

Parametric Sensitivity of the C2A1 Filter and Data Comparison with Four Filter Models

Dean O. Woolery¹, Nathan E. Lee¹, George Law¹, Darren M. Jolley¹, Deborah L. Beier², Michael L. Giessing², and John Peterson³

¹ U.S. Army Dugway Proving Ground, DTC-DP-WD-CT-C, MS #6, 4531 B Street, Dugway, UT 84022-5006
E-mail: dean.woolery@us.army.mil

² Dugway Data Services Team (DDST), P.O. Box 155, Dugway, UT 84022

³ Thatcher Company, 1905 Fortune Rd, Salt Lake City, UT 84109

ABSTRACT

There are limited data that accurately describe the effects of varying the temperature, air flow rate, relative humidity, and chemical concentration on respiratory protection filters. Varying the environmental parameters on the passage of a chemical through an individual filter will help identify the effects of these parameters on the breakthrough time. These effects can be quantified and used for future testing and modeling. Breakthrough times and concentration profiles for Freon-12[®] were measured using standard government-issue C2A1 Chemical, Biological, Radiological, and Nuclear filters under various controlled environmental conditions. Flow rate for Freon-12[®] was found to have a significant impact on breakthrough for the C2A1 filter.

The experimental data were used to evaluate the predictive capabilities of four filter life prediction models. Each model gave varied results. Of the four models considered, the recently released (2007) MultiVapor model from the National Institute of Occupational Safety and Health produced predictive breakthrough times that were the closest to the experimental data. However, none of the models performed well in producing predictive breakthrough times close to the experimental data breakthrough times over the entire range of environmental parameters that were used.

These results highlight two related and significant issues. First, this study illustrates the need to collect more empirical (i.e., experimentally measured) data about filter performance obtained by using multiple environmental parameters on various chemicals of interest to the respiratory protection community. Second, it also indicates the need for continued work refining the ability of filter-life prediction models to accurately reflect breakthrough time under combinations of multiple environmental parameters.

Keywords: C2A1 CBRN filter, breakthrough time, breakthrough prediction models, Freon-12[®], individual protection, collective protection, filter life.

INTRODUCTION

First responders, war fighters, or service personnel have the potential of encountering hazards in controlled, emergency, or battlefield situations. These hazards include a wide range of biological and chemical warfare agents, toxic industrial chemicals, battlefield contaminants, toxic industrial materials, and radioactive materials. Individual protection (IP) and collective protection (ColPro) air purification filters are designed to protect personnel from death or serious injury from inhalation of these hazards. Understanding how the filters perform under various environmental conditions aids in preparation for hazardous situations.

There are limited data that accurately describe the effects of varying the temperature, flow rate, relative humidity (RH), and chemical concentration on a chemical, biological, radiological, and nuclear (CBRN) filter. Varying the environmental parameters on a chemical passing through an individual filter will help identify the effects of these conditions. The effects on the breakthrough time can be quantified and used for future evaluations.

Four predictive models were chosen for evaluation. It was unknown which filter model most accurately predicted filter life when various combinations of environmental conditions were considered. Although filter life prediction models are commonly used across the respiratory protection community, the models were designed to simulate the performance of activated charcoal filters. The models do not take into consideration any effects that impregnates, chemical or otherwise, may have on the activated charcoal in the CBRN filters. In addition, few models account for more than one vapor and two environmental parameters. Four predictive models were compared with the trial data; (1) Wheeler-Jonas (Lodewyckx and Vansant, 1999; and Wood, 1994), (2) Gerry O. Wood mathematical model (OSHA; Wood 1994), (3) National Institute of Occupational Safety and Health's (NIOSH) MultiVapor (NIOSH 2007; Wood, 2004; and Wood and Snyder, 2007), and (4) Narayan-Harrison (Narayan and Harrison, 1991; and Harrison and Narayan, 1992).

METHODS

The test trials were conducted at West Desert Test Center (WDTC) – U.S. Army Dugway Proving Ground (DPG) Combined Chemical Test Facility. Freon-12[®], or R-12, is a chlorofluorocarbon (CFC) halomethane chemically known as dichlorodifluoromethane. Freon-12[®] was chosen over other chemicals because the compound is safe to work with, which allowed for easier test methodology development. The C2A1 CBRN filter has a P100 particulate filter in addition to treated, activated charcoal. The activated charcoal is impregnated with copper, silver, zinc, molybdenum, and triethylenediamine (ASZM-TEDA).

The volume of the test chamber, approximately 0.028 m³ (1 ft³), was sufficient to hold one filter at a time. The Freon-12[®] vapors entered the chamber before being drawn through the filter. Environmental conditions were allowed to stabilize in the chamber. Airflow containing Freon-12[®] was then drawn through the filter and sampled until the effluent reached the challenge concentration.

The test fixture schematic is given in Figure 1 and a photograph of the fixture in Figure 2. A Perma Pure Nafion[®] (Perma Pure LLC, Toms River, New Jersey) membrane humidifier was used to control the RH of the air stream into the test chamber. The temperature was controlled with thermally conductive heat tape on the sample transfer line between the membrane humidifier tube and the test chamber. A recirculation blower fan assisted in the mixing of the challenge gas and water vapor within the chamber.

The concentration of the Freon-12[®] penetrating the C2-A1 CBRN filter was measured with a Gasmeter™ DX-Series Fourier-Transform Infrared (FTIR) gas analyzer (Gasmeter Technologies, Helsinki, Finland). Two three-way valves, one placed upstream from the chamber and another placed downstream from the filter, allowed the FTIR to sample the flow entering the chamber system or exiting from the filter.

The air flow from the Nafion[®] humidifier, challenge gas cylinder, calibration system, and C2A1 CBRN filter was controlled with mass flow controllers (MFCs) and measured with a flow meter. To

prevent backpressure within the FTIR sample cell, a flow split line was also installed upstream from the instrument. This ensured that measurement errors were minimized.

A pump was not used downstream from the FTIR gas analyzer. It was found that the positive pressure in the chamber forced the effluent vapors from the filter and vented them to the chemical fume hood at 15 to 20 liters per minute (L/min), which accounted for all challenge air flow.

