

Correlating and Extrapolating Air-Purifying Respirator Cartridge Breakthrough Times – A Review

Gerry O. Wood

40 San Juan Street, Los Alamos, New Mexico, USA 87544
Corresponding author E-mail: GerryConsulting@earthlink.net

ABSTRACT

Air-purifying respirator cartridges for gas and vapor removal from breathed air have been tested for over a century. Usually gas or vapor breakthrough times have been measured with other conditions (air flow rate, humidity, temperature, concentration, etc.) fixed or varied systematically. With the accumulation of such data, various models have been proposed and used for correlating and extrapolating measured breakthrough times for air-purifying respirator cartridges and canisters. These models, ranging from simple equations to Rules of Thumb to elaborate computer programs, have been critically reviewed to 1) gather these models together into one document, 2) define their requirements and limitations, and 3) demonstrate their usability for extrapolating air-purifying respirator cartridge breakthrough time measurements to untested conditions (concentrations, humidities, temperatures, breathing rates, and covapors).

Keywords: Air-purifying respirator, cartridge, canister, breakthrough time, extrapolation.

BACKGROUND

Since it's not possible to test air-purifying respirator cartridges for all potential use conditions, it's often useful to have models to extrapolate measured breakthrough times to those for untested workplace conditions of air flow (breathing) rates, humidities, temperatures, gas/vapor concentrations, and other contaminants present. Such models include graphs, equations, Rules of Thumb, and computer programs of complex models based on correlations of data. These models need to be reexamined periodically as new data and understandings of adsorption and chemical removal of gases and vapors are developed. The fundamental equation for breakthrough time, t_b , based on mass conservation and first-order adsorption kinetics, is the Reaction Kinetic (modified Wheeler) equation containing a capacity (first) term minus a kinetic (removal rate) term (Wood and Moyer, 1989):

$$t_b = (W_e W / C_o Q) - (W_e \rho_B / k_v C_o) \ln[(C_o - C_b) / C_b] \quad (1)$$

where

t_b = breakthrough time at which vapor is observed in cartridge effluent air
 W_e = adsorption capacity (g vapor/ g sorbent)
 k_v = adsorption rate coefficient (min^{-1})
 W = weight of sorbent (g)
 Q = air flow rate (L/min)
 ρ_B = packed bed density (g/cm^3)
 C_o = vapor challenge concentration (g/L)
 C_b = breakthrough concentration (g/L)

Parameters in this equation are related to bed properties (ρ_B , W), use conditions (C_o , C_b , Q), and vapor/sorbent interactions (W_e , k_v). Capacities W_e and first-order vapor removal rate coefficients k_v are functions of concentration C_o , temperature T , properties of the vapor, properties of the sorbent, and concentrations (C_y) of other vapors present, including water vapor (at relative humidity, RH). If W_e and k_v can be derived from breakthrough time data, they can be used to calculate breakthrough times at different values of the other parameters in Equation (1). Note that the ratio W_e/C_o appears in both terms, so that breakthrough time is proportional to this capacity/concentration ratio.

CORRELATIONS OF BREAKTHROUGH TIMES BY EMPIRICAL RELATIONSHIPS

Empirical correlation equations are those derived from observed relationships between adjustable and measurable parameters with little or no understanding of why these relationships exist. A goal is to derive constants in such equations that can be used for interpolations and extrapolations.

Breakthrough Curve Analyses

A breakthrough curve is a plot of breakthrough concentration C_b (or ratio C_b/C_o) vs. time of air flow through a cartridge with all other test parameters fixed. When Equation (1) is rearranged to give C_b as a function of t_b the often-observed S-shaped breakthrough curve results.

Linear plots for adsorption of OV vapors have been obtained from breakthrough curve (t_b , C_b) data by plotting the logarithm $\ln[C_b / (C_o - C_b)]$ vs. t_b (Yoon and Nelson, 1984). The resulting Slope and Intercept allow extrapolation of t_b s to other C_b s.

Combined with Equation (1) the Slope and ($t_b = 0$) Intercept of such a plot give:

$$k_v = - \text{Intercept} * \rho_B Q / W \quad (2)$$

$$W_e = - (\text{Intercept}/\text{Slope}) * C_o Q / W \quad (3)$$

The absolute minimum number of (t_b , C_b) data sets needed to extract W_e and k_v using Equation (1) is two (e.g., at 1% and 10% breakthrough). However, two points are not enough to confirm the breakthrough curve symmetry (plot linearity) needed to confidently interpolate or extrapolate t_b to other values of C_b (or C_b/C_o) or validate the calculations of W_e and k_v . At least three breakthrough curve points are needed; more are preferable.

Alternately, Equation (1) can be fit to the breakthrough curve data by Nonlinear Least-Squares Regression (Yan, 2009) to extract values of W_e and k_v . If breakthrough curves are unsymmetrical (e.g., at high humidities) they may be better fit in the useful region $C_b/C_o \leq 0.5$ or fit to a related equation with more parameters (Wood, 1993).

