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Diffusion Effects Under Low Flow Conditions

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Under certain conditions, diffusion was found to be a significant positive bias when sampling for gases using sorbent tubes and pumps at reduced flow rates. Based upon a theoretical analysis, this bias is predicted to be significant for inlet Peclet numbers smaller than 3. The inlet Peclet number is defined as vL_1/D where: v = inlet velocity; L_1 = length to sorbent bed; D = diffusion coefficient. During experimental work, the analysis of sorbent tube samples collected at flow rates of 0.8 cm^3/min resulted in measured concentrations as much as 75% higher than sorbent tube samples collected at flow rates of 20 cm^3/min.

Introduction

In 1976, personal sampling pumps having flow rates as low as 0.5 cm^3/min became commercially available.(1) Currently the Anatole J. Sipin Co. and MDA Scientific Inc. market personal sampler pumps with flow rates as low as 2.0 and 0.5 cm^3/min, respectively.(1,2) Because approximately 30 NIOSH sampling and analytical methods use solid sorbents to collect air contaminants and recommend sample volumes of from 1.0 to 2.0 L,(3) sampling rates as low as 2 cm^3min are a real consideration for practicing industrial hygienists. A flow of 2 cm^3/min for an 8-hr sampling time would result in a sample size of nearly 1.0 L.

Such low flow rates may cause a positive bias in solid sorbent sampling. This bias is the result of diffusive mass flux at the solid sorbent tube sampling train inlet. In a flow system, the mass flux is computed from the following formula:(4,5)

$$F = vC(Z) - D\frac{\partial C(Z)}{\partial Z}$$

Total flux = Convective flux + Diffusive flux

F = total flux (moles or mass/(time-area))
v = velocity along Z axis (length/time)
C(Z) = concentration (moles or mass/volume)
D = diffusion or axial dispersion coefficient ($length^2$/time)
Z = distance along Z axis.

Convective flux is the result of the bulk flow of the fluid. The second term is the diffusive flux which is caused by a concentration gradient in the solid sorbent tube. At some distance into the sorbent tube, the sorbent is removing the analyte from the air stream and a concentration gradient results. As the bulk flow of the fluid or the sampling rate decreases towards zero, the contribution due to diffusive flux increases in magnitude and it will ultimately become an important bias in solid sorbent sampling. Immediately, the following question is asked: "At what flow does diffusive flux predominate?" An answer to this question is the purpose of this paper.

Theoretical

In order to estimate the diffusive flux at the sorbent tube inlet, the concentration gradient at the sorbent tube inlet must be found. The complete equation of continuity can be used to develop a mathematical model which describes the concentration profile in a sorbent tube. These equations are adequately explained in chemical engineering transport texts.(4,5) The system of equations shown in Table I is the result of applying the equations of continuity to different parts of a sorbent tube shown in Figure 1. In these equations the radial and angular velocity are assumed to be equal to zero and R refers to the rate of adsorption. It is unknown and may be different for each vapor and adsorbent. Consequently, solving the equations in Table I by numerical analysis would require experimental rate data that would be at least as difficult to acquire as the experimental measurement of diffusive flux. An exact analytical solution is impossible.

A review of the literature for solutions to the equations of continuity for fixed bed adsorption columns revealed no solutions to the equations of continuity given in Table I. A number of people have solved similar mass transfer equations. The problem of axial dispersion in relationship to breakthrough curves has been considered.(6-8) Bischoff(9) discussed boundary conditions in reactors such as fixed bed adsorbers. Kyte(10) developed a numerical solution for the breakthrough curve for an adsorption bed involving a non-linear isotherm. Lapidus and Amundson(11) and Van Deemter(12) studied longitudinal diffusion in gas chromatographs.

In order to obtain some preliminary estimates of the magnitude of diffusive flux, a simplified analysis can be made using the following assumptions:

1. The concentration of contaminant in the air at the front of the sorbent bed is zero.
2. The velocity profile is flat.
3. Steady state behavior exists.
4. Concentration does not depend on radial position.

TABLE I
Application of Equations of Continuity to Different Sections of Sorbent Tube

Section I: Empty section in front of sorbent bed.

$$\frac{\partial C^{I}(r,Z,t)}{\partial t} = -v(r)\frac{\partial C^{I}(r,Z,t)}{\partial Z} + D\frac{\partial^2 C^{I}(r,Z,t)}{\partial Z^2} + \frac{1}{r}\frac{\partial}{\partial}r\frac{\partial C^{I}(r,Z,t)}{\partial r}$$

Section II: Fluid stream in sorbent bed.

$$\frac{\partial C^{II}(Z,t)}{\partial T} = -\frac{v}{\epsilon}\frac{\partial C^{II}(Z,t)}{\partial Z} + D\frac{\partial^2 C^{II}(Z,t)}{\partial Z^2} - R$$

Section III: For the sorbent particles.

$$\frac{\partial C^{III}(r,Z,t)}{\partial t} = +R$$

Boundary conditions:

$t = 0, C^{I} = C^{II} = C^{III} = 0$

$Z = 0, t > 0; C^{I}(r,o,t) = C_0$

$Z = L_1; A_1 F_1 = A_2 F_2$ (what flows out of Section 1 flows into Section 2)

$0 < Z < L_1; \left.\frac{\partial C^{I}}{\partial r}\right|_{r=0} = 0$

$0 < Z < L_1; \left.\frac{\partial C^{I}}{\partial r}\right|_{wall} = 0$ (no diffusive flux through glass wall)

$Z = L_2; \frac{\partial C^{II}}{\partial Z} = 0$ (end of sorbent bed)

$Z = L_1; C^{I}(r, L_1, t) = C^{II}(L_1, t)$

A_1 = Cross sectional area of empty section (I), cm^2.
A_2 = Cross sectional area of sorbent bed open to flow, cm^2.
C_0 = Contaminant concentration at inlet, g/cm^3.
C^{I} = Contaminant concentration in Section I, g/cm^3.
C^{II} = Contaminant concentration in Section II, g/cm^3.
C^{III} = Contaminant concentration in Section III, g/cm^3.
D = Diffusion coefficient, cm^2/sec.
F_I = Flux in Section I at Z = L, g/cm^2/sec.
F_{II} = Flux in Section II at Z = L, g/cm^2/sec.
L_1 = Length from sorbent tube inlet to front of sorbent bed, cm.
L_2 = Length from sorbent tube inlet to back of sorbent bed, cm.
R = Rate of adsorption, g/cm^3/sec.
t = Time, sec.
v(r) = Velocity, cm/sec.
v = Average velocity in Section I, cm/sec.
Z = Axial coordinate (Z = 0 is at inlet to sorbent tube), cm/sec.
= Void fraction of sorbent bed.
r = Radial coordinate, r = 0 at center line of sorbent tube and r = r_1 at wall of sorbent tube, cm.

