DESIGN AND DEVELOPMENT OF AN ISOSTATIC TEST METHOD FOR DETERMINING GAS PERMEABILITY RATES OF PACKAGES

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ABSTRACT

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An accelerated isostatic permeability test method was developed for potential use as a tool for predicting package shelf life and studying the effects of closures on package permeability rates. The results of accelerated and normal tests run on 1 mil polyethylene pouches, 2 mil polyethylene/phenoxy/polyethylene pouches, and low density polyethylene bottles indicated that (1) normal package permeability rates can be predicted in relatively short periods of time and (2) package permeability rates are affected by heat seals and other closure types.

DESIGN AND DEVELOPMENT OF AN ISOSTATIC TEST METHOD FOR DETERMINING GAS PERMEABILITY RATES OF PACKAGES

By

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INTRODUCTION

Recently, industry has demonstrated a definite need for a realistic accelerated test method to determine the gas permeability rates of completed packages. Historically, attention has primarily been focused upon the permeability rates of only packaging materials as opposed to that of the total package system. This is evidenced by the fact that published permeability values are for materials in sheet form only; little data is available which indicates the effects of package fabrication processes upon permeability rates of completed packages. As a result, the usual method of designing a package system having specific barrier properties is to consider only permeability rates of prospective materials. Any compensations for the effects of closures, creases, and handling of the package must either be neglected or accounted for by the introduction of so called "fudge factors", which can be predicted only by experience and lengthy field testing. The net result is often over- or under-packaging and a significant loss of valuable lead time. The development of a widely applicable accelerated package test method for the determination of package system permeability rates would provide an extremely valuable tool for use in the design of packages having specific barrier properties.

Gas permeability test methods

In general, there are three test methods for determining gas permeability rates of packaging materials in sheet form. These are: (1) Volume increase, (2) Pressure increase, and

(3) Concentration increase. In each of these methods, volumes assumed by test cell cavities are placed in direct contact with each side of the test material. A gasketed hermetic seal is maintained between the cell halves and the material by an applied compressive force. This, however, is the extent of similarities among these methods. The characteristics of each are briefly described below; a more detailed discussion is offered by Taylor, Karel, and Proctor (1).*

Volume increase method

In this method, introduced in 1944, by Russell (2), the driving force of the permeating gas, usually oxygen, is obtained by applying a 1-atmosphere total pressure gradient across the test material. The gas moves from the high pressure to the low pressure side of the cell by permeating through the material. The volume change on the low pressure side of the cell is measured by the movement of a mercury bead in a horizontal capillary tube. Thus, the permeation rate of the gas of interest through the test material is recorded as this change in volume.

Pressure increase method

This test method (3), introduced in 1944, by Schuman (4), is similar to the volume increase method in that a 1-atmosphere total pressure gradient across the material is also required as

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*Numbers in parentheses correspond to literature cited.

the driving force for the permeating gas. As the gas permeates through the material, a resultant capillary pressure change in the low pressure side of the cell is manometrically measured. This pressure change serves as an indication of the volume of gas permeating through the material and is converted to appropriate units by subsequent calculations.

Concentration increase method

The concentration increase method is based upon an application of Dalton's law of partial pressures.* The driving force for the permeating gas is provided by a partial pressure gradient across the material, not a total pressure gradient as with the previously mentioned methods. Thus, if opposite sides of a membrane are each occupied by a different pure gas at ambient pressure, a 1-atmosphere partial pressure driving force is exerted by each gas; a total pressure gradient does not exist. The amount of gas A that permeates through the material is determined by measuring its increased concentration in a second gas, B.

This phenomenon was utilized by Davis (5) when he developed his isostatic test method for materials in sheet form. In this method, two gases, oxygen and nitrogen, were swept over either side of the test material. An increase in the oxygen concentration of the flowing nitrogen was caused by oxygen permeating through the material and into this stream. This

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*Dalton's law states that each gas in a mixture of gases behaves as if it alone occupied the volume occupied by the mixture.

concentration increase was measured and used to determine the oxygen permeability rate of the material.

Although these three test methods are adequate for determining gas permeability rates of materials in sheet form, their present cell designs cannot be adapted to total package testing. It was therefore the purpose of this study to develop a test apparatus and method to determine gas permeability rates of entire package systems.

Goals of the Study

Certain attributes must be incorporated into test apparatus design before any package permeability test method can become functional. These attributes are as follows:

(1) The package test method must permit the entire package to be tested under the same conditions under which its material was tested. This will enable the effects of package fabrication processes to be studied.

(2) The test method must have provisions for the introduction of humidity, temperature, and pressure variables actually present in product distribution channels.

(3) The test method should permit the package to be tested with minimum structural alterations.

(4) The test method should be applicable to all types of packages.

(5) The package should be subjected to maximum permeability acceleration at all times. This will keep test time to a minimum.

(6) The test method should permit testing by semi-skilled personnel.

Development and construction of a realistic accelerated total package permeability test method was undertaken with the incorporation of these attributes as primary objectives.

REVIEW OF LITERATURE

Numerous attempts at measuring the gas transmission rates of completed packages are illustrated in the literature. A brief review of these articles is in order.

In 1947, Cartwright (6) filled Ottawa test sand into packages; the resultant air space could then be flushed with a gas or evacuated. After exposure to air, the oxygen transmission rate was determined by measuring internal package pressure changes using a bell jar method.

Later, a test for the qualitative and quantitative determination of leaks in heat seal areas was designed by Hu and Nelson (7). Leaks were detected by placing a pouch having a known internal pressure under water. Seal porosity was indicated by the emergence of air bubbles from the pouch. By gradually increasing internal pouch pressure, heat seals could be evaluated as a function of the pressure at which leaks occurred.

In 1954, film was wrapped and sealed around acrylic forms by Ellickson, Hasenzahl, and Hussong (8). The form was wrapped while in a chamber containing either carbon dioxide, oxygen, or nitrogen. To study the passage of the gas from inside to outside the pouch, the wrapped form was placed in a gas-tight container. The wrapped form was surrounded by air; gas samples taken from the container void were analyzed for concentration of the gas of interest with a Pitts manometric analyzer. After completion of the test, the wrapped acrylic form was placed under water and the remaining gas was collected in a burett over a column of water; this gas was then analyzed by an Orsat apparatus. The gas transmission rate was determined from these gas concentrations.

In 1957, a test method somewhat similar to the one proposed by Ellickson, Hasenzahl, and Hussong, was introduced by Brickman (9). A molded styrene shell was inserted into a pouch, thus providing a basis for nearly constant volume. A small rubber patch was cemented to the pouch to provide a region for hypodermic needle insertion for pouch volume determination. The pouch was flushed and filled with nitrogen to a pressure that provided minimum distortion. Eight to ten units having equal surface areas were exposed to air for the duration of the test. Air was chosen as the test condition so as to maintain realistic partial and total pressures during the course of the test. The oxygen transmission rate was determined from the free gas space volume of the pouch, the area of the pouch, the elapsed test time, and the change in partial oxygen pressure within the pouch. Due to the extremely low transmission rates of many package systems, exposure times of twenty to thirty days were often required before any significant data was collected.

During 1954, a departure from strictly oxygen transmission rate determination for packages was made by Pinsky, Nielsen, and Parliman (10). In this method, four-ounce polyethylene bottles were weighed and filled to the shoulder with various organic liquids. The bottles were then subjected to various test conditions and weighed at intervals of one day, five days, ten days, one month, three months, six months, nine months, and twelve months. The recorded weight change was then converted to a permeability coefficient for each package/liquid combination.

In 1964, an acceleration test method for oxygen permeability rates of entire packages was described by Leonard (11). The theory behind the test was to expose the package to higher than normal concentrations of oxygen. In this method, pouches were filled with marbles or cork to represent and maintain a volume. The pouches were placed in a gasket-sealed 55 gallon drum flushed with oxygen to give a mean oxygen atmosphere of 90 percent. At selected intervals, one package was removed from the drum and analyzed for headspace oxygen content. The drum was reflushed with oxygen at the beginning of each sample interval. The package oxygen transmission rate was determined from the change in percent oxygen as a function of elaspsed test time.

Summary and proposal

Although each package permeability test method discussed above can meet at least one of the previously stated attributes of a desired package test method, none can meet all these requirements. Accelerability was lacking in those test methods using air as the exposure medium; no realistic quantitative permeability value could be obtained from Hu and Nelson's method of heat seal evaluation. The methods proposed by Ellickson *et al.* and Leonard, however, meet the stipulated requirements better than any other method cited. While keeping the above in mind, it was decided to proceed with the development of an isostatic, i.e., concentration increase, total package permeability test method. This method was most easily adaptable to all design attributes and afforded a good supplement to the existing Davis cell material test system at the Michigan State University School of Packaging.

DEVELOPMENT OF THE PACKAGE TEST APPARATUS

The development of an isostatic permeability test system was undertaken with the intention of providing a test apparatus in which the permeability rates of a wide variety of package types and sizes could be determined while at the same time minimizing alterations to the test package. It was felt that a test chamber constructed of acrylic plastic could not only meet all test requirements but could be easily worked into any desirable design with standard wood working tools.

The top of a Dura-Vac Plexiglas vacuum desiccator, manufactured by Ace Glass Incorporated, Vineland, New Jersey, was utilized as the base of the adopted test chamber. This portion of the chamber was hemi-spherical in shape, was equipped with a stopcock at its bottom, had an internal diameter of 10 inches, and enclosed a volume of 3700 cubic centimeters. A second desiccator top was reduced in volume by cutting off a portion of its bottom and inserting a paraffin sleeve. The volume of this base was thus reduced to 1400 cubic centimeters; with the paraffin sleeve not inserted, the volume was 3500 cubic centimeters. The stopcock was retained in this design. Both bases are illustrated in figure 1.

A flat sheet of 1/4-inch Plexiglas, fabricated into a flat disc 14 inches in diameter, served as the top of the test chamber. The top was sealed to the chamber base with "C" clamps and silicone stopcock lubricant, thus permitting access to the chamber interior.