Besides allowing extrapolation of t_b s to other C_b s, another application of such analyses to obtain W_e and k_v values is to observe how these values vary with other parameters (e.g., C_o , Q , RH, T). Knowing such mathematical functions allows extrapolations to other values of the latter parameters and corresponding cartridge use conditions. This is illustrated below.

Breakthrough Times Analyses

Sometimes instead of measuring a full or partial breakthrough curve, only breakthrough time t_b' for a preselected breakthrough concentration C_b' endpoint is measured for a controlled C_o . Values of W_e and k_v are then extracted from Equation (1) by varying another parameter (other than time) and keeping all other parameters (including C_b/C_o) fixed in a set of tests.

1. Varying the sorbent bed weight W (and so the bed volume V_B). As predicted by Equation (1) straight line plots of t_b vs. W have been observed. Such tests have been done using testing tubes packed with sorbent from a cartridge (Jonas and Rehrmann, 1973) or stacked cartridges (Moyer, 1987). From the Slope and Intercept of such a plot one can calculate:

$$k_v = -(\text{Slope/Intercept}) * \rho_B Q \ln[(C_o - C_b)/C_b] \quad (4)$$

$$W_e = \text{Slope} * C_o Q \quad (5)$$

2. Varying air flow rate Q . Plots of t_b vs. $1/Q$ for adsorbed vapors have been shown to yield straight lines with nearly zero intercepts (Nelson and Harder, 1972). Such plots of Equation (1) yield:

$$k_v = -(\text{Slope/Intercept}) * (\rho_B / W) \ln[(C_o - C_b)/C_b] \quad (6)$$

$$W_e = \text{Slope} * C_o / W \quad (7)$$

Since Intercepts are so small, k_v calculation by this method is very uncertain. Such nearly zero intercepts are the basis of the conclusion that breakthrough time is inversely proportional to flow rate (Nelson and Correia, 1976c). See later discussion of the second Rule of Thumb.

3. Varying bed residence time t_R . Closely related to the above is the varying the bed residence time t_R defined in units of seconds as:

$$t_R = (V_B / Q) (60 \text{ sec/min}) (1 \text{ L} / 1000 \text{ cm}^3),$$

by varying bed volume V_B and/or flow rate Q in tests (Ackley, 1985). A resulting linear plot of t_b vs t_R yields:

$$k_v = -(\text{Slope/Intercept}) * \ln[(C_o - C_b)/C_b] \quad (8)$$

$$W_e = \text{Slope} * C_o / \rho_B \quad (9)$$

A difficulty with methods 2 and 3 is that k_v is a weak function of Q (Wood and Lodewyckx, 2003), so that the values of W_e and k_v calculated by these methods will differ from those when Q is kept fixed (Wood and Moyer, 1989). They can still be used with Equation (1) for t_b extrapolation to other values of Q and V_B , but they should be used cautiously with different values of other variables.

Varying Concentration Data Analyses

Capacity W_e is always an increasing function of C_o for physical adsorption and usually so for reactive vapor removal which is a combination of adsorption and reaction. Note: Sometimes W_e is mistakenly assumed to be constant and it is incorrectly assumed that breakthrough time is inversely proportional to concentration, even over orders of magnitude of C_o . Unlike other parameters in Equation

(1), C_o can't be varied independently to derive W_e and k_v from a simple linear plot. It appears in both terms of Equation (1).

However, empirical linear plots of base 10 $\log t_b$ vs. $\log C_o$ for physically adsorbed vapors have been reported (Nelson and Harder, 1976a; Nelson et al., 1980). Combined with Equation (1),

$$t_b = 10^{\text{Intercept} * C_o^{\text{Slope}}} \quad (10)$$

gives capacity

$$W_e = W_{e1} * C_o^{\text{Slope}+1} \quad (11),$$

where W_{e1} is W_e at $C_o = 1$ unit (e.g., ppm). Equation (11) has the form of a Freundlich adsorption isotherm. This linear relationship between $\log t_b$ and $\log C_o$ allows the calculation of t_b at a third C_o if measured at two others. Again, a third or more reference value helps to establish linearity (or not) of such a plot, especially for reactive vapor removal mechanisms. Slopes varying from -0.108 to -1.040 have been reported for OV vapors physically adsorbed (Nelson et al., 1980).

Such linear plots of $\log t_b$ vs. $\log C_o$ have been observed and applied only with fixed breakthrough concentration ratios C_b/C_o (e.g., 10% breakthrough). However, in some cartridge testing a fixed breakthrough concentration (e.g., a detection limit or regulatory level) might be chosen as the breakthrough time endpoint as challenge concentration is varied. From the logarithm of Equation (1) and using Equations (10) and (11), the Intercept of such a plot corresponds to:

$$\text{Intercept} = \log W_{e1} + \log [(W/Q) - (\rho_B/k_v) \ln [(C_o - C_b)/C_b]] \quad (12)$$

If the ratio C_b/C_o is not kept fixed, then this Intercept is also a function of C_o and not invariant. This will affect the apparent Slope and perhaps even the linearity of the log-log plot. The resulting plot can still be useful, but will need more than two (C_o , t_b) data points to be established with enough certainty for calculation of t_b at another C_o .