The net effect of all these assumptions is that the flux of contaminant in the emply front section of a sorbent tube is constant. Therefore, the derivative of total flux with respect to axial distance from the inlet is zero. The resulting solution is shown in Table II.

Basically the simplified model estimates the diffusive flux during hypothetical steady state. The transient behavior has dissipated. For the rest of the sampling period, the diffusive flux is a maximum because the contaminant concentration in the sorbent is at or near zero. As time increases the sorbent tube will become loaded, the contaminant concentration at the start of the sorbent bed will increase and the concentration gradient and the diffusive flux will decrease. Obviously, the simplified analysis will overestimate the diffusive flux. Although this simplified analysis cannot be regarded as rigorous theory, it does estimate the maximum possible diffusive flux and it can serve as a criterion for insuring that diffusion is not a significant bias.

In Table II, the equation for diffusive flux is computed as a function of inlet Peclet number. The inlet Peclet is defined as:

$$N_1 = vL_1/D$$

where:

L_1 = distance from inlet to sorbent bed
v = average velocity at inlet
D = diffusion coefficient.

A plot of $1/|1 - \exp(N_1)|$ versus N_1 is a plot of bias due to diffusive flux versus inlet Peclet number. This plot is presented in Figure 3. The computed bias approaches zero for $N_1 > 3$.

An effective volumetric flow rate for total flux and for the diffusional flux into a sorbent tube can be computed by multiplying the respective flux times the area and dividing the result by the concentration. This diffusive flow rate and effective total flow rate are plotted as a function of bulk flow rate in Figure 4 for a sorbent tube with an inlet diameter of 0.04 cm, a length to the sorbent bed of 1.5 cm, and a pollutant gas diffusion coefficient of 0.1 cm^2/sec. The diffusive flux decreases as the bulk flow rate increases. With no bulk flow, the total effective and diffusive effective flow rates are computed by applying L'Hospital's rule to the equation for diffusive flux in Table II. This shows that the effective sampling rate of an unsaturated charcoal tube is never zero because of diffusion. However, as the bulk flow rate increases, the magnitude of the diffusive flow rate decreases. (By increasing the bulk flow rate from zero to 2 cm^3/min, the diffusive flow rate decreases from 0.5 cm^3/min to 0.04 cm^3/min.)

The simplified analysis can be extended to the case where the concentration is zero at some distance into the sorbent bed. The results of this analysis are shown in Table III. This model assumes an infinitely narrow mass transfer zone at some distance into the bed. The results of extending this analysis to a sorbent tube in a sorbent tube holder are presented in Table IV.

A more realistic model for diffusive flux was developed by solving the system of differential equations in Table V. These equations were developed from an incremented mass balance. Concentration is assumed to depend upon Z and t. The adsorption rate is assumed to be diffusion controlled and given by the following expression:

$$R = k_g a \frac{(1-\epsilon)}{\epsilon} C^{II}$$

R = adsorption rate
a = hydrodynamic surface area per volume of sorbent
ϵ = sorbent void fraction
k_g = mass transfer coefficient
C^{II} = concentration in sorbent bed voids.

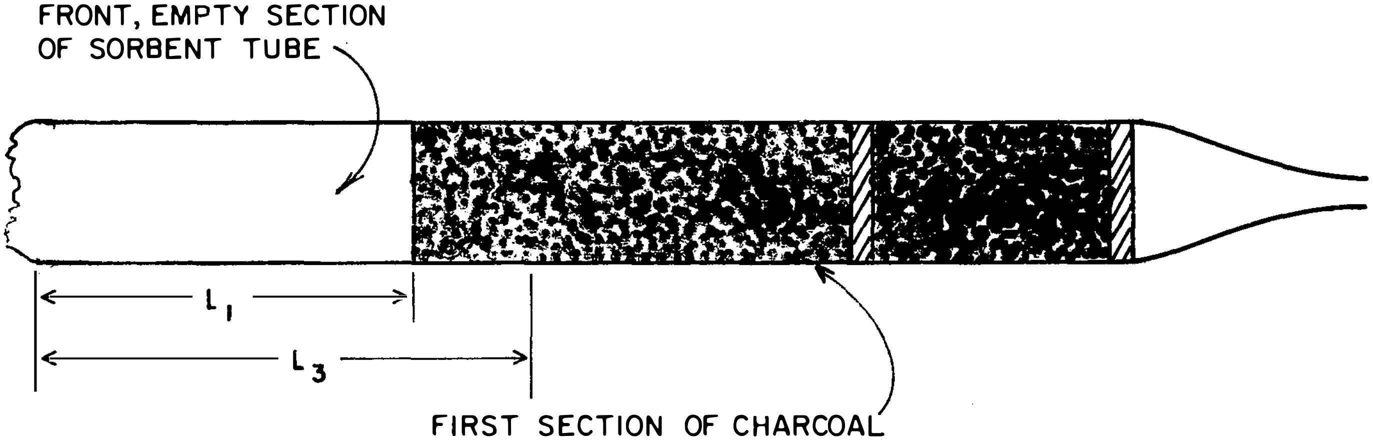

Figure 1 — Charcoal tube.

In Table V the terms "k_g" and "a" cannot be estimated precisely. The term "a" is computed from a formula which assumes that sorbent particles are spheres. The term "k_g" can be estimated from a number of dimensionless correlations available in the chemical engineering literature.(6-8)

The results of a simplified analysis suggest that diffusive flux is an increasingly important source of bias as the inlet Peclet number becomes smaller than 3. Several laboratory experiments were performed to confirm this conclusion and test only the simplified model and the more realistic model presented in Table V.

Experimental Work

The purpose of the experimental work is to determine whether diffusive flux is a bias for inlet Peclet (N_I from Table II) numbers less than 3. For typical sorbent tubes the simplified model predicts diffusion becomes a bias at flow rates less than 1.5 cm^3/min.

