VCP - ANALYTICAL PROCEEDURES

file VC - Analytical

Vinyl chloride permeation tubes have been utilized to provide a convenient and accurate standardization procedure for charcoal tube monitoring of atmospheric vinyl chloride. The procedure circumvents the need of determining charcoal desorption efficiencies and eliminates the handling of free vinyl chloride in the laboratory preparation of vinyl chloride standards.

Preparation of vinyl chloride standards using a permeation tube

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introduction

Since the original work ten years ago on the fabrication, calibration and use of permeation tubes, permeation tube systems have found increasing use in the preparation of dynamic gas mixtures for calibration and standardization purposes in the parts per million concentration range.[1-4] The simplistic nature of the permeation tube system and its fundamental physical means of operation characterize it as a primary standard system with precision and accuracy dependent only on gravimetric and temperature control parameters. Overall accuracy of the system has been reported to be of the order of 1-2% but more recent refinements in technology, utilizing a recording microbalance, may permit attainment of even greater accuracy.[3,5]

The basic physical chemistry mechanism involved in permeation tube technology is derived from the original investigations into diffusion.[6] Fick's first law established the role of concentration gradient as the potential function, or driving force, for movement of material in a physical system.

Formulation of this law required the introduction of a constant, D, which Fick designated as the Diffusion Coefficient ($l^2 t^{-1}$).

$$\left(\frac{dn}{dT}\right)_x = -DA\left(\frac{dc}{dx}\right)_T$$

The Diffusion Coefficient is an intrinsic property of the diffusing material and the validity of Fick's Law, as a basic diffusion equation, has been proven beyond question by its application to a variety of experimental problems. For practical purposes, a more useful form of Fick's Law is contained in the classical equation for Flux, F, where, at any instantaneous value of concentration,

$$F_{x,T} = \left(\frac{dn}{dT}\right)_x \bullet \frac{1}{A} = -D\left(\frac{dc}{dx}\right)_T$$

Flux has the dimension of $m\,l^{-2}\,t^{-1}$. In a system where the total diffusing mass is considered, rather than the mass per unit area, the Flux becomes the Permeation Rate (mt^{-1}).

In permeation tube technology the material of interest is sealed into a short length of plastic tubing and maintained in a constant temperature environment. Periodic weighings of the permeation tube provide weight loss data which are readily convertible to a permeation rate, usually expressed as micrograms per minute (mt^{-1}). If, in addition, a diluent gas flow is introduced into the permeation tube system, mixing with the diffusing material, a fully dynamic primary system is established.

Various plastics have been investigated for the fabrication of permeation tubes but the one most commonly used is fluorinated ethylene-propylene resin (FEP Teflon).® Tubes can be prepared in any laboratory or they can be purchased from several commercial sources at nominal cost ($20-$25). Liquifiable materials are most adaptable to permeation tube use and gases with critical temperatures above 20-25°C serve best.[7] Vinyl Chloride has a critical temperature of 156.5°C.

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TABLE I
Standardization History, Permeation Tube B-900
(September 1974 to May 1975)

STANDARDIZATION INTERVALS				WEIGHT LOSS, MILLIGRAMS	PERMEATION RATE MICROGRAMS MINUTE
9-18	to	9-24	142 42 hrs	53.9	6 308
9-24	to	9-27	73 38 hrs	27 1	6 155
9-27	to	9-30	72 23 hrs	27 3	6 299
9-30	to	10- 7	165 02 hrs	63 4	6 289
10- 7	to	10-14	168 32 hrs	63 4	6 278
10-14	to	11- 4	502 10 hrs	187 6	6 227
11- 4	to	12-10	864 30 hrs	325 2	6 271
12-10	to	2-27	1897 23 hrs	71[illegible]2	6 283
2-27	to	4-10	1001 76 hrs	375 9	6 254
4-10	to	4-17	168 08 hrs	62.2	6 168
4-17	to	4-24	168 10 hrs	63 2	6 266
4-24	to	5- 1	168 10 hrs	62 0	6.147
5- 1	to	5-14	316 47 hrs	118 0	6.214

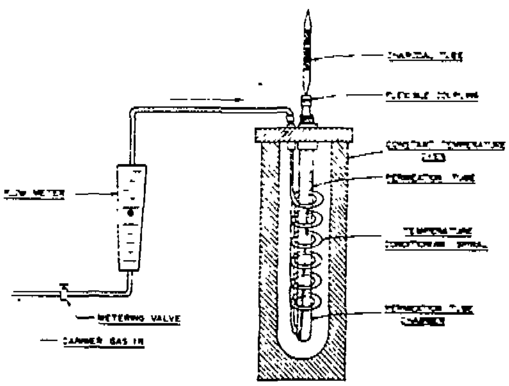

Figure 1 - Schematic of permeation tube system.

