EVALUATION OF A GAS CHROMATOGRAPHIC SEPARATION AND DETECTION TECHNIQUE FOR WATER VAPOR TRANSMISSION RATE STUDIES

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ABSTRACT

EVALUATION OF A GAS CHROMATOGRAPHIC SEPARATION AND DETECTION TECHNIQUE FOR WATER VAPOR TRANSMISSION RATE STUDIES

A chromatographic method for the separation and detection with quantitative measurement of water vapor was developed and evaluated. The applications of this specific method to packaging research are described. The applications of gas chromatography to packaging in general are reviewed.

Evaluation of a porous polymer chromatographic column packing material was carried out utilizing thermal conductivity and ionization detector gas chromatographs. The respective sensitivities to water and water vapor of the gas chromatographs were investigated and tabulated.

Several instrumental anomalies were encountered, explained, and effectively controlled.

The major finding of this research was that separations, detections, and measurements of water vapor in air by chromatography is a successful method. It is indicated that further development utilizing this method should be pursued actively. Also, many other separations may be uncovered by further investigation of the porous polymer beads, and packaging research should benefit greatly from these separations.

EVALUATION OF A GAS CHROMATOGRAPHIC SEPARATION AND DETECTION TECHNIQUE FOR WATER VAPOR TRANSMISSION RATE STUDIES

By

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TABLE OF CONTENTS

Introduction 1

Theory of Gas Chromatography 5

Experimental Procedure 16

Conclusions and Future Work 45

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LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Purpose of this research

The purpose of this research was to investigate and evaluate the practicality of using a chromatographic technique, preferably compatible with existing equipment at the School of Packaging, so that a statistically reliable method of measuring water vapor transmission rates would be available to the packaging engineer. A second goal of this research was to find a method by which a single measurement of the components, O_2, CO_2 and water vapor, in atmospheric air would be possible. The final area of interest was to investigate and describe applications of gas chromatography to packaging research in general.

Any gas chromatographic separation is dependent on the efficiency of the columns. The following characteristics must be inherent to the column material.

1) The column material must be easily prepared or commercially available.
2) The column material must be stable at temperatures above 200°C.
3) The separation agent cannot bleed or react with the instrument or components to be separated.
4) The column material must be easily packed into small diameter columns and it must allow necessary carrier-flow characteristics.

5) The material must separate a wide range of compounds such as N_2, O_2, CO_2, water vapor, and non-polar organic vapors.
6) The material must not only separate water but be able to yield smooth symmetrical peaks. Briefly, the column must minimize tailing (adsorption-desorption) of water.

At present, there is no permanent record made of water vapor measurements; this is not the case with the gas permeants. The gas chromatograph will enable absolute measurements to be performed. Simultaneous comparison of water vapor content and gas permeant content are but one reason for attempting this research project.

If a gas chromatographic technique may be developed for both gas permeants and water vapor measurements a source of instrumental error would be eliminated. This source of error is in using electric hygrometry for water vapor measurements. The many advantages of using one detection and measuring instrument for any given set of measurements has been demonstrated by Lockhart (13) in the utilization of gas chromatography for measuring permeability rates through barrier materials in the Davis cell (4).

Present WVTR detection methods

A degree of laboratory sophistication rarely found in technicians is involved in classical methods of measuring water vapor. Among these methods are gravimetric, chemical, electric hygrometric, dessicant-cup, and pressure increase methods (8,12,14,15,16). Gas chromatography has been demonstrated to be a simple straightforward measurement device. It is used for routine testing as well as research.

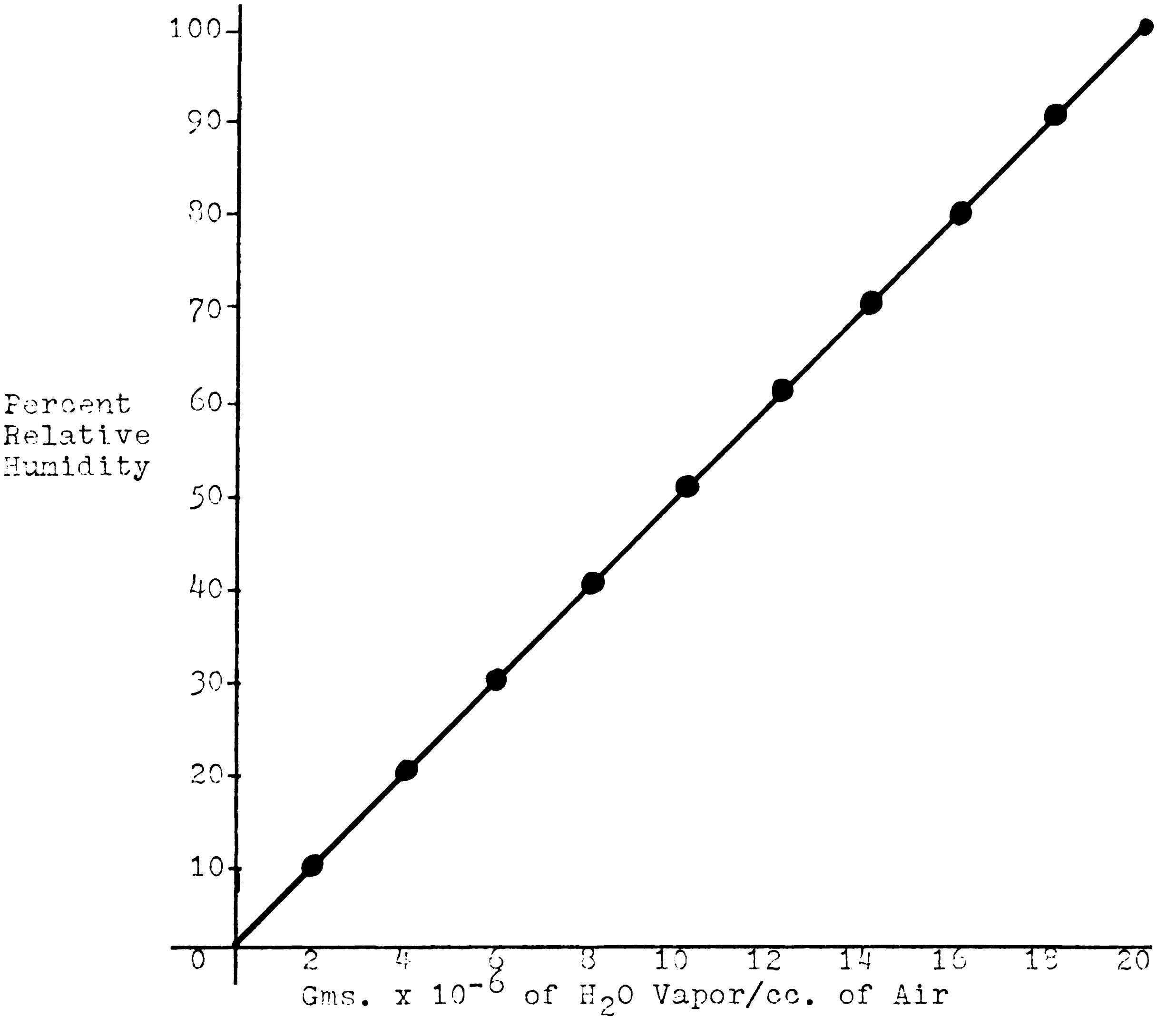
The School of Packaging is presently using a testing system developed by H. E. Lockhart that measures gas permeants by gas chromatography (13). The water vapor is measured by electric hygrometry (29). The level of detection is indicated by Figure I (20,26); a sensitivity of at least 1.0×10^{-6} gm./cc. for water must be obtained for gas chromatography to be a practical method of measuring water vapor in air.

The collection and tabulation of permeability data is essential for future design of packages as the main cause of product degradation in many cases is due to water vapor transmission and gas permeability.

FIGURE I

Weight of Water Vapor in 1.0 cc. Air vs. Percent Relative Humidity

23° C. (73.4° F.) $\frac{20.23 \text{ gms. } H_2O \text{ vapor}}{\text{cubic meter of air}}$



THEORY OF GAS CHROMATOGRAPHY

General Theory of Gas-Liquid and Gas-Solid Chromatography.

Small diameter columns of various solid supports, which may or may not have been previously coated with a thin layer of some organic compound have been used for chemical separations for years. If the solid support is coated, this coating is usually a high boiling liquid or solid. This coating is commonly called the liquid phase.

A sample of various components may be inserted into the front of the column by some suitable method. The sample is usually transported through the column by the use of an inert gas called the carrier gas. Separations are effected by differences in vapor pressure, solubility of the sample components in the high boiling liquid coating the column solid support, or in the case of using a solid support alone the elution and separations are dependent upon surface adsorption, molecular interaction between the sample and this support.

The eluting components are detected by some means, the more popular being thermal conductivity cells and ionization detectors. A series of signals are given by these detectors; when these signals are displayed as signal intensity versus time symmetrical peaks approximating Gaussian distribution curves are given, and the areas under these curves may then be normalized to obtain the percentages of the sample's components.

Columns: Their efficiency and resolution limitations.

Sufficient column length must be present to separate the desired components completely and quickly.