A controlled test atmosphere of ethanol was generated and then two different sets of samples were simultaneously collected on charcoal tubes. All samples within a set were collected at the same flow rate, inlet diameter, and length from inlet to sorbent bed. The inlet diameters were the inside diameter of the sorbent tube. Ethanol was collected one set of charcoal tubes at a rate of 0.8 cm^3/min. These samples were expected to have a diffusive bias. To provide a basis for comparison, a second set of samples was collected using flow rates of 20 cm^3/min. These samples should not have any diffusional bias since the Peclet number is greater than 15. Then, the concentrations measured by sampling at two different rates were compared statistically to determine whether there is a significant difference between the two sets of data. This difference is an estimate of the diffusive bias.

The ethanol samples were collected in the generation dilution system illustrated by Figure 4. The test atmosphere was generated by saturating a primary air stream with ethanol and mixing this stream with a known amount of dilution air. The flow rates of primary and dilution air were controlled by rotameters that were calibrated against bubblemeters. A constant temperature bath supplied cooling water to the condenser. A thermometer was inserted in the condenser to measure the temperature of the saturated ethanol stream. The saturated primary and dilution air were obtained untreated from compressors. The primary air flow rate was 0.5 L/min for the first two tests and 1.5 L/min for the latter tests. The dilution air flow rate was 10 L/min for the first two tests and 20 L/min for subsequent tests.

After the test atmosphere was generated, it flowed into a test manifold. The test manifold was made from a 0.91-m (3.0-ft) length of schedule 40, 7.62-cm (3.0-in.) diameter, type 304 stainless steel pipe. For sampling ports, 1.90-cm (0.75-in.) lengths of type 316, 3.49-cm (1.375-in.) diameter, stainless steel nipples were silver soldered to the pipe. The nipples were bored and tapped to accommodate 1.90-cm (0.75-in.) National Pipe Thread plugs made from Teflon® rod stock. The plugs were 2.54 cm (1.0 in.) long and were center-drilled to accommodate charcoal tubes and charcoal tube holders. The charcoal tubes were held in place by O-rings. The tube holders were held in place by compression of the plug when screwed into the nipple. The configuration of the plugs, nipples, and charcoal tubes was arranged so that the charcoal tube inlets were at least 3.0 cm from the walls of the sampling manifold.

One of the sampling ports was used to measure the manifold's static pressure while another port was used as a sampling port for a flame ionization detector. The static pressure within the manifold was maintained at +0.38 cm (0.15 in.) of H_2O static pressure with respect to the room. A Beckman 400 flame ionization detector (FID) was used to monitor ethanol concentration. During all experimental runs, the FID's response to the test atmosphere was stable to within 2-3% during a test. To obtain a nominal sampling rate of 0.8 cm^3/min, critical orifice personal samplers (COPS) were used.(13) The outlet of each COPS was removed and replaced with a Swagelock fitting. The outlet of the Swagelock fitting

TABLE II
Results of Simplified Analysis

$$\text{Flux} = C_0 v - \frac{C_0 v}{1 - \exp(N_I)}$$

$$\text{Diffusive flux} = \frac{C_0 v}{1 - \exp(N_I)}$$

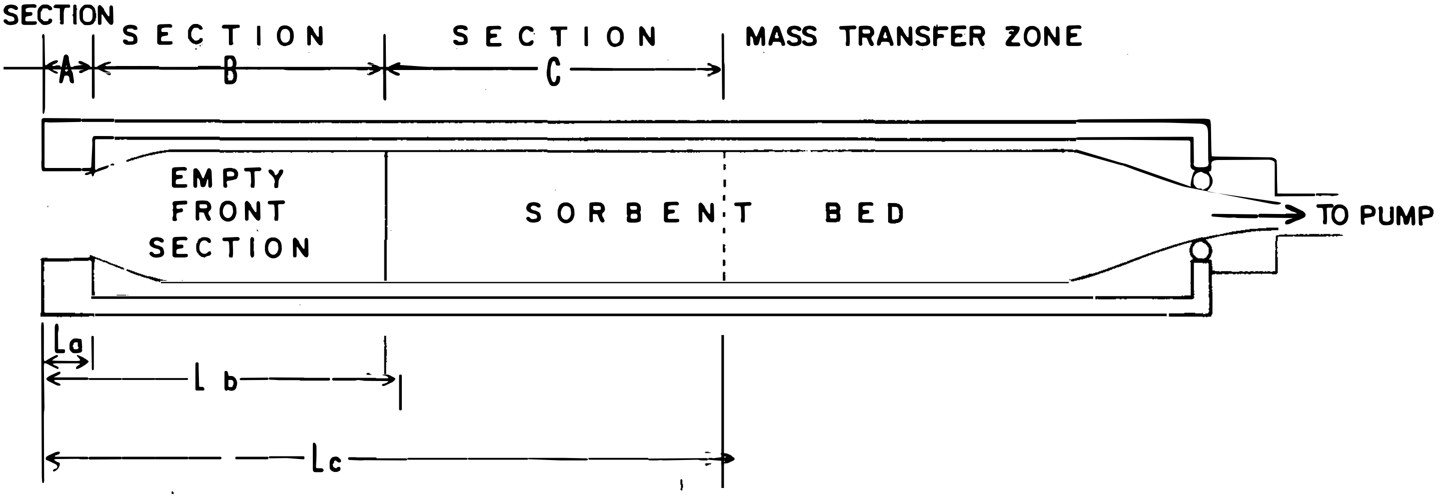

Figure 2 — Sorbent tube in sorbent tube holder.

was connected by tubing to a common vacuum manifold maintained at 500 mm (20 in.) of Hg vacuum. The inlet of each COPS was protected by a membrane filter.

Each COPS was calibrated by measuring the volume and then measuring the change in pressure over a period of time. The volume of the COPS was measured as follows:

1. Preweigh COPS.
2. Fill COPS with water by evacuation to one torr, submerge it in water, and then open the outlet valve.
3. Dry exterior of COPS and remove water that is above the level of the brass sealing ring in the outlet.
4. Reweigh the COPS.

For each COPS used, this procedure was repeated at least three times. Table V presents the mean COPS volumes and standard deviations for each COPS.