Relative Humidity Effects Analysis

Ratios of t_b for dry and "wet" conditions for 8 OVs have been fit to linear functions of fractional RH taken to a power (Wood, 1987).

$$t_b(\text{dry}) / t_b(\text{wet}) = 1 + \text{Slope} * (\text{RH})^n \quad (13)$$

where "dry" refers to a very low relative humidity fraction (e.g., < 0.1) and "wet" refers to a higher one. The value of n is chosen to make Equation (13) linear. If a linear relationship can't be forced, a nonlinear one can be established and confirmed with more RH data.

If linear, measuring t_b at very dry testing conditions and at two or more higher RHs can yield the parameters, Slope and n . Equation (13) can then be used to estimate t_b at another RH. Alternately, three $t_b(\text{wet})$ values at the widest possible range of RH can yield these parameters.

Another description of RH effects for adsorbed vapors has been proposed that conforms approximately to observations (Wood, 1987; Nelson et al., 1976b; and Backman, 1997). It can be expressed as:

$$t_b = t_b(\text{dry}) \text{ for } \text{RH} \leq \text{RH}_B \quad (14) \quad \text{and}$$

$$t_b = t_b(\text{dry}) - \text{Slope} * (RH - RH_B) \text{ for } RH > RH_B \quad (15),$$

where RH_B is the “breakpoint” where RH effects become significant. The difficulty is establishing this breakpoint without a lot of data. It depends on the relative adsorption affinities and concentrations of the vapor and water. A value of 0.5 is sometimes chosen for RH_B is not always the case (Wood, 1987).

Temperature Effects Analyses

Decreasing linear plots of t_b vs. temperature T ($^{\circ}\text{C}$) with negative slopes have been reported for vapor adsorption (Nelson et al., 1976b; Jonas et al., 1975) and reactive removal (Wood, 1985). Other parameters W , Q , ρ_B , and C_o were kept fixed, except in the case of Jonas (1975) where a correction for C_o can be made to get a linear plot. So,

$$t_b = t_b(\text{at reference } T) + \text{Slope} * T \quad (16)$$

Measuring t_b at two or more T s allows calculating t_b at another T , all other parameters being the same. Assuming linearity requires only duplicates at two temperatures; however, proving linearity or establishing a curve of t_b vs. T requires at least three temperatures.

Confidence Intervals

The reliability of extrapolations or interpolations of demonstrated linear correlations fit by Least Square Regression analysis can be estimated using equations or statistical computer programs (Yan, 2009). Commonly, 95% confidence limits and intervals are calculated for predicted values. Such intervals are smaller for more data points. Linear correlations coefficients can also be calculated to test for linearity. A spreadsheet for $\log t_b$ vs $\log C_o$ linear plots, available at www.GerryOWood.com, can be adapted for other linear correlations to predict extrapolated values and confidence limits.

Multiple Vapor Effects Analyses

For physical adsorption of mixtures of OV's a vapor breaking through later reduces the breakthrough time of an earlier one (Yoon, 1996, Swearengen and Weaver, 1988). A similar effect has not been reported, but can be expected, for covapors that compete for reaction with sorbent, impregnants, or adsorbed water.

Simple equations have been proposed for use to account for covapor reductions of breakthrough times, including:

1. Molar additivity (DOL/OSHA 1998). For an adsorbed vapor x with measured or estimated single vapor breakthrough time t_{bx} , replace C_o with

$$C_o = C_x + \sum C_y \quad (17)$$

where C_x is the molar (ppm) concentration of the vapor with the shortest breakthrough time and $\sum C_y$ is the sum of the molar concentrations of the covapors.

2. Mole fraction (Jonas et al., 1983; Robbins and Breysse, 1996). For an adsorbed vapor x with single vapor capacity W_e^o and single vapor breakthrough time t_b^o , use:

$$W_e = [C_x / (C_x + \sum C_y)] W_e^o \quad (18) \quad \text{and}$$

$$t_b = [C_x / (C_x + \sum C_y)] t_b^0 \quad (19).$$

Both these approaches neglect differences in volumetric adsorption capacities and affinities of vapors. Activated carbon is a micropore filling sorbent (Nelson and Correia, 1976c).

See Wood (2000) for a thorough discussion of other mixture calculation options. In that report a comparison of many theories of adsorbed vapor mixtures concluded that the Ideal Adsorbed Solution Theory combined with the Dubinin/Radushkevich isotherm equation is the best to use. However, calculations using these theories are complicated by requiring iterations instead of simple breakthrough time corrections for covapors (as above). An iterative computer program such as MultiVapor (CDC/NIOSH/NPPTL, 2015) is required (see next section).

EXTRAPOLATION AND INTERPOLATION USING COMPLEX MODELS

Complex predictive models (and their derived computer programs) have been developed and applied for estimating breakthrough times (Backman, 1997; DOL/OSHA, 2015; Wood and Snyder, 2007). They are based on Equation (1) and empirical equations for capacity W_e and adsorption rate coefficient k_v derived from fitting experimental data. Predictive models are those which do not require any breakthrough time data as inputs.

