

ESTABLISHING TEMPERATURE CHANGE CHARACTERISTICS ASSOCIATED WITH EQUILIBRIUM TIMES OF PERMEATION TUBES

Danet M. Vrazel
Technical Sales & Service Mgr.
Kin-Tek Laboratories, Inc.
504 Laurel St.
La Marque, TX 77568

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ABSTRACT

Teflon® permeation tubes are a proven method for making trace concentration gas mixtures when used in their equilibrium state. Permeation rates are established by a gravimetric weight loss method after equilibration at a stable temperature. Frequently, permeation tubes are subjected to drastic temperature changes when stored at low temperatures or used over a range of temperatures. Such changes can cause transient characteristics that result in substantial deviation from expected permeation rate data. Performing calibrations during non-equilibrated transient phases affect analyses and wastes time. This paper investigates transient temperature characteristics and establishes equilibrium times for disposable type permeation tubes containing hydrogen sulfide (H₂S), carbonyl sulfide (COS), toluene (C₆H₅CH₃), and water (H₂O).

INTRODUCTION

Teflon® permeation tubes have been an effective source of gas standards for the calibration of sensitive gas analyzers for over thirty years. Permeation tubes are effective for creating low concentration gas mixtures in the part per million to part per trillion range (1). Currently, over 400 compounds are commercially available as NIST traceable gas standards based on a gravimetric loss method at a specified stable temperature (1). However, documentation is limited detailing the characteristics of individual permeation tubes when subjected to non-equilibrium

conditions. Dynamic temperature changes cause transient characteristics that affect the permeation rates of the compounds investigated in this paper. However, the effect temperature has on certified permeation rates can be avoided by identifying the time lapse to controlled equilibrium. This paper investigates transient temperature characteristics and establishes equilibrium times for disposable type permeation tubes containing hydrogen sulfide (H₂S), carbonyl sulfide (COS), toluene (C₆H₅CH₃), and water (H₂O).

MATERIALS AND METHODS

Four previously certified disposable permeation tubes were subjected to drastic temperature changes in order to determine emission rate behavior and response times to equilibrium conditions. There were no special criteria for choosing the tubes other than availability, commercial popularity, and trends seen by laboratory technicians during a typical gravimetric weight loss certification procedure. The four tubes consisted of the following analytes and tube properties:

- 1). H₂S, supplied by Matheson Gas Products.
Tube properties: Teflon® FEP tube, 10 cm length membrane, 0.25" O.D., 0.0625" I.D., manufactured by Ain Plastics. (Cat# SRT-2-010.00-1002/50)
- 2). COS, supplied by AGA Gas Inc.
Tube properties: 7.5 cm stainless steel non-permeable reservoir, 2.54 cm Teflon® FEP, 0.10 cm length membrane, 0.25" O.D., 0.0625" I.D., manufactured by Ain Plastics. (Cat# ELSRT-2W-125.10-1003/30)
- 3). H₂O, distilled, supplied by Ozarka.
Tube properties: Teflon® TFE, 10 cm length membrane, 0.25" O.D., 0.030" I.D., manufactured by Zeus Industrial Products, Inc. (Cat# HRT-010.00-3019/100)
- 4). C₆H₅CH₃, supplied by Aldrich Chemical Company.
Tube properties: Teflon® TFE, 10 cm length membrane, 0.25" O.D., 0.030" I.D., manufactured by Zeus Industrial Products, Inc. (Cat# HRT-010.00-3019/100)

A permeation tube consists of a small volume of pure analyte liquid sealed inside an established length of Teflon® tubing (2). The tubing wall serves as a permeable membrane separating the pure analyte from an inert carrier gas flow. Pure analyte permeates through the tubing wall (membrane) as the tube is heated creating a small, very stable flow of vapor known as the permeation rate. The permeation rate is continuous and stable at equilibrium conditions and is directly dependent on temperature control (1, 2). The permeating vapor is further diluted by an inert carrier gas (i.e. Nitrogen) and carried through the permeation system at a controlled volume of flow. Changing dilution carrier gas volume creates different concentration levels for the calibration of gas analyzers (3).

