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The reference vinyl chloride charcoal tubes generated by a permeation technique are evaluated by collaborative testing. The statistical analysis of Youden's method provides an estimate of replication error, sample generation error, and interlaboratory error.

Collaborative study of reference vinyl chloride charcoal tubes

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introduction

The disclosure of a relationship between exposure to vinyl chloride monomer (VCM) and angiosarcoma of the liver has resulted in a drastic reduction in the allowable exposure of workers to vinyl chloride monomer by the Occupational Safety and Health Administration.[1] According to the new standard, exposure to VCM must be controlled so as not to exceed 1 ppm average over an eight-hour period and 5 ppm average over a 15-minute period. The most widely used technique for analysis of VCM is gas chromatographic separation followed by flame ionization detection (GC-FID). The sample to be analyzed is collected in a tube packed with activated charcoal adsorbent. The accumulated sample is then desorbed in carbon disulfide for analysis. A standard reference sample is needed for monitoring the accuracy of the laboratory test. A study was undertaken to develop standard reference charcoal tubes containing known amounts of vinyl chloride monomer at the current OSHA standard by a permeation technique.

The primary objective of this study was to determine the variation and stability of vinyl chloride collected on charcoal tubes as well as the accuracy and precision of the laboratory analytical result through a collaborative test. In this collaborative test, the reference charcoal tubes were carefully prepared by a permeation technique and sent to collaborative laboratories. Each laboratory analyzed a set of four charcoal tubes containing two concentration levels of vinyl chloride with two tubes at each concentration level. Replicate determinations were performed on each charcoal tube. The statistical analysis outlined by AOAC[2] was used to analyze the laboratory data. The statistical data analysis provided estimates of error for sample generation (sample variation), of instrument precision, and of interlaboratory error.

sample generation system

Vinyl chloride gas for this study was produced by a dynamic permeation tube system.[3,4] In permeation tube technology, the vinyl chloride is liquified and sealed into a short length of plastic tubing and by maintaining a constant temperature environment the VCM permeated at a constant rate. Various plastics can be used for the fabrication of permeation tubes, but the most commonly used is fluorinated ethylene-propylene resin (FEP Teflon). Periodic weighing of the permeation tube or using other indirect methods provide the permeation rate, usually expressed as micrograms per minute (μg/min) If, in addition, a diluent nitrogen gas or pure air flow is introduced into the permeation tube system and mixed with vinyl chloride gas, then a full dynamic system is established.

The permeation tube system is shown in Figure 1. The pure air, used as the carrier gas is generated by an AADCO 737 pure air generator (AADCO, Inc., Rockville, MD). The pure air is passed through a Hylan digital flow controller to maintain a constant mass flow, and then entered

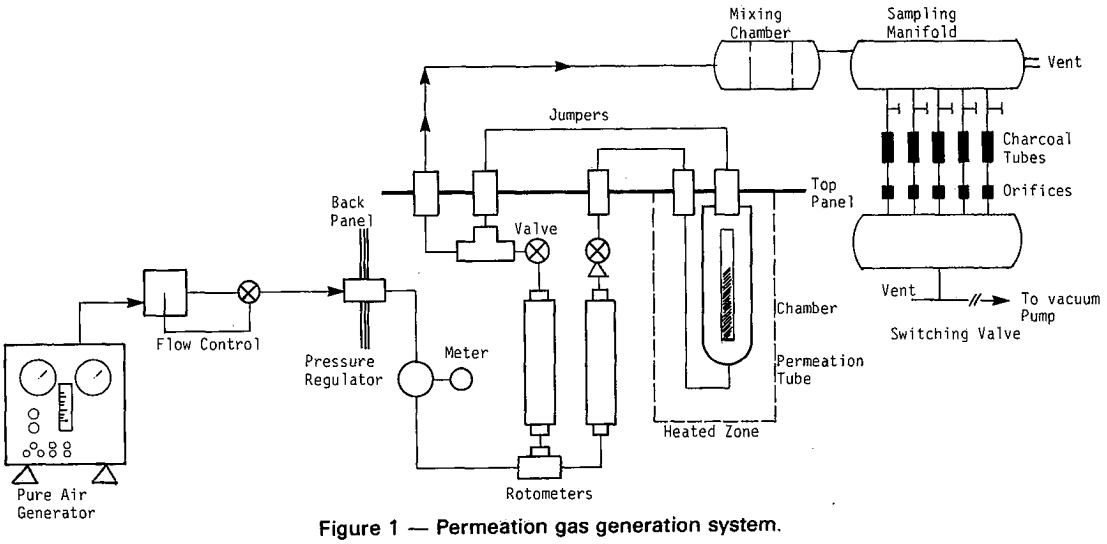

Figure 1 — Permeation gas generation system.

