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Ernest S. Moyer ^a & Jeffrey A. Peterson ^a

^a Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Safety Research, Protective Technology Branch, Respiratory Protection Section, 944 Chestnut Ridge Road, Morgantown, West Virginia, 26505-2888, USA

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Organic Vapor (OV) Respirator Cartridge and Canister Testing Against Methylene Chloride

Ernest S. Moyer and Jeffrey A. Peterson

Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Safety Research, Protective Technology Branch, Respiratory Protection Section, 944 Chestnut Ridge Road, Morgantown, West Virginia 26505-2888

The Occupational Safety and Health Administration (OSHA) has proposed amending its existing exposure regulations for methylene chloride. The National Institute for Occupational Safety and Health (NIOSH) tested organic vapor cartridges and canisters for their breakthrough characteristics against methylene chloride. These tests were conducted to determine breakthrough times for methylene chloride with commercially available, negative-pressure organic vapor cartridge and canister respirators. Various methylene chloride challenge concentrations, from a low of 50 ppm to a high of 1000 ppm, were employed. Cartridges and canisters were tested "as received" from the manufacturer at a flow rate of 64 L/min through the respirator; 50 percent and 80 percent relative humidities were used. Breakthrough times (t_b) were determined for individual cartridges and canisters, as well as for stacked cartridges. The results indicate that cartridge breakthrough times (t_b) were extremely short when tested at 80 percent relative humidity (RH) for all the challenge concentrations. The chin-style canisters, which contained 2.5–3.0 times more sorbent than the cartridges, gave a t_b of only 100 minutes when tested at 125 ppm and 80 percent RH. The front-mounted/back-mounted canisters (10.5–11 times more sorbent than cartridges) gave a t_b of more than 10 hours at 125 ppm and 80 percent RH, but the t_b was reduced to only 5 hours when the challenge concentration was increased to 1000 ppm. Moyer, E.S.; Peterson, J.A.: Organic Vapor (OV) Respirator Cartridge and Canister Testing Against Methylene Chloride. *Appl. Occup. Environ. Hyg.* 8(6):553–563; 1993.

Introduction

The Occupational Safety and Health Administration (OSHA) has issued a proposal (Federal Register, November 7, 1991, 29 Code of Federal Regulations (CFR), Part 1910, 1915, and 1926) to amend its existing regulations for employees who are exposed to methylene chloride. The existing 8-hour time-weighted average (TWA) of 500 ppm is to be lowered to 25 ppm under the proposed regulations. The short-term exposure limit (STEL) is also proposed to be lowered

from 2000 ppm to 125 ppm (measured as a 15-minute TWA). The current ceiling limit (CL) of 1000 ppm would be deleted. An "action level" of 125 ppm, measured as an 8-hour TWA, has been proposed by OSHA as a new criterion. The National Institute for Occupational Safety and Health (NIOSH) conducted tests on representative organic vapor cartridges and canisters to determine their breakthrough characteristics against methylene chloride. Activated charcoal is the sorbent used in these respirator cartridges and canisters. The results of these tests are given in this article.

The testing basically consisted of two types of experiments. The first type was determination of the breakthrough characteristics of a single cartridge, or of a canister "as received" from the manufacturer. These tests were conducted at various methylene chloride challenge concentrations at 50 percent and 80 percent relative humidity (RH) and at 25°C. The second set of experiments consisted of testing a stacked cartridge configuration that resembled a packed column or sorbent bed.¹⁰ These experiments were performed to determine if the Wheeler equation¹⁰ relationship holds true for the large range of sorbent weights tested. These tests were also performed at various methylene chloride challenge concentrations, at 50 percent and 80 percent RH and at 25°C. It should be noted that NIOSH does not recommend the use of organic vapor cartridges against methylene chloride for two reasons: (1) NIOSH considers methylene chloride a suspected carcinogen, and (2) methylene chloride does not have adequate warning properties.

Background

Organic vapor (OV) and gas, air-purifying respirators are designed to reduce the exposure of the wearer to toxic vapor or gas contaminants. Most gas/vapor devices remove the contaminant on inhalation by interaction of the molecules with granular, porous materials called sorbents. In general, organic vapors and gases are adsorbed by an activated charcoal sorbent. These chemical cartridge OV respirators are certified by NIOSH according to 30 CFR Part 11 and are tested against a single vapor (carbon tetrachloride).

According to 30 CFR Part 11, the most critical laboratory test datum obtained is the breakthrough time (t_b) against 1000 ppm carbon tetrachloride (CCL_4) at 50 ± 5 percent RH air and room temperature, approximately $25^\circ C$. A test air flow of 64 L/min for the "as received" cartridges is employed. These breakthrough data say little about the ability of the respirator cartridge to absorb other vapors and gases, or assess adsorption under more severe conditions of RH, temperature, and concentration. Unfortunately, information dealing with air-purifying cartridge performance under field conditions is limited. Yet it is known that many factors, such as flow rate, relative humidity, temperature, concentration, gas/vapor mixtures, and desorption can significantly affect the breakthrough time (t_b) or service life of sorbent cartridges.¹²

NIOSH Research Report 77-209, entitled "Development of Improved Respirator Cartridge and Canister Test Methods,"¹³ included a thorough review of the literature pertaining to sorbent adsorption capacity and dynamic breakthrough behavior. A recent derivation¹⁴ showed that the modified Wheeler¹⁵ equation is a special case of the Bohart-Adams¹⁶ equation proposed in 1920. Another approach uses the Yoon-Nelson^{17,18} equation, which can also be derived from the Bohart-Adams equation. The conditions that must be satisfied for the Wheeler utilization are that $C_o \gg C_x$ (C_o = inlet concentration, C_x = exit concentration at breakthrough) and that it must be a long bed where $\exp(k_v L/V_L) \gg 1$ (k_v = rate coefficient, L = height of the adsorbent bed, V_L = superficial linear velocity). These conditions were conformed to under the testing conditions conducted in this study.

