Performance of Permeation Tubes as Standard Gas Sources

Bernard E. Saltzman,[1] **William R. Burg, and Gopalakrishnan Ramaswamy**
Dept. of Environmental Health, University of Cincinnati, Cincinnati, Ohio 45219

■ Important factors affecting the accuracy of permeation tubes for nitrogen dioxide and several hydrocarbons were studied. Two new methods of sealing the tube ends were developed. Lifetimes of tubes were greatly extended by attaching to one end a glass or stainless steel bottle. Systems for their storage, calibration, and use were improved. Propane tubes required some aging at 30°C before reproducible rates in the 20–30°C range could be achieved. Humidity seriously affected the permeation rates of nitrogen dioxide tubes; even the past history of exposure was important. A convenient method for volumetric in situ calibration in the working flow dilution system was developed for rapid and precise results. Tubes for NO_2 were not reliable as precision primary standard gas sources, unless recently calibrated.

The rapidly expanding tempo of air pollution control activities has necessitated standardization of methods and critical review of their accuracies. Permeation tubes were recently developed (O'Keeffe and Ortman, 1966) as convenient calibration sources. Liquefied gases such as sulfur dioxide, nitrogen dioxide, hydrocarbons, and hydrogen sulfide, sealed in inert plastic tubing such as FEP Teflon (fluorinated ethylene propylene copolymer) or TFE Teflon (tetrafluoroethylene polymer) were found to permeate through the walls at relatively constant rates for long periods. Such tubes were used successfully for anhydrous ammonia (Scaringelli *et al.*, 1970), anhydrous hydrogen fluoride (Jacobson, 1967; Elfers and Decker, 1968), phosgene and organic mercury compounds (Linch *et al.*, 1968), and for hydrogen sulfide and mercaptans (Bamesberger and Adams, 1969). A critical study of sulfur dioxide permeation tubes was made by Scaringelli *et al.* (1967). These tubes also were successfully used by Thomas and Amtower (1966) and were collaboratively tested successfully (Saltzman, 1968; Tye *et al.*, 1968). Careful studies have been made for both gravimetric calibration techniques (Scaringelli, O'Keeffe *et al.*, 1970; Scaringelli, Rosenberg *et al.*, 1970) and volumetric calibration techniques (Saltzman *et al.*, 1969). High degree precision was the goal of these studies; however, variations of greater than known experimental errors still occurred. The purpose of this paper is to report further improvements in the design and use of permeation tubes and the improved degree of precision thus obtained.

Lifetimes of permeation tubes were extended to a year or more by attaching to one end a glass or stainless steel bottle to act as a reservoir. Two new methods of sealing the tubes were developed: use of Swagelok ferrules and fusion. Volumetric and gravimetric calibrations were compared and deviations and errors examined. Systems for storage and use of permeation tubes were studied. The permeation rates and their long-term stabilities for NO_2 and propane tubes were determined. Equilibration times for new tubes and adjustment times for change of temperature also were examined.

Improvements in Construction of Permeation Tubes

The lifetime of a permeation tube is a particularly important characteristic which is determined by the permeation rate and the volume to surface ratio of the tube. For a rapidly permeating material such as NO_2, inconveniently short lifetimes of only a few months have been reported. Longer life is desirable, since the calibration procedure itself consumes an appreciable amount of time. Heavy-wall Teflon bottles have been employed (Scaringelli, Rosenberg *et al.*, 1970). A glass bottle was recommended by O'Keeffe and Ortman (1967) for cases where slow rates were desired. This bottle was sealed by jamming into the tapered opening a Teflon tube containing a glass ball. Thus, only a small area of Teflon was available for the permeation process.

For our work with NO_2 permeation tubes, we have constructed a glass bottle by sealing one end of the bulb of a 5-ml Kimax transfer pipet (Kimble 37010) and cutting and fire-polishing the tube on the other side at about 1 in. from the bulb. A length of FEP Teflon tubing ($^3/_{16}$ in. i.d. × 0.030 in. wall thickness) can then be pushed on to the open end, which is of the proper outside diameter (0.25 in.) for adequate sealing at low pressures. The vapor pressure of NO_2 at room temperature is about 1 atm. The other end of the Teflon tube can be sealed after filling with another piece of glass tubing closed at the top. A finished assembly, illustrated in Figure 1A may have a lifetime of one year. The remaining amount of liquid NO_2 is readily visible. In later work, a tube with a fused Teflon seal at the top was pushed onto a bottle filled with liquid NO_2. Since the effective permeation length needed was only 1 cm, a bottle constructed of a glass tube 3 in. long × $^1/_4$ in. o.d. sufficed.

For materials such as propane, which has a vapor pressure at ordinary temperatures of about 10 atm, a stronger bottle was required. A $^1/_2$-in. stainless steel rod 3-$^1/_2$ in. long was turned down at one end to a stem of 0.197 in. o.d. × $^1/_2$ in. long. The inside of the rod was bored out to leave a wall thickness of 0.025 in. and the small end also bored out. The end of the reservoir was sealed with a press-fit stainless steel plug which then was silver soldered to produce an 8 ml bottle. The Teflon tubing was crimped to the open end with Swagelok ferrules. A finished assembly is shown in Figure 1B.