Each disposable permeation tube is typically certified by a weight loss method traceable to the National Institute of Standards and Technology (NIST). During the weight loss certification procedure, tubes are placed in permeation ovens that are calibrated using thermometers directly traceable to NIST (annual calibration assures +/-0.1 °C accuracy) and have a temperature range

of 30°C to 120°C. The amount of analyte emitted from each individual tube is measured gravimetrically after holding the tube at a constant specified temperature in a flow of inert carrier gas. Periodic weighing determines the rate of analyte loss over time resulting in the calculation of tube permeation rate values. General procedure dictates that a tube is considered certified when 3-4 consecutive weight loss measurements result in a stable repetitive rate of loss to +/- 2% accuracy.

Certified tubes are shipped to their respective buyers or stored in a manner that slows the emission rate until future purchase. Storage for each compound used in this experiment was as follows: Hydrogen sulfide tubes are stored in a freezer at a temperature of 0°C. Water tubes are stored at room temperature (~23°C). Carbonyl sulfide is stored at room temperature (~23°C), and toluene is stored in a refrigerator (4°C).

Each tube used in this experiment was taken from its respective storage facility to effectively determine initial perm tube response to temperature change. Tubes were weighed by conventional method using a standard five-decimal place microbalance, and immediately placed on a specially equipped Cahn electrobalance with a recorder and two glass enclosed scales. The weighing scale of the electrobalance was modified to slide easily into a permeation oven (temperature range of 30°C to 120°C) for easy temperature adjustment without disturbing the permeation tube or the electrobalance. Flowing nitrogen was applied to the weighing apparatus and a vent line was constructed to closely mimic the normal laboratory use of a disposable permeation tube. Nitrogen flow was set at approximately 200 cc/min with flow measurement verified by a calibrated flow measurement device. An adjacent chart recorder was set to record weight loss over time at a rate of 2 cm/hr.

Each tube was subjected to different temperature changes consistent to their allowable maximum operational ranges. Temperature dynamics ranged from 0°C to 80°C (freezer to oven) to temperature changes of ambient to an increase of only 10°C, dependant upon the respective permeation tube. Changes in permeation rates of tubes were identified as each tube was exposed to a temperature transition. Variations in permeation rates depict transient characteristics that occur until the tube stabilizes to a given temperature change. Tubes were given hours and sometimes days, if needed, to stabilize to a new temperature set point. High permeation rates depict sharp dynamics of permeation tube responses over a short period of time. Data was recorded sequentially to observe permeation tube responses until the permeation tube stabilized at the final recorded permeation rate.

No predetermined amount of temperature change was decided for this experiment. Temperature changes were randomly selected up or down in at least 10°C increments and were expected to illicit a verifiable response with respect to time. Permeation rates were calculated after the initial temperature change until a steady response and slope was seen for each temperature change. Permeation rates were calculated by dividing the amount of weight lost by the time lapse recorded.

Table I shows examples of temperature changes with respect to tube permeation rates for each analyte studied until equilibrium was achieved. Each tube had an initial increase in permeation

rate despite the action of an increase or a decrease in oven temperature. Additionally, each tube depicted a transient characteristic to temperature change defined by drastic permeation rate changes until equilibrium was achieved.

TABLE I – EMISSION RATE CHARACTERISTICS OF PERMEATION TUBES TO TEMPERATURE CHANGES

ANALYTE	OVEN TEMPERATURE	ACTION	PERMEATION RATE CHANGES (NG/MIN)
H ₂ S	50°C	Temperature Increase	13,636 4,110 4,167 10,789
		Equilibrium	7,500
H ₂ S	30°C	Temperature Decrease	11,111 4,856
		Equilibrium	4,490
COS	50°C	Temperature Increase	50,000 4,651 2,979
		Equilibrium	2,500
COS	40°C	Temperature Decrease	5,556 2,402
		Equilibrium	2,290
H ₂ O	80°C	Temperature Increase	88,889 9,195 6,311
		Equilibrium	4,815
H ₂ O	30°C	Temperature Decrease	2,068 1,675
		Equilibrium	1,012
C ₆ H ₅ CH ₃	80°C	Temperature Increase	72,222 9,848 7,692
		Equilibrium	4,688
C ₆ H ₅ CH ₃	40°C	Temperature Decrease	7,619 1,173
		Equilibrium	1,083