One such model for adsorption, MultiVapor, is available on the CDC/NIOSH/NPPTL (2015) website as a downloadable computer program. It improves on an earlier model (Wood, 1994) by including better established adsorption kinetics, all humidities, and possible covapors in the workplace. The current OSHA website has replaced the “Advisor Genius” calculator based on the earlier model with links to MultiVapor (DOL/OSHA, 2015). Several cartridge manufacturers have developed and posted applications of the earlier model for their products (see a list as Attachment 5 in DeCamp et al., 2004). MultiVapor has as input variables: vapor properties, carbon properties, and use conditions C_o , Q , RH , T , P_{atm} , and C_y (concentrations of up to 4 covapors).

Application: Breakthrough time prediction models can also be used with measured breakthrough time(s) to calculate t_b at untested conditions and even for covapors, other (surrogate) vapors, and other cartridges. The key is to “calibrate” the model or program. For example, with the MultiVapor program the steps would be:

- 1) Input as many vapor, cartridge, and use parameters corresponding to a measured breakthrough time as can be acquired.
- 2) If some of these parameters are not available, use best guesses (Wood and Snyder, 2004) or program default values for “typical cartridges” (Wood, 2009).
- 3) Do the calculation with MultiVapor, recognizing that it may initially yield a breakthrough time different from the measured one.
- 4) Adjust some model input parameters until the testing breakthrough time is reproduced by MultiVapor output. For capacity adjustments micropore volume W_o and, if necessary, polarizability P_e can be tweaked; for reproducing RH effects the water affinity coefficient β_{H_2O} is adjustable; for solubility S_b ; etc.
- 5) Then use the “calibrated” MultiVapor program with new input values to estimate breakthrough times for untested situations.

Some respirator manufacturers have modified predictive models in this way to better fit their products. For reactive removal of vapors there is another model and program, GasRemove (Wood, 2005). It can't be predictive since each removal reaction depends uniquely on the gas or vapor and what it reacts with. However, GasRemove is designed to summarize measured breakthrough times as a reactive

capacity parameter W_r which is derived as an empirical function of C_o and RH. For another set of C_o , RH, T, Q, and C_b , the appropriate W_r is inputted to the model to give an extrapolated t_b .

RULES OF THUMB

Four Rules of Thumb for estimating organic vapor cartridge service life were first cited in Chapter 36 of the American Industrial Hygiene Association (AIHA) publication "The Occupational Environment – its Evaluation and Control" (DiNardi, 1997). This publication cites the source as a Private Communication from Gary Nelson (1996). The bases of these generalizations were the extensive experimental studies and publications performed by Gary Nelson and others at the Lawrence Livermore Laboratory in the early 1970s (Nelson et al., 1972; 1974; 1976a; 1976b; 1976c). A subsequent report described additional work on the effects of vapor concentrations on cartridge breakthrough times (Nelson et al., 1980).

The four Rules of Thumb stated in this AIHA publication and its updates (DiNardi, 2003; Anna, 2011) are:

- 1) If the chemical's boiling point is $> 70^\circ\text{C}$ and the concentration is less than 200 ppm you can expect a service life of 8 hours at a normal work rate.
- 2) Service life is inversely proportional to work rate.
- 3) Reducing concentration by a factor of 10 will increase service life by a factor of 5.
- 4) Humidity above 85% will reduce service life by 50%.

The first rule provides a means of setting a minimum service life (an 8-hour work shift) if the chemical meets two conditions, minimum boiling point and maximum concentration. The other three provide means of extrapolating from one service life, experimental or calculated, to another at a different work rate, concentration, or humidity.

The second Rule of Thumb, "Service life is inversely proportional to work rate," will be examined first since it is required for discussion of the first Rule. What experimental data has actually shown is that the inverse proportionality of breakthrough time is to air flow rate, not work rate. In the summary paper of the Nelson et al. series it is stated,

"Figure 3 also shows that the breakthrough time is inversely proportional to flow rate. Thus halving the flow rate will essentially double the service life if the other conditions remain the same. We have observed no violations of the law during normal breathing conditions..." (Nelson et al., 1976c).

The conditions in which this was found to hold were both steady-state and pulsating flow (using a breathing simulator) and average breathing rates up to 75 L/min.

So, a correct statement of this second Rule of Thumb should be "Breakthrough time (service life) is inversely proportional to air flow rate."

Note that "work rate" and "air flow rate" are not proportional, as the original wording of the second rule would require. Silverman, et al. (1951) published a study of "Air Flow Measurements on Human Subjects with and without Respiratory Resistance at Several Work Rates". Figure 1 shows a plot of their results given in Table I for 6 mm water inspiratory and 3 mm water expiratory resistances. Clearly air flow rates are not proportional to work rates. An average subject is still breathing about 14 L/min at zero (sitting) work rate. An exponential fit ($y = 14.2 \exp[0.0015x]$) of this data provides a way of translating work rate x to air flow rate y . But how does one determine work rate for a specific job and person? Since it is even harder to measure work rate than air flow rate, Nelson and Correia (1976c) provided the category labels in Table I for six of Silverman's work levels and related breathing rates. Note: in earlier work Nelson and Harder (1974) categorized 53.3 L/min as corresponding to moderately heavy work rate.