More convenient methods of sealing permeation tubes also were developed. In the original report, glass or stainless steel balls were pressed into the ends as seals; later, aluminum and stainless steel collars were crimped around the ends to hold Teflon plugs. A convenient method was developed to utilize readily available Swagelok ferrules and thus avoid the need for special collars and crimping equipment. The Teflon permeation tubes used were of $^3/_{16}$ in. i.d. and 0.030 in. wall thickness, plugged at the ends with solid FEP Teflon rod, 0.200 in. o.d. The $^1/_4$-in. ferrules were assembled on the plugged end of the tube and then crimped down with a standard $^1/_4$-in. stainless steel Swagelok fitting. A split nut clamped together in a socket was used. After the crimping was com-

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[1] To whom correspondence should be addressed.

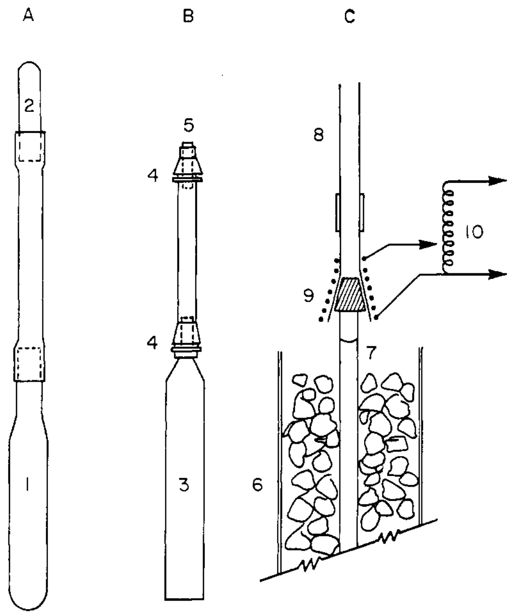

Figure 1. Construction and sealing of permeation tubes. Teflon tubing used had a 0.1875-in. i.d. and a 0.030-in. wall thickness

A. Glass bottle-type for NO_2
  (1) 5-ml glass bottle
  (2) glass plug (later, fused Teflon plugs were used)
B. Stainless steel bottle-type for C_3H_8
  (3) 8-ml stainless steel bottle
  (4) crimped Swagelok $^1/_4$-in. ferrules
  (5) Teflon plug
C. Technique for fusion sealing
  (6) cardboard container containing Dry Ice
  (7) filled FEP Teflon permeation tube with FEP Teflon plug
  (8) glass tube clamped at top and flared at bottom
  (9) heater winding
  (10) Variac transformer

pleted, the split nut was opened and removed, as was the socket end of the fitting, so that only the two ferrules remained on the permeation tube. The brass front ferrule was soft enough to be easily crimped onto the tubing. Because a brass rear ferrule cut the plastic tube when tightened, stainless steel rear ferrules were used. In later work, aluminum ferrules (both front and rear) were used, crimped by turning the nut three-quarters past the finger tight position. These were more corrosion resistant than brass ferrules for SO_2 (and probably for hydrogen sulfide) tubes. Tests showed that after practice, good seals could be obtained with this technique.

The second new method of sealing developed successfully for FEP Teflon was to fuse the plug with the tubing. The end of the permeation tube was rotated and pushed into a clamped glass tube which had a slightly tapered open end heated to approximately 260°C with about six turns of no. 24 nichrome wire attached to a Variac autotransformer (Figure 1C). Careful adjustment of the heat was essential. About 10 V kept the wire below any visible red glow and softened the Teflon but did not decompose it (i.e., produce visible bubbles in the tubing). When the plug became clear and was compressed to a taper for its entire length, it was sufficiently hot to be properly sealed; this process required 5 to 10 min. The Teflon has some tendency to stick to the glass especially if decomposition has taken place. If necessary, the glass and Teflon were allowed to cool for 5 to 10 min before separating them. The fusion technique was not successful with TFE Teflon.

By use of Dry Ice, propane tubes were filled and sealed at atmospheric pressure as follows: The stainless steel reservoir was crimped to a TFE Teflon tube with Swagelok ferrules. The assembly was then cooled with Dry Ice only in a towel or cardboard container. A cooling slurry with liquids such as acetone was not used, to avoid possible contamination. The propane was allowed to flow from a cylinder into the tube at a rate sufficiently slow so as not to build up pressure. Adequate volume was left for expansion of the liquid propane (approximately 25%) in warming from Dry Ice temperature to room temperature as well as an allowance for trimming the end and for insertion of the plug. When sufficient propane had been condensed, the tube was disconnected from the cylinder and the Teflon plug was inserted. The tube was kept at the Dry Ice temperature until the seal was completed as described above.

Since the liquid level in the stainless steel bottle cannot be observed, it was difficult to get the desired amount of propane into it. A torsion balance can be used if it is prepared ahead of time for support of the tube with several layers of towels for thermal insulation. A more convenient method, however, was to attach a longer tube to the bottle than needed for the permeation. The system was cooled and propane added until the liquid was visible in the Teflon tube. The open end was sealed and the tube was allowed to warm to room temperature. The actual volume of the liquid at room temperature was observed. The tube was again cooled, the liquid level adjusted if necessary, and the tube cut off and resealed at the proper length for the total permeation rate and lifetime desired.

Studies of NO_2 Permeation Tubes

Many NO_2 permeation tubes were constructed by various methods and calibrated over periods of up to a year, both volumetrically and gravimetrically at different temperatures. The objective was to eliminate unaccounted for deviations in calibrations. The gas used was from Matheson cylinders, minimum purity 99.5%. Originally, crimped aluminum bands were used for the tube seals. Since these were found to corrode, the design ultimately selected as best was that shown in Figure 1A. A lifetime of one year was achieved. Figure 2 shows the weights of the tube over a 35-week period. About four weeks were required to attain a steady rate through the FEP Teflon.

