204 disc integrator (DISC Instruments, Incorporated).

Chemicals: The organic sulfur compounds used in the analyses were of questionable purity due to decomposition with age. In calculating the results of this procedure, experimental data is compared with data obtained from a commercial analysis performed by Childers Microanalytical Laboratories.

Procedure: Because of the rather complex nature of the trapping and separation system shown in Figure 2, it would seem advisable to illustrate, by means of a series of diagrams, the procedure followed in each analysis. In every instance, the sample to be oxidized was introduced into the system at point D in Figure 1. In the first section, a liquid nitrogen filled Dewar is in place around trap C of Figure 2. All gaseous combustion products would be condensed at that point. Figure 3 pictures the position of all elements of the trapping and separation system at the time that the combustion products are being swept into trap C. In order to avoid plugging the trap with liquid nitrogen, a vacuum pump is kept in operation while the contents of the combustion tube are carried into the trap. The pump is allowed to evacuate the trap for five minutes after the stopcock between the combustion tube and trap C is closed (Figure 4).

At the end of the five minute evacuation period, the stopcock positions are altered until the arrangement is the

FIG. 2



Section of system heated to prevent water condensation.



24 inch section of glass tubing, $\frac{1}{2}$ inch O.D., containing activated 5A molecular sieves.

- A Helium carrier gas cylinder.
- B From combustion tube.
- C U-tube trap containing glass wool.
- ^o D 20 cm. section of Cu^o turnings,
500 C.
- E Tube furnace operating at 500°C.
- F U-tube trap containing activated
13X molecular sieves.
- G Gas outlet and soapfilm flowmeter.
- H Vacuum pump and soapfilm flowmeter.
- I Combustion by-pass injection port.
- J Aerograph A-90-P.
- K 6 foot, $\frac{1}{4}$ inch O.D. S.S. column with
Porapak Q, 50-80 mesh.
- L Gas outlet.
- M Helium by-pass.

