Respirator Canister Evaluation for Selected Organic Vapors and Sorbent Performance Against Vinyl Chloride

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by

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ABSTRACT

The protection afforded by one commercial organic vapor respirator canister (MSA/GMA) against chloroform, benzene, epichlorohydrin, acrylonitrile, propargyl alcohol, 1,2-dibromoethane, acrolein, chloromethyl methyl ether, and N-nitrosodimethylamine was determined. Six canisters simultaneously were challenged at 64 actual liters per minute with test atmospheres of these compounds at both 80% and <15% relative humidity (RH). The challenge concentrations were, in general, the greater of 50 times the threshold limit value or 1 ppm. Breakthrough volume was defined as that volume of air which passed through the canister before the downstream concentration was 1% of the challenge concentration. Tests were continued until at least this concentration was attained or 16 h had elapsed, whichever occurred first.

Under a moderate workload, these canisters should afford adequate protection against chloroform, benzene, and acrylonitrile for at least 4 h, epichlorohydrin for at least 8 h, and the remaining compounds (except chloromethyl methyl ether) for at least 16 h. Chloromethyl methyl ether at 80% RH exhibited a minimum penetration of 30% after only 34 min, and it appears that this and similar canisters will not provide adequate protection against atmospheres containing this compound. In all tests in which breakthrough occurred, the decrease in breakthrough time with increase in relative humidity was greater than would be expected from published literature. On the basis of these results, suggestions are made for changes in the present National Institute for Occupational Safety and Health/Mine Safety and Health Administration certification procedures.

The capacities of a charcoal and Ambersorb 347 for vinyl chloride were determined. Challenge atmospheres were 10-ppm vinyl chloride at both 80% and <15% RH. The capacities were calculated from the amount of vinyl chloride sorbed in beds of two different weights at a given penetration. At 1% penetration, the calculated charcoal capacity was 2.0 mg of vinyl chloride per gram of sorbent at <15% RH, and 0.52 mg/gm at 80% RH. The

corresponding capacities for Ambersorb 347 were 0.68 and 0.36. Both sorbents, when used in respirator equipment, appear only marginally useful against vinyl chloride.

I. RESPIRATOR CANISTER EVALUATION FOR SELECTED ORGANIC VAPORS

A. Introduction

Respirators have long been employed to prevent the inhalation of toxic materials. For the most effective and efficient use of these devices, the useful life of the canister (or cartridge) needs to be known. If this is not the case, the canister might be used so long that its efficiency is degraded, thus endangering the wearer, or it might be replaced sooner than necessary resulting in an economic and material waste.

There is a lack of sufficient quantitative information concerning the penetration/breakthrough that commercially available air-purifying respirator canisters exhibit against hazardous compounds. The current National Institute for Occupational Safety and Health/Mine Safety and Health Administration (NIOSH/MSHA) method for approval of organic vapor respirator cartridges and canisters is specified in 30 CFR 11, subparts I and L.[1] In brief, approval is granted on the basis of breakthrough time for carbon tetrachloride from either a 5000-ppm (canister) or 1000-ppm (cartridge) challenge atmosphere. If the downstream concentration has not reached 5 ppm (0.1 % penetration) after 12 min for a canister, or 50 min (0.5% penetration for a cartridge) the item is approved for all organic vapors. (Penetration is the ratio of downstream to challenge concentration.) Unfortunately, the results for carbon tetrachloride are not necessarily indicative of the protection that is afforded against other compounds.

The published literature[2-4] shows that for many compounds, particularly those of low molecular weight and boiling points, breakthrough may be much faster than for carbon tetrachloride under identical test conditions. For example,[3] in experiments in which canisters were challenged with 50% relative humidity (RH), 1000-ppm challenge atmospheres at 53 liters per minute (LPM), downstream concentrations of 10 ppm (1% penetration) were observed at the following times: carbon tetrachloride, 90 min; vinyl chloride, 7 min; dichloromethane, 16 min; chloroform, 52 min; and methyl chloroform, 59 min. It is obvious, at least in these cases, adequate protection is not always afforded.

A number of theoretical expressions have been derived to calculate breakthrough times or capacities of various sorbents.[2,4,5] Unfortunately, none of these are completely successful. Probably the most successful is a semiempirical equation, a result of a series of experiments by Nelson and coworkers.[3,4,6-8] Breakthrough data for 131 compounds were obtained under a number of different experimental conditions. From these data, an expression for the time at which 10% breakthrough occurred was derived. This expression was applicable to 10 different classes of organic compounds using the constants that were listed in the paper.[4] The calculated breakthrough times for individual compounds usually agreed within 20% of the experimentally determined times. However, particularly in the case of low molecular weight, volatile compounds, the calculated times usually overestimated the breakthrough times, sometimes by more than a factor of 2. There were also indications that actual breakthrough times at high humidity or very low challenge concentrations might be shorter than would be predicted. Finally, using the published equation allows breakthrough estimates to be calculated for only 10% penetration, the 10 classes of compounds, and the same type cartridges which were used in the study.

Ideally, every canister type should be tested with every compound against which it is supposed to offer protection under conditions simulating all field conditions. Obviously, this is an unrealistic task. The next best approach would be to test each canister type against every compound under the most severe field conditions that are to be expected. This method would go far in guaranteeing worker protection, but would not allow for the greatest possible use of individual canisters.

Following this latter approach, we have tested a common organic vapor canister, MSA Type GMA, part No. 448974, against the following nine hazardous organic vapors: chloroform, benzene, epichlorohydrin, acrylonitrile, propargyl alcohol, 1,2-dibromoethane, acrolein, chloromethyl methyl ether, and N-nitrosodimethylamine. The challenge atmospheres were, in general, 50 times the threshold limit value (TLV), at both 80% and <15% RH, and the flow through the canisters was a nominal 64 actual liters per minute (ALPM). [Because of the altitude of Los Alamos, 7000 ft., 64 ALPM corresponds to approximately 49 standard liters per minute (SLPM).]

B. Summary

Six MSA Type GMA canisters were tested simultaneously against nine different organic vapors. These nine compounds were: chloroform, benzene, epichlorohydrin, acrylonitrile, propargyl alcohol, 1,2-dibromoethane, acrolein, chloromethyl methyl ether, and N-nitrosodimethylamine. All of these compounds, except propargyl alcohol and acrolein, have recognized or suspected carcinogenic potential. The challenge atmospheres were 50 times the assigned TLV or 100 times the smallest concentration which could be reliably monitored if there were no assigned value. This latter case existed for chloromethyl methyl ether, recognized to have carcinogenic potential, and N-nitrosodimethylamine, suspected of carcinogenic potential. For these tests, challenge atmospheres were 1 ppm. Tests were run at both 80% and <15% RH with nominal flow through the canisters of 64 ALPM. Breakthrough was defined as 1% penetration (1/2 the TLV) and the tests were continued until, at least, this concentration was detected downstream of the canisters or for 16 h, whichever occurred first.

All evaluation tests were carried out in a controlled access laboratory.[9] The challenge atmosphere was produced by injecting the compound of interest into a 325 SLPM flow of compressed "house" air (Fig. 1). This air then passed into a stainless steel chamber, which contained the canisters to be tested. For the majority of the tests, the test chamber was placed in a ventilated glove box. The exhaust from the test chamber was vented up the stack of a laboratory hood with a face velocity of 150 ft/min. The total airflow and the flows through each individual canister were measured with mass flow transducers. The concentration of the compound in the challenge atmosphere and downstream of each canister was measured with a flame ionization detector (FID). In those cases in which the challenge concentration might be so low that 1% penetration could not be detected, provision was made to take batch samples downstream of the canisters during the first and then second 8-h period of the tests. In practice, this latter feature was not required. A summary of the test results, Table I, shows that including a safety factor and under a moderate workload these canisters should afford adequate protection against chloroform, benzene, and acrylonitrile for at least 4 h, epichlorohydrin for at least 8 h, and the remaining compounds (except chloromethyl methyl ether) for at least 16 h. Because of very rapid breakthrough, it appears that this and similar canisters will not provide adequate protection against atmospheres containing chloromethyl methyl ether. These tests suggest the need for changes in the certification procedure that include: testing based on the chemical functionality of the compounds to be sorbed, humidity pretreatment at 80% RH, and abandonment of tests with as received and 25% RH pretreated canisters.

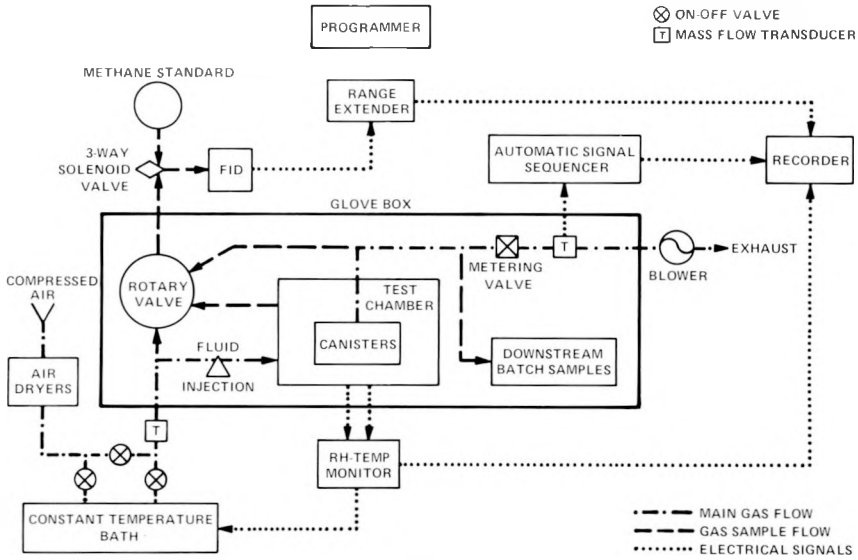

Fig. 1.
Block diagram of test system.

TABLE I

SUMMARY OF CANISTER BREAKTHROUGH TESTS

Compound	TLV (ppm)	Challenge Conc (ppm)	RH (%)	Canister Flow (ALPM)[a]	Average Breakthrough - 1% Penetration: Volume ($L \times 10^{-4}$)	Time (min)	Amount Collected (g)	Approximate Calculated Breakthrough Time for 30 SLPM Flow (h)
Chloroform	10	525	< 15	65.4	2.9	437	56.9	12
Chloroform	10	494	79	65.6	1.8	274	34.0	8
Benzene	10	498	< 15	65.8	3.6	547	44.2	15
Benzene	10	495	80	64.7	3.0	387	30.6	13
Epichlorohydrin[b]	5	250	< 15	64.4	7.0	1080	50.8	> 29
Epichlorohydrin	5	251	80	67.5	5.2	765	37.4	22
Acrylonitrile	2[c]	101	< 15	64.1	6.9	1078	11.9	29
Acrylonitrile	2[c]	98	80	64.8	3.2	488	5.2	13
Propargyl Alcohol[b]	1	50	< 15	64.0	6.5	1020	5.8	> 28
Propargyl Alcohol[b]	1	49	79	64.0	7.3	1140	6.4	> 31
1,2-dibromethane[b]	0.13[d]	6.5	< 15	63.7	7.3	1140	2.8	> 31
1,2-dibromoethane[b]	0.13[d]	6.5	80	64.7	7.0	1080	2.7	> 30
Acrolein[b]	0.1	4.9	< 15	64.5	8.5	1320	0.8	> 36
Acrolein[b]	0.1	5.0	80	60.8	6.6	1080	0.6	> 29
Chloromethyl methyl ether[e]	N.A.	1.0	< 15	63.7	0.76	119	2×10^{-2}	3
Chloromethyl methyl ether[f]	N.A.	1.0	80	63.8	0.22	34	6×10^{-3}	0.9
N-nitrosodimethylamine	N.A.	1.0	< 15	63.8	14.5	2280	0.33	> 62
N-nitrosodimethylamine	N.A.	1.0	81	65.7	10.2	1560	0.24	> 43

[a] Actual liters per minute.

[b] Breakthrough not detected.

[c] OSHA permissible exposure limit.

[d] NIOSH proposed 15-min ceiling.

[e] Breakthrough defined as 10% penetration.

[f] Breakthrough defined as 30% penetration.

N.A. = No assigned value.

C. Experimental

1. Airflow. A schematic of the test system is shown in Fig. 2. The air used to make up the test atmospheres was supplied from the building compressed air supply. After regulating the pressure to approximately 40 psi (276 kPa), it was dried with two heatless air dryers (Puregas, model HF-200) in parallel. Because the dryers required about 40 psi and the incoming air cycled between approximately 45 and 65 psi (310 to 448 kPa), it was necessary to try to regulate the air close to the lower end of the pressure cycle. Even with two compressed gas regulators in series, some fluctuation in the pressure was still present. As a consequence, there was approximately a ±2% variation in the total airflow through the system and a ±1% variation in the flow through the canisters. Another fluctuation was caused by the cycling of the air dryers and consisted of short pulses approximately every 15 s. These pulses resulted in about a 1% drop in the measured flow. These flow fluctuations are discussed more fully in Sec. I.C.4.a.

After passing through the dryers, the air could follow one of two paths: either directly to the total mass flow transducer (Kurz Instruments, Inc., model 505-9) and then to the test chamber for runs with dry air, referred to as dry runs, or first over the surface of a temperature controlled water bath to increase the water vapor content for the 80% RH tests. In both cases, the humidity and temperature in the test chamber were monitored. For the high humidity tests, the humidity signal from the monitor was used to control the temperature of the water bath and thus the humidity.

The compound of interest was injected into the airstream downstream from the total mass flow monitor but before the air entered the test chamber. Three different methods of injection were used and these are described in Sec. I.C.3 below. The test atmosphere then entered the chamber through 12 holes in the bottom. Upstream of the chamber, the pressure in the test atmosphere line was approximately 1-1/2 psi (10.3 kPa) while the pressure in the chamber was controlled to a few inches positive with the exhaust blower. The air left the chamber either through the canisters or through a 12-port manifold in the top of the chamber. The flow through each individual canister was controlled with a metering valve and measured with a mass flow transducer (Kurz Instruments, Inc., model 505 DC-7). After the metering valve, the individual flows joined, passed through a normally closed solenoid valve ("canister valve"), and were then connected to the exhaust blower. While approximately 290 SLPM of air was leaving the chamber through the canisters, 325 SLPM was entering. The excess passed through the manifold in the top of the chamber, through a metering valve ("bypass metering valve") and into the exhaust line downstream of the canister valve. The bypass metering valve permitted control of the total flow passing through all six canisters while the individual metering valves in each canister line allowed the flow through each canister to be adjusted.

Another bypass line connected the top manifold to a normally open solenoid valve ("main bypass valve") and then to the exhaust line downstream of the canister valve. The canister and main bypass valves were wired so that one or the other was always open. In this way, the chamber was always open to the exhaust line either through the main bypass valve or the canisters and bypass metering valve.