To measure the volumetric flow rates, the rate of pressure increase was determined using a pressure transducer and valving as shown in Figure 5. The procedure allowed for the calculation of the volume of the lines between the transducer and the COPS. The procedure is as follows:

1. Evacuate the COPS and fore line tubing between the COPS and transducer. Record pressure (P_1).
2. Close the COPS outlet.
3. Open the atmosphere inlet to the tubing between the COPS and the transducer and allow the tubing to

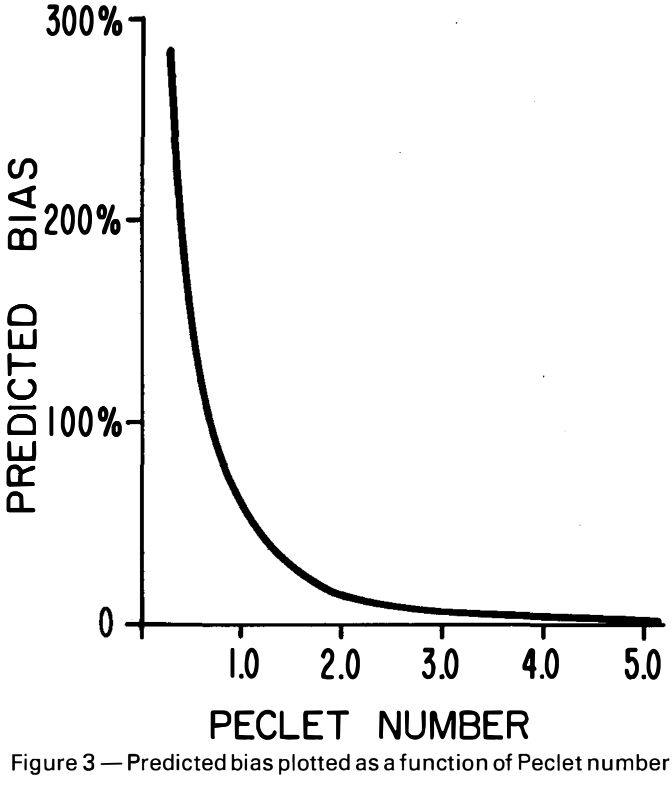

Figure 3 — Predicted bias plotted as a function of Peclet number.

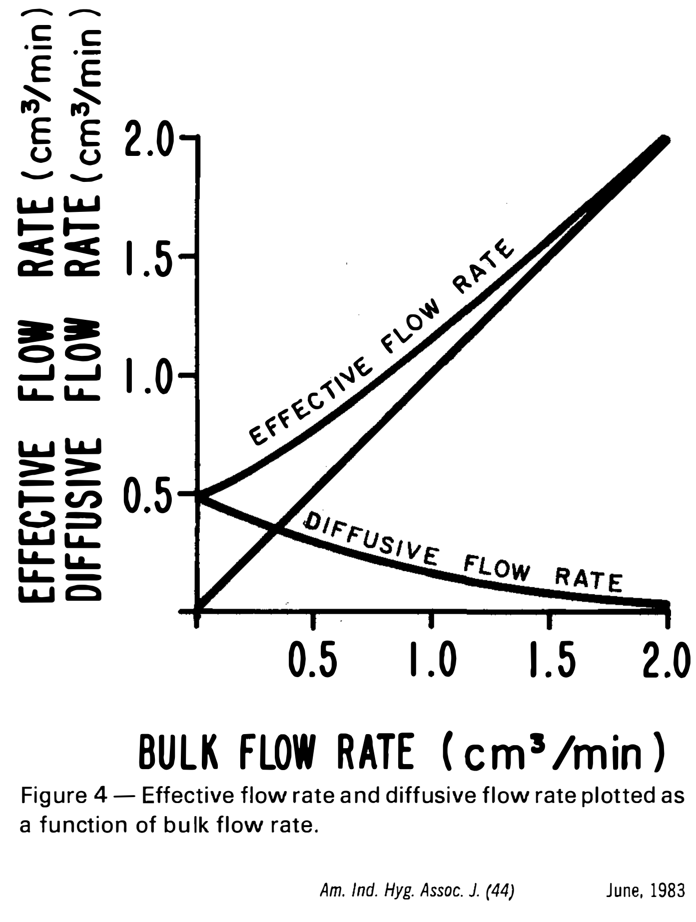

Figure 4 — Effective flow rate and diffusive flow rate plotted as a function of bulk flow rate.

TABLE III
Results of Simplified Analysis Extended to Case Where Air Contaminant Concentration is Zero at Some Distance, L_3, Into the Sorbent Bed

$$\text{Total flux} = C_0\, v - (C_0 - C(L_1))\, v/(1 - \exp(N_1))$$

$$\text{Diffusive flux} = \frac{[C_0 - C(L_1)]v}{1 - \exp(N_1)}$$

$$C(L_1) = \frac{C_0\, A}{A + B}$$

where

$A = \exp(N_1)/[\exp(N_1) - 1]$

$B = \exp(N_1/\epsilon)/\exp(N_2/\epsilon) - \exp(N_1/\epsilon)]$

$N_2 = v\, L_3/D$

L_3 = length from inlet of sorbent tube to some distance where contaminant concentration is zero, cm.

return to atmospheric pressure. Close the atmospheric inlet.

4. Open the COPS outlet. Record the pressure (P_2).
5. Open the COPS inlet and start timer.
6. Record pressure (P_3) and time at predetermined intervals until pressure rises above 100 torr.

The sampling rates were computed from the following formula:

$$Q = V\left(1 + \frac{P_2 - P_1}{P_{atm} - P_2}\right)\left(\frac{P_3 - P_2}{P_{atm}}\right)/t$$

Q = sampling rate

V = volume of COPS

t = time

P_1 = pressure to which COPS is initially evacuated

P_2 = pressure in COPS after returning fore line to atmospheric pressure, closing fore line, and reopening the COPS

P_3 = final pressure in COPS

P_{atm} = atmosphere pressure

The correction for the fore line volume was always between 3 and 4% of the sampler volume.

Flow rates of 20 cm^3/min were obtained by using jeweled orifices as limiting orifices rather than as critical orifices. A needle valve was used to set the amount of vacuum in the manifold for the limiting orifices. The vacuum in the manifold was measured with an Hg manometer. Ports on this manifold were connected by tubing to 13 mm Swinnex filter holders which contained the orifices. The orifices were protected by fiber glass filters. The flow rates through the orifices were measured using a stop watch and a 10-mL bubblemeter.