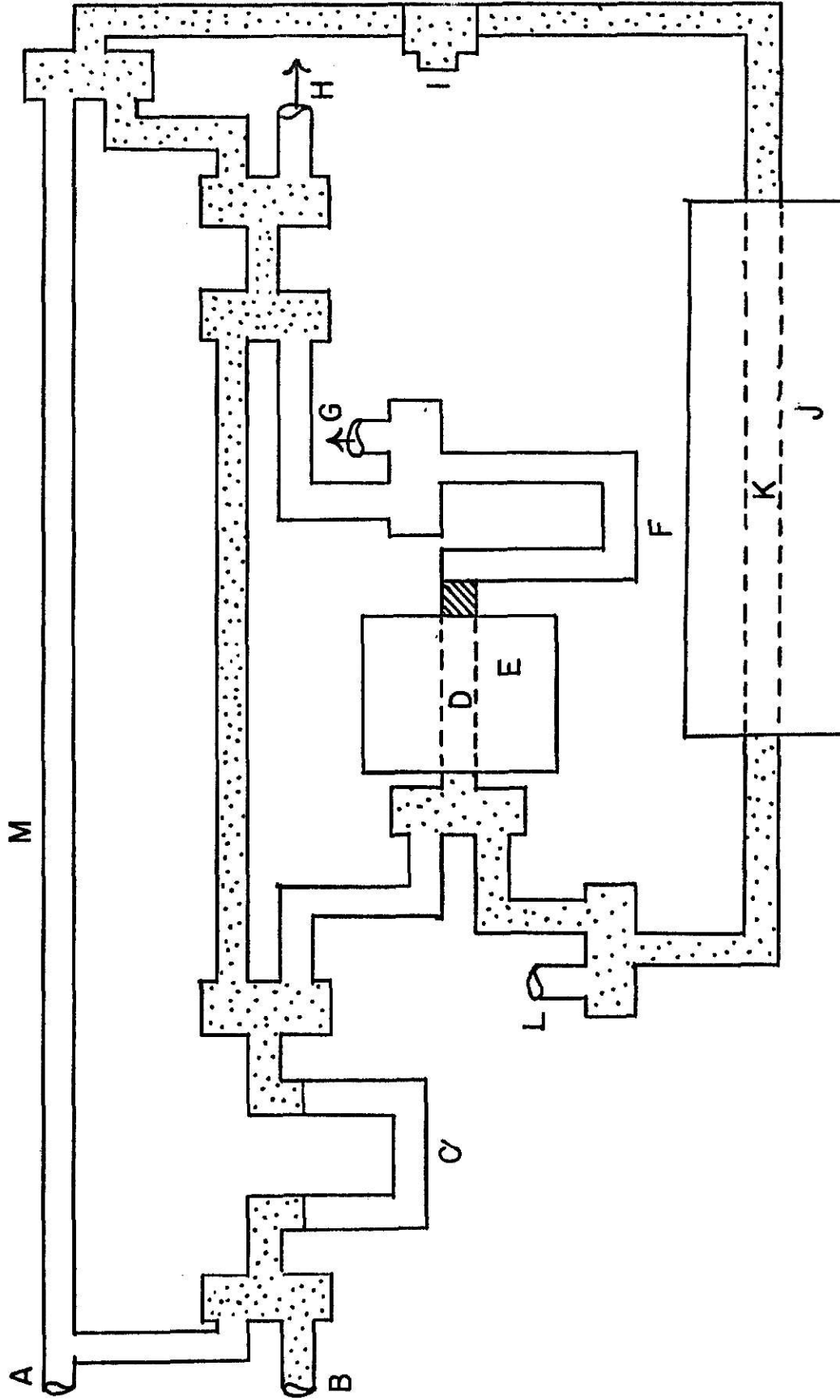


FIG. 2

FIG. 3

Combustion products are swept into trap C by oxygen flow. At this stage, a liquid nitrogen containing Dewar is in place around trap C and the vacuum pump at H is operating in order to minimize oxygen condensation at C.