Two lines were connected downstream of each canister but upstream of its flow transducer. One of each of these pairs of lines led to a 10-port, air-operated, rotary valve (Valco Instruments Co., type ASD). Other inputs to this valve were the challenge atmosphere from the test chamber and the make-up air, before the challenge compound was injected, referred to as "clean" air. The output of this valve was connected to a FID (Beckman Industries, Inc., model 400 hydrocarbon analyzer). The valve was controlled by a timer (Valco Instruments Co., digital valve sequence timer) to advance, in most tests, every 90 s. This time period was a reasonable comprise between obtaining a stable, readable signal, the physical length of the strip-chart record, which would be produced in a 16-h test, and the time between consecutive readings on the same valve port. The

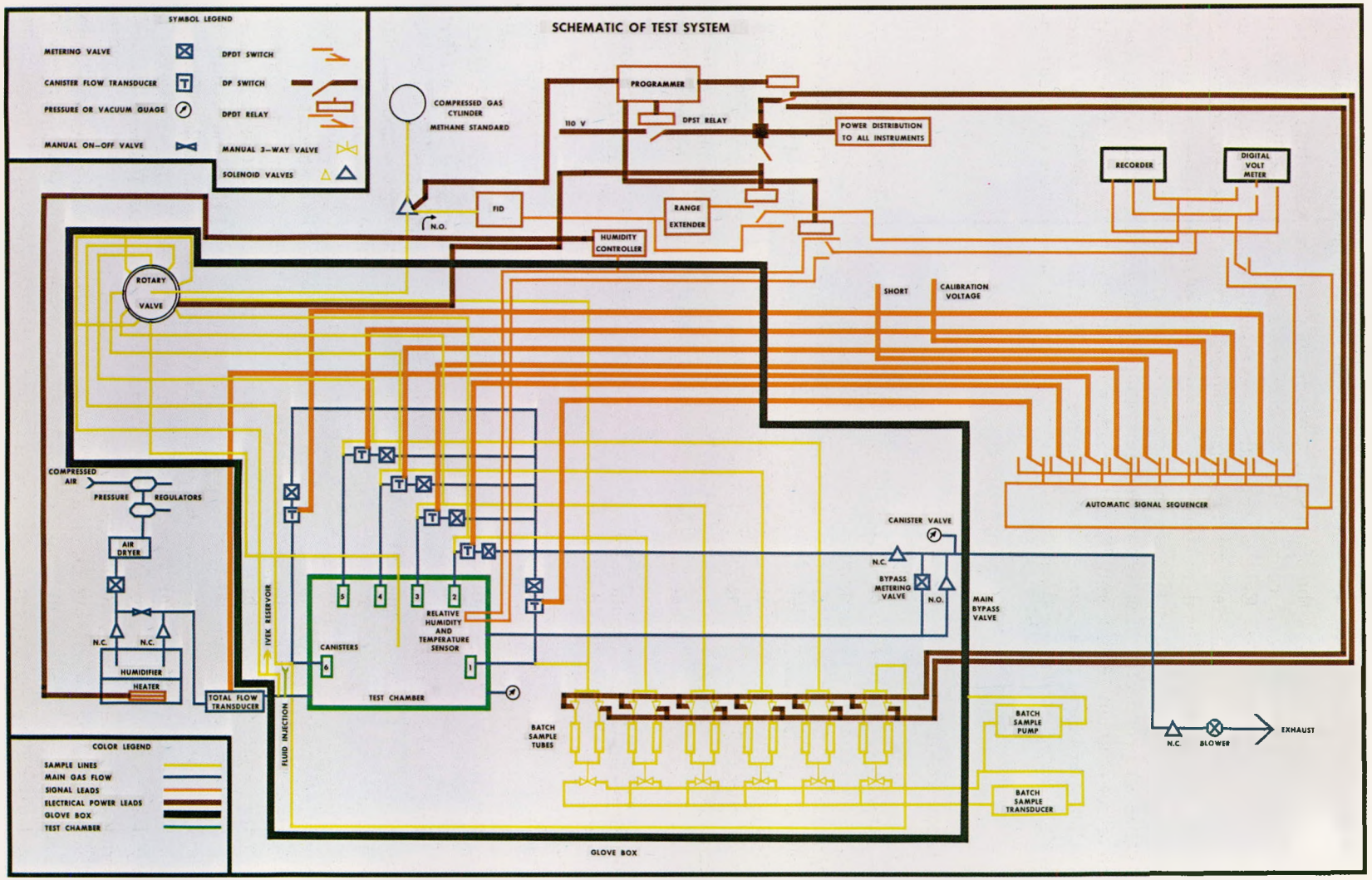

Fig. 2.
Schematic of test system.

order of sampling was as follows: canister No. 1, canister No. 2, challenge atmosphere, clean air, canister No. 3, canister No. 4, clean air, canister No. 5, canister No. 6, clean air.

To take batch samples of the air passing through the canisters, when that was required, the other lines of each pair were connected to six four-way solenoid valves (Skinner Precision Industries, No. V933 DB 2075). Each of these valves was actually a pair of two-way valves in a single body with the inputs connected and the outputs separate. The outputs were adapted to take 10-mm-o.d. sample tubes. The downstream end of each pair of sample tubes was connected to a critical orifice in the common side of a manual, three-way valve. One output side of each of these six valves was connected directly to a vacuum pump which maintained a critical flow through each orifice of about 180 mL/min. The other side was connected to the vacuum pump through a mass flow transducer (Teledyne Hastings-Raydist, model ALL-500/H-500M). By switching the flow through the transducer, the actual flow through any one sample tube could be measured at any time.

2. Electrical.

a. Automatic Operation of Test System. Automatic operation of the test system was accomplished with a programmable timer (Lindburg Enterprises, Chrontrol). Nine simple programs could be entered that turned four individual 110-V outlets on or off. These 110-V signals were used to control the following functions: (1) turn off all power to the test system at the end of the test; (2) periodic calibration of the FID by connecting it, through a three-way solenoid valve, to a cylinder of 9-ppm methane in air; (3) sequential monitoring of the temperature and relative humidity in the test chamber; and (4) collecting 8-h batch samples of the air downstream of the canisters by operating first one-half and then the other half of the four-way solenoid valves.

b. Data Handling. All data were recorded on one three-pen, strip-chart recorder (Linear Instruments, model 595). The data were handled as described below.

One pen of the recorder recorded the FID signal. If the challenge concentration, usually 50 times the TLV, gave a full-scale deflection, then the breakthrough concentration, 1/2 the TLV or 1% penetration, would give only 1% of full scale or one division. To increase the sensitivity, a range extender (Caltronics Industries, Inc., model 410 linear auto-expander) was placed in the signal line between the FID and the recorder. This unit automatically expanded the effective display width of the recorder by a factor of 10. Only when the challenge atmosphere was being sampled was the extender bypassed. This was accomplished by closing a switching relay, which was activated by a signal from a switch on the rotary, sample valve. Thus, in terms of recorder chart divisions, when the challenge atmosphere gave a full-scale, 100 divisions, reading, the air downstream of the canisters would give a 10 division response at 1% penetration.

The signals from the six canister flow and the total airflow transducers were connected to an automatic sequencer (Hampshire Controls Corporation, Dataplex). Also sequenced were a short (zero signal) and a constant calibration voltage. During a test, one pen of the recorder recorded these inputs, at approximately 3-min intervals, in the following sequence: canister No. 1, canister No. 2, total, canister No. 3, short, canister No. 4, calibrate, canister No. 5, canister No. 6. Thus, every flow was recorded approximately every 27 min for 3 min. Provision was incorporated to override this sequence so as to be able to read any input at any time.

The temperature and relative humidity in the test chamber were monitored (General Eastern Instruments Corp., model 400). These two signals were switched at 20-min intervals by a relay controlled with the main timer and recorded with the third recorder pen.

3. Fluid Injection. As noted earlier, three different means were used to inject the challenge compound: syringe and syringe pump (Sage Instruments, model 355) and two positive displacement pumps [IVEK Corporation, S-LOX Precision Metering System; Instrumentation Specialties Co., (ISCO), model 312]. The factors that determined the system used were the rate and total amount of compound to be injected and the constancy of the injection.

As we have had favorable experiences with the syringe and syringe pump method in the past,[10,11] the greatest reliance was placed on this system, and it was used whenever possible. Knowing the total airflow past the syringe needle, the rate of injection was calculated by:

$$R = (C_c\ M\ F_t)/(2.40 \times 10^7\ \rho)\ , \tag{1}$$

where

R = injection rate: mL/min,
C_c = challenge concentration: ppm (volume),
M = molecular weight of liquid being injected: gm/mole,
F_t = total airflow into chamber: SLPM,
ρ = density of liquid being injected: gm/mL.

The required speed of the syringe pump carriage was then found by:

$$\upsilon = R/A\ , \tag{2}$$

where

υ = syringe pump carriage speed: mm/min,
A = linear syringe capacity: mL/mm.

This system was used whenever the challenge concentration was 50 ppm or less. For higher concentrations, the syringe required for a 16-h test would have been larger than the syringe pump could conveniently handle.

For higher concentrations, except chloroform, the IVEK, S-LOX Precision Metering system, was used. This system mated a rotating, reciprocating piston pump (Fluid Metering, Inc., model RHO or RH1) to a stepping motor and electronic control. The pump, which had a ceramic piston and cylinder, was adjustable to deliver from almost 0 to 25 μL/stroke for the RHO or from almost 0 to 100 μL/stroke for the RH1 head. The electronic control was digitally adjustable to give from 0 to 600 strokes/min. Thus, the system was capable, theoretically, of delivering from 0 to 60 mL/min with simple adjustment of the actual delivery rate. However, some leakage around the piston caused the following difficulties: First, the delivery rate for one compound was not necessarily the same as the delivery rate for another compound with the same pump and control settings. Second, it was not always possible with any one compound to predetermine the control setting for a given delivery rate particularly at very low rates. Third, with chloroform, the delivery rate slowly decreased with time. These problems were particularly noticeable when there was a pressure differential across the pump head. This was always the case when generating a test atmosphere as the pump was delivering into the make-up air, at about 1-1/2 psi, while the compound supply reservoir was at ambient pressure. Finally, the pressure fluctuations of the make-up air, noted in Sec. I.C.1, caused marked changes in the challenge concentration because the

pump head was subjected to a changing pressure differential. The problems caused by this pressure differential were largely overcome by connecting a static pressure line between the compound reservoir and the clean air supply which equalized the pressure across the pump head.

One final problem encountered with the acrylonitrile tests was contamination of the clean air, as monitored by the FID, with vapors of the compound. This occurred for the following reason. As noted earlier, the operation of the air dryers caused short pressure pulses in the clean air pressures. The static line to the compound reservoir was attached to the air inlet system in close proximity to the clean air sample line. When the clean air pressure suddenly dropped, a small amount of the air in the reservoir static line, containing some acrylonitrile, was pushed out and picked up by the clean air sample line. This problem was noted only with acrylonitrile because of the moderately low challenge concentration (100 ppm) and relatively high vapor pressure of the compound. Placing a small, charcoal sorbent bed in the reservoir static line cured the problem.

Because there were still uncertainties in the calculated delivery rates of the IVEK system, the syringe and syringe pump were used as a standard. That is, the FID response was determined, both directly and with an integrating recorder, when a known challenge concentration was being produced with the syringe and syringe pump. The final adjustments of the IVEK system then were made to give the same FID response.

The final fluid injection system, used only with chloroform, was the ISCO (Instrumentation Specialties Co., model 312) metering pump. While leakage past the pumping mechanism, in this case check valves, was very noticeable,once established the rate was constant. Further, as the check valves employed O-rings, material compatibility with the fluids being pumped could have been a problem. As with the IVEK system, the ISCO was set by comparison to the syringe and syringe pump.

4. Calibrations and Errors.

a. Airflow. The total mass flowmeter was calibrated by passing dry air through a calibrated orifice (traceable to NBS) and then through the flowmeter. The estimated uncertainty in the calibrated flow did not exceed about 4% at 325 SLPM.

The individual mass flowmeters downstream of the canisters were calibrated periodically with a dry test meter (American Meter Co., model DTM-115), which was itself calibrated with the same NBS traceable system used to calibrate the total mass flowmeter. The estimated uncertainty in the calibration of the dry test meter did not exceed 2% at 50 SLPM. The outputs of the flowmeters, nominally 50 SLPM maximum flow, were nonlinear and at 50 SLPM were approximately 27 SLPM per volt. Although the overall response was nonlinear, linear calibration curves were determined for the range from about 44 to 53 SLPM. The results of these calibrations, as well as that for the total flow transducer, are shown in Table II. Each calibration curve, for both the dry and wet atmospheres, is the result of approximately 10 or more individual calibration points. F-tests at the 10% significance level showed no difference between the dry and 80% calibrations.

As noted in Sec. I.C.1., there were two fluctuations in the airflow, both a result of changes in the air pressure. One of these, with a very regular period of about 6 min, was caused by changes in the supply to the air dryers and resulted in approximately a ±2% variation in the total flow and ±1% fluctuation in the flow through the canisters. The average between the maximum and minimum flows was used in all flow calculations.

The other fluctuation was a short pulse, about every 15 s, caused by the operation of the air dryers. These pulses, which lasted for less than 2 s, resulted in about a 1% drop in the measured

TABLE II

CALIBRATIONS OF MASS FLOW TRANSDUCERS

Flow in SLPM = a(volts) - b

Relative Humidity	Dry				80%				Combined			
Transducer	No. of Points	Slope a	Intercept b	Regression Coefficent	No of Points	Slope a	Intercept b	Regression Coefficient	No. of Points	Slope a	Intercept b	Regression Coefficient
Canister No. 1	15	24.2	81.5	0.983	11	23.5	78.5	0.964	26	23.7	79.2	0.970
Canister No. 2	15	31.4	120.6	0.991	10	27.4	98.9	0.954	25	29.4	109.6	0.975
Canister No. 3	15	24.9	86.0	0.969	9	28.2	103.2	0.969	24	26.2	92.8	0.973
Canister No. 4	11	25.3	88.7	0.991	10	26.5	95.7	0.964	21	24.4	84.2	0.983
Canister No. 5	18	30.1	113.4	0.982	10	28.8	106.7	0.912	28	29.1	108.2	0.965
Canister No. 6	14	26.5	97.4	0.978	11	29.3	112.4	0.998	25	27.8	104.2	0.987
TOTAL	Flow in SLPM = -0.31 + 94.02 (volts) - 1.74 (volts)^2											

total and individual flows. As the output of the individual and total flow transducers were recorded on and read from the strip-chart record both during calibration and the canister testing, the effect of these pulses was compensated for.

