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### A REVIEW OF PERMEATION TUBES AND PERMEATORS

Gerald D. Mitchell<sup>a</sup>

<sup>a</sup> Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.

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## A REVIEW OF PERMEATION TUBES AND PERMEATORS

**Gerald D. Mitchell**

Chemical Science and Technology Laboratory,  
National Institute of Standards and Technology,  
Gaithersburg, MD

### ABSTRACT

In this review, the basic principles underlying the design and application of permeation tubes and permeators are discussed. The fundamental theory is cast in terms of Fick's Laws and Henry's law. The various types of polymer materials and permeation tube devices are then discussed, with a view toward the final application of the devices. Finally, calibration and lifetime issues are treated.

*Keywords:* Calibration, permeators, permeation tubes.

### INTRODUCTION

Over the last four decades, the trend in environmental studies has been toward monitoring ever-lower concentrations of trace impurities. Permeation tubes

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and permeators offer a simple method for preparing low concentrations of gas mixtures. Known concentrations of a variety of air pollutants may be prepared by passing clean air or nitrogen over permeation tubes that contain the compound of interest. Since 1966, the uses of permeation tubes and other permeation devices have grown to such an extent that they are now produced commercially for more than 400 compounds. The underlying technology has branched out into controlled-release devices used in medical applications, membrane separation technologies and the dynamic blending of gas mixtures.

Permeation tubes are polymeric tubes containing a hermetically sealed liquid. The most common polymeric materials used for permeation tubes, TFE Teflon (tetrafluoroethylene) and FEP Teflon (Fluorinated ethylene propylene) are chosen because of their durability, low reactivity and availability. Other materials used to construct permeation tubes are polyethylene, polyvinyl acetate, polyvinylidene chloride, polyamide, polyester, nylon, and silicones. To fabricate a tube, one end of the polymeric tube is plugged with a solid rod. The tube is filled with liquid and sealed with another section of rod. Additional support is given to the plugged areas to reinforce the seal. The permeation process consists primarily of the dissolution of the gas in the polymer, the diffusion through the polymer wall and the passing of the gas into the atmosphere surrounding the outer surface of the tube. The main driving force for permeation is the difference in the partial pressure between the inner and outer walls of the tube. Permeation processes are highly sensitive to temperature, and therefore temperature must be carefully controlled to maintain stable permeation rates. In practice, permeation tubes and permeators are primarily used to generate low concentrations of reagent gas mixtures.

Permeation devices come in a variety of designs and configurations. The most common configurations are the sealed Teflon tube, the Teflon tube with a stainless steel or glass reservoir (microbottle), and the wafer device. Many other devices have been designed and reported. Wafer devices are designed to be used with fluids that have extremely high vapor pressures and low permeation rates. The gas permeates through a polymer membrane inserted into a stainless steel device. The only difference in the Teflon tube and reservoir devices is the reservoir used to hold a larger quantity of the permeating fluid.

The processes behind the operation of permeation tubes and permeators are best described by Fick's Law of Diffusion and Henry's Law of Solubility. The behavior of a device is characterized by three distinct stages: saturation, steady-state and depletion or decay. The saturation stage is best understood as a combination of solubility and diffusion of the gas molecules in the wall of the tube material. The steady-state stage in the useful life of a permeation tube occurs when the permeation rate of the tube is controlled and constant. Physically, the steady state-stage represents that period after initial fabrication when the permeation rate is constant and a liquid remains in the tube. A new saturation stage occurs whenever there is a change in condition away from constant permeation. The depletion stage

occurs when the liquid in the tube vanishes and the permeation rate trend is toward zero. During the saturation and depletion stages, the permeation rate of the tube is not reliable. During the steady-state stage, the tube can be used as a reliable gas delivery device.

The simplicity of permeation devices has made them an integral part of field-work in environmental air pollution studies. Gravimetric, volumetric, and manometric techniques have been developed to calibrate permeation devices and permeators as primary analytical standards.