The vinyl chloride permeation tube has been found to be convenient, accurate and reasonable in cost as a calibration system for atmospheric vinyl chloride determinations.

experimental design

The permeation tube system used in our laboratory is diagrammed in Figure 1. The specific permeation rate must be determined for each separate permeation tube. Table I presents detailed data for one permeation tube, B-900 and Table II summarizes permeation data for tubes B-900, B-1136 and B-1272. Once the permeation rate is known, charcoal tube standards can be prepared by varying the residence time of charcoal tubes in the system.

The single most important element of the permeation tube system is the constant temperature oven housing the permeation tube and chamber. The oven used in our work provided internal temperature control of at least ±0.5°C. Oven temperature is critical since permeation rate is a function of temperature. Scaringelli has reported that a change in temperature of 0.1°C will produce an error in permeation rate of approximately 1%.[3]

The top of the oven is removable for access to the permeation tube and chamber (Figure 2) permitting the permeation tube to be removed for weighing. The net loss of vinyl chloride between weighings, divided by the corresponding time interval, yields the permeation rate for that specific tube. (Tables I & II).

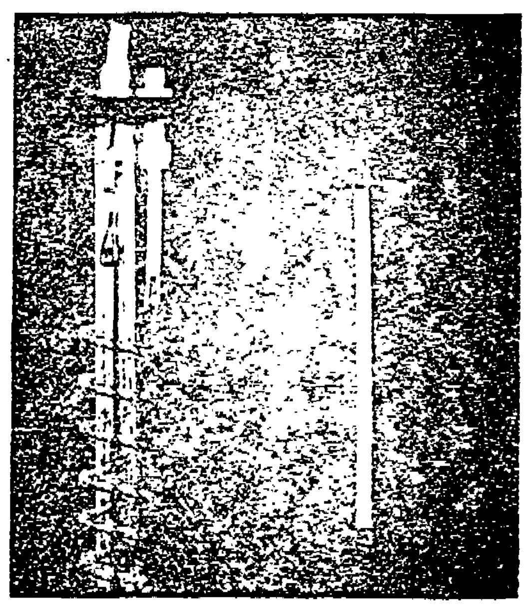

Figure 2 - Permeation tube and chamber.

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TABLE II
Summary of Standardization Data
for
Three Permeation Tubes

PERMEATION TUBE IDENTIFICATION	PERIOD OF USE	NUMBER OF WEIGHINGS	PERMEATION RATE, MICROGRAMS/MINUTE			
			RANGE	MEAN	STD DEV	COEFFICIENT OF VARIATION*
B-900	9-18-74 to 5-14-75	13	6.147-6.308	6.243	±0.056	0.897%
B-1136	5-19-75 to 11-25-75	22	7.370-7.557	7.443	±0.057	0.766%
B-1272	12-2-75 to 2-24-76	14	6.470-6.731	6.600	±0.084	1.273%

*Relative Standard Deviation

Factory air, used as the carrier gas, was passed through a metering valve adjusted to maintain a flow rate of 100 cc/min. The carrier gas enters the constant temperature oven through the temperature conditioning spiral, passes into the permeation tube chamber and mixes with the vinyl chloride gas permeating through the walls of the permeation tube.

The diluted vinyl chloride - air mixture exits through the top of the oven. Charcoal tubes placed in the exit stream can be charged with known quantities of vinyl chloride.

results and discussion

permeation rate

Permeation tube B-900 was purchased in September, 1974 from Analytical Instrument Development, Inc.* The tube was placed in the constant temperature oven and allowed to equilibrate for several days at 30°C. and 100 cc/min air flow. On September 18, the initial weight of the tube was measured as 9.7715 g, using a Mettler H51AR five place balance and the exact time recorded. Six days later, September 24, the tube was weighed again, the time recorded and the tube immediately placed back inside the oven. The tube weighed 9.7176 g for a loss of 53.9 mg. of vinyl chloride over a 142.42 hour period. The permeation rate was calculated as 6.308 μg/min. Table I gives the standardization history for permeation tube B-900 over a 9 month period at 30°C and 100 cc/min air flow.