Humidity was found to be a serious problem. O'Keeffe,

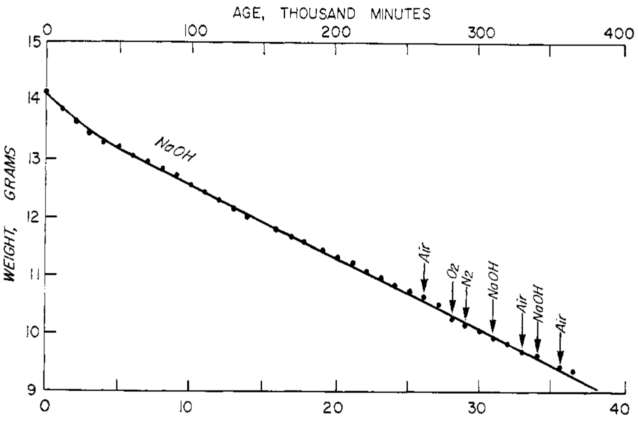

Figure 2. Weight history of an NO_2 permeation bottle

Constructed of FEP Teflon, effective length 4.76 cm. Storage was in a closed container over NaOH, or in a stream of flowing gas starting at the times indicated

and Ortman, (1966) reported that nitrogen dioxide permeation tubes became blistered when exposed to moisture. Scaringelli, O'Keeffe *et al.* (1970) reported that when the NO_2 permeation tubes were used in a flow dilution system, the concentrations observed by colorimetric analysis decreased linearly as much as 30% as the relative humidity of the system increased from 0 to 100%. They assumed, however, that the gravimetric calibration obtained when the tube was stored in a slow stream of cylinder dry nitrogen or air was correct.

Many gravimetric calibrations were made on a permeation tube that was stored in streams of various flow rates of cylinder air, nitrogen and oxygen as well as of purified air from the house compressor system. They indicated that gravimetric calibrations also were seriously reduced (by as much as 30%) according to the moisture content of these flowing gases. Exposing a tube for as short a period as 15 min to gas containing 100% relative humidity produced a visible whitening of the Teflon as well as a drop in the rate. The tube only partially recovered its original rate after storage for as long as a week.

The moisture contents of various gases were determined gravimetrically by passing a metered volume of each gas through two U-tubes in series, each containing Anhydrone. Results are given in Table I. It is evident that there are marked differences in these moisture contents.

Table I. Moisture Content of Various Gases

Sample description	Volume, liters	Weight gain, mg First U-tube	 Second U-tube	Moisture, mg/liter
Cylinder nitrogen	1123	16.3	2.3	0.0166
Cylinder oxygen	142.4	18.1	6.1	0.170
Cylinder breathing air	180.1	43.0	6.9	0.277
House system air dried with regenerated silica gel	168.2	154.1	2.0	0.928
House system air dried with spent[a] silica gel	837.9	1015.4	4.9	1.218

[a] Indicator chemical changed color from blue to pink.

The final conclusion of all of these studies was that there was no precise fixed permeation rate for a tube even at a fixed temperature. Since the tubes may be permanently affected by brief exposures to moisture and since they may be exposed in flow systems to gases of various humidities, the calibration was most accurately done while exposing the tube to a flow of the actual gas to be used. Gravimetric calibrations required careful control of the brief exposures to different humidities during the weighings. The tubes were stored in 250 ml all-glass gas washing bottles submerged in a thermostated water bath. For weighing they were briefly transferred to tared glass-stoppered tubes to protect them and the balance. More precise results were obtained, however, by calibrating without removing them from the system.

The volumetric system reported by Saltzman *et al.* (1969) was adapted for in situ calibration as shown in Figure 3. It was thus unnecessary to handle the tube or expose it to room air. The flow rate of gas over the permeation tube was immaterial as long as it exceeded about 50 ml/min. Conveniently, this gas was dry nitrogen from a cylinder, which exhibited a low and reproducible humidity. The connection to the dilution mixing bulb should be by Teflon tubing, or glass tubing connected butt to butt with short pieces of Tygon tubing. A larger stream of dilution air was introduced just upstream from the mixing bulb. Reproducible volumetric calibrations also required a dry microgasometer. Even traces of moisture reduced the observed permeation rates. A commercial Gilmont Warburg compensated syringe manometer was used; dodecane was a convenient manometer liquid of negligible vapor pressure for use in the apparatus. Only the side arm test tube for containing the permeation tube required special fabrication.

During calibrations, the microgasometer was sensitive to temperature fluctuations because the enclosed volume containing the permeation tube was about 50 ml. The manometer fluid meniscus moved back and forth past the reference line in synchronism with the operation of the thermostat when the apparatus was immersed directly in the main water bath, even though the temperature of the latter fluctuated only a few hundredths of a degree between heating and cooling. Apparently the temperature-compensating bulb did not adequately cancel these fluctuations, probably because of a differing temperature distribution in this portion of the syringe manometer. Accurate calibration required a more stable temperature. Therefore, the microgasometer was immersed in water in a 4-liter beaker thermally insulated by foamed packing material in a plastic pail or waste paper basket. The beaker contained a coil of $^3/_8$-in. o.d. aluminum tubing through which thermostated water from a heated-refrigerated water bath was circulated. It was also necessary to have an electric stirrer in the beaker. To eliminate the effect of air currents, a sheet of transparent vinyl plastic, appropriately slotted for the various parts, was used to cover the top of the beaker. The thermal capacity of this system effectively dampened the temperature fluctuations and permitted precise measurements. In a later, simpler system for smoothing out temperature fluctuations, the microgasometer was immersed in the main water bath, but was surrounded by a water-filled plastic bag.