Two 1/4-inch copper tubing fittings were secured in the chamber top with epoxy cement. The first was a tee located approximately 2 inches from the center. The tee was fitted with a silicone rubber septum in one end of its straight-through opening; a 2 inch long piece of 1/4-inch copper tubing with Hoke valve attached was soldered to the branch opening of the tee. The assembly was then secured in the chamber top so as to permit sampling of the internal chamber environment through the septum.

A brass Swagelok bulkhead female connector (tube O. D. 1/4-inch; female pipe size 1/8 inch), with a 2-inch long piece of 1/4-inch copper tubing soldered into the side of its female end, was secured in the dead center of the chamber top. The bulkhead connector was arranged so as to have its female end exposed to the interior of the assembled test chamber. The side tube of the connector was fitted with an elbow which was placed through a third hole in the chamber top; a Hoke valve was fastened to the end of this tube. The end of the bulkhead connector exterior to the chamber, after having its lock nut secured, was cut off even with the nut and fitted with a silicone rubber septum. The septum was provided to permit sampling from the internal environment of the test package. All joints between the chamber top and tubing fittings were made gas-tight by using epoxy cement and black glyptal paint. The chamber top is illustrated in figure 2.

A brass Swagelok male connector (tube O. D. 1/4-inch; male pipe size 1/8-inch) was altered to permit its use as an

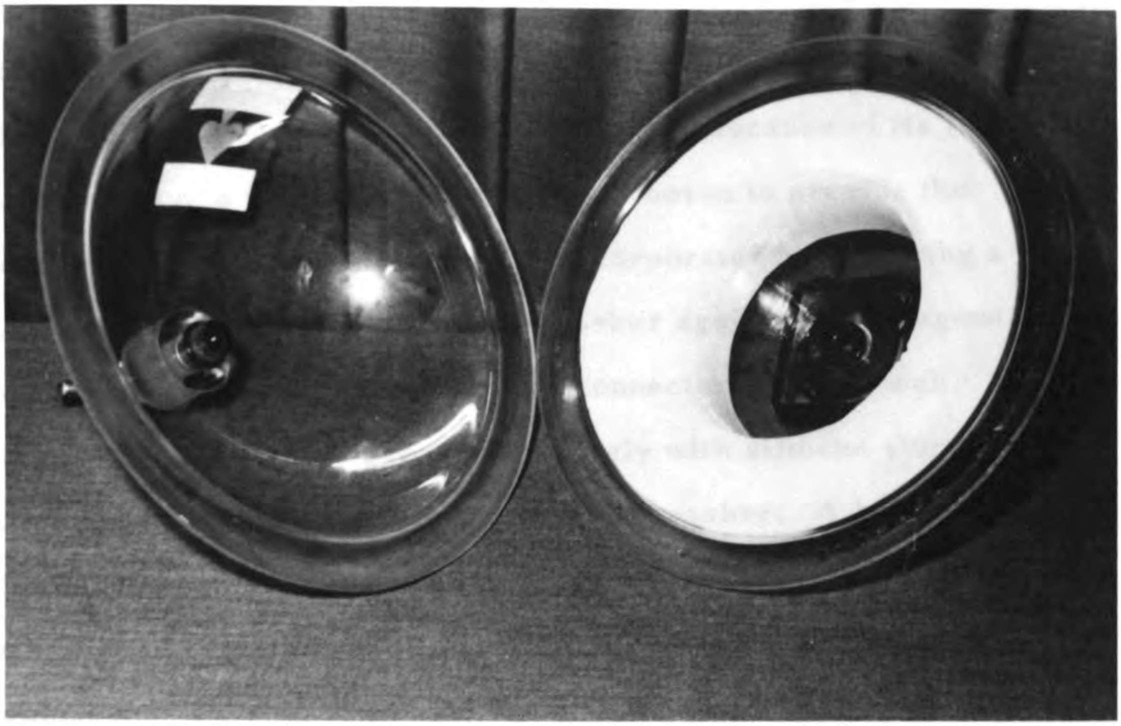

Fig. 1 -- 3700 cubic centimeter (left) and 1440 cubic centimeter test chamber bases.

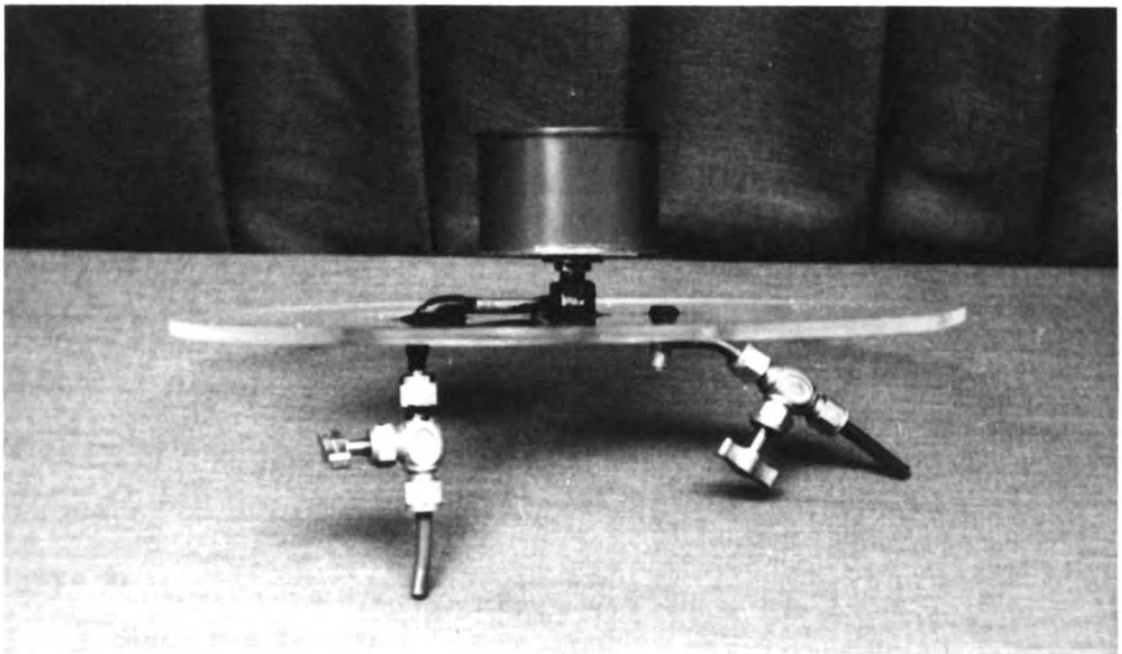

Fig. 2 -- Test chamber top with an absolute gas barrier package in test position.

adapter fitting for connecting the test package to the female end of the bulkhead connector described above. Because of its low permeability, a neoprene "O" ring was chosen to provide the seal for this connection. This was incorporated by soldering a 7/16-inch (1-inch O. D.) flat steel washer against the hexagonal portion of the female end of the male connector. A 3/4-inch diameter "O" ring was greased sparingly with silicone stopcock lubricant and placed against the soldered washer. A 1/2-inch diameter hole was made in one wall of a test package; this hole was slipped over the end of the adapter fitting and pressed against the "O" ring with a second washer and lock nut. Provisions were required to permit the application of the test package closure only after the package adapter fitting had been properly fastened to the package. The bulkhead connector and assembly sequence of the package adapter fitting are illustrated in figure 3.

The completed test package, with the package adapter fitting in place, was suspended from the chamber top by screwing the male end of the package adapter fitting into the female bulkhead connector. Although this connection was via pipe threads, a small amount of silicone stopcock lubricant was placed on the threads prior to tightening to insure a hermetic joint. The test chamber top was placed on the chamber base and sealed as illustrated in figure 4.

Since the driving force of the permeating gas in isostatic permeability test methods is the partial pressure gradient of that