Means of describing a column's efficiency are approached by many workers in various ways (11,23). The method described here is based on the theoretical plate treatment of James and Martin in which N, the number of theoretical plates, is found by using peak dimensions.

$$\text{(A)} \quad N = 16(X/Y)^2$$

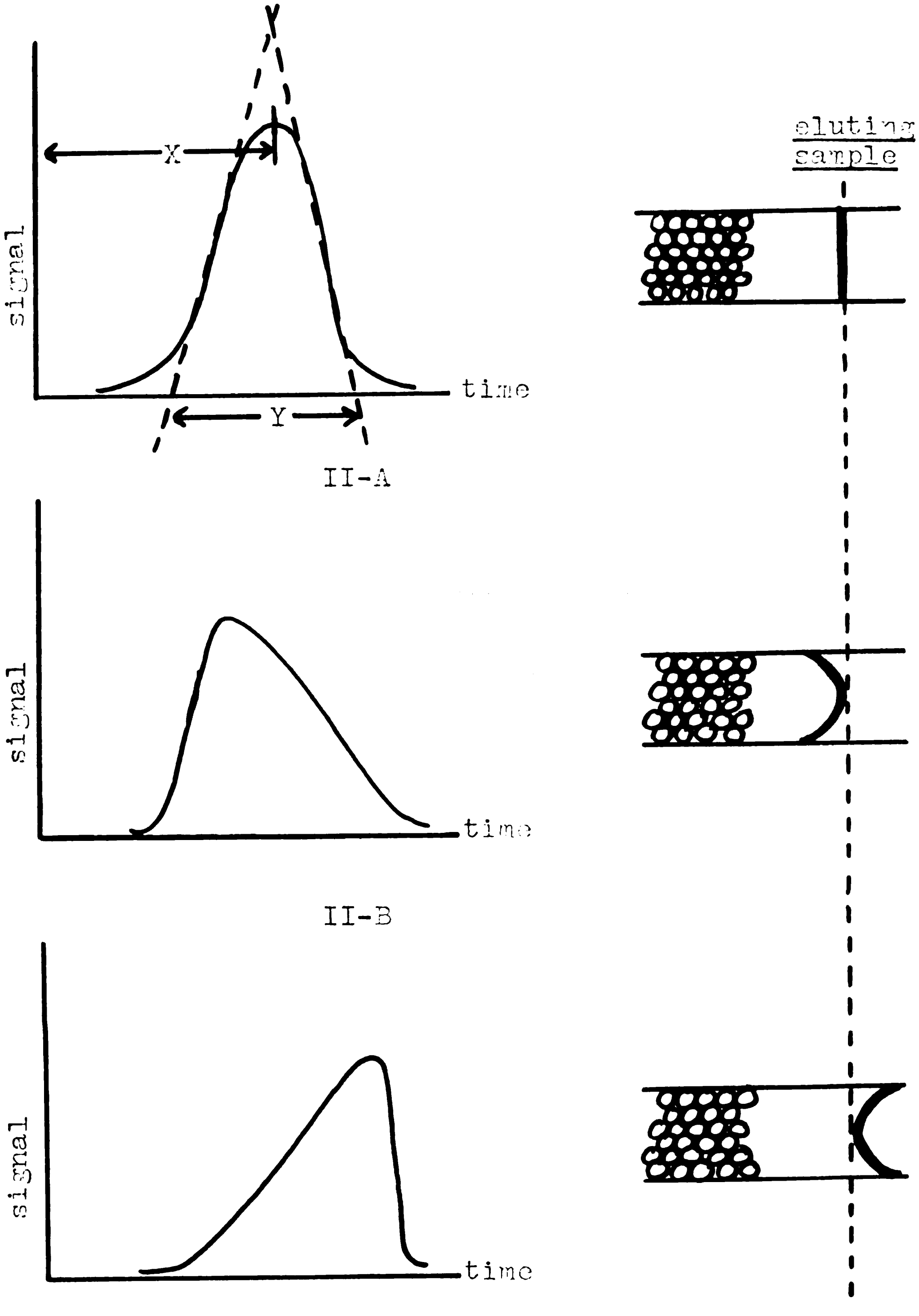
N may be calculated using Equation (A) where X is the retention time and Y is the baseline width intercepted by tangents to the points of inflection of the peak. (See Figure II-A). In general, the separation requiring N plates by normal distillation is given by N^2 theoretical plates. One other comparative method of measuring column efficiency is commonly used (11,23). This measurement $\bar{H}$ is defined as the height equivalent to a theoretical plate. It is obtained from N and the length of the column, L.

$$\text{(B)} \quad \bar{H} = L/N$$

In Equation (B) a measure of band broadening is essentially given as width of peak base, Y, during time of elution, X. See Figure II-A. A means of comparing column resolution is

FIGURE II

Illustrations of Normal, Langmuir, and Anti-Langmuir Curves



II-A

II-B

II-C

given by

$$(C) \quad R = \sqrt{N} \cdot (X_2/X_1 - 1)$$

This expression for R, the distance between peak maxima, is expressed as a multiple of the standard deviation of the first peak. It is clear from Equation (B) and Equation (C) that if the resolution, R, is to be doubled, the column length must be increased by a factor of 4. Also the effective resolution may be increased by increasing the ratio of liquid phase to solid support within practical limits.

Along with the resolution the symmetry of the peak for the eluted component is dependent on adsorption-desorption effects taking place on the surface of the solid support and on the instrument walls. The instrument must be non-reactive, clean, and it must possess small hold up volume in order to minimize tailing and spreading effects (2,10,11).

The shape of the curve obtained in gas chromatography may be varied in three ways (11,23,24). The first variation is shown in Figure II-A. The nearly Gaussian peaks are obtained when the concentration of the solute in the stationary phase is directly proportional to the concentration of the solute in the gas phase. It is seen that the retention time is independent of concentration. The type called Langmuir or Classical Isotherm as shown in Figure II-B is caused by the main portion of the solute band being eluted more rapidly than the leading front edge due to a limited area of adsorption available. Langmuir curves are given by all columns to some degree. Peaks of the Langmuir type are usually observed in gas-solid chromatography. In this type of column the retention time is a function of sample size and normal narrow peaks are obtained with micro amounts. A third type is shown in Figure II-C. Its shape is due to the main portion eluting more slowly than the extremities. Again, retention time is a function of sample size which is, of course, dictated by sample volume available and the sensitivity of the detector.

The column is the heart of a gas chromatograph because the actual separations are obtained in the column. In gas-liquid chromatography high thermal stability and low vapor pressure at the operating temperature of the instrument must be possessed by the liquid phase. The separation of homologous mixtures is easy, and, of most importance, azeotropes are not formed in homologous series.

The injection of samples must be done in such a manner as to approximate a "plug" introduction of vapor. For optimum results the smallest possible sample consistent with detection sensitivity is desirable, but this efficiency is reduced if the sample vapor is excessively diluted with carrier gas.

The rate of elution as well as the degree of separation is affected by the temperature of the column and the flow rate of the carrier gas. It is necessary to optimize these variables in such a manner that a rapid, precise, and yet simple technique may be available to the packaging engineer.

Throughout the remainder of this paper the term "gas chromatography" is used instead of the limiting terms "gas-solid" or "gas-liquid". Since the development of solid supports which will separate both polar and non-polar substituents the scope of the field is widened in gas chromatography--both gas-solid and gas-liquid.

Instrumentation

Thermal conductivity detectors.

A thermal conductivity cell is basically a balanced differential bridge by which the unbalance caused by various characteristic thermal conductivities of materials flowing over one arm of the electrical bridge is measured. These are of two types--the hot wire filament and the thermistor thermal conductivity cell. Samples as low as 10^{-9} to 10^{-10} grams can be detected using small volume thermal conductivity cells (6,11,23,24).

Ionization detectors.

There are two popular types used: the direct ionization detector and the hydrogen flame detector. The hydrogen flame is completely insensitive to water (23) and will not be discussed here. The argon detector is a type of ionization detector which operates on the principle of forming metastable argon ions (6,23) as a source of energy by which free electrons similar to those described by Ryce and Bryce (22) are produced. The separated components are ionized by the free electrons not much differently from the way a sample is ionized by a mass spectrometer (3). Ionization detectors are characterized by their fast response in the range of milliseconds (23,24) and high sensitivity; 10^{-12} gram determinations are not uncommon for non-reactive organic compounds (23).

Any material capable of being heated to incandescence and emitting free electrons will constitute a filament for an ionization source. These free electrons are accelerated by a positive potential which gives them enough kinetic energy to ionize molecules. The molecules are ionized by removing electrons from the electron orbits of the molecules. The ions formed migrate to the collector plate by virtue of their positive charge. Upon striking the negative collector the ions discharge by accepting electrons from the collector. This electron flow amounts to a minute current and this current, when amplified by an electrometer, is a statistical representation of the sample introduced into the device.

In the case of a filament manufactured from pure tungsten it is necessary to precondition it with a hydrocarbon. The basic reaction is to form two distinct tungsten carbides.

$$4W + 2H_2C{=}CH_2 \longrightarrow W_2C + WC + W + 2CH_4$$

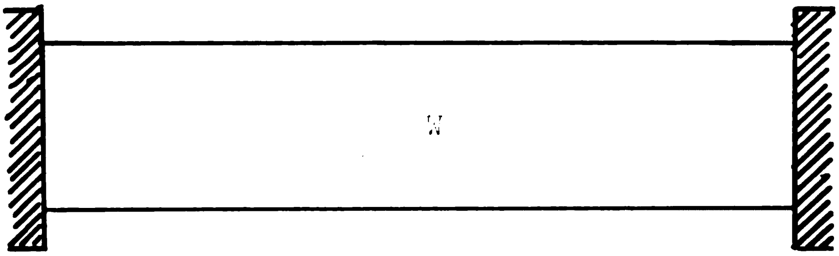
A diagramatic presentation of this may be seen in Figures III-A, III-B, and III-C. Figure III-B is the ideal filament which has been described by Sharkey and many others (3,7,23,27). It is possible to overcondition a filament and this filament structure is represented by Figure III-C. The reaction involved is similar to the above but it is driven further to the right causing a larger percentage of WC to be formed at the surface. Supposedly the carbon permeates (diffuses) through the tungsten metal and WC forming a large build-up of W_2C in the center of the filament (3).

A graph of conductance (reciprocal of resistance) is shown in Figure IV. The minimum conductance, which is the maximum resistance, is found at the point where the filament has the greatest amount of W_2C present at the emitting surface. Briefly, this is the point where the electron emission is optimum with respect to a constant filament heating current. As previously mentioned, the filament is the source of free electrons. These free electrons when given

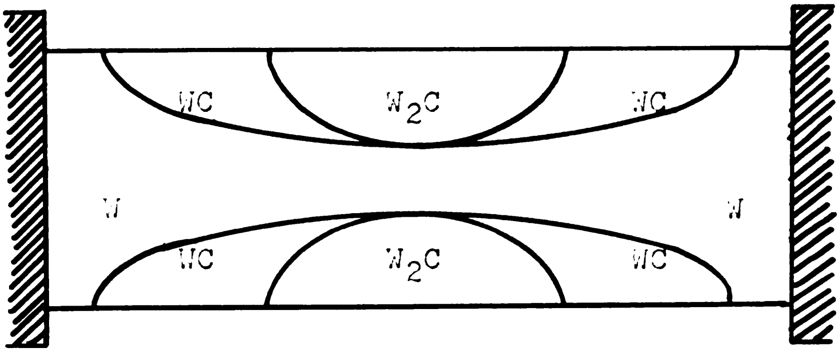
Figure III

Composition Profiles of Tungsten Filaments

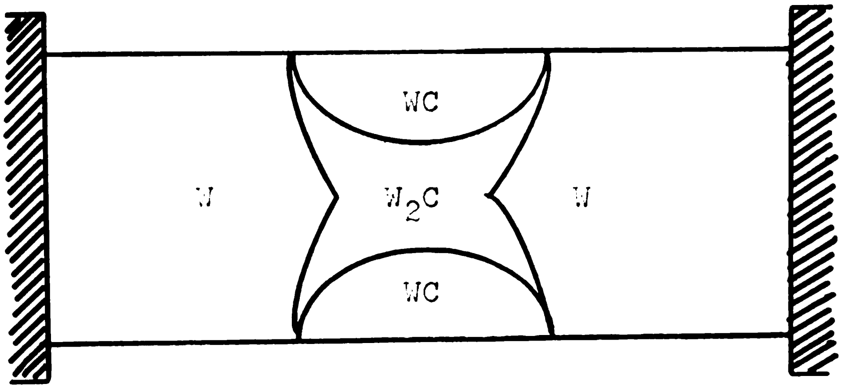
Taken from Beynon. *Mass Spectrometer and Its Applications to Organic Chemistry*. p. 108.