## TECHNICAL PRINCIPLES

Diffusion is the process by which gaseous substances are transported by means of random molecular motion. In the mid-1800's, a series of equations (Fick's Laws) was introduced that quantified transport of material through a membrane. Fick's First Law states that the flux of the concentration of a component across a membrane of unit area, in a predefined plane, is proportional to the concentration differential across that plane. From the Fick's first law, the rate of diffusion,  $J$ , is given by the expression:

$$J = -Ddc/dx, \quad (1)$$

where  $D$  is the diffusion coefficient,  $c$  is the concentration of the diffusing species, and  $x$  is the distance. Under steady-state conditions in which the flux,  $J$ , is invariant with time, the integral value of  $J$  is inversely proportional to the thickness,  $L$ , of the solid material.

Fick's Second Law states that the rate of change of concentration in the volume element of a membrane, within the diffusion field, is proportional to the change of concentration gradient at that point in the field. Mechanistically, the process is the dissolution of the substance within the tube into and through the wall material of the tube. After diffusion through the wall of the tube, a diluent gas stream sweeps the permeated molecules away from the outer surface. During the saturation stage a permeation tube undergoes processes governed by Henry's Law and Fick's Second Law, occurring within the tube material.

In the gas-polymer system, a Henry's-law-type equilibrium is exhibited between the external gas pressure and the concentration of the gas dissolved in the solid material. This is expressed as follows:

$$C = S \cdot p \quad (2)$$

where  $C$  is concentration,  $S$  is solubility, and  $p$  is pressure for a particular gas-polymer system. The permeability,  $P$ , is given by the product of Henry's Law constant,  $S$ , the solubility coefficient, and  $D$ , the diffusion coefficient. Equation 3

relates the permeability, P, to the solubility coefficient, S, a thermodynamic property, and to the diffusion coefficient, D, a kinetic property.

$$P = D \cdot S \quad (3)$$

Temperature dependence of the permeability, diffusion, and solubility coefficients over small temperature ranges are given by Equations 4, 5, and 6. ( $E_p$  and  $E_d$  are activation energies for the overall permeation and diffusion processes. ( $H_s$  is the heat of solution, and  $P_o$ ,  $D_o$  and  $S_o$  are pre-exponential constants related to the permeating molecules for each process respectively.

$$P = P_o \cdot e^{-\Delta E_p/RT} \quad (4)$$

$$D = D_o \cdot e^{-\Delta E_d/RT} \quad (5)$$

$$S = S_o \cdot e^{-\Delta H_s/RT} \quad (6)$$

The permeation process depends on both kinetic and thermodynamic properties of the system. It is expected that gas permeation through polymeric materials is not solely dependent upon specific properties of the permeating material or the substrate, but upon the interaction between them.

To use a permeation tube as a predictable source of a gas, it must be maintained in the steady-state stage. At steady state, the diffusion potential of the permeating gas (the difference in its partial pressure across the tube wall) and the diffusion transport must remain constant. In the steady state stage, both the diffusion potential and transport are directly dependent on temperature, thus it is extremely important to control specific operating conditions. At steady-state, the quantity of gas permeating through the wall of the tube is expressed by

$$q_s = P \cdot A \cdot (p_i - p_o)/d \quad (7)$$

$q_s$  = sample emission rate

P = permeability

A = surface area

$p_i$  = pressure of reagent gas inside the tube

$p_o$  = pressure of reagent gas outside the tube

d = thickness of the tubes wall.

The permeation rate of any gas through a permeation tube of length, L, and radius, r, can be expressed by the following equation.

$$q_s = 2\pi r L P_o \cdot e^{\Delta E_p/RT} (p_i - p_o)/d \quad (8)$$

Equation 7 allows the rate to be calculated theoretically, however, the actual permeation rate of a device is determined gravimetrically, volumetrically, or manometrically.

## DEVICE CHARACTERIZATION AND LIMITATIONS

### Material and Configuration

A typical tubular permeation device may have a wall thickness between 0.75 mm and 1.75 mm and vary between 1 cm and 30 cm in length. Common permeation rates for tubes range from 5 to 50 ng/min depending on device size and operating temperature. Practical departures from the theoretical performance of permeation devices are the result of restrictions caused because of the device size, the membrane wall thickness, operating temperature, or properties of the polymeric material. The polymer must be able to withstand the internal pressure of the liquefied gas and not go through any physical transitions at the operating temperature that would effect it's permeation rate.

