

THE DETERMINATION OF ORGANIC HALOGENS
USING GAS CHROMATOGRAPHY

by

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INTRODUCTION

The study of the combustion products of organic halogen containing compounds has not been studied extensively. It is assumed in most cases that the organically bound halogens are converted into their respective molecular forms during combustion. No further proof is offered to support this fact. Considering that a combustion is carried out at high temperatures of 650°C to 850°C in an atmosphere of oxygen in the presence of red-hot platinum catalysts, the question is being raised as to the possibility of the formation of the halogen oxides under such oxidizing conditions.

This paper is concerned with the study of the combustion gases of the organic halogens utilizing gas chromatographic techniques. The retention times of the combustion gases were compared with those of oxygen, carbon dioxide, chlorine, and bromine gas samples. The combustion gases of organic compounds containing chlorine and bromine in the sample were also studied. Furthermore, the combustion gases were analyzed using the method worked out by Beuerman and Melan (7) for the determination of organically bound sulfur.

Fluorine containing organic compounds have not been included in this work.

REVIEW OF LITERATURE

There is a wide variety of methods employed for the determination of the halogen content of organic compounds. The methods of decomposing the organic material alone ranges from the use of peroxide (3), lime (17), caustic fusion techniques in a sealed bomb (28), sodium fusion (10), sodium dispersions in organic solvents (10, 22), wet oxidation methods which include the Van Slyke method (33), the Carius method (33), and combustion in an at-

mosphere of oxygen in the presence of platinum catalysts, known as the Pregl method (33). It has also been shown that sodium diphenyl (23) can decompose certain halogenated compounds into their corresponding halides. Besides, chemical methods of analysis, physical methods of analyzing organically bound halogens have been utilized such as X-ray absorption techniques (15).

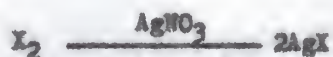
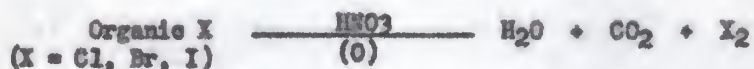
With the advent of gas chromatography, Duswalt and Brandt (11) and Sundenberg and Marash (34) developed methods of determining carbon and hydrogen utilizing gas chromatographic techniques. The combustion gases were passed through calcium carbide to convert the water to acetylene and the issuing gases were trapped in liquid nitrogen. After combustion is complete, the trapped gases were allowed to vaporize and then injected into the gas chromatographic column of silica gel for its separation. Ceramic thermistors were used for the detection of the gases. Their methods reduced the time for a carbon-hydrogen determination to one fifth the time for that of the standard Pregl method. Scott, et al. (32) modified the method to determine oxygen and nitrogen. Marash (8) using the same principles determined simultaneously carbon, hydrogen, and nitrogen. Beuerman and Melcan (7, 6) adapted a combination of the Pregl catalytic combustion method with gas chromatography for the simultaneous determination of carbon and sulfur.

Hightangale and Walker (28) used a high frequency induction furnace for the combustion of the organic samples and used gas chromatographic techniques for the analysis of the combustion gases. The sample was mixed with a sufficient amount of oxidizing agent, which is silver permanganate, and was combusted in a helium atmosphere. Rapid combustion eliminated the need for a liquid nitrogen trap. With this method, they were able to complete a simultaneous carbon, hydrogen, and nitrogen determination in one hour and forty five minutes. The column used was a 5-A molecular sieve with a ther-

mal conductivity detector.

Gas chromatographic work on inorganic halogens were done by several workers. Ellis and Iveson (12), Runge (31), and Iveson and Hamlin (16) have all worked on corrosive inorganic gases using gas chromatography. Neely (26) developed a gas chromatographic method for determining the percentage composition of the gases that are present in a chlorine cell. Phillips and Owens (30) worked out a gas chromatographic analysis of the halogens on capillary columns coated with Kel-F oils. Bergman and Martin (5) developed a method for determining a mixture of chloride and bromide ions in solution by converting the ions to their respective covalent and volatile hydrogen halides and analyzing these gases by gas chromatography. The column used was a 5.0% n-heptane and 2.3% toluene on granular teflon at a temperature of -78°C .

The most generally accepted methods of analyzing organically bound halogens are the Carius method and the Pregl catalytic method. The Carius method consists of combusting the organic compound in nitric acid and silver nitrate. The nitric acid destroys the organic matter and the resulting halogen is converted to the corresponding silver halide by the silver nitrate. The reactions are as follows:

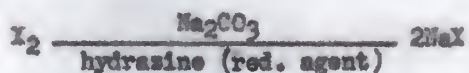


The silver halide formed is then determined gravimetrically. The method takes about nine to ten hours for completion of the analysis.

Besides the length of time involved in the method, there is the necessity of learning the techniques of sealing and breaking the tubes. Extra precautions should also be taken to protect the precipitate from photochemical

decomposition.

The Pregl method consists of combusting the organic compound in an oxygen atmosphere in the presence of red-hot platinum contact stars. The resulting halogen is absorbed and reduced simultaneously in an alkaline reducing medium. The solution is then acidified and the halide precipitated as the silver halide. The silver halide is determined gravimetrically. The reactions are as follows:



A number of modifications are introduced in determining the halide concentration. Titrimetric techniques using silver nitrate and Volhard indicator (14), Fajans indicator (14), and potentiometric end-point detection (18) have been used. However, Steyermark (33) has found the end-point detection utilizing the Volhard method rather unsatisfactory for very dilute solutions. Mercuric titrations have been used by other workers (20). Coulometric methods (24), colorimetric methods (9), and chromatographic methods (13) have been utilized. Other modifications include amperometric titrations (21), polarographic methods (19), and radiochemical procedures (2) for determining the halide concentration.

Alicino, *et al.* (1) determined bromine in the presence of chlorine by converting the bromine to the bromate state iodometrically, using sodium hypochlorite as the oxidizing agent.

Chlorine and bromine can also be determined simultaneously (27) by col-

lecting the two silver halides, weighing the mixture and then treating it with about six times its weight of ammonium iodide (or bromide). The mixture is heated to 300°C for conversion to silver iodide (or bromide) and reweighed. The treatment is repeated to insure complete conversion. Chlorine and bromine are calculated from the increase in weight of the precipitate.

The halogens and sulfur are analyzed simultaneously by Friedrich (33) using a modified Carius method. The silver halide is removed and the sulfate is precipitated with barium nitrate. Belcher and Spooner (4) did a simultaneous determination of carbon, hydrogen, sulfur and chlorine.

The length of time involved in the Carius and Pregl methods is quite considerable. The Carius method takes about nine to ten hours and the Pregl method about two to three hours for a complete halogen determination. Besides this disadvantage, there are several sources of errors that may come in. One major source of error is the photochemical decomposition of the silver chloride or silver bromide precipitate. Besides the inconvenience of transferring the precipitate quantitatively to the filter tube, there is the possibility of losing some of the material during the transfer. Errors may also be introduced in the drying and weighing of the precipitate.

This work is an attempt to shorten the determination of the organic halogens by directly analyzing the combustion gases, using gas chromatographic techniques. The direct analysis of the gases minimizes the introduction of errors encountered in the classical gravimetric and titrimetric methods of analysis. Furthermore, the work may be modified to include the simultaneous determination of carbon, hydrogen, oxygen, sulfur, nitrogen, and the halogens.

EXPERIMENTAL

Apparatus

The apparatus used in this work was the same as that used by Beuerman (8) in the determination of organic sulfur by gas chromatography. Slight modifications were introduced in the combustion train and the column used. The apparatus consisted of a combustion train (Figs. 1 and 2), a trapping system (Figs. 1 and 3), and a gas chromatograph (Figs. 4, 5, 6, and 7).

The combustion train consisted of an oxygen supply, furnace, combustion tube, and drying tubes. The supplied oxygen was prepared from the distillation of air. The cylinder of oxygen was equipped with a 2-stage pressure regulator and needle valve. The oxygen was passed through a pressure regulator to keep the oxygen pressure in the combustion train at constant pressure. From the pressure regulator, the oxygen passes the bubble counter which determines the rate of flow of oxygen, into the U-tube filled with anhydrous in one arm and with ascarite in the other. The anhydrous removes the water out of the oxygen and the ascarite removes carbon dioxide.

The combustion tube is made of Pyrex glass and is filled according to Fig. 2. The pyrex glass beads (20 mesh) was introduced first to about 3 centimeters from the end of the tube. The beads offer resistance to the flow of oxygen. A plug of 10% platinum asbestos was added to a depth of 5 centimeters and then one of the platinum contact stars was put into place followed with another 2 centimeters of 10% platinum asbestos. The other platinum contact star was placed next and finally about 2 centimeters of the platinized asbestos was plugged in.

The furnace used was a Sargent Micro-Combustion furnace capable of obtaining temperatures of 900°C.

The drying tube was a Pregl absorption tube filled with anhydrous calcium sulfate. The drying tube is necessary to remove the water out of the combustion gases so as to prevent its reaction with the halogens, halogen oxides, or hydrogen halides that may be formed during the combustion.

The connections are all glass to glass joined by thick-walled tubing specially treated with paraffin. The trap is connected to the drying tube by a one-hole silicone rubber seal. The other drawn-out end of the trap is also connected to a drying tube by the same means.

The cold trap was constructed of 7 mm. pyrex glass tubing as shown in Fig. 3. The stopcocks were lubricated with the minimum amount of vacuum grease Kel-F No. 90 and held in place by Todd tension clips. The tension clips prevent the loss of gases due to increased pressure upon vaporization of the trapped gases. The trap was immersed in a one-quart Dewar flask filled with liquid nitrogen. The trap is connected to a vacuum system with a drying tube in between to prevent any moisture to come inside the trap from any outside source. Vacuum was applied to decrease the partial pressure of the oxygen in the trap and at the same time to maintain a constant flow of oxygen through the combustion train. The vacuum was regulated by means of a Hoffman screw.