Typical permeation ovens have digital temperature controllers that increase or decrease at the push of a button and are accurate to +/- 0.1°C. The average response time required for the oven to stabilize to a 10°C to 40°C temperature increase or the response time required for the oven to stabilize after decreasing the temperature 10°C to 50°C ranged from 40 minutes to 180 minutes, respectively. It takes longer for the oven to cool to a given temperature decrease than it does to a given temperature increase.

The purpose of the electrobalance recorder is to chart even the slightest weight changes using a pen recorder equipped with rolling chart paper adjustable from 1cm/hr to 60 cm/min. Recordings can be charted daily without interruptions to the apparatus. A scale measurement was determined by placing tare weights on the scale and noting the recorder response to each weight increment to

establish a quantified chart recorder response to weight changes. Chart paper recordings were adapted to actual weight change measurement; one milligram of tare weight moved the recorder pen a total of 20 millimeters in length on the chart paper (1 mg = 20 mm). The recorder setting for time lapse was 2 cm/hr, equivalent to 20 millimeters in paper length. Each recorded temperature response per tube was standardized to the same weight and time scale and were converted to permeation rates in nanograms per minute for comparison.

Permeation rates were noted at specific points of each permeation tube response in order to determine any relationship or pattern resulting from an increase or decrease in oven temperature. See Table I for permeation rate patterns. Other measurements were taken verifying slope of a recorded line with emission rate values.

RESULTS

Permeation rates of tubes used in this experiment were calculated from an initial point of equilibrium (or recorder zero line) to a point of visible response or elicited response. See Figure 1 parts A through D for an example of a recorded weight loss response of a toluene tube measured from 80°C to a temperature decrease of 40°C.

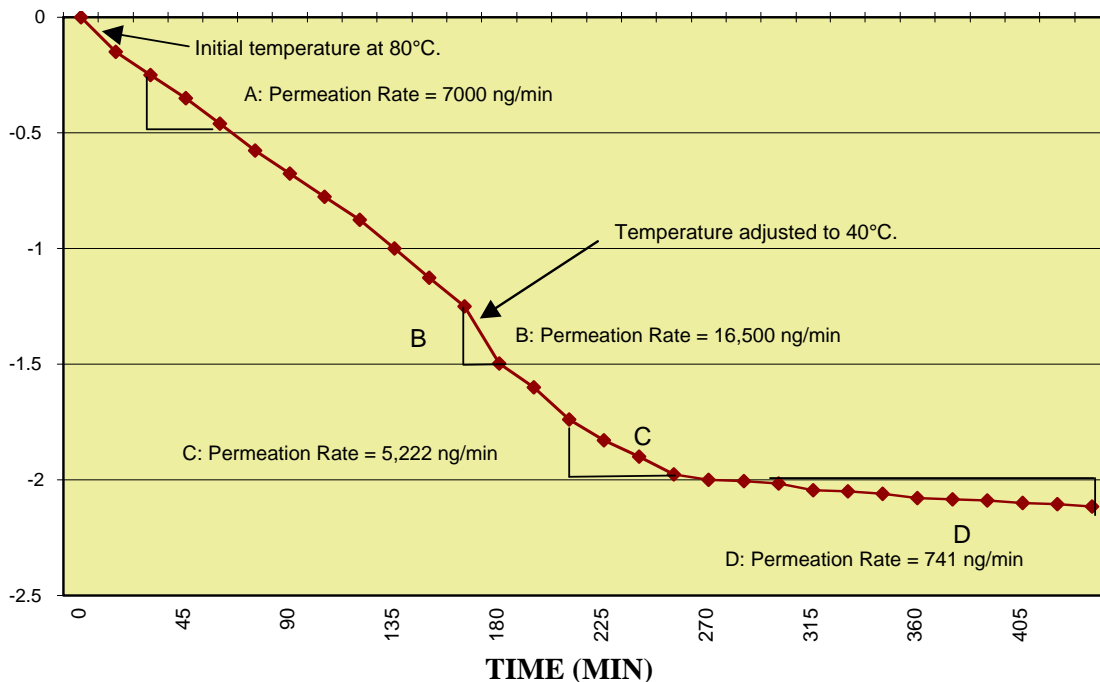


FIG. 1 - TOLUENE RESPONSE TO TEMPERATURE CHANGE FROM 80°C TO 40°C.