In summary, the total airflow measurements were accurate to better than ±6% and reproducible to ±2%. The flows through the individual canisters were accurate and reproducible to ±3%.

b. Fluid Injection and Challenge Concentration. The carriage speed of the syringe pump and the linear capacities of the syringes were measured to within ±2%. Combining the uncertainty in the total flow, ±6%, with the uncertainties in the injection rate, the challenge concentration should have been accurate to better than ±7%.

With the IVEK and ISCO delivery systems, the challenge concentrations were determined by comparison with challenge atmospheres prepared with the syringe pump. While the error in this comparison is well within ±2%, there is more uncertainty in the constancy of the injection rates over long time periods. However, there was no evidence during any of the canister tests that the concentration changed by as much as 5%.

c. Downstream Concentration. The major instrumental source of error in determining downstream concentrations was the linearity of the FID. This was checked experimentally by integrating the signal produced from test atmospheres of different concentrations. Epichlorohydrin and acrylonitrile atmospheres were produced using the syringe pump and different syringes to produce atmospheres with the test challenge concentrations and 10% and 1% of these concentrations. For each compound the maximum deviation from linearity was 5%. As this test also included uncertainties in the challenge concentrations, the linearity of the FID is no worse than ±5%.

A noninstrumental uncertainty arose from contaminants in the make-up air and is discussed more fully in Sec. I.C.5 below. In this air were contaminants that gave an FID signal corresponding to about 2 to 3 ppm of methane. About 80% of this contaminant readily passed through the canisters while about 20% was taken out. However, over a 24-h period there was no indication that the percentage that passed through the canisters changed markedly. This contaminant was only a problem with the very low challenge concentrations of chloromethyl methyl ether and N-nitrosodimethyamine.

5. Experimental Procedure. Before actual tests with a new compound were begun, the sensitivity of the FID to the compound was determined and the range and gain of the analyzer set to give 70 to 80% of full scale on the recorder. One per cent penetration would then give 7 to 8 divisions with the range extender. If the IVEK (or ISCO) was to be used to produce the final test atmosphere, the approximate setting of the delivery system, to give the proper challenge concentration, was determined. Details of the chemicals used and the injection methods are given in Table III.

TABLE III

CHEMICALS AND INJECTION METHODS USED

Compound	Relative Humidity (%)	Source of Compound	Method[a]	Syringe[b] mL	Rate mL/min
Chloroform	Dry	Burdick and Jackson Laboratories, Inc.	ISCO	50	0.579
Chloroform	79	Burdick and Jackson Laboratories, Inc.	ISCO	50	0.537
Benzene	Dry	Burdick and Jackson Laboratories, Inc.	IVEK	50	0.609
Benzene	80	Burdick and Jackson Laboratories, Inc.	IVEK	50	0.595
Epichlorohydrin	Dry	Eastman Organic Chemicals; Cat. No. 507	IVEK	20	0.265
Epichlorohydrin	80	J. T. Baker Chemical Co. Cat. No. 0-8260	IVEK	20	0.267
Acrylonitrile	Dry	Eastman Chemical Co., Cat. No. P5161	IVEK	2.5	0.089
Acrylonitrile	80	Eastman Chemical Co., Cat. No. P5161	IVEK	5	0.087
Proparygl Alcohol	Dry	Aldrich Chemical Co.,Inc., Cat. No. P5080-3	Syringe	50	0.039
Proparygl Alcohol	79	Aldrich Chemical Co.,Inc., Cat. No. P5080-3	Syringe	50	0.039
1,2-Dibromoethane	Dry	Aldrich Chemical Co.,Inc., Cat. No. D-4075-2	Syringe	10	0.0075
1,2-Dibromoethane	80	Aldrich Chemical Co.,Inc., Cat. No. D-4075-2	Syringe	10	0.0075
Acrolein	Dry	Eastman Organic Chemicals, Cat. No.-2037	Syringe	5	0.0046
Acrolein	80	Eastman Organic Chemicals, Cat. No.-2037	Syringe	5	0.0045
Chloromethyl methyl ether	Dry	Aldrich Chemical Co., Cat. No. 10-033-1	Syringe	0.5	0.0010
Chloromethyl methyl ether	80	Aldrich Chemical Co., Cat. No. 10-033-1	Syringe	0.5	0.0010
N-nitrosodimethylamine	Dry	Aldrich Chemical Co., Cat. No. N2,500-1	Syringe	0.5	0.0010
N-nitrosodimethylamine	81	Aldrich Chemical Co., Cat. No. N2,500-1	Syringe	0.5	0.0010

[a]ISCO - Instrumentation Specialties Co., model 312.
IVEK - IVEK Corporation, S-LOX Precision Metering Systems.

[b]When the ISCO or IVEK were used, the syringe listed is the one used for calibration.

Before starting the actual canister test, all airflows and electrical signals were allowed to stabilize. Just before starting, the total airflow and the flows through the individual canisters were checked and adjusted if necessary. When the IVEK injection system was to be used, the challenge concentration was checked by comparing an approximate 20-min integrated FID signal with that produced with the syringe and syringe pump. If the challenge concentration was off by more than 5%, the IVEK rate was adjusted and the comparison repeated. This same procedure was used with the ISCO system.

When the proper injection rate had been attained, the fluid metering system was turned off, the canister valve closed, and the canisters installed. The canisters were not pretreated but used as they came from the manufacturer. In the first few tests, the flow of clean air through the canisters was then checked. However, particularly with moist atmospheres, when the canister valve was first opened, the indicated flow would change for a number of minutes nullifying any attempt at adjustment. The final procedure adopted was to start the test and then wait until the indicated flows had stabilized to make any necessary adjustment, usually only with the canister bypass valve.

With canisters installed and the canister valve closed, compound injection was started. If the IVEK (ISCO) system was used, the FID signal from the challenge atmosphere usually was compared again with the signal from the syringe generated atmosphere and any needed adjustments made.

When all preliminary checks had been completed and the concentration of challenge compound in the test atmosphere had stabilized, the test was started by: opening the canister valve, starting the timer, and, if batch samples downstream of the canisters were to be taken, starting the sample pump on the first 8-h set. The indicated flow through canister No. 1 was monitored until it had stabilized and then the flow through each canister was recorded for at least 7 min. Any needed flow adjustments were made after this time. The flows were checked periodically, when personnel were present, and adjusted if needed.

The timer was programmed to perform the following operations: shut off all electrical power at the end of the test; direct the standard methane mixture to the FID for 1 min every hour; switch the temperature and relative humidity signals to the recorder every 20 min; switch the sample pump from the first to the second set of downstream batch samples after 8 h. If the test was still in progress at the end of the regular work day or at the end of the test if personnel were available, the FID signal from the challenge atmosphere was integrated.

At the end of the test, the pertinent data were taken from the strip-chart record. It was first determined that the challenge concentration had not changed markedly during the test. There

were always some fluctuations caused by the fluid injection system and by the fluctuating airflow, but there was never any apparent long-term trend. Airflows, both total and through the individual canisters, were checked and no long-term change in the total airflow was ever noted. With humid atmospheres, the individual canister transducers showed an approximate 0.2 ALPM/h increase with time. This increase occurred in all humid tests and for clean, wet make-up air passing through the canisters but not when canisters were not installed or for dry atmospheres. This indicates an interaction between the water vapor and the canisters and that the flow increase was real and not an artifact of the flow transducers. To calculate the volume of air that passed through the canisters, average flows were used.

The concentration of challenge compound downstream of the canisters was calculated by:

$$C_D = (D_D - D_B)/S \quad , \tag{3}$$

where

C_D = concentration downstream of canisters: ppm (volume),
D_D = FID signal from challenge atmosphere downstream of canisters: recorder divisions,
D_B = FID signal from clean air downstream of canisters: recorder divisions,
S = sensitivity of the FID to the compound: recorder divisions/ppm.

With high challenge concentrations, D_B was considered to be identical to the signal from the clean air. However, because some of the clean air contaminant was taken out by the canisters, there was a significant difference in the downstream and clean air signals when low concentrations were being measured. In these cases, D_B was assumed to be equal to the signal from the clean air minus the difference in the clean air and downstream signals at the beginning of the run before any measurable breakthrough had occurred. That is,

$$D_B = D_M - \triangle D \quad , \tag{4}$$

where

D_M = FID signal from clean air: recorder divisions,
$\triangle D$ = difference in signals from clean air and air downstream of canisters when no or negligible penetration had occurred: recorder divisions.

Substituting Eq. (4) into (3)

$$C_D = [D_D - (D_M - \triangle D)]/S \quad . \tag{5}$$

We believe the major component of this contaminant was methane for the following reasons: The great majority was not taken out by the canisters, approximately the same level of contaminant was present in the laboratory air, and a few ppm is not an unreasonable methane concentration in the ambient atmosphere. The identity of the remaining contaminant is completely unknown. Only with chloromethyl methyl ether and N-nitrosodimethylamine, at 1 ppm challenge

concentrations, was the contaminant a concern. First, with chloromethyl methyl ether, it was difficult to determine the value of $\triangle D$. This was particularly true for the 80% RH test when breakthrough occurred very rapidly. Second, while the fraction of the contaminant removed by the canisters remained constant, the total contaminant level fluctuated by as much as 1/2 ppm methane equivalents, and the changes were most severe from late afternoon to mid-morning. At times when concentrations of a few parts per billion (ppb) methane equivalents were being measured, the signal from the range extender could change by as much as 10% during the short time any one sample stream was being monitored. This was true for signals from both make-up air and air downstream of the canisters.

Since chloromethyl methyl ether penetrated so rapidly, errors in measuring the downstream concentrations had little pragmatic effect on determining the usefulness of the canisters for this compound. N-Nitrosodimethylamine, on the other hand, showed no sign of breakthrough in 16 h so the variation in background contaminant was not important.

To debug the system, the first five canister tests (two chloroform, the dry benzene, and the two acrolein) were conducted with the test chamber and injection system outside the glove box. For these tests, a specially constructed Plexiglas box, vented to a laboratory hood, was placed over the chamber and injection system. All electrical and gas flow lines were attached to the same points they would be connected to when the chamber was in the glove box. The humid benzene test was carried out after the chamber had been installed in the glove box but before the windows were replaced. During this test, polyethylene sheet was taped over the window opening. All other tests were conducted in the completely enclosed glove box.

D. Results

In Figs. 3 through 11 the data for tests in which breakthrough was achieved are plotted as the concentration downstream of the canisters vs the volume that had passed through the canister. Only the 80% RH acrylonitrile test was taken to almost 100% penetration. One per cent breakthrough volumes were determined graphically from similar plots with much expanded ordinates. Breakthrough times were calculated by dividing the breakthrough volumes by the average canister flow. The data from these tests are listed in Table IV. Because of the fluctuating background levels and rapid breakthrough, the breakthrough values for chloromethyl methyl ether are for a minimum of 30% penetration in the 80% RH test and 10% penetration in the dry test. The data from those tests in which breakthrough was not achieved are given in Table V. While all flow calibrations and test measurements were made on the basis of standard liters per minute, the results are shown as actual liters per minute which, at Los Alamos, are ~30% larger than the corresponding standard values. Thus, the nominal 64 ALPM corresponds to ~49 SLPM.

The first thing to note in Table IV is the precision in each of the tests in which breakthrough occurred, as shown by the standard deviation. In all cases, except the humid chloromethyl methyl ether test, the relative standard deviation is 6% or less. This includes the experimental precision and is an indication of good quality control during manufacture. Even in the case of chloromethyl methyl ether, the relative standard deviation is only 9%.

Rather than plotting downstream concentration as was done above, the log of the penetration may be plotted instead. This has been done in Figs. 12 through 20. There are two reasons why this is a better presentation than the linear plots. First, it allows all data to be plotted on one reasonable size graph without losing data obtained at small penetrations. A more basic reason is most theoretical equations describing breakthrough predict such a plot will yield a straight line.[2,12] Most of these expressions are based on the Mecklenburg equation:

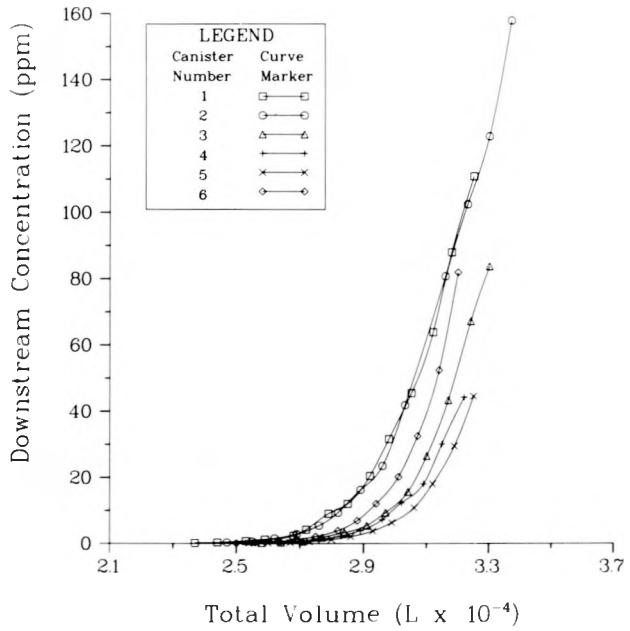

Fig. 3.
Chloroform, 525 ppm, dry: downstream concentration vs volume.

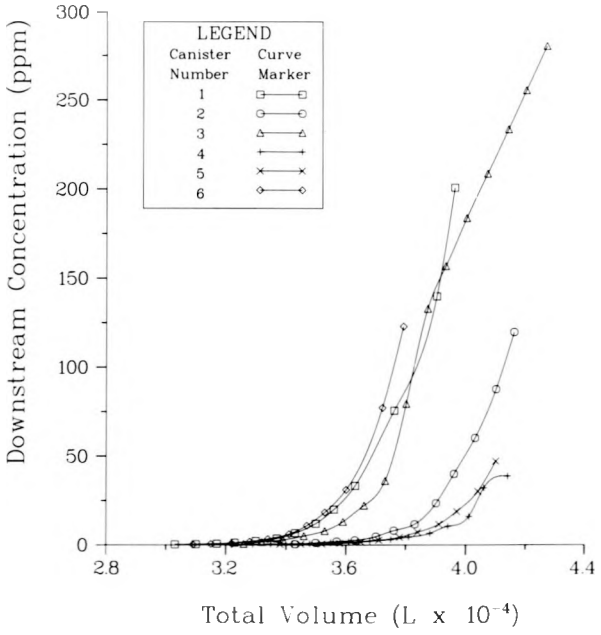

Fig. 5.
Benzene, 498 ppm, dry: downstream concentration vs volume.