During each experimental run, one set of samples was collected at 0.8 cm^3/min, and another set were collected at a sampling rate of 10-20 cm^3/min. For samples collected at 0.8 cm^3/min the sample volumes and times were chosen to obtain a loading of 2.0 to 2.5 mg per charcoal tube. This resulted in sampling periods of about 7.0 to 8.0 hr. During each experimental run, at least five replicate samples per experimental treatment were taken. The samples used to measure the effect of diffusion were taken on standard charcoal tubes. These tubes have an inside diameter of 4-mm and contain 100 and 50 mg of activated coconut shell charcoal in the front and backup sections, respectively.

During each of the first two tests, samples were taken at 20 cm^3/min on jumbo charcoal tubes (SKC 226-16). These charcoal tubes had an 8-mm inside diameter and contained 700 mg and 300 mg of SKC lot 107 charcoal in front and backup sections, respectively. The two sets of 4-hr samples were taken sequentially during the same time period as the samples collected at 0.8 cm^3/min. After the first two tests, the 20 cm^3/min samples were taken sequentially on the same type of charcoal tube used to collect the 0.8 cm^3/min samples. These 20 cm^3/min samples were collected for periods between 20 and 30 min. This was done because the desorption efficiency of the samples collected on the larger tubes was different from the charcoal tubes used to test the effect of diffusion. To eliminate desorption efficiency as a potential source of experimental error, sample volumes for both sets of samples were selected to provide the same loading of ethanol on the same type of charcoal tube.

The ethanol samples were analyzed by gas chromatography. The samples collected during the first two experimental runs were analyzed by the Measurements Support Branch of NIOSH's Division of Physical Sciences and Engineering. They analyzed the charcoal tubes as described by NIOSH Method S56. Method S56 was modified slightly for analysis of the jumbo charcoal tube. The jumbo charcoal tubes were desorbed in 4.0 mL of a 1% n-butanol in carbon disulfide solution.

TABLE IV
Results of Simplified Analysis Extended to Sorbent Tube Holder

$$\text{Flux at inlet} = V_A C_0 - \frac{V_A(C_0 - C_1)}{1 - \exp(N_A)}$$

$$C_1 = \frac{C_0 I}{I + J[1 - G/(H + G)]}$$

where

$I = \exp(N_A)/[\exp(N_A) - 1]$

$J = \exp(N_A/\epsilon_B)/[\exp(N_B) - \exp(N_A/\epsilon_B)]$

$G = \exp(N_B)/[\exp(N_B) - \exp(N_A/\epsilon_B)]$

$H = \exp(N_B\, \epsilon_B/\epsilon_C)/[\exp(N_C) - \exp(N_B\, \epsilon_B/\epsilon_C)]$.

Figure 2 illustrates geometry of situation:

$N_A = v_A\, L_A/D$

$N_B = v_B L_B/D$

$N_C = v_C\, L_C/D$

$$\epsilon_B = \frac{\text{cross sectional area Section B}}{\text{cross sectional area Section A}}$$

ϵ_C = (cross sectional area of Section C open to flow) by (cross sectional area of Section A)

L_A = length from inlet to sorbent tube entrance, cm

$L_B = L_A + L_1$

$L_C = L_A + L_3$

$v_{A,B,C}$ = average air velocities in Sections A, B, C, respectively, cm/sec.

TABLE V
A More Realistic Estimate of Diffusive Flux Based Upon an Estimated Adsorption Rate

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Two simultaneous differential equations were solved to estimate the diffusive flux at the sorbent tube inlet. These equations describe the conservation of mass in the fluid stream within the empty section in front of the sorbent bed and within the sorbent bed's voids. These equations are:

In the empty section in front of sorbent bed (Section I);

$$Dd^2C^I/dz^2 - vdC^I/dz = 0.$$

In the fluid stream in sorbent bed (Section II);

$$Dd^2C^{II}/dz^2 - (v/\epsilon)dC^{II}/dz - ((1 - \epsilon)/\epsilon)k_g aC^{II} = 0.$$

To solve this system of equations, the following boundary conditions were invoked:

$z = L_1,\ C^I = C_0$

$z = L_s,\ dC/dz = 0$,

$z = 0,\ C^I = C^{II}$ (concentrations are equal)

$F_I = \epsilon F_{II}$ (fluxes are equal).

The expression for diffusive flux at the inlet ($z = -L_1$) is:

$$\text{diffusive flux} = -vK\exp(-N_1),$$

where

$$K = \frac{C_0(DEM_2/v)\,(1 - \exp(M_2 - M_1)L_s))}{[\exp((M_2 - M_1)L_s)((D\epsilon M_2/v)(1 - \exp(-N_1)) - M_2/M_1) + 1 - (1 - \exp(-N_1))D\epsilon M_2/v]}$$

$M_1 = (O - (O^2 + 4P)^{1/2})/2$

$M_2 = (O + (O^2 + 4P)^{1/2})/2$

$O = v/(\epsilon D)$

$P = k_g a(1 - \epsilon)/(\epsilon D)$

a = hydrodynamic surface area per volume of bed, cm^{-1}

k_g = mass transfer coefficient, cm/sec

L_s = length of sorbent bed, cm

L_1 = distance between inlet and sorbent bed, cm

v = average fluid velocity in empty section, cm/sec

z = axial coordinate ($z = 0$ at interface between empty section and start of solid sorbent bed), cm.

The remaining samples were analyzed by the author in a method similar to NIOSH Method S56. The procedure used for the analysis of the samples was as follows:

1. Transfer the front and backup sections of the charcoal tube to separate 1-mL reaction vials.
2. Pipet 1 mL of CS_2 containing 1%-n-butanol into a reaction vial, cap with cap lined with Teflon, and desorb for at least 1 hr.
3. Inject 5-μL aliquot into Perkin-Elmer 900 gas chromatograph.
4. Record peak area using Varian CDS 111 integrator.