Before a satisfactory volumetric calibration could be performed, the stream of about 50 ml/min of dry nitrogen was allowed to flow over the permeation tube for a day or more to bring it and the microgasometer to constant humidity. When the tube was to be calibrated, the nitrogen flow was

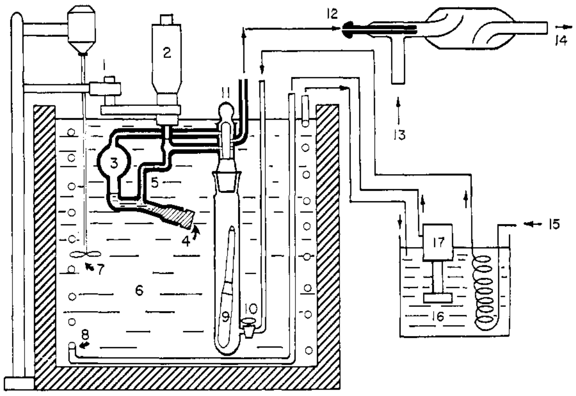

Figure 3. Schematic diagram of permeation tube in flow system with in situ volumetric calibration by Gilmont Warburg compensated syringe manometer

(1) clamp (2) 200-μl micrometer syringe (3) compensating bulb (4) adjustment screw for manometric fluid (5) reference line (6) insulated water bath (7) propeller stirrer (8) metal coil for circulating thermostated water (9) permeation tube (10) gas inlet stopcock (11) gas outlet stopcock (12) connection for permeated gas flow (13) connection for metered dilution air flow (14) gas mixture outlet (15) connection for metered dry nitrogen from gas cylinder (16) thermostated water bath (17) water circulating pump

disconnected from the microgasometer and the inlet stopcock of the test tube was closed. The outlet stopcock of the gasometer was then turned 180° from the venting position to the closed position and the calibration run was begun as described by Saltzman *et al.* (1969). The moment the meniscus of the manometer fluid crossed the reference line, a stopclock was started. The microgasometer syringe was then readjusted from the fully extended position to a new setting about 25 μl lower. When the meniscus again crossed the reference mark, the time was noted without stopping the clock. This process was repeated until the sufficient number of readings for a calibration were obtained. As little as 30 min to 1 hour sufficed. The two stopcocks were then opened and the nitrogen flow reconnected. After allowing a few minutes to flush the system, the diluted mixture was used for the test desired.

The calculations for a volumetric run were made as follows: First a plot was made of the permeated volume vs. time and the best slope was determined. The volumetric rate was then converted to gravimetric rate by means of Equation 1:

$$G = \left(\frac{S}{L} \times \frac{P}{760} \times \frac{273.16}{T} \times \frac{\text{M.W.}}{22.4146}\right)\left(\frac{1}{z^2}\right)\left(\frac{1}{1-r}\right) \tag{1}$$

Note the two parenthesized correction terms on the extreme right side of the equal sign. The first one compensates approximately for the deviations by NO_2 from ideal gas volumes because of its dimerization. The correction may also be necessary for hydrogen fluoride (which would require a non-glass apparatus). This correction is negligible for other substances which follow the usual pattern of volumetric deviations due only to physical forces. The second correction term is for backward permeation of the gas from outside to inside the tube. This correction ordinarily is small except for a long run in the closed system with a rapidly permeating gas of relatively low vapor pressure, such as NO_2.

Values of compressibility of nitrogen dioxide were calculated with the equilibrium constant for the dimerization reaction. The experimental measurements from which this constant was determined were actually of deviations from the ideal gas law. The constant was calculated (Verhoek and Daniels, 1931) on the basis of the assumption that the deviations were entirely due to the dimerization. In the present work, the calculations were reversed and the deviations calculated from the equilibrium constant. The needed value of K was calculated from:

$$\log \frac{K}{0.1328} = 6.8393\left(\frac{1}{298.16} - \frac{1}{T}\right) \tag{2}$$

where 0.1328 is the equilibrium constant at 25°C. These constants were calculated from free energy data for the reaction ("International Critical Tables," 1930).

The compressibility was calculated from the ideal partial pressure of nitrogen dioxide outside of the permeation tube, given by Equation 3. Values of K and p were entered into Equation 4.

$$p = \frac{S \times A \times P}{V \times 1000 \times 760} \tag{3}$$

$$z = \frac{\sqrt{1 + 8\,p/K} - 1}{8\,p/K} + \frac{1}{2} \tag{4}$$

Results calculated by use of Equations 2 and 4 are plotted in Figure 4. Either this plot or the equations may be used to obtain the compressibility correction factor.

The back pressure ratio was computed as follows, by definition:

$$r = p/P_{NO_2} \tag{5}$$

The needed value of P_{NO_2} was calculated from vapor pressure data.