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

The helium was supplied from a cylinder equipped with a two-stage pressure regulator and a vee-type needle valve. The helium was passed to an absorption bottle filled one-half with anhydrous calcium chloride and the other half with ascarite. The helium entering the gas chromatograph is thus freed of any water or carbon dioxide. The helium passed the reference side of the

detector block first (See Fig. 4). The helium from the reference side of the detector block was then passed through the trap carrying with it the combustion gases in the trap into the column and finally through the sample side of the detector block. The emerging helium gas was passed through a soap bubble flow meter to measure its flow rate. The flow diagram of the helium gas in the gas chromatograph is shown in Fig. 4.

The control box, detector block, and the constant temperature cabinet for the column are described in Beuerman's work (8). Figs. 5, 6, and 7 were reproduced from his paper.

As shown in Fig. 6, the circuit provided a source of direct current to the thermistors with the proper sensitivity control and attenuation to send the correct signal to the recorder.

The constant temperature cabinet was constructed of 16 gauge galvanized iron and insulated with about one fourth inch asbestos covered with heavy-duty aluminum foil. A 4-inch fan powered by a 1/100 horsepower motor forced the air over a 500 watt heating tape installed in front of the fan. The cabinet is made up of an inner and outer chamber to establish a definite pattern of circulation of heated air.

The recorder was equipped with a one millivolt sensitivity plug. The recorder was adjusted to give the best pen response and the right attenuation and sensitivity.

Preparation of the Column Packing

A weighed quantity of the liquid phase was dissolved in diethyl ether. The resulting solution was mixed thoroughly with a weighed quantity of inert phase which had been acid washed and dried. The ether was then allowed to evaporate from the mixture. To hasten the evaporation of the solvent, the

Figure 1. Flow diagram of the combustion train

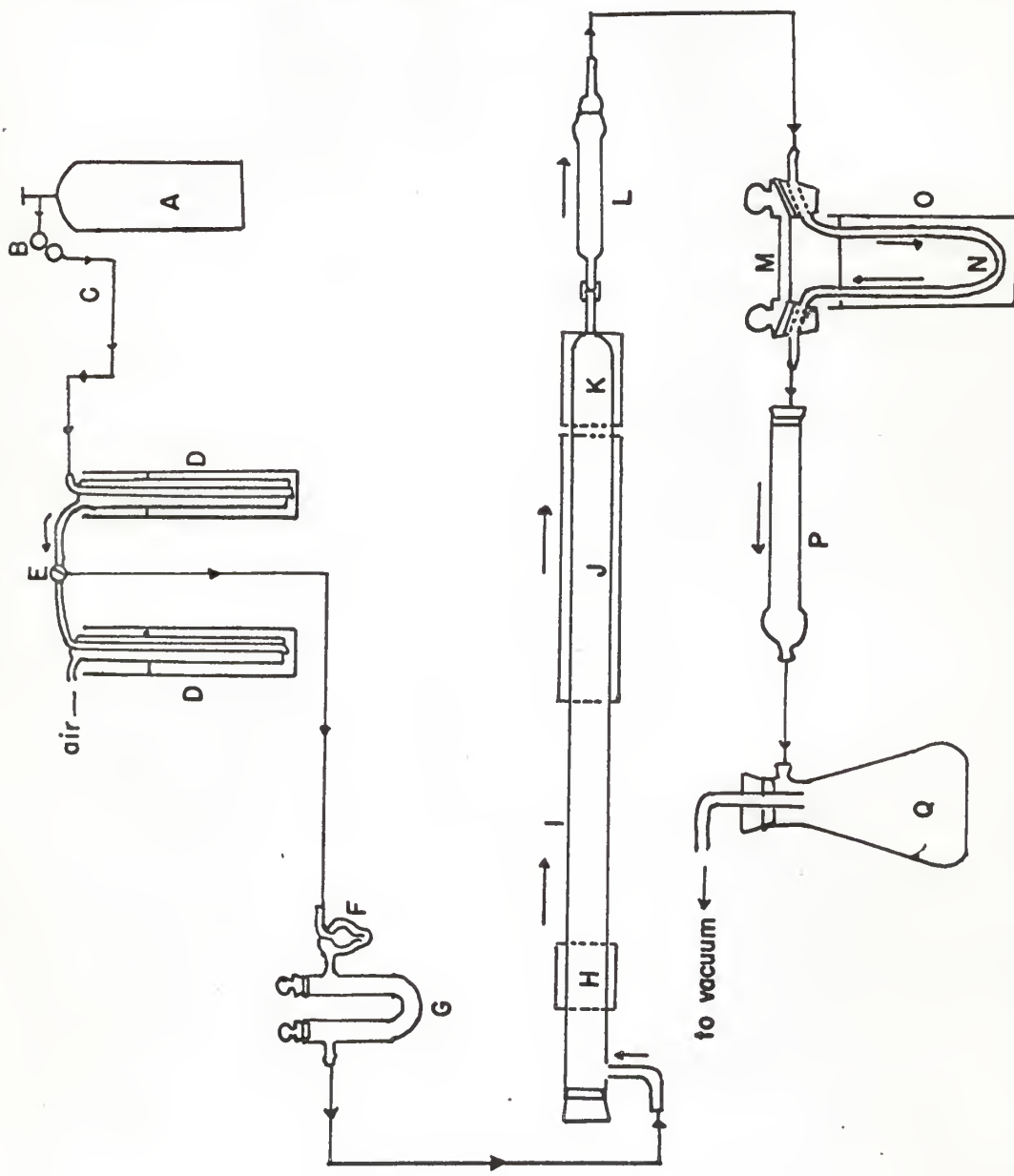


Table 1. Parts of the combustion train.

- A. Cylinder of oxygen
- B. Two stage pressure regulator
- C. Ves point type needle valve
- D. Pressure regulators with 5% sodium hydroxide or dilute sulfuric acid solution
- E. Three way stopcock
- F. Bubble counter with concentrated sulfuric acid (5-7 mm. deep)
- G. U-tube with anhydrous in one arm and ascarite in the other
- H. Short movable furnace
- I. Pyrex combustion tube
- J. Long stationary furnace
- K. Heating mortar
- L. Absorption tube with anhydrous calcium sulfate
- M. Bypass of trap
- N. Cold trap
- O. One quart Dewar flask filled with liquid nitrogen
- P. Drying tube with desiccant
- Q. Trap of vacuum system

Figure 2. The combustion tube filling

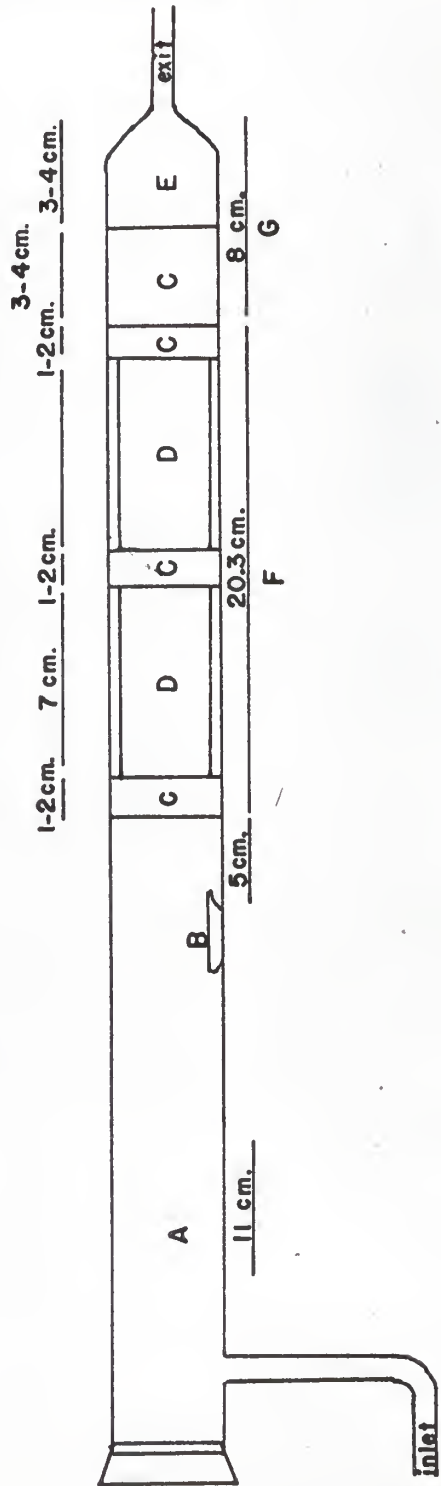
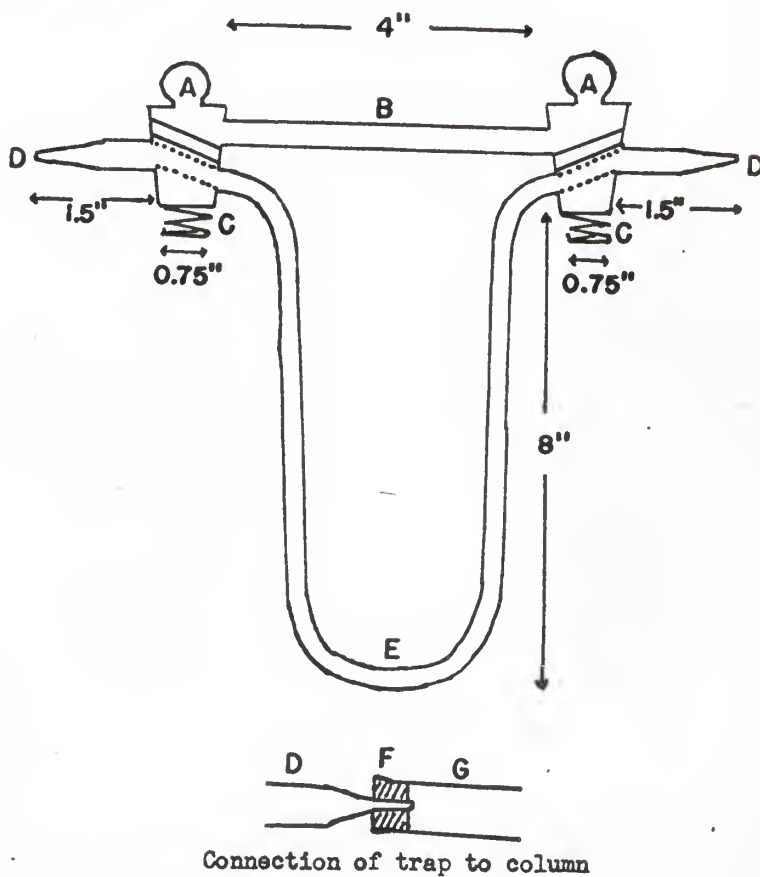