The reservoir tube limitations are essentially the same as those of tubular devices. The major differences are the size and nature of the reservoir used and the permeation area of the polymer. The microbottle device usually has a lower permeation rate because of its smaller polymer surface area. This type of permeation device is commonly used to deliver a wide range of permeation rates while significantly increasing its useful life.

Wafer devices are used for materials that are not liquid at ordinary temperatures, such as nitric oxide, methane and carbon monoxide; however, the full range of gases usable with tube and reservoir devices may be used in wafer devices. The major limitation associated with the wafer device is in the calibration technique used to quantify the permeation rate. With conventional gravimetric techniques, the large mass of the device coupled with a low permeation rate may cause the calibration process to take more than a year to complete.

### Equilibration and Stability

Equilibration and stability are the two most important periods in the life cycle of a permeation tube. Equilibration periods are required when the permeation tube is first filled, after a small change in temperature, or when the tube has been exposed to a high concentration of the permeating gas for an extended period. In the later case, if a permeation tube is stored in a closed container, the gas builds up on the outer wall of the tube to the point where it affects the permeation rate. When this happens, the permeation rate decreases and the diffusion and solubility processes within the polymer shift in the direction of decreased permeation. A shift in the rate due to a change in temperature involves two processes: a change in the diffusion rate of the permeating gas through the polymer that is governed by Fick's First law and a change in the solubility of gas in the polymer.

The time for equilibrium to be reached after a temperature change may be anywhere from a few minutes to a few days depending on the gas, the polymer

wall-thickness, and the polymeric material. It has been shown that permeation tubes made of TFE and FEP Teflon® containing inorganic gases must be conditioned at a temperature of above 40 °C for a minimum of 24 hours to assure stable and reproducible operation. Once conditioned, the equilibration time from a storage temperature at –15 °C to an operation temperature of 30 °C for sulfur dioxide and other inorganic gas permeation tubes range from 24 hours to 48 hours. For smaller step changes in temperature, the permeation rate reaches 95 % of the new value in approximately 30 minutes. The remaining 5% is achieved within the following 24 hours. Hydrocarbon permeation tubes behave differently: longer equilibration times are required after a step change in temperature. Gas-membrane interactions have to be considered when using hydrocarbon compounds as the active reagent in a permeation device. With certain highly fluorinated or chlorinated compounds, the Teflon® tube material is not truly inert and the permeation rate is affected.

Stability (Steady State Stage) occurs when the permeation tube is maintained under constant conditions for an extended period. At steady state, a permeation device will maintain a constant permeation rate as long as the liquid/vapor equilibrium within the device is maintained. When no liquid is present, the device enters the Decay Stage where the permeation rate falls toward zero.

### Temperature Limitations

The permeability coefficient,  $P_o$ , shown in Equation 4 is a pre-exponential constant related to the permeating gas characteristics and the polymer properties. The permeability coefficient of the gas determines the temperature response characteristics of permeation tubes or permeators. Under normal operating conditions, permeation tubes are maintained during the steady state stage at a constant temperature. The permeability characteristics of the membrane affect all aspects of the permeation tube process because of their effect on the permeability coefficient of the gas passing through it. This is the primary design parameter when selecting the optimum polymer membrane material for the fabrication of a permeation tube. However, wall-thickness is also a parameter that must be taken into consideration when designing a device for a specific application. Gases with high permeability through the polymer may require a heavier wall. Permeation devices have restrictions related to the pressure limitations of the polymer material. The device must also maintain a two-phase liquid/vapor equilibrium at and above room temperature without fracturing the polymer.

Because of a temperature transition effect of Teflon material reported at 30 °C, the majority of studies performed on permeation devices have been confined to the 20 to 30 °C temperature range. Recent findings have shown that the temperature transition reported at 30 °C occurs in fact at 39.6 °C for both TFE and FEP Teflon® materials. For sulfur dioxide permeation tubes, the rate of change in

the permeation rate with temperature increases above the transition temperature. It was also shown that the permeation rate at a given temperature above or below the transition temperature is repeatable once the initial conditioning above 40 °C has taken place. When a permeation device is initially fabricated, it should be conditioned by placing it in a constant temperature environment at 40 to 43 °C with dry nitrogen or air flowing over its outer surface for a period 48 hours.