The modified Wheeler approach was used by Jonas and co-workers.¹⁹⁻¹⁴ They worked on small columns of charcoal sorbent and determined the breakthrough time as a function of sorbent weight. Moyer¹⁵ confirmed that the Jonas approach for evaluating small sorbent beds at low flow rates was applicable to the characterization of respirator cartridges at high flow rates. Further, Wood and Moyer¹⁶ analyzed breakthrough data using three applications of the Wheeler equation: (1) varying bed weight, (2) varying residence time, and (3) fitting the breakthrough curve. When the adsorption capacity values, W_e , were compared, they observed excellent agreement among the three methods. The kinetic parameter, K_v , however, differed from method to method and was influenced by flow rate and selected penetration fraction. Some guidelines were stated for consideration when using the modified Wheeler equation.

Jonas and co-workers¹⁹⁻¹³ showed that a linear relationship existed between gas breakthrough time and sorbent weight. The functional equation is the modified Wheeler equation (Equation 1):

$$t_b = \frac{W_e}{C_o Q} \left[W - \frac{\rho_\beta Q}{k_v} \ln \left(\frac{C_o}{C_x} \right) \right] \quad (1)$$

where t_b = breakthrough time (min)
 C_x = exit concentration (g/cm^3)
 C_o = inlet concentration (g/cm^3)

Q = volumetric flow rate (cm^3/min)

W = weight of adsorbent (g)

ρ_β = bulk density of the packed bed (g/cm^3)

W_e = kinetic adsorption capacity or equilibrium adsorption capacity at an arbitrary ratio of C_x/C_o (g/g)

k_v = first order rate constant of adsorption (min^{-1})

C_o , C_x , and Q are established by the experimental test conditions, as is the temperature. The value of ρ_β is determined experimentally.

W_e and k_v are calculated from experiments using charcoal beds of different weights and determining breakthrough time (t_b). The breakthrough time (t_b) is a linear function of bed weight; therefore

$$W_e = \text{slope} (C_o) (Q) \quad (2)$$

and

$$k_v = - \frac{W_e \rho_\beta}{(y - \text{intercept}) (C_o)} \ln \frac{C_o}{C_x} \quad (3)$$

The critical bed thickness (W_c), which is the weight of sorbent that gives instantaneous breakthrough, equals $\rho_\beta Q \ln (C_o/C_x)/k_v$. Values for W_e and k_v permit the Wheeler equation to be used to calculate breakthrough times for carbon beds of larger weight (e.g., canisters); it is discussed in the Results and Discussion section.

Experimental Method

The laboratory configuration is shown in Figure 1 and has been described previously.¹⁹ Basically, house air is passed through an in-line dryer/sorbent system to remove residual moisture and contaminants. The inlet air is controlled to regulate the temperature, humidity, and flow rate. A syringe pump is used to feed solvent to the air stream at a predetermined rate, thus generating the desired challenge concentration (C_o).

Fluctuations in the upstream concentration are reduced by employing a buffer tank. Both the upstream methylene chloride concentration (C_o) and the downstream concentration (C_x) are continually monitored by a Miran 1A (Foxboro, South Norwalk, Connecticut) infrared gas (IR) analyzer (analytical wavelength, $13.5 \mu m$ and minimum detectable limits with a 20-meter cell, 4 ppm). The conditioned air stream (50% or 80% RH at $25^\circ C$) containing the challenge methylene chloride is pulled through the cartridge cell housing, which can contain from one to four cartridges in series. The downstream Miran 1A IR detector monitors the breakthrough concentration as a function of exposure time.

The cell consists of anodized aluminum¹⁵ machined to accept a specific OV respirator cartridge. One to four cartridges can be stacked in series to resemble a packed column of varying bed length and sorbent weight. Consecutive sampling ports allow four breakthrough time versus breakthrough concentration measurements to be made during a single experiment.

The updated data collection system consisted of a Hewlett-Packard (HP) Series 200 computer in combination with an HP 3497A Data Acquisition System. This system operated similarly to the preceding system.^{15,16} In addition, the HP