Table 2. Details of the combustion tube filling

- A. Area of movable short furnace
- B. Platinum sample boat
- C. 10% platinum asbestos
- D. Platinum contact stars
- E. Pyrex beads (20 mesh)
- F. Area of long stationary furnace
- G. Area of heating mortar

Figure 3. The cold trap



Connection of trap to column

Table 3. Details of the cold trap

- A. Stopcocks, Pyrex, Fisher catalog No. 14-587**
- B. Bypass constructed of 7 mm. glass tubing**
- C. Todd tension clips, Fisher catalog No. 14-631-50**
- D. Drawn-out end for connection to combustion train or column**
- E. Trap constructed of 7 mm. glass tubing**
- F. Burrell seal, one hole-silicone rubber, Burrell catalog No. 261-9**
- G. Gas chromatograph column tube**

Figure 4. Flow diagram of the gas chromatograph

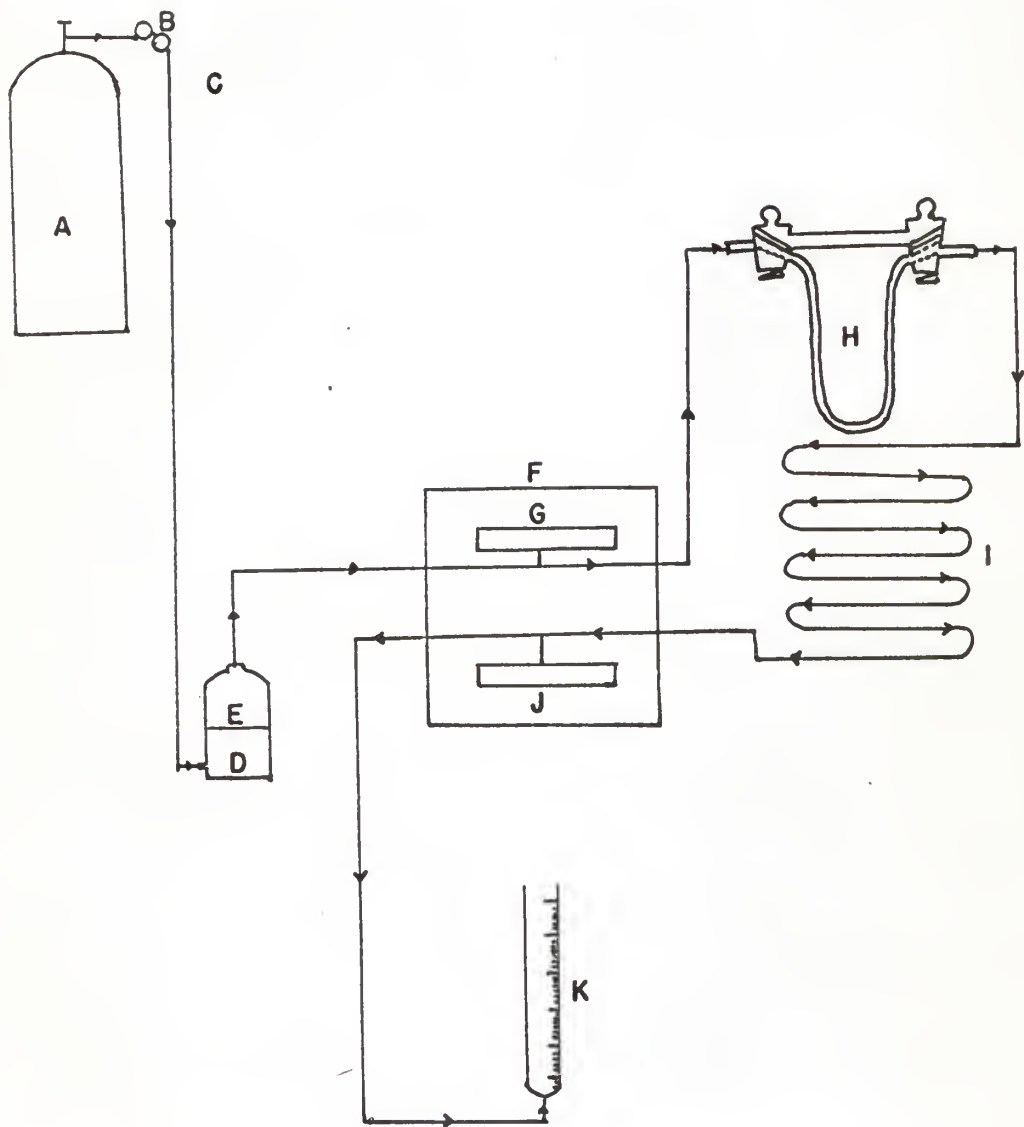
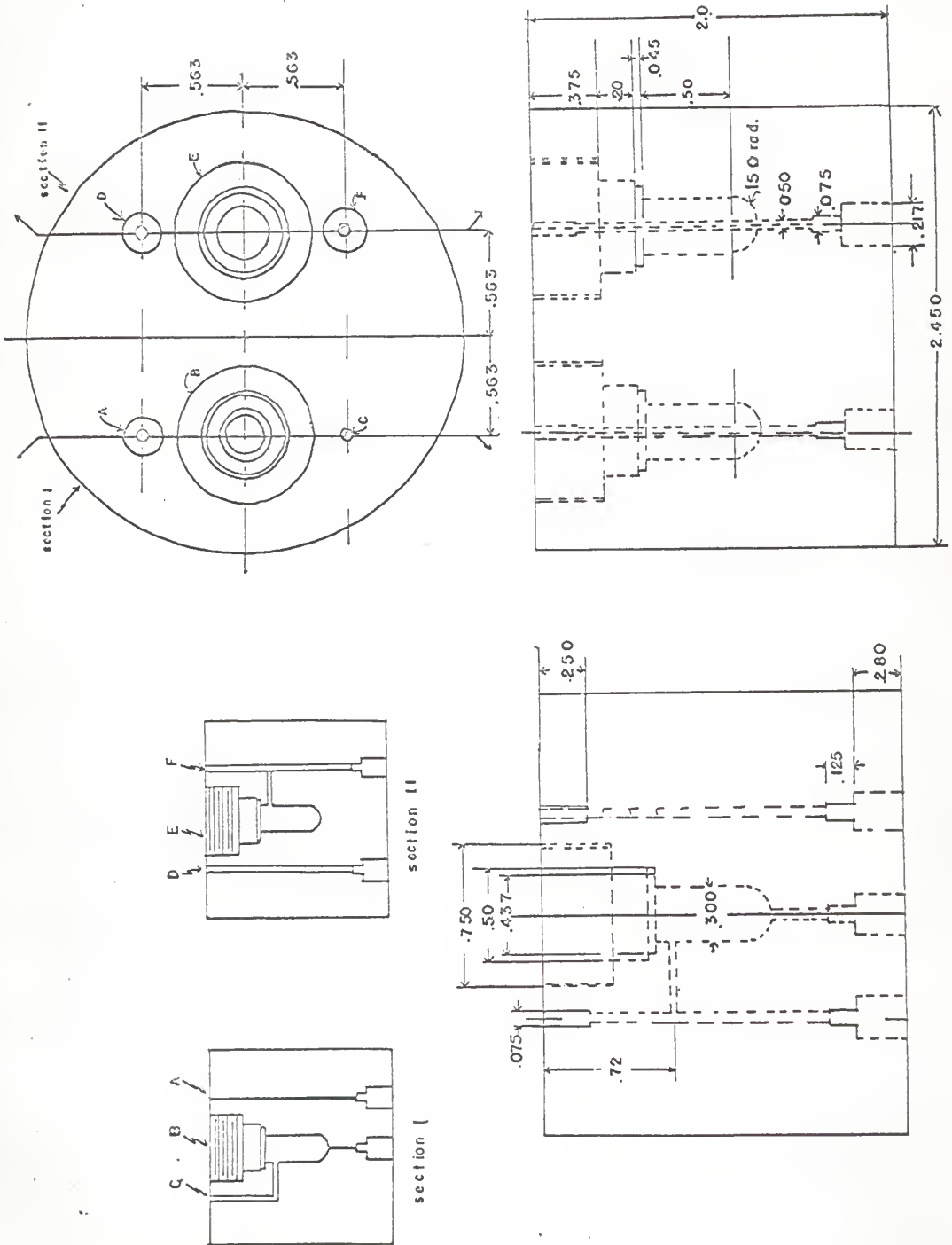


Table 4. Components of the flow diagram of the gas chromatograph.

- A. Cylinder of helium**
- B. Two stage pressure regulator**
- C. Vee point, brass needle valve**
- D. Anhydrous or calcium chloride**
- E. Ascarite**
- F. Detector block**
- G. Reference side of detector block**
- H. Sample trap**
- I. Chromatographic column**
- J. Sample side of detector block**
- K. Soap bubble flow meter**

Detector Block



* Reproduced from Beuerman's master's thesis.