III-A Pure tungsten before any conditioning



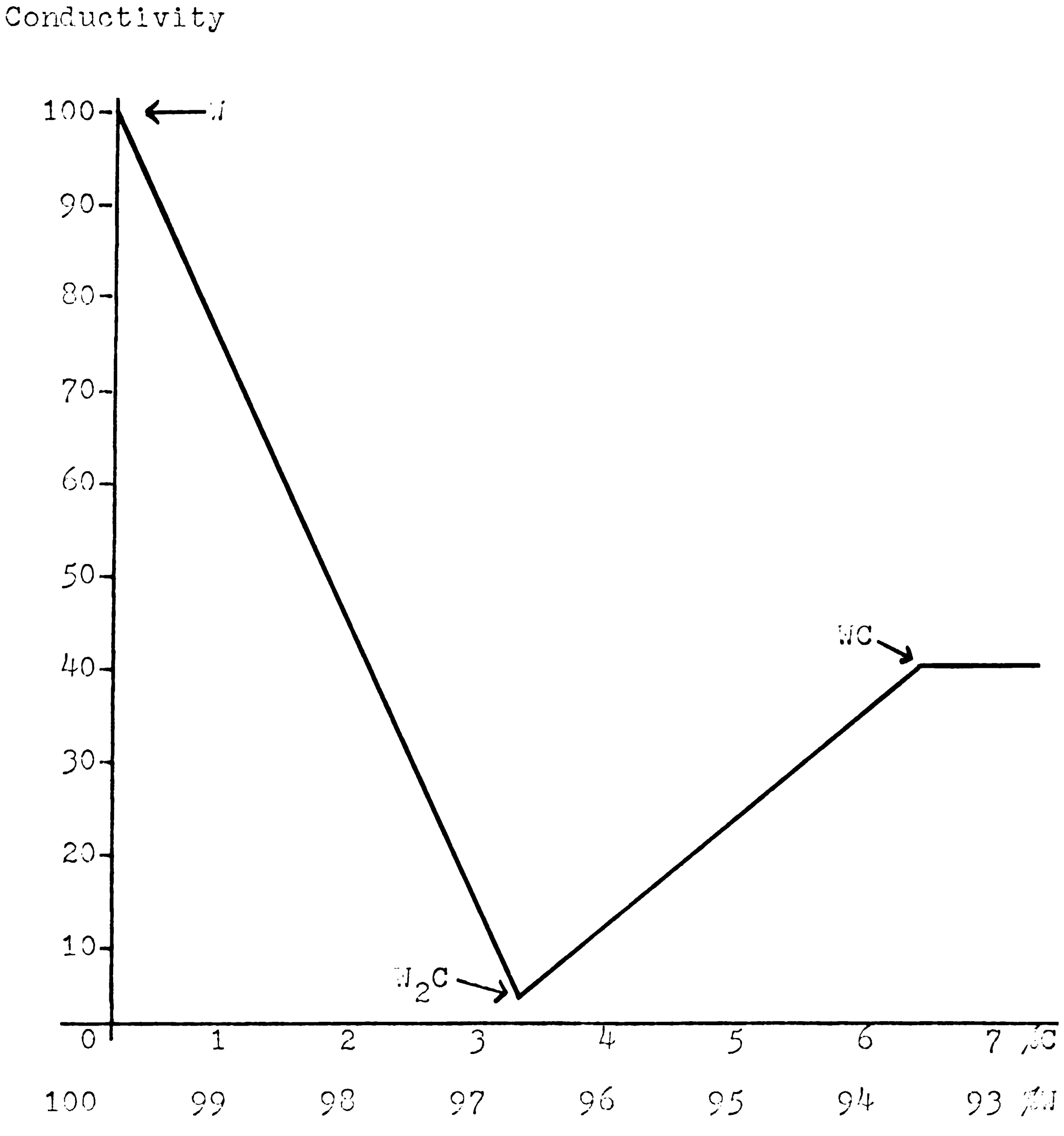
III-B A properly conditioned filament
(III-A + hydrocarbons)



III-C An overconditioned filament
(III-B + excess hydrocarbons)

Figure IV

Conductance of Various Tungsten-Carbon Compositions
Measured at Room Temperature



Taken from Beynon. *Mass Spectrometry and Its Applications to Organic Chemistry*. page 109.

enough kinetic energy will ionize sample molecules.

As part of the description of the ionization source it must be stated that the ionization of materials present in the source will give rise to one ionization signal unless the ions are separated by some electrical or magnetic means. A chromatograph will, in most cases, allow just one single component to be eluted at a time; in turn, this single component is ionized and the ions detected are representative of that particular specie plus any residual components present in the ionization source at the time of ionization.

There are two gas chromatographs available at the School of Packaging. The Fisher Gas Partitioner is a thermal conductivity instrument which operates at ambient temperatures (stabilized by a constant differential heater). The other instrument available utilizes an ionization detector and is equipped with a programmed column heating element. It is the Burrell Kromo-tog K-7. Most of the evaluation was performed using the Burrell instrument in order to utilize its high sensitivity and column heating equipment.

A tungsten filament is utilized in the Burrell Kromo-tog K-7. This tungsten filament is heated by a potential of 18 volts, and an emission of 0.8 milliampere is obtained when 5.0 to 6.0 amperes current is passed through the tungsten filament causing it to become an electron emitter (Edison effect).

EXPERIMENTAL PROCEDURE

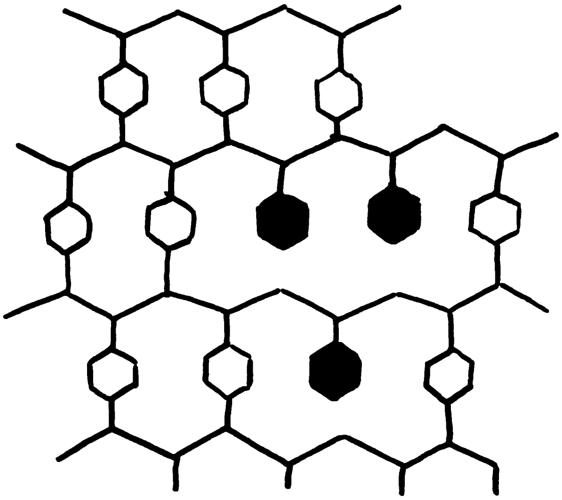
Effect of water on ionization detector response

The first step in this procedure involved the selection and preparation of a suitable chromatographic column. Initially, 5% Carbowax coated on Teflon powder was considered to be the best water separation column. It has been reported by Kirkland (10) that this column packing separated liquid water with minor tailing. Kirkland also describes cooling the Teflon powder (after coating) to 0°C. and vibration packing 3/16" and 1/4" one meter columns successfully. Attempts to pack columns at room temperature invariably result in aggregated Teflon and undesirable plugging.

In the past few years at The Dow Chemical Company gas chromatograph methods of measuring water were tried and evaluated using the common technique of coating a fluorine containing polymer with a suitable liquid phase. That much of the tailing (Langmuir effect) might be eliminated by the use of a uniformly sized support (microspheres) was confirmed in a personal interview with L. B. Westover (30). A solid porous support had been developed by O. L. Hollis (9) and was being released by Waters Associates, Inc. of Framingham, Massachusetts under the name of Porapak was also made known in this interview. Two of the more common Porapak structures are graphically demonstrated in Figures V-A and V-B (9, 17,

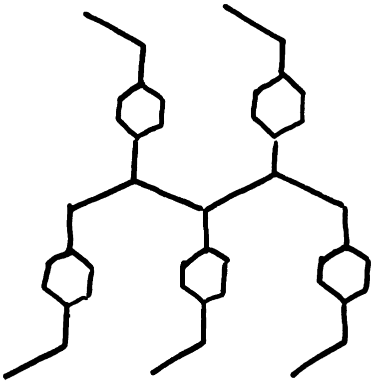
FIGURE V

Structure of Porapak R and Porapak Q



V-A

Porapak R----a copolymer of divinylbenzene and styrene. The styrene molecules are those with solid rings.



V-B

Porapak Q----a polyethylvinylbenzene.

18,19,30). Both the liquid phase and solid support functions in the column are actually served by the porous polymer beads (17) for chromatographic separations.

Due to the availability of this chromatographic column packing, Porapak, which packs easily and needs no liquid phase coating, Teflon powder support was not investigated further. The Porapak column had been recommended by Westover (30) and Hollis (9) for the separation of water vapor from air. Hollis suggested using a small diameter column at least 6 feet long and operating the column above 100°C. Past experience with coated Teflon indicated that bleeding of the liquid phase would be another disadvantage with the Teflon column. The Porapak does not bleed even at temperatures of 250° C for it has no liquid phase to bleed. Porapak exhibits the unique property of separating polar and non-polar compounds with virtually no tailing of either type.

A column 6.5 ft. x 3/16 in. O.D. aluminum was packed with 18.3 ml. of Porapak Q by vibration. This column was conditioned at 230° C. for 4 hours while being continuously purged with helium. This column was bent in the hairpin shape common to the Burrell instrument and attached to it. While optimum column conditions were being sought, the emission current was noticed to drop by a factor of 25% (0.8 to 0.6) during detector response. Due to this loss of emission current, the chromatograms were in no way reproducible.