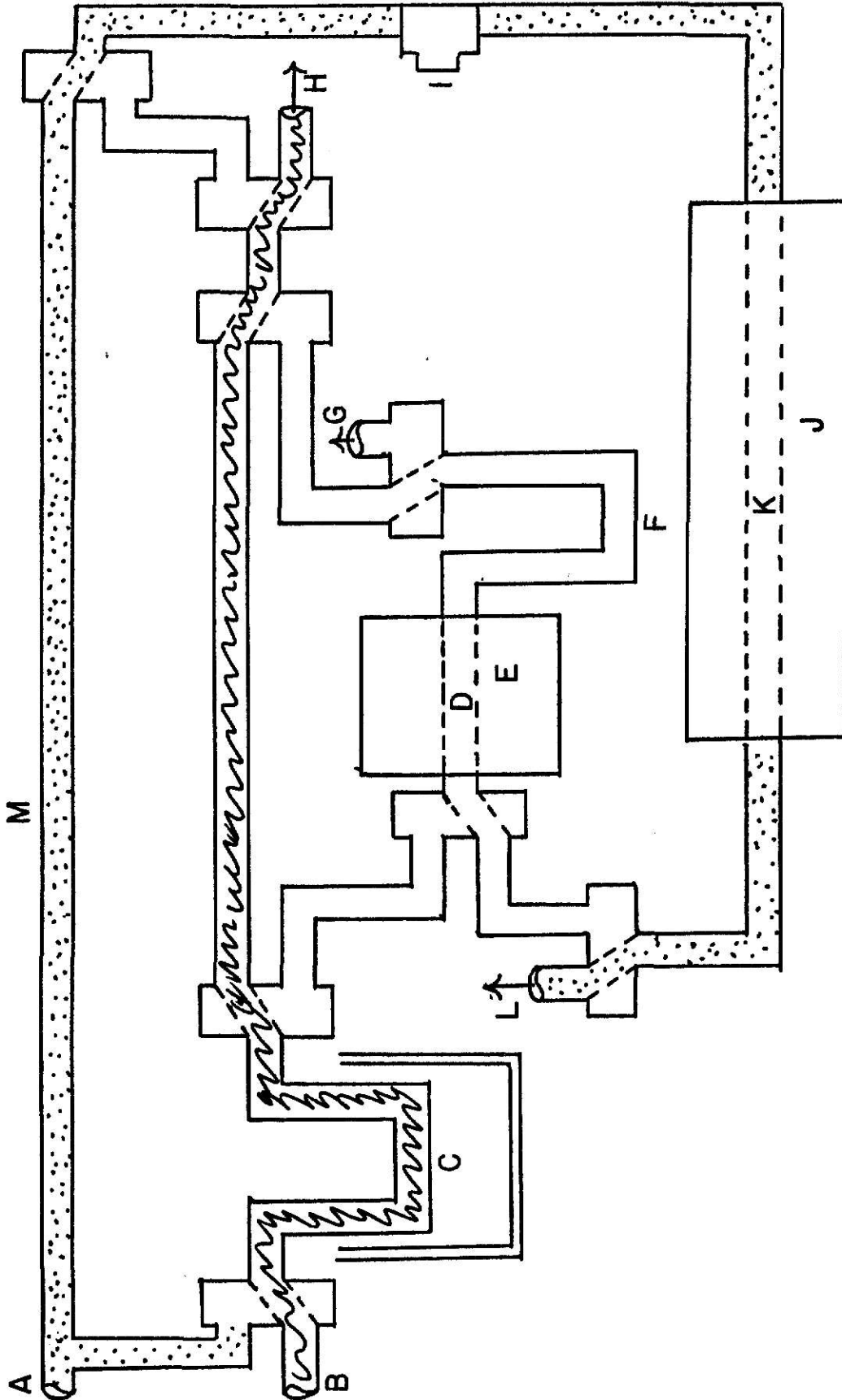


FIG. 3

FIG. 4

Excess oxygen is removed from trap C by creating a partial vacuum. At this stage, the stopcock at B is closed.