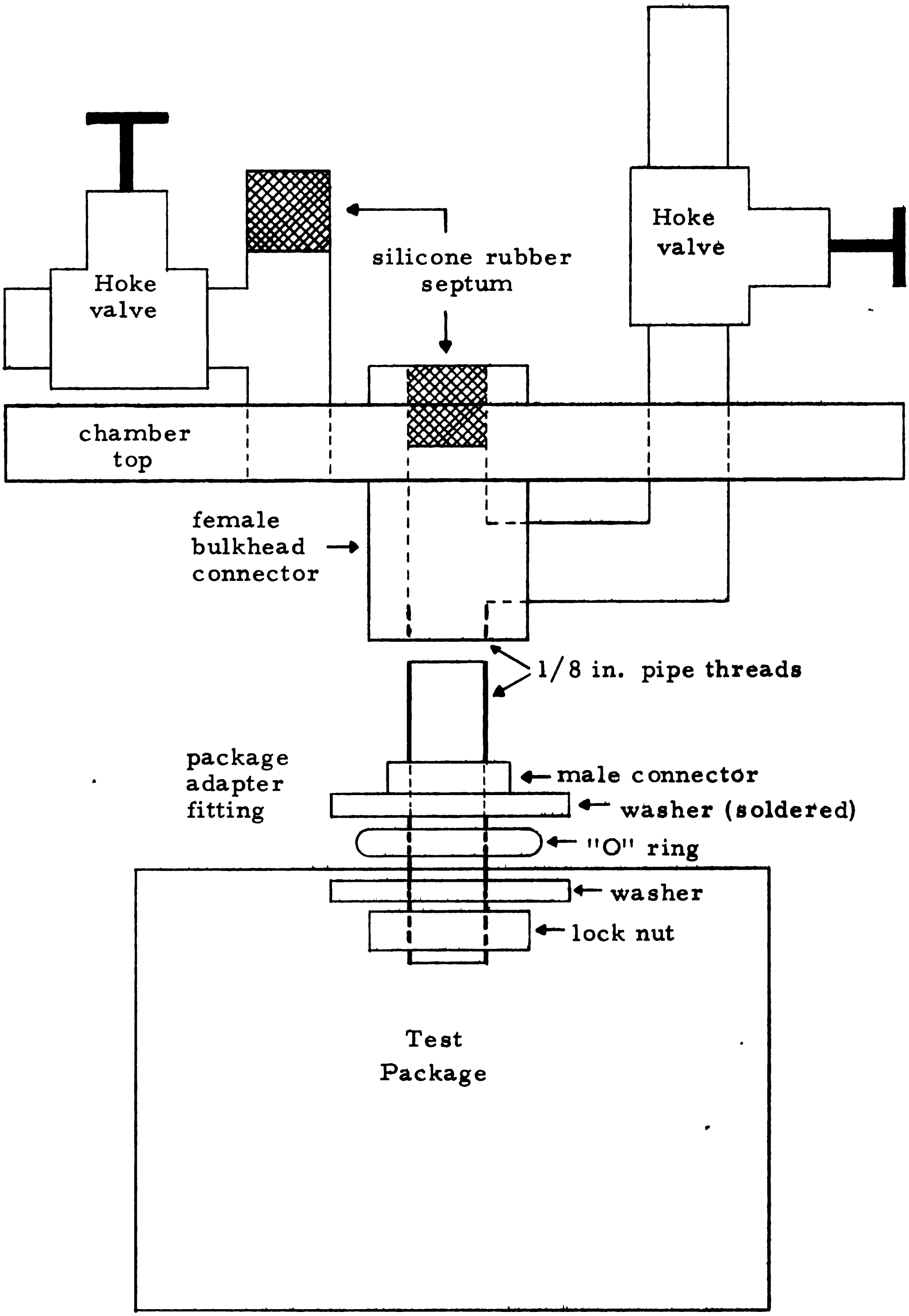

Figure 3. Female bulkhead connector/package adapter fitting assembly sequence.

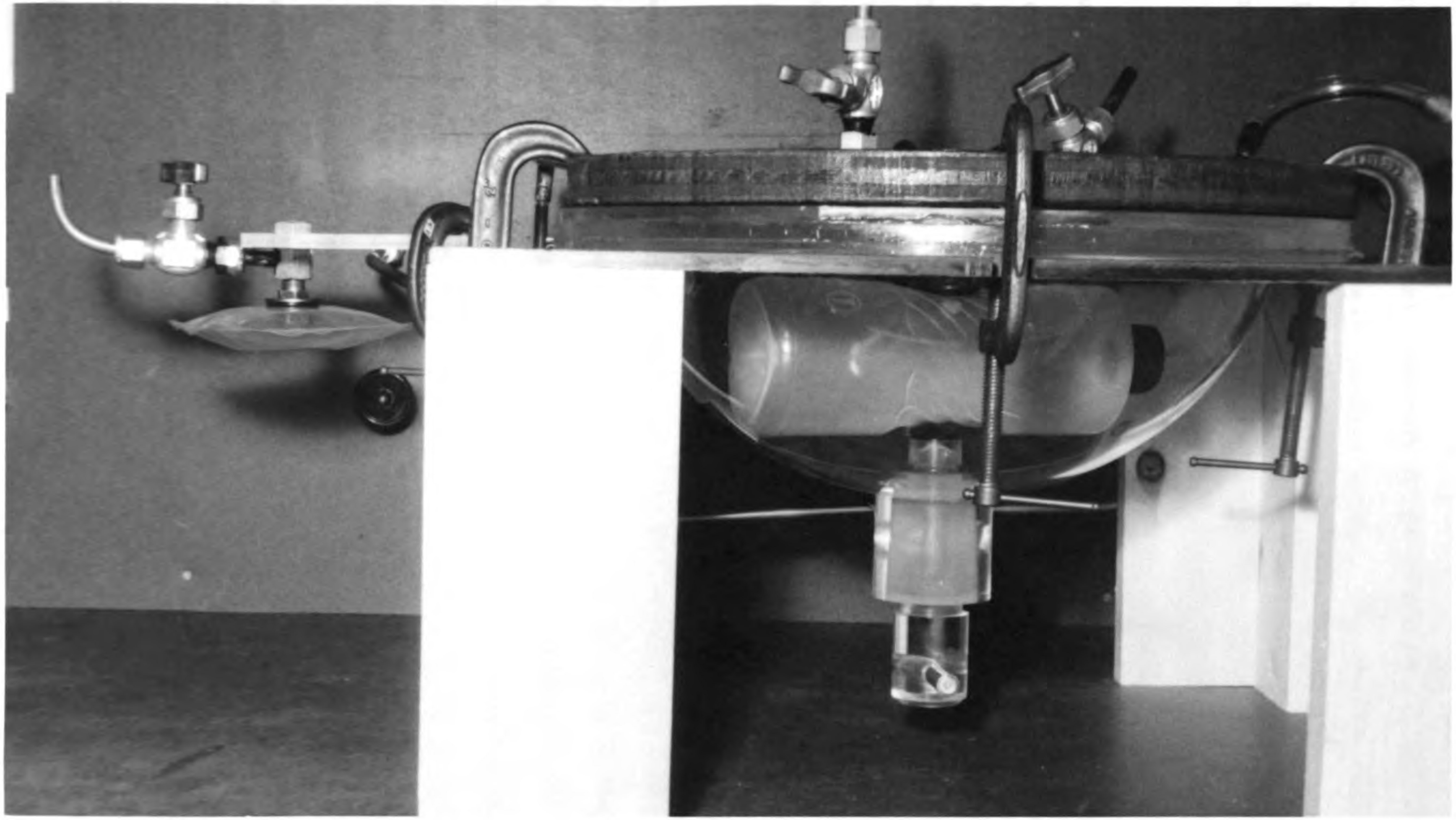

Fig. 4 -- Assembled package test apparatuses with (left) a pouch being subjected to normal test conditions and a polyethylene bottle being subjected to accelerated test conditions.

gas across the material, different gases must occupy the test package interior and test chamber proper. The test package was flushed with nitrogen for a period long enough to insure an approximate nitrogen concentration of 100 percent. This was accomplished by inserting a 2-inch X 25-gauge hypodermic needle through the bulkhead connector septum and into the test package. This needle was connected to an extension of the nitrogen side of the Davis test cell flow system described by Lockhart (12). Flushing of the test package was accomplished by the flow of nitrogen through the flush needle, into the package, and out through the tubing soldered into the female bulkhead connector. The package interior was secluded (sealed) from atmosphere by closing the Hoke valve on this tube.

The high percentage oxygen atmosphere in the test chamber was provided by the introduction of oxygen through the stopcock located in the bottom of the chamber. It was felt that the arrangement of four holes placed in the end of the stopcock core by the manufacturer would provide a good flow and distribution pattern for the test gas. The source of oxygen was an extension of the oxygen side of the same Davis cell flow system cited above.

Several preliminary checks of the test apparatus were required before accelerated permeability testing of packages could begin.

The purpose of the first check was to determine the flow pattern of the test gas, oxygen, over the surface of the test package. This was accomplished by coating a test pouch with lead sub-acetate. The pouch was secured in the test position inside the test chamber and had hydrogen sulfide introduced around it. Upon reaction with hydrogen sulfide, the lead sub-acetate, a white powder, was converted to lead sulfide, a black power.

$$\underset{\text{White}}{Pb(C_2H_3O_2)_2} + H_2S \longrightarrow \underset{\text{Black}}{PbS} + 2C_2H_3O_2 + 3H_2O$$

Thus, the color change of the lead sub-acetate on the pouch served as an indication of the test gas flow pattern. It was shown by visual observation that the test gas flowed from the bottom to the top of the chamber in a pattern evenly distributed about the vertical axis of the chamber.

A second check was conducted to determine the length of time required to develop and maintain a high oxygen concentration within the test chamber. This was determined by analyzing the test chamber atmosphere at selected intervals after initial introduction of oxygen into the chamger. Test gas flow rates of 1050 cc./min. and 310 cc./min. were examined. Chromatographic analysis showed that for both flow rates, a chamber atmosphere of approximately 98 percent oxygen was obtained and maintained after forty minutes. It was therefore decided to run all permeability tests with an oxygen flow rate of 500 cc./min. and a sweep gas (nitrogen flush) flow rate of 100 cc./min.

Determining the total package oxygen permeability rate

It was decided that the accelerated package test chamber should be proven practical by testing several package types for their respective oxygen permeability rates.

The preliminary step in the determination of such permeability rates was to measure the aggregate leakage rate of the package adapter fitting/package seal, the bulkhead septum, and the Hoke valve in the tube branching from the bulkhead fitting. This was measured by securing an absolute gas barrier package, a 214 X 200 sanitary can cut down to 214 X 100, in the test position. (See figure 2.) The can was flushed with nitrogen and then "sealed" by removing the flush needle and closing the Hoke valve described above. Two-tenths cubic centimeter gas samples taken from the can interior at selected intervals were analyzed for oxygen content; the resulting oxygen percentages were plotted as a function of elapsed test time. The volume of the bulkhead connector, the copper tube to the Hoke valve, and the package adapter fitting was determined by mercury displacement and found to be 3.50 cubic centimeters; the volume of the can was 54.4 cubic centimeters, again measured by mercury displacement. Thus, the total volume of the leak blank was 58.0 cubic centimeters. The total leakage rate, expressed as cc. O_2/24 hr., of the adapter fitting, the Hoke valve, etc., was given by the product of the plot slope and the leak blank volume. A mean leakage rate of 0.041 cc. O_2/24 hr. was found in two test runs. Except for those packages with extremely low oxygen permeability rates, this value was found to be insignificant and could therefore be neglected.

Although the primary purpose of the initial accelerated package permeability tests was to determine if a given permeability acceleration factor applicable to all packages could be used to accurately predict shelf life, it was decided that a cursory examination of the effect of various package fabrication processes upon the oxygen permeability rate of the completed package would also be beneficial. To accomplish this, two flexible packaging materials, 1 mil polyethylene (Dow Polyfilm, Type 114T-1) and 2 mil polyethylene/phenoxy/polyethylene (Pollock Paper Company, P.S.G.P. No. 6A), were fabricated into 3-1/2-inch X 3-1/2-inch four-sided pouches and tested for oxygen permeability under both accelerated and normal conditions. The same materials were also tested in sheet form with the School of Packaging's Davis test cell. Two, blow-molded, low density polyethylene bottles (Owens-Illinois Plastainer) were also tested.