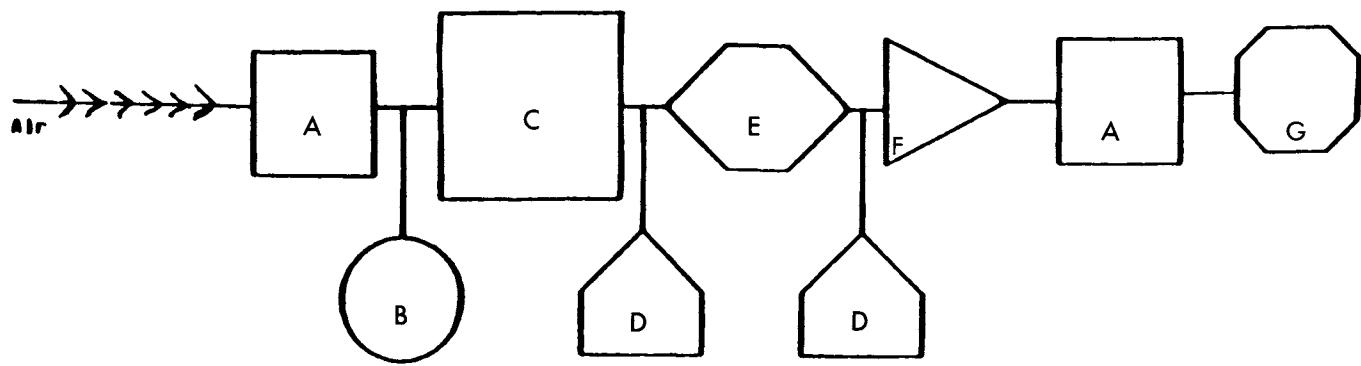


FIGURE 1. Experimental apparatus for monitoring organic vapor cartridge and canister breakthrough. A = flow control mechanism; B = vapor generator; C = buffer reservoir tank; D = vapor detector; E = cartridge cell; F = cold trap or sorbent trap; G = vacuum source

system calculated the Wheeler constants of interest. All data were stored on a 3.5-inch disk.

The methylene chloride (dichloromethane) was purchased from Fisher Scientific (Pittsburgh, Pennsylvania) and was certified as American Chemical Society Spectrally analyzed. Air used in the system was house air that was passed through a dryer/sorbent system to remove contaminants.

Two manufacturers' cartridges, each of which contained coconut-based charcoal, were tested. Manufacturer A used

a single cartridge on its respirator; thus, a flow rate of 64 L/min was employed, as required in 30 CFR, Part 11. Manufacturer B used a pair configuration, and single cartridges were tested at a flow rate of 32 L/min. Two sizes of canisters produced by manufacturer B—chin-style canisters and front mounted/back-mounted (FM/BM) canisters—were tested at 64 L/min. All tests were conducted on "as received" cartridges or canisters at $25 \pm 1.5^\circ\text{C}$ and $50 \pm 5\%$ RH or $80 \pm 5\%$ RH. Where possible, cartridges or canisters from a single lot (which contained carbon from the same processing run)

TABLE I. Summary of All Cartridge and Canister Breakthrough Time (t_b) Data Against 1000 ppm Methylene Chloride at Equivalent 64 L/min

Manufacturer	Type	Lot	Charcoal Wt (g)	% RH	t_b Corrected to 1000 ppm (min)		
					5 ppm	10 ppm	15 ppm
A	Cartridge	A	69.223	50	11.4	13.0	13.7
		A	69.522	50	12.3	13.8	14.3
		A	71.247	50	12.5	14.0	14.7
		A	71.988	50	13.7	15.0	15.9
		B	74.176	50	11.3	12.8	13.9
		C	71.914	50	11.7	14.0	14.7
		D	74.838	50	14.0	15.9	17.1
		D	73.851	50	12.6	14.0	15.0
		A	70.127	80	10.2	11.4	12.1
		A	71.686	80	11.3	12.5	13.3
		A	70.352	80	11.0	12.3	13.1
		A	69.906	80	11.4	12.5	13.2
		A	69.827	80	11.0	12.2	12.9
		D	76.425	80	10.5	11.8	12.6
		D	74.922	80	10.2	11.5	12.3
B	Cartridge*	A	34.430	50	21.1	22.9	24.0
		A	35.104	50	22.8	24.4	25.4
		A	34.483	80	19.2	20.6	21.5
		A	36.180	80	18.4	19.9	20.7
B	Chin canister	AC	193.0	50	71.4	76.6	79.1
		AC	196.5	50	77.0	82.0	84.2
		AC	195.7	80	49.8	53.0	55.5
		AC	194.8	80	46.1	49.0	51.2
B	FM/BM canister	SS	745.0	50	440.4	450.8	455.3
		SS	738.0	50	437.5	449.2	455.2
		SS	745.0	80	299.6	309.5	319.6
		SS	797.0	80	317.8	328.5	335.3

*Single cartridge of pair (32 L/min).

were used to reduce variability. The methylene chloride challenge concentrations were varied from a low of 50 ppm to 1000 ppm.

Results and Discussion

The breakthrough data for manufacturer A's and B's cartridges, and B's chin-style and FM/BM canisters (64 L/min) at a 1000-ppm methylene chloride challenge, and 50 and 80 percent RH, are presented in Table I. Table I also includes some breakthrough data for the first cartridge of the stacked cartridge experiments. The 500 ppm, 250 ppm, and 125 ppm methylene chloride breakthrough data are given in Tables II, III, and IV, respectively. The mean challenge concentration in parts per million, the test humidity, charcoal weight, and corrected breakthrough times (t_b) at 1 percent of the challenge concentration, at 5 ppm breakthrough, 10 ppm breakthrough, and 15 ppm breakthrough, are listed.

A summary of the 5 ppm breakthrough time values is given in Table V. The relatively short t_b values observed for the cartridges and chin-style canisters were expected for methylene chloride because it has a low boiling point and a high vapor pressure and would not be expected to strongly adsorb on charcoal. Further, the data show that breakthrough times at 80 percent RH¹⁷⁻²⁰ are always significantly faster than those at 50 percent RH for all challenge concentrations.