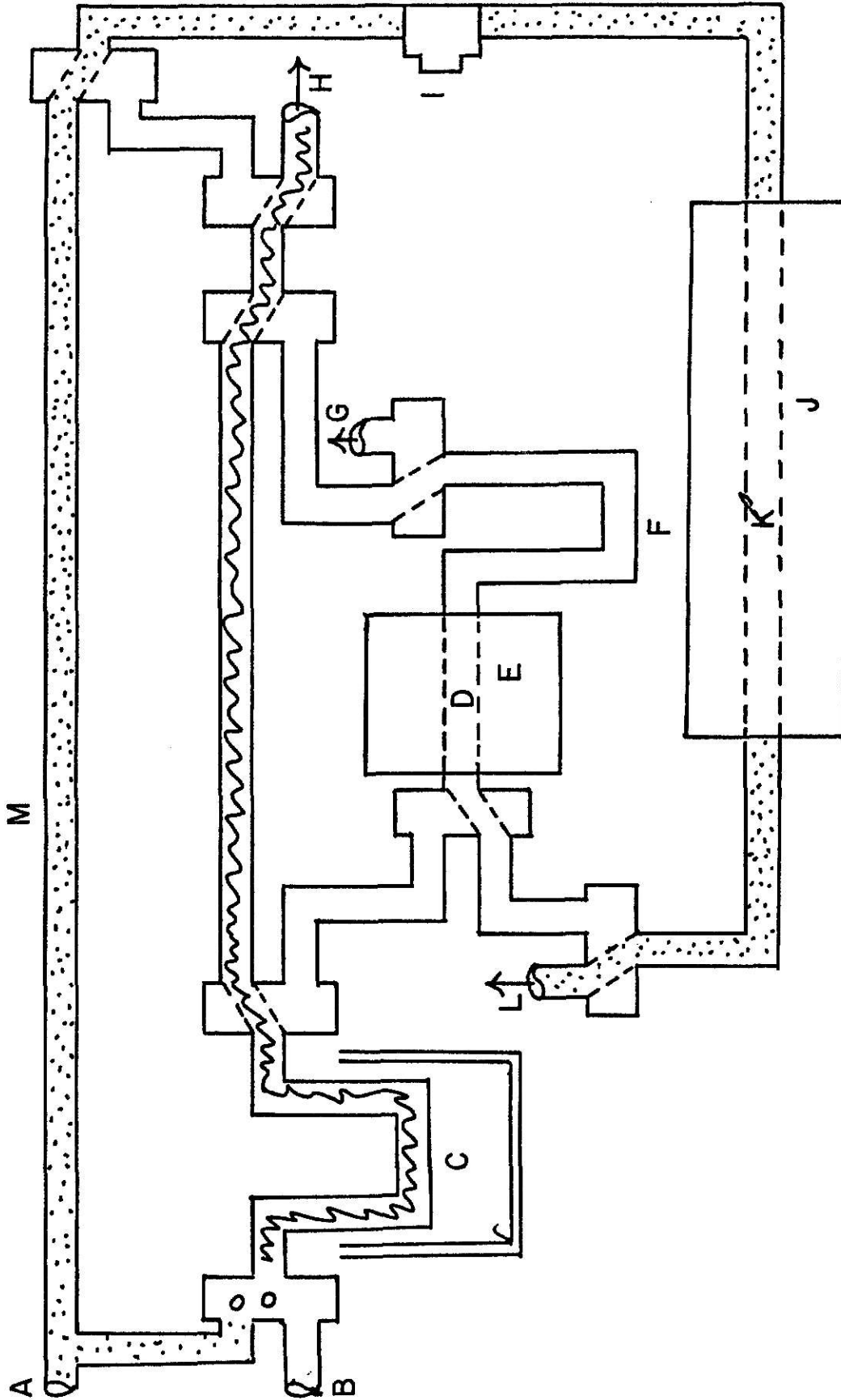


FIG. 4

same as that shown in Figure 5 and the recorder is turned on. As soon as the helium flow reaches equilibrium throughout the system, the liquid nitrogen Dewar is removed and replaced by a bath of hot mineral oil. The oil bath is heated to about 120°C in order to cause the condensed water to vaporize rapidly. The column is operating at room temperature initially, but as soon as the sulfur dioxide peak emerges, the column oven is turned on in order to raise the oven temperature to 120°C and cause the water peak to elute. Operating the column at higher temperatures throughout the course of the analysis causes poor resolution of the carbon dioxide and sulfur dioxide peaks.

Enough time elapses between the appearance of the carbon dioxide, sulfur dioxide and water peaks to allow for an attenuation change. The area under each peak is read directly from the integrator trace and then multiplied by a factor correcting for attenuation changes. Figure 6 is a representative chromatogram.

RESULTS AND DISCUSSION

The analyses of three organic compounds are given in Table 2. The values are reported in terms of mean error from the theoretical values for an average of three determinations. The precision of this method is given at the bottom of the table as the standard deviation for carbon, sulfur and hydrogen. It is obvious that the standard deviations leave something to be desired. The fact was mentioned previously that any glass to

FIG. 5

After the helium flow has reached equilibrium, the liquid nitrogen containing Dewar is removed and replaced by a hot bath of mineral oil. The combustion products are then swept from trap C onto the column I.