How can one use this revised Rule of Thumb? 1) The work rate category can be estimated by observing the worker and the job. 2) The corresponding average air flow rate can be taken from the table or calculated from the formula. 3) Then a known breakthrough time for a certain air flow can be adjusted to the worker's average breathing rate. This inverse relationship can also be useful for adjusting data for analysis (as shown below).

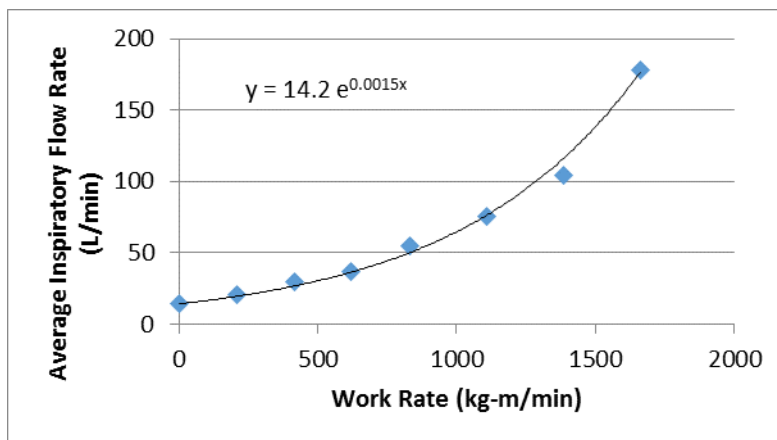


Figure 1. Average breathing rate as a function of work rate.

Table I. Work Rate Descriptions and Corresponding Average Breathing Rates

Work Rate Description	Work Rate (kg-m/min)	Average Breathing Rate (L/min)
per Nelson et al. (1976c)	per Silverman et al. (1951)	
Sitting	0	14.2
Light	208	20.8
Moderate	415	29.9
Moderately heavy	622	37.3
Heavy	830	54.7
Extremely heavy	1107	75.3
	1384	104
	1660	178

The first Rule of Thumb, "If the chemical's boiling point is $> 70^{\circ}\text{C}$ and the concentration is less than 200 ppm you can expect a service life of 8 hours at a normal work rate," has a glaring problem: What is a "normal work rate" with its corresponding average breathing rate? It's likely that for an entire 8-hour shift only an average moderate work rate (corresponding in Table I to an average 30 L/min) could be maintained. (This assumption will be used for calculations below). Higher average work rates could be maintained for shorter work periods and shorter cartridge change schedules.

How does this first Rule of Thumb hold up to the data? In the original data of Nelson et al. (summarized in 1976c) there is only one test below 200 ppm for a compound with a boiling point above

70 °C. It's for 125 ppm benzene (BP = 80.1 °C) with a breakthrough time of 5.9 hours at 53.3 L/min. This fails the Rule prediction, but passes (10.5 hours) when adjusted to 30 L/min. For a more extensive test of this Rule we can use data extrapolated to 200 ppm. Nelson et al. (1976a; 1980) reported linear plots of log (10% breakthrough time in min) vs. log (challenge concentration in ppm) for a variety of chemicals and cartridges. The best fit intercepts (A) and slopes (B) of such log-log plots are reproduced in Columns 13 and 14 of Table II. From these parameters 200 ppm breakthrough times have been extrapolated and listed in column 5 of the table. Column 6 shows that only 6 of the 17 chemicals with BP > 70 °C also have breakthrough times > 480 min (test passed) at the test air flow. When adjusted to a moderate work rate (30 L/min in column 7) still only 11 of the 17 pass the 480 min test (column 8). The conclusion is that even at a "normal (moderate) work rate" the first Rule of Thumb does not hold up very well.

Can this first Rule of Thumb be salvaged? Column 9 shows that if the breakthrough time is changed to 6 hours instead of 8 hours all the tests pass at adjusted 30 L/min air flow. Columns 10-12 show that if the 200 ppm criterion is reduced to 140 ppm for 8 hours all the 17 tests likewise pass. So, reliable restatements of this Rule could be:

1a) If the chemical's boiling point is > 70 °C and the concentration is less than 200 ppm you can expect a service life of 6 hours at a moderate work rate. Or,

1b) If the chemical's boiling point is > 70 °C and the concentration is less than 140 ppm you can expect a service life of 8 hours at a moderate work rate.

Caution: These rules come from data for chemicals that are removed by physical adsorption on carbon. They are not likely to apply to cases of reactive removal by reactions with carbon impregnants or adsorbed water. Also, these rules may not hold up as data for more chemicals become available. The unreliability for basing breakthrough time predictions on the single parameter, boiling point, is seen in the second data set in Table II where hexane and methanol have similar boiling points (69 and 65 °C, respectively) but very different 200 ppm extrapolated breakthrough times (383 and 7 min, respectively).