To establish a control test method, i.e., the exposure of packages to normal atmospheric conditions, a second Swagelok female bulkhead connector/male connector arrangement was constructed. With the exception of volume, this arrangement was identical in every respect to the setup on the test chamber. The bulkhead connector was secured in a small sheet of Plexiglas which was in turn clamped to the chamber frame with "C" clamps. (See figure 4.) The volume of this assembly was determined by mercury displacement and found to be 2.00 cubic centimeters.

The package adapter fittings were fastened to each respective material sheet as illustrated in figure 3; pouches were then fabricated with a Sentinal model 12TP impulse heat sealer. Heat sealing variables of 30 psi. jaw pressure, 0.7 second dwell time, and 6 seconds cooling time were maintained for all pouches. A small corrugated fibreboard jig was utilized to control pouch dimensions, which were separately measured for each pouch. Each pouch was secured to its respective bulkhead connector, placed in its appropriate test environment, flushed with nitrogen, and closed in a manner identical to that of the leak test. Although the control test package was exposed to the same temperature as the accelerated test package, the relative humidity of the control environment was 50 percent while that of the accelerated environment was 0 percent. This difference in humidities presented a potential problem as far as the validity of the control test was concerned. However, oxygen permeability tests conducted on 1.5 mil polyethylene in relative humidities ranging from 0 percent to 83 percent yielded mean rates ranging from 2980 cc./24 hr. M^2 to 3100 cc./24 hr. M^2. Thus, it was concluded that relative humidity had no significant effect upon the permeability rate of polyethylene. The volume of each pouch was determined at the end of each test run by withdrawing its contents with a hypodermic needle and 50-cubic centimeter syringe. The volume was indicated on the syringe barrel by the position of the syringe plunger after complete extraction of the gas within the pouch. Each pouch was tested only once, as the method of volume determination introduced numerous wrinkles and creases in the pouch walls.

Except for the method of volume determination, the polyethylene bottles were tested in a manner identical to that of the pouches. A package adapter fitting was placed in the side of each respective bottle midway between the shoulder and base. The bottles were closed via screw-caps, which were applied with a 10 in. lb. torque, and fastened to the chamber top in the usual manner. Due to the relatively large bottle diameter, a 1/4-inch donut-shaped Plexiglas spacer was placed between the chamber top and the 3700 cubic centimeter base. Thus, 1/4 inch in depth and approximately 300 cubic centimeters in volume were added to the test chamber. Each bottle was tested twice, once under accelerated test conditions and once under control or normal test conditions. After completion of the tests, the bottle volumes were determined by water displacement.

At selected intervals during the course of each test run, samples of the test package volume were analyzed for percentage oxygen concentration. A plot was made of percentage oxygen as a function of elapsed time. The quantity of oxygen permeated was yielded by the product of the plot slope ($\% \ O_2/24$ hr.) and test package volume. The permeability rate of each pouch was converted to cc. $O_2/24$ hr. M^2 by dividing the above product by the pouch surface area (in square meters); bottle permeability rates were expressed as cc. $O_2/24$ hr. The method of permeability rate calculation is described in appendix B.

DISCUSSION OF TEST RESULTS

The permeability rates of the packages and films tested are tabulated in tables 1, 2, and 3. The versatility of the accelerated package permeability test chamber was revealed upon examination of these tables.

TABLE 1

OXYGEN PERMEABILITY RATES MEASURED FOR 1 MIL POLYETHYLENE IN SHEET AND POUCH FORMS

Test run	Oxygen permeability rate (cc./24 hr. M^2)		
	Sheet form	Package form	
	Accelerated test	Accelerated test	Normal test
1	4710	5890	1180
2	4210	8520	1400
3	----	7010	----
$\overline{X}$	4460	7140	1290

TABLE 2

OXYGEN PERMEABILITY RATES MEASURED FOR 2 MIL POLYETHYLENE/PHENOXY/POLYETHYLENE IN SHEET AND POUCH FORMS

Test run	Oxygen permeability rate (cc./24 hr. M^2)		
	Sheet form	Package form	
	Accelerated test	Accelerated test	Normal test
1	189	247	38.8
2	188	242	43.0
$\overline{X}$	189	245	40.9

TABLE 3

OXYGEN PERMEABILITY RATES MEASURED FOR LOW DENSITY POLYETHYLENE BLOW MOLDED BOTTLES

Bottle	Oxygen permeability rate (cc./24 hr.)	
	Accelerated test	Normal test
A	9.29	1.66
B	8.45	1.42
$\overline{X}$	8.87	1.54

When the accelerated and normal permeability rates of a given material or package tested under identical conditions, i.e., temperature, etc., are compared, it would be expected that the normal oxygen permeability rate would be accelerated by a factor equal to the ratio of the oxygen concentration of the accelerated test condition to the oxygen concentration of the normal test condition. Since the oxygen concentration of the accelerated package test chamber was maintained at approximately 98 percent as compared to 21 percent for normal conditions, an acceleration factor of 98%/21% or 4.7 would be obtained. Thus, the oxygen permeability rate of a package exposed to 98 percent oxygen would be expected to be 4.7 times greater than the rate resulting from exposure of the same package to air.

However, when the accelerated oxygen permeability rates of the pouches and bottles tested in this study are compared to the normal oxygen permeability rates of the same packages, mean acceleration factors of 5.3, 5.9, and 5.8 are obtained for the 1 mil polyethylene pouches, 2 mil polyethylene/phenoxy/polyethylene pouches, and low density polyethylene bottles respectively. Thus, any package, when tested according to the accelerated method put forth in this study, yielded an oxygen permeability rate approximately 5.7 times greater than the rate resulting from exposure of the same package to air.

Several investigations were made in an attempt to explain this discrepancy between the predicted acceleration factor of 4.7 and the actual acceleration factor of 5.7. It was first thought that because of the greater permeability rate of oxygen than nitrogen, the volume of a pouch under test would increase as elapsed time increased. Since the pouch volume was determined only at the termination of the test run, the volume measured would be maximum at that time. Thus, the product of the plot slope (% O_2/24 hr.) and the pouch volume would give an oxygen permeability rate fictitiously high. The net result would then be an acceleration factor greater than 4.7. This theory, however, was refuted when the same logic was applied to the polyethylene bottles. These bottles, having a relatively rigid structure, could not increase in volume as elapsed test time increased. Instead, a decrease in the oxygen partial pressure gradient across the bottle walls would be the only change. The net result would be a reduction in the oxygen permeability rate, which in turn would yield a lower than expected acceleration factor. As was noted earlier, an acceleration factor of 5.8 was obtained from bottle data.

A second theory, which considered a possible pressure build-up in the test gas portion of the test chamber, was also investigated. It was thought, that due to the relatively high oxygen flow rate, i.e., 500 cc./min., through the test chamber and the comparatively small orifice of the test gas exit port, a chamber pressure greater than atmospheric pressure would create an oxygen partial pressure gradient greater than expected. If this was true, the test gas gauge pressure within the test chamber would be approximately 190 mm.* However, when the test gas pressure was measured with a mercury manometer, no measurable pressure was recorded. This measurement was supported when air was substituted for oxygen as the test gas; an acceleration factor of 5.9 was again obtained. Thus, this theory was also rejected.

It was also thought that the test gas flow rate, i.e., the velocity of oxygen over the surface of the package in the accelerated test chamber, could be used to explain the unexpected acceleration factor. However, as was noted above, an acceleration factor of

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*This was calculated from the actual acceleration factor and the partial pressures of oxygen in atmospheres of air and 98 percent oxygen, each at 760 mm. pressure.

5.9 was obtained when air was substituted, at an identical flow rate, for the oxygen test gas.

Although the above explanations of the higher than expected acceleration factor did not prove fruitful, it is hoped that more detailed inspection will yield the underlying factors contributing to the problem.

The effect of heat sealing upon the oxygen permeability rates of polyethylene and polyethylene/phenoxy/polyethylene films was revealed by a dissection of tables 1 and 2 respectively. The oxygen permeability rate of 1 mil polyethylene increased 83 percent when tested in pouch form as compared to the sheet test; the oxygen permeability rate of 2 mil polyethylene/phenoxy/polyethylene increased 30 percent when subjected to identical tests. These results indicate that the application of heat seals to these materials caused an increase in oxygen permeability rates. Witte (13), however, reported that permeability rates for the same materials were unaffected by the application of fin and overlap heat seals. Although at a glance it appeared as if the results of Witte's work were in direct contradiction with the results of this study, a closer examination of test methods revealed that he tested only the linear portion of seals; both the linear portion and overlap corners were tested in this study. Thus, it seems as if pouch corners and heat seal overlaps are possible weak points in the barrier properties of pouches constructed of the two materials tested.

It also appears that heat sealing produced wider variations in oxygen permeability rates of polyethylene than polyethylene/phenoxy/polyethylene. Table 4, shows that oxygen permeability rates varied as much as 19 percent of the mean for the former while varying only 5.1 percent for the latter.

A situation similar to polyethylene film can be observed for the polyethylene bottles. It appears as if screw-cap closures caused some, although less than the polyethylene pouches, variability in bottle permeability rates.

Since it was not the purpose of this study to evaluate the effects of heat seals and other closures upon package permeability rates per se, more intense examination was not attemped at this time. The data obtained in this study does, however, provide an interesting starting point for future study.