The reason for this was that the tungsten filament was being stripped by the oxygen-containing samples. This tungsten stripping effect is well known in mass spectrometry and is referred to frequently in the literature (1,3,11,27,28). Also, insulating deposits will be released by accelerated decomposition in the ionization chamber due to the presence of oxygen-containing compounds. Erratic operation will be caused by the release of these deposits, especially if these deposits are subsequently exposed to electron bombardment from the filament, and the background will be high. The filament itself will be damaged by some of these materials in this process of decomposition. As an example, water vapor is decomposed when contact is made with the filament; the oxygen is chemically combined with the filament and hydrogen is evolved as atomic hydrogen.

$$H_2O + W_2C \longrightarrow WO + WC + 2H$$

$$H_2O + W \longrightarrow WO + 2H$$

$$2H_2O + WC \longrightarrow WO + CO + 4H$$

At the operating temperature of a tungsten filament the tungsten oxide is distilled to the walls of the ionization chamber. There it is reacted with the atomic hydrogen to reform tungsten metal and water so that the process is repeated. The process is not reversible because the tungsten metal is now deposited on the wall surface.

$$WO + 2H \longrightarrow W + H_2O$$

This effect is readily noticed in a mass spectrometer after many water samples are run, and the effect is shown as a loss of total emission and then the filament must be reconditioned by purging with a hydrocarbon. The loss of tungsten is irreversible, and in order to obtain the same total emission level the filament current must be continuously increased. This type of reaction proceeds readily at pressures of 10^{-12} mm. Hg, and as the pressure of the ionization chamber is increased the loss of emission becomes noticeably greater.

If carbon-containing compounds alone were present, the surface of the filament would be chemically changed to mainly WC, the other carbide of tungsten, and the carbon would permeate to the center of the filament forming W_2C. This type of filament is shown in Figure III-C. An entirely different work function of electron emission is possessed by this filament, and this emission will be much less than that of the case shown in Figure III-B for the same amount of input current. All these reactions take place in mass spectrometers operating at pressures of 10^{-12} mm. Hg. In the case of the Burrell K-7 this deleterious effect will be accelerated due to higher ionization pressures of 0.1 and 1.0 mm Hg (6).

The effect would be observed for small amounts of an oxygen-containing sample. When a large amount is suddenly introduced the emission current decreases sharply, and erratic non-reproducible chromatograms are caused by this decrease. To obtain reproducible ionization of samples some source of hydrocarbon must be introduced to maintain the filament as shown in Figure III-B. The chemical composition of a properly conditioned filament has been determined by Sharkey (13,27,28) as previously mentioned (See Figure III).

The optimum emission will take place when the carbon content is 3.16%. This may be seen in Figure IV. One is not concerned with the exact chemical composition of the tungsten filament being exactly 3.16% carbon, but rather that the filament easily reaches some stable reproducible level of carbonization. It may be readily demonstrated that when a slightly conditioned tungsten filament is exposed to an excess of any hydrocarbon a further production of W_2C will take place and the resistance of the filament will increase (1,27). This resistance increase will cause the filament to be maintained at a satisfactory emission level by successively lower quantities of filament heating current needed. Conversely, if oxygen is introduced, the filament heating current must be increased to maintain this same level of electron emission. The exact reverse behavior would be observed with an over-conditioned filament (3,28). The

Burrell instrument has no provisions for automatic electronic control of the emission level (6) and drastic decreases and increases in the total emission current are noted during the operation of the instrument. In this research, water vapor decarbonized and methanol vapor carbonized the tungsten filament in the Burrell K-7.

Of interest is the section entitled "Analytical Results" found in <u>Performance Data on a New Ionization Detector</u>, a Burrell Corporation publication (6). The analysis of hydrogen, oxygen, nitrogen, methane, carbon monoxide, argon, carbon dioxide, ethylene, and acetylene is referred to as the analysis of a "fixed gas." These gasses were adsorbed on molecular sieve and silica gel giving reproducible quantitative chromatograms. The reproducibility is caused by the presence of hydrocarbons in this "fixed gas" sample. In general usage, the constituents N_2, O_2, CO_2, and water vapor are found in atmospheric samples, and are denoted by the term "fixed gas." Atmospheric samples do not generally contain methane, ethylene, or acetylene in any great amount. A filament having a coating of tungsten carbides W_2C and WC coated on pure W is obtained in the presence of those hydrocarbons.

Also shown in the Burrell publication (6) is a chromatogram which contained 90% water and the remaining 10% made up of the hydrocarbons methanol and ethanol. The ionization energy was reduced after the methanol and ethanol were eluted; Figure VI is an exact scale drawing of reference (6) with the dotted line drawn in to indicate water. If this experiment were to be repeated with ionization energy great enough to ionize the water, erratic chromatograms should be obtained. It is not stated in the Burrell publication anywhere that water-containing compounds may be quantitatively analyzed in the absence of hydrocarbons. The non-reproducible situation noted in this research may be overcome by properly conditioning the filament by the use of hydrocarbons during the analysis of small amounts of oxygen-containing compounds. It is seen that, unless a proportional amount of hydrocarbon is present when oxygen-containing samples are ionized, the electron emission will not be linear; thus, the signal measured will be non-linear also.

Sensitivity determination of chromatograph with respect to water

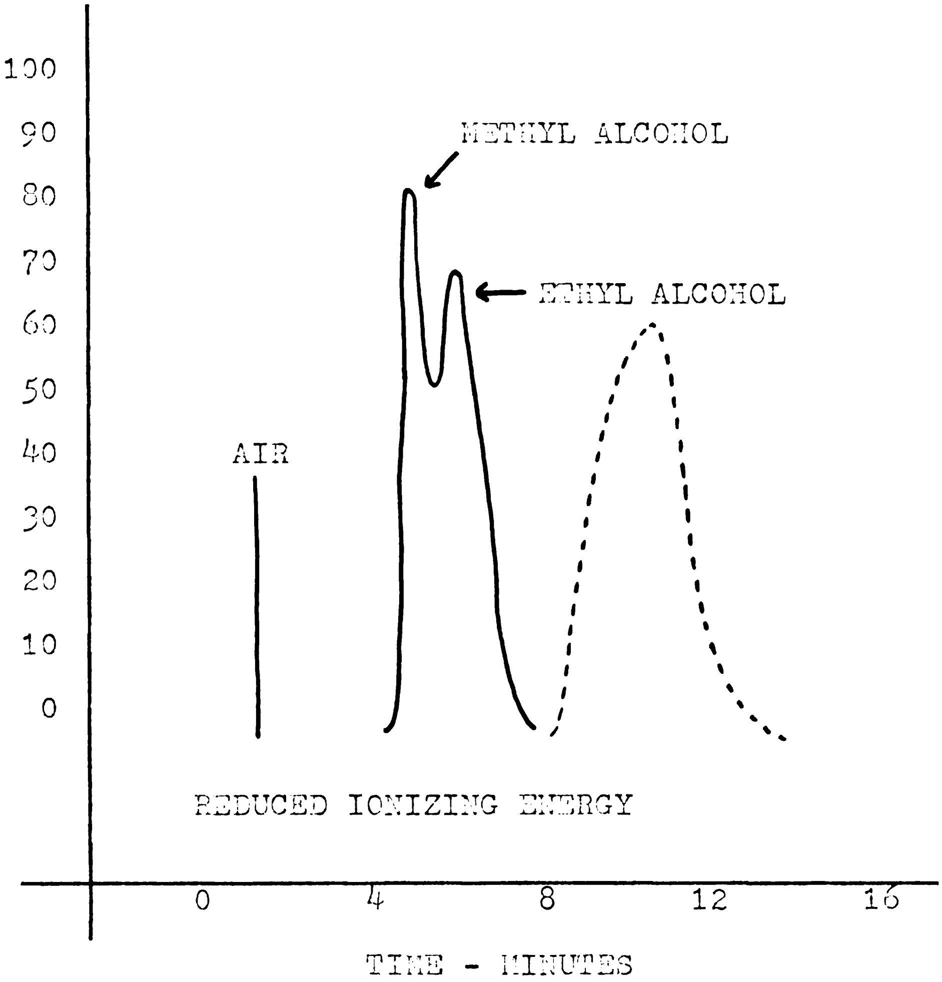
Even though the Burrell ionization instrument gave less than completely successful results, the anomalous conditions are instrumental in nature and would be eliminated by careful conditioning or instrumental design changes. These changes are covered in detail in the section on further work.

Excessive high background was observed at maximum sensitivity and minimum attenuation settings. The background

FIGURE VI

Performance Data on a New Ionization Detector

Burrell Corporation



was in the same order of magnitude as that of water vapor in air. Due to high background levels the water vapor detection experiments were performed at lower sensitivity and higher attenuation settings. The values obtained are relative values, and, in fact, will be 50 times lower than could be obtained by operating at the maximum sensitivity of the Burrell instrument.

Various solutions of water in methanol were prepared to determine the minimum practical limit of sensitivity of the Burrell K-7 for water. The use of methanol was dictated by the observed deleterious effect of water alone upon the tungsten filament in the Burrell Kromo-tog instrument. There was still a noticable drop in emission current, but this was due to the cooling of the filament below its most efficient emission temperature, and, as there would always be a hydrocarbon (methanol) present, the normal behavior of a properly conditioned filament will be experimentally created.

A series of chromatographic experiments were performed on the Burrell K-7 using a 3/16 in. O. D. aluminum column 6½ ft. long packed with 18.3 ml. of Porapak Q resin. The column was tested between 75° C. and 200° C. with varying helium flow rates in order to obtain relatively "tail-free" curves. All tables have the exact instrument operating conditions specified on them. The first experiments (EXP BK-7-1A and EXP BK-7-1B) were performed to observe the variation of the peak area for pure water when no organic compounds were present. The 1.0 μl. sample was injected by a microliter syringe through the Burrell syringe port. To eliminate any question of loading error, the syringe was loaded, weighed to the nearest 0.1 of a milligram, and injected; the syringe was immediately weighed again. The 1.0 μl. load showed no detectable variation to 0.1 milligram when the loads were weighed and injected carefully. Also the sample was drawn up through the syringe by a squeeze bulb. This was to insure that no air bubbles were trapped in the syringe needle. Due care was taken in injecting the sample through the syringe port, as this port was operated at temperatures in excess of 100° C. for all of this project. The method used was to insert the syringe fully into the port, immediately to depress the plunger, and to remove it in one swift motion. If this were not rapidly done, the needle would become hot and preferentially volatilize lower boiling constituents. The results of these two experiments are shown in Table I. A variation of -49.4% to +31.3% is demonstrated by these experiments, and this variation is due to the water stripping problem mentioned previously.

