THE ANALYSIS OF SOME VOLATILE PHOSPHORUS COMPOUNDS BY GAS-LIQUID CHROMATOGRAPHY

by

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TABLE OF CONTENTS

INTRODUCTION

It is sometimes necessary to analyze various mixtures of volatile phosphorus compounds. It would therefore be desirable to have a method of analysis available that is both rapid and reasonably accurate. Gas chromatography would appear to meet these requirements and be further enhanced by the fact that quantitative analysis and qualitative analysis are simultaneously determined.

Keeler and coworkers (6) analyzed mixtures containing phosphorus trichloride and phosphoryl chloride. Because this method was quite lengthy and restricted to the above compounds, a more rapid and general determination was desired. It was the purpose of this investigation to develop such a method by utilizing gas chromatographic techniques.

LITERATURE REVIEW

Bernhart and Rattenberg (1) succeeded in determining total di-and trialkyl phosphites in the presence of each other by taking advantage of the rapid hydrolysis of dialkyl phosphites. In an alkaline alcoholic medium dialkyl phosphites are instantly hydrolyzed to form sodium monoalkyl phosphites, while trialkyl phosphites react very slowly. The rates of reaction of the two components are far enough apart to permit determination of dialkyl phosphites in the presence of trialkyl phosphites by adding excess alcoholic sodium hydroxide and immediately titrating the excess base with a standard acid. In an alcoholic acid medium trialkyl phosphites are rapidly hydrolyzed to form dialkyl phosphites. The phosphite is then present entirely as dialkyl phosphite and may be determined by alkaline hydrolysis.

Gehauf and coworkers (5) developed a colorimetric method of estimation of certain pentavalent compounds, not found in the presence of each other, that could be applied to $POCl_3$ only.

Keeler and coworkers (6) analyzed mixtures containing phosphorus trichloride and phosphoryl chloride. Advantage is taken of the difference in oxidation states of phosphorus. The mixture is hydrolyzed, thus producing phosphorous acid and phosphoric acid. The phosphorous acid is quantitatively oxidized to phosphoric acid by a known excess of standard iodine solution. The amount of iodine reduced enables the number of moles of phosphorous acid present to be determined which is equal to the number of moles of PCl_3 originally present. An aliquot of the original mixture is then entirely converted to phosphoric acid which is determined as the molybdiphosphate. The amount of $POCl_3$ in the original mixture is then determined by difference.

Ellis and Iveson (3) used gas chromatography to analyze very reactive mixtures of volatile halogen and interhalogen compounds. The main problems involved were to find suitable materials for construction of the apparatus. They found that polytetrafluoroethylene (Teflon) and polytrifluoromonochloroethylene (Kel-F) were suitable for use as inert stationary phase and partitioning liquid respectively. The detectors employed were a Martin gas density balance and a thermal conductivity cell constructed from a nickel block with Teflon fittings and nickel wires for the sensing elements. This work was further improved upon by Ellis and coworkers (4) who limited their work to the use of the Martin gas density balance.

EQUIPMENT

Many of the phosphorus compounds of interest, such a PCl_3, react quite readily with the integral parts of commercial chromatographs. This necessitated

the use of an instrument especially constructed of materials which do not react with the compounds under investigation.

In the chromatograph the sample normally comes into contact with the column and the detector. The detector chosen for this investigation was a hot wire thermal conductivity cell. Pyrex glass proved suitable for use as a column and thermal conductivity cell. Tantalum wire, being very inert, was used for the filaments. In addition, tantalum possesses a desirable resistivity and temperature coefficient of resistance.

Because $(CH_3O)_2POH$ and $(C_2H_5O)_2POH$ are not reactive, they could be analyzed with a Gow-Mac Model 9285 hot wire thermal conductivity cell.

A schematic drawing of the system appears in Plate I.

Description of the Column

The columns were constructed from Pyrex tubing, one 246 cm long by 7mm diameter and the other 86 cm by 8mm, used for the inorganic and organic compounds respectively. Each end was fitted with a 12/5 socket joint and provision was made for sample injection by placement of a rubber serum cap at the entrance of the column. The glass tubing was wound into a coil in such a fashion that it fit into the constant temperature box without being too near the heating strips which lined the inside.

Description of the Cell

The cell was designed such that two branches of the Wheatstone bridge circuit were directly in the path of the gas flow, the remaining two branches being present to complete the bridge circuit. Figure 3 of Plate II illustrates the circuit employed.

The filaments were made from unannealed 2 mil tantalum wire and 3.1 mil

nichrome wire. Each filament was coiled by placing a 26 gauge hypodermic needle in a hand drill and winding the wire around the needle. The proper length of each filament was then spot welded to a filament support assembly.

