D-R Plots and Typical Parameters for Several OV and Multigas Cartridges and Canisters

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ABSTRACT

Dubinin-Radushkevich (D-R) plots have been prepared from published data and measurements for several organic vapor air-purifying respirator cartridges or the carbons they contain: 3M 6001, 3M 7251, MSA GMA-OV, MSA GMC-H, MSA GME-H, North N7500-1, Scott 642-OV, Willson T01, Survivair 100100, and the CBRN C2A1 with ASZM-TEDA impregnated carbon. Such plots provide micropore volumes and benzene-reference adsorption potentials for service life estimation models and computer programs such as Breakthrough and MultiVapor. Typical parameters for OV cartridges and multigas canisters have been developed for approximations when carbon bed and D-R parameters are not readily available for particular items.

Keywords: air-purifying, organic vapor, respirator, cartridge, canister, parameter

INTRODUCTION

Adsorption capacity of an air-purifying respirator cartridge carbon bed for organic vapor (or gas) must be known to estimate service life and set a changeout schedule. Adsorption capacity is a measure of how much vapor an adsorbent can contain at a certain set of conditions. It depends on vapor concentration, temperature, properties of the vapor, and properties of the adsorbent.

The Dubinin-Raduskevich (D-R) adsorption equation describes adsorption of organic vapors on microporous activated carbons, such as are found in air-purifying respirator organic vapor (OV) cartridges or multigas (chemically impregnated carbon) canisters:

$$\ln\left(\frac{W_e}{d_L}\right) = \ln\left(W_o\right) - \left[\left(\frac{R\,T}{\beta E_o}\right)\ln\left(\frac{p_{sat}}{p}\right)\right]^2 \qquad (1)$$

where W_e (g/g) is the equilibrium carbon capacity for the vapor,
W_o (cm^3/g) is the micropore volume of the carbon, and
E_o (kJ/mol) is its adsorption potential (relative to benzene);
d_L (g/cm^3) is the liquid density of the adsorbate,
β is its affinity coefficient (relative to benzene), and
p_{sat} is its vapor pressure at temperature T (^{o}K),
p is the vapor pressure (concentration) in units of p_{sat} and
R is the ideal gas constant in units of E_o (0.0083145 kJ/mol).

Two parameters of this equation, micropore volume W_o and adsorption potential E_o, are characteristics of the carbon used. They are required inputs to the Breakthrough (Wood, 2004) and

MultiVapor (Wood and Snyder, 2007) models and service life estimation computer programs (NIOSH, 2005 and 2009) and adaptations (e.g., 3M, 2008, and Cossement, 2008) of an earlier version of Breakthrough (Wood, 1994). A linear D-R plot of the above equation yields these parameters from the exponential of the intercept and the reciprocal square root of the slope:

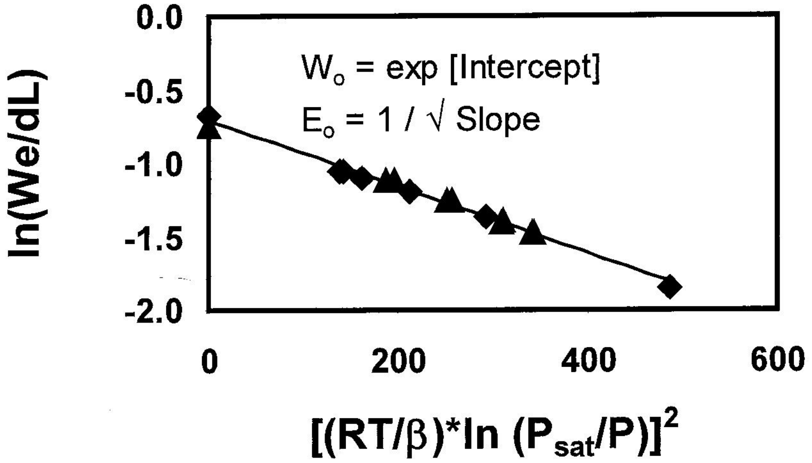

Figure 1. An example of a D-R plot and how to obtain parameters from it.

Saturation vapor pressures are readily available for most common chemicals. Affinity coefficients (relative to benzene) have been tabulated and correlated (Wood, 2001). For this work the following correlation with molar polarizability P_e has been used: $\beta = P_e^{0.75}$ (Wood, 2004 and 2007).

Capacities W_e at selected concentrations (p in pressure units) can be obtained by the following four experimental methods and plotted to extract parameters. Important: Measurements should be done at the driest conditions to remove the influences of adsorbed and vaporous water. Supplemental studies at high humidities are useful for defining the effects of water and summarizing them as a water affinity coefficient β_{H20} (Wood, 2004).