A consistent pattern of weight loss was charted over 165 minutes at 80°C. The calculated permeation rate at 80°C was 7000 ng/min until a temperature change was made to 40°C. The

toluene tube then experienced transient temperature characteristics for 120 minutes until it reached equilibrium again at 40°C. Chart recorder measurements were converted to permeation rates to determine permeation rate deviations during a temperature change. The calculated rates of 16,500 ng/min and 5,222 ng/min (See Figure 1, parts B and C, respectively) indicate drastic deviations in tube permeation rates during temperature instability. Calibrating an analyzer during a temperature instability phase would result in unreliable data or false readings.

Transient temperature characteristics were also observed when permeation tubes were subjected to extreme temperature changes common to normal use. Figure 2 shows the response of a H₂S permeation tube taken from its recommended storage facility of 0°C and immediately placed in an oven preheated to 50°C. Part A on Figure 2 indicates an odd occurrence observed within the first 230 minutes of oven exposure; the permeation tube appeared to have gained weight before stabilizing. The H₂S tube later reached the equilibration permeation rate of 10,200 ng/min (See Figure 2, part B) at 50°C.

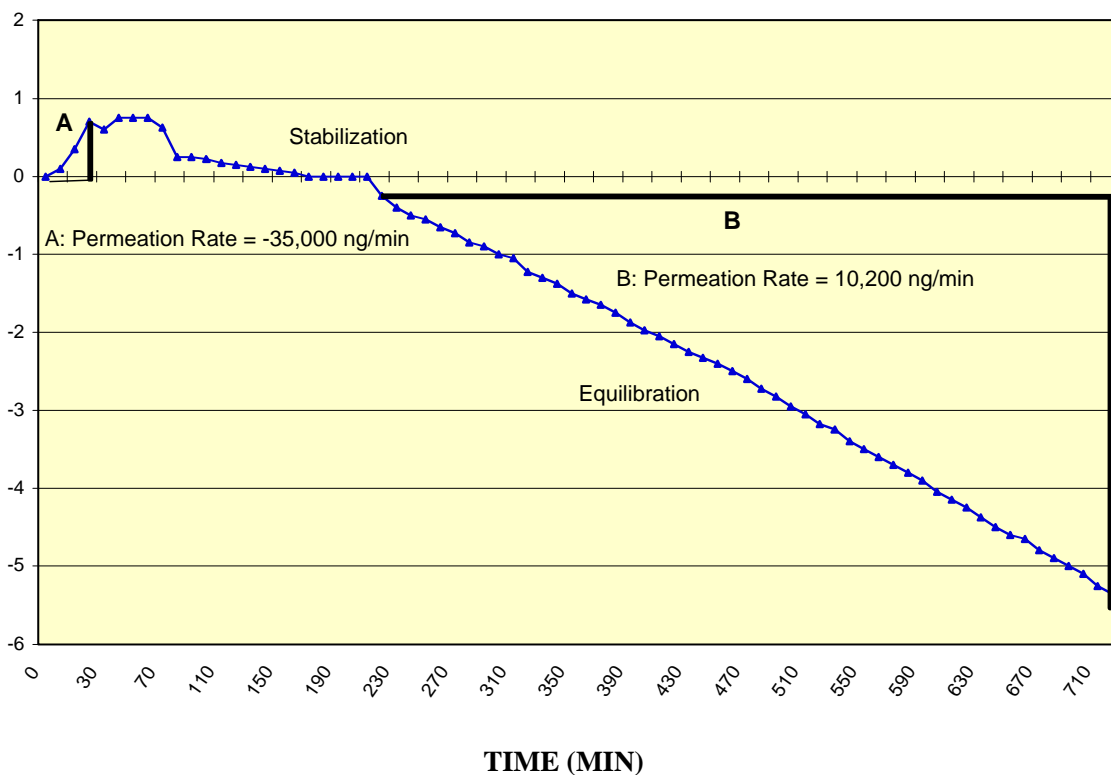


FIG. 2 – H₂S RESPONSE TO TEMPERATURE CHANGE FROM 0°C TO 50°C.