The support assemblies for the filaments in the gas stream were made from two parallel molybdenum wires with tungsten leads, the tungsten portion of each sealed in a short length of glass tubing and the tantalum filaments spot welded to the molybdenum portions. The glass fittings were then added to the cell. The remaining pair of filaments, made from nichrome wire, were spot welded to two Gow-Mac type 9225 filament support assemblies and mounted in a U tube. Figure 1 and Figure 2 of Plate II illustrates these components.

The cell was designed with the filaments directly in the path of the gas flow. This gives rise to excellent response time but has the drawback of being very sensitive to fluctuations of the flow rate of the carrier gas. The pressure regulating devices employed, however, were sufficient to overcome this problem.

To increase the heat stability of the cell a 3/16 inch layer of 28 gauge copper wire was wound around each of the two branches of the cell containing the sensing elements, the effectiveness of which was not evaluated. This envelope is not shown in Plate II.

The completed cell was wired and fitted to an aluminum bracket which enabled the unit to be conveniently mounted inside the chromatograph. Current was supplied to the cell by means of a Gow-Mac constant voltage supply unit.

Description of the Constant Temperature Box

The constant temperature box was made from sheet iron, double walled, with rock wool insulation between the walls. The inside of the box was lined with a one inch layer of asbestos which provided sufficient insulating

qualities. Constant temperature was maintained by the use of four 250 watt strip heaters wired in parallel and an 180 inch, open coiled, 20 mil nichrome wire heater which was regulated by an American Instrument Company "Quickset" thermostat enabling the temperature to be controlled to within $\pm$ 0.2°C. The voltage across the strip heaters was controlled by a General Radio Company Variac. Air circulation was achieved by the use of a 1/40 horsepower electric motor turning a 6 inch, 4 bladed aluminum fan at 1540 revolutions per minute.

Pressure Regulation

A Matheson number 8 automatic regulator and a Hoke precision valve proved sufficient to obtain a constant flow rate. No regulator was required on the outlet side of the system.

The flow rate was accurately measured by means of a soap film meter similar to that described by Keulemans (7).

Recording Device

A Sargent recorder, catalogue number S-72150, was used for the $(CH_3O)_2POH$ - $(C_2H_5O)_2POH$ mixture while a Sargent recorder, Model S-R, was used for the PCl_3-$POCl_3$ and PCl_3-$PSCl_3$ mixtures.

EXPERIMENTAL PROCEDURE

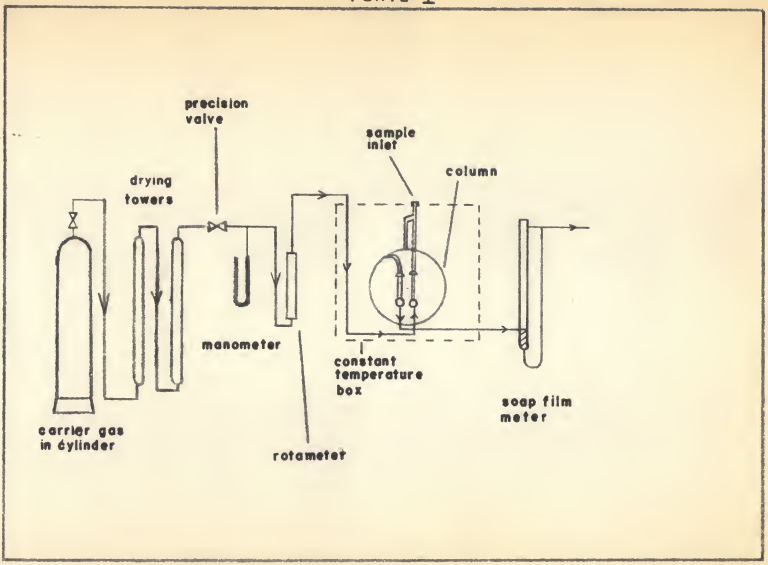
Preparation of the Column Packing

The material used for the inert stationary support was "Fluoropak 80," 20-80 mesh, a commercial brand of ground Teflon. The inert stationary phase was spread out in a shallow dish, the liquid phase dissolved in a suitable solvent and applied to the column packing. The resulting slurry was stirred until the solvent was completely evaporated.

EXPLANATION OF PLATE I

Arrangement of gas-liquid chromatography apparatus for the analysis of volatile phosphorus compounds using a thermal conductivity cell as detector.

PLATE I


precision valve
sample inlet
column
drying towers
manometer
constant temperature box
soap film meter
carrier gas in cylinder
rotameter

EXPLANATION OF PLATE II

Fig. 1: Illustrates one of the two identical branches of the cell that is in the gas stream. These are fitted side by side to an aluminum mounting bracket which enables convenient mounting within the constant temperature box.

Fig. 2: Illustrates the remaining two branches of the cell which are mounted in a Pyrex glass U tube.

Fig. 3: Wiring diagram of the circuit employed for the cell.