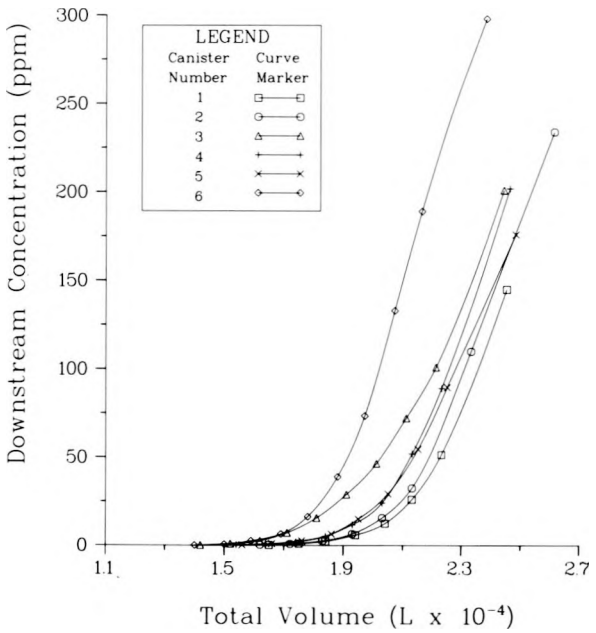

Fig. 4.
Chloroform, 494 ppm, 80% RH: downstream concentration vs volume.

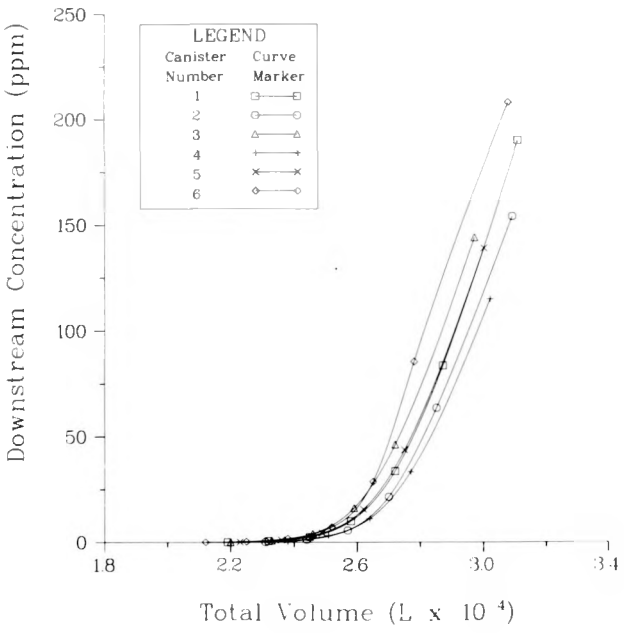

Fig. 6.
Benzene, 495 ppm, 80% RH: downstream concentration vs volume.

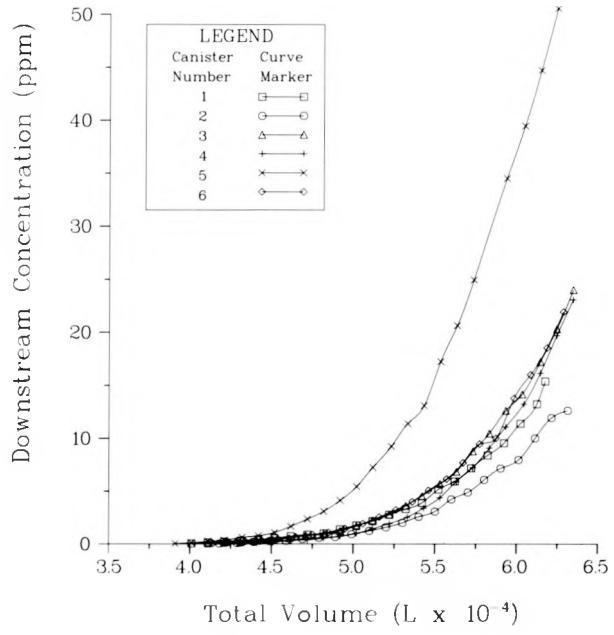

Fig. 7.
Epichlorohydrin, 251 ppm, 80% RH: downstream concentration vs volume.

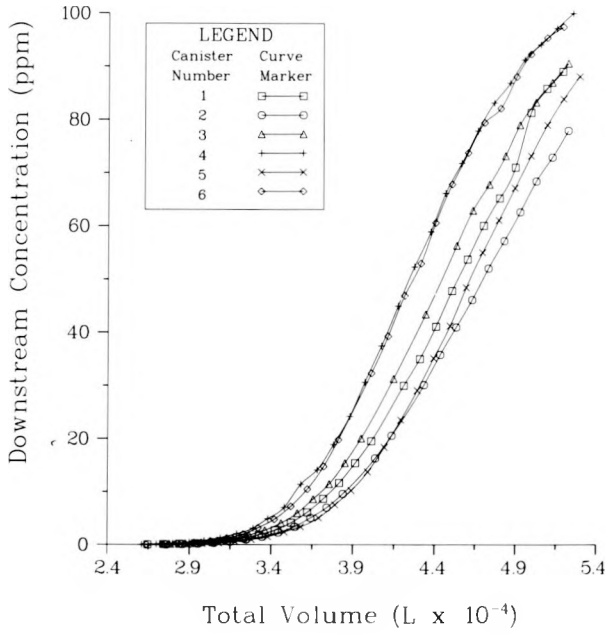

Fig. 9.
Acrylonitrile, 98 ppm, 80% RH: downstream concentration vs volume.

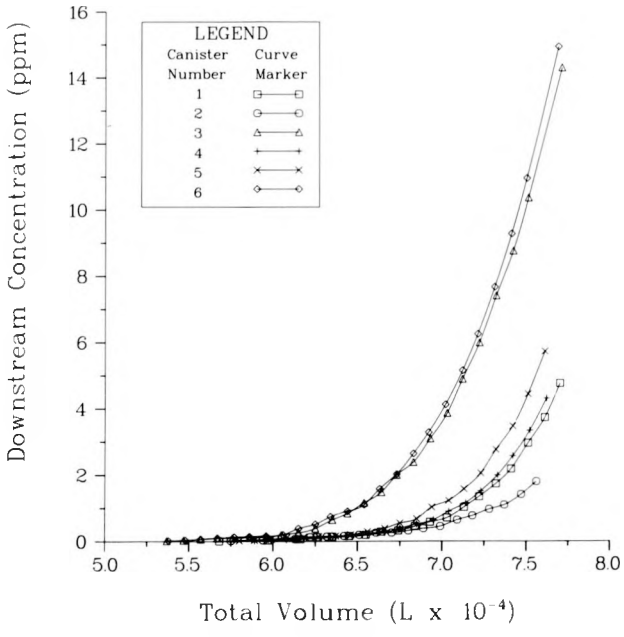

Fig. 8.
Acrylonitrile, 101 ppm, dry: downstream concentration vs volume.

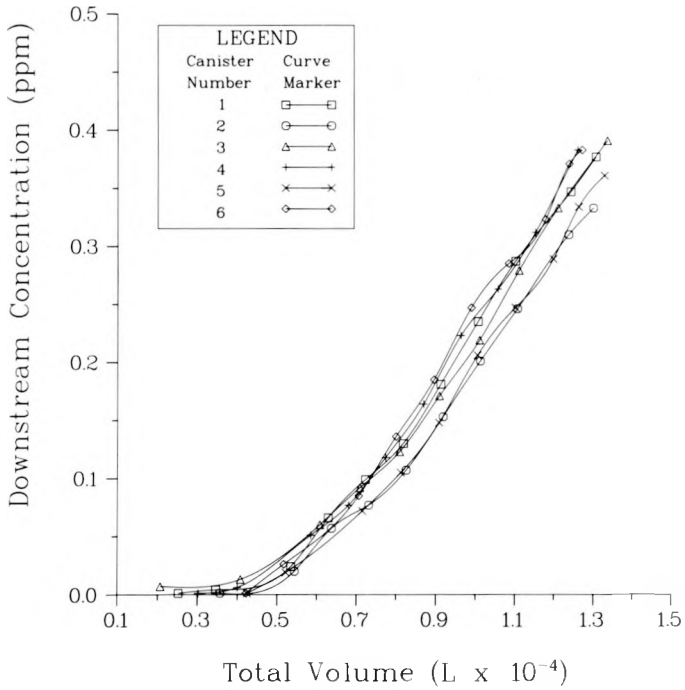

Fig. 10.
Chloromethyl methyl ether, 1 ppm, dry: downstream concentration vs volume.

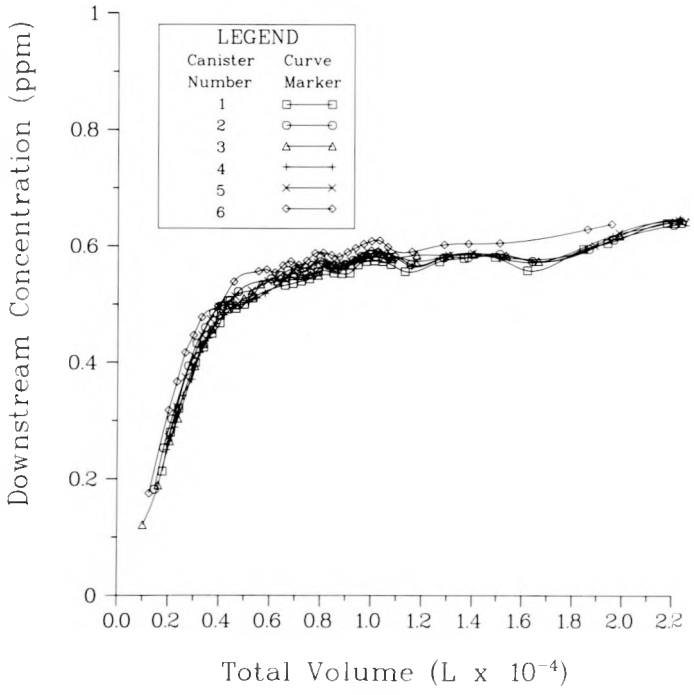

Fig. 11.
Chloromethyl methyl ether, 1 ppm, 80% RH: downstream concentration vs volume.

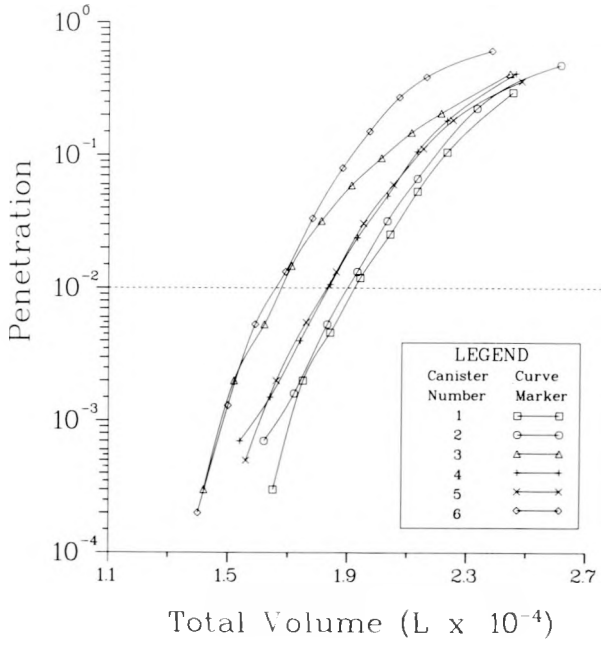

Fig. 13.
Chloroform, 494 ppm, 80% RH: penetration vs volume.

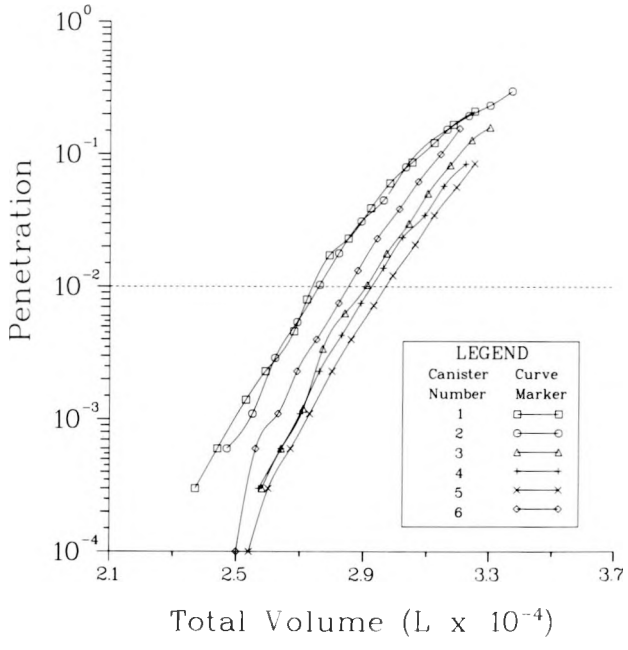

Fig. 12.
Chloroform, 525 ppm, dry: penetration vs volume.

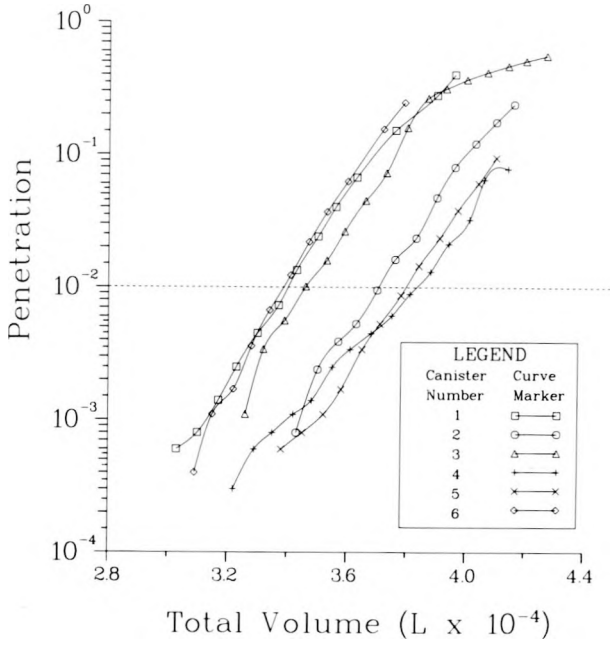

Fig. 14.
Benzene, 498 ppm, dry: penetration vs volume.