TABLE 4

PRECISION OF THE TEST METHOD EXPRESSED AS MAXIMUM PERCENT DEVIATION OF INDIVIDUAL PERMEABILITY RATES FROM THE MEAN RATE

	Test method		
	Sheet form	Package form	
Material	Accelerated test	Accelerated test	Normal test
1 mil polyethylene	5.5%	19%	8.5%
2 mil polyethylene/ phenoxy/ polyethylene	0.53%	1.2%	5.1%
Low density polyethylene bottle	----	5.0%	9.4%

Precision of the test method

The precisions of the Fisher Gas Partitioner and Heathkit Servo-Recorder were published as ± 0.5 percent and ± 1 percent respectively. Thus, any additional variations were introduced as probable error Q, where $Q = 0.645\ \sigma$, in gas sampling technique and chromatogram evaluation. The above equation was applied to the data obtained from chromatograph calibrations (figure 8) and yielded a probable error of ± 1.3%. Thus, relatively high precision was obtained from the quantitative analysis technique.

An indication of the precision of the test method itself, i.e., test chamber, is illustrated for each type of test in table 4. These figures, although showing the general reproducibility of the test method, have no statistical significance and should be treated accordingly.

Conclusions

The potential use of this test chamber, not only as a package design tool for predicting the shelf life of a given package, but also as a research tool for heat seal and other closure studies, was fully supported by data obtained from preliminary tests. The introduction of product into the test package will provide vital information for an even more accurate prediction of shelf life. A more complete study of the permeability rates of a given material in sheet versus pouch form and an investigation of the effect of crisscrossed heat seals on the permeability rate of the same material in sheet form provides a logical starting point for additional heat seal studies.

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APPENDICES

APPENDIX A

DEVELOPMENT AND CONSTRUCTION OF AN ELECTRONIC INTEGRATOR FOR VAPOR PHASE CHROMATOGRAPHY

Due to the large number of chromatograms requiring measurement and calculations, the Michigan State University School of Packaging found it necessary to either hire additional employees or develop a more rapid, less tedious method of differential chromatogram area determination. It was decided to solve this problem by electronically integrating the differential chromatogram peaks.

The chromatograph commonly used at the School of Packaging is the Fisher Gas Partitioner, model 25V, a thermal conductivity unit equipped with a Fisher Thermal Stablizer base. The base is held at 50° C., which the Fisher Scientific Co. reports to give a column temperature of 37° C. Although room temperature is controlled to 73° F, ± 3° F, greater thermistor stability is achieved when using the thermal stabilizer.

The column/thermistor system is arranged such that one thermistor follows 30 X 1/4-inch HMPA (hexamethyl phosphoramide) column. This column is followed in series by a 78 X 3/16-inch 13X molecular sieve column. Helium is used as the carrier gas and flows at 80cc./min. This column system, which Fisher designates as "standard", will separate carbon dioxide, oxygen, and nitrogen in approximately two and one-half minutes, but is normally used for only oxygen-nitrogen analysis. When used for carbon dioxide-oxygen-nitrogen analysis, the carbon dioxide peak is not completely separated from the composite peak. Carbon dioxide analysis is satisfactorily achieved by lengthening the HMPA column to 60 inches and the molecular sieve column to 93 inches. Although analysis time is increased to approximately three and one-half minutes, the latter system affords complete separation of all peaks.

A Bristol Dynamaster one-millivolt recorder is used for producing differential chromatograms. A chart speed of four inches per minute is used with the "standard" column system while two inches per minute is more desirable when the longer column system is in operation.

Normally, area determination of conventional chromatograms, described in Appendix B, takes approximately three minutes each. Ofttimes, fifty or more chromatograms are evaluated daily, which becomes not only time consuming, but also extremely tedious. This prompted the development of another method of differential chromatogram area determination.

An idle Heathkit analog computer and a Heathkit model EUW-20A Servo Recorder were made available and thus provided a starting point for electronically integrating the chromatographic signal. The computer was equipped with fifteen model ES-201 DC operational amplifiers. For each, open loop gain is 50,000, drift is 10 mv./hr., and noise is equal to or less than 2 mv.

It was decided, so as to minimize the effect of final amplifier drift, to record the integrated chromatogram in volts. Recorder sensitivity could be set at 4, 10, 20, 40, and 100 percent full scale. Thus, a completely versatile system for analysis of extreme gas concentrations was assured. Since the maximum voltage emitted from the chromatograph for a given 0.2 cc. gas sample is approximately 25 mv., a total gain of 1000 would be required to record the final signal in volts. Keeping this in mind, it was decided to have a three-amplifier open loop integrator.

The first two amplifiers were each equipped with a 1 megohm input resistor and a 10 megohm feedback resistor. The third amplifier was equipped with a 1 megohm input resistor and a 0.01 microfarad feedback capacitor. The net result was a gain of ten in each of the three amplifiers, the third also integrating. The required 1000 gain was delivered by this circuit.

While attempting to calibrate the system, it became evident that operational amplifier drift would force abandonment of this arrangement. If the complete system, i.e., the chromatograph and operational amplifier, was properly balanced, the recorder pen would trace a straight line while the operational amplifier was integrating. This, however, was extremely difficult to achieve and introduced significant random error which often completely cancelled or doubled the indicated amount of oxygen in a sample of air.

When the published operational amplifier drift and the respective gains of each amplifier were evaluated, it became evident that this error was to be expected. For example, using an oscilloscope, it was found that with the standard column system, the maximum voltage emitted by the Fisher instrument for the oxygen in a 0.2 cc. air sample was 4 mv. If the assumption was made that this signal approximated a half-sine wave, then the maximum possible recorded area would be 4 volts. If the published amplifier drift was followed through the integrating circuit, it could be seen that 0 to 5.5 mv. drift would exit amplifier two of the circuit. This random value would once again be multiplied by ten and then integrated over time. It can therefore be seen that the Heathkit drift is unacceptable for integration in gas vapor phase chromatography.

The same three-amplifier integration circuit was patched into an Applied Dynamics analog computer. This instrument has twenty-four, model 111-2DC operational amplifiers. Each has an open loop gain of 200,000 and a published drift value of no greater than 2 mv./hr. Although a fivefold reduction over the Heathkit instrument, the Applied Dynamics operational amplifier drift also proved too great. Only slightly greater precision was obtained for air analysis.

Electronic integration with available analog computers proved to be fruitless. The only method of thwarting the effects of operational amplifier drift was to: (1) limit the integration circuit to one operational amplifier, and (2) utilize a more sophisticated operational amplifier.

A Philbrick, model USA-3, DC operational amplifier was made available, thus satisfying the above requirements. The Philbrick amplifier has an open loop gain of at least ten million

and a long-term drift no greater than 100 μv.

To produce an integrated output signal in volts, a gain of 1000 was required in the one-amplifier circuit. This was accomplished by using a 0.1 megohm input resistor and a 0.01 microfarad feedback capacitor. A small control module was constructed incorporating appropriate banana jacks, a reset-operate switch, and a balance potentiometer with bias reference. Banana jacks were utilized to add versatility to the system; the 0.1 megohm resistor and 0.01 μf capacitor were fastened to banana plugs. The integration circuit and amplifier power supply connections are illustrated in figures 5 and 6 respectively.

Preliminary integrator tests indicated extremely precise analysis could be obtained provided both the integrator and chromatograph were properly balanced.

The integrator can be balanced most effectively by grounding the input terminal and placing the reset-operate switch to the "operate" position. The recorder pen should trace a straight line for at least twenty seconds. A similar procedure should be followed for balancing the chromatograph. This is accomplished with the entire system adjusted to maximum sensitivity and the reset-operate switch on the "operate" position. The pen should once again trace a straight line. It was found that chromatograph balancing was markedly enhanced with the introduction of a 10K ohm helipot around the existing 25 ohm balancing helipot. This provides both coarse and fine balance controls. The 10K helipot is shown relative to the Gas Partitioner bridge circuit in figure 7.