The methylene chloride 5-ppm breakthrough times for manufacturer A's cartridge ranged from 108 minutes at 1000 ppm and 80 percent RH to 46.6 minutes at 125 ppm and 50

percent RH. Manufacturer B's cartridges gave t_b values that ranged from 18.8 minutes at 1000 ppm and 80 percent RH to 54.7 minutes at 125 ppm and 50 percent RH. The average chin-style canister breakthrough time to 5 ppm is less than 1 hour at 1000 ppm challenge and 80 percent RH. These relatively fast breakthrough times are attributed to the physical characteristics of methylene chloride (high volatility and high vapor pressure; low molecular weight and boiling point). Notice that as the percentage relative humidity increases, the t_b values become shorter for all given challenge concentrations.

The FM/BM canister's breakthrough time to 5 ppm is just over 5 hours at 1000 ppm and 80 percent RH. The FM/BM canisters gave a 5-ppm t_b time of greater than 10 hours at 125 ppm and 80 percent RH, and these breakthrough times would all decrease as RH increased. Further, factors like face-fit, weight, wearer acceptability, breathing resistance, and expense must be considered when choosing FM/BM canisters. The FM/BM canisters do heat up considerably due to adsorption on the large amount of charcoal present. Further low-level (<1 ppm) methylene chloride concentrations were detected downstream of the FM/BM canisters prior to breakthrough. This result was seen at the 1000, 500, and 250 ppm challenge concentrations.

Some additional methylene chloride breakthrough data were generated for various other challenge concentrations for manufacturer A cartridges. All data were combined to determine if a correlation between breakthrough time (t_b) and challenge concentration existed. The additional data at methylene chloride challenge concentrations of 775 ppm,

TABLE II. Summary of All Cartridge and Canister Breakthrough Time (t_b) Data Against 500 ppm Methylene Chloride at Equivalent 64 L/min

Manufacturer	Type	Lot	Charcoal Wt (g)	% RH	t_b Corrected to 500 ppm (min)		
					5 ppm	10 ppm	15 ppm
A	Cartridge	A	69.451	50	24.9	27.1	28.6
		A	71.188	50	24.8	27.0	28.6
		A	71.633	50	24.5	26.5	27.9
		A	70.773	50	26.0	28.4	29.9
		B	78.159	50	19.4	22.0	23.5
		D	77.300	50	24.8	27.9	29.4
		D	75.453	50	19.4	22.8	24.3
		A	70.146	80	18.4	20.6	21.7
		A	70.943	80	17.8	19.7	20.9
		A	70.669	80	14.9	16.8	17.9
		A	71.040	80	15.7	17.6	18.9
		B	73.310	80	16.9	18.7	19.9
		D	76.027	80	16.0	17.9	19.7
		D	74.477	80	17.5	19.9	21.5
B	Cartridge*	A	34.486	50	33.0	35.0	36.4
		A	33.783	50	39.9	43.0	45.3
		A	33.638	80	25.4	27.5	28.4
		A	34.884	80	24.0	25.8	26.8
B	FM/BM canister	SS	749.2	50	506.2	537.1	549.0
		SS	746.5	80	383.4	398.1	407.4
		SS	740.4	80	382.1	396.8	408.1

*Single cartridge of pair (32 L/min).

TABLE III. Summary of All Cartridge and Canister Breakthrough Time (t_b) Data Against 250 ppm Methylene Chloride at Equivalent 64 L/min

Manufacturer	Type	Lot	Charcoal Wt (g)	% RH	t_b Corrected to 250 ppm (min)			
					1%	5 ppm	10 ppm	15 ppm
A	Cartridge	A	71.404	50	33.1	36.5	40.5	42.8
		A	71.984	50	29.4	32.7	36.7	39.0
		A	69.598	50	31.7	34.7	38.6	40.8
		A	70.353	50	33.1	36.2	40.3	42.6
		A	70.915	80	22.3	25.0	27.9	29.8
		A	70.868	80	24.2	26.8	30.1	32.0
		A	71.336	80	25.1	27.9	31.5	33.5
		A	70.527	80	24.0	26.6	30.0	31.5
B	Cartridge*	A	34.210	50	36.8	39.0	42.6	44.7
		A	34.686	50	38.6	40.9	44.6	46.4
		A	35.064	80	29.9	32.4	35.2	36.8
		A	33.335	80	27.6	29.6	32.4	33.7
B	Chin Canister	AC	194.5	50	144.6	156.8	167.0	177.7
		AC	197.0	50	134.5	146.8	157.8	168.4
		AC	188.8	80	70.2	76.9	84.5	88.6
		AC	198.0	80	75.5	83.6	91.6	95.7
B	FM/BM canister	SS	725.0	50	850.4	865.6	882.7	892.5
		SS	730.8	80	394.2	419.4	450.3	473.3
		SS	734.0	80	511.2	531.8	553.2	565.2
		SS	734.0	80	459.3	483.2	505.6	521.9

*Single cartridge of pair (32 L/min).