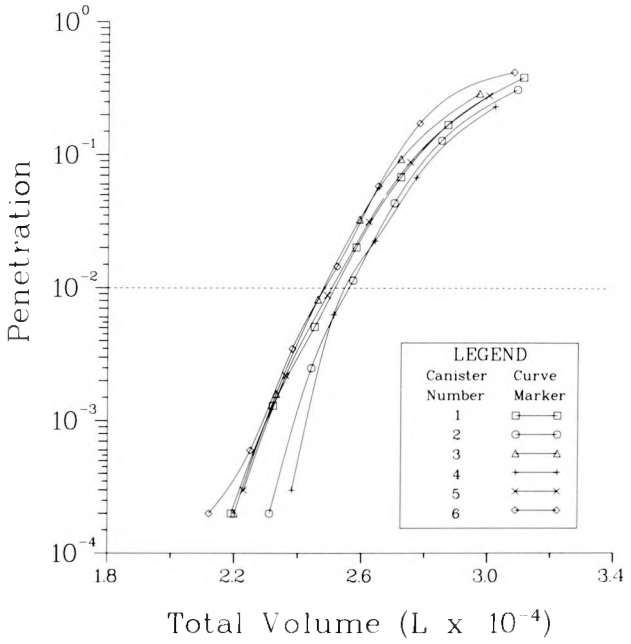

Fig. 15.
Benzene, 495 ppm, 80% RH: penetration vs volume.

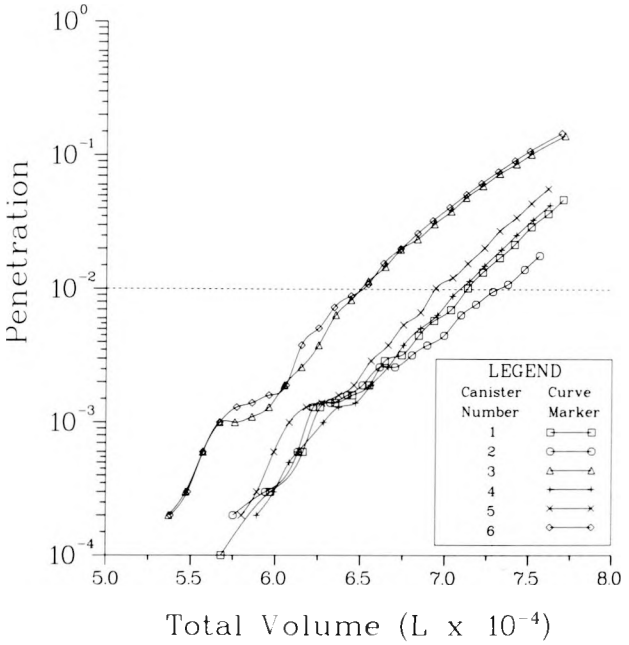

Fig. 17.
Acrylonitrile, 101 ppm, dry: penetration vs volume.

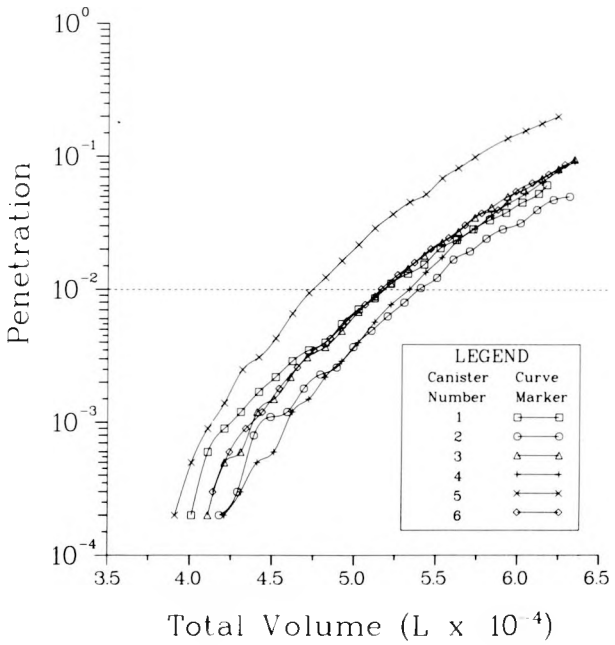

Fig. 16.
Epichlorohydrin, 251 ppm, 80% RH: penetration vs volume.

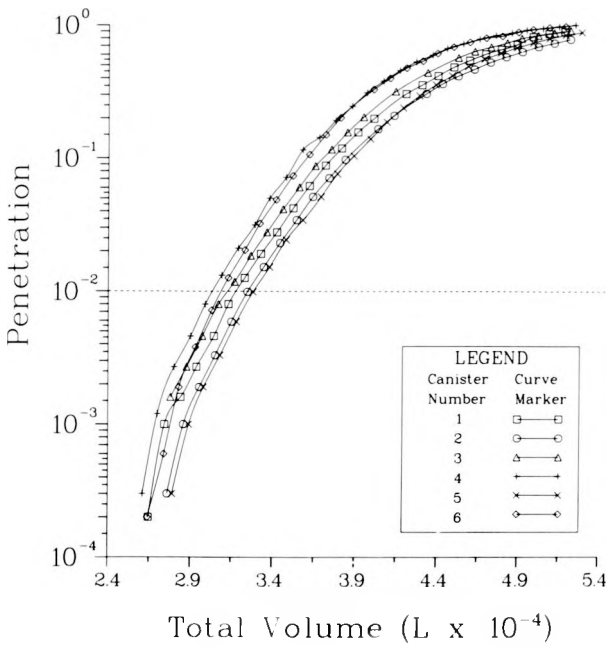

Fig. 18.
Acrylonitrile, 98 ppm, 80% RH: penetration vs volume.

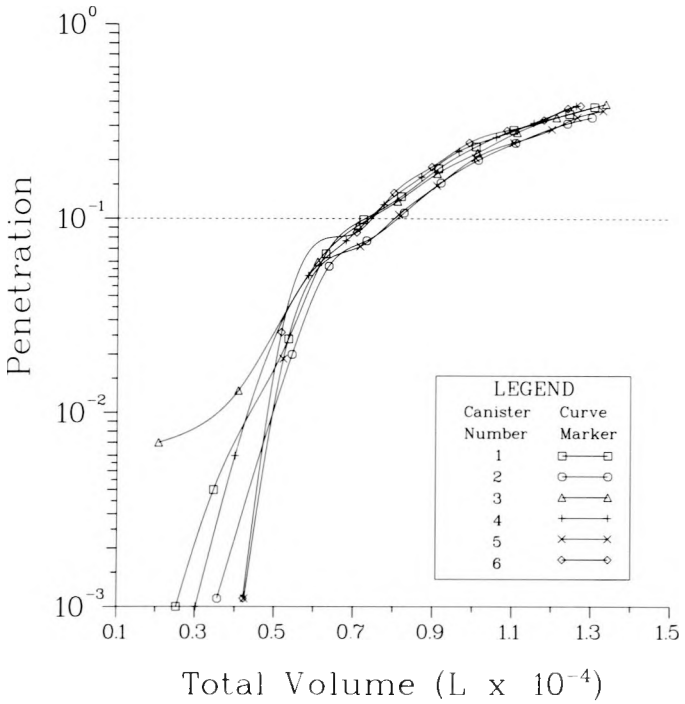

Fig. 19.
Chloromethyl methyl ether, 1 ppm, dry: penetration vs volume.

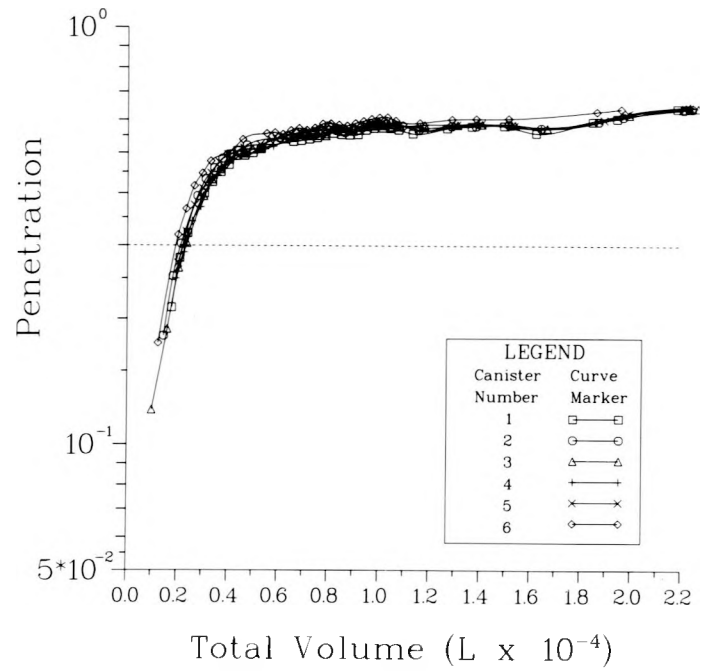

Fig. 20.
Chloromethyl methyl ether, 1 ppm, 80% RH: penetration vs volume.

TABLE IV

CANISTER EVALUATION TESTS IN WHICH BREAKTHROUGH WAS MEASURED

Canister No.	Clean Air[a] (min)	Test Atmosphere[b] (min)	Av Flow Through Canister (ALPM[c])	Volume (L X 10^{-4})	Time (min)	Amount Collected Before Breakthrough (g)	Approximate Calculated Breakthrough Time for 30 SLPM Flow (hours)
Chloroform							
Challenge atmosphere: 525 ppm; less than 15% RH; 23-1/2°C							
1	40	21	65.6	2.73	416		
2			67.9	2.76	406		
3			66.2	2.90	438		
4			64.3	2.92	454		
5			64.8	2.97	458		
6			63.6	2.85	448		
	Average[d]		65.4±1.5	2.86±0.09	437±21	56.9	12
Challenge atmosphere: 494 ppm: 79% RH: 26-1/2°C							
1	15	13	64.7	1.91	295		
2			67.4	1.89	280		
3			65.7	1.67	254		
4			66.3	1.83	276		
5			66 3	1.82	275		
6			63.3	1.65	261		
	Average[d]		65.6±1.4	1.80±0.11	274±15	34.0	8
Benzene							
Challenge atmosphere: 498 ppm; less than 15% RH; 25°C							
1	15	13	66.4	3.40	512		
2			66.2	3.71	560		
3			67.8	3.46	510		
4			65.5	3.83	585		
5			65.4	3.80	580		
6			63.5	3.38	532		
	Average[d]		65.8±1.4	3.60±0.21	547±33	44.2	15
Challenge atmosphere: 495 ppm; 80% RH; 26°C							
1	6	55	65.5	2.49	380		
2			64.7	2.55	394		
3			64.1	2.45	382		
4			65.1	2.54	390		
5			64.1	2.50	390		
6			64.5	2.47	383		
	Average[d]		64.7±0.6	2.50±0.04	387±5	30.6	11
Epichlorohydrin							
Challenge atmosphere: 251 ppm; 80% RH; 26°C							
1	2	8	66.8	5.18	778		
2			67.5	5.38	797		
3			67.7	5.18	765		
4			67.6	5.32	787		
5			67.5	4.75	704		
6			68.2	5.16	757		
	Average[d]		67.5±0.4	5.16±0.22	765±33	37.4	22
Acrylonitrile							
Challenge atmosphere: 101 ppm; less than 15% RH; 23°C							
1	0	52	64.3	7.13	1109		
2			63.8	7.31	1145		
3			64.8	6.49	1002		
4			63.8	7.08	1109		
5			63.7	6.96	1093		
5			64.3	6.48	1007		
	Average[d]		64.1±0.4	6.91±0.35	1078±59	11.9	29

TABLE IV (cont)

Acrylonitrile							
Challenge atmosphere: 98 ppm; 80% RH; 26°C							
1	0	4	64.4	3.18	494		
2			64.5	3.25	504		
3			64.5	3.13	485		
4			64.6	3.03	469		
5			66.1	3 29	498		
6			64.6	3.09	478		
	Average[d]		64.8±0.7	3.16±0.10	488±13	5.2	13
Chloromethyl methyl ether[e]							
Challenge atmosphere: 1.0 ppm; less than 15% RH; 23-1/2°C							
1	0	8	62.7	0.74	118		
2			62.5	0.80	128		
3			66.7	0.74	111		
4			62.7	0.74	118		
5			64.5	0.80	124		
6			63.3	0.74	117		
	Average[d]		63.8±1.6	0.76±0.03[e]	119±6[e]	1.9X10-2 [e]	3[e]
Challenge atmosphere:[f] 1.0 ppm; 80% RH; 26°C							
1	1	10	63.4	0.22	35		
2			63.8	0.21	33		
3			64.2	0 24	37		
4			63.7	0.24	37		
5			64 1	0.22	34		
6			63.3	0.20	31		
	Average[d]		63.8±0.4	0.22±0.02[f]	34±2[f]	5.6 X 10-3 [f]	0.9[f]

[a]Time clean air passed through canisters before run began.
[b]Time canisters were in challenge atmosphere with no air passing through them.
[c]Actual liters per minute.
[d]Average ± standard deviation.
[e]Breakthrough values are for 10% penetration.
[f]Breakthrough values are maximum for 30% penetration.

$$t_B = (a/C_o)\ (b - h) \quad , \tag{6}$$

where:

t_B = time at which a particular penetration occurs,
C_o = challenge concentration,
a, b = constants, a function of the sorbent bed and challenge compound,
h = a function of the mass transfer zone or dead layer.

This equation can readily be converted to one in terms of volume by:

$$V = t_B F = (aF/C_o)(b - h) \quad , \tag{7}$$

where

V = volume which has passed through the sorbent bed when a given penetration occurs,
F = volume flow through the sorbent bed.

A number of different expressions have been proposed for h. The majority of these, Klotz, Sillen, Wheeler, and van Dongen, are of the form:

$$h = -a_1 \ln P \quad , \tag{8}$$

where

P = penetration = (downstream concentration/challenge concentration),

a_1 = constant.

Substituting Eq. (8) into Eq. (7),

$$V = A + B \log P \quad , \tag{9}$$

where

$A = (abF)/(C_o)$,

$B = (2.303aa_1F)/(C_o)$.

As can be seen from Figs. 12 through 20, the straight line predicted from Eq. (9) holds quite well in the middle range of the penetration curves. At high penetrations, approaching 100% as seen in Fig. 18, it does not. This must be the case as penetrations >100% are predicted with continued flow. At low penetrations discrepancies between the data and the predicted linearity also appear but with no obvious explanation. Still, between about 0.2 and 10% penetration, it holds well enough to be useful for predicting volumes that will produce a given penetration. The intercepts and slopes, calculated by combining all the data from the six canisters in each test over the linear range, are listed in Table VI.

As noted above, the 80% RH, chloromethyl methyl ether breakthrough values are for a minimum 30% penetration. In this test, Figs. 11 and 20, it appears the curves are leveling off at about 0.60 ppm. Since in time a sorbent will exhibit 100% penetration, this indicates 100% penetration was actually approached at a calculated 60% penetration. Because breakthrough was so rapid, $\triangle D$ of Eq. (5) could not be determined and downstream concentrations were calculated from Eq. (3). Thus it appears that $\triangle D$, if it could have been determined, would have corresponded to about 0.40 ppm of chloromethyl methyl ether and all plotted data should be increased by this amount. This means that when the first reliable data were collected at about 15 min (1000 L) ~40% penetration had already been achieved.