Table II shows the high degree of reproducibility that was obtained over a one month period for volumetric calibrations, averaging 2.071 μg/min cm. A straight line was fitted by least-squares method to these values. It showed a decrease in rate by 0.054%/day. The initial intercept was 2.084 μg/cm min, which agreed well with the gravimetric permeation rate of 2.088 obtained before starting these runs. The standard deviation of the experimental rate from the fitted line was 0.008, or 0.4%.

The effect of temperature on the permeation rates through Teflon followed the pattern expected for a rubberlike polymer. This permeation process requires an activation energy sufficient for the diffusing molecule to rupture the weak intermolecular bonds of the polymer and jump to a new equilibrium position. Presumably the bonds recombine behind the molecule as it moves in a series of discontinuous jumps, and the energy is dissipated. Activation energy of permeation, which we have found generally exceeds the heat of vaporization of the substance, has been discussed by Brubaker and Kammermeyer (1952), Waack *et al.* (1955), Stern *et al.* (1965), and Scaringelli *et al.* (1967).

Temperature affected the permeation rates according to the usual Arrhenius-type equation:

$$\log\left(\frac{G_2}{G_1}\right) = \frac{E}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{6}$$

The value of the activation energy was 14.6 kcal/g-mol.

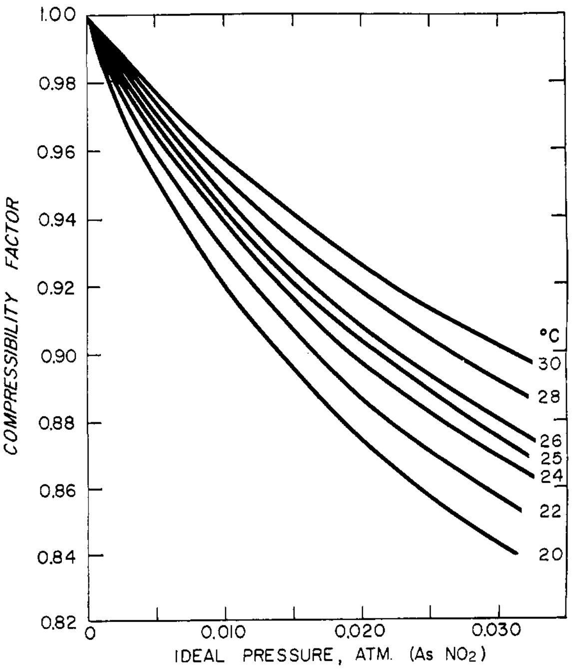

Figure 4. Compressibility of NO_2 at various temperatures and partial pressures

Compressibility is the ratio of the actual to ideal volume as NO_2 gas

Table II. In Situ Volumetric Calibrations of an NO_2 Permeation Tube

Tube age, days	Permeation rate, µg/min cm	
	Exptl	Calcd[a]
279.81	2.082	2.084
280.96	2.085	2.082
281.85	2.096	2.081
282.85	2.074	2.080
285.86	2.078	2.077
286.84	2.067	2.076
295.84	2.054	2.066
299.97	2.059	2.061
300.84	2.072	2.060
302.82	2.051	2.058
309.91	2.056	2.050
Mean	**2.071**	

SD from fitted line = 0.008
Relative SD = 0.4%

[a] From fitted line, with slope of 1.11×10^{-3} µg/min cm/day and initial intercept of 2.088 µg/min cm (at age 279.81 days).

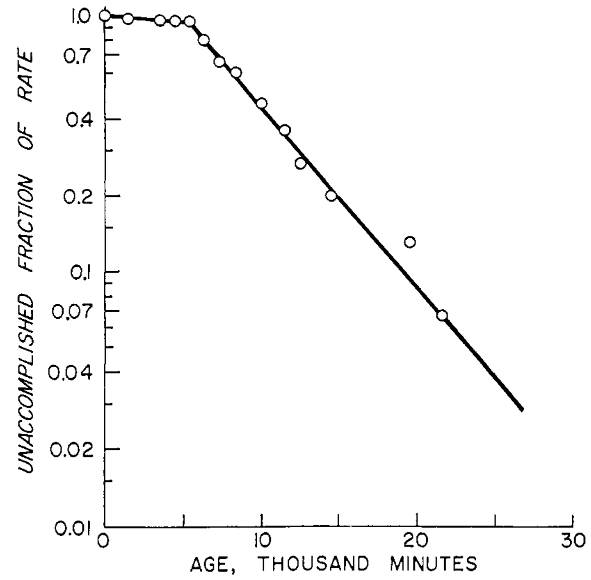

Figure 5. Equilibration of a new propane permeation tube at 25°C

Constructed of FEP Teflon, 12.5 cm effective length. Intercept at ordinate 0.1 is 90% equilibration time; at 0.05 is 95% time

Other values ranging above and below this also were obtained. Part of this scatter may have been due to the effects of humidity which were not clearly understood when the work was done.

Studies of Hydrocarbon Permeation Tubes

Although standard mixtures of hydrocarbons can be conveniently made and stored in gas cylinders, extensive studies were made of permeation tubes containing hydrocarbons in order to elucidate the factors affecting their performance. Such tubes also have the useful practical advantages of compactness, flexibility, and low cost. The bulk of the work to be described was conducted with tubes containing propane. These were filled as described above at atmospheric pressure using Dry Ice cooling. Propane and butane were Matheson instrument grade, 99.5% minimum purity; propene and butene-1 were Matheson C.P. grade, 99.0% minimum purity. Calibrations were made both gravimetrically and volumetrically on many tubes stored at various temperatures, over extensive time periods.