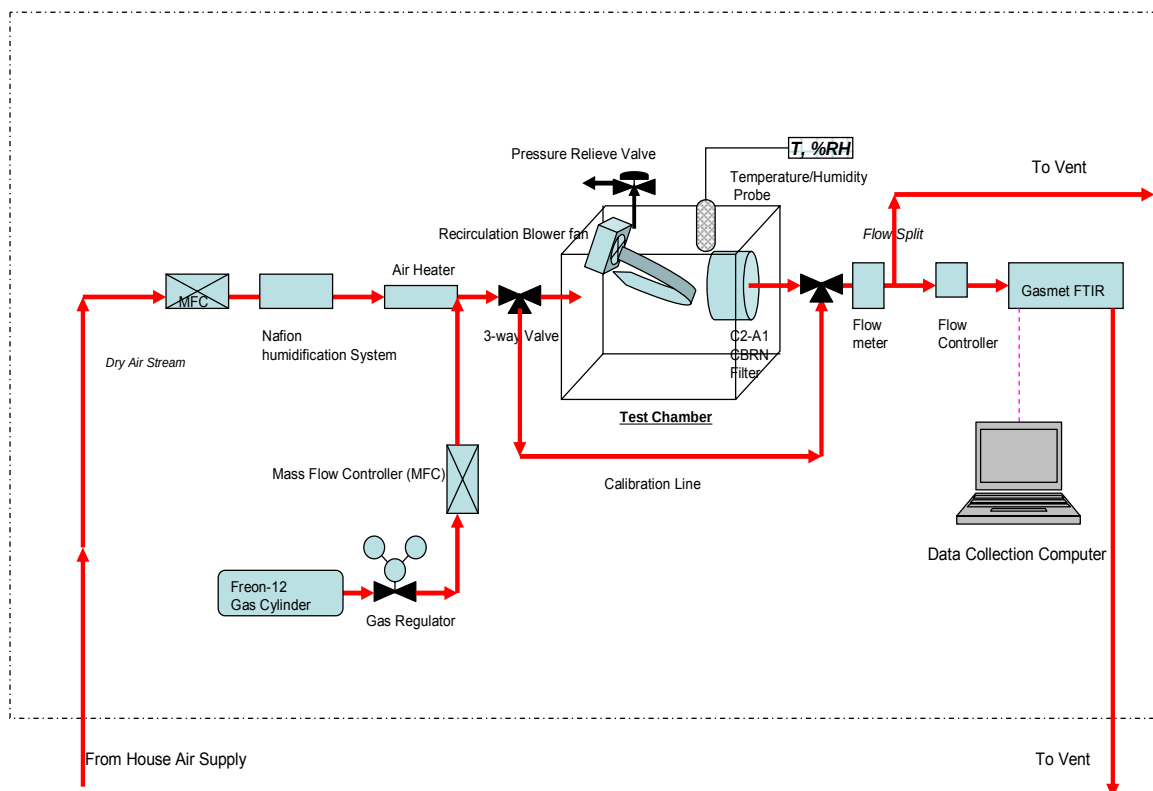


Figure 1. Schematic diagram of the parametric sensitivity fixture (MFC – mass flow controller; CBRN – chemical, biological, radiological, nuclear; T – temperature; RH – relative humidity; FTIR – Fourier-transform infrared gas analyzer.

Test Procedures

Desired target values for each environmental parameter were determined by selecting from a range of possible usage conditions and a test matrix was developed to accommodate more than one trial for each parameter. Parameter values were randomized among the trials to avoid bias.

Before testing began, the time required for the concentration, temperature, and humidity to reach a steady state within the test chamber was determined.

The FTIR was also calibrated using a multipoint calibration method before testing. Two separate calibration trials were completed, one for higher concentrations above 100 parts per million (ppm), and another for concentrations lower than 100 ppm, which generated a piecewise linear curve. The FTIR provided verification of clean out and that cross contamination of C2A1 filters did not occur. In addition, the air stream into and out of the test chamber was monitored with the FTIR before installation of a new filter.

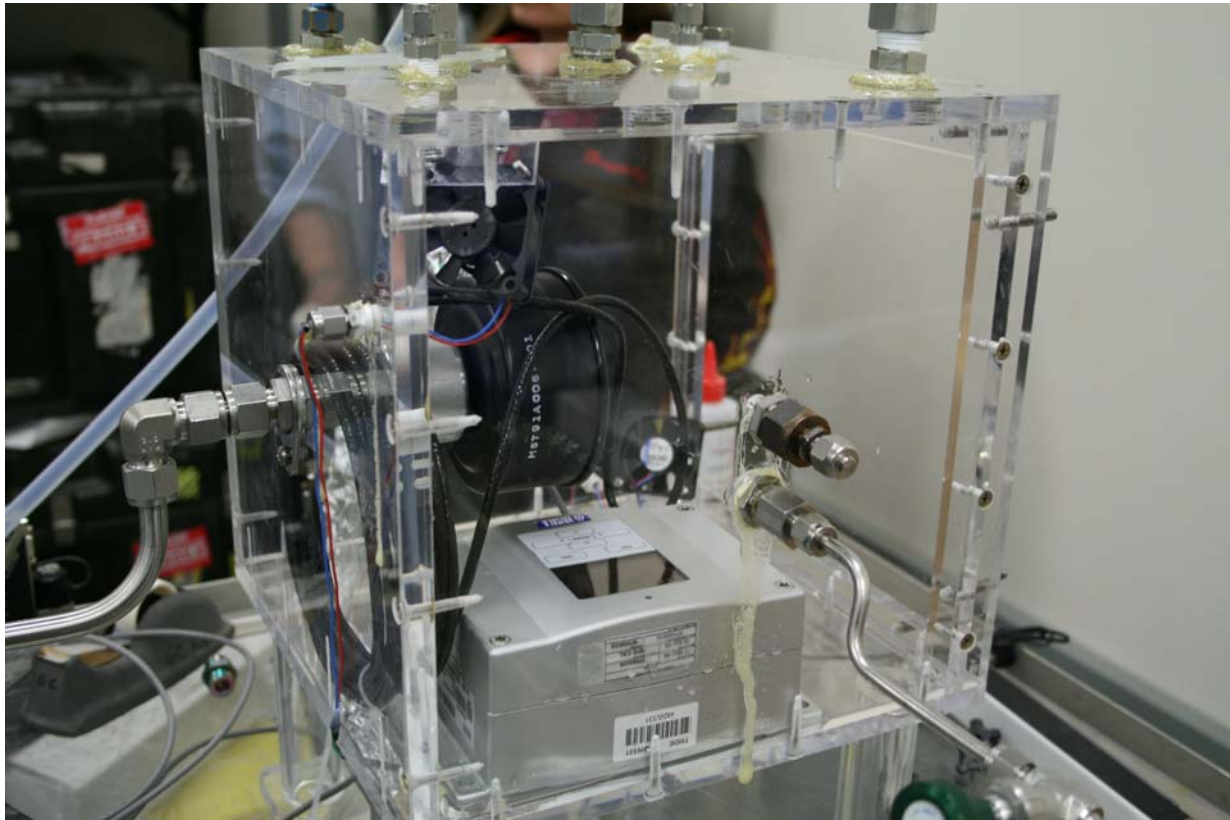


Figure 2. Photograph of the parametric sensitivity fixture.