Figure 6. Wiring diagram of gas chromatograph (8)

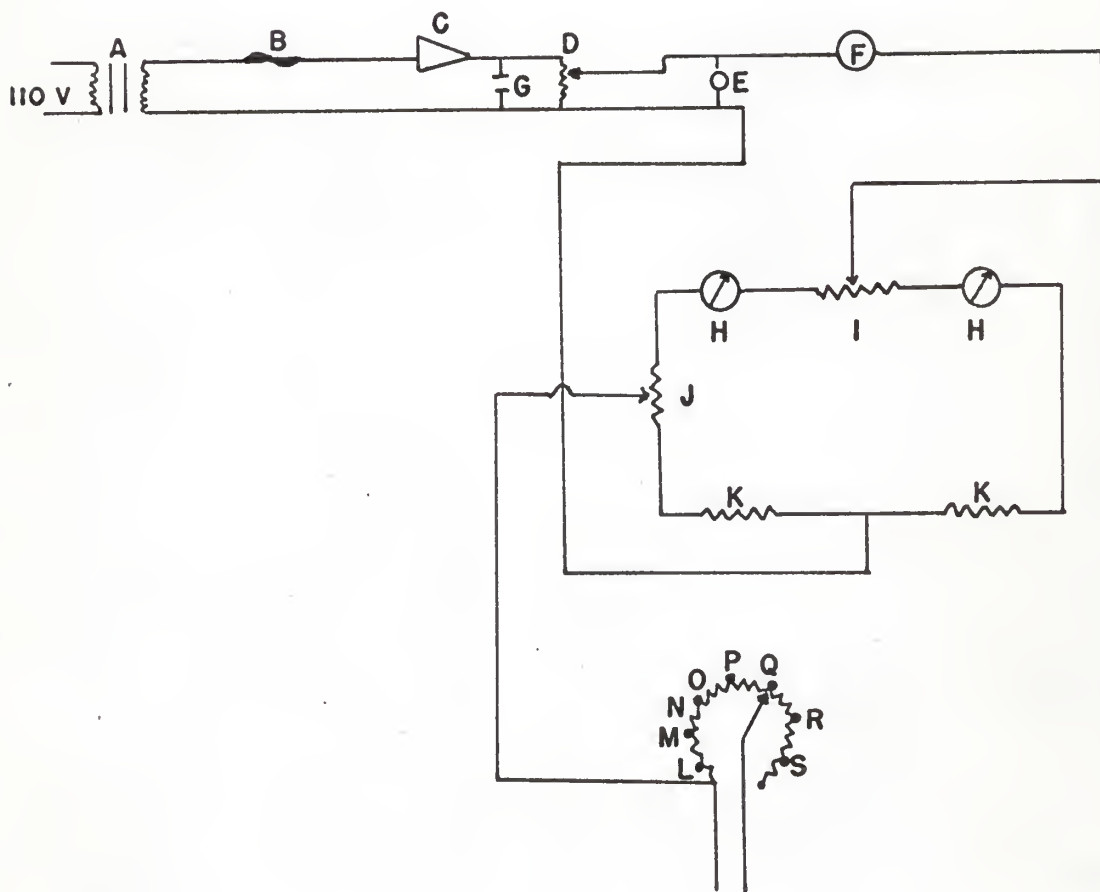


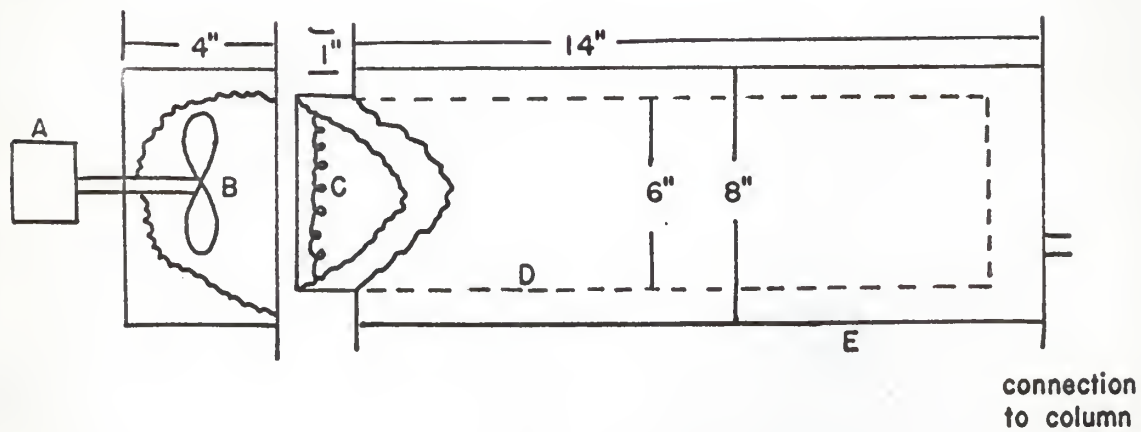
Table 5. Components of Wiring Diagram*

- 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. 1.80 ohm resistor, 1%
- P. 3.50 ohm resistor, 1%
- Q. 7.00 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

*(8)

Figure 7. Constant temperature cabinet (8)



- A. 1/100 horsepower motor
- B. 4 inch fan
- C. 500 watt heating coil
- D. Inner chamber
- E. Outer chamber

mixture was heated over a water bath under the hood. After all the solvent had evaporated, the mixture was packed into the desired tube length whose other open end was plugged with a wad of glass wool. The packing was done with constant vibration either by tapping or by means of a vibrator to insure uniform packing. When the tube was filled, the other end was plugged with another wad of glass wool. The column was then coiled into the proper diameter which fits the constant temperature inner chamber and then fitted with the proper swagelock fittings.

Preparation of the Gas Samples

Carbon dioxide. Carbon dioxide was prepared by the acidification of reagent grade sodium carbonate. The liberated gas was trapped in liquid nitrogen together with some air. The trapped gas was allowed to vaporize and then flushed into the column to determine its retention time.

Sulfur dioxide. Sulfur dioxide was prepared by the acidification of reagent grade sodium sulfite. The same procedure for carbon dioxide was followed for the liberated gas.

Chlorine. Chlorine was prepared by acidification of sodium hypochlorite. The reaction of hydrochloric acid on sodium hypochlorite is as follows:



Bromine. Liquid bromine was used. The bromine vapors were trapped in liquid nitrogen. Gentle vacuum was used to help collect the vapors into the trap. The same procedure for the above gases was followed for the trapped vapors.

Iodine. Iodine crystals were heated and the vapors collected in the trap. Most of the vapors recrystallized at room temperature and had to be heated first before injection into the column.

Combustion of Halogen Containing Organic Compounds

Organic compounds containing chlorine, bromine, and iodine were combusted in platinum boats at a temperature of 800°C and their combustion gases trapped in liquid nitrogen. The trapped gases were allowed to vaporize and then passed into the column. The retention times of the combustion gases were compared with the retention times of the prepared gas samples. Organic compounds containing chlorine and bromine, chlorine and sulfur, hydrogen, and oxygen in the same compound were also combusted.

For the quantitative aspect of the work, the organic compounds were purified either by sublimation, crystallization from their saturated solutions, or distillation. The purified compounds were dried over phosphorus pentoxide. The purified and dried samples were kept in small tightly stoppered vials. The compounds were weighed to the nearest 0.001 of a milligram on an Ainsworth microbalance. The area of the peaks in the chromatograms obtained from the combustion gases of the compounds were measured with a Kauffel and Esser Co. No. F 4236 planimeter.

RESULTS AND DISCUSSION

The results of the columns prepared are tabulated in Table 6.

Table 6. Retention times of the gas samples.

Column description: Liquid phase Column support Tube material Length and O.D.	Chromatograph parameters: Temperature, °C Flow rate, ml/min.	Retention times in minutes					
		O ₂	CO ₂	SO ₂	Cl ₂	Br ₂	I ₂
33% fluorelube grease (LG-160) Columpak (30-60) 20' Cu, O.D. 1/4"	120°C 33 ml/min.	2.4	2.75	2.9	2.9	*	*
16' Ni, O.D. 1/4"	60°C 33 ml/min.	1.8	2.00	2.8	3.0	8.3	*
22.5' Al, O.D. 1/4"	50°C 33 ml/min.	3.0	3.4	4.4	5.3	15.5	*
33% fluorelube grease (LG-160) on Chromosorb W (80-100) 30' Al, O.D. 1/4"	90°C 20 ml/min.	7.4	8.0	9.1	11.1		
30% fluorelube grease (LG-160) Columpak (30-60) 12' Cu, O.D. 1/4"	30°C 33 ml/min.	1.6	1.75	2.8	2.8	*	
	70°C 33 ml/min.	1.6	1.75	2.2	2.2	*	*
33% dinonyl phthalate Columpak (30-60) 5' stainless steel	50°C 33 ml/min.	0.6	0.6	2.0	1.8		
2.5% Kel-F No. 40 on glass beads (120-170) 6' Cu, O.D. 1/4"	100°C 33 ml/min.	At this flow rate and temperature, there was no separation of O ₂ and CO ₂ .					
2.5% silicone stopcock grease (Dow-Corning) Columpak (30-60) 12' Al, O.D. 1/4"	50°C 33 ml/min.	No separation of O ₂ and CO ₂					
15% silicone stopcock grease (Dow-Corning) Columpak (30-60) 12' Al, O.D. 1/4"	30°C 33 ml/min.	1.6	1.8	2.45	3.30	21.5	
	70°C 33 ml/min.	1.4	1.4	1.7	2.1	6.2	*

Table 6. (cont.)