The gas chromatograph conditions were as follows:

1. Detector — flame ionization
2. Gas inlet pressures: hydrogen 24 psig (30 mL/min)
   oxygen 36 psig (30 mL/min)
   nitrogen 50 psig (50 mL/min)
3. Column — 10% SP-1000 on 100/120 mesh chromosorb WAW, 10 ft long, 1/8 in. diameter
4. Temperature program mode settings:
   70 °C isothermal for 4 min
   70 ° - 150 °C at 24 °C/min
5. Electronic settings:
   Attenuation: × 256
   Amplifier: × 10
   Integrator attenuation: 256
6. The ethanol retention time was 3.2 min

Ethanol standards covering the range 1.0-5.0 μL ethanol per mL solution were made from ethanol, 100% United States Pharmaceutical Grade analytical reagent. A 10-μL syringe was used to transfer the ethanol to the 10-mL volumetric flasks containing the carbon disulfide.

Desorption efficiency was determined at a level corresponding to 2.0 μL of ethanol per 100 mg of charcoal. The procedure for determining desorption efficiency was as follows:

1. Transfer the front section of a charcoal tube to 1.0-mL reaction vial and cap;
2. Inject 5.0 μL of a solution 40% by volume ethanol in CS_2 into capped reaction vials. Six reaction vials contained charcoal and three contained 1.0 mL of desorbing solution;
3. Allow 2.0 hr for adsorption;

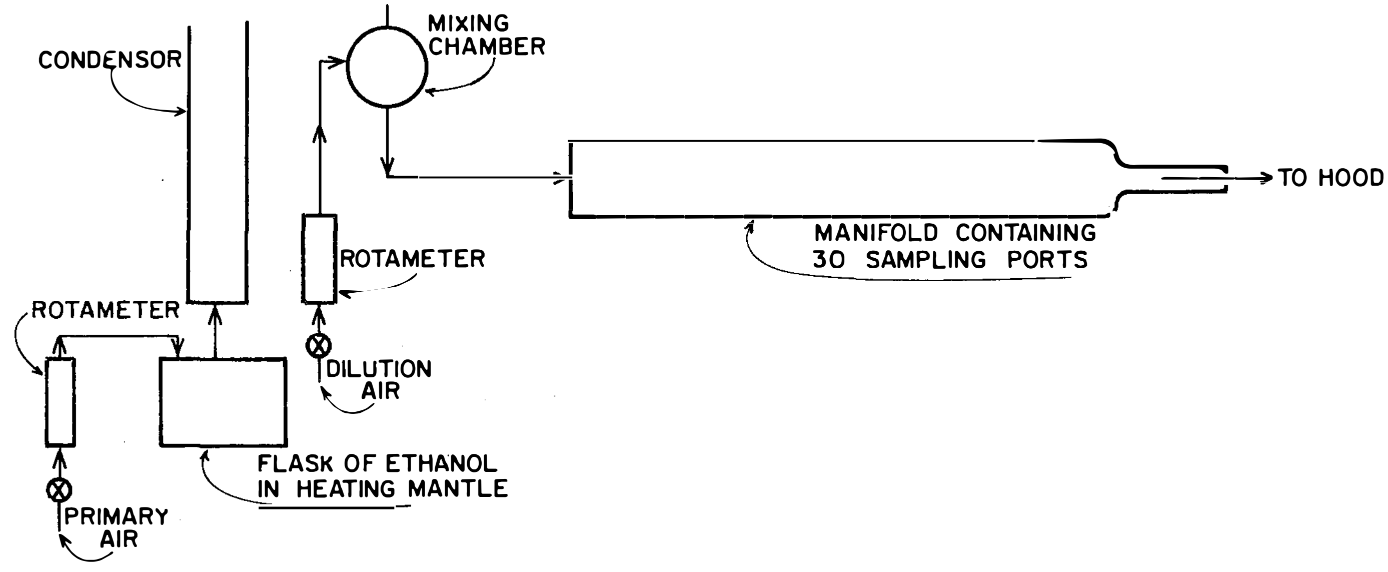

Figure 5 — Schematic of test apparatus.

4. Remove cap, pipette 1.0 mL of desorbing solution into the reaction vial, recap, and allow at least 30 min before analysis;
5. Analyze as described earlier.

In order to estimate the width of the mass transfer zone, a breakthrough test was conducted by recording the response of a flame ionization detector (FID) to the combined effluent of eight standard charcoal tubes with the backup sections removed. These tubes sampled 5.5 mg/L ethanol at a 20 cm^3/min nominal flow rate. Limiting orifices connected to a common vacuum manifold were used to control the sampling rate. A metal bellows pump and a needle valve maintained a vacuum of 3.0 in. of Hg in the manifold. The effluent of the bellows pump was the input for the FID.

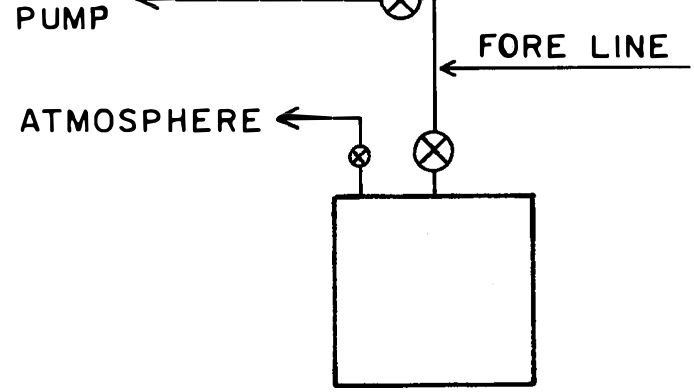

Figure 6 — Schematic of pressure transducer and tubing used to calibrate COPS.

Experimental Results and Their Statistical Analysis

Table VI summarizes the calibration of the COPS. The total volume of each COPS was determined with volumetric flow rates of the COPS. The pooled standard deviation for all these COPS was 0.03 cm^3/min. The coefficient of variation for flow rates is 0.043.

The comparison between sampling at a rate of 0.8 cm^3/min and at a rate of 20 cm^3/min is summarized in Table VII. The desorption efficiency correction was not applied to the samples collected in Sipin charcoal tube holders because the desorption efficiency was not determined at the level corresponding to the loadings of these tubes, 3.0 to 4.5 μL of ethanol. For the three sets of data collected, sampling at a rate of 0.8 cm^3/min resulted in significantly higher mean concentrations and standard deviations than the 20-cm^3/min samples.