The shortest standardization interval was a three day period from September 27 to September 30, in which 27.3 mg of vinyl chloride were lost over 72.23 hours, resulting in a permeation rate of 6.229 μg/min.

In comparison, the longest standardization interval was a 79 day period from December 10, 1974 to February 27, 1975 in which 715.2 mg of vinyl chloride were lost over 1897.23 hours, resulting in a permeation rate of 6.283 μg/min. Data listed in Table I effectively illustrate the consistent permeability characterisitcs of permeation tube B-900 over the entire life history of the tube.

Permeation rates for two other permeation tubes, B-1136 and B-1272, were also determined. Table II summarizes the standardization data for all three permeation tubes and presents various statistical parameters for each of the individual tubes. Combining the Coefficients of Variation that have been calculated for each tube, an overall Coefficient of Variation of 1.0% is obtained for the vinyl chloride permeation tube system.

standards

After the permeation rate for a specific permeation tube has been established, analytical standards can be prepared by charging charcoal tubes with known quantities of vinyl chloride. In Table I, the permeation rate for tube B-900 on September 24, 1974 was 6.308 μg/min. Therefore, charging charcoal tubes on the permeation system for 0, 1, 3, 5, 10, 15 and 20

*Analytical Instrument Development, Incorporated, 250 South Franklin Street, West Chester, Pennsylvania, 19380.

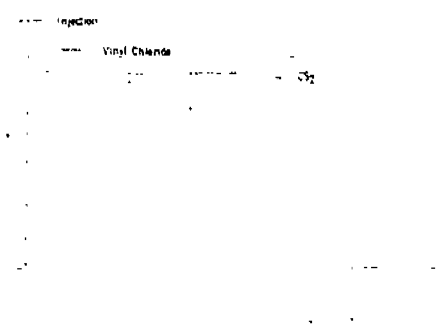

Figure 3 - Gas chromatographic elution of vinyl chloride.

minutes would result in charcoal tube standards containing 0, 6.3, 18.9, 31.5, 63.1, 94.6 and 126.2 micrograms of vinyl chloride. A stop watch is used to measure residence time of a charcoal tube on the system. It is important to make certain that the carrier gas flow is not altered when a charcoal tube is placed on the system.

Since some variability in permeation rate does exist, the permeation tube should be weighed prior to preparing a set of standards. As an example, the permeation rate for tube B-900 on May 1, 1975 was 6.147 micrograms/min. Standards prepared on this day would contain 6.1, 18.4, 30.7, 61.5, 92.2 and 122.9 micrograms of vinyl chloride rather than the quantities indicated in the paragraph above.

After charging, both sections of the charcoal tube standards were desorbed with 1 milliliter of carbon disulfide for at least thirty minutes. One microliter injections of each standard were made on a Model 5170A Hewlett-Packard Gas Chromatograph, equipped with a flame ionization detector, at the following conditions:

Column:	10 ft. 10% Silicone Oil DC-200 on 80-100 WHP.
Column Temperature:	75°C
Injection Temperature:	200°C
Detector Temperature:	250°C
Range:	10
Attenuation:	8

An actual chromatogram of the elution of vinyl chloride is shown in Figure 3. Peak heights are obtained directly from the chromatogram and are used to draw a standard curve for the data by the least squares method. The equations used to obtain the standard curve in Figure 4 are:

$$\Sigma y = na + b(\Sigma x)$$
$$\Sigma xy = a(\Sigma x) + b(\Sigma x^2)$$

which reduces to:

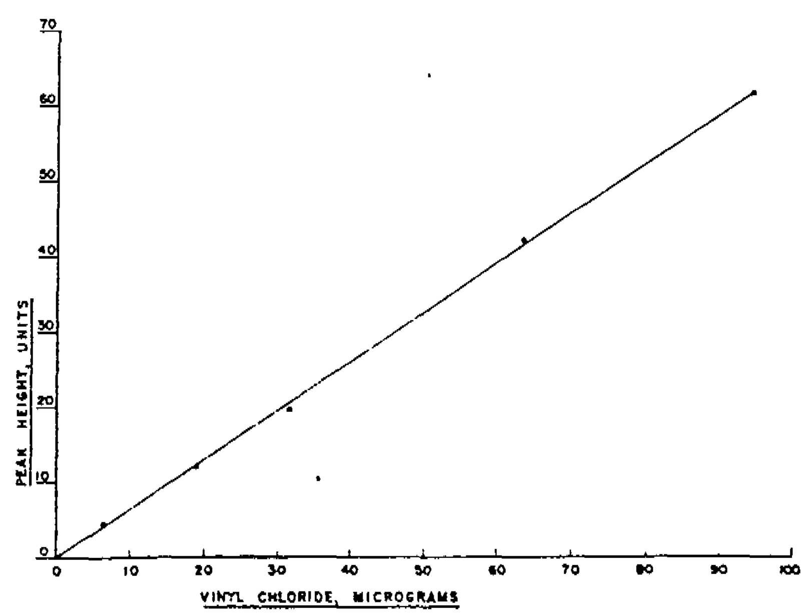

Figure 4 - Peak height versus vinyl chloride for permeation tube B-900.