Column description: Liquid phase Column support Tube material Length and O.D.	Chromatograph parameters: Temperature, °C Flow rate, ml/min.	Retention times in minutes					
		O ₂	CO ₂	SO ₂	Cl ₂	Br ₂	I ₂
15% silicone stopcock grease (Dow-Corning) Columpak (30-60) 12' Al, O.D. 1/4"	120°C 33 ml/min.					3.4	**
	50°C 33 ml/min.	2.1	2.4	3.4	3.8	*	*
25% silicone stopcock grease (Dow-Corning) Columpak (30-60) 18.5' Cu, O.D. 1/4"	120°C 33 ml/min.	1.9	2.2	2.6	2.8	*	*
	45°C 33 ml/min.	1.1	1.3	1.7	2.4	13.2	
12' Al, O.D. 1/4"	60°C 33 ml/min.	1.1	1.1	1.6	1.9	6.9	*
	140°C 28 ml/min.	1.6	1.6	1.6	1.6	3.7	*
	150°C 25 ml/min.					3.5	
30' Al, O.D. 1/4"	85°C 33 ml/min.	3.0	3.3	4.8	5.5		
	100°C 33 ml/min.	3.0	3.2	3.7	4.6		
33% silicone stopcock grease (Dow-Corning) Chromosorb W (80-100) 12' 2" Ni, O.D. 1/4"	50°C 33 ml/min.	2.1	2.4	3.1	5.7	12.8	*
	65°C 25 ml/min.	4.2	4.9	7.0	10.5		
33% silicone stopcock grease (Dow-Corning) Chromosorb P, acid washed, (30-60), 30' Al, O.D. 1/4"	68°C 24 ml/min.	4.3	5.0	7.5	11.0	40.0	
	23 ml/min.	4.5	5.5	7.7	12.0	44.0	
	70°C 25 ml/min.	4.0	4.5	6.2	8.0		
	80°C 25 ml/min.	3.8	4.3	5.5	7.8		

*No peak after 1 hour

**Poor peak

From the results shown in Table 6, it was decided to use the column with 33% silicone stopcock grease (Dow-Corning) on Chromosorb F, acid-washed (30-60), at 68°C with a helium flow rate of 24 ml/min. Typical gas chromatograms of the combustion products of the organic compounds containing the halogens are shown in Figs. 8, 9, and 10. The retention times of the combustion gases of some organic halogen compounds are shown in Table 7.

Table 7. Retention times of the Combustion gases.

Compounds	Retention time of the peaks			
Monochloroacetic acid 65°C, 25 ml/min.	4.2	4.9		10.5
2,4-dichlorobenzoic acid 68°C, 24 ml/min.	4.2	4.9		11.0
2,4-dichloroquinoline 68°C, 24 ml/min.	4.3	5.0	10.0	10.8
p-toluensulfonfyl chloride 68°C, 24 ml/min.	4.2	5.0		11.0
1-bromo-3 chloropropane 68°C, 24 ml/min.	4.3	5.0		11.0 40.0
p-bromochlorobenzene 68°C, 24 ml/min.	4.3	5.0		11.0 40.0
Helium flow rate of 25 ml/min:				
4-chlorophenyl sulfone 68°C, 25 ml/min.	4.0	4.5	7.3	9.7
Trichloroacetic acid 70°C, 25 ml/min.	4.0	4.5		8.0
Trichloroacetic acid 80°C, 25 ml/min.	4.0	4.4		7.8

Based on the retention times of the combustion gases of the halogen containing compounds, it is seen that the organic halogens are converted to their

respective molecular state since the retention times of the last two peaks coincided with those for pure chlorine gas and bromine gas.

The combustion of iodine containing organic compounds showed iodine crystals depositing in the trap. Due to the difficulties encountered in determining the iodine vapors by means of the type of gas chromatograph used and the techniques involved, work on the determination of iodine vapors was discontinued. A type of programmed temperature gas chromatograph would be suitable for the simultaneous determination of chlorine, bromine and iodine vapors.

No evidence of chlorine oxides or bromine oxides were shown in the chromatograms. If ever the respective oxides were formed, they must have decomposed to the respective halogens and oxygen at the temperature of combustion of 800°C. In general, the halogen oxides are known for their instability (25).

Chlorine monoxide, Cl_2O , explodes on heating to a mixture of chlorine and oxygen. Chlorine dioxide, ClO_2 , is extremely reactive. In the pure state it explodes violently and therefore has to be diluted with carbon dioxide or air for safe handling. Chlorine hexoxide, Cl_2O_6 , decomposes appreciably to chlorine dioxide and oxygen even at the melting point. Chlorine heptoxide, Cl_2O_7 , detonates when heated or subjected to shock. The existence of chlorine tetroxide, ClO_4 , is only postulated by Comberg (25) but not yet proven.

The oxides of bromine have properties similar to the oxides of chlorine. Bromine monoxide, Br_2O , decomposes into bromine and oxygen at any temperature above -40°C . Bromine dioxide, BrO_2 , decomposes to bromine and oxygen at higher temperatures (above -40°C).

The formation of hydrogen chloride and hydrogen bromide occurred when the oxygen flow rate in the combustion tube was slow, but upon increasing the oxygen flow rate, the hydrogen chloride reacts to form water and chlorine, and the hydrogen bromide to water and bromine. Hydrogen chloride is converted to

chlorine and water when heated in an atmosphere of oxygen in the presence of catalysts even at temperatures of 450°C (25). The hydrogen chloride and the hydrogen bromide peaks come after the carbon dioxide peak.

Considering the dissociation constants of chlorine gas which is 10^{-8} and that of bromine gas, 10^{-3} at 1000°C, it is then seen that these gases could exist as such at temperatures of 750°-800°C.

There was no evidence of a BrCl peak in the chromatograms of the combustion gases of organic compounds containing chlorine and bromine. The interhalogen, BrCl, that may have formed, may have been dissociated into bromine and chlorine, at the temperature of combustion. Furthermore, bromine monochloride undergoes photochemical decomposition. Its instability is indicated by its small heat of formation which is $+0.75 \pm 0.5$ kcal per mole (25).

The formation of sulfur dioxide from the combustion of 4-chlorophenyl sulfone was evident but for the combustion products of benzenesulfonyl chloride and p-toluenesulfonyl chloride, the sulfur dioxide peak was missing. This may be due to a lower combustion temperature used (800°C for the short furnace and 750°C for the long furnace). Most of the sulfur dioxide that may have formed may have been converted to sulfur trioxide. No attempts were made to verify the sulfur trioxide peak.

It was found that the oxygen flow rate of the combustion tube is critical not only because of the formation of hydrogen chloride and hydrogen bromide but also the possibility of the newly formed halogens attacking the platinum catalysts if they are not removed right away from the vicinity of the platinum catalysts. It was observed that in the combustion of compounds with a large number of chlorine atoms, like hexachloroethane and hexachlorobenzene, there was a reddish-brown deposit at the end of the combustion tube. This deposit must have come from the reaction of chlorine and the platinum catalysts

to form platinum tetrachloride which is a reddish-brown compound. Increasing the oxygen flow rate by applying a slight vacuum and lowering the temperature of the long furnace to 750°C - 800°C, gave no such deposit.

Based on the results of the performances of the different columns, it was noted that copper and stainless steel can no be used for bromine determination because of the property of these metals to hold bromine vapors tenaciously especially in the presence of even a trace of moisture. Nickel and aluminum were found to be able to resolve a mixture of bromine and air. Shorter columns of nickel and aluminum can be utilized to determine chlorine and bromine if the separation of carbon dioxide from oxygen is not to be considered. The separation of the oxides of nitrogen from chlorine may be obtained if a lower column temperature or longer column is used.

The utmost precautions were taken to prevent water from getting inside the trap and the gas chromatograph because the presence of water leads to erratic results due to its reaction with the combustion gases.

CONCLUSIONS

Combustion

The oxygen flow rate was adjusted from 15 - 20 ml/min. in the combustion train to insure complete combustion of the sample, and at the same time oxidize all the organic halogens to their molecular forms. If there is no excess of oxygen during combustion, hydrogen chloride and hydrogen bromide are being formed and swept out of the combustion tube together with the halogens; also the platinum catalysts are liable to be attacked when the active halogens are not removed right away from their surfaces.

The combustion temperature of the short movable furnace was adjusted to

Figure 8. Typical gas chromatogram of combustion gases of organic chlorine compounds.