The air flow rate through the filter was controlled by MFCs and measured by a flow meter. The concentration of Freon-12[®] penetrating the filter was measured at real time during each of the 17 trials. The operator observed the readings every 5-10 minutes; if the flow deviated (+/-10 percent) from the target, the trial was aborted. Each trial generated one set of data and each breakthrough curve required approximately 2 to 3 hours to capture.

Trials ended when the Freon-12[®] concentration penetrating the C2A1 was at a steady state for approximately 0.5 hour, as timed by the laboratory computer clock. After each new test filter was installed and the new air flow rate commenced, up to 1 hour elapsed before the start of the trial to allow the system to equilibrate at the new temperature, flow rate, and RH before a new challenge concentration was introduced.

One cylinder containing Freon-12[®] (Scott Specialty Gasses, Plumsteadville, Pennsylvania) at a concentration of 5,000 milligrams per meter cubed (mg/m³) (high concentration) and certified at +/- 5 percent was used for each trial. The intermediate concentration (2,000 mg/m³) and the lower concentration (500 mg/m³) were achieved by diluting the higher concentration from the cylinder with a separate air stream. The diluted airstream was checked before each trial by sending the Freon-12[®] stream directly to the FTIR. The acceptable tolerances were +/-20 percent of the target concentration.

Data Analysis and Model Comparison Procedures

Breakthrough was considered to have occurred when the concentration of Freon-12[®] penetrating the filter reached 10 percent of the actual challenge concentration for each trial. The results help determine what effects or changes in the breakthrough times can be anticipated when varying the temperature, RH, concentration, or flow rate. The test matrix, target values, and trial results are provided in Table I.

Breakthrough times for each environmental condition, the test matrix, and the trial results have been used to generate comparisons with the models.

After all trials were completed, graphs and tables were created and used to compare the profiles for each trial with the predictions from the models. The results from the models were also compared with each other to identify which model provided better prediction.

List of Key Parameters

The following table (Table II) contains a list of key parameters and their values that are not readily available for the model equations. Some are unique to specific models.

RESULTS

The effects of RH, temperature, chemical concentration, and flow rate on breakthrough time were analyzed by fixing two of the parameters and varying the other two in accordance with the matrix developed for optimal statistical reliability. This split the trials into five groups for comparison. Individual trials within the groups were also compared to one another. Trials from other groups with similar temperature and RH were also compared. Measured breakthrough times for Freon-12[®] ranged from 17 to 273 minutes. Table 1 summarizes trial results, and includes breakthrough times and the environmental data from each trial for the effects of each environmental condition.

Predictive Models and Experimental Data Comparison

The *Wheeler-Jonas model*, the oldest model in this comparison, has been used by the respiratory protection community to determine the effectiveness of both IP and ColPro filters (Lodewyckx and Vansant, 1999; Wood, 1994). However, this model is not capable of predicting the breakthrough time for more than one chemical at a time and does not consider water vapor (RH) in addition to the challenge. The Wheeler-Jonas model also requires an actual data run to estimate some of the unknown parameters in the equation (see additional discussion of predictive models in the Discussion section). One trial for each temperature (trials 1, 2, and 4) was used as the basis for the equation parameters for other trials at the same temperature. Instrument reading anomalies (outliers) in the real data could not be included for finding the unknowns. The information from the C2A1 CBRN trials based on the test matrix and the calculated information for each temperature group was entered by DPG personnel into the model developed by Wheeler-Jonas, and the results were compared with the data from the trials.

The Wheeler-Jonas model predicted breakthrough times for Freon-12[®] averaging nearly 475 percent greater than what were experimentally measured. Although the model's simulated data output was a close match for the empirical data of trials used for base information, it was not a predictive tool for the other trials in each temperature group. A possible reason this model does not match experimental data is that this model only considers a few physical properties of the organic vapor and temperature. Because of the problems and usage conditions described above, the Wheeler-Jonas model was determined to be not as practical for predictive use as newer models.

Table I. Trial Results Data Summary with Times to Breakthrough

Trial	Time to Breakthrough ^a (hh:mm:ss)	Mean Concentration (mg/m ³)			Mean Flow Rate (L/min)		Mean Temperature (°C)			Mean Relative Humidity (percent)		
		Level	Target	Actual	Level	Rate	Level	Target	Actual ^b	Level	Target	Actual ^b
1	00:46:25	High	5000	4713	High	15	Low	25	25.5	Low	20	23.9
2	00:50:20	Mid	2000	1752	Mid	10	Mid	30	30.7	Mid	50	50.7
3	01:19:40	High	5000	5090	Low	5	Low	25	24.8	High	80	76.5
4	01:42:20	High	5000	4409	Low	5	High	35	35.5	Low	20	21.6
5	00:55:43	Mid	2000	2100	Mid	10	Mid	30	30.6	Mid	50	50.6
6	00:17:00	High	5000	5020	High	15	High	35	36.1	High	80	72.8
7	01:01:40	Mid	2000	1829	Mid	10	Mid	30	31.0	Mid	50	50.4
8	00:52:32	Mid	2000	1786	Mid	10	Mid	30	31.2	Mid	50	50.8
9	01:09:33	Low	500	606	Low	5	High	35	35.8	High	80	75.5
10	00:53:58	Mid	2000	1836	Mid	10	Mid	30	31.6	Mid	50	50.4
11	00:45:55	Low	500	544	High	15	High	35	35.4	Low	20	21.9
12	04:32:40	Low	500	580	Low	5	Low	25	25.8	Low	20	23.5
13	00:40:44	Low	500	600	High	15	Low	25	25.7	High	80	75.7
14	00:59:50	High	5000	5438	Low	5	High	35	35.1	High	80	75.5
15	02:15:14	Low	500	700	Low	5	Low	25	25.0	High	80	80.0
16	00:29:35	High	5000	5486	High	15	Low	25	25.5	High	80	75.9
17	00:23:21	Low	500	586	High	15	High	35	35.5	High	80	71.2

^aSeconds for breakthrough times are estimated from times that bracket the measured breakthrough times. Breakthrough concentration is defined as 10 percent of the challenge (measured) concentration.

^bDetection limits of the temperature and humidity instrumentation are rated for accuracy in the hundredths; we are rounding to the tenth.