TABLE IV. Summary of All Cartridge and Canister Breakthrough Time (t_b) Data Against 125 ppm Methylene Chloride at Equivalent 64 L/min

Manufacturer	Type	Lot	Charcoal Wt (g)	% RH	t_b Corrected to 125 ppm (min)			
					1%	5 ppm	10 ppm	15 ppm
A	Cartridge	A	69.345	50	38.5	48.1	53.9	58.8
		A	70.460	50	35.4	45.3	51.2	56.3
		A	71.015	50	36.6	46.8	53.1	58.3
		A	71.992	50	36.0	46.2	52.3	57.5
		A	70.248	80	27.5	34.8	39.4	43.3
		A	70.314	80	25.6	33.4	37.8	41.5
		A	70.543	80	25.1	33.1	37.8	41.7
		A	70.964	80	26.5	34.7	39.6	42.0
B	Cartridge*	A	35.393	50	42.0	51.7	56.9	60.2
		A	35.238	50	48.2	57.7	63.6	59.2
		A	34.208	80	31.6	37.4	41.4	43.6
		A	35.622	80	33.1	41.1	45.0	47.1
B	Chin Canister	AC	196.0	50	183.5	228.3	255.5	269.6
		AC	188.5	50	151.0	190.8	208.1	217.8
		AC	197.2	80	83.0	101.0	110.4	117.9
		AC	191.2	80	89.8	107.8	117.5	124.7
B	FM/BM canister	SS	746.4	80	601.7	623.6	701.1	—
		SS	754.3	80	649.7	728.6	752.2	—
		SS	742.4	80	515.2	607.1	656.9	—
		SS	744.9	80	587.8	676.3	707.9	—

*Single cartridge of pair (32 L/min).

TABLE V. Average 5-ppm Breakthrough Times at Various Methylene Chloride Challenge Concentrations

Type	Manufacturer	Challenge Conc. (ppm)	50% RH				80% RH			
			# Lots Tested	Total Points	Avg t_b (min)	S.D. \pm	# Lots Tested	Total Points	Avg t_b (min)	S.D. \pm
Cartridge	A	1000	4	8	12.4	1.0	2	7	10.8	0.5
Cartridge	B	1000	1	2	22.0	1.2	1	2	18.8	0.6
Chin canister	B	1000	1	2	74.2	4.0	1	2	48.0	2.6
FM/BM canister	B	1000	1	2	439.0	2.1	1	2	308.7	12.9
Cartridge	A	500	3	7	23.4	2.8	3	7	16.7	1.3
Cartridge	B	500	1	2	36.5	4.9	1	2	24.7	1.0
FM/BM canister	B	500	1	1	506.2	—	1	2	382.8	0.9
Cartridge	A	250	1	4	35.0	1.7	1	4	26.6	1.2
Cartridge	B	250	1	2	39.5	0.7	1	2	31.0	2.0
Chin canister	B	250	1	2	151.8	7.1	1	2	80.3	4.7
FM/BM canister	B	250	1	1	865.6	—	1	3	478.1	56.4
Cartridge	A	125	1	4	46.6	1.2	1	4	34.0	0.9
Cartridge	B	125	1	2	54.7	4.2	1	2	39.3	2.6
Chin canister	B	125	1	2	209.6	26.5	1	2	104.4	4.8
FM/BM canister	B	125	—	—	—	—	1	4	658.9	55.0

275 ppm, 100 ppm, 75 ppm, and 50 ppm at 50 percent RH and 80 percent RH are presented in Table VI. A plot of $\log t_b$ (at 5 ppm) versus log challenge concentration for the 50 percent RH and 80 percent RH data are shown in Figure 2 along with the least squares regression lines. The 50 percent RH least squares regression analyses gave: $r^2 = 0.950$; slope = -0.5186 ; $T = -13.08$; $Pr > /T/ = 0.0001$; intercept = 2.7138 ; $T = 27.63$; $Pr > /T/ = 0.0001$. The 80 percent RH least squares regression analyses gave: $r^2 = 0.934$; slope =

-0.4311 ; $T = -11.28$; $Pr > /T/ = 0.0001$; intercept = 2.3645 ; $T = 24.99$; $Pr > /T/ = 0.0001$. Similar plots for manufacturer B cartridges and canisters at 50 percent RH and 80 percent RH were obtained. The r^2 values ranged from 0.899 to 0.986, which indicate high correlation between $\log t_b$ and log challenge concentration. The least squares regression lines are useful for predictive purposes over limited concentration ranges.

The Wheeler equation establishes a relationship be-

TABLE VI. Additional Organic Vapor Cartridge Breakthrough Time (t_b) Data for Methylene Chloride at Various Concentrations for Manufacturer A

Concentration (ppm)	Lot	Charcoal Wt (g)	% RH	t_b (min)			
				1%	5 ppm	10 ppm	15 ppm
775	B	74.345	50	16.2	14.9	16.8	17.9
775	D	76.842	50	20.7	19.0	21.5	22.8
775	D	78.075	50	19.4	18.0	20.1	21.3
775	D	77.180	80	13.4	12.4	14.1	15.1
775	D	78.327	80	14.4	13.3	15.0	16.2
275	B	74.390	50	24.7	26.4	30.0	32.3
275	C	75.010	50	22.8	27.2	33.4	35.9
275	C	74.315	50	25.9	27.5	29.9	32.6
275	B	74.104	80	19.7	20.9	22.0	24.8
275	C	74.758	80	17.8	18.9	21.5	23.5
275	C	74.537	80	16.6	18.6	22.0	24.0
100	C	74.970	50	33.0	43.5	50.5	58.8
100	C	75.414	50	28.5	37.0	45.4	50.5
100	C	72.990	80	20.5	26.5	31.0	35.4
100	C	74.769	80	25.8	33.6	38.4	43.1
75	C	70.737	50	38.5	54.4	63.1	68.0
75	C	70.429	50	42.2	58.3	67.4	74.4
75	C	71.701	50	43.3	59.0	67.9	75.3
75	C	71.317	80	27.8	38.8	45.4	49.4
75	C	71.744	80	25.3	36.0	42.6	46.7
50	C	72.759	50	—	65.8	78.6	89.1
50	C	72.201	50	—	58.2	69.9	78.6
50	C	69.392	80	—	36.3	43.6	49.4
50	C	68.998	80	—	33.5	39.4	44.9