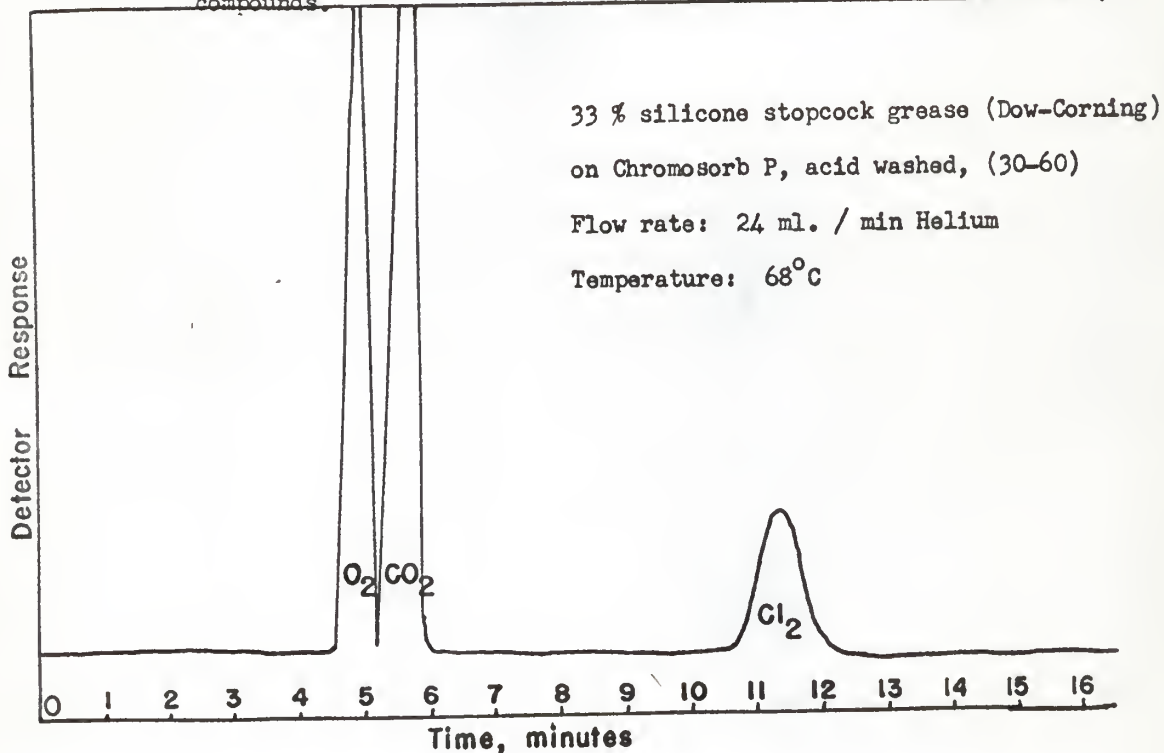
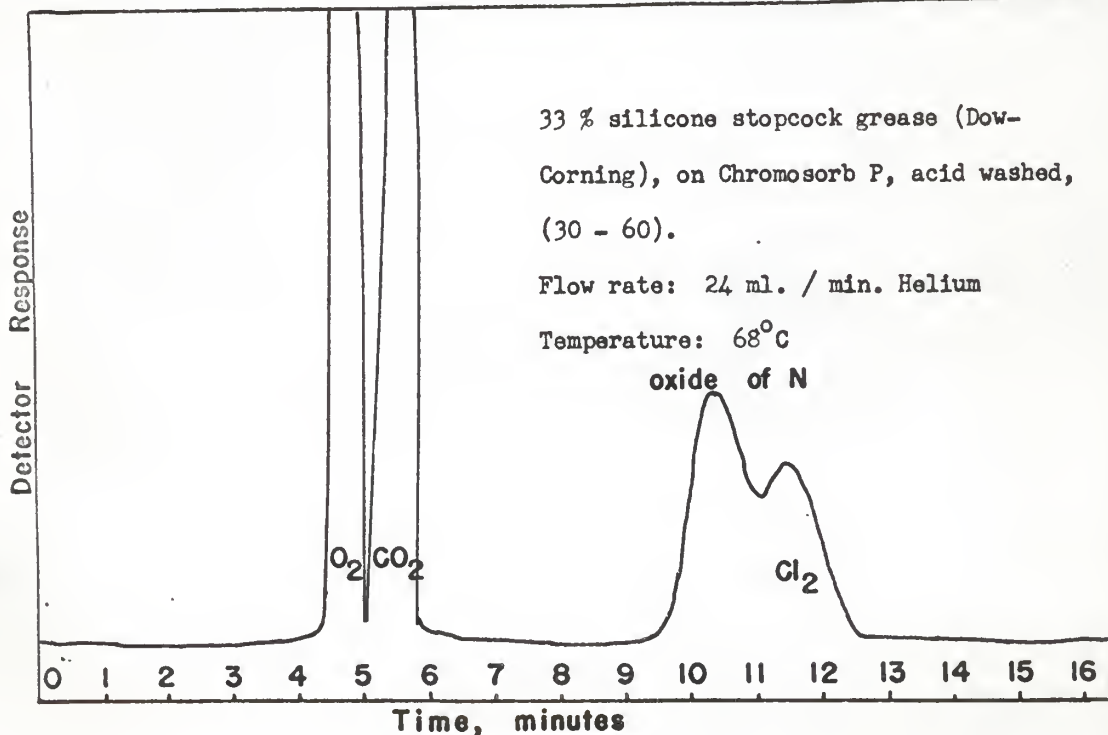


Figure 9. Chromatogram of combustion gases of organic compounds with Cl and N.



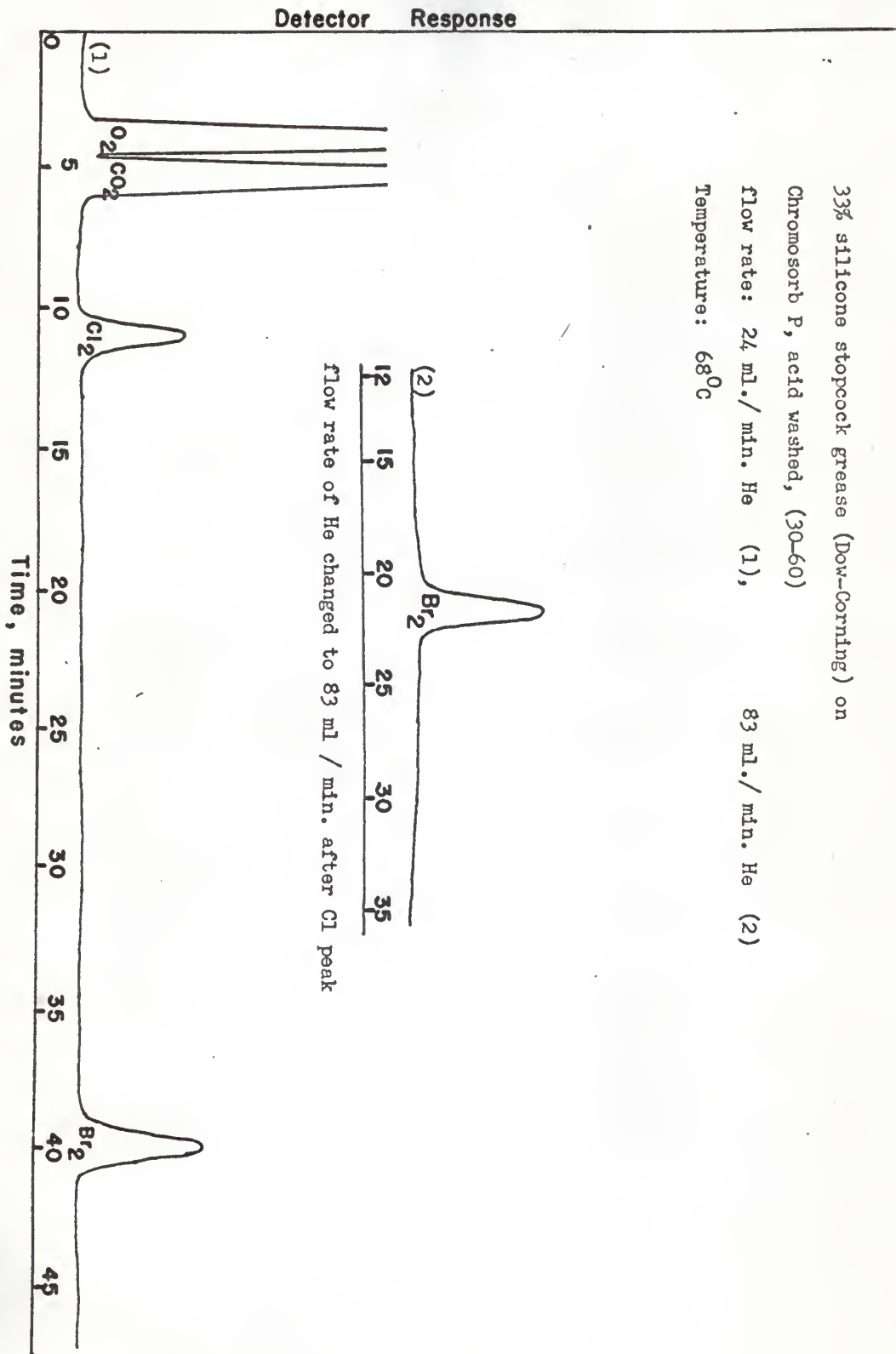


Figure 10. Typical gas chromatogram of combustion gases of organic compounds containing chlorine and bromine.

33% silicone stopcock grease (Dow-Corning) on
 Chromosorb P, acid washed, (30-60)
 Flow rate: 24 ml./min. He (1), 83 ml./min. He (2)
 Temperature: 68°C

Flow rate of He changed to 83 ml / min. after Cl peak

800°C and the long furnace to 750° - 800°C. At this temperature, the sample was completely combusted. The desiccant used was anhydrous calcium sulfate without the indicator. Anhydrous was not used because of its strong oxidizing property. Calcium chloride (anhydrous) also may be used.

Trapping System

Liquid nitrogen was used to trap the gases. According to Beuerman (8), only liquid nitrogen was found to trap sulfur dioxide quantitatively. Sulfur dioxide has a boiling point of -10°C as compared with that of chlorine, -34.6°C, therefore it was assumed that the other coolants will not quantitatively trap chlorine. Vacuum was applied to decrease the partial pressure of oxygen in the trap. Despite the application of vacuum, there was still some condensation of oxygen. Bromine may be quantitatively trapped by other coolants considering its boiling point of 58.78°C.

Chromatographic Column

Based on the results of Table 6, and the work of Iveson and others (16, 29, 30), copper and stainless steel columns can not be used for determining bromine because of the strong attraction of these metals for bromine and hydrogen bromide. Nickel, monel tubing, and teflon were found to work with chlorine and bromine. It was found in this work that aluminum could be used too, provided the prepared column is conditioned for several days at some elevated temperatures (about 70°C - 100°C) and the determinations are made under completely anhydrous conditions. This may be due to the formation of a film of aluminum oxide on the aluminum surface. The film of aluminum oxide is inert to the dry halogen gases.

Thirty three percent (33%) silicone stopcock grease (Dow-Corning) which

is inert to the gases tested was chosen as the liquid phase and chromosorb P (30-60), acid washed, as the column support. Teflon powder (Haloport) may be used as a support but care should be taken that its friable condition be maintained because it easily forms sticky particles due to absorption of moisture by the powder. When this happens, the packing is very hard to put into the tube uniformly.