into an AID Model 309 Permeation System (AID, Inc., Avondale, PA). The pure air supply to the Model 309 enters the system through a 1/4" tube fitting mounted on the rear panel. At this point the pure air splits into two: one, the chamber flow, passes through a 0-2 liter/min rotameter and into a precision flow controller which provides flow adjustment over the required flow range; the second, the diluent air flow, enters a 0-8 liter/min rotameter. This flow is connected to the vent of the heated chamber via a jumper tube which allows further dilution of the stream containing the known vinyl chloride. The chamber which is located in the precisely controlled temperature zone, contains a high emission permeation tube with 3/8 inch OD and 5.91 inch length, supplied by Medronics Associates, Inc., Palo Alto, CA. The permeation tube releases a very precise and known amount of vinyl chloride into the pure air stream. Because the permeation rate is temperature dependent, the tube must be maintained in a very stable thermal environment. The heat zone is controlled by a fully proportional feedback temperature controller which can be varied from 30 to 80° C and maintained within ±0.1° C of the set temperature, indicated on a dial thermometer.

The gas mixture, after exiting from the permeation system, enters a mixing chamber featuring small entrance and exit ports and baffle plates with apertures. The well-mixed vapor finally enters the sampling manifold with an exit end vent to the exhaust hood. The underside of the manifold is equipped with 10 short lengths of 6 mm OD glass tubing to which are attached very short (8 mm) lengths of 4.76 mm ID PVC tubing. The tubing permits secure attachment of the sampling tubes.

Sampling of the vinyl chloride vapor is accomplished by drawing the vapor through a charcoal tube at a rate determined by a selected orifice downstream of the sampling device. The flow-determining orifices operate with a downstream vacuum maximum of 200 mm Hg absolute, which is substantially less than the required 0.53 ratio of downstream pressure to upstream pressure for the critical flow; thus, flow will be insensitive to variations in downstream pressure and will remain constant with a constant upstream pressure (sampling manifold pressure in this case). The sampling tubes and orifices are mounted on a two-inch diameter vacuum receiver manifold; ten may be mounted simultaneously. The receiver may be rapidly changed from atmospheric pressure to 200 mm Hg by a switching valve at the manifold outlet. Sampling orifices are constructed from 23-gauge, 1-inch, hypodermic needles, and are matched for flow characteristics as a group to a mean flow of 0.592 liter/min with an upstream pressure of 745 mm Hg. The group flow rate has a 0.7% coefficient of variation. Filters upstream of the orifices protect them from particulates which could alter their flow characteristics; this set of orifices has demonstrated unchanged flow characteristics over a 6-month period.

sample production

Samples in a given mass range may be produced by selecting values for the three variables in the system: diluent air flow rate, VCM permeation rate and sampling duration. The selection of values for the diluent flow rate and VCM permeation rate is limited as compared with that of sampling duration. Firstly, diluent air flow rate can not be less than the total sampling rate. Secondly, the permeation rate is limited by the tubing material and oven temperature. Oven temperature can not be set much higher than the ambient temperature in order to maintain a steady oven temperature. Once the first two variables have been properly set, sampling duration can be easily varied. Several sets of samples with different weights can be produced by varying sampling time as long as the break-through time for vinyl chloride adsorbed in the charcoal tube is not exceeded.

The permeation tube was placed in the constant temperature chamber and allowed to condition for several days at 40°C and 100 cc/min pure airflow. After the permeation rate for a specific permeation tube has been established, the proper diluent flow is adjusted and then the system is allowed to equilibrate for at least one hour. When the system is equilibrated and verified, six charcoal sampling tubes are prepared, labelled, and attached to both the sampling manifold and vacuum receiver. Vacuum is then applied and an electronic digital stopwatch is used to measure the residence time of charcoal tubes in the system. After the desired time interval has elapsed, the vacuum receiver value is switched to return the receiver to atmospheric pressure and the tubes are removed and capped.

quality control

The accuracy of vinyl chloride concentration output from the permeation system was estimated by comparing GC results with a reference certified vinyl chloride cylinder, purchased from Scott Specialty Gases, which was prepared gravimetrically by actually weighing the gas component on a high load, high sensitivity analytical balance. All weights were traceable to National Bureau of Standards. The mixture prepared by weight was verified by gas analysis and then certified by Scott. The certified value was 49.5 ppm ± 1% and was assigned as the true value. The stability of the generation system was monitored using a 32 mm (1/8 inch) O.D. Teflon tube to withdraw gas from the permeation assembly and the gas was pulled through the gas chromatography sampling valve with a vacuum pump at 100 mL/min. Sampling is maintained at 5 min. intervals. For a six hour sample generation period, vinyl chloride concentrations was 6.08 ppm ± 2.03% relative standard deviation.