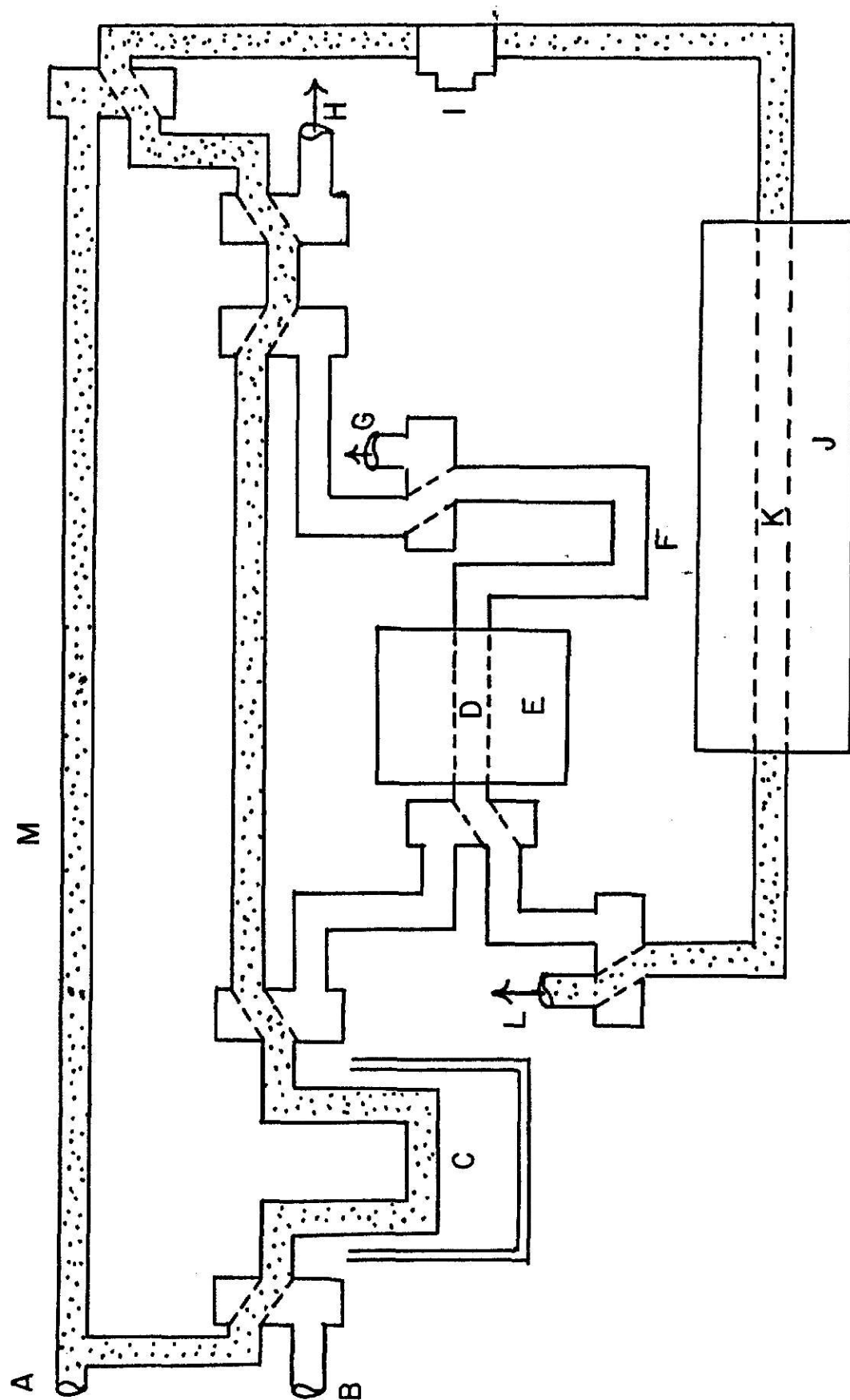


FIG. 5

FIG. 6

Chromatograms of combustion products.