At a 95% level of confidence, the variances of the means for the samples collected at 20 cm^3/min and 0.8 cm^3/min are statistically different. For the first two tests, two standard deviations are reported for the measurements taken at 20 cm^3/min. The higher of these two was used to conduct the F test[14] in Table IX. When all variances for the 20 cm^3/min-measurements are tested for homogeneity by Bartlett's test, they are found to be non-homogeneous. When the value for test 2, set 1 is removed, Bartlett's test indicates homogeneous variances. The pooled standard deviation computed from the homogeneous variances is 0.31 mg/m^3. Using the pooled

TABLE VI
Volume of COPS Calibration Data

Sampler	Mean (mL)	Standard Deviation (mL)	Number of Determinations	Flow Rate Mean (mL/min)	Flow Rate Std. Dev. (mL/min)	n
32	95.3	0.7	3	0.77	0.04	5
34	95.16	0.4	3	0.81	0.04	5
12551	96.56	1.2	3	0.72	0.04	5
12553	90.96	0.73	3	0.76	0.01	5
12554	89.2	0.201	3	0.83	0.03	5

TABLE VII
Summary of Ethanol Concentrations Measured Using Flow Rates of 0.8 cm^3/min and Contrasting Measurement

		Samples Collected at 0.8 cm^3/min				Samples Collected at 20 cm^3/min			
Test No.	Treatment	Inlet Peclet Number	$\bar{x}$ (mg/L)	s (mg/L)	n	$\bar{x}$ (mg/L)	s (mg/L)	n	Computed Conc. (mg/L)
1	Standard charcoal tube length from inlet to bed 1.5 cm	1.36	6.99	0.82	5	a. 6.38 b. 5.60	0.32 0.14	5 5	6.0
2	Standard charcoal tube length from inlet to bed 1.0 cm	0.9	9.4	2.54	5	a. 5.78 b. 6.2	0.81 0.33	5 6	6.0
3	Standard charcoal tube in Sipin holder	0.6	9.77	2.66	4	5.56	0.306	12	5.5

value instead of individual values for the contrasting methods to do the F-test, sampling at 0.8 cm^3/min significantly increased the standard deviation of the measured concentration at a level of confidence greater than 99.5% in each case.

The results of pooled t-tests conducted under conditions of heterogeneous variances are presented in Table IX. The procedure in Snedecor and Cochran(14) is used to calculate the test statistic "t". This value is compared to critical values of "t" available from tables. For the three tests, the observed difference in means was significant at a 95% level of confidence. For the first two tests in Table IX, the mean of the contrasting measurement was the average of the two means reported.

Table X shows the difference between the observed and predicted bias in concentration measurements for the tests summarized in Table VIII. The predicted concentrations were determined from the simplified model presented in Tables II and IV from the model involving mass transfer coefficients in Table X. For the latter model, 3 different values of k_ga were estimated from the correlation in the literature. These resulted in predicted biases which either over- or underestimated the bias.

The breakthrough test resulted in a plot of time versus FID response to the charcoal tubes effluent. Breakthrough occurred after 2.5 hr of sampling at a rate of 20 cm^3/min. After a total of 3.5 hr, 100% breakthrough had occurred. Removing the charcoal tubes from the sampling lines did not change the response of the FID. Based upon an analysis of breakthrough curves presented by Treybal,(15) a mass transfer zone of 0.5 cm is computed.

At a loading of 2.0 μL ethanol per 100 mg of charcoal, the desorption efficiency was 0.794 with a standard deviation of 0.021. All of the tube loadings with the exception of samples collected in Sipin sorbent tube holders were within 20% of the loading at which desorption efficiency was determined.

Discussion

Based upon the experimental results, diffusive flux can be a positive bias at flow rates of 0.8 cm^3/min. As suggested by the simplified analysis this bias increases with decreasing Peclet number. However, the difference in variances is not completely understood. The simplified analysis indicates that the amount of bias caused by diffusive flux is very sensitive to changes in the inlet Peclet number. As the inlet Peclet number drops below 1.5 the amount of bias rises rapidly with decreasing Peclet number. This is illustrated in Figure 3. The samples collected at a nominal rate of 0.8 cm^3/min actually varied from 0.83 to 0.73 cm^3/min. In addition, the length of empty space in front of the charcoal bed could only be held within 2.0 to 3.0 mm. Consequently, the inlet Peclet number may only be known to within 20%. For a Peclet number of 1, this would cause a ± 20% variation in the amount of material collected by diffusive flux.

Although the imprecision in the length of empty space in front of the sorbent bed may cause increased variances, other experimental sources of error have not been ruled out. The data presented in Table VI show that the flow rate through the COPS was relatively stable and not an important source of error. In order to determine whether the increased variances are caused by diffusion or other unknown experimental fac-

TABLE VIII
F-Tests to Determine Whether Variances are Homogenous Between Treatment and Contrast at the 95% Confidence Level

	Degrees of Freedom		F		
Test	Treatment	Contrast	Critical	Computed	Difference
1	4	4	6.4	6.5	Significant
2	4	4	6.4	10	Significant
3	3	11	3.7	72	Significant

TABLE IX
Student's "t" Test to Determine Significance of Difference Between Treatment and Contrasting Means at a Level of Confidence of 95%

Test	Degrees of Freedom	Critical	Calculated	Difference
1	4	2.13	2.5	Significant
2	4	2.13	2.9	Significant
3	3	2.51	2.7	Significant

tors, further experiments need to be conducted which compares samples with low flow rates and high Peclet numbers to those with low flow rates and low Peclet numbers.

Other experimental sources of error appeared to be reasonable and below 5%. The coefficient of variation for most NIOSH sampling and analytical methods is between 5% and 10%. The coefficient of variation for the flow rate of the COPS was 4.3% which is in agreement with the coefficient of variation for flow rates in the NIOSH manual of analytical methods.(3) The standard deviation for the desorption efficiencies was between 0.02 and 0.03 which is typical of desorption efficiencies reported elsewhere.

The results of the breakthrough tests show that the mass transfer zone is relatively wide in relation to the total length of the charcoal tube's front section. Consequently, the assumption of very narrow mass transfer zone is probably not appropriate. Because this breakthrough test was conducted at 20 cm^3/min, application of this test to 1 cm^3/min is questionable because the resistance to mass transfer increases as flow rate decreases. Nevertheless, this breakthrough test does illustrate that the width of the mass transfer zone is not always small with respect to the length of sorbent in a charcoal tube.