In the dry run with this same compound, there appeared to be no increase in the downstream, FID signals, except for canister No. 3, for about the first 50 min (3000 L) and a value for $\triangle D$, in Eq. (5), could therefore be determined. However, because of the background signal fluctuations, this was only approximate and, at low penetrations, it resulted in fluctuations in the calculated downstream concentrations. For this reason, the points plotted at 0.1% penetration are the estimated volumes at which penetration first started. The tabulated breakthrough values are for 10% penetration. Although this introduces some possibility for error, from these results and those from the humid test, it is concluded this canister should not be used in a chloromethyl methyl ether environment.

In the N-nitrosodimethylamine tests with 1 ppm challenge atmospheres (although 10 ppb, 1% penetration was well within the sensitivity of the FID with the range extender) the fluctuating background would have made it extremely difficult to pinpoint 1% penetration. However, in the dry test there was no overall increase in $\triangle D$ during 40 h; at 81% RH, $\triangle D$ actually increased, if anything, during a 26-h test. If 1% penetration had actually been achieved by the end of 16 h, by the conclusion of these tests the compound should have been readily detected in the downstream air. Further, $\triangle D$ should have decreased which it did not. Therefore, we feel confident 1% penetration was not achieved at the end of 16 h.

TABLE V

CANISTER EVALUATION TESTS IN WHICH BREAKTHROUGH DID NOT OCCUR

Canister No.	Clean Air[a] (min)	Test Atmosphere[b] (min)	Av Flow Through Canister (ALPM[c])	Volume (L X 10^{-4})	Time (min)	Amount Collected Before Breakthrough (g)	Approximate Calculated Breakthrough Time for 30 SLPM Flow (hours)
Epichlorohydrin							
Challenge atmosphere: 250 ppm; less than 15% RH; 23°C							
1	0	6	64.2	6.93	1080		
2			64.0	6.91	1080		
3			64.5	6.97	1080		
4			64.6	6.98	1080		
5			64.4	6.96	1080		
6			64.5	6.97	1080		
	Average[d]		64.4±0.2	6.95±0.02	1080	>51	>29
Propargyl Alcohol							
Challenge atmosphere: 50 ppm; less than 15% RH; 23°C							
1	0	5	63.6	6 49	1020		
2			63.9	6.52	1020		
3			64.0	6.53	1020		
4			64.0	6.53	1020		
5			64.6	6.59	1020		
6			63.9	6.52	1020		
	Average[d]		64.0±0.3	6.53±0.03	1020	>5.8	>28
Challenge atmosphere: 49 ppm; 79% RH; 26°C							
1	6	21	63.8	7 27	1140		
2			64.0	7.30	1140		
3			64.0	7.30	1140		
4			63.2	7.20	1140		
5			65.5	7.47	1140		
6			63.6	7.25	1140		
	Average[d]		64.0±0.8	7.30±0.09	1140	>6.4	>31
1,2-Dibromoethane							
Challenge atmosphere: 6.5 ppm; less than 15% RH; 22°C							
1	0	7	63.1	7.19	1140		
2			63.7	7.26	1140		
3			64.0	7.30	1140		
4			63.9	7.28	1140		
5			64.0	7.30	1140		
6			63.9	7.28	1140		
	Average[d]		63.7±0.4	7.27±0.04	1140	>2.8	>31
Challenge atmosphere: 6.5 ppm; 80% RH; 26°C							
1	0	14	64.6	6.98	1080		
2			64.3	6.94	1080		
3			65.2	7.04	1080		
4			64.4	6.96	1080		
5			65.4	7.06	1080		
6			64.4	6.96	1080		
	Average[d]		64.7±0.5	6.99±0.05	1080	>2.7	>30

TABLE V (cont)

Acrolein							
Challenge atmosphere: 4.9 ppm; less than 15% RH; 25°C							
1	10	9	64.2	8.47	1320		
2			67.5	8.91	1320		
3			63.6	8.40	1320		
4			63.9	8.43	1320		
5			64.2	8 47	1320		
6			63.6	8.40	1320		
	Average[d]		64.5±1.6	8.51±0.20	1320	>0.74	>36
Challenge atmosphere: 5.0 ppm; 80% RH; 26°C							
1	20	16	62 4	6.74	1080		
2			61.6	6.65	1080		
3			59.8	6.46	1080		
4			60.8	6.57	1080		
5			59.5	6.43	1080		
6			60.9	6.58	1080		
	Average[d]		60.8±1.1	6.57±0.12	1080	>0.58	>29
N-nitrosodimethylamine							
Challenge atmosphere: 1.0 ppm; less than 15% RH; 24°C							
1	0	18	64.0	14.6	2288		
2			64.2	14.6	2280		
3			63.7	14.5	2280		
4			63.6	14.5	2280		
5			62.8	14.3	2280		
6			64.3	14.7	2280		
	Average[d]		63.8±0.5	14.5±0.1	2280	>0.33	>62
Challenge Atmosphere: 1.0 ppm; 81% RH; 26°C							
1	0	6	66.1	10.3	1560		
2			66.5	10.4	1560		
3			66.1	10.3	1560		
4			65.1	10.2	1560		
5			65.0	10.1	1560		
6			65.4	10.2	1560		
	Average[d]		65.7±0.6	10.2±0.1	1560	>0.24	>43

[a]Time clean air passed through canisters before run began.
[b]Time canisters were in challenge atmosphere with no air passing through them.
[c]Actual liters per minute.
[d]Average ± standard deviation.

E. Discussion

The following empirically derived equation for calculating breakthrough times for 10% penetration was published by Nelson and coworkers[4] following an extensive series of experiments:

$$t_{10\%} = [2.4 \times 10^6 W_c (a + bT)]/ (C_o^{2/3} M F) \quad , \tag{10}$$

where

W_c = weight of sorbent,
M = molecular weight of the compound,
a, b, T = constants relating to the compound.

TABLE VI

CONSTANTS FOR EQUATION 9

Volume = A + B log Penetration

Compound	Challenge Concentration (ppm)	Relative Humidity (%)	Assumed Linear Range of Penetration	Intercept A	Slope B
Chloroform	525	<15	$6X10^{-3}$-10^{-1}	3.43	0.29
Chloroform	491	79	$2X10^{-3}$-10^{-1}	2.38	0.28
Benzene	498	<15	10^{-3}-$2X10^{-1}$	4.21	0.30
Benzene	495	80	$2X10^{-4}$-10^{-1}	2.93	0.20
Epichlorohydrin	251	80	10^{-3}-10^{-1}	6.98	0.88
Acrylonitrile	100	<15	10^{-3}-$5X10^{-2}$	8.44	0.77
Acrylonitrile	99	80	$2X10^{-3}$-10^{-1}	4.18	0.50
Chloromethyl methyl ether	1.0	<15	Inadequate data		
Chloromethyl methyl ether	1.0	80	Inadequate data		

Although this equation was derived for 10% penetration, there appears no reason a similar expression should not be just as valid for other penetrations. The general expression is

$$t_B = (2.4 \times 10^6 W_c K)/(C_o^m MF) = Z/C_o^m F \quad , \tag{11}$$

where

K = constant dependent upon sorbent and challenge compound,

m = constant, possibly a function of the penetration,

$Z = (2.4 \times 10^6 W_c K)/M$.

The first thing to note is the time to breakthrough is inversely proportional to the flow. This permits breakthrough times for flows other than those used in an experiment to be calculated. Applying this to our data, breakthrough times for a moderate work rate, 30 SLPM, were calculated for our experiments and are shown in the last columns of Table IV and V. These times indicate the canisters would afford adequate protection against chloroform, benzene, and acrylonitrile for 4 h, epichlorohydrin for 8 h, and the remaining compounds, except chloromethyl methyl ether, for at least 16 h. These times incorporate a safety factor to account for different conditions that may exist under actual use conditions. These and similar canisters should not be used in a chloromethyl methyl ether environment.

When moisture is present in the challenge atmosphere, water molecules are also sorbed and there is a competition between the water and the challenge compound for the available sorption sites. This results in a reduction in the maximum amount of challenge compound that can be removed and a subsequent decrease in the breakthrough time and volume. From our data, under humid conditions, breakthrough volumes are reduced 30% for benzene, 54% for acrylonitrile, and >70% for chloromethyl methyl ether.

Many variables affect breakthrough and the quantitative effect of these variables, except for canister flow, have not been well established. Because of this it is usually difficult, if not impossible, to compare data taken under different experimental conditions. However, we have tried to do this with some of our data and that previously published by Nelson and coworkers[3,4,7,8] and Henry, Wilhelme, and Wilhelme.[13]

In Nelson, et al.[8] the effects of pretreatment and challenge humidity on breakthrough times were published. Assuming that our canisters were stored under dry conditions, we would predict that by using their data, only a 10% decrease in breakthrough volume between dry and 80% RH challenge atmospheres. Our data actually show much larger decreases than this.

In the recent article by Henry, et al.,[13] breakthrough data for GMA chin-style canisters by acrylonitrile were published. Some of these data were for 10% breakthrough of 10-ppm challenge atmospheres at 7, 50, and 90% RH. Interpolating these data to 80% RH, a 50% reduction in breakthrough volume would be predicted, which compares favorably to our 54%. As the challenge concentrations and penetrations both differed by a factor of 10 between the experiments by Henry and ourselves, this might indicate the reduction in breakthrough volume with increasing relative humidity is dependent on the downstream concentration as in both cases this was 1 ppm. Unfortunately, there is no obvious reason this should be true.

In this same article, the 10% penetration time for a 100 ppm, 50% RH challenge atmosphere was reported as 30 h. Canister flow was 60 LPM, which we assume was for standard conditions. Again interpolating their data for decrease in breakthrough time with increasing relative humidity, and assuming the time is inversely porportional to canister flow, we calculate 10% penetration should have occurred at 22 h in our experiment. We actually found 9.5 h. While this is a significant difference, interpolating their 10-ppm relative humidity data to 80% can introduce a significant error. Also, the charcoal in the two canisters may have been different as they did not list the manufacturer.

This same comparison can be calculated in a different way. By Eq. (11) and assuming m is 2/3, as Nelson found for 10% penetration,

$$t_{10\%} = (t_{B,80}\ C_o^{2/3}\ F)_H\ /\ (C_o^{2/3}\ F)_S\ , \qquad (12)$$

where

$t_{B,80}$ = interpolated breakthrough time for 10 ppm, 80% RH challenge atmosphere,

$_{H,S}$ = refer to data from Henry, et al.[13] and this work respectively.

This calculation gives a breakthrough time of 12 h, which provides reasonably good agreement between Henry's data and our results. However, if this is a valid calculation, then the explanations for the previous poor comparisons are not correct and the effect of relative humidity is a function of the challenge concentration.

Whichever of the above calculations is correct, if either, the comparison of our results with that of Henry et al.[13] is no worse than might be expected. It also indicates the relative humidity effect, as reported by Nelson, is suspect. Finally, it points up the difficulty in not only comparing but, more importantly, predicting breakthrough performance.

F. Suggested Changes to NIOSH/MSHA Certification Procedure

The results of the chloromethyl methyl ether tests argue for a change in at least part of the current NIOSH/MSHA testing and certification procedures for canisters and cartridges. The present procedure for canisters is outlined in Table VII. Certification is based on tests with only one

TABLE VII

CANISTER CERTIFICATION TESTS

Challenge Atmosphere: 5000 ppm (v) Carbon Tetrachloride
50% relative humidity

Maximum Allowable Penetration: 5 ppm(v), 0.1% penetration
Minimum Allowable Time: 12 min

	Tests	
Number of Canisters	Preconditioning	Canister Flow
3	None (as received)	64 LPM
2	25% relative humidity at 64 LPM for 6 h	32 LPM
2	85% relative humidity at 64 LPM for 6 h	32 LPM

compound, carbon tetrachloride. Admittedly the challenge concentration, 5000 ppm, is high and the maximum penetration which is allowed, 0.1%, is low. Even the high humidity pretreatment used in one test is, in some respects, quite stringent. While the canisters used in our experiments were certified by this procedure for use in chloromethyl methyl ether environments, we believe the data show they do not afford adequate protection. This may also be true of other hazardous compounds.

It has long been known that, in general, low molecular weight, volatile compounds penetrate more rapidly than do higher molecular weight, lower vapor pressure compounds. However, it has not yet been possible to calculate, a priori, breakthrough based on these or any other properties. As an example from our data, acrolein, with a lower molecular weight and lower boiling point (implying higher volatility) than chloromethyl methyl ether, did not penetrate in even 18 h from a challenge concentration five times as large. This inconsistency and the need to assure worker protection argues for a restriction on the use of any canister or cartridge with low molecular weight, volatile compounds until it has been subjected to further tests.

In the NIOSH publication "Development of Improved Respirator Cartridge and Canister Test Methods," (Ref. 2) five proposed certification schemes are outlined. The second of these is to "test each device against certain gases and vapors representative of chemical structure groups." In essence this method is based on dividing the compounds, for which protection is needed, into classes based on chemical functionality. Tests would be performed with the lowest molecular weight compound in each class for which protection is required. If the canister gave an acceptable service life, it would be approved for this compound and any of higher molecular weight of that class. If it did not, the next higher molecular weight compound would be tested and so on. The compounds from each class which gave an acceptable service life in tests with one canister could then be used as the test compound for that class when testing other cartridges and canisters. While this procedure would require more testing to approve a canister or cartridge than is presently the case, it would assure greater safety in certain environments.

Another possible fallacy in the present certification procedure is the use of 50% RH challenge atmospheres. Referring again to the article by Nelson and coworkers,[8] their data show the relative humidity of pretreatment is not as important as that of the challenge atmosphere. Although it was argued above that their data on the effect of humidity appear to be very conservative, nothing was said to negate their conclusions on the relative importance of pretreatment

and challenge humidity. It is also true that static pretreatment was used in Nelson's experiments while dynamic pretreatment is required for the certification tests. However, until such time as it is shown severe pretreatment followed by a 50% RH challenge atmosphere produces as large a decrease in service life as does an 80-90% challenge atmosphere, a change in the certification procedure to include a test with, at least, an 80% RH challenge atmosphere is indicated. As there is little indication in the literature that breakthrough times at low relative humidities are significantly shorter than at high, consideration might also be given to abandoning the low humidity preconditioning and as received tests. This would decrease the amount of testing required for certification, which would help in instituting the generic testing described above. Until a better testing and certification procedure can be implemented, the same risk of inadequate worker protection remains.