PLATE II

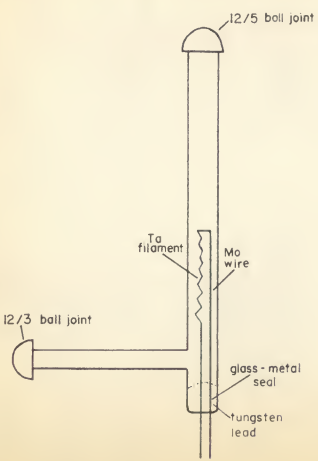


fig. 1

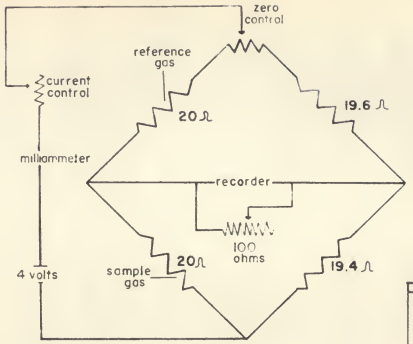


fig. 3

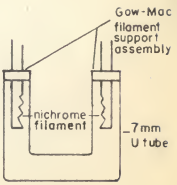


fig. 2

Table 1. Composition of column packing

Mixture	Weight of Fluoropak 80	Weight of Liquid Phase	Solvent
PCl_3-$POCl_3$	90.0gms	9.0gms Kel-F #90 grease	250ml benzene
PCl_3-$PSCl_3$	90.0gms	9.0gms Kel-F #90 grease	250ml benzene
$(CH_3O)_2POH$-$(C_2H_5O)_2POH$	38.7gms	5.4gms di-n-butyl phthalate	150ml benzene
$(CH_3O)_2POH$-$(C_2H_5O)_2POH$	70.0gms	9.4gms Apiezon K oil	250ml diethyl ether

Method of Packing Columns

A small amount of column packing was loaded into one end of the column, the other end being sealed with a small plug of glass wool. The column was then rotated, thereby moving the packing to the plugged end. The packing was then gently tamped down by means of a length of copper wire, one end of which was curled to present a flat surface at the end of the wire. About 1½ inches of untamped packing was added each time and compressed to about 1 inch after tamping. This procedure was followed until the column was completely filled.

The filled column was fitted to the cell, and with the carrier gas flowing, the temperature was raised to 150°C in order to purge the column of water. The course of this operation was followed by the recorder which was operating at maximum sensitivity. The column was considered to be completely purged when the base line became steady, an operation that took approximately two hours.

Purification of Materials and Preparation of Mixtures

Dimethyl phosphite (Virginia Carolina 0413402) and diethyl phosphite (Virginia Carolina 0401802) were carefully distilled at 17mm pressure. Center cuts were run through the chromatograph which showed approximately one per cent by weight impurity remaining in each compound. These compounds were judged to be sufficiently pure for this work.

Reagent grade phosphorus trichloride (Mallinckrodt 6640) was distilled under nitrogen at atmospheric pressure, and reagent grade phosphoryl chloride (Mallinckrodt 6628) was taken directly from a freshly opened bottle. The purity of each was checked mass spectrometrically. Thiophosphoryl chloride, synthesized at this laboratory (2), was redistilled shortly before use.

All mixtures, with the exception of the first three listed under Table 2 were prepared by weighing each component on an analytical balance. The composition of each of the three exceptions was determined by volume - density calculations.

Operating Procedure

The equipment was assembled and wired. After the system was checked for leaks, the flow rate adjusted and measured with the soap film meter, the chromatograph was brought up to temperature. The system came to equilibrium after approximately two hours. This was checked by operating the recorder at maximum sensitivity and obtaining a straight base line.

One quarter ml syringes were used to inject the sample under the surface of the column packing, thereby obtaining a plug injection.

The areas of the peaks obtained were used to determine the composition of each mixture. It was found that the area per cent of each peak closely

agreed with the weight per cent of the corresponding component of the mixture. All areas were measured 6 times with a compensating polar planimeter, the average value being used for the calculations.

RESULTS AND DISCUSSION

The results appear in tabulated form under Tables 2, 3 and 4.

A Gow-Mac pretzel type hot wire thermal conductivity cell constructed from a monel block with tungsten filaments proved satisfactory for analysis of the $(CH_3O)_2POH$ - $(C_2H_5O)_2POH$ mixture. However, after 3 runs with the inorganic compounds the base line became extremely erratic. Examination of the cell showed that the filaments had reacted with the compounds and a green deposit had formed on the walls of the cell. Replacement of the tungsten filaments with silver plated tungsten filaments gave similar results. It is likely that these filaments were not completely plated as it is very difficult to plate a 1 mil wire such as employed in this cell. For these reasons it was necessary to construct a cell of inert materials.