Table II. List of Key Parameters for Models

Symbol	Definition	Units	Value
C _o	Inlet concentration	mg/m ³	(From Table I)
p	Atmospheric pressure	atmospheres (atm)	0.9
b	Breakthrough	percentage (%) of challenge concentration	10
Q	Volumetric flow rate	L/min	(From Table I)
T	Temperature	°C or K	(From Table I)
RH	Relative humidity	percent (%)	(From Table I)
W	Weight of carbon absorbent	g	112
L	Length of carbon bed	cm	2.2
A	Cross-sectional area of carbon filter	cm ²	85
ρ _b	Bulk density of the packed bed	g/cm ³	6.0×10 ⁻¹
dL	Liquid density of adsorbate	g/cm ³	1.31
W _o	Carbon micropore volume	cm ³ /g	4.54×10 ⁻¹
d _p	Carbon average granule diameter	cm	0.11
W	Weight of carbon in filter	g	112
E _o	Reference adsorption potential for benzene	kJ/mol	18.0
β	Affinity coefficient of water	(no units)	0.06
β _{ov}	Affinity coefficient of organic vapor	(no units)	3.31
P _e	Polarizability of Freon-12 [®]	cm ³ /mol	16.77
Q _{ao}	Heat of adsorption for Freon-12 [®]	calories/gK	.036
k _c	Mass transfer coefficient	s ⁻¹	0.9

The Gerry O. Wood mathematical model (OSHA; Wood, 1994), although based on Wheeler-Jonas, was found to have important differences from the Wheeler-Jonas model; therefore this original Wood model from 1994 was added as a further comparison. This model is used by the Occupational Safety and Health Administration (OSHA) and is one of several tools available online for public use and information. The information from the C2A1 CBRN trials based on the test matrix was entered by DPG personnel into this model and the results compared to the data from the trials.

The 1994 Wood/OSHA model predicted breakthrough times for Freon-12[®] averaging 62 percent greater than what were experimentally measured. It seemed better suited for high concentrations and high flow rates, and does reasonably well for other concentrations and flow rates.

The MultiVapor model (NIOSH, 2007) software released in March 2007, is the replacement for NIOSH's earlier model, Breakthrough (NIOSH, 2005). MultiVapor is designed to simultaneously model multiple vapors with water vapor (RH), whereas Breakthrough could only model one vapor plus RH. Breakthrough (Wood, 2004; NIOSH, 2005) was used to estimate the amount of Freon-12[®] needed to perform the trials. The Breakthrough software from NIOSH proved somewhat unstable, and because it was officially replaced by MultiVapor it was not included in the final modeling calculations. Wood and Snyder (2007) improved Wood's earlier models (Wood, 1994; Wood, 2004); the MultiVapor model is a software program based on this advanced model and developed for public accessibility for filter life prediction (NIOSH, 2007) (see additional discussion of predictive models in the Discussion section). The environmental information from each trial was entered into the NIOSH MultiVapor model. The MultiVapor

program was not able to simulate a breakthrough for some of the environmental conditions for the trials due to limitations in this version of the software.

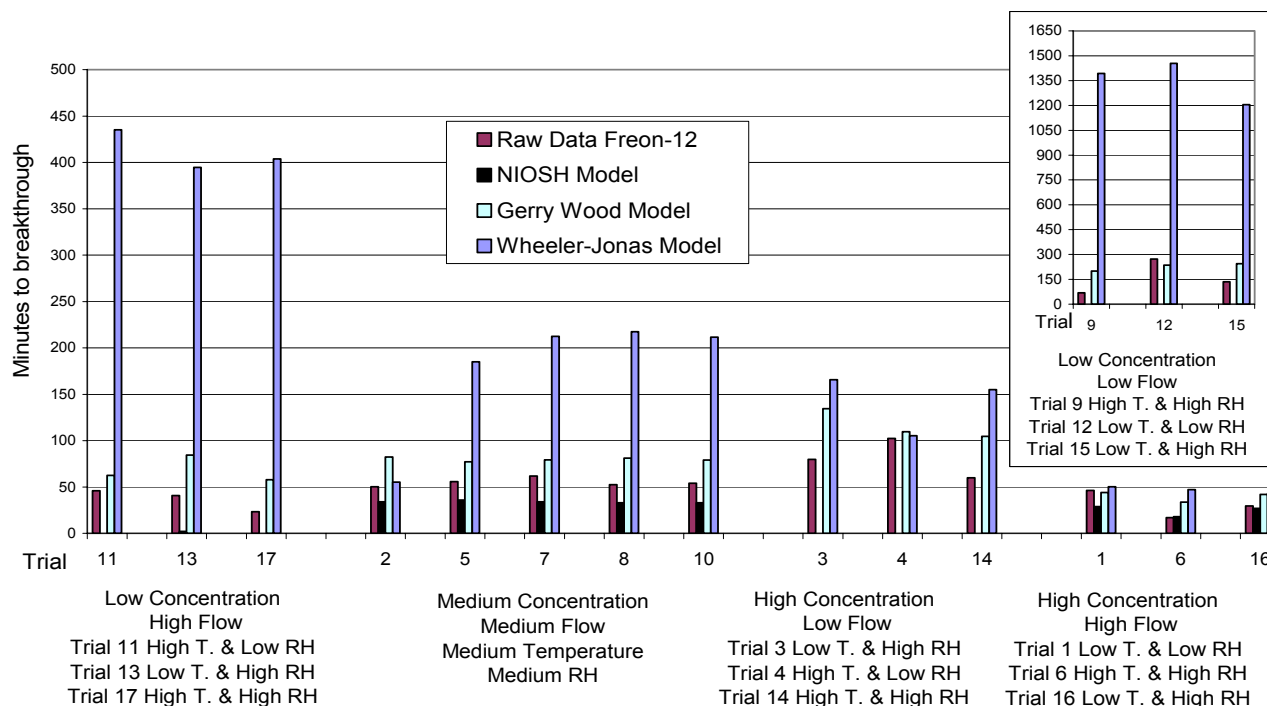
The NIOSH MultiVapor model's average predicted breakthrough time was approximately 30 percent less than what was experimentally measured (see note). In all trials except one, the MultiVapor model predicted breakthrough times that were before actual breakthrough times by an average of 21 minutes. This model closely predicted the breakthrough times of trials with high concentrations and high flow rates and on average performed within 38 percent for the mid concentrations and mid flow rates. However, if either the concentration or the flow rate was low, the NIOSH program had limitations, and did not accept flow rates below 10 L/min or low concentrations even when coupled with the high flow rate (high, mid, and low flow rates and concentrations are defined in Table 1). Overall, based on the trial conditions accepted by the NIOSH program, predictions were closer to the actual breakthrough times than predictions of the other models. [NOTE: Including three questionable returns gives an average predicted breakthrough time of 47.7 percent less than experimentally measured values. If the trials in the low concentration group (trials 11, 13, and 17) are also considered as no return due to program boundary problems, the average predicted breakthrough time difference instead would be 28.6 percent less than experimental measurements. The authors believe that this version of the NIOSH software has boundary condition limitations, and including the low concentration/low flow rate trials for the average calculation gives a false idea of the underlying model's (Wood and Snyder, 2007) performance.]