A second experiment was designed to demonstrate the effect an organic compound has upon stabilizing the emission characteristics of the filament. The results of this

TABLE I

Filament Stripping Experiment

Trial	Sample Weight mg.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average	
							Pk. Ht.	Area
EXP BK-7-1A								
1	1.0	1.10	13.20	14.80	7.26	5.53	-10.80	+31.3
2	1.0	0.35	16.00		2.80		+ 8.12	-49.4
3	1.0	0.40	16.30		5.36		+13.50	- 3.08
4	1.0	1.00	13.40		6.70		- 9.46	+21.2
EXP BK-7-1B								
1	1.0	0.60	39.50	32.38	11.85	12.06	+21.98	-10.05
2	1.0	1.00	26.50		13.25		-18.15	+ 9.87
3	1.0	1.00	29.00		14.50		- 8.59	+20.21
4	1.0	0.55	34.50		8.64		+ 6.56	-28.40

EXP BK-7-1A: Speed $\frac{1}{2}$, 3/16" aluminum column at 175° C., flow rate Helium 68.5 cc./min., 1 μl. sample load, S = 10, A = 10, no organic present, nonlinear experiment.

EXP BK-7-1B: Same conditions as 1-A except S = 10 and A = 5.

experiment are given in Table II, and it is interesting to note that between Trial #1 and #2 no organic was introduced to the previously conditioned system, and a drop of 15.40 cm.^{2} in the water peak area is noted. This is calculated to be a variation of 45.5%. The organic (methanol) 1.0 μl. load was injected between all of the other trials and after four injections of methanol (each followed by a 1.0 μl. load of water) steady state conditions were again attained by the instrument. The importance of properly conditioning this instrument before attempting analysis work cannot be overstated.

An experiment designed to determine the minimum water sensitivity of the Burrell was carried out by using a blend of methanol and water. A conditioned filament was created by the introduction of a source of organic material (methanol) and progressively smaller amounts of water. These injections were performed without sacrificing the previously demonstrated precision obtained by using 1.0 μl. sample loads. The results of these experiments are given in Tables III and IV. The practical minimum sensitivity of the Burrell K-7 instrument with electrometer set at a sensitivity of 10, and the attenuation set at 5 was no greater than 3.000 x 10^{-4} gm./5 cm.^{2} for water in the presence of an ionizable hydrocarbon. A graphic display of this data from Tables III and IV is shown in Figure VII. It is shown in Figure VIII where

TABLE II

Conditioning Experiment

Trial	Weight	Full Band	Peak Height	Area ca. Triangle
1	1.0 mg.	2.90 cm.	23.30 cm.	33.78 cm.^{2}
2	1.0 mg.	1.75 cm.	21.00 cm.	18.38 cm.^{2}
3	1.0 mg.	2.70 cm.	16.30 cm.	27.00 cm.^{2}
4	1.0 mg.	3.00 cm.	19.20 cm.	28.80 cm.^{2}
5	1.0 mg.	3.65 cm.	18.50 cm.	33.76 cm.^{2}
6	1.0 mg.	3.50 cm.	18.50 cm.	32.38 cm.^{2}
7	1.0 mg.	3.60 cm.	18.50 cm.	33.30 cm.^{2}

NOTE: No methanol introduced after Trial 1. 1 μl. methanol introduced after each other trial until instrument rapidly approached steady state.

EXP BK-7-2: Speed 2, 3/16" aluminum column at 200° C., Helium flow 68.5 cc./min., S = 10, A = 10.

TABLE III

Burrell K-7 Minimum H_2O Detection Limit Experiment
Using a 6.5 ft. x 3/16" column

Trial	Sample Weight mg.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average Pk. Ht.	Area
1	0.4989	1.60	16.10	16.05	12.880	12.028	+0.311	+ 6.24
2	0.4989	1.30	15.90		10.285		-0.933	-14.50
3	0.4989	1.60	16.15		12.920		+0.311	+ 7.40
1	0.2975	1.45	7.20	7.50	5.220	5.145	-4.00	+ 1.50
2	0.2975	1.30	7.80		5.070		+8.00	- 1.50
1	0.2153	1.40	4.70	4.42	3.290	2.964	+6.35	+11.00
2	0.2153	1.35	4.60		3.105		+4.07	+ 8.14
3	0.2153	1.30	4.30		2.795		-2.72	- 5.71
4	0.2153	1.30	4.10		2.665		-7.25	-10.10

EXP EK-7-3: 3/16 in. x 6.5 ft. aluminum column with Porapak Q, speed 1, Helium flow 68.5 cc./min., 75° C., S = 10, A = 5, filament conditioned with MeOH.

TABLE IV

Burrell K-7 Minimum MeOH Detection Limit Experiment
Using a 6.5 ft. x 3/16" Column

Trial	Sample Weight mg.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average Pk. Ht.	Area
1	0.3988	3.40	15.50		26.350		+5.05	+ 6.57
2	0.3988	3.45	14.10	14.85	23.820	24.713	-5.05	- 3.62
3	0.3988	3.40	14.10		23.970		-5.05	- 2.64
1	0.5570	3.15	19.10	19.1	30.082	30.321	-----	- 0.789
2	0.5570	3.20	19.10		30.560		-----	+ 0.789
1	0.6240	3.40	20.50		34.850		+8.93	+14.7
2	0.6240	3.10	19.60	18.82	30.380	30.387	+4.14	------
3	0.6240	3.20	18.10		28.960		-3.82	- 4.71
4	0.6240	3.20	17.10		27.360		-9.14	- 9.97

EXP BK-7-4: 3/16" x 6.5 ft. aluminum column with Porapak Q, speed 1, Helium flow 68.5 cc./min., 75° C., S = 10, A = 5.

FIGURE VII

Measured Area vs. Weight Loaded for Water Sensitivity Determination on the Burrell K-7 Instrument Using a 6.5 ft. x 3/16" column

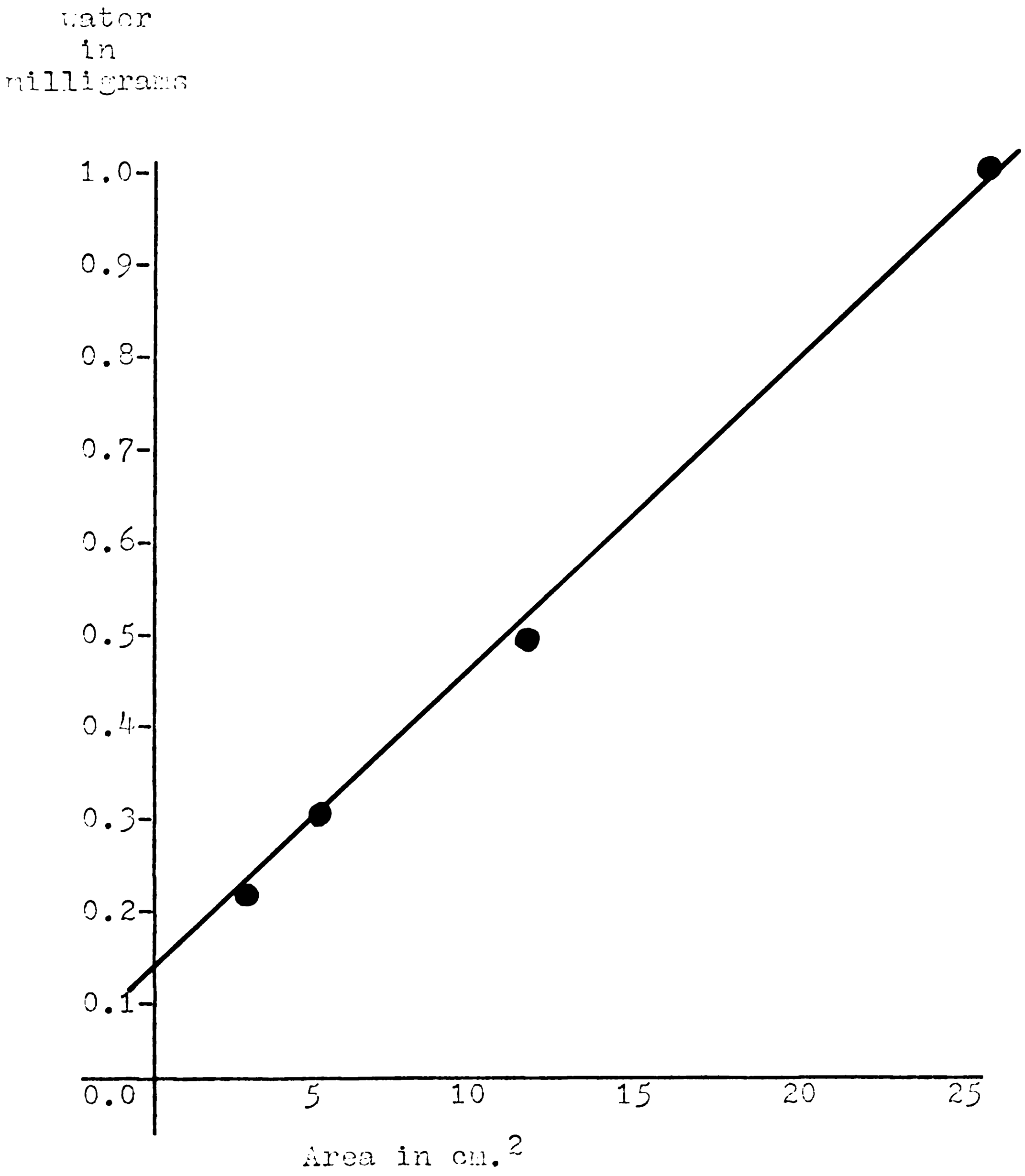
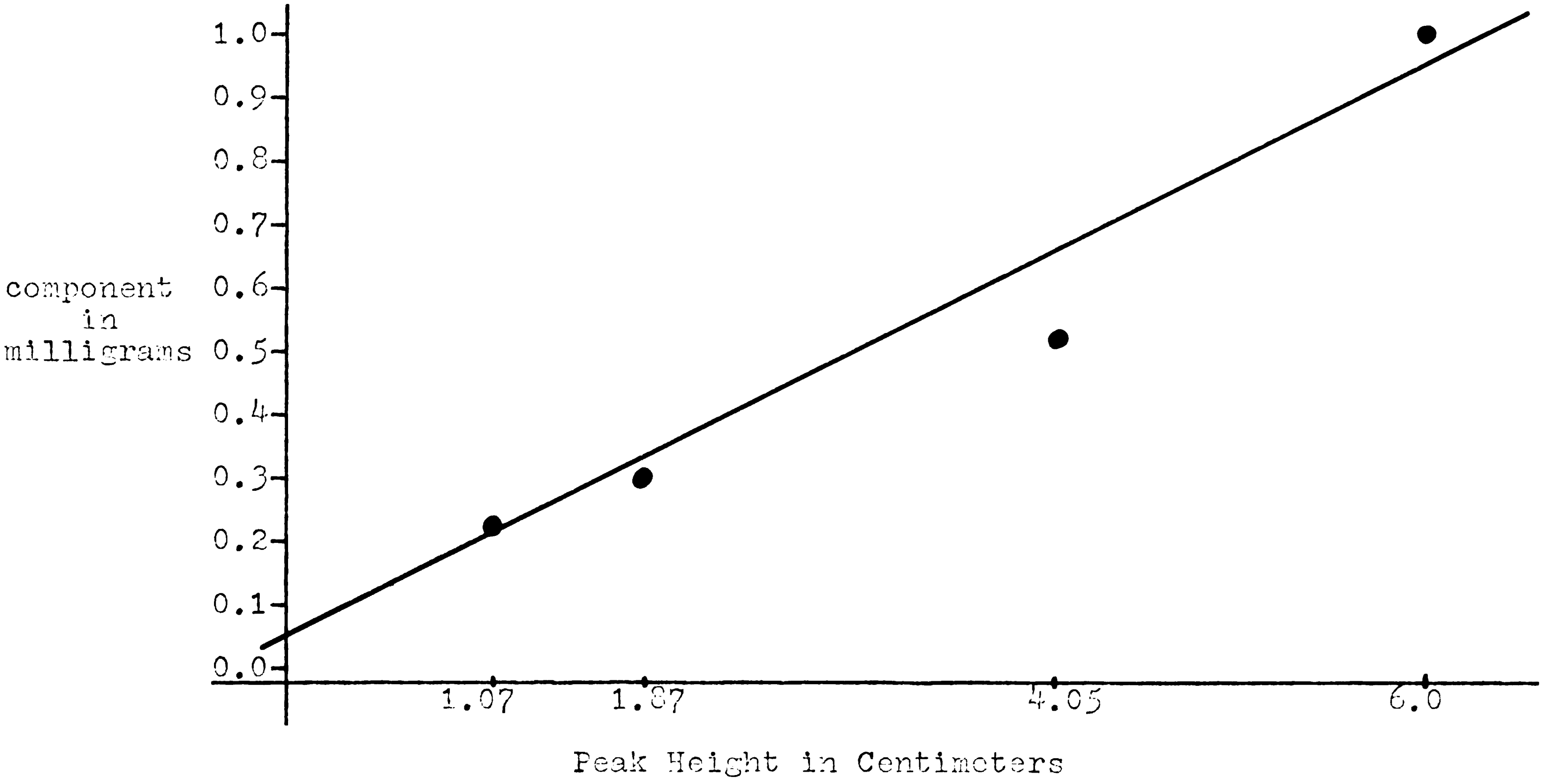