Dimethyl Phosphite - Diethyl Phosphite

Four mixtures of dimethyl phosphite - diethyl phosphite were analyzed. Each analysis of the first three mixtures listed under Table 2 and Table 3 was made at a different flow rate (from 57 to 91 ml min^{-1}). For this reason retention time and H.E.T.P. data are not listed for these mixtures under Tables 3 and 4. Each analysis of the fourth mixture was made at the same flow rate. The first three mixtures were analyzed immediately after the compounds were purified while the last was analyzed at a later date. By this time the impurities originally present had increased in concentration. Each of the components of the mixture was run through the chromatograph and the

impurity present in each compound was found to have identical retention times and in both cases was present in the same proportion to its major component. For this reason it was believed that the errors introduced by these impurities cancel out. The results of the analysis bear this out.

Plate III illustrates a typical chromatogram obtained with the fourth mixture. It is seen that complete separation of the two components was not quite achieved. This, however, did not interfere with an accurate quantitative evaluation because the peak areas could be determined by the method of Brace as described by Pecsok (10). The minimum between the peaks was used as a dividing line, the areas remaining under each peak being measured for the calculations. The first peak which appears was due to the impurities present in both consituents of the mixture and was ignored, the reasons for this being explained earlier. Plate III illustrates the peaks obtained for Trial 2 and the method of determining the areas to be measured.

The major difficulty encountered during this analysis was that of tailing. The use of Chromosorb produced tailing to such an extent that quantitative analysis was not possible. It is believed that the tailing was due to adsorption of phosphite molecules on the surface of the support. Ormerod and Scott (9) deactivated Chromosorb by coating it with silver. This approach appears to be highly effective in covering the active sites; the method, however, suffers from the difficulty of preparing the silvered support. The use of ground Teflon provided the necessary inertness. This produced columns of low efficiency but nevertheless enabled the analysis to be carried out.

While using the Teflon packing it was observed that after repeated analyses the tailing reappeared. This was caused by a deposit of a colorless, viscous material formed inside the cell and on the glass wool packing on the

Table 2. Tabulation of Data

Mixture	% of each constituent added	% of each constituent found						
		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7
$(CH_3O)_2POH$-	52.6	53.6	53.9	55.3	53.8	51.8	51.1	
$(C_2H_5O)_2POH$	47.4	46.4	46.1	44.7	46.2	48.2	48.9	
$(CH_3O)_2POH$-	46.0	47.4	47.8	46.9	46.6	46.8	46.2	
$(C_2H_5O)_2POH$	54.0	52.6	52.2	53.1	53.4	53.2	53.8	
$(CH_3O)_2POH$-	38.6	38.3	35.9					
$(C_2H_5O)_2POH$	61.4	61.7	64.1					
$(CH_3O)_2POH$-	51.4	51.3	51.8	51.8	51.4	51.4	51.6	51.4
$(C_2H_5O)_2POH$	48.6	48.7	48.2	48.2	48.6	48.6	48.4	48.6
PCl_3-	27.1	27.5	26.3	27.9	27.7	27.2	27.4	
$PSCl_3$	72.9	72.5	73.7	72.1	72.3	72.8	72.6	
PCl_3-	44.1	45.6	45.7	45.6	43.8	44.8	44.1	
$PSCl_3$	55.9	54.4	54.3	54.4	56.2	55.2	55.9	
PCl_3-	36.8	36.9	36.9	37.1	36.6	38.5	37.3	
$PSCl_3$	63.2	63.1	63.1	62.9	63.4	61.5	62.7	

Table 2 (concl.) Tabulation of Data

Mixture	% of each constituent added	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7
PCl_3-a	36.4	36.5	35.2	36.2	34.4			
$POCl_3$	63.6	63.5	64.8	63.8	65.6			
PCl_3-	27.1	27.2	26.8	26.9	26.9	26.9	27.3	27.6
POCl3	72.9	72.8	73.2	73.1	73.1	73.1	72.7	72.4
PCl_3-	53.9	53.4	54.1	52.5	53.3	55.3		
$POCl_3$	46.1	46.6	45.9	47.5	46.7	44.7		

a. Using an 81 cm x 7 mm column.

Table 3. Tabulation of Data

Mixture	Temp. (°C)	Flow Rate (ml min^{-1}	Inlet Pressure (mm Hg)	Retention Time (min)
$(CH_3O)_2POH$-$(C_2H_5O)_2POH$	101.0	*	120	*
$(CH_3O)_2POH$-$(C_2H_5O)_2POH$	101.0	*	120	*
$(CH_3O)_2POH$-$(C_2H_5O)_2POH$	101.0	*	120	*

* Flow rate and therefore retention time was different for each trial.