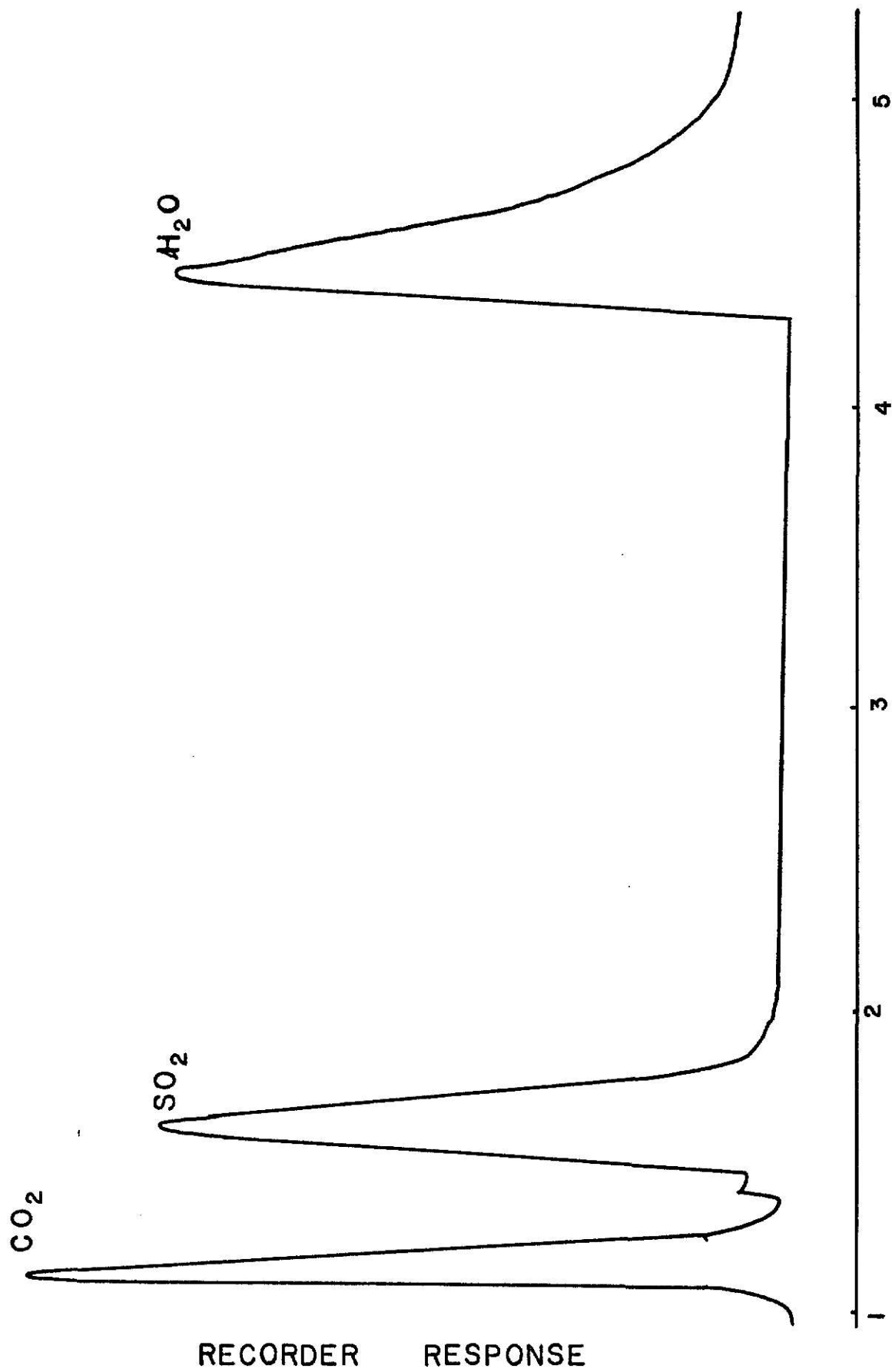


TABLE 2

Results of Analysis of Three Liquid Organic Compounds

Compound	Percent deviation from the calculated va.		
	% Carbon	% Sulfur	% Hydrogen
Carbon disulfide	-0.34%	+0.34%	
Tetramethylene sulfoxide	-1.03%	+0.53%	+0.51%
Tetramethylene sulfone	+0.03%	+1.13%	-1.17%
Standard deviation	$\pm 7.59\%$	$\pm 1.36\%$	$\pm 7.99\%$

metal connections in the system were made with Cajon Ultra-Torr fittings. Throughout the course of this work, a major problem has been preventing leaks in the system at those points where metal to glass connections were made. It is the opinion of the author that the precision of this method could be greatly improved by eliminating the need for these fittings. Since procedures similar to that presented in this study have been found to result in much better precision, this opinion would seem to be well founded.

In spite of the seeming difficulties inherent in this procedure, the author feels that the method could be improved so as to compare favorably with the classical methods of analysis.

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VITA

Mary Jane Jackson was born July 22, 1943, in St. Louis, Missouri, the daughter of John and Alberta Jackson. She had one brother, Roland Otto. Living in the St. Louis area for the early part of her life, the author attended both grade school and high school in the city.

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A procedure is presented that makes possible the determination of the amount of carbon, hydrogen and sulfur present in an organic compound. The sample to be analyzed is combusted in a stream of oxygen at 850°C and the gaseous combustion products are trapped at liquid nitrogen temperature before introduction onto a chromatographic column. The method has a standard deviation of $\pm 7.59\%$ for carbon, $\pm 1.36\%$ for sulfur and $\pm 7.99\%$ for hydrogen. The analysis time for this system is 15 minutes.