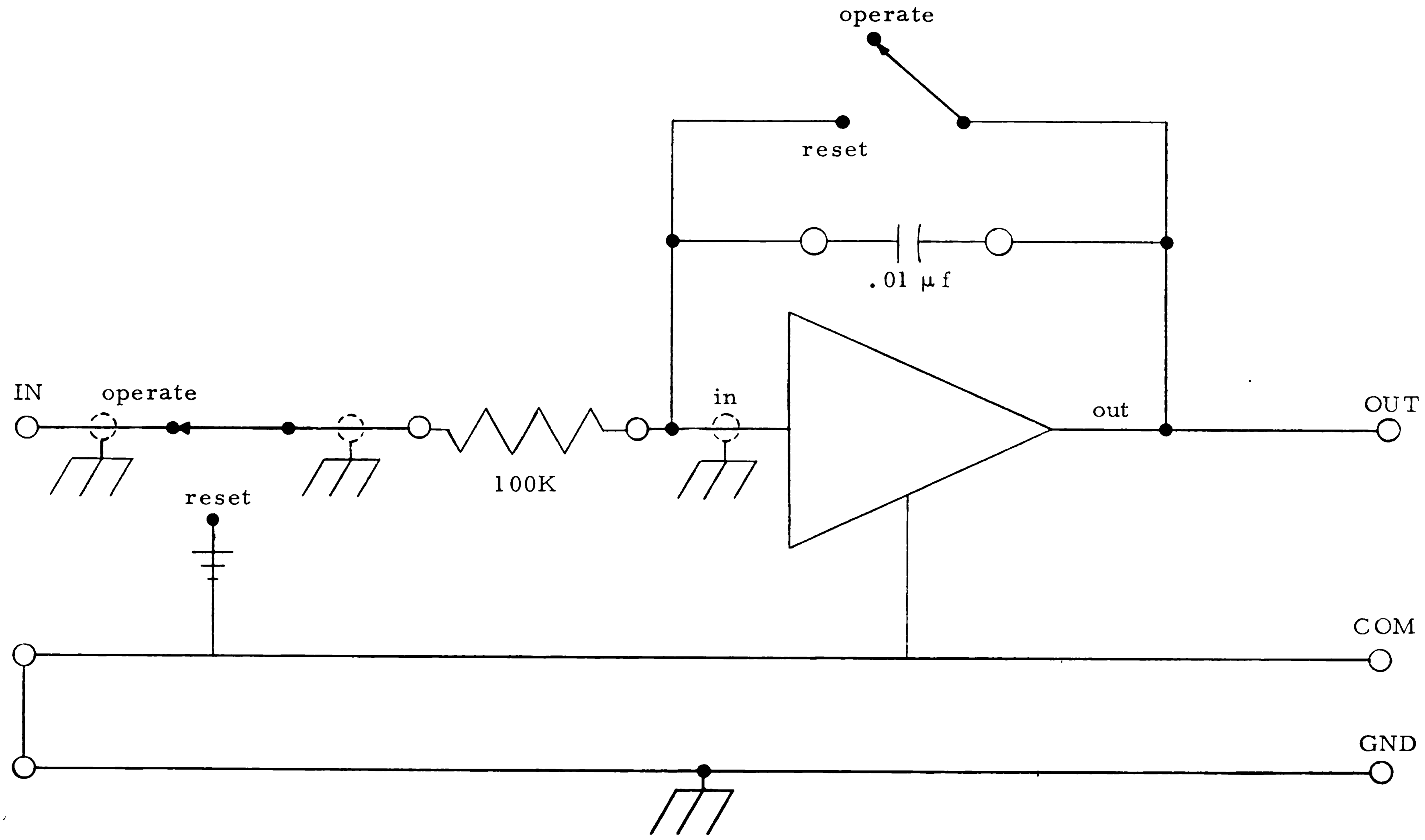

Figure 5. Single-amplifier integration circuit.

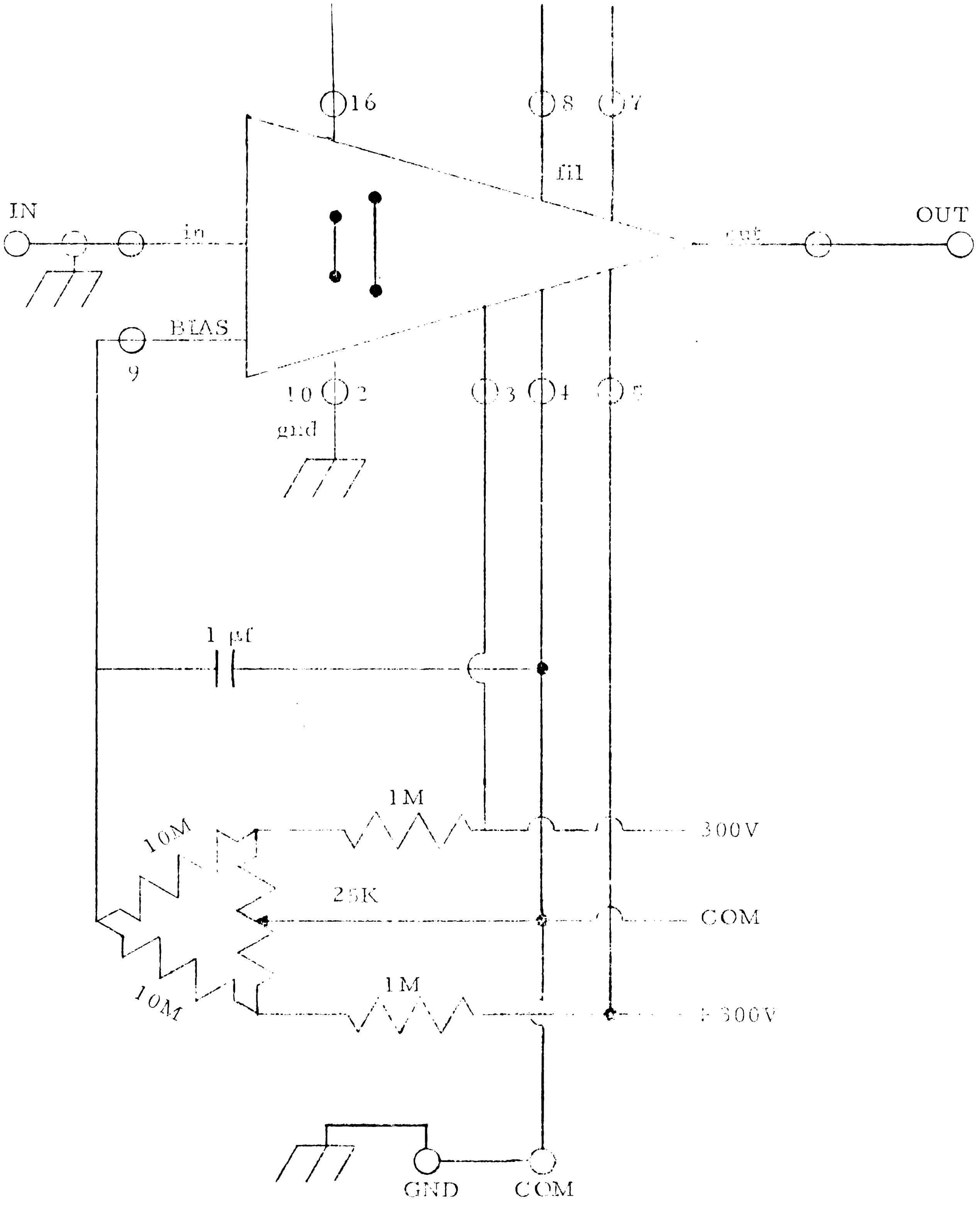

Figure 6. Philbrick operation amplifier power supply and bias connections.

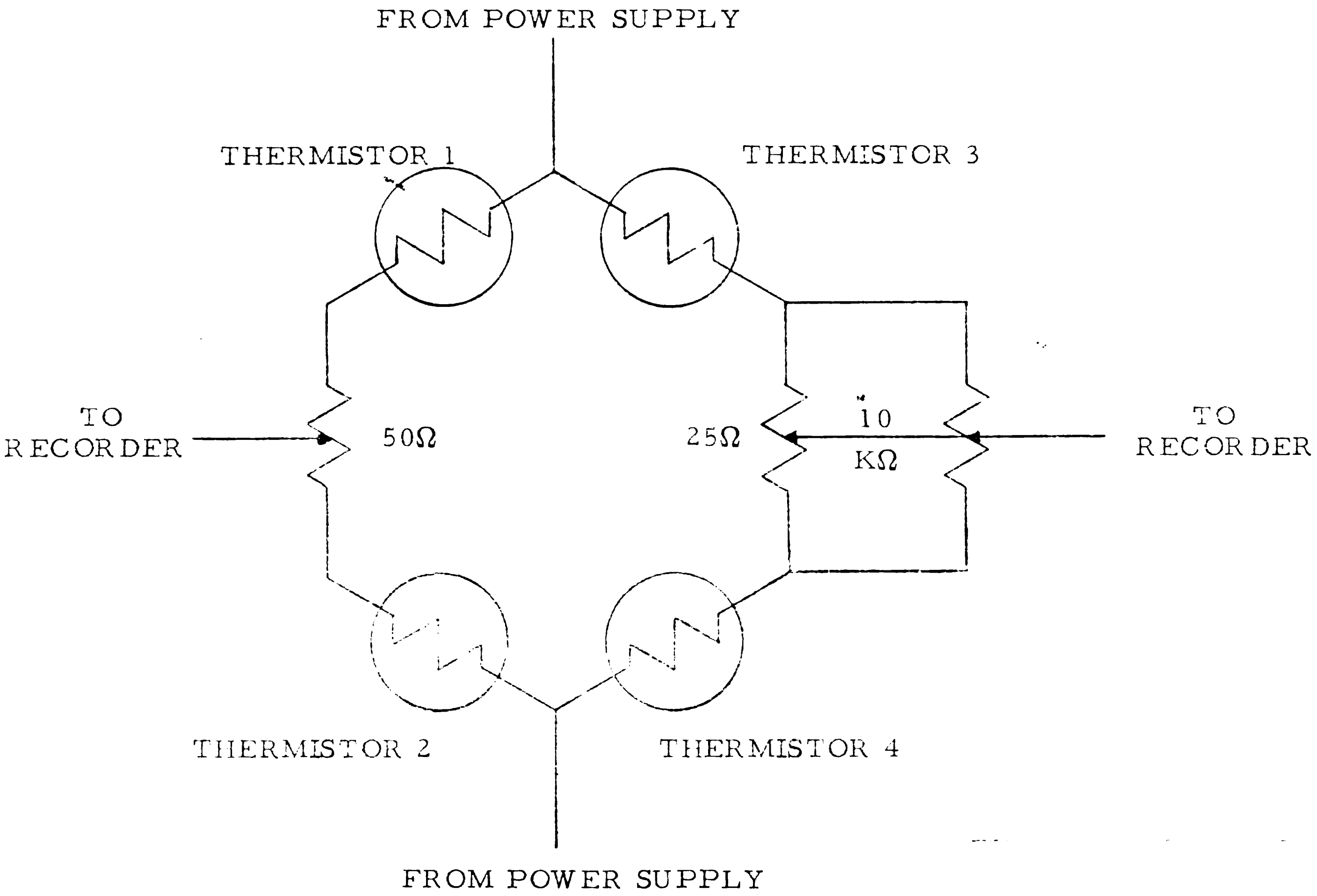

Figure 7. Fisher Gas Partitioner bridge circuit with added 10K helipot.

It was also found helpful to know the exact time the signal for each respective gas is emitted from the chromatograph. The integrator reset-operate switch should be kept on "reset" until just prior to signal emission. When integration is complete, the recorder pen will once again track a straight line. The pen may be returned to the base line by switching the reset-operate switch to the "reset" position. The same procedure is followed until each peak of the chromatogram is integrated. In contrast to the triangular peaks in a differential chromatogram, illustrated in figure 9, the integrated chromatogram results in S-shaped curves, illustrated in figure 10. Thus, the area of the oxygen peak in figure 9 is represented by the height of the oxygen peak in figure 10; this also holds for the nitrogen peaks of the same figures.