The third Rule of Thumb states, "Reducing concentration by a factor of 10 will increase service life by a factor of 5." This comes from an analysis of the first data set in Table II (Nelson et al., 1976a). Slopes B of base 10 log-log plots of 10% breakthrough time and concentration represent how much a change in concentration affects breakthrough time. For example, the first acetone data set with a pair of cartridges containing 62.2 g total carbon gave a slope B of -0.452 (column 14). This means that a concentration 10 times higher results in a breakthrough time $10^{0.452} = 2.8$ times lower (column 15). It seemed that these slopes could be averaged (-0.668 in column 14) and used to calculate a corresponding breakthrough time change of a factor of $10^{0.668} = 4.7$ (about 5) for a 10 times concentration change for a variety of chemicals (Nelson et al., 1976a). This is the source of the third Rule of Thumb.

Unfortunately, such parameter B averaging covers up the actual range of the concentration effects. The values of B in the first set of data in Table II range from -0.395 to -0.937, corresponding to factors of 2.5 to 8.6. Those in the second set of data (Nelson et al., 1980) range from -0.108 to -1.040, corresponding to factors of 1.3 to 11.0. Clearly, a factor of 5 does not represent all the chemicals and could lead to very erroneous concentration extrapolations for any one chemical. This makes this third Rule of Thumb totally useless.

Table II. Experimental Results of Nelson et al. (1976a; 1980) for Testing Rules of Thumb

Chemical	Boiling Point (°C)	Total Carbon Weight (g)	Air Flow Rate (L/min)	Extrapolated 10% Breakthrough Time at 200 ppm (min)	Test Passed at 8 hours	With Air Flow Adjusted to 30 L/min	Test Passed at 8 hours
Acetone	56	62.2	53.3	95		169	
Acetone	56	70.6	53.3	166		295	
Benzene	80	52.5	53.3	304	no	540	yes
Carbon Tetrachloride	77	52.5	53.3	230	no	409	no
Dichloromethane	40	52.5	53.3	44		78	
Diethylamine	55	52.5	53.3	113		201	
Hexane	69	52.5	53.3	274		487	
Hexane	69	70.6	53.3	317		563	
Isopropanol	83	52.5	53.3	227	no	403	no
Methyl acetate	57	52.5	53.3	104		185	
Methyl chloroform	74	52.5	53.3	252	no	448	no
Acetone	56	80	40	247		329	
Amyl acetate	149	80	40	453	no	604	yes
Butyl acetate	126	80	40	492	yes	656	yes
Chloroform	61	80	40	303		404	
Cyclohexane	81	80	40	334	no	445	no
Dichloromethane	40	80	40	136		181	
Dioxane	101	80	40	510	yes	680	yes
Ethanol	78	80	40	307	no	409	no
Ethylene dichloride	84	80	40	376	no	501	yes
Freon TF	118	80	40	273	no	364	no
Hexane	69	80	40	383		511	
Methanol	65	80	40	7		9	
Methyl cellosolve	124	80	40	903	yes	1204	yes
Methyl chloroform	74	80	40	456	no	608	yes
Methyl ethyl ketone	80	80	40	476	no	635	yes
Pentane	36	80	40	451		601	
Tetrahydrofuran	66	80	40	326		435	
Trichloroethylene	87	80	40	506	yes	675	yes
Toluene	111	80	40	607	yes	809	yes
m-Xylene	139	80	40	667	yes	889	yes
					6 of 17		11 of 17

Table II (continued).

Test Passed at 6 hours	Extrapolated 10% Breakthrough Time at 140 ppm (min)	With Air Flow Adjusted to 30 L/min	Test Passed at 8 hours	A	B	10 ^B	Chemical
	111	197		1.04E+03	-0.452	2.8	Acetone
	207	368		4.46E+03	-0.621	4.2	Acetone
yes	397	705	yes	1.56E+04	-0.743	5.5	Benzene
yes	292	519	yes	8.04E+03	-0.671	4.7	Carbon Tetrachloride
	50	89		3.53E+02	-0.395	2.5	Dichloromethane
	146	260		5.36E+03	-0.729	5.4	Diethylamine
	382	679		3.92E+04	-0.937	8.6	Hexane
	438	778		3.89E+04	-0.908	8.1	Hexane
yes	281	499	yes	5.53E+03	-0.603	4.0	Isopropanol
	126	225		1.84E+03	-0.542	3.5	Methyl acetate
yes	329	585	yes	1.30E+04	-0.744	5.5	Methyl chloroform
				Average	-0.668	4.7	
					Range	2.5 to 8.6	
	319	426		1.12E+04	-0.720	5.2	Acetone
yes	647	862	yes	9.10E+04	-1.001	10.0	Amyl acetate
yes	687	917	yes	6.98E+04	-0.935	8.6	Butyl acetate
	373	498		6.59E+03	-0.581	3.8	Chloroform
yes	448	598	yes	2.71E+04	-0.830	6.8	Cyclohexane
	163	218		1.99E+03	-0.506	3.2	Dichloromethane
yes	673	897	yes	3.16E+04	-0.779	6.0	Dioxane
yes	392	523	yes	1.17E+04	-0.687	4.9	Ethanol
yes	475	633	yes	1.19E+04	-0.652	4.5	Ethylene dichloride
yes	368	490	yes	2.30E+04	-0.837	6.9	Freon TF
	531	708		5.01E+04	-0.920	8.3	Hexane
	7	9		1.17E+01	-0.108	1.3	Methanol
yes	1215	1620	yes	7.38E+04	-0.831	6.8	Methyl cellosolve
yes	626	835	yes	5.09E+04	-0.890	7.8	Methyl chloroform
yes	660	880	yes	6.10E+04	-0.916	8.2	Methyl ethyl ketone
	635	847		7.26E+04	-0.959	9.1	Pentane
	421	561		1.44E+04	-0.715	5.2	Tetrahydrofuran
yes	666	887	yes	2.99E+04	-0.770	5.9	Trichloroethylene
yes	825	1100	yes	5.87E+04	-0.863	7.3	Toluene
yes	967	1290	yes	1.65E+05	-1.040	11.0	m-Xylene
				Average	-0.777	6.0	
17 of 17			17 of 17		Range	1.3 to 11.0	