By the gravimetric calibration procedure it was found that the flow rate and the humidity of the ambient gas did not affect the permeation rates. However, in an ordinary dry system, substantial electrostatic charges developed as a result of the permeation process. Errors in weight averaged 2, but sometimes as large as 20 mg resulted. By moving a polonium-strip static charge eliminator briefly around the tube, the charges were readily dissipated for accurate weighings. In the absence of this equipment, satisfactory results were also obtained by wrapping the tube with a tared aluminum foil, which was grounded just before the weighing.

A number of problems also were noted in the volumetric calibration procedure. The Kel-F fluorocarbon grease was found on occasion to emit puzzling microliter quantities of gas that invalidated the calibrations. Use of Hi Vac silicone grease instead gave good results. The manometer fluid must move smoothly past the calibration mark. Although it seemed logical that aqueous wetting agents or salt solutions would be suitable, better results were obtained with dodecane as a manometer fluid. The solubility of the propane in the latter under ordinary conditions was negligible. The glass apparatus was cleaned as required with hot alcoholic potassium hydroxide and oven dried at 120°C.

As in the case of the NO_2, a certain period of time was required for a newly constructed propane tube to reach a steady permeation rate. The Dry Ice treatment may have affected the equilibration processes. In Figure 5 a plot is given for an FEP Teflon tube showing equilibration at 25°C. The ordinate scale was chosen so that the intercept at ordinate 0.1 was the 90% equilibration time; that at 0.05 the 95% time, etc. After a 5000-min (3.5-day) lag, equilibration followed a first-order relationship (a straight line on the plot) with a half-life of 4200 min (2.9 days); 95% of the ultimate rate was achieved in 23,200 min (16.1 days). After complete equilibration was achieved, the tube maintained a pseudostable rate as long as the temperature was maintained at 25°C. However, in subsequent studies involving raising and lowering of temperature in stages between 20–30°C, a different and more permanent rate at 25°C was achieved, provided that the tube was held first for a period at 30°C. The permeation rates then followed closely the Arrhenius relationships.

Table III shows the effects of temperature cycling for two tubes; similar results were obtained for others. A line was fitted to the data subsequent to the 30°C aging periods, by the least-squares method, using Equation 6. The same line was used for both volumetric and gravimetric data. The table indicates that both methods are in substantial agreement.

In Table IV, data are given for these and other tubes for the stable permeation rates and activation energies. The activation energies for propane permeation differed for FEP and TFE Teflon. Also, the rate through the latter was greater by a factor of 14. The propane-FEP data in the table showed no significant differences between tubes sealed by fusion and those sealed with Swagelok ferrules. The relationship between the total permeation rate (rate/cm × tube length) and the tube length also was examined by fitting a line to the calculated data by the least-squares method. The total rate was proportional to the tube length plus a small correction of 0.004 cm. This correction was regarded as not significant, within the accuracy of the data.

Also shown in the table are the data for other hydrocarbons. In the case of butene-1, again the permeation rate through TFE Teflon was much greater than that through FEP Teflon and the activation energy was somewhat lower. These tubes exhibited equilibration properties similar to those described above.

An interesting experiment was conducted with the propane–stainless steel bottle–TFE Teflon tube. The permeation rates were measured in two positions, first with the bottle on bottom, and then inverted. In the former case the Teflon tube was filled with propane vapor and in the latter with liquid. The two rates showed no significant difference.

Table III. Effects of Temperature Cycling

			Permeation rates, μg/cm min						
Mean temp, °C	Final tube age, days	Holding period, days	Calcd[a]	Grav.	No. points	% Dev.[a]	Vol.	No. points	% Dev.[a]
Heat sealed, FEP Teflon, 17.7 cm effective length									
25.10[b]	119[b]	55.3[b]	0.1273[b]	0.1213[b]	23	−5.8[b]	0.1226	11[b]	−3.7[b]
29.80	130	9.8	0.1954	0.1979	5	+1.3	0.1939	7	−0.8
19.95	139	7.9	0.0784	0.0777	4	−0.9	0.0790	3	+0.7
25.15	216	43.0	0.1279	0.1248	11	−2.5	0.1283	1	+0.2
29.18	229	13.3	0.1848	0.1860	3	+0.5			
19.90	250	15.0	0.0780	0.0790	6	+1.2			
					Av. dev.	**−0.1**[c]			**0.0**[c]
Swagelok ferrule sealed, TFE Teflon, 4.2 cm effective length, stainless steel bottle									
29.80	66	10.7	2.569	2.581	6	+0.5	2.626	8	+2.2
19.95	75	7.9	1.246	1.259	4	+1.0	1.266	3	+1.6
25.10	87	6.7	1.830	1.800	4	−1.6	1.849	4	+1.0
25.15	152	43.0	1.837	1.808	11	−1.6			
29.18	165	13.3	2.458	2.422	3	−1.5			
19.90	186	15.0	1.241	1.224	6	−1.4			
					Av. dev.	**−0.8**[c]			**+1.6**[c]

[a] From line fitted to data by the least-squares method.
[b] This line of data excluded from calculations.
[c] Average, including signs.