TABLE III
95% Confidence Intervals for Single Points on Standard Curve
(Permeation Tube B-900, 6.308 ug/min)

VINYL CHLORIDE MICROGRAMS	OBSERVED PEAK HEIGHT, UNITS	CALCULATED PEAK HEIGHT UNITS	CONFIDENCE INTERVAL	DEVIATION FROM OBSERVED PERCENT
6.3	4.2	4.14	3.17-5.10	1.4
18.9	12.6	12.42	11.60-13.23	1.4
31.5	19.8	20.70	19.96-21.43	4.5
63.1	42.3	41.46	40.52-42.40	2.0
94.6	61.9	62.15	60.68-63.63	0.4

TABLE IV
Statistical Summary of Standard Curve Data
for
Three Permeation Tubes at 95% Confidence Level

PERMEATION TUBE	PERMEATION RATE, ug/min	SLOPE, UNITS/ug	CONFIDENCE INTERVAL	ANALYTICAL C.V.	TOTAL C.V.
B- 900	6.308	0.657	0.635-0.679	0.02	0.05
B-1136	7.474	0.376	0.355-0.397	0.03	0.06
B-1272	6.616	0.414	0.365-0.463	0.06	0.08

$$\Sigma y = b\,(\Sigma x)$$
$$\Sigma xy = b\,(\Sigma x^2)$$

When a = 0, (y - intercept)

The standard curve shown in Figure 4 is for permeation tube B-900, permeating at a rate of 6.308 micrograms/minute. The six points represent the 0, 1, 3, 5, 10 and 15 minute standards, equivalent to 0, 6.3, 18.9, 31.5, 63.1 and 94.5 micrograms of vinyl chloride. Table III presents this data, along with the observed and calculated peak heights and 0.95 confidence intervals for each point on the standard curve. The final column, the percent deviation from observed, is the difference between the calculated and observed peak heights.

Table IV is a statistical summary of standard curve data for permeation tubes B-900, B-1136 and B-1272, at the 95% confidence level. The slope of the standard curve for each permeation tube at a specific permeation rate was calculated, along with a 0.95 confidence interval. Calculation of a confidence interval is important since the slope of the standard curve is the critical factor in determining vinyl chloride quantities. Subsequently, a coefficient of variation for the entire analytical method is derived from the slope/confidence interval data.

The total coefficient of variation considers the sampling coefficient of variation in addition to the analytical coefficient of variation. Therefore, considering 0.05 as the coefficient of variation for the sampling pump,[8] we obtain a total coefficient of variation for tube B-900 by:

$$CV_T = \sqrt{(CV_P)^2 + (CV_A)^2}$$
$$= \sqrt{(0.05)^2 = (0.02)^2}$$
$$CV_T = 0.05$$

The total coefficients of variation for tubes B-1136 and B-1272 were calculated in the same manner. For tube B-1136, $CV_T = 0.06$ and for tube B-1272, $CV_T = 0.08$. 95% of our measurements will fall within plus or minus 10%, 12% and 16% respectively, of the true concentration, depending on the specific permeation tube being used for preparation of the standards.

The data presented in Table V, again for permeation tube B-900, demonstrate three important points. First, that vinyl chloride breakthrough, although less than 10%, occurs after a 20 minute residence time on the permeation system. This corresponds to 126.0 micrograms of vinyl chloride adsorbed on the charcoal tube. A second point of interest is the sensitivity of the permeation tube system. The atmospheric concentrations represented by the listed microgram quantities of vinyl chloride, if contained in a 48 liter sample (8 hrs at 100 cc/min), range from 50 parts per billion to 1 part per million. This range includes the important "action level" and "permissible exposure values" of the current OSHA Standard for Vinyl Chloride (CFR 1910.1017). The OSHA required accuracy, at the 95% confidence level is ± 50% from 0.25 ppm through 0.5 ppm, ± 35% from over 0.5 ppm through 1.0 ppm and ± 25% over 1.0 ppm. A third point to be emphasized is that