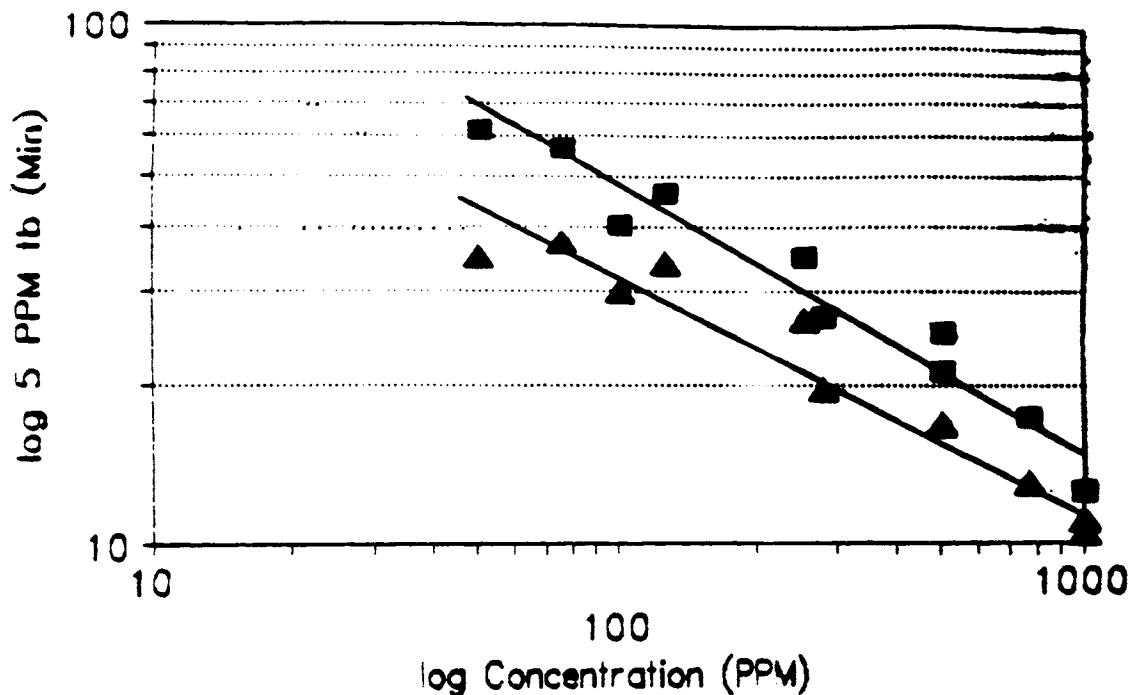


FIGURE 2. Plot of log 5 ppm breakthrough time versus log challenge concentration for manufacturer A's cartridges. ■ = 50 percent RH; ▲ = 80 percent RH.

tween breakthrough time and sorbent (charcoal) weight. Experiments were performed to confirm this relationship over the large sorbent weight range from cartridge to canister for manufacturer B. The flow velocities through the cartridges and canisters were comparable, and visual inspection of the charcoal showed it to be similar. Tables VII-X present the data for the stacked cartridge experiments (4 cartridges in series) at 1000 ppm, 500 ppm, 250

ppm, and 125 ppm, respectively. The canister data were presented in Tables I-IV. Plots of breakthrough time versus sorbent weight for the stacked cartridge experiments were linear. Table XI shows the values of the least squares fitted regression lines for 1000 ppm, 500 ppm, 250 ppm, and 125 ppm. The correlation obtained was high. The r^2 values ranged from 0.969 to 0.998.

The cartridge Wheeler constants presented in Table XI

TABLE VII. Organic Vapor Cartridge Breakthrough Time (t_b) Against 1000 ppm Methylene Chloride for Stacked Cartridges of Manufacturer B at Equivalent of 64 L/min for Pair Configuration

%	RH	Cumulative Charcoal Wt (g) *Single Cartridge	Cumulative Charcoal Wt (g) Pair Configuration	t_b Corrected to 1000 ppm (min)		
				5 ppm	10 ppm	15 ppm
50	34.430	68.860	21.1	22.9	24.0	
	70.165	140.330	56.2	58.0	59.4	
	105.031	210.062	94.2	95.8	97.1	
	140.455	280.910	133.9	136.4	137.7	
50	35.104	70.208	22.8	24.4	25.4	
	66.784	133.568	59.0	60.7	61.8	
	101.326	202.652	96.0	97.8	99.0	
	135.762	271.524	136.3	139.3	140.7	
80	34.483	68.966	19.2	20.6	21.5	
	69.366	138.732	47.4	48.9	49.8	
	105.390	210.780	76.9	78.3	79.4	
	140.104	280.208	106.6	108.1	108.9	
80	36.180	72.360	18.41	19.9	20.7	
	70.603	141.206	46.2	47.5	48.3	
	103.824	207.648	75.7	77.1	78.0	
	136.460	272.920	107.8	109.5	110.5	

*Stacked single cartridges run at 32 L/min.