Table 3 (concl.) Tabulation of Data

Mixture	Temp. (°C)	Flow Rate (ml min^{-1})	Inlet Pressure (mm Hg)	Retention Time (min)
$(CH_3O)_2POH$-	107.0	64.0[a]	120	2.4[b]
$(C_2H_5O)_2POH$				5.3[b]
PCl_3-	103.0	66.0	163	1.4
$PSCl_3$				2.9
PCl_3-	103.0	66.0	163	1.4
$PSCl_3$				2.9
PCl_3-	103.0	66.0	163	1.4
$PSCl_3$				2.9
PCl_3-	66.0	62.4[a]	80	.9[b]
$POCl_3$				2.4[b]
PCl_3-	72.0	90.0	186	1.3
$POCl_3$				3.5
PCl_3	72.0	75.0	172	1.4
$POCl_3$				3.8

a. Flow rate for trial 2. Flow rate differed for other trials.
b. Calculated for trial 2.
c. Outlet pressure for all trials was atmospheric.

Table 4. Column Performance

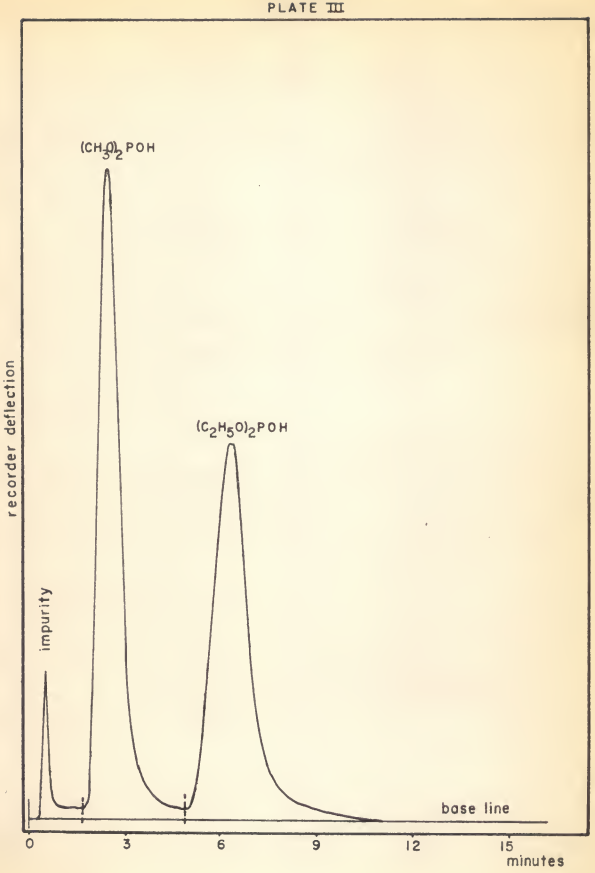
Compound	Column Length (cm)	Column Diameter (mm)	Liquid Phase	Flow Rate (ml min^{-1})	Retention Time (min)	Number of Theoretical Plates	H.E.T.P.[d] (cm)
$(CH_3O)_2POH$[a]	86	8	Di-n-Butyl Phthalate	64	2.4	58	1.5
$(C_2H_5O)_2POH$[a]	86	8	"	64	6.3	140	.62
PCl_3[b]	246	7	Kel-F 90 Grease	90	1.4	85	2.9
PCl_3[c]	246	7	"	66	1.4	170	1.4
$POCl_3$	246	7	"	64	3.8	140	1.8
$PSCl_3$	246	7	"	66	2.9	170	1.4

a. Data for fourth mixture only. First three mixtures analyzed at various flow rates.
b. Data for PCl_3-$POCl_3$ mixture.
c. Data for PCl_3- $PSCl_3$ mixture.
d. Height equivalent to a theoretical plate. For calculation see Appendix.

EXPLANATION OF PLATE III

Chromatogram of $(CH_3O)_2POH$-$C_2H_5O)_2POH$ mixture. Column packing: 5.4 parts di-n-butyl phthalate on 38.7 parts Fluoropak 80; column length: 86 cm; temperature: 107°C; carrier gas: helium; flow rate: 64ml min^{-1}; filament current: 175 milliamperes; chart speed 1/3 inch min^{-1}; detector: Gow-Mac thermal conductivity cell.

PLATE III


(CH3O)2POH
(C2H5O)2POH
impurity
recorder deflection
base line
0
3
6
9
12
15
minutes

inlet end of the column. This difficulty was overcome by frequent cleaning of the cell and replacement of the glass wool. The material in question was not identified. It was not found necessary to change the column packing.

Tricresyl phosphate and Kel-F 90 grease also proved satisfactory for use as liquid phase. It is interesting to note that there was no essential difference in retention times when polar and non-polar liquid phases were used.

Phosphorus Trichloride-Thiophosphoryl Chloride

Three mixtures of PCl_3- $PSCl_3$ were analyzed at constant flow rate and constant temperature. Plate IV illustrates a typical analysis.