A common trend to a temperature increase was observed in all four tubes used in this experiment and was depicted by a peak drawn in the positive direction on the Cahn electrobalance recorder. A peak in the positive direction depicts a gain in weight as opposed to an expected loss of weight, and converts to high emission rate values due to extreme changes over a the small lapse

of time. Although unexpected, this response was characteristic to 16 of the 20 temperature increases (80%) throughout the experiment. Also, of a combined total of 8 temperature decreases in all four tubes, all 8 responses (100%) resulted in a positive curve from the zero line before equilibrium was reached and the expected linear weight loss trend was observed.

The average time for all of the tubes to equilibrate after a temperature increase ranged from 99 minutes to 275 minutes. The average time for the tubes to equilibrate after a temperature decrease ranged from 28.5 minutes to 303 minutes. Equilibration times were calculated based on the recorder readings at initial exposure to oven temperature (zero line or equilibrium point) until the tube depicted a stable weight loss. Mean equilibration times were calculated per tube with response to an increase or decrease in temperature.

The Teflon® FEP tube with hydrogen sulfide took an average of 275 minutes to equilibrate after an initial temperature increase of 10°C or more and 99 minutes to reach equilibrium after initial temperature decrease of 10°C or more. For the Teflon® FEP carbonyl sulfide tube (COS), the average equilibration time after temperature increase of 10°C or more was 173 minutes with 28.5 minutes being the average equilibrium time after a temperature decrease of 10°C or more. The Teflon® TFE water tube took an average of 128 minutes to equilibrate to an increase in temperature of 10°C or more and 303 minutes to equilibrate to a temperature decrease of 10°C or more. Similar to the response of the water tube, the Teflon® TFE toluene tube also had a lower average equilibration time after a temperature increase of 10°C or more (99 minutes) than that of the average temperature decrease of 10°C or more (214 minutes).

DISCUSSION

Several variables can contribute to the final interpretation of data. Three different types of permeation tubes were used varying in thickness, length, and type of Teflon®. Four different analytes were examined without concern to any known solubility or diffusivity properties. Real scenarios of permeation tube use include removing a tube from storage and placing it directly in an oven. This paper purposely disregards controlling variables. However, given the results of the experiment, several aspects must be considered.

Firstly, the time for the oven to independently respond to temperature changes has an effect on tube equilibrium time. This is obvious when comparing equilibrium times of individual tubes taken directly from storage or when the tube is already in the oven at the time of a temperature change. Secondly, the initial transient characteristic weight loss curve seen in all of the temperature decreases and increases resulted in an increase in emission rate when converted from the linear recorder response. The emission rate increase is real but is misleading since calculation is based on the slope of the line drawn over time. A curved or peak response indicates the slope of the line is constantly changing, converting to a high and unstable permeation rate (See Figure 2 and Table I). Hence, the rapid weight loss seen at the time of a temperature decrease contributes to the notion of a transient characteristic since calibration attempts during this time period would easily result in false readings. However, an observed curve is a response to continued weight loss of the tube at initial temperature equilibrium, and the transition in temperature between the oven and the tube until equilibrium is met again. This transient

characteristic can be avoided by determining oven and tube equilibrium times to temperature change or by taking a series of weight change measurements over time until consistency is seen. Thirdly, solubility rates of the analyte and properties relating to tube membrane composition may contribute to final interpretations of permeation abilities at varying temperatures (4).