Table IV. Permeation Rates and Activation Energies for Gravimetric Calibrations (20–30 °C)

Gas	Teflon type	Seal type[a]	Tube length, cm	No. of runs	Rate at 25 °C, μg/cm min	Activation energy, kcal/g-mol
Propane	FEP	F	4.2	29	0.167[b]	14.7[b]
Propane	FEP	F	7.1	29	0.126	16.5
Propane	FEP	F	10.5	29	0.126	15.8
Propane	FEP	F	12.2	29	0.133	15.4
Propane	FEP	F	16.2	28	0.139	16.3
Propane	FEP	F	17.7	37	0.126	16.4
Propane	FEP	SW	7.2	22	0.126	16.5
Propane	FEP	SW	8.5	24	0.137	16.3
Propane	FEP	SW	11.5	24	0.138	16.7
Propane	FEP	SW	14.0	24	0.135	16.3
				Mean	**0.1318**	**16.24**
				Rel SD	**4.4%**	**2.5%**
Propane	TFE	SW[c]	4.2	49	1.859	13.0
Propene	FEP	SW	12.5	3	5.13	15.4
Butane	FEP	SW	14.9	2	0.0243	15.8
Butene-1	FEP	SW	14.2	2	0.0316	14.8
Butane	TFE	SW	13.7	2	0.2579	12.7
Butene-1	TFE	SW	13.5	2	0.3679	12.4

[a] F = fused seal, SW = Swagelok ferrules.
[b] This data excluded as outlying.
[c] With stainless steel bottle.

The typical results obtained by in situ volumetric calibrations of propane calibration tubes are given in Table V. They show the accuracy and the degree of constancy that can be achieved. A relative 0.8% SD was observed for FEP Teflon tubes and 0.1% for TFE Teflon tubes. The lower precision of the former was probably due to the lower rate.

Performance of Flow Dilution System

Studies were made of the operating characteristics of the flow dilution system indicated in Figure 3. The propane–stainless steel bottle–TFE Teflon permeation tube was used. The mixture was monitored with a Beckman Model 109 hydrocarbon analyzer, operating at 1 × attenuation and 1.34 psi sample pressure. It was found that after a calibration run, 2 or 3 min sufficed to flush completely the microgasometer and reach a steady state in the dilution system. Good performance was obtained from the system. The instrument response was closely proportional to the calculated concentrations in the flow system. It was necessary, of course, to make sure that the flow rate of the mixture exceeded that drawn by the instrument so that no outside air entered.

Because the response of the system to changes in water bath temperature is an important operating characteristic, several experiments were conducted with results shown in Figure 6. In these experiments the water bath temperature was changed as rapidly as possible. A mercury thermometer was used to measure the temperature of the water bath alongside of the test tube. For each temperature that was observed, the theoretical permeation rate was calculated. The corresponding calculated gas concentration in the dilute mixture is shown in the dashed line of the figure. The monitored concentrations lagged behind these as indicated by the solid line. The lag, probably representing the time required for the permeation tube to reach the water bath temperature, was usually less than 15 min. This demonstrates the convenience of the system, even with changes in temperature. To guarantee complete equilibration, an hour or so should be allowed.

Part of the lag described above could be due to the response characteristics of the hydrocarbon analyzer. To determine these characteristics, the sample inlet to the analyzer was alternately switched from a blank to a bag containing propane–air mixture. The calculated results are given in Figure 7. This is plotted in the same manner as was Figure 5. A more rapid response was obtained when the instrument was going to higher concentrations than when the instrument was going to lower concentrations; the 95% response times were 0.9 and 2.7 min, respectively. The difference may be due to the diffusion of hydrocarbons into and out of the dead volume in the instrument plumbing. During the decreasing concentration period, this process had a greater effect on the low blank reading than it had on the high readings during ascending conditions. These results indicate that only a small part of the lag shown in Figure 6 can be due to the monitoring instrument. The remainder must therefore be interpreted as the response characteristic of the dilution system.

Table V. In Situ Volumetric Calibration of Propane Permeation Tubes

FEP Teflon[a]		TFE Teflon[b]	
Final tube age, days	Rate, at 25 °C, μg/cm min	Final tube age, days	Rate, at 25 °C, μg/cm min
278	0.1252	217	1.8046
279	0.1259	217	1.8073
279	0.1241	218	1.8044
279	0.1233	223	1.8041
281	0.1248	**Mean**	**1.80510**
284	0.1255	Rel. SD	**0.1%**
284	0.1258		
Mean	**0.12494**		
Rel. SD	**0.8%**		

[a] Heat sealed, FEP Teflon tube, 17.7 cm effective length.
[b] Swagelok ferrule sealed, TFE Teflon tube, 4.2 cm effective length, with stainless steel bottle.

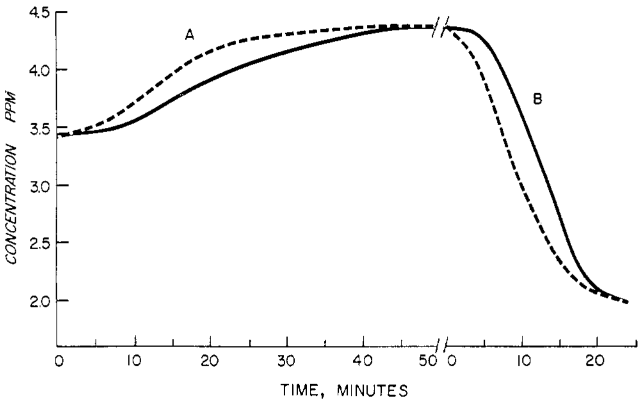

Figure 6. Responses of flow dilution system to changes in water bath temperature setting