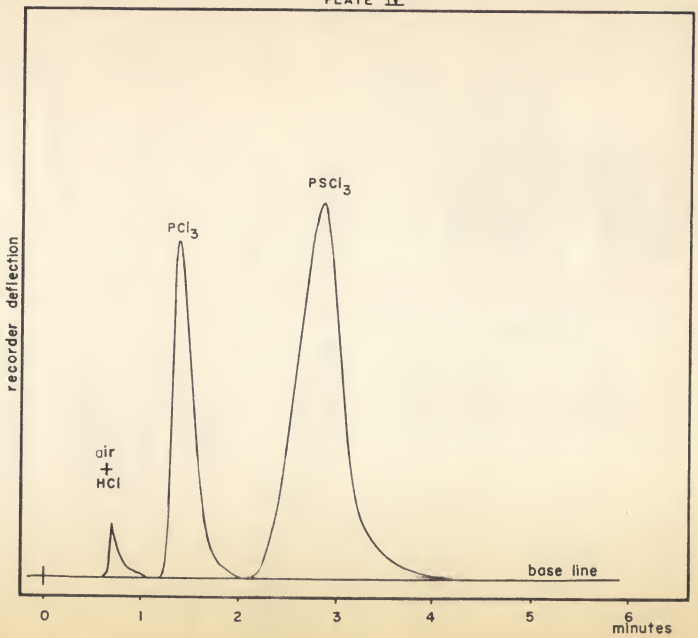
After several analyses were run a yellow-brown deposit appeared on the inlet side of the column. Prolonged use showed that this did not interfere with the performance of the column.

Examination of Plate IV shows an impurity which was not always present, and when present appeared before the PCl_3 peak. This was believed to be due to air and HCl, the HCl probably forming by reaction of the sample at the tip of the needle with moisture in the air. Hydrogen chloride vapors were collected and injected into the chromatograph. The vapors had a retention time identical to that of air, and like air, did not tail. It is evident from the chromatogram that tailing did occur. A tentative explanation offered is that the tailing is due to hydrogen bonding between the hydrogen atom of the HCl and either the phosphorus, oxygen, sulfur or chlorine atoms of the other compounds present. This peak was ignored when measuring the areas under the other peaks.

EXPLANATION OF PLATE IV

Chromatogram of PCl_3-$PSCl_3$ mixture. Column packing: 9.0 parts Kel-F 90 grease on 90 parts Fluoropak 80; Column length: 246 cm; temperature: 103°C; carrier gas: helium; flow rate: 66ml min^{-1}; filament current: 120 milliamperes; chart speed: 1 inch min^{-1}; detector: glass thermal conductivity cell.

PLATE IV


recorder deflection
PSCl3
PCl3
air
+
HCl
base line
0
1
2
3
4
5
6
minutes

A ½ ml syringe was filled with the mixture and small aliquots were successively injected into the chromatograph. It was found that the impurity peak became smaller with each injection thereby lending support to the suggestion that the HCl present is formed at the tip of the syringe needle. This peak was ignored when measuring the areas under the other peaks, its presence or absence not interfering with the analysis.

Phosphorus Trichloride - Phosphoryl Chloride

A mixture of PCl_3 - $POCl_3$ was analyzed using an 81 cm column. Complete separations were obtained below flow rates of approximately 63 ml min^{-1}. Flow rates as high as 111.3 ml min^{-1} gave rise to peaks which were not completely separated but which could be utilized by application of Brace's (10) method of determining peak areas.

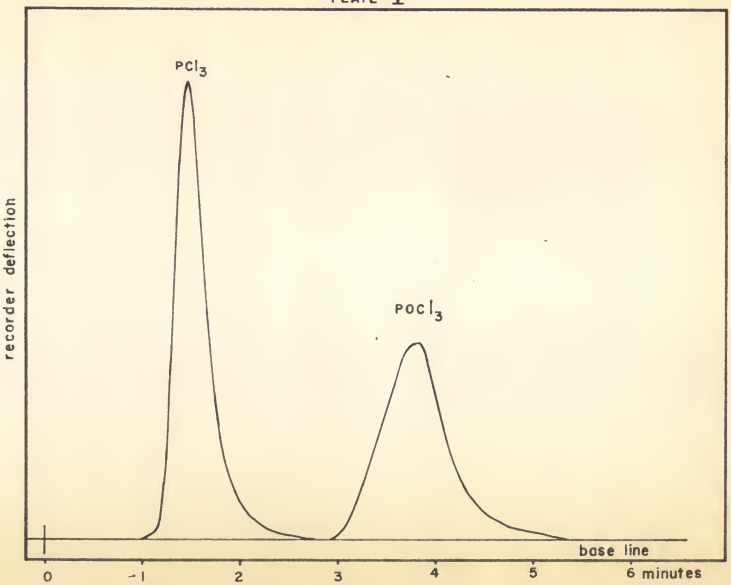
Two other mixtures were analyzed using the 246 cm column, one at 75 ml min^{-1} and the other at 90 ml min^{-1}. No difficulties were encountered during the course of these analyses. The air - HCl peak was entirely absent from the analysis run at 75 ml min^{-1}.