The Narayan-Harrison model (Narayan and Harrison, 1991; Harrison and Narayan, 1992) is extremely complex, but was suggested for inclusion in this study because in addition to considering the effect of humidity, temperature, concentration, and flow rate on the adsorption performance of the filter, it incorporates other factors, such as the heat capacity for the filter housing, that could influence the filter performance. Computer code was written to solve the system of partial differential equations. Because of strict stability conditions for the implementation of the equation and the uncertainty of some of the equation parameters, several parameter, mathematical, and code checks were performed, and a third paper by Narayan and Harrison (1994) was used to confirm the equations. As a further verification, the parameter values provided in their 1994 report were used in attempts to replicate their experiment; however, replication of the simulation profiles or output they reported was not achieved. After reviewing the mathematics and comparing them with what was presented in the papers, it was concluded that this model as it was presented by Narayan and Harrison (1991, 1992, and 1994) cannot simulate the adsorption of significant amounts of organic vapor (see additional discussion of predictive models in the Discussion section). Nevertheless, simulations using this model (as presented) were run for comparison with the other models. Quantitatively, the Narayan-Harrison model predicts breakthrough times that are 99.9 percent too short regardless of any coefficient adjustments recommended. Simulated breakthrough times occurred in seconds (1.2 to 2.6 seconds) rather than minutes, and none were relatively close to the experimental data.

Side-by-Side Comparisons of Data and Model Output

Figure 3 shows the comparison of the actual breakthrough times for each trial and the predicted breakthrough times from the models for the different environmental conditions studied. The graph shows the five comparison groups that resulted from sorting the trials by common concentration and flow rate. Missing bars in trial sets 3, 4, 9, 11, 12, 13, 14, 15, and 17 imply numbers approaching zero. The actual breakthrough times for each trial and the predicted breakthrough times from each simulation model are in Table III.

Before the start of the test, an assumption was made that the output from the models would be close to the empirical data; but this was not the case. Error is defined as the difference between what was predicted from the model and what was observed from experimental data. The closer the error is to zero the better the prediction. Table IV compares model predictions to the experimental data and the overall average difference for each model. A negative value indicates a predicted breakthrough time that was shorter than the actual breakthrough time.



Note: Missing bars imply numbers approaching zero. NIOSH model would not accept low flow rates (<10 liters per minute). T=Temperature; RH=Relative Humidity; NIOSH=National Institute for Occupational Safety and Health

Figure 3. Comparison of Breakthrough Times for Data and Models

DISCUSSION

The Wheeler-Jonas Model

The Wheeler-Jonas model has been used to determine the effectiveness of both IP and ColPro filters (Lodewyckx and Vansant, 1999; Wood, 1994; Wu 2004). However, this model is not capable of predicting the breakthrough time for more than one chemical at a time, and does not consider water vapor / RH in addition to the challenge. The basic model developed by Wheeler-Jonas (Equation 1) is as follows:

$$t_b = \left(\frac{W_e \cdot W}{C_o \cdot Q} \right) - \left(\frac{W_e \cdot \rho}{C_o \cdot k_v} \right) \ln \left(\frac{C_o - C_x}{C_x} \right) \quad \text{Equation 1}$$

Where,

t_b = breakthrough time;
 W = weight of carbon in filter;
 C_o = challenge concentration;
 Q = filter flow rate;

W_e = adsorption capacity
 ρ = bulk density of the carbon
 C_x = breakthrough concentration
 k_v = first order mass transfer rate

Table III. Comparison of Measured and Predicted Breakthrough Times for Trials and Models

Trial	Measured Breakthrough ^a Time (minutes)	Predicted Breakthrough Time			
		Wheeler-Jonas Model (minutes)	Gerry O Wood Model (minutes)	NIOSH ^b Multi Vapor Model (minutes)	Narayan-Harrison Model (minutes)
1	46.42	50.24	44.12	29	0.025
2	50.33	55.34	82.18	34	0.024
3	79.67	165.70	134.57	-- ^c	0.041
4	102.33	105.38	109.46	--	0.024
5	55.72	184.98	77.14	36	0.024
6	17.00	47.18	33.82	18	0.038
7	61.67	212.40	79.27	34	0.024
8	52.53	217.49	81.18	33	0.024
9	69.55	1392.20	199.12	--	0.027
10	53.97	211.59	79.00	33	0.024
11	45.92	435.24	62.38	0	0.021
12	272.67	1454.15	236.36	--	0.022
13	40.73	394.66	84.32	2	0.033
14	59.83	155.10	104.58	--	0.037
15	135.23	1204.87	244.68	--	0.029
16	29.58	43.16	42.00	27	0.043
17	23.35	403.76	57.87	0	0.025

^a Breakthrough concentration is defined as ten percent of the challenge (measured) concentration.

^b National Institute for Occupational Safety and Health.

^c NIOSH MultiVapor program would not accept some trial conditions, resulting in no output. The MultiVapor program reports negative calculated values of breakthrough times as zeros. Trials 11 and 17 (breakthrough time of 0 minutes) and trial 13 (time of 2 minutes) may also be reflecting program limitations with low concentration.

The Gerry O. Wood Mathematical Model

The Gerry O. Wood mathematical model has important changes from the Wheeler-Jonas model. Different equations are used to calculate the parameters W_e and k_v for the base equation, and molar polarization is taken into account (OSHA; Wood, 1994). For example, the Dubinin-Radushkevich (DR) equation (Cal, 1995; Wood, 1994 and 2002; Wu, 2004), which is used to calculate adsorption, is modified and used to calculate W_e . A further discussion of Wood's basic model can be found in Wood's 1994 paper and at the OSHA site.