Because the areas of peaks in differential chromatograms are often approximated by triangles, any "tailing" of the peak will introduce error. For example, in a sample of gas containing only oxygen and nitrogen, let X represent error resulting from the area approximation of the oxygen peak. Similarly, let Y represent error in the area approximation of the nitrogen peak. Thus, when the triangle approximation method is used, the resultant error in the ratio, R, of the total amount of oxygen to the total amount of gas in the sample is $\frac{X}{X+Y}$. This can be represented by the following expression:

$$\frac{\text{Oxygen area} + X}{\text{Oxygen area} + X + \text{Nitrogen area} + Y} = R + \frac{X}{X+Y} \qquad \text{(A-1)}$$

The integrated chromatogram, however, completely eliminates this error. This can be seen by statistical analysis of one-percent oxygen calibration factors (Appendix B) for air samples. When using the triangle method to approximate peak areas in differential chromatograms for fifty-three air samples, the mean one-percent oxygen calibration factor was 0.01002; the standard deviation σ was 0.00024. On the other hand, when integrating the chromatograms of fifty additional air samples, taken under identical conditions, the mean one-percent oxygen calibration factor was 0.01010 while σ = 0.00004 (see figure 8). Thus, we can verify the increased precision of the integrated method by a six-fold reduction of the standard deviation. At the same time, chromatogram computation time was reduced three-fold.

The cost of the integration system described above compares very favorably to integrators now available on recorders. The cost of the entire system, including power supply, operational amplifier, recorder, and installation labor, is approximately five-hundred dollars. Recorder integrators, on the other hand, cost in excess of one-thousand dollars.

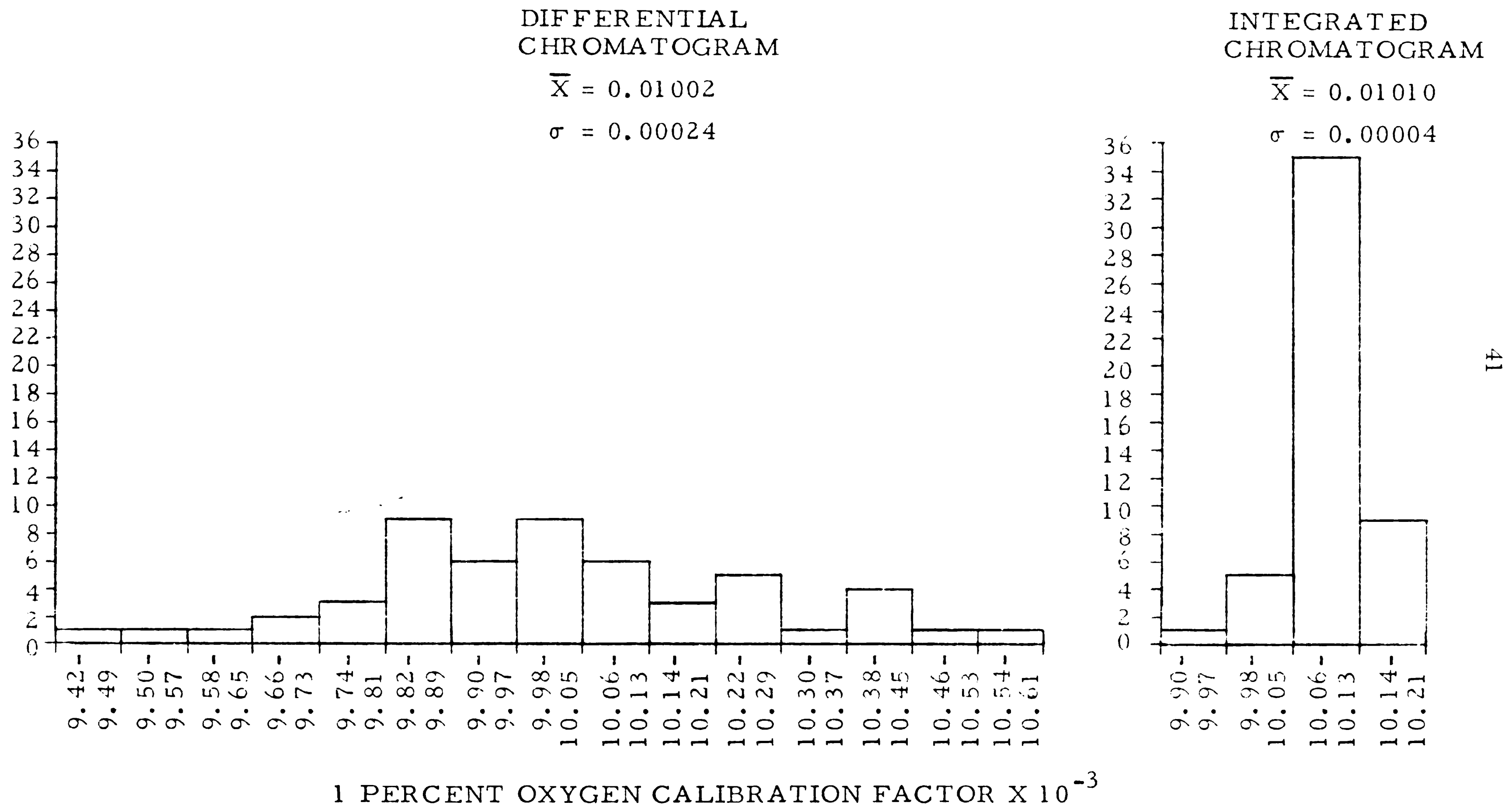

Figure 8. Frequency distributions of 1 percent oxygen calibration factors when using differential and integrated chromatograms.

APPENDIX B

GAS PERMEABILITY OF PACKAGES AND PACKAGE MATERIALS: AN ISOSTATIC TEST PROCEDURE

The isostatic permeability test method is composed of two basic components: (1) a material test cell or package test chamber, (2) vapor phase chromatograph or other suitable gas analyzer.

The Davis isostatic test cell, an isostatic package test chamber, and a Fisher Gas Partitioner were utilized in the test procedure described below. It should be noted, however, that several calculations must be considered before material and package permeability rates can be determined.

Measurement and Calculation of Chromatograms Produced in Vapor Phase Chromatograph

Determination of areas of chromatogram peaks

The area under any peak of a differential chromatogram is approximated by the product of the height of the peak and the width of the peak at half its height. These dimensions are respectively illustrated by dotted lines H and W in the oxygen peak of figure 9. The area under a peak representing any other gas in the sample is similarly approximated.

The area under the peaks of any differential chromatogram may more accurately be determined by integrating the chromatographic signal before it is recorded. When this method is utilized, the height of the recorded peak is the discrete area of the differential

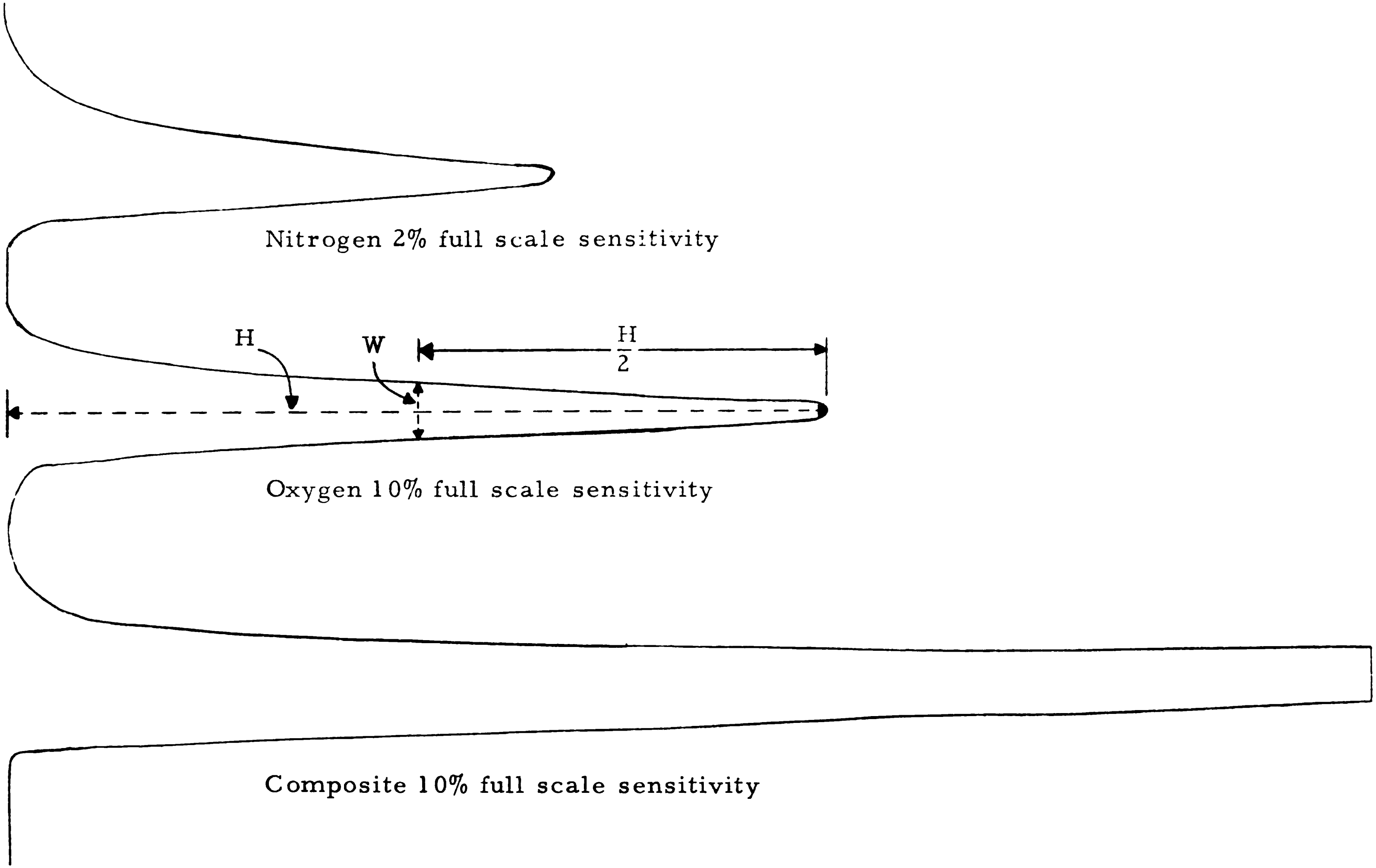

Figure 9. Differential chromatogram of a 0.2 cc. air sample.

peak it represents. This is illustrated by dotted line H' in figure 10.