TABLE VIII. Organic Vapor Cartridge Breakthrough Time (t_b) Against 500 ppm Methylene Chloride for Stacked Cartridges of Manufacturer B at Equivalent of 64 L/min for Pair Configuration

% RH	Cumulative Charcoal Wt (g) *Single Cartridge	Cumulative Charcoal Wt (g) Pair Configuration	t_b Corrected to 500 ppm (min)		
			5 ppm	10 ppm	15 ppm
50	34.486	68.972	33.0	35.0	36.4
	69.124	138.248	87.2	89.7	91.6
	102.411	204.822	145.6	148.1	150.0
	137.593	275.186	206.1	209.5	211.7
	33.783	67.566	39.9	43.0	45.3
	68.546	137.092	105.8	109.3	111.5
80	102.260	204.520	172.4	176.1	178.5
	136.096	272.192	238.5	242.4	245.1
	33.638	67.276	25.4	27.5	28.4
	65.455	130.910	65.8	67.9	68.9
	97.915	195.830	106.0	108.3	109.3
	131.869	263.738	145.3	147.7	148.9
80	34.884	69.768	24.0	25.8	26.8
	69.848	139.696	59.3	61.6	67.2
	104.817	209.634	98.6	100.7	101.9
	139.082	278.164	139.0	141.4	142.8

*Stacked single cartridges run at 32 L/min.

were used to calculate breakthrough times for both chin and FM/BM canisters, using Equation 2 to determine if the relationship was valid over large sorbent weight ranges. The results are shown in Table XII, where they are compared to the values determined experimentally. These results confirm that only a rough estimate of breakthrough times can be obtained (range % deviation, -17% to +46%). The predictions for the FM/BM canisters appear to be better than the predictive values for the chin-style canisters. Also, the calculated values for FM/BM canisters are generally conservative, but not always. An approximation was obtained that was in the range of from -25 percent to +27

percent of the actual value for the FM/BM canisters. Such an approximation might be helpful for preliminary analysis in certain cases, using extreme care. Subsequent experimental confirmation would be essential. The only values that needed to be determined to perform these calculations other than the measured cartridge t_b are canister sorbent weight and fill volume.

Conclusions

Methylene chloride breakthrough data have been generated for two manufacturers' cartridges and for one manu-

TABLE IX. Organic Vapor Cartridge Breakthrough Time (t_b) Against 250 ppm Methylene Chloride for Stacked Cartridges of Manufacturer B at Equivalent of 64 L/min for Pair Configuration

% RH	Cumulative Charcoal Wt (g) *Single Cartridge	Cumulative Charcoal Wt (g) Pair Configuration	t_b Corrected to 250 ppm (min)			
			1%	5 ppm	10 ppm	15 ppm
50	34.210	68.420	36.8	39.0	42.6	44.7
	68.122	136.244	—	94.5	98.4	100.8
	100.085	200.170	—	154.6	158.7	161.7
	133.203	266.406	—	220.9	225.5	228.5
	34.686	69.372	38.6	40.9	44.6	46.4
	69.737	139.474	96.5	100.5	104.8	106.8
80	103.196	206.392	165.4	169.0	173.7	161.9
	136.937	273.874	233.7	238.2	243.2	245.5
	35.064	70.128	29.9	32.4	35.2	36.8
	65.397	130.794	81.5	84.2	87.7	89.3
	100.495	200.990	132.8	135.0	138.3	139.7
	134.598	269.196	185.8	188.2	191.8	193.8
80	33.335	66.670	27.6	29.6	32.4	33.7
	65.906	131.812	71.2	73.2	76.6	78.1
	97.387	194.774	117.4	120.3	123.6	125.6
	130.971	261.942	163.7	165.6	168.8	171.3

*Stacked single cartridges run at 32 L/min.

TABLE X. Organic Vapor Cartridge Breakthrough Time (t_b) Against 125 ppm Methylene Chloride for Stacked Cartridges of Manufacturer B at Equivalent of 64 L/min for Pair Configuration

% RH	Cumulative Charcoal Wt (g) *Single Cartridge	Cumulative Charcoal Wt (g) Pair Configuration	t_b Corrected to 125 ppm (min)			
			1%	5 ppm	10 ppm	15 ppm
50	35.393	70.786	41.9	51.7	56.9	60.2
	69.737	139.474	119.8	132.0	138.2	142.5
	104.200	208.400	207.0	218.9	225.1	229.7
	139.109	278.218	294.2	308.8	316.3	321.2
50	35.238	70.476	48.4	57.7	63.6	67.2
	69.524	139.048	130.9	141.6	148.0	151.9
	104.654	209.308	215.8	227.5	234.7	239.4
	139.981	279.962	305.3	318.4	327.1	334.8
80	34.208	68.416	30.2	37.4	41.4	43.6
	69.413	138.826	84.9	94.5	98.9	101.9
	105.259	210.518	142.1	151.4	155.9	159.2
	140.933	281.866	202.6	212.0	217.4	221.0
80	35.622	71.244	34.8	41.1	45.0	47.1
	71.099	142.198	87.2	95.9	101.0	103.5
	104.532	209.064	145.6	154.4	159.6	162.6
	138.104	276.208	205.1	215.1	220.9	224.6

*Stacked single cartridges run at 32 L/min.

facturer's chin and FM/BM canisters, at various challenge concentrations. The cartridge data confirm that at 80 percent RH the breakthrough times are extremely short, even for low challenge concentrations (50 ppm challenge, 80 percent RH, t_b approximately 0.5 hour). This observation is consistent with the physical characteristics of methylene chloride (high volatility and high vapor pressure; low molecular weight and boiling point), which result in weak charcoal adsorption.