The fourth Rule of Thumb states, "Humidity above 85% will reduce service life by 50%." This again comes from Lawrence Livermore studies of humidity effects (Nelson et al., 1976b; 1976c). Looking at tabulated averages of effects reveals that "humidity" in this statement refers to cartridges that have been preconditioned at and then tested at 80-90% RH. The data were only obtained for 1000 ppm. The authors state,

"It must be emphasized that these factors were determined from a rather small cross section of solvent vapors and cartridge types as well as only one concentration. At lower concentrations past data...indicate that these multiplication factors increase as the concentration decreases below 1000 ppm" (Nelson et al., 1976b).

Furthermore, humidity effects greater than those reported by Nelson et al. (1976b) have been observed for other carbon types and vapors (Wood, 1987; Werner, 1985; Jonas, 1975). These effects start below 85% RH. Neglecting other important parameters (e.g., vapor type and concentration, carbon type and preconditioning) makes the fourth Rule of Thumb too simplistic to be useful.

CONCLUSIONS

Decades of measuring breakthrough times of air-purifying chemical respirator cartridges and the carbons they contain have resulted in many correlations expressed as equations and Rules of Thumb. Some correlations can be predicted from a theoretical equation; others are simply empirical. Such correlations, if verified by sufficient data, allow breakthrough time measurements for selected testing conditions to be interpolated and extrapolated to untested conditions. One set of Rules of Thumb has been shown to be of questionable usefulness without modifications.

REFERENCES

- Ackley MW. (1985) Residence Time Model for Respirator Sorbent Beds, *Am. Ind. Hyg. Assoc. J.* 46:679-689.
- Anna, DH, editor. (2011) The Occupational Environment – Its Evaluation, Control, and Management. 3rd edition, American Industrial Hygiene Association, Falls Church, VA.
- Backman L. (1997) The Practical Use of Some Existing Models for Estimating Service Life of Gas Filters, presented at the 1997 International Society for Respiratory Protection Conference, Amsterdam, Netherlands. Available online at <http://www.sea.com.au/docs/papers/isrplb1.pdf>.
- CDC/NIOSH/NPPTL. [Centers for Disease Control and Prevention/National Institute for Occupational Safety and Health/National Personal Protection Testing Laboratory]: (2015) MultiVapor Version 2.2.3 Application, website <http://www.cdc.gov/niosh/npptl/multivapor/multivapor.html>.
- DeCamp DS, Constantino J, and Black JE. (2004), Estimating Organic Vapor Cartridge Service Life, IOH-RS-BR-SR-2005-0005, U.S. Air Force Institute for Operational Health. Available from NTIS and DTIC.
- DiNardi SR, editor.(1997) The Occupational Environment – Its Evaluation and Control, Chapter 36, "Respiratory Protection," 988-999, American Industrial Hygiene Association Press, Falls Church VA.
- DiNardi SR, editor. (2003) The Occupational Environment – Its Evaluation and Control, 2nd edition, American Industrial Hygiene Association Press, Falls Church, VA.
- DOL/OSHA [U.S. Department of Labor/Occupational Safety & Health Administration]. (1998) Instruction Directive Number CPL 2-0, 120, Inspection Procedures for the Respiratory Protection Standard.
- DOL/OSHA. (2015) Respiratory Protection eTool, Respirator Change Schedules, website: https://www.osha.gov/SLTC/etools/respiratory/change_schedule.html.
- Jonas LA and Rehrmann JA. (1973) Predictive Equations in Gas Adsorption Kinetics, *Carbon* 11:59-64.
- Jonas LA, Boardway JC, and Meseke EL. (1975) Prediction of Adsorption Behavior of Activated Carbons,