The quality of vinyl chloride charcoal tubes was determined by GC analysis. In general, GC measurement is carried out by means of comparison with a standard. Two common methods of making primary calibration standard solution for vinyl chloride are the volumetric method and the gravimetric method: in the volumetric method a gas-tight syringe is used to measure a fixed volume of pure vinyl chloride and then dissolved in carbon disulfide liquid (CS_2). In the gravimetric method, either bubble pure vinyl chloride into a tared vial containing toluene, weigh and dissolve in CS_2 or condense vinyl chloride into a tared narrow neck ampule in dry ice, seal, and weigh it then dissolve in CS_2 by breaking the ampule. The vinyl chloride working standard solution is prepared by diluting various aliquots of this primary standard.

In our laboratory, the volumetric method was used to prepare the primary standard. After the vinyl chloride working standard was prepared, 5 μl of liquid sample with duplicate injections were made by a Varian Model 8000 auto-sampler on a Model 2440 Varian chromatograph with a Varian 485 digital integrator at the following conditions:

Column: chromosorb 102 column, 2′ 1/16″ O.D. stainless steel
Column temperature: 140°C
Injection Port Temperature: 160°C
Detector Port Temperature: 170°C
Range: 10^{-10} Amp/mv
Attenuation: 1X

Peak areas were obtained from the printout of digital integrator and were used to draw a standard curve for the data by the least squares method.

TABLE I
Analytical Result of Quality Control Samples

Sample	Target Value* $\bar{X} \pm$ S.D. μg/tube	Observed Analytic Result of Samples $\bar{X} \pm$ S.D. (n) μg/tube	Deviation From Target Value
A	12.68 ± 0.16	12.70 ± 0.327 (10)	0.16%
B	19.07 ± 0.23	19.16 ± 0.590 (10)	0.47%

*Standard deviation estimated based on the uncertainty of the concentration measurement and uncertainty of the flow variation.

TABLE II
The Stability of Reference Charcoal Tubes

Concentration Level	VCM Found Initially in Charcoal Tube $\bar{X} \pm$ S.D. (n) μg/tube	VCM Found From Return Charcoal Tube Stored 3 Months $\bar{X} \pm$ S.D. (n) μg/tube	Vinyl Chloride Recovered %
A	12.70 ± 0.327 (10)	13.02 ± 0.425 (14)	102.5
B	19.16 ± 0.590 (10)	19.29 ± 0.775 (14)	100.7

Ten vinyl chloride charcoal tubes at each of two concentration levels were randomly selected and desorbed with 1.5 milliliters of carbon disulfide for at least 30 minutes. Charcoal tubes were analyzed by GC in the same manner as that of calibration standard. The amount of vinyl chloride in charcoal tube was obtained by comparing GC results with calibration standard.

The analytical result of samples are shown in Table I. The target value with the uncertainties inherent in the preparation procedures was estimated based upon the gas phase concentration, sampling rate, and sampling time. The analytical result is considered to be in agreement with target values within the uncertainties assigned to each other.

The stability of the charcoal tubes were investigated as follows: five sets of charcoal tubes were analyzed in the Chemical Reference Laboratory (CRL) on the second and third days

TABLE III
Calculation Details of the Parameters of Youden's Analysis for a Study Involving Two Determinations On Duplicate Sets of Samples, A and B

BLOCK	Laboratory Number i =	1	2	3. . .n
	First Determination on Sample A	x_{1A}	x_{2A}	x_{3A}. .x_{nA}
	Second Determination on Sample A	x_{1A}'	x_{2A}'	x_{3A}'. . .x_{nA}'
	Difference of Two Determinations $x_{iA} - x_{iA}'$	d_1	d_2	d_3. . .d_n
TYPE I	Sum of Two Determinations $x_iA + x_iA'$	t_1	t_2	t_3. . .t_n
	First Determination on Sample B	X_{1B}	X_{2B}	X_{3B}. .X_{nB}
	Second Determination on Sample B	X_{1B}'	X_{2B}'	X_{3B}'. .X_{nB}'
	Difference of Two Determinations $X_{iB} - X_{iB}'$	d_1'	d_2'	d_3'. . .d_n'
	Sum of Two Determinations $X_{iB} + X_{iB}'$	t_1'	t_2'	t_3'. . .t_n'
	Mean of Two Determinations on Sample A = $\frac{^{x}iA + ^{x}iA'}{2}$	$\bar{X}_{1A}$	$\bar{X}_{2A}$	$\bar{X}_{3A}$. .$\bar{X}_{nA}$
	Mean of Two Determinations on Sample B = $\frac{^{x}iB + ^{x}iB'}{2}$	$\bar{X}_{1B}$	$\bar{X}_{2B}$	$\bar{X}_{3B}$. .$\bar{X}_{nB}$
TYPE II	Difference of Two Means $\bar{X}_{iA} - \bar{X}_{iB}$	D_1	D_2	D_3. . .D_n
	Sum of Two Means $\bar{X}_{iA} + \bar{X}_{iB}$	T_1	T_2	T_3. . .T_n