FIGURE VIII

Measured Height vs. Weight for Burrell K-7 Water Sensitivity Determination on 6.5 ft. x 3/16" Column



sample weight in milligrams is plotted against peak height in cm. that 0.05 μl. (5 x 10^{-5} gm.) of water must be present before water detection (any signal) is observed. There must be enough signal to measure area before the water percentage may be calculated in any case.

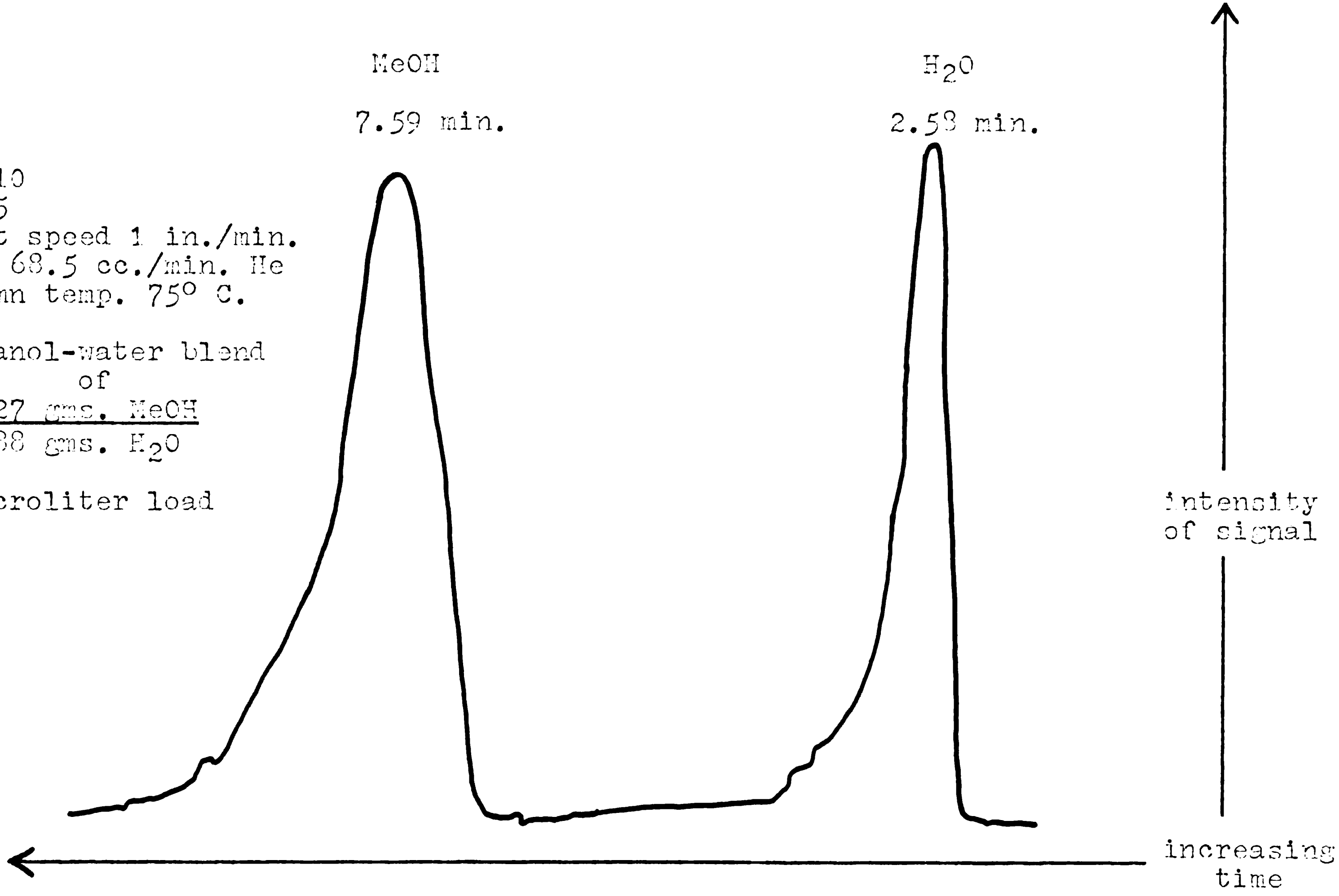
A graph of grams of water per cubic centimeter versus relative humidity at 23° C. (73.4° F.) was given in Figure I; it is indicated that at least a sensitivity of 1.0 x 10^{-5} gm. of water at 50% relative humidity must be present in any instrument for detection at the 50% R. H. level.

In order to compare the resolution efficiency of the Porapak column Figure IX is included. This is a reduced scale drawing of Trial #1 (EXP BK-7-3). The elution time for water is 2.58 minutes at 75° C. column temperature with a flow of ~68.5 cc./min. of helium in the Burrell K-7 instrument using the 3/16 in. x 6¼ ft. aluminum column.

A second column of stainless steel, 2.0 mm. I. D. x 2.5 meters long was packed with 10.2 cc. of Porapak Q and conditioned at 230° C. for 4 hours constantly being purged with helium. On this column an experiment was run to determine the relative sensitivity of this column versus the 3/16 in. column. The chart speed was set at ¼, the sample load was 2.0 μl. of distilled water, and the column flow was 40.0 cc./min. with a column temperature of 125° C. The average of three determinations was 164.1 cm.^{2}/μl. of

FIGURE IX

A Typical Chromatogram using Porapak Q



S = 10
A = 5
Chart speed 1 in./min.
Flow 68.5 cc./min. He
Column temp. 75° C.

Methanol-water blend of

$$\frac{1.0127 \text{ gms. MeOH}}{1.0088 \text{ gms. } H_2O}$$

1 microliter load

water loaded. These figures may be found in Table V.

One last experimental procedure was attempted with the Burrell instrument. The instrument was stabilized at 125° C. column temperature and a flow rate of 40.0 cc./min. He was established. The sensitivity was set at 10 and the attenuation at 1. These settings gave very high noise to signal ratios. A sample of 1.0 cc. of room air was injected. The instrument did not give a response for water. The emission current dropped to such a low level that it was not possible to increase the filament heater current high enough to obtain 0.8 milliampere emission current. This experiment was attempted 5 times and no meaningful water separation chromatograms were obtained.

At this point it was necessary to evaluate the thermal conductivity detector using the same column packing material in order to complete column and instrumental evaluations. A survey of the literature indicated that thermal conductivity is not as sensitive as ionization detection for organic vapors. A study of thermal conductivities of various gases and vapors indicated that the detection of water vapor appeared possible by thermal conductivity provided a large enough sample is used. See Table VI.

Table VI is a compilation of selected thermal conductivities taken from <u>International Critical Tables, Vol. 5</u> "Thermal Conductivity: Gases and Vapors," pages 213 - 216.

TABLE V

Burrell K-7 Minimum H_2O Detection Limit Experiment
Using a 2.5 meter x 2.0 mm. Stainless Steel Column

Trial	Sample Weight mg.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average	
							Pk. Ht.	Area
1	2.0	1.45	20.4		14.75		+4.15	+10.01
2	2.0	1.40	20.5	21.3	14.35	16.41	+3.74	+13.18
3	2.0	1.75	23.0		20.12		-7.89	-23.19

EXP BK-7-2mm: Speed ¼, 2.0 mm. stainless steel column 2,5 meter length,
Helium flow 40.0 cc./min., 125° C., S = 100, A = 5, 2 µl. load.

TABLE VI

Thermal Conductivities of Various Gases at 0° C.

$K = \text{kilo} \cdot \text{erg} \cdot \text{cm}^2 \cdot \text{sec}^{-1} (^\circ\text{C}, \text{cm}^{-1})^{-1}$

GAS	K
He	13.9
Air	~2.23
H_2	~15.9
H_2O	~209.0
O_2	~2.33
N_2	~2.28

The values are given at 0° C. which is a common reference point for which all could be compared meaningfully. That thermal conductivity is very sensitive to water vapor has been verified by much previous experimentation (2,9,10,11,23).