The permeation rates of a device may be estimated at different temperatures when the rate is known at a given temperature. The rule of thumb is that for each 1 °C increase in temperature, the rate increases by 10%. Considering the new findings reported above, the rule of thumb should not be used to estimate the rate of a permeation device beyond the transition temperature 39.6 °C of a Teflon® polymer. For more precise calculations of the permeation rate, manufacturers provide for each tube type (high or low emission) a temperature coefficient for the permeating material. The generalized equation for calculating a rate at a new temperature is:

$$\text{Log } R_2 = \text{Log}_1 + \alpha(T_2 - T_1) \quad (9)$$

where,  $R_1$ , is the rate at,  $T_1$  (°C),  $R_2$ , is the new rate at,  $T_2$  (°C). The temperature coefficient of the device,  $\alpha$ , is a function of the gas and the permeable material. For Teflon® tube material it has been shown that the permeation rate can be reproduced to within 1% when the temperature is raised or lowered and cycled back to its original set point. For sulfur dioxide tubes, this feature is observed even for repeated temperature excursions above the transition temperature of the Teflon® polymers.

## CALIBRATION METHODS

To determine the permeation rate of a device accurately the device must first be calibrated at a specific temperature or over a specific temperature range. Several different calibration methods have been developed that allow permeation devices to be used as primary analytical standards. Gravimetric, volumetric, and manometric techniques have been used as reference methods for calibrations. A gravimetric calibration involves the periodic weighing of the device. The time between weighing is governed by the output of the device and the limitations of the balance. The balance used must be capable of measuring a weight loss to a milligram or better. For wafer devices, where the permeation rates may be as low as 5 ng/min, the gravimetric process may take weeks or months to complete, if several temperatures are involved in the calibration.

An alternative to the static gravimetric rate determination is a dynamic determination using an electrobalance. The capacity of the electrobalance also limits the maximum weight of the permeation device. The tube to be calibrated is suspended from the balance inside a temperature-controlled jacket held at a fixed temperature. The weight loss is continuously recorded versus time, and a permeation rate is calculated as the slope of the weight-time curve.

The volumetric method uses a compensating microgasometric technique. The permeation tube is housed in a sealed, compensating Warburg syringe manometer submerged in a water bath. The meniscus of the manometric fluid is adjusted to a reference position after the Warburg apparatus and the tube have come to thermal equilibrium. As the gas permeates, it displaces the manometric fluid and this displacement is recorded with time. Permeation rates are calculated from the pressure and volume measurement taken during the calibration. Limitations associated with this method are:

- (1) Correcting all measurements to standard conditions,
- (2) Correcting for the solubility of the permeating gas in the manometric fluid,
- (3) Correcting for the vapor pressure of the manometric fluid,
- (4) Correcting for those gases having large deviations from the ideal gas volume, and
- (5) Having a substantial partial pressure of the permeating gas in the chamber surrounding the permeation tube.

The absolute pressure method can also be used to calibrate permeation tubes. The apparatus used consists of a permeation tube chamber, and a calibrated pressure transducer, an accurate method for measuring the volume of the chamber is also needed. The method has been shown to provide rapid and accurate calibrations of all types of permeation devices using both condensable and noncondensable gases. Table 1 gives a comparison of the different calibration techniques. The

**Table 1.** Comparison of Calibration Methods

Method	Permeation Rate (ng/min)	Time (Hours)	Time (Days)
Gravimetric-microbalance	2,000	100	4
	200	1,000	40
	20	10,000	400
Volumetric	2,000	2.5	0.1
	200	25	1
	20	250	10
	2	2,500	100
Gravimetric-electrobalance	200	10	0.4
	20	100	4
	2	1,000	40
Absolute pressure	200	1	0.04
	20	10	0.4
	2	100	4

data presented are for wafer devices and are intended to show the time required for a calibration with a precision of 2% at a given a specific permeation rate. Each calibration method is accurate and requires inexpensive apparatus, but it is recommended that the calibration method be chosen to match the specific application.