Table IV. Comparison of Predicted Breakthrough Time - Differences from Measured Trial Data

Trial	Wheeler-Jonas Model Time Difference		Gerry O Wood Model Time Difference		NIOSH ^a MultiVapor Model Time Difference		Narayan-Harrison Model Time Difference	
	Minutes	Percent	Minutes	Percent	Minutes	Percent	Minutes	Percent
1	3.82	8.2	-2.30 ^b	5.0	-17.42	-37.5	-46.40	-99.95
2	5.01	10.0	31.85	63.3	-16.33	-32.5	-50.31	-99.95
3	86.03	108.0	54.90	68.9	-- ^c	--	-79.63	-99.95
4	3.05	3.0	7.13	7.0	--	--	-102.31	-99.98
5	129.26	232.0	21.42	38.4	-19.72	-35.4	-55.70	-99.96
6	30.18	177.5	16.82	98.9	1.00	5.9	-16.96	-99.78
7	150.73	244.4	17.60	28.5	-27.67	-44.9	-61.65	-99.96
8	164.96	314.0	28.65	54.5	-19.53	-37.2	-52.51	-99.96
9	1322.65	1901.7	129.57	186.3	--	--	-69.53	-99.96
10	157.62	292.1	25.03	46.4	-20.97	-38.9	-53.95	-99.96
11	389.32	847.8	16.46	35.8	-45.92	-100.0	-45.90	-99.95
12	1181.48	433.3	-36.31	-13.3	--	--	-272.65	-99.99
13	353.93	869.0	43.59	107.0	-38.73	-95.1	-40.70	-99.92
14	95.27	159.2	44.75	74.8	--	--	-59.79	-99.96
15	1069.64	791.0	109.45	80.9	--	--	-135.20	-99.98
16	13.58	45.9	12.42	42.0	-2.58	-8.7	-29.54	-99.85
17	380.41	1629.2	34.52	147.8	-23.35	-100.0	-23.33	-99.89
Average Difference	325.70	474.5	32.68	62.5	-21.02	-47.7 ^d	-70.36	-99.95

^a National Institute for Occupational Safety and Health.^b Negative values reflect predicted breakthrough before measured breakthrough.^c NIOSH MultiVapor program would not accept trial conditions, resulting in no output.^d If trials 11 and 17 (with breakthrough times of 0 minutes) are considered a no return due to program boundary problems, the average would be -36.0 percent difference. If trial 13 (time of 2 minutes), part of the low concentration group, is also dropped, the difference would be -28.6 percent.

The NIOSH MultiVapor Model

The MultiVapor (NIOSH, 2007) software, released March 2007, is the replacement for NIOSH's earlier model, Breakthrough (NIOSH, 2005). Breakthrough, based on work by Wood that included an expanding zone model, was able to account for one vapor with humidity (Wood, 2004). There are two zones in the Breakthrough model: the first zone contains organic vapor and water at equilibrium, the second contains only water. The first zone expands, pushing its wave front to the end of the filter. Wood and Snyder (2007) improved the concepts behind Breakthrough, and this improvement became incorporated into NIOSH's MultiVapor model. MultiVapor is unique in its ability to model multiple vapors and humidity at the same time.

MultiVapor assumes a particular wave front shape determined by the adsorption rate given by Equations 2 and 3:

$$k_{v0.1\%} = 800\beta_{ov}^{0.33}v_l^{0.75}d_p^{-1.5}(W_e/M_w)^{0.5} \text{ for } c/c_o = 0.001 \quad \text{Equation 2}$$

$$k_v(c/c_o) = \left[\frac{1 + b \ln(c_o/c - 1)}{1 + b \ln(999)} \right] k_{v0.1\%} \text{ for } c/c_o \leq 0.5 \quad \text{Equation 3}$$

Where, $k_{v0.1\%}$ is the adsorption rate for c/c_o at 0.1 percent, $k_v(c/c_o)$ is the adsorption rate for c/c_o less than 50 percent, β_{ov} is the affinity coefficient for organic vapor, d_p is the average carbon granule diameter (cm), v_l is the superficial velocity, M_w is the molecular weight, W_e is the adsorption capacity, and b is a root of a correlation for the skew parameter.

The output of the model returns a predicted, a minimum, and a maximum breakthrough time. The minimum and maximum form a confidence interval for the time estimate, derived from experimental data provided by the 3M™ Company (St. Paul, Minnesota) (Wood, 2004). Therefore, when looking at the output graph, the breakthrough time is determined by the position of the center plot, and the maximum and minimum lines plot the confidence interval.

MultiVapor uses a special form of the DR equation that combines DR with DR-IAST (Ideal Adsorbed Solution Theory) and the Bering equation (Wood and Snyder, 2007) to calculate the equilibrium molar capacities of each zone (Equation 4):

$$n_T = \frac{W_o}{V_{mT}} \exp \left[- \left(\frac{RT}{E_o} \right)^2 \left(\frac{\sum x_i \ln(x_i p_{sati} / p_i)}{\beta_T} \right)^2 \right] \quad \text{Equation 4}$$

Where, W_o is the micropore volume, V_m is the liquid molar volume for the mixture of organic vapors, E_o is the adsorption potential, x is the molar fraction of an organic vapor, the subscript i denotes the i^{th} vapor, the subscript sat denotes saturation, the subscript T denotes the total over all vapors, p is the partial pressure of an organic vapor, and n is the molar capacity. For one vapor plus water (our case), Equation 4 reduces to the usual DR equation.

The Narayan-Harrison Model

Description. The Narayan-Harrison model (Narayan and Harrison, 1991; Harrison and Narayan, 1992), unlike the other models, is a continuous dynamical system that is primarily derived from first principles. It uses three basic ideas: first, there is a conservation of mass; second, energy is conserved; and third, the rate of adsorption is proportional to the difference between the amount adsorbed and the amount that could be adsorbed at equilibrium. These three ideas create a system of five partial differential equations. This allows the Narayan-Harrison model to treat space and time continuously, model a continuous temperature profile in the filter bed, and model continuous concentration profiles in the filter of both humidity and the adsorbate. One feature of the model is not derived from first principles,

which is the adsorption equilibrium (which is denoted by *). Like the other models, it models the adsorption process directly, and only models physical adsorption.