TABLE IV
Summary of Accuracy Study of Laboratory Data Vinyl Chloride Found μg/tube

Concentration Level	CRL Reference Value ± S.D. (n)	Laboratory Mean Value ± S.D. (n)	Deviation From CRL Reference Value	Percent Relative Error	t calc	t Value	Remark
A	12.70 ± 0.327 (10)	12.43 ± 2.328 (33)	-0.270	-2.13%	0.357	$t_{95} = 2.021$ $t_{99} = 2.704$	$t < 2.021$ no difference can be established
B	19.16 ± 0.590 (10)	19.15 ± 2.877 (33)	-0.010	-0.05%	0.011	$t_{95} = 2.021$ $t_{99} = 2.704$	$t < 2.021$ no difference can be established

after the samples were generated. Seven sets of charcoal tubes were sent by mail to randomly selected laboratories at different geographical locations in the USA and returned by mail to CRL. Upon return they were stored in a refrigerator and analyzed 3 months after their preparation. The analytical results for the returned charcoal tubes are tabulated in Table II and indicate no aging and shipping effects.

experimental design of collaborative test

The collaborative test involved 42 laboratories. Each laboratory analyzed duplicate sets of charcoal tubes containing vinyl chloride at two concentration levels. The analytical data obtained from participating laboratories were used to calculate interlaboratory error, replication error, and sample generation error, as well as accuracy at each concentration level for the vinyl chloride samples.

The statistical analysis outlined[2,5] was used. A set of replicate determinations performed on one of the duplicate samples comprised a "unit block" which will be referred to as Unit Block Type I. The results of replicate determinations performed on each of the duplicate samples were also averaged and the pair of averages comprised Unit Block Type II. The calculation details of the parameters of analysis[2] for this study are shown in Table III. Analysis of these two types of unit blocks by this method provides estimates of replication error, interlaboratory error, and sample generation error.

statistical analysis of collaborator's results

Prior to subjecting the data obtained from the collaborative laboratories to statistical analysis, the outlier laboratories were identified and eliminated. The individual outliers were determined by means of maximum normal residual test.[6] This test detects gross error and also excess intralaboratory random variability. Laboratories which had one or more extreme values as detected by this method[6] were eliminated. A total of 4 laboratories had one or more extreme values by the test. After the test, the studentized deviate test (Grubbs' test) was used for the remaining laboratories to eliminate any laboratory which was consistently high or low in its results. Five laboratories were eliminated by this test.

The accuracy of laboratory data was established by comparison of mean values at each concentration level with reference values established by the Chemical Reference Laboratory. A t-test, where standard deviation (σ) is unknown but believed to be the same for the two populations, was used to check for statistically significant differences between the Chemical Reference Laboratory samples mean and the mean from the collaborative laboratories. The results are shown in Table IV. There is no difference between CRL Reference Value and Laboratory Mean Value.

The precision of the laboratory data was estimated by the Youden analysis of variance.

The estimation of total variance of data in Youden's treatment can be accomplished by analyzing the sums of the two terms of each unit block, i.e.,

$$S_t^2 = \frac{\sum_{i=1}^{n} (t_i-\bar{t})^2}{2(n-1)}; \quad S_T^2 = \frac{\sum_{i=1}^{n} (T_i-\bar{T})^2}{2(n-1)} \qquad (1)$$

where:

S_t^2 = variance component of total error for data in Unit Block Type I

S_T^2 = variance component of total error for date in Unit Block Type II

t_i = sum of two terms in Unit Block Type I

T_i = sum of two terms in Unit Block Type II

$\bar{t}$ = mean of the sum quantities in Unit Block Type I

$\bar{T}$ = mean of the sum quantities in Unit Block Type II

n = number of laboratories

The variance component of the replication error can be computed by analysis of the difference of the two terms of each unit block, i.e.,

$$S_r^2 = \frac{\sum_{i=1}^{n} (d_i-\bar{d})^2}{2(n-1)}; \quad S_R^2 = \frac{\sum_{i=1}^{n} (D_i-\bar{D})^2}{2(n-1)} \qquad (2)$$

where:

S_r^2 = variance component due to random errors in Unit Block Type I

S_R^2 = variance component due to random errors in Unit Block Type II

d_i = difference of two terms of Unit Block Type I

D_i = difference of two terms of Unit Block Type II

$\bar{d}$ = mean of n d_i'S

$\bar{D}$ = mean of n D_i'S

Variance component of total error contains two components, variance component of random errors and variance component of systematic errors. The estimate of the variance component for systematic errors can be obtained from the following equation:

$$S_t^2 = 2\,S_b^2 + S_r^2\ ;\ S_T^2 = 2\,S_B^2 + S_R^2 \qquad (3)$$

where:

S_b^2 = variance component for systematic errors in Unit Block Type I

S_B^2 = variance component for systematic errors in Unit Block Type II

In Unit Block Type I, the random error, S_r, represents replication error and is obtained by analyzing the difference between replicate determinations made on the sample. By taking the difference, the resulting d term contains no systematic error components and the difference quantities are then used to calculate replication error from Equation 2. The estimates of the replication error and total errors obtained for two sets of samples at each concentration level are assumed to be homogeneous and the results of these estimates can be pooled for that level. The systematic errors, S_b, consist of interlaboratory error and sample generation error and can be obtained for Equation 3. In the Unit Block Type II, the S_R terms in Equation 2 contain both replication error, S_r, and sample generation error, S_s. The systematic errors, S_B, in Equation 3 contain only interlaboratory errors, S_L.

The table below summarized the relations between the different estimates of variance

Estimates of Various Variance

ANALYSIS	RANDOM ERROR	SYSTEMATIC ERROR
Unit Block Type I (Not Averaged)	S_r^2	$S_s^2 + S_L^2 = S_b^2$
Unit Block Type II (Average of Replicate)	$\frac{S_r^2}{2} + S_s^2 = S_R^2$	$S_L^2 = S_B^2$

TABLE V
Summary of Youden's Analyses
(The Standard Deviation and Percent Relative Error Contribution of Variance Components)

Concentration Level	Average Amount Found μg/tube	Replication Error		Sample Generation Error		Interlaboratory Error		Total Error	
		S.D.	R.S.D.	S.D.	R.S.D.	S.D.	R.S.D.	S.D.	R.S.D.
A	12.43	0.178	1.43%	0.554	4.45%	2.256	18.16%	2.328	18.37%
B	19.15	0.162	0.85%	0.473	2.48%	2.836	14.80%	2.877	15.03%

components for results obtained by not averaging the replicate (Unit Block Type I) and from results obtained by averaging the replicates (Unit Block Type II).
where:

S_r^2 = replication error
S_L^2 = interlaboratory error
S_s^2 = sample generation error

From the above analyses, all three variance components can be individually estimated. The replication error, S_r, can be directely calculated from the first analysis. The sample generation error, S_s, can be obtained by combining both analyses. The interlaboratory error, S_L, can be obtained from the second analysis or from the first analysis, provided S_s is known from the second analysis.

discussion of results

The variance analysis shows that the replication error varies from 0.85% to 1.43%. Sample variation (generation error) varies from 2.48% to 4.45%. The interlaboratory systematic error varies from 14.8% to 18.16%. A detailed summary of the statistical results is shown in Table V.

The replication error arises from noise, drift, integration error, and syringe reading error. The sample variation arises from the variation of permeation rate, the fluctuation of sample volume flow rate caused by the variation of temperature and pressure of the system, and variation of individual charcoal tubes.

The between-laboratory error comprises a large part of the total experimental errors. This is probably due to large systematic errors, such as errors in making standard calibration curve, instrument calibration, and sample handling and preparation. How well the calibration standard can be made greatly affects the accuracy of sample analytical results.

Since vinyl chloride is a gas at normal ambient temperature and pressure, it is difficult to accurately measure the volume and to prevent the vinyl chloride gas losses during weighing and preparing the primary standard and also the working standard. This kind of systematic error sometimes is difficult to foresee and is a major part of interlaboratory error. This error can often be determined by comparison of the value obtained with the true value of standard.

This collaborative test demonstrates that the premeation method is adequate to generate accurate, uniform, and stable vinyl chloride reference samples. It can be used to evaluate the instrument performance, calibration curve, and analytical procedures. If vinyl chloride reference samples are used for this purpose, they can play an invaluable role in the reduction of between-laboratory variability of the analysis and can considerably improve the accuracy of the results.

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