METHOD

Combustion Procedure

1. A clean pyrex combustion tube was packed with 10% platinum asbestos and platinum contact stars as shown in Fig. 2.
2. The prepared combustion tube was placed in the Sargent microfurnace. A Pregl absorption tube filled with anhydrous calcium sulfate was attached to the exit end of the combustion tube using specially treated tubing to join a glass-to-glass connection. The inlet tube was connected to the U-tube containing anhydrous and ascarite and the bubble counter which in turn was attached to the two pressure regulators leading to the oxygen supply as shown in Fig. 1. The other open end was sealed with a cork.
3. The long burner was heated to 750° - 800°C and the heating mortar to 180°C to prevent condensation in the exit end of the tube.
4. The trap was connected to the Pregl absorption tube by pushing the drawn-out end of the trap through a one-hole silicone rubber attached to the absorption tube. The other drawn-out end of the trap was attached to a drying tube connected to the vacuum trap. The bypass of the trap was opened and oxygen allowed to flow at about 10 ml. per minute. The system was purged with oxygen for about 30 minutes.
5. The trap was immersed in a Dewar flask containing liquid nitrogen after

the system had been purged. The trap was then opened to the system and the oxygen flow rate adjusted to about 15-20 ml. per minute (85 - 90 bubbles per 10 seconds).

6. The stopcocks of the trap were turned to deadhead the oxygen flow and the cork was removed. A 3-10 mg. sample which was weighed to the nearest of a 0.001 mg. in a platinum boat was introduced and placed one or two inches before the long burner. The cork was put back and the stopcocks opened to let the gases pass through the trap.

7. The short movable furnace was heated to 800°C and allowed to move to the sample boat at slow speed. After combustion was complete, the movable furnace was again allowed to traverse the sample at a fast rate to sweep all the remaining gases into the long furnace. The combustion may be speeded up by using an additional burner to vaporize the sample and using the movable furnace to sweep out any remaining combustion gases.

8. The system was flushed with oxygen for another 3-5 minutes after combustion is complete. This was to insure that all the combustion gases were swept out of the combustion tube and absorption tube into the trap.

9. The trap was closed and the bypass was opened and the trap removed from the combustion train. The trapped gases were allowed to vaporize at room temperature. For bromine gases, the trap may be warmed gently over a hot plate adjusted to "low" after the trap had reached room temperature.

10. A second combustion may be started while waiting for the trapped gases to vaporize.

Gas Chromatographic Analysis of the Combustion Gases

1. The column to be used was previously installed in the constant temperature

cabinet and allowed to come into equilibrium with the cabinet temperature of 68°C. This may be installed during the weekend since it takes two or more days for the temperature to be constant. A 30 foot column of 33% silicone stopcock grease (Dow-Corning) on Chromosorb P was used.

2. The detector (thermistors) potential was set at 8 volts and the current was 44 milliamperes at this voltage. The recorder was turned on. The recorder had a sensitivity of 1 millivolt full scale deflection with an attenuation of 2 in the control box.

3. The trap was connected to the column by pushing the drawn-out ends of the trap into one-hole silicone rubber seals as shown in Fig. 3.

4. The helium gas was allowed to pass the bypass for several minutes. During this time, the flow rate of the helium gas was adjusted to 24 ml. per minute. In determining combustion gases containing bromine, the flow rate would be 24 ml. per minute until after the chlorine peak when the flow rate may be increased to 83 or 85 ml. per minute to hasten the emergence of the bromine peak.

5. The stopcocks were opened to the column by opening the stopcock nearest the helium supply so as to develop a pressure in the trap which is released to the column upon opening the other stopcock. In this way the combustion gases are swept into the column by the helium gas.

6. The area of the chlorine and bromine peaks of the chromatograms obtained from the combustion gases was measured with a Keuffel and Esser Co. No. F 4236 planimeter.

Evaluation of the Method

The results of the analysis of a number of organic compounds containing chlorine and bromine are shown in Table 8 and Table 9.

A linear relationship was obtained between area of peak and milligrams of

chlorine in the sample from the analysis of different sample weights of dichloromethane using the method, as shown in Fig. 11. From the analysis of the dichloromethane samples, a factor was obtained for converting the area of chlorine peak in square inches to milligrams chlorine. The factor was obtained by dividing the number of milligrams of chlorine present in the sample by the area of the chlorine peak in square inches. The calculations are shown as follows:

$$\frac{0.669 \text{ mg. chlorine in the sample}}{0.860 \text{ sq. inches}} = 0.777 \text{ mg. chlorine per sq. in.}$$

$$\frac{1.411 \text{ mg. chlorine in the sample}}{1.82 \text{ sq. in.}} = 0.775 \text{ mg. chlorine per sq. in.}$$

$$\frac{1.185 \text{ mg. chlorine in the sample}}{1.153 \text{ sq. in.}} = 0.774 \text{ mg. chlorine per sq. in.}$$

$$\text{Average} = 0.775 \text{ mg. chlorine per sq. in.}$$

The weight of chlorine present in the sample was calculated as: area of Cl peak in sq. in. x 0.775 mg. per sq. in. = mg. Cl in sample.

$$\text{Percent Cl in sample} = \frac{\text{mg. Cl in sample}}{\text{weight of sample in mg.}} \times 100$$

The same calculations were done for the bromine determinations. The bromine factor was obtained from the analysis of different sample weights of bromoethane.

$$\frac{3.162 \text{ mg. bromine in sample}}{1.29 \text{ sq. in.}} = 2.451 \text{ mg. bromine per sq. in.}$$

$$\frac{6.535 \text{ mg. bromine in sample}}{2.68 \text{ sq. in.}} = 2.438 \text{ mg. bromine per sq. in.}$$

$$\text{Average} = 2.445 \text{ mg. bromine per sq. in.}$$

The weight of bromine in the sample was calculated as: Area of Br peak in sq. in. x 2.445 mg. Br per sq. in. = mg. Br in the sample.

$$\text{Percent Er in sample} = \frac{\text{mg. of Er in the sample}}{\text{weight of sample in mg.}} \times 100$$

The average deviation calculated for the chlorine determinations between the theoretical and the determined percentage of chlorine is: (n = number of determinations)

$$\text{Average deviation} = \frac{\text{deviations}}{n} = \frac{5.19}{18} = 0.29\%$$

The average deviation calculated for the bromine determinations is:

$$\frac{4.02}{16} = 0.25\%$$

Fig. 12 shows the linear relationship between the area of the bromine peak and the weight of bromine in the analysis of different sample weights of bromoethane.

This method may be used to determine carbon, chlorine, and bromine simultaneously if the carbon dioxide peak is not allowed to go off-scale. Furthermore, the method may be modified to include the simultaneous determination of carbon, hydrogen, oxygen, sulfur, nitrogen, and the halogens. If iodine is to be determined, a programmed temperature type of gas chromatograph may have to be utilized for a faster determination.

Table 8. Evaluation of the method for determining organic chlorine.

Compounds	Weight of compound, ng.	Area of peak, in. ²	mg. Cl present		Percent Cl	
			Theory	Found	Theory	Found
Dichloromethane	4.755	5.12	3.970	3.968	83.49	83.45
Dichloromethane	4.995	5.38	4.170	4.170	83.49	83.49
Trichloroacetic acid	3.720	3.12	2.422	2.418	65.10	65.00
Trichloroacetic acid	3.041	2.55	1.980	1.976	65.10	64.99
Monochloroacetic acid	4.310	2.06	1.617	1.597	37.52	37.05
Monochloroacetic acid	4.510	2.14	1.692	1.658	37.52	36.63
Hexachlorobenzene	5.122	4.93	3.826	3.821	74.70	74.60
Hexachlorobenzene	4.875	4.69	3.642	3.677	74.70	74.40
Chlorobenzene	4.100	1.64	1.291	1.271	31.50	31.00
Chlorobenzene	3.560	1.44	1.121	1.116	31.50	31.35
2,4-dichlorobenzoic acid	2.553	1.22	0.948	0.945	37.12	37.02
2,4-dichlorobenzoic acid	3.410	1.59	1.266	1.232	37.12	37.13
Benzenesulfonyl chloride*	5.080	1.31	1.019	1.015	20.06	19.98
Benzenesulfonyl chloride*	5.344	1.38	1.072	1.068	20.06	19.98
4,7-dichloroquinoline**						
1-bromo-3-chloropropane	6.653	1.91	1.498	1.480	22.52	22.25
1-bromo-3-chloropropane	5.512	1.58	1.241	1.225	22.52	22.22
p-bromochlorobenzene	5.456	1.27	1.010	0.984	18.52	18.04
p-bromochlorobenzene	3.440	0.81	0.637	0.628	18.52	18.26

*No sulfur dioxide peak in the chromatogram; sulfur dioxide may have been converted to sulfur trioxide.

**Chlorine peak not fully resolved from an unknown peak which may be an oxide of nitrogen either nitrogen dioxide or nitric oxide.

Table 9. Evaluation of the method for determining organic bromine.

Compounds	Weight of sample, mg.	Area of peak, in. ²	mg. Br present		Percent Br	
			Theory	Found	Theory	Found
m-bromotoluene	4.819	0.92	2.251	2.249	46.71	46.67
m-bromotoluene	4.190	0.82	1.957	1.956	46.71	46.68
Bromoethane	5.638	1.69	4.134	4.132	73.33	73.29
Bromoethane	5.470	1.64	4.011	4.009	73.33	73.29
1-bromoheptane	3.581	0.65	1.598	1.589	44.62	44.37
1-bromoheptane	3.585	0.65	1.600	1.589	44.62	44.32
O-bromobenzoic acid	7.343	1.19	2.919	2.910	39.75	39.63
O-bromobenzoic acid	7.440	0.55	1.367	1.345	39.75	39.10
1-bromonaphthalene	3.318	0.52	1.280	1.271	38.59	38.31
1-bromonaphthalene	5.862	0.92	2.262	2.249	38.59	38.36
1,1,1-tribromo-2-methyl propanol	6.471	2.02	4.991	4.976	77.13	76.90
1,1,1-tribromo-2-methyl propanol	6.558	2.05	5.058	5.017	77.13	76.50
1-bromo-3-chloropropane	6.653	1.37	3.377	3.350	50.76	50.35
1-bromo-3-chloropropane	5.512	1.14	2.798	2.787	50.76	50.56
p-bromochlorobenzene	5.456	0.93	2.280	2.274	41.78	41.68
p-bromochlorobenzene	3.440	0.58	1.437	1.421	41.78	41.31

Figure 11. Relationship between area of peak and milligrams of chlorine in dichloromethane samples.