The Narayan-Harrison model uses a large number of parameters: β is the affinity coefficient of the organic vapor, B is the structural parameter, w_o is the micropore volume, T is the temperature, k_c is the mass transfer coefficient, ρ_o is the liquid density of the organic vapor, ρ_b is the density of the carbon bed, L is the length of the bed, ε is the bed voidage, K is the heat transfer constant, and v_l is the superficial velocity. The model's equations, initial conditions (IC) and boundary conditions (BC) are:

Equation Set 1:

$$\left\{ \begin{array}{ll} v_l \frac{\partial c_o}{\partial x} + \varepsilon \frac{\partial c_o}{\partial t} + p_b \frac{\partial n_o}{\partial t} = 0 & \text{(Mass balance for vapor)} \\ \frac{\partial n}{\partial t} = k_c (n_o^* - n_o) & \text{(Adsorption rate for vapor)} \\ v_l \frac{\partial c_w}{\partial x} + \varepsilon \frac{\partial c_w}{\partial t} + p_b \frac{\partial n_w}{\partial t} = 0 & \text{(Mass balance for water)} \\ \frac{\partial n}{\partial t} = k_c (n_w^* - n_w) & \text{(Adsorption rate for water)} \\ \rho_g c_{pg} v_L \frac{\partial T}{\partial x} = \rho_b \left(Q_{ao} \frac{\partial n_o}{\partial t} + Q_{aw} \frac{\partial n_w}{\partial t} \right) - K \frac{\partial T}{\partial t} & \text{(Energy balance)} \end{array} \right.$$

The adsorption equilibria for organic

vapor and water (n^*) in Equation Set 1 are:

$$n_o^* = w_o \rho_o \left(1 - \frac{n_w^*}{w_o \rho_w} \right) \exp \left(\frac{BT^2}{\beta^2} \log^2 \left(\frac{c_{so}}{c_o} \right) \right) \quad \text{Equation 5 (vapor)}$$

$$n_w^* = \left(1 - \frac{n_o^*}{w_o \rho_o} \right) \sum_{i=1}^{i=8} a_{i-1} \left(\frac{c_w}{c_{sw}} \right)^i \quad \text{Equation 6 (water)}$$

The following are the IC and BC equations:

$$n_w(x,0) = n_w^*, n_o(x,0) = 0, T(x,0) = T_0, c_o(x,0) = 0, c_w(x,0) = RH \times c_{sw} \quad \text{Equation 7(IC)}$$

$$n_w(0,t) = n_w^*, \frac{\partial n_w(L,t)}{\partial x} = 0, c_w(0,t) = RH \times c_{sw}, \frac{\partial c_w(L,t)}{\partial x} = 0 \quad \text{Equation 8 (BC)}$$

$$n_o(0,t) = n_o^*, \frac{\partial n_o(L,t)}{\partial x} = 0, c_o(0,t) = c_o, \frac{\partial c_o(L,t)}{\partial x} = 0 \quad \text{Equation 9 (BC)}$$

$$T(0,t) = T(L,t) = T_0 \quad \text{Equation 10 (BC)}$$

These differential equations with IC and BC are solved through a numerical integration scheme. These equations have the three types of state variables: c the concentration in gas phase (g/mL), n the concentration in adsorbed phase with respect to grams of carbon (g/g_c), and T the temperature (K). The subscripts o and w denote organic vapor and water respectively. The parameter Q_a denotes heat of adsorption. The subscript s denotes saturation concentrations and the subscript 0 means this is the challenge value. The coefficients a_{i-1} are the result of eighth order polynomial regression. It should be noted that the model might have some problems resulting from this unusual choice.

Adsorption Problem

Overall, the modeling of adsorption processes is not adequate. The simulation work of Narayan and Harrison does not correspond to the parameters that they provide in their 1994 report. Using the given parameter values of $\beta = 5.4120 \times 10^{-1}$, $B = 7.3664 \times 10^{-7}$, $w_o = 4.5966 \times 10^{-1} \text{ mL/g}$, $T = 298\text{K}$, $k_c = 2.5 \times 10^{-1} \text{ s}^{-1}$, and $\rho_o = 3.1284 \times 10^{-1} \text{ g/mL}$, $\rho_b = 5.874 \times 10^{-1} \text{ g/mL}$, $L = 1.963 \text{ cm}$, $c_o = 2.1 \times 10^{-6} \text{ g/mL}$, $c_{so} = 3.1671 \times 10^{-2} \text{ g/mL}$, $\varepsilon = 3.038 \times 10^{-1}$, and $v_l = 5.77 \text{ cm/s}$, the model itself provides for the escape of at least $2.50 \times 10^{-4} \text{ g}$ of ethane, which is close to the $2.51 \times 10^{-4} \text{ g}$ challenge amount.

To verify that it adsorbs so little, consider a scenario that would adsorb many times more ethane than the scenario modeled in Narayan and Harrison's January 1994 report. Assume that the concentration is a constant $2.1 \times 10^{-6} \text{ g/mL}$. This allows more adsorption than possible with an ethane pulse [$2.1 \times 10^{-6} \geq (2.1 \times 10^{-6} \times e^{-tQ/V})$ for all $t \geq 0$ where Q is the flow rate and V is the chuck volume]. The equilibrium is determined by the parameter values and the concentration of adsorbate in gas phase using the DR equation (Narayan and Harrison, 1994; Wood, 2002; Cal 1995). Also, this value is dependent on temperature. Narayan and Harrison used 298K (25°C). To obtain an upper bound on what is physically reasonable, the temperature 273K (0°C) was chosen for this proof. The low temperature will allow more adsorption in the model and is far below any temperature likely to occur under these test conditions.

$$n_o^* = w_o \rho_o \exp \left(-\frac{BT^2}{\beta^2} \ln \left(\frac{c_o}{c_{so}} \right)^2 \right) = 4.112 \times 10^{-9} \frac{\text{g}}{\text{g}_c} \quad \text{Equation 11}$$

With this answer and the second equation from Equation Set 1, we can find an upper bound on adsorption rate:

$$\frac{\partial n_o}{\partial t} = k_c (n_o^* - n_o) \leq .25(4.112 \times 10^{-9} - 0) = 1.028 \times 10^{-9} \frac{\text{g}}{\text{g}_c \cdot \text{s}} \quad \text{Equation 12}$$

Where k_c is the mass transfer coefficient (1/s), n_o is the concentration of adsorbed organic vapor (g/g_c), and n_o^* is the equilibrium amount of adsorbed organic vapor (g/mL).

We can assume that the vapor only resides in the filter as long as it takes the carrier gas to pass through the filter. If the assumption is wrong, the amount of vapor adsorbed will be significant and the proof will fail. Thus nothing is lost through this assumption. The air takes less than $L/v_l = 1.963/5.77 = 0.34$ seconds to pass through the filter. Ensuring that most of the ethane pulse has subsided ($c_o(0, t) \leq 10^{-14}$) will require another 29 seconds. The total time required is less than 30 seconds, therefore, let $\tau = 30$ seconds.