Despite the obvious effects of oven temperature change versus tube equilibration time, the type of tubing does seem to play a definitive role in average equilibration time, as expected. An overall comparison of equilibration times at a temperature decrease results in longer equilibration times for the Teflon® TFE tubes investigated compared to that of the Teflon® FEP type tubes investigated. A plausible and noted explanation is given as known permeability differences in membrane composition between Teflon® FEP and Teflon® TFE permeation tubes (5). It may also be considered that equilibration times of Teflon® TFE tubes after temperature decrease would be consistent to that of the oven equilibration time, since Teflon® TFE tubes used in this experiment were thin walled, highly permeable tubes. The average response time for oven stabilization to a temperature decrease of 10°C to 50°C ranged from 40 minutes to 180 minutes, respectively. Oven equilibration time and Teflon® TFE tube equilibration time to lower temperatures seem to actually overlap each other causing a longer delay.

The thicker walled Teflon® FEP type tubes had an opposite effect with regards to average equilibration time after a temperature decrease. Equilibration time was actually reduced because the thicker tube membrane possibly contained vapor molecules longer and the weight loss curve is not as dramatic. Also, the effect of a temperature change takes longer in a thicker membrane and the permeation rate of the tube stays more consistent to the previous temperature setting. Due to tube membrane composition differences affecting vapor permeability rates (6), by the time the oven reaches the lower temperatures and equilibrates, vapor inside the tube has already adjusted, and the new emission rate is seen in less time creating a gradual change in the recorder. A curve still exists at the initial change depicting a high emission rate, but a linear response takes less time.

The same concept can also explain the differences in equilibration times after an increase in temperature, but in an opposing manner. A longer time is required for equilibration of Teflon® FEP type tubes due to the thickness of the tube as compared to that of the thinner type Teflon® TFE tubes. The thicker Teflon® FEP type tube is not as responsive to direct temperature changes, and time is needed for equilibration to a dramatic change in temperature. Additionally, the time required for the oven alone to equilibrate directly relates to the observed responses of the thinner Teflon® TFE tubes since these tubes are quickly affected by initial temperature changes. Both oven and tube take a considerable time to reach the newly set temperature decrease, but not as much time to adjust to a temperature increase.

A peak was drawn (suggesting an actual weight gain) by the balance recorder in 80% of the temperature increases of all the tubes investigated in this experiment. This permeability phenomenon can also be attributed to membrane composition, molecular interactions taking place inside and outside the permeation tube, or simply by a balance artifact related to rapid temperature increase. Linear peak measurements as seen in Figure 2 varied with temperature increments and tube types and also resulted in very high emission rates but in a direction of

weight gain. These unexpected peaks seen on the recorder definitely deserve further investigation.

CONCLUSION

A typical gravimetric weight loss certification procedure involves recording weight loss over time for a given temperature until three closely repetitive permeation rates are observed. An average of these measurements results in the final certified emission rate. A gravimetric weight loss procedure is acceptable for certification purposes because enough time for equilibration is given to each tube and tube equilibration is noted by several consistent weight loss recordings. Additionally, there are no temperature variations other than the few minutes the tubes are removed from respective ovens and weighed at room temperature. Certain analyte properties may be responsive to ambient room conditions during a weight loss measurement, however, the tube is isolated in a closed system and held at controlled conditions for most of the certification time. Typically, when permeation tubes are being used for calibrating an analyzer they are often taken from storage and placed in a heated permeation oven without adequate time for equilibration. Transient temperature characteristics cause emission rate variations resulting in false calibration values when tubes are used prior to equilibration.

This study aids in recognizing a minimum equilibration time required for using Teflon® permeation tubes with similar properties. The values reported above show that a Teflon® permeation tube with similar properties should be given at least 303 minutes (~5 hours) to equilibrate in order to avoid transient characteristics associated with temperature changes.

The temperature changes in this paper created permeation rate deviations related to different types of Teflon® disposable permeation tubes without direct regard to analyte properties. The transient temperature characteristics described after an initial temperature change lasted several minutes and resulted in drastic permeation rate differences until the permeation tube reached equilibrium. The best way to prevent inaccurate calibrations due to permeation rate deviations is to allow enough time for tube equilibrium to be achieved. Further investigation of permeation tube equilibration times is required to compare tube materials with respect to analyte behavior and to adequately address specific time frames associated with various permeation tubes.

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