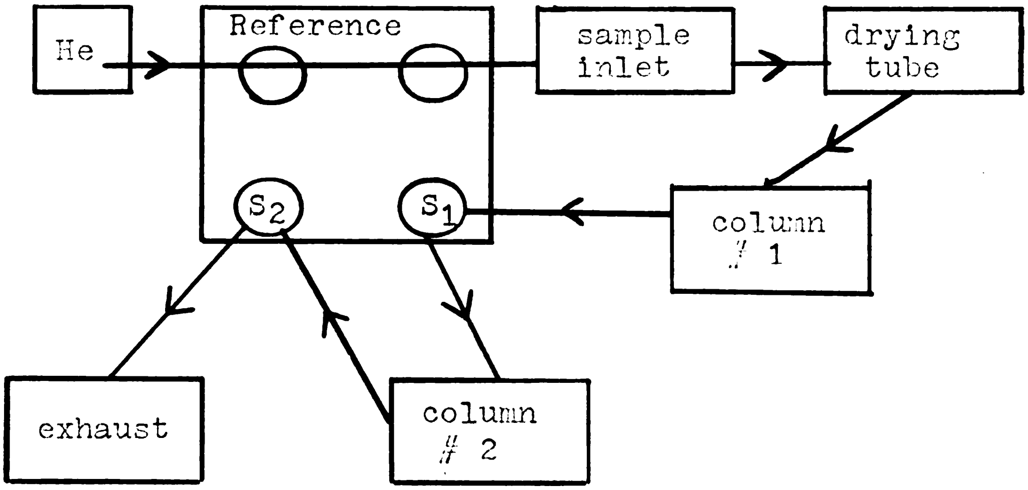
Due to favorable thermal conductivity of water vapor and the fact that thermal conductivity does not destroy the sample being analyzed as does ionization detection, an experiment to determine the Fisher Gas Partitioner (Model 25V) water sensitivity was performed.

An aluminum column 3/16 in. O. D. x 3 ft. was packed with 10.0 cc. of Porapak Q and it was conditioned at 230° C. for 4 hours. This column was installed in the Fisher Gas Partitioner. This instrument was used as a one column instrument by removing the drying tube and column #1 (see Figure X). A short 7½ in. copper tube was substituted for column #1 and the Porapak Q column substituted for column #2. The instrument was run at room temperature with the temperature held constant by a thermal stabilizer operating at 50° C. The column flow (helium) was adjusted between flow rates of 80 cc./ min. and 125 cc./min. for optimum separation and minimum elution times.

Three distinct component areas on the chromatogram were given at the 100 percent sensitivity range with the introduction of 1.0 cc. of laboratory room air. The first area is due to the composite peak measured by thermistor S_1,

FIGURE X

Present Chromatographic System



Column # 1: 30 in. x ¼ in. filled with 30% hexamethylphosphoroamide

Column # 2: 6½ ft. x 3/16 in. O. D. filled with Molecular Sieve 13X

S_1 and S_2 are detecting thermistors.

the second component is air measured by S_2, and the third small component is water also measured by thermistor S_2. The quantitative confirmation of the third component was done by using three separate measurement techniques. The first technique was to carefully set the helium carrier flow at 125 cc. per minute and inject multiple air samples, carefully measuring the elution time of the third component which was observed to be 0.60 minute. The second measurement technique was to introduce the same sample size of air from the humidity chest. The peak for the third component was observed to have the same elution time, 0.60 minute, but increasingly larger area. The third confirmation was to introduce a small sample of pure water and air by a microsyringe and to observe the elution time of the third component. It was 0.60 minute.

Great care must be used in this latter verification step due to the necessity of over-loading this instrument by the introduction of such a large sample; damage to the measuring thermistors may be caused. The controlled environmental room was at 47% relative humidity and 75° F. when the air samples were taken; this corresponds to 1.0×10^{-5} gm. of water in 1.0 cc. of air. The results of this data are tabulated in Table VII and instrumental conditions are specified in the table.

A reduced scale drawing of the chromatogram obtained

TABLE VII

Compilation of Data from the Fisher Gas Partitioner

Trial	Sample Volume cc.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average Pk. Ht.	% Deviation from Average Area
1	1.0	1.00	1.30		0.650		- 3.85	+25.5
2	1.0	0.90	1.30		0.595		- 3.85	+15.0
3	1.0	0.90	1.40		0.630		+ 3.85	+21.5
4	1.0	0.70	1.30		0.456		- 3.85	-11.9
5	1.0	0.70	1.30	1.350	0.456	0.518	- 3.85	-11.9
6	1.0	0.70	1.40		0.490		+ 3.85	- 5.40
7	1.0	0.75	1.35		0.507		------	- 2.12
8	1.0	0.65	1.45		0.472		+ 7.70	- 8.89

1.00 cc. air, 47% relative humidity, 75° F., equals 1.02 x 10^{-5} gm./cc. of air on a 3.0 ft. x 3/16" aluminum column with Porapak Q, flow 125 cc./min. He, column temperature at room temperature stabilized by a 50° C. differential bulb heater.

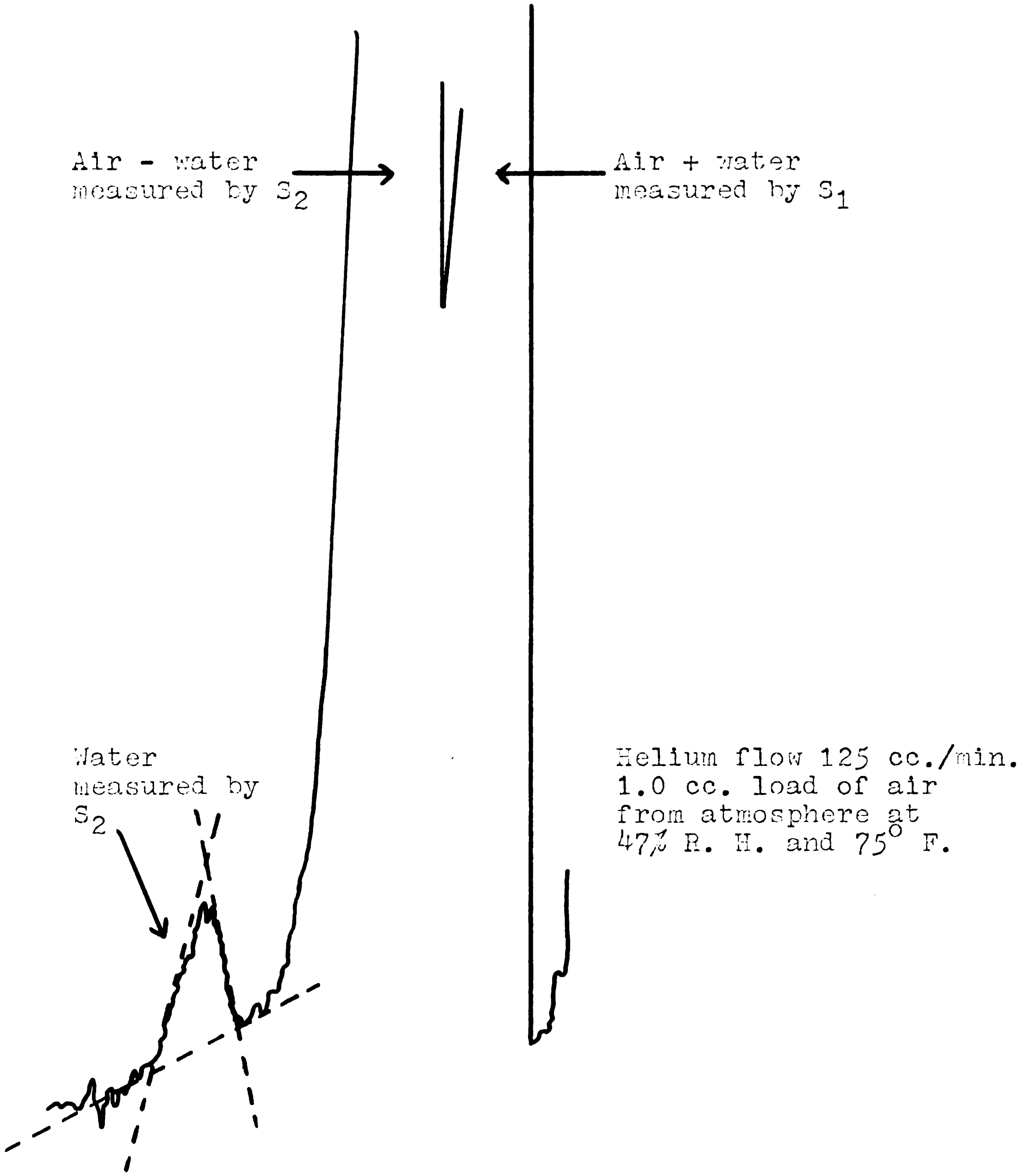
Trial	Sample Volume cc.	Full Band cm.	Peak Height cm.	Average Pk. Ht. cm.	Area ca. Triangle cm.^{2}	Ave. Area cm.^{2}	% Deviation from Average Pk. Ht.	% Deviation from Average Area
1	1.0	1.50	1.90		1.460		+16.94	+29.61
2	1.0	1.30	1.50		0.974		- 7.71	-16.62
3	1.0	1.30	1.70	1.625	1.110	1.148	+ 4.62	- 3.63
4	1.0	1.50	1.40		1.050		-13.85	- 9.36

Four samples taken from humidity cabinet and run between the above eight trials--no control over the temperature of the syringe.

by the Fisher instrument may be seen in Figure XI. It should be noted that the noise to signal ratio is high and some loss of precision may be inherent in the calculation of peak areas by using the normal chromatographic calculation method based on triangulation of the peak areas (11,23).

FIGURE XI

Fisher Chromatogram of Water in Air



Helium flow 125 cc./min.
1.0 cc. load of air
from atmosphere at
47% R. H. and 75° F.

CONCLUSIONS AND FUTURE WORK

Results and conclusions

A support material Porapak has been evaluated and found to possess excellent stability in a wide temperature range (up to 250° C.). These porous polymer beads are physically stable and they vibration pack well in small diameter columns at room temperature. Porapak did not bleed and it yielded excellent high temperature sensitivities. This material can be conditioned completely in four hours at 230° C. with a helium purge. Porapak has demonstrated the ability to separate water both in the liquid and vapor phase from other polar and non-polar compounds; the packing has shown the ability to separate water cleanly with minimum tailing and rapid elution times (0.60 to 5.0 minutes) dependent on column dimensions, carrier flow, and temperature. Porapak may be coated as any other column packing material and by possessing geometrical uniformity excellent chromatographic separations result.