G. Conclusions

Although all experimental data were obtained at an elevation of 7000 ft. and an average atmospheric pressure of 585 torr (78 kPa), we believe the following conclusions are applicable to standard conditions as well:

- At concentrations of 50 times the appropriate TLV and a moderate breathing rate, the MSA type GMA chin-style canister provides protection against:
  (1) chloroform, benzene, and acrylonitrile for at least 4 h,
  (2) epichlorohydrin for 8 h, and
  (3) propargyl alcohol, 1,2-dibromoethane, and acrolein for 16 h.

- At 1 ppm challenge concentration, this canister provides protection against N-nitrosodimethylamine for 16 h.

- This and similar canisters should not be used in a chloromethyl methyl ether environment.

- Comparing breakthrough data from different experiments is fraught with difficulties unless identical test conditions are employed.

- The decrease in breakthrough time with increasing relative humidity may be greater than has been reported in the literature.

- A new testing and certification procedure for respirator canisters and cartridges is badly needed. Certification tests based on chemical functionality are suggested.

II. THE CAPACITY OF TWO SORBENTS FOR VINYL CHLORIDE

A. Introduction

Vinyl chloride is a substance recognized as having carcinogenic potential.[14] Because it is a low molecular weight compound and a gas at standard temperature and pressure, it is probably not readily removed from the air by most canister sorbents. In a preliminary effort to find a suitable sorbent for use in respirator, chin-style canisters and cartridges, the capacities of two sorbents for this compound were determined.

B. Summary

The capacities of two different sorbents for vinyl chloride for possible use in respirator canisters and cartridges were determined. These sorbents were activated charcoal, taken from SKC West, No. 226-01 sample tubes, and Ambersorb 347. Small beds of these sorbents were challenged with 10-ppm vinyl chloride atmospheres of both 80% and <15% RH. Flow through the beds, which were 4-mm diam, was 70 standard cubic centimeters per minute (SCCM). This flow gave a linear velocity of about 725 cm/min at Los Alamos, which corresponds to the linear velocity in a typical canister at 64 LPM. A summary of the results is given in Table VIII.

C. Experimental

The sorbent sample tubes shown in Fig. 21 consisted of 4-mm-i.d. Pyrex tubes within which a weighted amount of sorbent was placed. The sorbent was held in place by stainless steel screens and Teflon rings. These tubes were, in turn, sealed into 10-mm-o.d Pyrex tubes with plastic sleeves. The 10-mm tubes were inserted, one at a time into a chamber (Fig. 22) through which the test atmosphere passed. The downstream ends of the sorbent tubes were connected to the same FID used in the canister test system. The test atmosphere was pulled through the sorbent tubes with the pump, which was a part of the FID.

A schematic of the test atmosphere generation and sampling system is shown in Fig. 23. To generate the test atmosphere, ~125 SLPM of compressed "house" air was first conditioned as with the canister test system except that ~25 SLPM was removed before the air dryers. This air

TABLE VIII

SUMMARY OF CAPACITY MEASUREMENTS FOR VINYL CHLORIDE

Sorbent	Relative Humidity (%)[a]	Weight Sorbent (mg)	Bed Depth (cm)	Amount (μg) Vinyl Chloride Sorbed at Given Penetration				Calculated Capacity of Sorbent at Given Penetrations: (mg vinyl chloride / g sorbent)			
				(First Sign)[b]	(1%)	(5%)	(10%)	(First Sign)[b]	(1%)	(5%)	(10%)
Charcoal[c]	Dry	50	0.94	40	51	67	78	--	--	--	--
Charcoal[c]	Dry	75	1.38	83	101	126	141	--	--	--	--
Charcoal[d]	Dry	--	--	--	--	--	--	1.7	2.0	2.4	2.5
Charcoal[c]	80	50	0.94	12	15	20	22	--	--	--	--
Charcoal[c]	80	100	1.88	36	41	47	51	--	--	--	--
Charcoal[d]	80							0.48	0.52	0.54	0.58
Ambersorb 347	Dry	65	0.85	12	20	36	52	--	--	--	--
Ambersorb 347	Dry	90	1.20	22	37	66	93	--	--	--	--
Ambersorb 347[d]	Dry	--	--	--	--	--	--	0.40	0.68	1.20	1.64
Ambersorb 347	80	150	1.93	19	24	33	38	--	--	--	--
Ambersorb 347	80	200	2.57	36	42	54	60	--	--	--	--
Ambersorb 347[d]	80	--	--	--	--	--	--	0.34	0.36	0.42	0.44

[a] Dry: less than 15%.

[b] First indication of vinyl chloride from visual inspection of the strip-chart record.

[c] Charcoal taken from SKC West 226-01 charcoal sample tubes.

[d] Capacity calculated using Eq. (7).

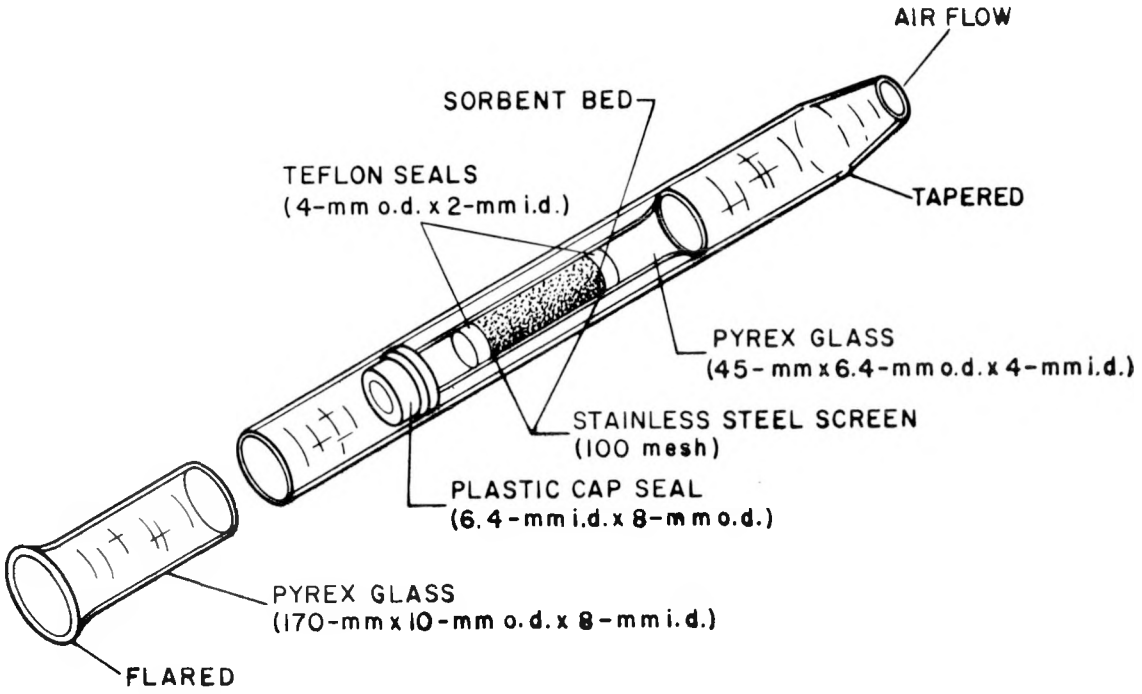

Fig. 21.
Sorbent sample tube.

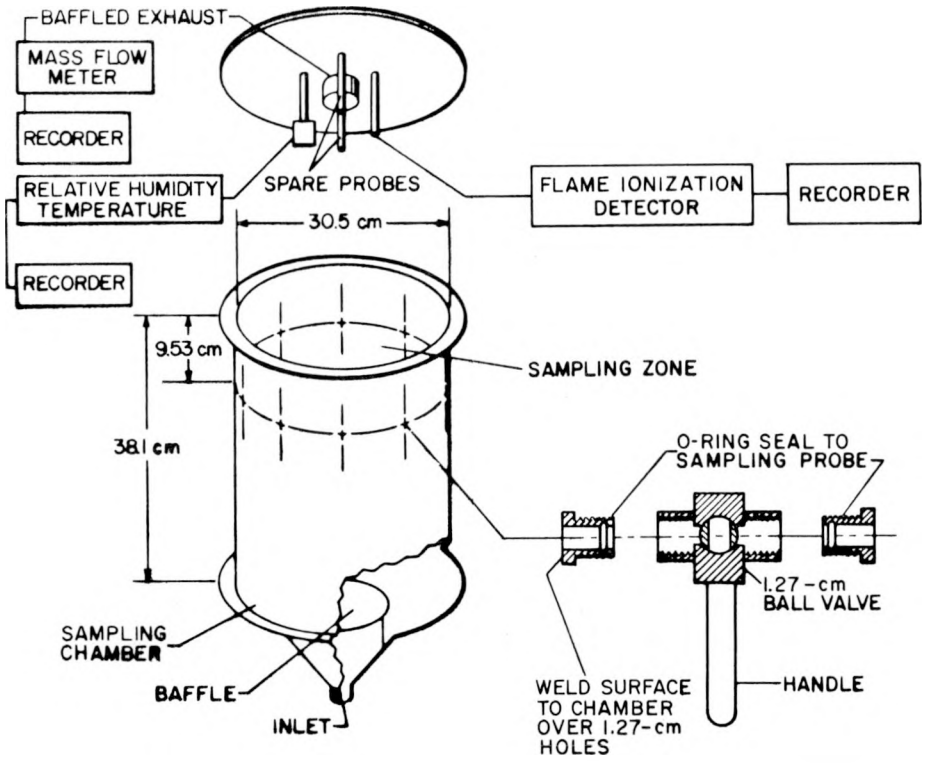

Fig. 22.
Sampling chamber.

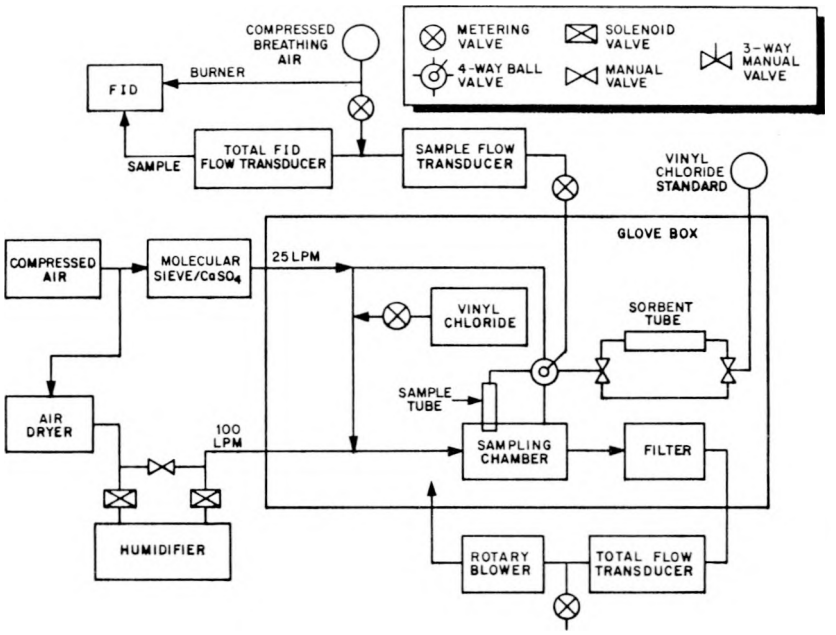

Fig. 23.
Schematic of generation and sampling system.

passed through a molecular sieve-$CaSO_4$ drying tube and then into the glove box where it rejoined the main airflow. Enough vinyl chloride from a compressed gas cylinder was metered into the 25 SLPM airstream to produce a 10-ppm challenge atmosphere in the sampling chamber. After passing through the sampling chamber and a charcoal filter, the total airflow was measured with a mass flow transducer (Hastings-Raydist, model AHL-10). It then passed through a rotary blower and was exhausted back into the glove box. The rotary blower/metering valve arrangement was provided to adjust the pressure in the sampling chamber to ambient.

The amount of test atmosphere that was pulled through the sorbent beds was controlled with a metering valve to 70 SCCM and measured with a mass flow transducer (Hastings-Raydist, model ALL500/H-500 M). Because the FID required a greater flow than this to operate properly, compressed air was added to the sample flow to bring the total to 500 SCCM and this total was measured with another mass flow transducer (Hastings-Raydist, model ALL-IK/H-IKM). This dilution air was from the same cylinder that supplied the air for the FID burner.

To produce the 10-ppm test atmosphere, the response of the FID to a 9.0 ± 0.5-ppm vinyl chloride in nitrogen, certified standard was first determined. This was accomplished by switching the four-way valve in the FID inlet line to the vinyl chloride standard and adjusting the sample and dilution flows to 70 and 500 SCCM, respectively. As was the case with the respirator canister tests, the FID responds to the organic contaminants in the make-up air and any that may also be in the vinyl chloride standard. We assume the only contaminant that will pass through the sorbent beds and the only contaminant in the vinyl chloride standard is methane. To determine the response of the FID to the vinyl chloride, the standard was first passed through a bed of Ambersorb 347 to establish the vinyl chloride background. The difference between this signal and that from the standard that has not passed through the sorbent, and thus still has the original 9 ppm vinyl chloride, is the FID response to 9 ppm of vinyl chloride. The test atmosphere is then produced by metering "pure" vinyl chloride, from a compressed gas cylinder, into the flowing make-up air to give an FID signal 1.1 times the standard signal.

D. Calculation of Capacity

Whenever a sorbent removes a material from a flowing gas stream and before all the sorbent is saturated with the compound, there exists a region in the sorbent bed where there is a concentration gradient of the compound in the gas stream. Upstream of this region, the sorbent is saturated and the concentration in the gas is the same as the challenge concentration. Downstream the concentration in the gas is essentially zero. That is, all of the compound has been removed. This region is often called the mass transfer zone (MTZ) or dead layer.

As the challenge atmosphere continues to flow through the sorbent bed, the MTZ moves toward the downstream end and after some time starts to emerge. The velocity and concentration profile of the MTZ can be determined by measuring the change in the downstream concentration as a function of time.

Assuming the MTZ profile does not change with bed depth, the capacity of the sorbent can be calculated by determining the amount of the compound that is sorbed in beds of two different weights, but the same cross-sectional area, and at the same penetration. These capacities will apply only to the same humidity, challenge concentration, and linear velocity as used in the tests.

The capacity is given by:

$$C = (g_2 - g_1)/(G_2 - G_1) \quad ,$$

where

C = capacity of sorbent: g sorbate/g sorbent,

g = weight of compound sorbed: g,

G = weight of sorbent: g,

Subscripts 1 and 2 refer to the different bed weights.