The first equation ($v_l \frac{\partial c_o}{\partial x} + \varepsilon \frac{\partial c_o}{\partial t} + p_b \frac{\partial n_o}{\partial t} = 0$) from Equation Set 1 in the Narayan-Harrison model can be analyzed to obtain a lower bound on the amount of escaping vapor. First, integrate this with respect to x and t from 0 to L and 0 to τ respectively to obtain:

$$v_l \int_0^{\tau} c_o(L, t) - c_o(0, t) dt + \varepsilon \int_0^L c_o(x, \tau) - c_o(x, 0) dx + \rho_b \int_0^L \int_0^{\tau} \frac{\partial n_o}{\partial t} dt dx = 0. \quad \text{Equation 13}$$

Next, use initial conditions and the assumption that the ethane pulse has subsided to get:

$$v_l \int_0^{\tau} c_o(L, t) dt - v_l \int_0^{\tau} c_o(0, t) dt + \rho_b \int_0^L \int_0^{\tau} \frac{\partial n_o}{\partial t} dt dx = 0. \quad \text{Equation 14}$$

The three terms of the equation correspond to the escaping ethane, the entering ethane, and the amount adsorbed, respectively. Then, rearrange and substitute Equation 12 for the adsorption rate to obtain the inequality:

$$\int_0^{\tau} c_o(L, t) dt \geq \int_0^{\tau} c_o(0, t) dt - \frac{\rho_b L \tau}{v_l} 1.28 \times 10^{-9}. \quad \text{Equation 15}$$

The ethane pulse has the form $c_o(0, t) = 2.1 \times 10^{-6} \times e^{-tQ/V}$. Substituting this expression in Equation 15, and evaluating the integral, we obtain:

$$\int_0^{\tau} c_o(L, t) dt \geq 2.1 \times 10^{-6} \frac{V}{Q} (1 - e^{-\tau Q/V}) - \frac{\rho_b L \tau}{v_l} 1.028 \times 10^{-9} = 2.89 \times 10^{-6} g/cm^2 \quad \text{Equation 16}$$

Next, multiply by the cross-sectional area of the filter (86.6 cm²) to get the amount of ethane in grams.

$$86.6 \int_0^{\tau} c_o(L, t) dt \geq 2.50 \times 10^{-4} g \quad \text{Equation 17}$$

The left hand side is now the total amount of ethane to escape in grams. This shows that at least $2.50 \times 10^{-4} g$ of the $2.51 \times 10^{-4} g$ ethane that enters the filter escapes in less than 30 seconds. This is in agreement with ethane simulations run at DPG using this model.

This proof shows that the mechanisms of adsorption represented by the DR isotherm are not sufficient to retain a significant amount of organic vapor. Another mechanism, such as chemisorption, is needed to create the adsorption rates necessary to prevent breakthrough. A better understanding of adsorption equilibrium could allow the model to make predictions that are similar to empirical data.

CONCLUSIONS AND RECOMMENDATIONS

Effects of Environmental Parameters on Breakthrough Times

Conventional wisdom might suggest that high temperature, especially in combination with high RH, would cause fast breakthrough times for filters. Based on the analysis of data from trials using multiple environmental parameters (see Table I and Figure 3) on the C2A1 CBRN filter, it appears that flow rate has the greatest influence on breakthrough time for Freon-12[®], followed (in descending order of influence) by concentration, RH, and temperature (see Figure 3).

Various combinations of these environmental parameters accelerate the breakthrough time. Not surprisingly, high values for all environmental parameters led to the shortest breakthrough time, and low values for all parameters led to the longest breakthrough time. It is likely that these effects would be

similar for other ColPro or IP filters that contain treated, activated carbon. For example, it is likely that service personnel, war fighters, or first responders using non-self-contained breathing apparatus [non-(SCBA)] IP gear, to include the M40 mask and other equipment with this type of filter, would have the shortest filter breakthrough time when they are engaged in strenuous activity (or hyperventilation) because of the increased flow rate (breathing rate) through the filter. Added to a high flow rate, high concentration of chemical vapor and high RH would accelerate the breakthrough process. Situations with low temperatures and high RH also speed up breakthrough compared with situations with high temperatures and low RH.

These statements are not meant to minimize the considerable impact of temperature and humidity on the comfort, performance, and/or safety of the service personnel, war fighters, or first responders that must wear IP gear in hazardous situations.

Comparison of Predictive Models with Experimental Data

None of the models performed well in producing predictive breakthrough times that were consistently close to the trial data, and most models predicted longer times to breakthrough than experimental values (see Figure 3, and Tables III and IV). Changing the environmental parameters according to the matrix emphasized the differences between the models as well as the limitations of the models (see Figure 3).

Recommendations for Predictive Model Application

The newer, more advanced filter life prediction models should be preferentially used instead of the older models even though Wheeler-Jonas and Wood's 1994 model have been used for several years.

The Narayan-Harrison model used a combination of first principles and empirical modeling methods (see additional discussion of predictive models in the Discussion section above), and considered many factors that could affect the breakthrough and service life of filters. Unfortunately, predicted breakthrough times occurred in seconds rather than minutes, making this model (as it was presented) impractical for current use. However, the Narayan-Harrison model has several promising ideas, for example, the continuous treatment of time and space, and continuous modeling of temperature and concentration profiles, which may prove useful for future filter model development.

Although beyond the scope of our investigation, it is possible that the Narayan-Harrison model could be extended to model chemical adsorption. Because the DR equation for physical adsorption works better with other more empirically based models, it is possible that the first principles foundation of the Narayan-Harrison model could be used to determine the adsorption mechanism more precisely. It is also possible that use of this dynamic model might have some hope of explaining hysteresis (chaotic behavior, differences in adsorption and desorption curves) in adsorption. Obviously, some of these ideas are interesting speculations at this point, but are mentioned to illustrate that this model may warrant further investigation.

The NIOSH MultiVapor model represents the most recent improvements. This initial release version of the software program (Beta 2.1.3, March 2007) could not accommodate low flow rates and low concentrations in the test matrix. In spite of this software problem, MultiVapor's breakthrough time prediction was closer overall to the experimental data than the prediction of any other model. The MultiVapor program generally predicted breakthrough times that were shorter than the actual times, so in most cases there would be a margin of safety instead of false security. For safety reasons, the MultiVapor model would be the best of the models under consideration to use for filter life prediction.

Overall Recommendations

Although excellent progress has been made during the past few years, there is a definite need for further development of predictive filter models. These refined models will need to reflect the actual response of IP and ColPro filters under chemical challenges combined with multiple environmental

conditions. Further investigational studies using other organic vapors and chemicals of interest to the protection community may need to be conducted to see whether the effects of these multiple environmental parameters are consistent with those obtained with Freon-12[®]. Until more is known about the actual response of the various IP and ColPro filters to combined environmental conditions and the models are refined, informed caution should be exercised when using any of the models to predict breakthrough times for CBRN filters.

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