## APPLICATIONS

Permeation tubes and permeators are used today in a variety of applications such as gas calibration systems, atmospheric air pollution measurements, the controlled release of drugs for medical uses, and in process control technology. For gases such as sulfur dioxide ( $\text{SO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ), and hydrogen sulfide ( $\text{H}_2\text{S}$ ), permeation-device technology is routinely used to produce reliable and stable gas mixtures for analytical service. At low concentrations, the instability of these and other reactive gases in cylinders make it imperative that permeation tubes be used to prepare gas mixtures dynamically. The most commonly used application of permeation tubes is as a calibration gas source. This particular application is responsible for the development of automated continuous air pollution analysis.

One example of the use of permeation tubes is in the study of atmospheric levels of nitric oxide (NO) and nitrogen dioxide. A calibrated  $\text{NO}_2$  permeation tube can be used as a calibration source of both NO and  $\text{NO}_2$ . The NO is generated from  $\text{NO}_2$  through the quantitative catalytic action of a molybdenum converter. The output of the  $\text{NO}_2$  permeation tube is directly determined through weight loss using a calibrated balance. The NO is quantified through the conversion efficiency of the molybdenum converter.

Permeation technology and the use of permeators have expanded to the point where polymeric materials are designed commercially for specific membrane separation applications. The refinement of such materials has reached the point where the solubility or permeability selectivity for one material over another may be magnified hundreds of times. This property permits some polymers to be more permeable to one material over another while being more solubility-selective to other materials. One application of this technology is the design of gas separation membranes that are more permeable to larger molecules than smaller. Using permeability and solubility selectivity, membrane materials are designed that exhibit high permeability to toxic volatile organic compounds in natural gas and at the same time a high selectivity to other unwanted components of the natural gas mixture. These applications of permeability and solubility technologies have also been applicable to water purification, electrodialysis, chemical and food preparation, drug delivery, and medical treatments. The application of permeation tubes and permeators is only limited by the imagination of the experimentalist.

## BIBLIOGRAPHY

1. O'Keefe, A.E. and Ortman, G.C., "Primary Standard for Trace Gas Analysis," *Anal. Chem.*, 38, 1966, 760-763.
2. Scaringgelli, F.P., O'Keefe, A.E., Rosenberg, E. and Bell, J.P., "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically," *Anal. Chem.*, 1970, 42, 871-876.
3. Purdue, L.J. and Thompson, R.J., "A Rapid, Sensitive Method for Calibration of Permeation Devices," *Anal. Chem.*, 1972, 44 1034-1036.
4. Williams, D.L., "Permeation Tube Equilibration Tines and Long-Term Stability", *Calibration in Air Monitoring*, ASTM STP 598, American Society for Testing and Materials, 1976, 183-197.
5. Hughes, E.E., Rook, H.L., Deardorff, E.R., Margeson, J.H. and Fuersty, R.G., "Performance of a Nitrogen Dioxide Permeation Device," *Anal. Chem.*, 1977, 49, 1923-1829.
6. Namiesnik, J., "Generation of Standard Gaseous Mixtures", *Journal of Chromatography*, 1984.300, 79-108.
7. Nelson, G.O. *Gas Mixtures Preparation and Control*, Lewis Publishers, Boca Raton, 1992.
8. Mitchell, G.D., Dorko, W.D., Johnson, P.A., "Long-Term Stability of Sulfur Dioxide Permeation Tube Standard Reference Materials", *Fresenius J. Anal.Chem.*1992, 344, 229-233.
9. Hsien-Wen, K., Jund-Der, W., "Collection and Determination of 4,4'-Bipyridine Vapor Using XAD-2 Resin", *Chemsphere*, 1996, 32, 2057-2065.10.McKinley, J.J., Merriman, D.C., "Permeation Tube Sources for Internal Standards in Process Samples", *Process Control and Quality*, 1996, 8, 69-74.