Conclusions and Recommendations

The study shows that diffusive flux can be a bias in solid sorbent sampling at low sampling rates for typical sorbent tubes. In addition, it may cause a sampling and analytical methods' precision to deteriorate. To avoid these problems, the inlet Peclet number should be kept above five. Based on this criterion and a diffusion coefficient of 0.13 cm^2/sec, Table XI contains a set of recommended minimum solid sorbent sampling rates for sorbent tubes of different diameters and different sorbent tube holders.

Diffusion coefficients do vary with temperature and pressure according to empirical correlations of the following form:(16)

$$D = n(T/P_{atm})^{1.75}$$

n = a constant

T = absolute temperature

A diffusion coefficient could increase by 30% because of an ambient temperature of 40 °C and an elevation of 7000 ft.

TABLE X
Predicted and Observed Biases

Test Inlet Peclet No.	1 1.4	2 1.0	3 0.6
Observed bias	15%	56%	75%
Predicted biases:			
Simplified model (Table II and III)	30%	80%	110%
Model involving rate term (Table V):			
$k_g a$ = 0.18 sec^{-1} (Ref. 6)	5%	10%	17%
9 sec^{-1} (Ref. 7)	22%	40%	97%
52 sec^{-1} (Ref. 8)	27%	50%	102%

TABLE XI
Recommended Minimum Sampling Rates to Maintain an Inlet Peclet Number Above 5^A for Different Sorbent Tube Holders and Sorbent Tube Diameters

Sampling Train Inlet	Assumed Distance to Sorbent (cm)	Recommended Minimum Sampling Rate (mL/min)
4.0-mm i.d. Sorbent Tube	1.5	5
6.0-mm i.d. Sorbent Tube	2.0	5
8.0-mm i.d. Sorbent Tube	2.5	7
Sipin Sorbent Tube Holder (inlet diameter 10 mm)	2.0	10
Accuhaler Sorbent Tube Holder (inlet diameter 4.0 mm)	2.0	2.5
DuPont Sorbent Tube Holder (inlet diameter 4.0 mm)	2.0	2.5
SKC Sorbent Tube Holder (inlet diameter 2.0 mm)	2.0	1.0

^A Presume a diffusion coefficient of 0.13 cm^2/sec.

Under these conditions sampling at flow rates stated in Table XI would result in a predicted bias of 0.5%. However, most diffusion coefficients are less than 0.1 cm^2/sec at sea level and the recommendations contained in Table XI should be valid in most circumstances.

By minimizing the inlet opening, a further margin of safety over what is provided in Table XI can be obtained for solid sorbent tubes used without holders. This reduces the surface area through which diffusive flux can occur. An opening diameter of 1.0 to 2.0 mm should be large enough for flow rates as small as 5 cm^3/min.

Additional data need to be taken at flow rates between 0.7 and 2.0 cm^3/min to document further the nature of diffusion as a bias. At those flow rates inlet areas should be varied to determine whether this minimizes bias and possible random effects attributable to diffusive flux. These conditions should be varied so that inlet Peclet numbers for test methods vary between 1 and 5. Methods collected under these conditions should be contrasted against samples taken under conditions so that the inlet Peclet number is larger than 10.

Detecting statistically significant differences between treatments would require a relatively large amount of replication to detect differences of 10%. The pooled coefficient of variation for such tests probably will not be smaller than 10%. Consequently 23 samples per treatment would be needed to reduce the beta error to 5%. (Beta error is the probability of saying that there is no difference when, in truth, there is a difference). This result is obtained from consulting operating characteristic curves for a 1-sided student's t-test for a pooled t test.(17)

Notation Used in Equations

$A = \exp(N_1)/[\exp(N_1) - 1]$

A_1 = cross sectional area of empty section, cm^2

A_2 = cross sectional area of sorbent bed open to flow, cm^2

a = hydrodynamic surface area per volume of bed, cm^{-1}

$B = \exp(N_1/\epsilon)/[\exp(N_2/\epsilon) - \exp(N_1/\epsilon)]$

C^I, C = concentration in Section I, the empty section in front of sorbent bed, g/cm^3

C^{II} = concentration in Section II, the voids in sorbent bed, g/cm^3

C^{III} = concentration in sorbent bed, g/cm^3

D = diffusion coefficient, cm^2/sec

ϵ = sorbent bed void fraction

ϵ_B = cross sectional area of space in front of sorbent bed divided by cross sectional area of sorbent tube holder

ϵ_C = cross sectional area open to flow in sorbent bed divided by cross sectional area of sorbent tube holder

F_I, F_{II} = flux in sections 1 and 2, respectively, $g/cm^2/sec$

k_g = mass transfer coefficient, cm/sec

L_1 = distance between inlet and sorbent bed, cm

L_2 = distance between sorbent tube inlet and back sorbent bed, cm

L_3 = distance between sorbent tube inlet to point where concentration in bed is zero, cm

L_A = distance from inlet of sorbent tube holder to sorbent tube inlet, cm

$L_B = L_A + L_1$

$L_C = L_A + L_3$

L_s = length of sorbent bed, cm

$M_1 = (O - (O^2 + 4P)^{1/2})/2$

$M_2 = (O + (O^2 + 4P)^{1/2})/2$

$N_1 = vL_1/D$ (inlet Peclet number)

$N_2 = vL_3/D$

$N_A = v_A L_A/D$

$N_B = v_B L_B/D$

$N_C = v_C L_C/D$

$O = v/(\epsilon D)$

$P = k_g a((1 - \epsilon)/(\epsilon D))$

R = adsorption rate, $g/cm^3/sec$

r = radial coordinate; $r = 0$ at center line of sorbent tube; $r = r_1$ at wall of sorbent tube, cm

t = time, sec

$v(r)$ = fluid velocity as a function of r, cm/sec

v = average fluid velocity in empty section, cm/sec

$v_{A,B,C}$ = average air velocity in space between sorbent tube holder inlet and sorbent tube (A), sorbent tube inlet and sorbent bed (B); and in the sorbent bed voids, cm/sec

Z = axial coordinate; $Z = 0$ at inlet to sorbent tube, cm

z = axial coordinate ($z = 0$ at interface between empty section and start of solid sorbent bed), cm

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