TABLE V
Comparable 8-Hour Atmospheric Concentrations
for
Various Charcoal Tube Residence Times
(Permeation Tube B-900; 6.308 ug/min)

RESIDENCE TIME MINUTES	PEAK HEIGHT, UNITS	VINYL CHLORIDE MICROGRAMS	VINYL CHLORIDE PARTS PER MILLION [1]	OSHA REQUIRED ACCURACY
1	4.2	6 3	0.05	-
3	12.6	18 9	0.15	-
5	19.8	31.5	0.26	50%
10	42.3	63.1	0.51	50%
15	61.9	94 6	0.77	35%
20	[2]	126 0	1.03	25%

[1] Eight hour sample at 100 ml min.
[2] Less than 10% breakthrough.

TABLE VI
Interplant Comparison
of
Charcoal Tube Vinyl Chloride Analyses

	VINYL CHLORIDE, MICROGRAMS								
	LOW RANGE			MID RANGE			HIGH RANGE		
PLANT	TRUE VALUE	FOUND	PERCENT RELATIVE ERROR	TRUE VALUE	FOUND	PERCENT RELATIVE ERROR	TRUE VALUE	FOUND	PERCENT RELATIVE ERROR
		37.0			76.0			106.0	
	31.5		+15.9	63.0		+18.3	94.5		+10.1
		36.0			73.0			102.0	
A	34.0	38.0	+11.8	68.0	70.0	+ 2 9	102.0	100 0	- 2.0
		37.5						111.1	
	37.2		+ 0.8	-	-	-	111.5		+ 0.72
		37 5						113 5	
		35.6			70.0			105.6	
	31.5		+ 1.4	63.0		+12.9	94.5		- 0.7
		28.3			72.2			82.1	
B	34.0	32.0	-5.9	68.0	62.0	- 8.8	102.0	89.0	-12.8
		34 0						99.0	
	37.2		-11.3	-	-	-	111.5		-13.5
		32.0						94.0	

our sampling/analytical accuracies of plus or minus 10%, 12% and 16%, at the 95% confidence level, are well within the OSHA required accuracies.

interplant round robin

Table VI contains data from vinyl chloride round robin analyses conducted among 2 Goodyear Plants and the Corporate Industrial Hygiene Department. Three series of charcoal tube standards were prepared approximately six months apart and sent to Plants A and B for analysis. Two of the three series contained a low, mid and high range of vinyl chloride. A third series contained only low and high range standards. Two of the series, contained duplicate standards to check precision of the Plant's analytical methods.

The accuracy and precision of Plant A improved with each series of analysis, achieving a relative error (accuracy) of less than 1% in the final series. The performance of Plant B was just the opposite, with accuracy and precision decreasing. Both Plants performed all analyses using standards prepared by the regular volumetric method.

summary

Permeation tubes offer a convenient and accurate means of preparing primary vinyl chloride standards for use in a charcoal tube, air monitoring program. The need is eliminated for handling free vinyl chloride in the laboratory during the customary volumetric preparation of standards. Preliminary statistical evaluations also indicate a satisfactory level of accuracy is attainable for the sampling analytical method.

The nominal cost of the complete calibration system and the capability of preparing standards for many different atmospheric contaminants, makes the permeation tube standardization method a valuable analytical tool for the industrial hygienist.

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metrication comes to the JOURNAL

In keeping with the national trend to metrics, the American Industrial Hygiene Association JOURNAL will undergo metrication in 1977.

Effective with the January, 1977 issue, the official policy of the JOURNAL is that all units of measure previously shown in conventional fashion will now be shown both in metrics according to the ICS system and in conventional units. For example, **XX feet per minute (or fpm)*** will appear as **XX meters per second (or mps)***, FOLLOWED by **XX feet per minute (or fpm)*** in parentheses. All such measurements will be expressed as units metric (units conventional). Typically, **.508 mps (100 fpm).**

***Note:** Either the full expression of the unit of measure or its abbreviation should be used, NOT both.

Manuscripts approved for publication and in file will be returned to authors for insertion of metric measurements, where necessary. Manuscripts in the review or revision process also will be returned for the same purpose.

New manuscripts being prepared for submission should incorporate metrics, as outlined above.

In all cases, measurements now traditionally shown in metrics need not be converted to conventional equivalents.

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