(A) Water bath temperature raised from 26.55° to 30.10 °C
(B) Water bath temperature lowered (with addition of ice) from 30.10° to 19.20 °C

Solid line gives concentration readings of monitoring instrument; dashed line, those calculated from theoretical permeation rates at measured temperatures of bath

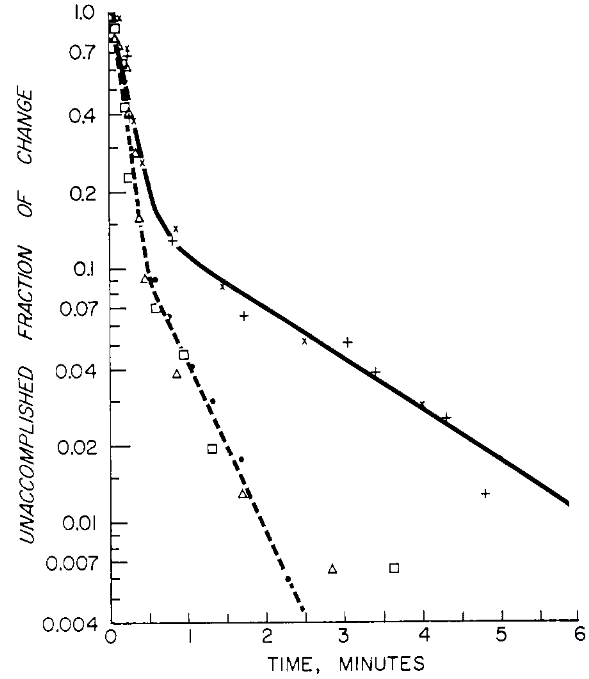

Figure 7. Response characteristics of Beckman Model 109 hydrocarbon analyzer

Dashed line—sample connection switched from blank to 8.2 ppm propane
Solid line—sample connection switched from 8.2 ppm propane to blank

Nomenclature

A = mean age of air mixture during run, min (from time of closing vent)
E = activation energy of permeation process, cal/g-mol
G = gravimetric rate, μg/min cm, at test temp
K = equilibrium constant, atm, for the dissociation reaction $N_2O_4 \rightleftharpoons 2\ NO_2 = (NO_2)^2/N_2O_4$
L = effective tube length, cm
M.W. = molecular weight (46.0067 for NO_2)
p = ideal partial pressure of NO_2 outside of permeation tube, atm
P_{NO_2} = vapor pressure of liquid NO_2 inside tube at test temperature, atm
P = barometric pressure, torr
r = mean back pressure ratio (partial pressure of gas outside of permeation tube to vapor pressure inside)
R = gas constant, 1.9872 cal/g-mol °K
S = measured volumetric rate, μl/min (slope of plot)
T = test temperature, °K (°C + 273.16)
V = volume of air mixture, ml (volume of test tube and connections)
z = compressibility factor, mean for run

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Effects of Hydrogen Fluoride on Production and Organic Reserves of Bean Seed

Merrill R. Pack
College of Engineering Research Division, Washington State University, Pullman, Wash. 99163

■ The response of bean fruiting to HF gas was investigated in a series of experiments in growth chambers. No response was found when plants were fumigated at 4.5 to 8.0 μg (F)/m^3 for 7 to 14 days during or near flowering. Bean plants exposed from seeding to harvest to as little as 2.1 μg (F)/m^3 produced fewer fruit and (or) fewer seed per fruit than control plants. In lower HF treatments and in one experiment at 2.2 μg (F)/m^3, no effects were evident. Where fruiting was affected, the mature seed had a somewhat faded, shriveled appearance, weighed less, and had a markedly lower starch content than seed of control plants. There were no definite differences in reducing sugars, total sugars, protein, or ether extract. The effects on bean fruiting were independent of visible injury to the foliage.

Atmospheric fluorides have been suspected of affecting plant fruiting, but there has been little research to investigate the possibility. Brewer and associates (1960, 1967, 1969) consistently obtained lower yields of Washington navel orange fruit in response to fluoride treatments applied either as HF gas in the atmosphere of greenhouses or as HF or NaF in solution sprayed on trees growing outdoors. They attributed the lower yields to less photosynthetic area on the fluoride-treated trees resulting from smaller leaf size and premature leaf drop. Studying Valencia oranges in a grove exposed to relatively high levels of airborne fluorides, Leonard and Graves (1966) found that trees enclosed in plastic greenhouses receiving unfiltered ambient air produced 21% less fruit than trees in greenhouses receiving air filtered through calcium carbonate filters to remove fluorides. Unenclosed trees in the grove produced 78% less fruit than those in the greenhouses with filtered air.

If fluoride reduces the total leaf area or injures the leaves of plants, fruit production logically may be less, simply because of reduced photosynthetic capacity of the foliage; but the author found evidence of a direct effect of fluoride on tomato fruiting (Pack, 1966). Tomato plants exposed to HF at 6 μg (F)/m^3 from 45 days after seeding till harvest produced smaller fruit than plants grown in a filtered atmosphere. The smaller fruit was partially or completely seedless, suggesting that the fluoride was interfering with some phase of fertilization or seed development. Tomato fruiting was not affected at 3 μg (F)/m^3.

The investigation reported here shows that the production and organic reserve composition of bean seed can be affected by growing the plants in an atmosphere containing HF.