The research has yielded water sensitivity data for both of the instruments presently used at the School of Packaging. The data from the evaluation of the Burrell instrument supports the statement that water in liquid form as well as water vapor may be detected. The Burrell was operated at a sensitivity level of 10 and an attenuation of

5. The data shows that a level of 3.00×10^{-4} gm./5 cm.^{2} (See Figure VII) would be obtained with the 6.5 ft. x 3/16 in. O. D. aluminum column. The data obtained using the 2.5 meter x 2.00 mm. I. D. stainless steel column further indicates separations using this column yield approximately 6.8 times as much signal as the 3/16 in. aluminum column does. From this data it appears that the 2.5 meter x 2.00 mm. I. D. stainless steel would have an easily attainable sensitivity of 2.1×10^{-5} grams per 5 cm.^{2} for water. This figure is relative in that an arbitrary area (5 cm.^{2}) is defined as the necessary minimum area required for chromatographic calculations. Even with this requirement the increase of the Burrell sensitivity by 50 times (the electronic maximum sensitivity level) would put the level of detection at 1.05×10^{-7} gm./5cm.^{2}, well below the minimum necessary to detect water between 1 - 100 % Relative humidity range in 1.0 cc. air at 73° F. This sensitivity indicates that indeed one may use the Burrell for water vapor measurements in air. It must be stressed that long and arduous conditioning and many instrumental corrections will be necessary before the Burrell instrument may be used quantitatively for either water or water vapor measurements. The Burrell instrument is extremely sensitive and reproducible to most organic compounds, and, with the non-bleeding characteristics of Porapak, this instrument appears better suited at present

for organic vapor separation and detection applications.

The Fisher instrument uses a thermistor thermal conductivity cell for detection and from the experimentation and the reduced scale drawing (Figure XI) there is undeniable evidence of the ability to measure water vapor in air. The obvious candidate for a chromatographic detection system of water vapor is a small cavity thermal conductivity cell fitted with nonreactive thermistors.

A reason for obtaining different instrumentation is that the preferred level of detection isin the order of 5 - 10% relative humidity. The Fisher Gas Partitioner appears to be limited at higher levels of water vapor due to the overloading and damaging of the metallic oxide thermistors. Liquid water sample measurements are presently prohibited using the Fisher instrument as there are no provisions for heating the columns and many adsorption-desorption (tailing) effects would be noted with liquid water samples. Because the column could not be heated, a flow rate of 125 cc./min. helium was necessary to minimize tailing when water vapor was separated on the Fisher instrument. Another reason for using thermal conductivity that is just as important as the sensitivity requirements is that ionization detectors destroy the sample whereas thermal conductivity cannot. One other advantage in thermal conductivity detection may be in the intrinsic simplicity of this detector which means that lower sensitivity but more stability and reliability in operation are usually noted.

As a means of comparing the Fisher with the Burrell K-7 the minimum sensitivity of the Fisher was calculated from the 8 trials of room air and using the arbitrary requirement of 5 $cm.^2$ area for the water peak. The Fisher will yield a maximum sensitivity of 1.01×10^{-4} grams per 5 $cm.^2$ compared with the maximum theoretical Burrell sensitivity of 1.05×10^{-7} gm./5 $cm.^2$.

From the summarized results four major conclusions may be stated.

1. Detection of water vapor in air has been accomplished using the Fisher Gas Partitioner.

2. The Burrell experiments indicate that under ideal instrumental operation the detection of water vapor in air would be easily accomplished.

3. The preliminary work with the Burrell indicates much developmental and instrumental conditioning will be necessary for use of this instrument for water measurement studies.

4. The reproduction of the Fisher chromatogram provides the School of Packaging with evidence of thermal conductivities sensitivity and ease of water vapor detection.

The best choice of detection for water vapor in air appears to be a small cavity thermal conductivity cell fitted to a temperature programmed two column gas chromatograph utilizing a system such as shown in Figure XII.

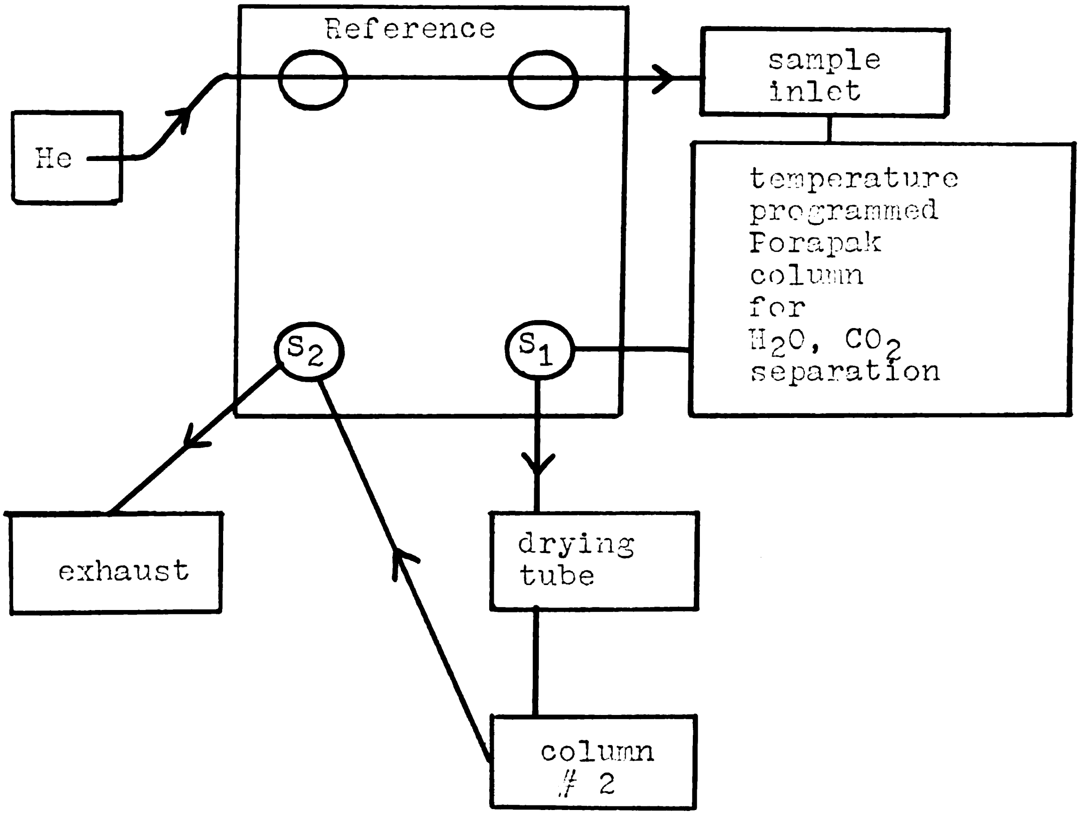
Future work

This section will first deal with suggestions to improve existing equipment, taking into consideration that the suggestion of acquisition of a temperature programmed small cavity thermal conductivity gas chromatograph appears to be the best approach to obtaining the desired sensitivity and versatility.

The suggestions for improving the Fisher apparatus are as follows: First, a system of columns such as shown in Figure XII would be successful if some external means of temperature programming the column were to be developed. Secondly, the sensitivity increase noted when column volume was reduced on the Burrell would also be noted in a thermal conductivity instrument such as the Fisher. The sensitivity of the Fisher Gas Partitioner was found to be 1.01×10^{-4} gm./5 $cm.^2$ **using** a 3.0 ft. x 3/16" column. If the volume of both the column and the thermal conductivity cell were reduced by a factor of 10, the sensitivity would be increased by 10. The cell volume may be changed easily and will not affect the separation efficiency; however, the column dimensions must be such that clean separations will be made.

FIGURE XII

Proposed Chromatographic System



S_1 and S_2 are detecting thermistors.

Water vapor and carbon dioxide would be trapped after detection at the S_1 detector by the drying tube and column #2; other separations (O_2, N_2) would be done on the #2 column utilizing the S_2 detector.

If the Burrell instrument is to be used for measuring oxygen-containing compounds (such as water vapor using the standard tungsten filament equipment), it must have some means of electronically maintaining stable electron emission levels. Another method less preferable would be to incorporate a method of injecting a hydrocarbon to chemically create a suitable filament environment.

Another way to eliminate this emission level instability would be to substitute a non-reactive material for the reactive tungsten. The tungsten filament may be changed to a non-reactive material such as rhenium (21,22) which does not form stable carbides; its nitrides are also unstable; its oxides are conducting and it is not involved in a water cycle in the same way as tungsten. A rhenium filament is limited by one drawback. This is that its vapor pressure is 156 times that of tungsten at the same electron emission, but the electrical resistivity of the material is higher so a larger diameter wire may be used. The life of rhenium is limited by evaporation, but it may be used for long periods quite well if proper electronic controls are observed. The life of the tungsten filament is not normally limited by evaporation, but rather by the fragility of tungsten recrystallized by prolonged heating at high temperature, and tungsten is caused to distill as the oxide by the forementioned water cycle phenomenon. Acceleration of the normal (brittle) hardening is also caused by this water cycle. With this filament material change one may also want to increase the amount of sample introduced into the ionization detector which would increase detector sensitivity.

One last instrumental change is recommended. The Burrell electronics, especially the electrometer circuit, should be stabilized.

This research dealt primarily with the chromatographic separation and detection of water vapor, and secondly with the application of this chromatographic separation and detection method to packaging research. The results of this work may be directly applied to further the technique of water vapor transmission rate measurements. This specific chromatographic technique may be also used in determining the water content of packaging materials. It may be used to analyze water absorbed by hygroscopic products as well as materials giving the package researcher another way of studying package performance. A third area of interest was to determine the other area in which gas chromatography may be applied to packaging research.

The time spent with the ionization detector instrument indicated that the Porapak material coupled with ionization detection will be an excellent way to study product degradation such as those found in food products (25). This area alone would yield a wealth of information and developmental data. The study of odor transmission rates as well as permeants such as O_2, N_2, CO_2, and water vapor would give design data to extend shelf life. The use of chromatography in studying residual solvents by S. G. Gilbert (5) illustrates but another area of application to packaging research. One more tool for the packaging engineer is found in gas chromatography. This research has enabled the School of Packaging to evaluate and plan for further use of this valuable tool in packaging research. Hopefully, this type of research will continue and the results utilized for solving packaging problems.

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