This equation is derived as follows:

Let

g_1 and g_2 = grams of material sorbed when a given penetration first occurs,

g_{1s} and g_{2s} = grams of material sorbed when bed is saturated,

$$(g_{1s})/(G_1) = (g_{2s})/G_2) = \text{capacity of sorbent.} \tag{13}$$

g_x = the difference, in grams, between the amount sorbed at saturation and the amount sorbed at a given penetration.

If it is assumed the MTZ profile does not change with bed depth, g_x is constant so that:

$$g_x = g_{1s} - g_1 = g_{2s} - g_2 \quad , \text{ and} \tag{14}$$

$$g_{2s} = g_{1s} + g_2 - g_1 \quad . \tag{15}$$

From Eq. (13) and (15)

$$g_{2s} = g_{1s}\,[(G_2)/(G_1)] = g_{1s} + g_2 - g_1 \quad . \tag{16}$$

Rearranging

$$g_{1s}[(G_2)/(G_1) - 1] = g_2 - g_1, \text{ and} \tag{17}$$

$$g_{1s} = G_1\,[(g_2 - g_1)/\,(G_2 - G_1)] \quad . \tag{18}$$

Thus

$$C = (g_{1s})/G_1 = [(g_2 - g_1)/\,G_2 - G_1] \quad . \tag{19}$$

E. Results and Discussion

The detailed results of the capacity measurements are shown in Tables IX and X. The data shown are the length of time to reach various penetrations, the amount sorbed at these penetrations, the time intervals between successive penetrations, and the capacities calculated at these penetrations.

As is evident from the data, the calculated capacity depends upon the penetration used for the calculation. As the degree of penetration increases, so does the calculated capacity. This should not be the case if the original assumptions of the derivation are correct. However, as is also clear, the assumption of an MTZ profile independent of bed depth is not correct as the elapsed times between successive penetrations is not the same for the different bed depths. From chromatography theory this is not unexpected as in a chromatograph, peaks tend to broaden and the leading edge profile becomes less steep as the column length increases. Referring back to the above derivation, this implies that,

$$g_{x2} > g_{x1} \quad , \tag{20}$$

$$g_{2s} - g_2 > g_{1s} - g_1 \quad , \tag{21}$$

and

$$C = (g_{1s})/(G_1) > (g_2 - g_1)/(G_2 - G_1) \quad . \tag{22}$$

TABLE IX

CHARCOAL CAPACITY FOR VINYL CHLORIDE

Sorbent: Charcoal taken from SKC West 226-01 charcoal sample tubes

Test Condition: Less than 15% relative humidity

Tube No.	Time (min) to Achieve Given Penetration				Amount (μg) Vinyl Chloride Absorbed at Given Penetration				Time (min) Interval Between Given Penetrations		
	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign→1%)[a]	(1-5%)	(5-10%)
	50-mg Sorbent Beds (Average Bed Length: 0.94 cm)										
41	25	30	38-1/2	45	45	55	69	80	5	8-1/2	6-1/2
42	20-1/2	27	36-1/2	42	37	49	66	75	6-1/2	9-1/2	5-1/2
43	19	27	38	44	34	49	68	78	8	11	6
44	19	28	36-1/2	46	34	51	66	82	9	8-1/2	5-1/2
45	23	27	35	42	42	49	63	75	4	8	7
46	26	30	37-1/2	45	47	55	67	80	4	7-1/2	7-1/2
Av[b]	22±3	28±1	37±1	44±2	40±6	51±3	67±2	78±3	6±2	9±1	6±1
	75-mg Sorbent Beds (Average Bed Length: 1.38 cm)										
67	42	53	73	81	76	97	131	145	11	20	8
68	50	55	69	77-1/2	90	100	124	139	5	14	8-1/2
74	49	58	75	83	89	106	135	149	9	17	8
75	42	53	70	79	76	97	126	142	11	17	9
76	47	56	68	74-1/2	85	102	122	134	9	12	6.5
77	46-1/2	55-1/2	67	75	84	101	120	135	9	11-1/2	8
Av[b]	46±3	55±2	70±3	78±3	83±6	101±3	126±6	141±6	9±2	15±3	8±1
Capacity[d]					1.7	2.0	2.4	2.5			

Test Condition: 80% relative humidity

Tube No.	Time (min) to Achieve Given Penetration				Amount (μg) Vinyl Chloride Absorbed at Given Penetration				Time (min) Interval Between Given Penetrations		
	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign→1%)[a]	(1-5%)	(5-10%)
	50-mg Sorbent Beds (Average Bed Length: 0.94 cm)										
50	7-1/2	9	11-1/2	13	14	16	21	23	1-1/2	2-1/2	1-1/2
51	4-1/2	7	9	10-1/2	8	13	16	19	2-1/2	2	1-1/2
53	6	8	10-1/2	11-1/2	11	15	19	21	2	2-1/2	1
55	6-1/2	9	11-1/2	13-1/2	12	16	21	24	2-1/2	2-1/2	2
56	7	8-1/2	11	12-1/2	13	16	20	22	1-1/2	2-1/2	1-1/2
57	6	7-1/2	11-1/2	13	11	14	21	23	1-1/2	4	1-1/2
Av[b]	6±1	8±1	11±1	12±1	12±2	15±1	20±2	22±2	1.9±0.5	2.7±0.7	1.5±0.3
	100-mg Sorbent Beds (Average Bed Length: 1.88 cm)										
64	21-1/2	24	27-1/2	29-1/2	39	44	50	53	2-1/2	3-1/2	2
65	21	25	27	30	38	46	49	54	4	2	3
78	21-1/2	23	27-1/2	30	39	42	50	54	1-1/2	4-1/2	2-1/2
79	20	22-1/2	26	29	36	41	47	52	2-1/2	3-1/2	3
80	20	23	28	30	36	42	51	54	3	5	2
81	11[c]	16[c]	23-1/2	26	20[c]	29[c]	42	47	5[c]	7-1/2[c]	2-1/2
46	17	20	25-1/2	27	31	36	46	49	3	5-1/2	1-1/2
45	19	20-1/2	24	26	34	37	43	47	1-1/2	3-1/2	2
Av[b]	20±2	23±2	26±2	28±2	36±3	41±4	47±3	51±3	2.6±0.9	3.9±1.2	2.3±0.5
Capacity[d]					0.48	0.52	0.54	0.58			

[a] First indication of vinyl chloride from visual inspection of the strip-chart record.

[b] Average ±1 standard deviation.

[c] These values excluded on basis of Grubbs Test.

[d] $\frac{\text{mg vinyl chloride}}{\text{g charcoal}}$.

TABLE X

AMBERSORB 347 CAPACITY FOR VINYL CHLORIDE

Sorbent: Ambersorb 347

Test Condition: Less than 15% relative humidity

Tube No.	Time (min) to Achieve Given Penetration				Amount (μg) Vinyl Chloride Absorbed at Given Penetration				Time (min) Interval Between Noted Penetrations		
	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign → 1%)[a]	(1-5%)	(5-10%)
	65-mg Sorbent Bed (Average Bed Length: 0.85 cm)										
18	5	9	17	25	9	16	30	44	4	8	8
19	5-1/2	11	25	35	10	20	45	62	5-1/2	13	10
24	5	7-1/2	15	22-1/2	9	14	27	40	2-1/2	7-1/2	7-1/2
25	5	8	17	25-1/2	9	15	30	45	3	9	8-1/2
26	7-1/2	12	21	30-1/2	14	22	38	54	4-1/2	9	9-1/2
27	8	11	21-1/2	32	15	20	38	56	3	10-1/2	10-1/2
28	9	15	25	36	16	27	45	63	6	10	11
29	9	15-1/2	27	38	16	28	48	67	6-1/2	11-1/2	11
31	9	13	23-1/2	34	16	24	42	60	4	10-1/2	10-1/2
34	7	11	21	30-1/2	13	20	38	54	4	10	9-1/2
33	6	9-1/2	18	26-1/2	11	17	32	47	3-1/2	8-1/2	8-1/2
32	6	9	15	22	11	16	27	39	3	6	7
35	7	11	20	29-1/2	13	20	36	52	4	9	9-1/2
36	6	9	16-1/2	24	11	16	30	42	3	7.5	7-1/2
Av[b]	7±2	11±2	20±4	29±5	12±2.7	20±4	36±7	52±9	4.0±1.2	9.3±1.8	9.2±1.4
	90-mg Sorbent Bed (Average Bed Length: 1.20 cm)										
22	11	17	39	53	20	31	70	93	6	12	14
37	11	15	25	41	20	27	45	72	4	10	16
40	13	21	38	54	24	38	68	95	8	17	16
41	10	18	38	56	18	33	68	99	8	10	18
42	13	20	36	51	24	36	64	90	7	16	15
52	12	19	37	55	22	34	66	97	7	8	18
53	16	24	39	55	18	44	70	97	8	15	16
54	19	27	44	58	34	49	79	102	8	17	14
Av[b]	13±3	20±4	37±5	53±5	22±5	37±7	66±10	93±9	7.0±1.4	13.1±3.6	15.9±1.6
Capacity[c]					0.40	0.68	1.20	1.64			

Test Condition: 80% relative humidity

Tube No.	Time (min) to Achieve Given Penetration				Amount (μg) Vinyl Chloride Absorbed at Given Penetration				Time (min) Interval Between Noted Penetrations		
	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign)[a]	(1%)	(5%)	(10%)	(First Sign → 1%)[a]	(1-5%)	(5-10%)
	150-mg Sorbent Bed (Average Bed Length: 1.93 cm)										
58	12-1/2	15	21	24	22	27	38	43	2-1/2	6	3
83	10	12	17	19-1/2	18	22	31	35	2	5	2-1/2
86	9	13-1/2	19-1/2	22-1/2	16	24	35	40	4-1/2	6	3
88	9	12	17	20-1/2	16	22	31	36	3	5	3-1/2
87	10	12	17-1/2	20-1/2	18	22	32	36	2	5-1/2	3
21	11-1/2	14-1/2	19	21-1/2	21	26	34	38	3	5-1/2	2-1/2
Av[b]	10±1	13±1	19±2	21±2	19±3	24±2	33±3	38±3	2.8±0.9	5.5±0.5	2.9±0.4

TABLE X (CONT)

200-mg Sorbent Bed (Average Bed Length: 2.57 cm)

61	22-1/2	26	31	34-1/2	41	47	56	62	3-1/2	5	3-1/2
1	16	19	28	32-1/2	29	34	51	58	3	9	4-1/2
2	16	18	28	32	29	33	51	57	2	10	4
4	17	21	30-1/2	34	31	38	56	61	4	8-1/2	3-1/2
3	21-1/2	26-1/2	31	34-1/2	39	48	56	62	5	4-1/2	3-1/2
5	24	27	32-1/2	36	44	49	59	65	3	5-1/2	3-1/2
6	22-1/2	25-1/2	30	34	41	46	54	61	3	4-1/2	4
7	18	22	26-1/2	30	33	40	48	54	4	4-1/2	3-1/2
Av[b]	20±3	23±4	30±2	34±2	36±6	42±6	54±6	60±3	3.4±0.9	6.4±2.3	3.8±0.4
Capacity[c]					0.34	0.36	0.42	0.44			

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[a]First indication of vinyl chloride from visual inspection of the strip-chart record.

[b]Average ±1 standard deviation.

[c]Capacity = $\frac{\text{mg vinyl chloride}}{\text{g ambersorb 347}}$.

Thus, the calculated capacities are a minimum.

The capacity of the charcoal, as calculated at 1% penetration, is 2.0 μg/g under dry conditions decreasing to 0.52 μg/g at 80% RH. The Ambersorb shows a much smaller decrease in capacity with increasing relative humidity, 0.68 to 0.36 μg/g. For canister or cartridge use, the volume of the required amount of sorbent is important. Because the Ambersorb has a higher packing density than the charcoal, 0.63 vs 0.42 gm/cm^3, 50% less volume of the Ambersorb would be required to remove a given quantity of vinyl chloride. As a result, for a given volume of sorbent the Ambersorb has a greater total capacity at 80% RH while the charcoal has a greater capacity under dry conditions. In terms of absolute quantities, assuming a 10-ppm, 80% RH challenge atmosphere and 64-LPM canister flow, 147 g (350 cm^3) charcoal or 212 g (337 cm^3) of Ambersorb 347 would be required to limit the penetration to 1% at the end of 1 h. These calculated values are based on the tabulated capacities and ignore the existence of the MTZ, consideration of which would increase the actual amount of sorbent needed.

The principle source of error in the capacity measurements was the challenge concentration. First, the concentration in the standard was known only to ±6% (9 ± 0.5 ppm). Also, the amount of vinyl chloride injected into the airstream was difficult to adjust so that data were collected whenever this calculated concentration was within 5% of 10 ppm. Sample flow was accurate to ±2%. Thus, the total error in the challenge concentration was ±9%.

The precision of the data also depended upon the reproducibility of the sorbent beds and reading the strip-chart record on which the downstream concentrations were recorded. Particular difficulty was encountered with the Ambersorb 347. The sorbent acquired a large static charge, which made accurate weighing and packing difficult. Further, the particles are hard spheres ranging in size from greater than 20 mesh to smaller than 55 mesh. This not only produces the possibility of channeling but also may result in a different mix of particle sizes, and thus surface area, in different sorbent samples. Finally, particularly in the dry tests, the MTZ profile is greatly elongated as shown by the long times between successive penetrations. This results in greater error in determining exactly when a given penetration occurs. In some cases, in an attempt to improve the precision, more than six samples were run.

At 80% RH, the charcoal exhibited unexpected behavior. When sampling was continued to reach 100% penetration, the FID signal increased to ~160% of the challenge concentration signal. It then slowly decreased to the same value as for the challenge concentration. We believe this apparently excess organic material was vinyl chloride, which was originally sorbed but was later replaced with water molecules. If this is the case, about 60% of the originally sorbed vinyl chloride was desorbed.

F. Conclusions

- In all cases, the charcoal exhibited a larger capacity than did the Ambersorb 347. However, the packing density of the Ambersorb 347 (0.63 gm/cm^3) was 50% larger than the charcoal (0.42 gm/cm^3). Thus, for a given volume of sorbent, the Ambersorb 347 has a greater total capacity at 80% RH while the charcoal has a greater capacity under dry conditions.
- Because of the change in the MTZ profile with bed depth, the calculated capacities are minimum values.
- The fact that continued passage of humid air through the charcoal desorbs originally sorbed vinyl chloride argues against its use.
- Because of the shape and size distribution of the Ambersorb 347 particles, it may be more difficult to achieve good quality control in the manufacture of units with this sorbent than with charcoal.

From the above conclusions it would be difficult to choose one of these sorbents over the other for use in canisters or cartridges for protection against vinyl chloride. It is true that the sorbent beds used in these experiments were not as deep as those in most protective equipment, and it is not possible to extrapolate the data accurately to greater depths. However, both sorbents appear only marginally useful for this application.

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