MEASUREMENTS AND PLOTS

Static Equilibrium

The simplest measurement of equilibrium capacity is done in a closed container. Vapor concentration is controlled or measured after equilibration. The carbon sample is weighed initially and at increasing exposure times until a constant weight is reached.

For example, in a study at the Los Alamos National Laboratory (Wood, 1997) researchers weighed duplicate samples of carbons from MSA GMC-H, MSA GME-H, and C2A1-TEDA (ASZM-TEDA) canisters were placed in sealed glass jars along with open containers of either liquid hexane or liquid ethyl acetate. Vapor saturation and adsorption equilibration required a week to obtain constant weights. The liquids were then removed and the jars were flushed with air and resealed. Vapor loss and desorption resulted in a lower equilibrium vapor concentration and corresponding lower adsorption capacity of vapor on carbon. The equilibrium vapor concentration was measured with an infrared spectrometer after several weeks of reweighings. This process was repeated several times to get capacities at lower vapor concentrations.

D-R plots of the results of these experiments for the MSA GMC-H and GME-H carbons are shown in Figures 2 and 3. They resulted in the parameters listed in Tables I and II. The ASZM-TEDA results will be shown later (Figure 9).

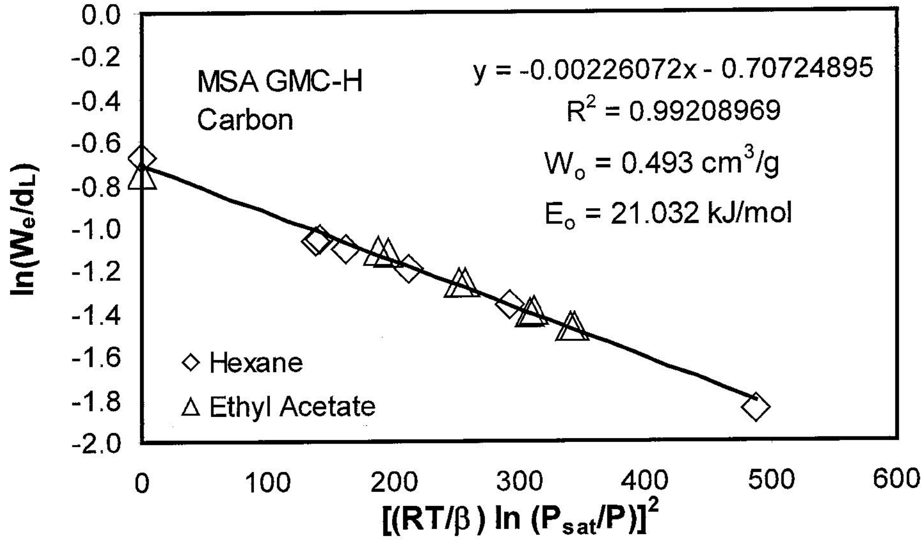

Figure 2. D-R Plot for MSA GMC-H carbon.

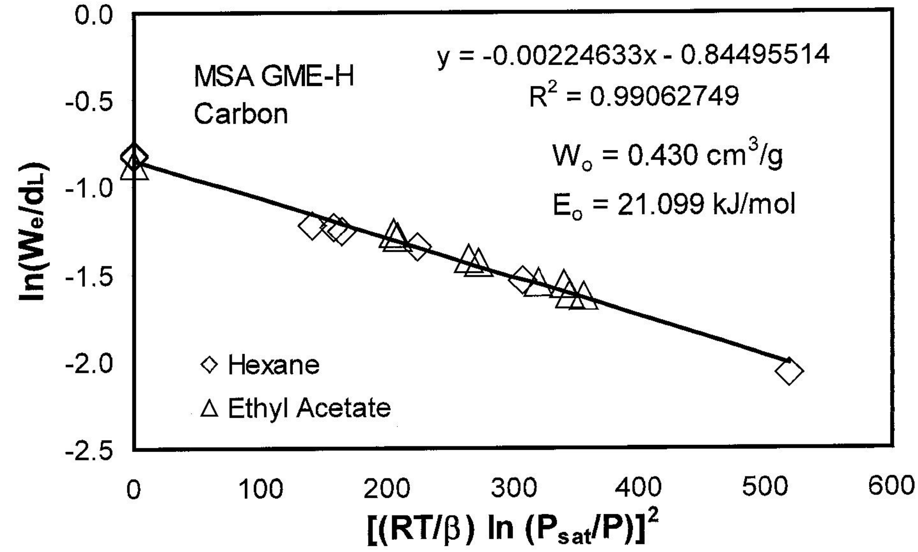

Figure 3. D-R plot for MSA GME-H carbon.