- Journal of Colloid and Interface Science* 50:538-544.
- Jonas LA, Sansone EB, and Farris TS. (1983) Prediction of Activated Carbon Performance for Binary Vapor Mixtures, *Am. Ind. Hyg. Assoc. J.* 44:716-719.
- Moyer ES. (1987) Organic Vapor (OV) Respirator Cartridge Testing – Potential Jonas Model Applicability, *Am. Ind. Hyg. Assoc. J.* 48:791-797.
- Nelson GO, and Harder CA. (1972) Respirator Cartridge Efficiency Studies IV. Effects of Steady-State and Pulsating Flow, *Am. Ind. Hyg. Assoc. J.* 33:797-805.
- Nelson GO, and Harder CA. (1976a) Respirator Cartridge Efficiency Studies VI. Effect of Concentration, *Am. Ind. Hyg. Assoc. J.* 37:205-216.
- Nelson GO, Correia AN, and Harder C. (1976b) Respirator Cartridge Efficiency Studies VII. Effect of Relative Humidity and Temperature, *Am. Ind. Hyg. Assoc. J.* 37:280-288.
- Nelson GO, and Correia AN. (1976c) Respirator Cartridge Efficiency Studies: VIII, Summary and Conclusions, *Am. Ind. Hyg. Assoc. J.* 37: 514-525.
- Nelson GO, Carlson GJ, and Johnson JS. (1980) Service Life of Respirator Cartridges at Various Concentrations of Common Organic Solvents, Report UCRL-52982, Lawrence Livermore Laboratory, Livermore, CA.
- Nelson GO. (1996) Rules of Thumb for Cartridge Service Life, July 29, 1996. [Private Communication]. Miller-Nelson Research, 8 Harris Court, Suite C-6, Monterey, CA 93940.
- Robbins CA and Breyse PN. (1996) The Effect of Vapor Polarity and Boiling Point on Breakthrough for Binary Mixtures on Respirator Carbon, *Am. Ind. Hyg. Assoc. J.* 57:717-723.
- Silverman L, Lee G, Plotkin T, Sawyers LA, and Yancey AR. (1951) Air Flow Measurements on Human Subjects With and Without Respiratory Resistance at Several Work Rates, *A.M.A. Arch. Ind. Hyg. Occup. Med.* 3:461-478.
- Swearingen PM and Weaver SC. (1988) Respirator Cartridge Study Using Organic Vapor Mixtures, *Am. Ind. Hyg. Assoc. J.* 49:70-74.
- Werner, MD (1985) The Effects of Relative Humidity on the Vapor Phase Adsorption of Trichloroethylene by Activated Carbon, *Am. Ind. Hyg. Assoc. J.* 46:585-590.
- Wood GO. (1985) Effects of Air Temperatures and Humidities on Efficiencies and Lifetimes of Air-Purifying Chemical Respirator Cartridges Tested Against Methyl Iodide, *Am. Ind. Hyg. Assoc. J.* 46:251-256.
- Wood GO (1987) A Model for Adsorption Capacities of Charcoal Beds I. Relative Humidity Effects, *Am. Ind. Hyg. Assoc. J.* 48:622-625.
- Wood GO and Moyer EM. (1989) A Review of the Wheeler Equation and Comparison of Its Applications to Organic Vapor Respirator Cartridge Breakthrough Data, *Am. Ind. Hyg. Assoc. J.* 50:400-407.
- Wood GO. (1993) Organic Vapor Respirator Cartridge Breakthrough Curve Analysis, *J. Int. Soc. Resp. Prot.* 10:5-17.
- Wood GO. (1994) Estimating Service Lives of Organic Vapor Cartridges, *Am. Ind. Hyg. Assoc. J.*, 55: 11-15.
- Wood GO (2000) Reviews of Models for Adsorption of Single Vapors, Mixtures of Vapors, and Vapors at High Humidities on Activated Carbon for Applications Including Predicting Service Lives of Organic Vapor Respirator Cartridges, Report LA-UR-00-1531, Los Alamos National Laboratory, Los Alamos, NM.
- Wood GO, and Lodewyckx P. (2003) An Extended Equation for Rate Coefficients for Adsorption of Organic Vapors and Gases on Activated Carbons in Air-Purifying Respirator Cartridges, *Am. Ind. Hyg. Assoc. J.* 64:646-650.
- Wood GO and Snyder JL. (2004) Estimating Service Lives of Organic Vapor Cartridges II: A Single Vapor at All Humidities, *J. Occup. Environ. Hyg.*, 1: 472-492. See Appendix.
- Wood GO. (2005) Estimating Service Lives of Air-Purifying Respirator Cartridges for Reactive Gas Removal, *J. Occup. Environ. Hyg.*, 2:414-423. A downloadable program, GasRemove, for such estimates with parameters for a variety of common gases has been submitted to NPPTL for online publication. In the meantime it is available at www.GerryOWood.com.
- Wood GO and Snyder JL. (2007) Estimating Service Lives of Organic Vapor Cartridges III: Multiple Vapors at All Humidities, *J. Occup. Environ. Hyg.*, 4: 363-374.

-
- Wood GO. (2009) D-R Plots and Typical Parameters for Several OV and Multigas Cartridges and Canisters, *J. Int. Soc. Resp. Prot.* 26:71-81.
- Yoon HY and Nelson JH. (1984) Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life, *Am. Ind. Hyg. Assoc. J.* 45:509-516.
- Yan X and Su X. (2009) Linear Regression Analysis: Theory and Computing, World Scientific Publishing Company, Pte. Ltd., Singapore.
- Yoon HY. (1996) Respirator Cartridge Service-Life: Exposure to Mixtures, *Am. Ind. Hyg. Assoc. J.* 57:809-819.