Throughout this entire study a problem concerning the use of syringes was encountered. The use of a micro syringe was not satisfactory with the inorganic phosphorus compounds because a slight amount of heat, presumably produced by hydrolysis with moisture in the air, caused the plunger to seize inside the barrel. One quarter ml, all glass, syringes were entirely satisfactory in this respect. No reaction was observed with the needles employed if they were cleaned immediately after use.

EXPLANATION OF PLATE V

Chromatogram of PCl_3- $POCl_3$ mixture. Column packing: 9.0 parts Kel-F 90 grease on 90 parts Fluoropak 80; column length: 246 cm; temperature: 72°C; carrier gas: helium; flow rate: 75 ml min^{-1}; filament current: 125 milliamperes; chart speed: 1 inch min^{-1}; detector: glass thermal conductivity cell.

PLATE V



Phosphorus Pentachloride

An attempt was made to analyze PCl_5 in a manner similar to that of the other compounds. Phosphorus pentachloride sublimes at 160°C and would seem to be suitable for analysis by gas-liquid chromatography.

Samples of PCl_5 were dissolved in both CCl_4 and benzene and run through the chromatograph. There was no indication that the PCl_5 was eluted at temperatures from 75°C to 180°C while normal peaks were obtained for both the CCl_4 and benzene. It is not considered likely that the PCl_5 was eluted coincidently with its solvent as these solvents have considerably different retention times. An unusually heavy yellow deposit was observed to form inside the cell after these attempted analyses indicating that the PCl_5 decomposed or reacted within the system.

SUMMARY

The purpose of this investigation was to develop a general and rapid method of analysis for volatile phosphorus compounds. Gas chromatography was chosen because it meets the requirements of rapid analysis time and is applicable to a wide range of compounds.

Analysis of very reactive phosphorus compounds necessitated the use of inert materials. Glass was used to construct the column and the body of the cell, with tantalum wire as the filaments. Ground Teflon and Kel-F 90 grease were satisfactory as the inert solid support and liquid phase respectively for the inorganic compounds while ground Teflon and di-n-butyl phthalate or Apiezon K oil was used for the organic compounds.

The following synthetic mixtures were analyzed: $(CH_3O)_2POH$-$(C_2H_5O)_2POH$, PCl_3-$PSCl_3$ and PCl_3 - $POCl_3$. The area per cent of each peak of the

chromatograms closely agreed with the weight per cent of the corresponding component of the mixture. When the latter two mixtures were analyzed, an impurity peak was sometimes present, which was believed to be due to air and HCl. Quantitative results were obtained by disregarding this peak, if present, when computing the area per cent of each peak in the chromatogram.

Gas chromatography did not prove suitable for analysis of PCl_5. Solutions of PCl_5 in both CCl_4 and benzene were injected into the instrument but the PCl_5 was not eluted. Heavy yellow deposits formed in the cell after the analysis indicating that the PCl_5 either decomposed or reacted within the system.

ACKNOWLEDGMENTS

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He is also grateful to the Fansteel Metallurgical Corporation for providing samples of tantalum wire and to the Virginia Carolina Chemical Corporation for their generous supply of organo-phosphorus compounds.

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BIBLIOGRAPHY

(1) Bernhart, D. N. and K. H. Rattenbury.
Determination of di- and trialkyl phosphites in the presence of each other. Anal. Chem. 28: 1765-66. 1956.

(2) Clark, T. J.
Reactor irradiated phosphoryl chloride. Ph.D. Thesis, Kansas State University, 1958.

(3) Ellis, J. F. and G. Iveson.
The application of gas-liquid chromatography to the analysis of volatile halogen and interhalogen compounds. D. H. Desty (ed.) Gas Chromatography, pp300 - 309, Butterworth Publications, London, 1958.

(4) Ellis, J. F., C. W. Forrest and P. L. Allen.
The quantitative analysis of mixtures of corrosive halogen gases by gas liquid chromatography. Anal. Chim. Acta 22: 27-33. 1960.

(5) Gehauf, B., J. Epstein, G. B. Wilson, B. Witten, S. Sass, V. E. Bauer and W. H. C. Rueggeberg.
Reaction for colorimetric estimation of some phosphorus compounds. Anal. Chem. 29:278-81. 1957.

(6) Keeler, R. A., C. J. Anderson and D. Satrianis.
Analysis of mixtures of white phosphorus, phosphorus oxychloride and phosphorus trichloride. Anal. Chem. 26: 933-4. 1954.