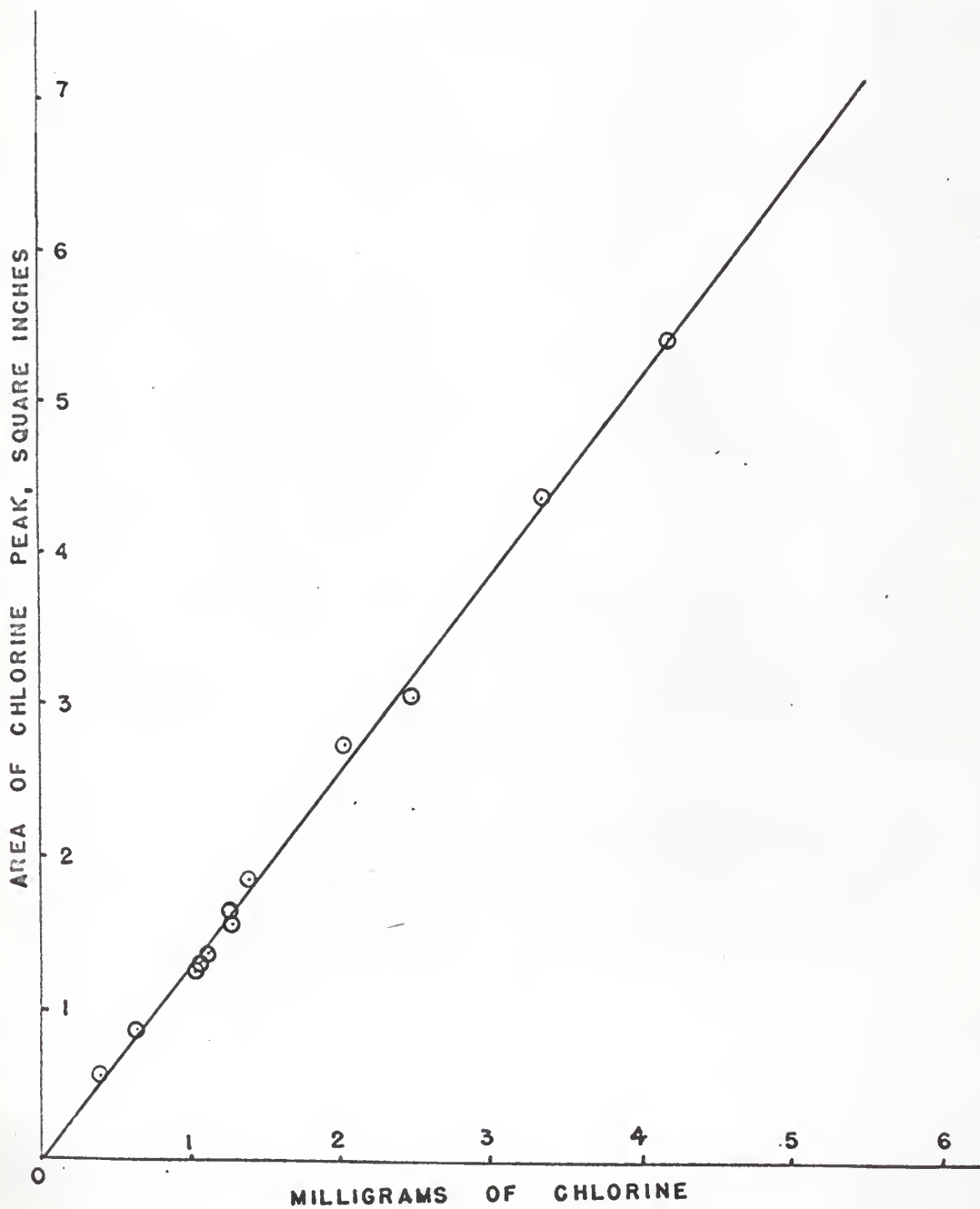
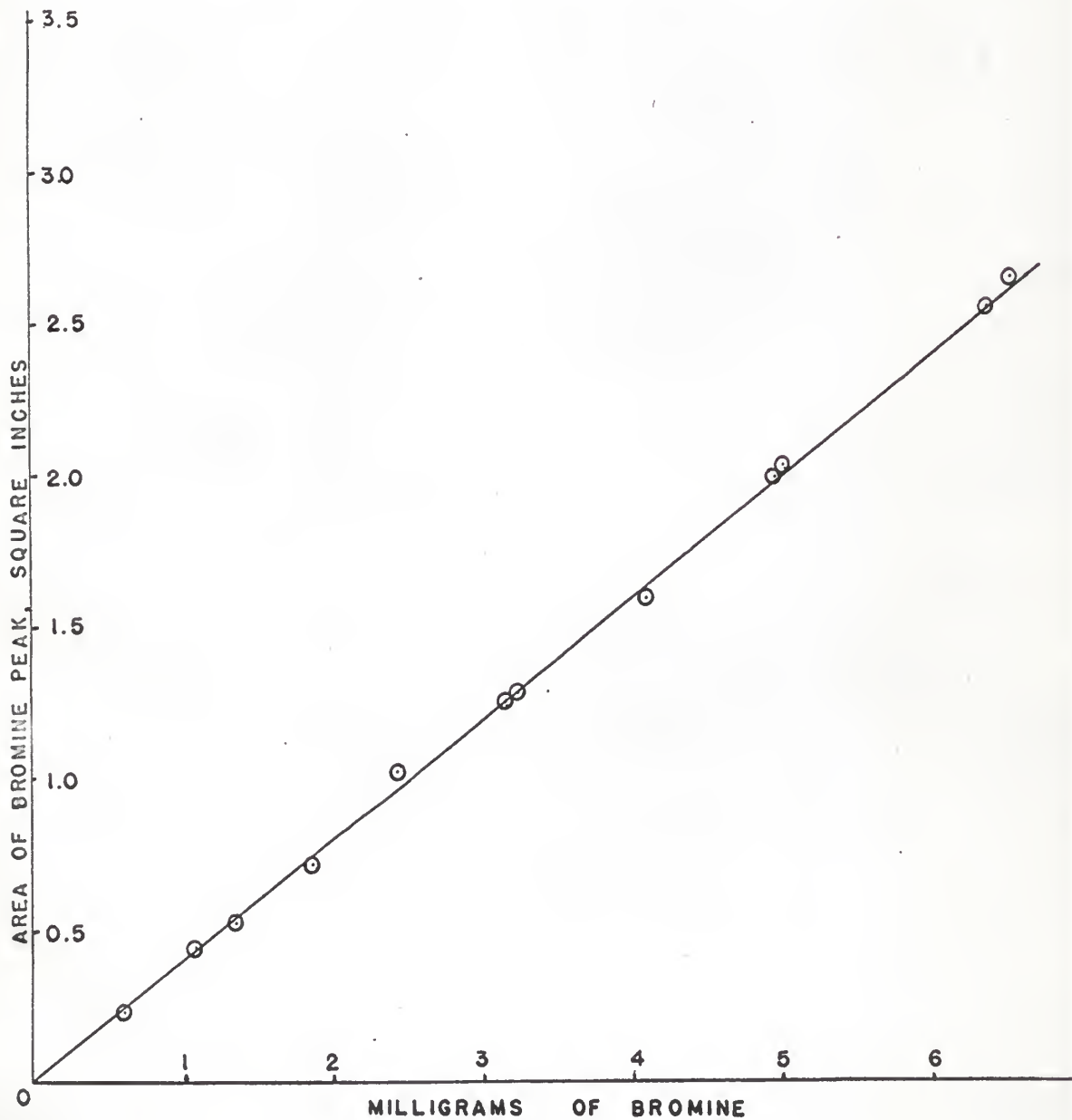


Figure 12. Relationship between area of peak and milligrams of bromine in bromoethane samples.



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THE DETERMINATION OF ORGANIC HALOGENS
USING GAS CHROMATOGRAPHY

by

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B.S.Chem., University of the Philippines, 1955

AN ABSTRACT OF A THESIS

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Organic halogen compounds were combusted at 800°C to carbon dioxide, water, and to their respective molecular forms using a modified Pregl method. The combustion gases were dried over anhydrous calcium sulfate and trapped in a trap immersed in liquid nitrogen. The trapped gases were allowed to vaporize and the components determined by gas chromatography. A thirty foot column of 33% silicone stopcock grease (Dow-Corning) on Chromosorb P, acid washed (30-60) was used at a temperature of 68°C. Helium gas was used at a flow rate of 24 ml. per minute. If bromine was present, the flow rate was increased to 83 ml. per minute, after the chlorine peak. The retention times for oxygen, carbon dioxide, chlorine, and bromine at a helium flow rate of 24 ml./min. were 4.3, 5.0, 11.0, 40.0 minutes respectively. Retention time for bromine at a flow rate of 83 ml. He per minute after the chlorine peak was 21.5 minutes. The percentage chlorine was determined by multiplying the area of the chlorine peak by a factor of 0.775 milligram chlorine per square inch, dividing by the sample weight and multiplying by 100. The percentage of bromine was determined using a factor of 2.445 milligrams bromine per square inch. The average deviation for 18 chlorine determinations was 0.29% and for 16 bromine determinations was 0.25%. An average chlorine determination takes about thirty minutes and a simultaneous determination of chlorine and bromine about forty minutes. Oxygen and sulfur do not interfere in this method. Nitrogen may not interfere if its oxide peak is fully resolved from the chlorine peak.