When measuring peak dimensions using either of the above two methods, any convenient linear unit may be used; all units cancel in subsequent calculations.

If the chromatographic system is on maximum full scale sensitivity, any signal that represents a relatively high quantity of a given gas in the sample will be too great to be recorded. To compensate for this, the signal emitted by the chromatograph detectors must be reduced to a recordable level. For a differential chromatogram, fractional multipliers in either the chromatograph or recorder may be used to adjust the full scale sensitivity; only recorder sensitivities may be manipulated when recording integrated signals. For example, in the differential chromatogram of a 0.2 cc. air sample, illustrated in figure 9, the oxygen peak was recorded at 10 percent full scale sensitivity; the nitrogen peak was recorded at 2 percent full scale sensitivity. Similarly, the integrated chromatogram in figure 10 shows the oxygen and nitrogen peaks recorded at 10 percent and 4 percent full scale sensitivities respectively.

Before actual evaluation of the chromatogram, each peak must be adjusted to the same full scale sensitivity setting. This adjustment can be made by using the expression

$$A_c = A_a \left(\frac{100\%}{X} \right) \tag{B-1}$$

where A_c = the corrected area of the peak, A_a = the area of the

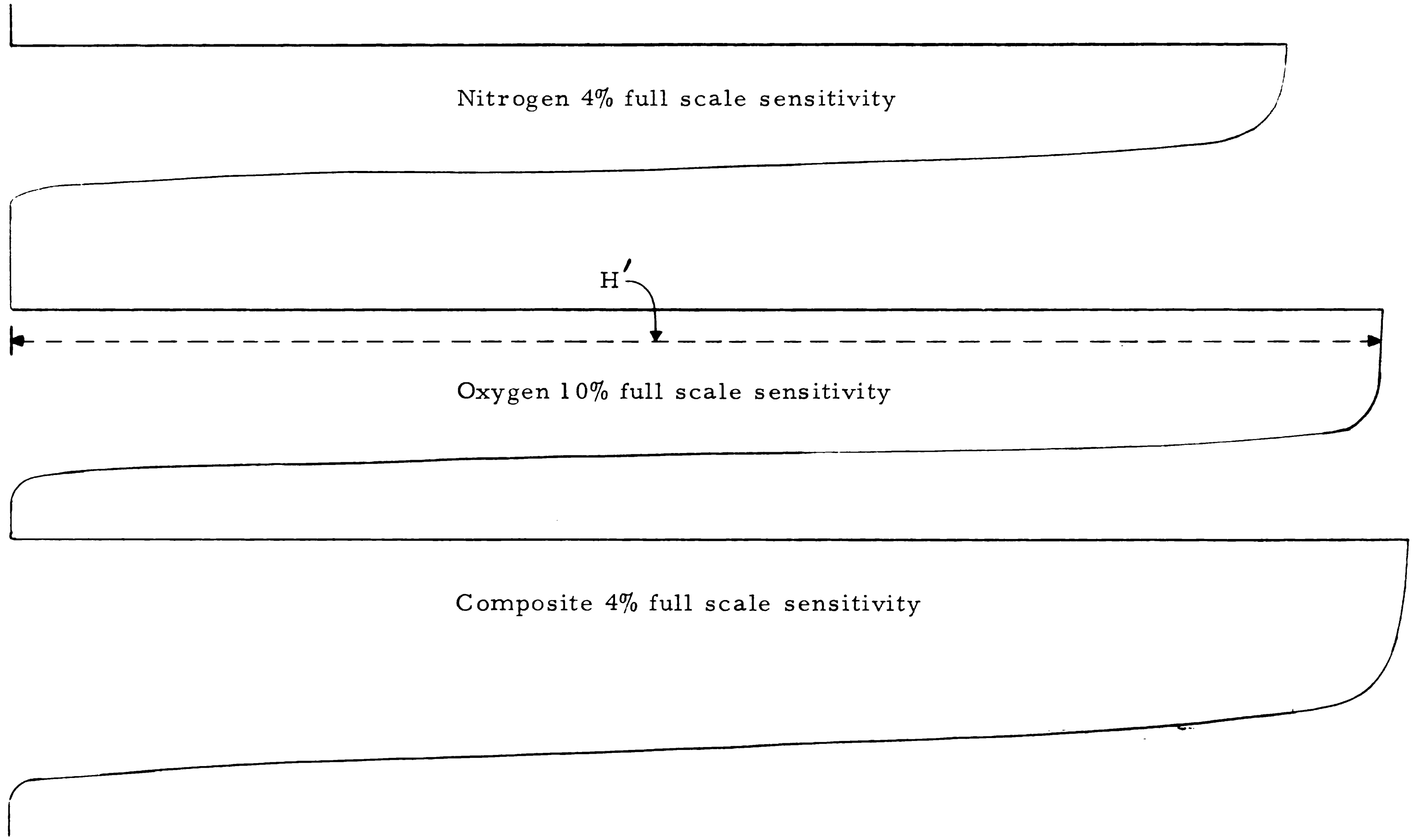

Figure 10. Integrated chromatogram of a 0.2 cc. air sample

peak as measured in the chromatogram, and x = the percent full scale sensitivity at which the peak was recorded.

Calibration of the chromatograph

The chromatograph may be calibrated by using a gas mixture having known concentrations of the gas or gases of primary interest. Air, for example, was used to calibrate the Gas Partitioner for analysis of gas samples containing unknown concentrations of oxygen.

It is known that air contains predominately oxygen and nitrogen, each present in concentrations of approximately 21 percent and 79 percent respectively. Thus, for a given sample of air analyzed by the chromatograph, the expression

$$\frac{A_0}{A_0 + A_N} = 21\% \qquad \text{(B-2)}$$

is true, where A_0 = the corrected area of the oxygen peak, and A_N = the corrected area of the nitrogen peak. From equation (B-2),

$$\frac{A_0}{21(A_0 + A_N)} = 1\% \qquad \text{(B-3)}$$

is also true and shall be designated the 1% oxygen calibration factor. Gas mixtures containing more than two gases may be used to determine the 1% calibration factor for each gas having a known concentration in the mixture.

Determination of the oxygen concentration of an unknown gas sample

Let it be assumed a given gas sample contains unknown concentrations of oxygen and nitrogen and no other gases are present in the mixture. Thus, from the chromatogram of this sample, the expression

$$R = \frac{A_0}{A_0 + A_N} \qquad \text{(B-4)}$$

indicates the ratio R of the amount of oxygen to the total amount of gases in the sample. Hence, the percentage of oxygen present can be determined using the expression

$$\text{Percent oxygen} = \frac{R}{1\% \text{ oxygen calibration factor}} \qquad \text{(B-5)}$$

Oxygen Permeability Test Procedure

Determination of leak rate

(1) Secure an absolute barrier material, e.g., aluminum foil, in the material test cell or to the package test chamber adapter fitting. The neoprene "O" ring must be sufficiently compressed so as to form a gas-tight seal.

(2) Flush the sweep* and test gas sides of the test apparatus with nitrogen and oxygen respectively. Flow rates should be such that elimination of air from both sides of the test appratus can be achieved within forty minutes.

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*For package testing, the inside of the package is the sweep gas side of the test system.

(3) Isolate or close off the sweep gas side of the test system while permitting the test gas to flow.

(4) Using a hypodermic needle and syringe flushed free of air, withdraw gas samples at selected intervals. Sample size should be small relative to the volume of the sweep gas side of the system. The accumulated sample volume should not exceed ten percent of the volume of the sweep gas side of the system.

(5) Immediately after sample withdrawal, analyze each sample for oxygen concentration; plot the results as percent oxygen as a function of elapsed time.

(6) Determine the slope of the plot and express as $\Delta \% O_2/24$ hr. The product of the slope and volume of the sweep gas side of the system yields the leak rate expressed as cc./24 hr.

The permeability test

(1) Condition the material to be tested at the desired test conditions until equilibrium is achieved between test conditions and the material.

(2) Secure the material in the test cell or the package to the test chamber adapter fitting. The neoprene "O" ring must be sufficiently compressed so as to form a gas-tight seal.

(3) Flush the sweep and test gas sides of the test apparatus with nitrogen and oxygen respectively. Flow rates should be identical to those used for leak rate determination.

(4) Isolate or close off the sweep gas side of the test system while permitting the test gas to flow over the material or package surface.

(5) Using a hypodermic needle and syringe flushed free from air, withdraw gas samples at selected intervals. Sample size should be small relative to the volume of the sweep gas side of the system. The accumulated sample volume should not exceed ten percent of the sweep gas volume.

(6) Analyze each sample for oxygen concentration, plot the results as percent oxygen as a function of elapsed time.

(7) Determine the slope of the plot and express as $\Delta \% 0_2/24$ hr. The product of the slope and the volume of the sweep gas side of the system yields the gross permeability rate expressed as cc./24 hr.

Determination of the permeability rate

The permeability rate P may be determined by the expression

$$P = \frac{P_G - L}{A} \qquad \text{(B-6)}$$

where P_G = the gross quantity of oxygen permeated into the sweep gas side of the test system per 24 hours (expressed as cc./24 hr.), L = the leak rate of the system in cc./24 hr., and A = the surface area of the material or package, in square meters, exposed to the test conditions. P usually is reported in cc./24 hr. M^2, but often cc./24 hr. 100 in.^{2} is preferred. The conversion from square meters to 100 square inches is made by dividing the metric permeability rate by 15.5.