(7) Keulemans, A. I. M.
Gas Chromatography, p60, Reinhold Publishing Company, New York. 1959.

(8) Laitinen. H. A.
Chemical Analysis, p506, McGraw Hill Book Company, New York. 1960.

(9) Ormerod, E. C. and R. P. W. Scott.
Gas Chromatography of polar compounds using a non-polar liquid phase. J. Chromatography 2: No. 1, 65-68. 1959.

(10) Pecsok, R. L.
Analytical methods. R. L. Pecsok (ed.) Principles and Practice of Gas Chromatography, pp 145-149, John Wiley and Sons, Inc., New York. 1959.

APPENDIX

Calculation of the Number of Theoretical Plates and Height Equivalent to a Theoretical Plate

An expression of column performance in terms of theoretical plate number n can be calculated by the equation

$$n = 16 \left[\frac{IC}{AB}\right]^2$$

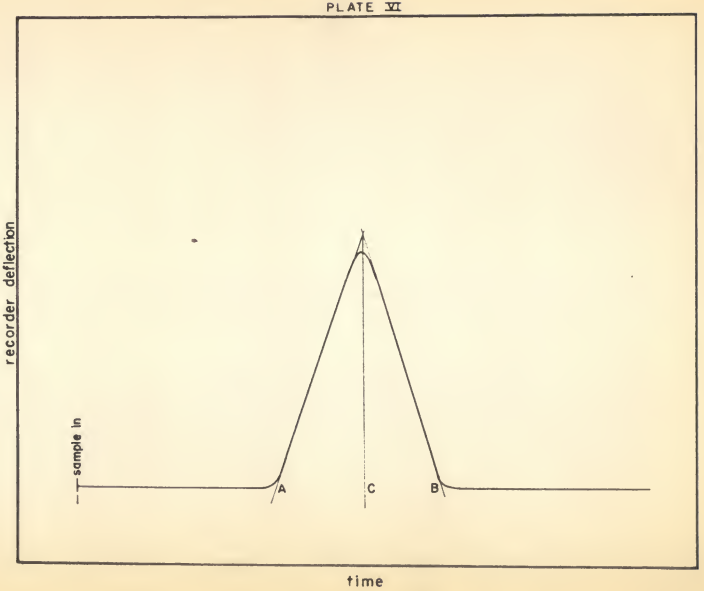
where the quantities IC and AB are the distance along the recorder chart from the sample injection point to the peak maximum and the width of the peak base in the same units, respectively (8). Plate VI, an idealized elution diagram, illustrates the method of measuring these values.

The height equivalent to a theoretical plate, H.E.T.P., is calculated by dividing the column length by the number of theoretical plates.

EXPLANATION OF PLATE VI

Plate VI illustrates an idealized chromatogram for one component obtained with a differential detector.

PLATE VI



THE ANALYSIS OF SOME VOLATILE PHOSPHORUS COMPOUNDS BY GAS-LIQUID CHROMATOGRAPHY

by

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A method of analysis based on gas chromatography was developed for some mixtures of volatile phosphorus compounds.

Because some of the compounds investigated were very reactive, it was necessary to construct an instrument of inert materials. Pyrex glass proved suitable for use as a chromatographic column and body of the thermal conductivity cell, and tantalum wire was employed for the sensing elements.

The column packing for the inorganic compounds was made from ground Teflon and Kel-F 90 grease for inert phase and partitioning liquid respectively, while ground Teflon and either di-n-butyl phthalate or Apieson K oil was suitable for the organic compounds studied.

The constant temperature box was constructed from sheet iron, double walled, with rock wool insulation between the walls. Constant temperature was maintained by the use of four 250 watt strip heaters and an open coiled nichrome wire heater which was regulated by a thermostat.

The liquid phase was coated on the inert solid support and packed into the column. The filled column was fitted to the cell, and with the carrier gas flowing, the temperature was raised to 150°C in order to purge the column of water. The column was then ready for operation.

Reagent grade PCl_3 was redistilled under nitrogen at atmospheric pressure, and reagent grade $POCl_3$ was taken directly from a freshly opened bottle. The purity of each was checked mass spectrometrically.

Thiophosphoryl chloride was synthesized at this laboratory and redistilled shortly before use. Dimethyl phosphite and diethyl phosphite were redistilled at 17mm pressure and chromatograms of center cuts showed the presence of approximately 1% impurity remaining in each compound.

The equipment was assembled, checked for leaks, the flow rate adjusted and brought to temperature. Known mixtures of various compounds were made and analyzed. Quantitative results were obtained for the following mixtures: $(CH_3O)_2POH$-$(C_2H_5O)_2POH$, PCl_3-$PSCl_3$ and PCl_3-$POCl_3$. Analysis of PCl_5 was not successful. Heavy yellow deposits were observed in the cell after attempting this analysis thereby indicating decomposition or reaction within the system.