The chin-style canisters contained 194.3 grams (standard deviation 3.2) of charcoal, which is approximately 25–30 times more sorbent than cartridges. Still, the t_b at 125 ppm and 80 percent RH was only on the order of 100 minutes. Finally, the FM/BM canisters, 744.9 grams (S.D. 16.3) of sorbent, which contain 105–11 times more charcoal than the cartridges, gave a t_b of more than 10 hours at 125 ppm and 80

percent RH, but a t_b of only 5 hours was observed when the concentration was increased to 1000 ppm.

It must be remembered that (1) as the RH increases above 80 percent, the t_b will subsequently decrease; (2) as the contaminant concentration decreases, the water vapor has a more pronounced influence on t_b ; and (3) other critical factors for canisters like face-fit, weight, balance, wearer acceptability, air resistance, and expense must be addressed.

The effect of challenge concentration and relative humidity on t_b for methylene chloride has been characterized. The cartridges' breakthrough times are extremely short when tested at 80 percent RH; these times would decrease at humidities above 80 percent. Likewise, the breakthrough times for the chin-style canisters were relatively short. Only the FM/BM canisters gave prolonged breakthrough

TABLE XI. Wheeler Constants for Manufacturer B Cartridges Against Methylene Chloride at 5 ppm Breakthrough

Challenge Conc. (ppm)	% RH	# Points	R ²	Slope	T	Pr > /T/	Intercept	Intercept		W _e Kinetic Adsorption Capacity (g/g)	k _v Rate Constant (–min ⁻¹)	W _c Critical Bed Weight (g)	Cartridge Wheeler Constants	
								T	Pr > /T/					
125	50	8	0.998	1.240	55.13	0.0001	−34.63	−8.05	0.0002	0.0345	2737	27.90	0.0262	
125	80	8	0.998	0.833	58.69	0.0001	−20.29	−7.47	0.0003	0.0232	3145	24.31	0.0176	
250	50	8	0.996	0.947	37.24	0.0001	−28.88	−6.11	0.0009	0.0526	2910	30.52	0.0399	
250	80	8	0.989	0.741	22.99	0.0001	−19.35	−3.31	0.0162	0.0412	3387	26.11	0.0313	
500	50	8	0.969	0.906	13.73	0.0001	−26.40	−2.14	0.0765	0.1007	3681	29.14	0.0765	
500	80	8	0.981	0.575	17.48	0.0001	−14.52	−2.38	0.0549	0.0639	4204	25.26	0.0485	
1000	50	8	0.995	0.545	34.42	0.0001	−16.47	−5.51	0.0015	0.1212	4122	30.21	0.0920	
1000	80	8	0.998	0.428	49.20	0.0001	−12.32	−7.43	0.0003	0.0952	4335	28.77	0.0723	

TABLE XII. Comparison of Calculated Breakthrough Times for Manufacturer B with Experimental Values

Type	Challenge Conc. (ppm)	Charcoal Wt (g)	% RH	Experimental 5 ppm t_b (min)	Calculated t_b Eq. 2	% Deviation from Exper.
Chin canister	1000	193.0	50	71.4	81.8	+15
	1000	196.5	50	77.0	83.3	+8
	1000	195.7	80	49.8	66.1	+33
	1000	194.8	80	46.1	65.8	+43
FM/BM canister	1000	745.0	50	440.4	385.2	-13
	1000	738.0	50	437.5	381.6	-13
	1000	745.0	80	299.6	303.4	+1
	1000	797.0	80	317.8	324.6	+2
FM/BM canister	500	749.2	50	506.2	644.7	+27
	500	746.5	80	383.4	410.3	+7
	500	740.4	80	382.1	407.0	+7
Chin canister	250	194.5	50	156.8	141.3	-10
	250	197.0	50	146.8	143.1	-3
	250	188.8	80	76.9	112.0	+46
	250	198.0	80	83.6	117.5	+41
FM/BM canister	250	725.0	50	865.6	649.2	-25
	250	730.8	80	419.4	516.7	+23
	250	734.0	80	531.8	519.0	-2
	250	734.0	80	483.2	519.0	+7
Chin canister	125	196.0	50	228.3	193.8	-15
	125	188.5	50	190.8	186.4	-2
	125	197.2	80	101.0	135.5	+34
	125	191.2	80	107.8	131.3	+22
FM/BM canister	125	746.4	80	623.6	597.5	-4
	125	754.3	80	728.6	603.8	-17
	125	742.4	80	607.1	594.3	-2
	125	744.9	80	676.3	596.3	-12

times, but other factors would influence their applicability.

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