Dynamic Saturation

The next best method is to equilibrate the carbon bed with a flow of vapor in air at a controlled concentration and temperature. The effluent from the bed is monitored with some instrument until the vapor breakthrough concentration reaches the influent vapor concentration. A plot of these breakthrough concentrations vs. time is a full breakthrough curve (Figure 4). An advantage of this method is that the carbon can be left in the cartridge; however, an empty cartridge body must be weighed and subtracted to get the initial and final bed weights to calculate the correct equilibrium capacity.

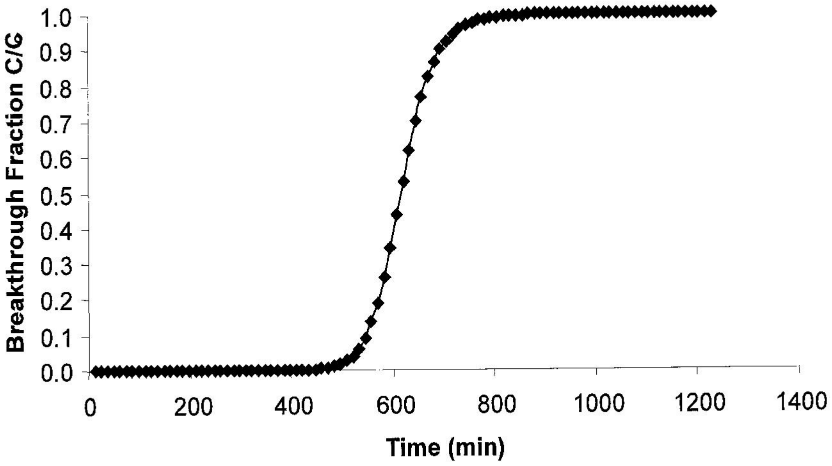

Figure 4. A full breakthrough curve example.

An example of this method is from measurements of equilibrium capacities of 6 commercial OV cartridges with 10 vapors at about 500 ppm (Cossement et al., 2008). Note that the vapor can be a variable instead of or in addition to the challenge concentration. Figure 5 shows the D-R plot for a Willson T01 cartridge from this data. The other five plots were equally good. Resulting D-R parameters for all six cartridges are listed in Table I.

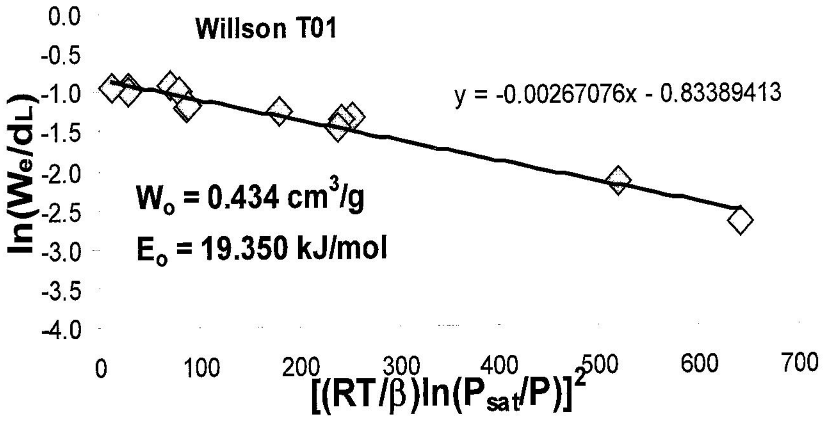

Figure 5. D-R Plot for a Willson T01 cartridge.

Table I. D-R Parameters for OV (only) Cartridges

Cartridge	Micropore Volume W_o (cm^3/g)	Adsorption Potential E_o (kJ/mol)
MSA GMC-H	0.493	21.032
3M 7251	0.783	15.862
3M 6001	0.584	19.063
MSA GMA-OV	0.526	18.381
North N7500	0.526	18.516
Scott 642-OV	0.563	18.462
Willson T01	0.434	19.350
Survivair 100100	0.571	18.406

Breakthrough Curve Midpoint Time

A third method can be used if only half the breakthrough curve or the 50% breakthrough time $t_{50\%}$ is measured. The stoichiometric center of the breakthrough curve can be obtained by integrating the entire breakthrough curve. Only if the breakthrough curve is completely symmetrical (rare) is the stoichiometric time t_{sto} equal to the time at 50% breakthrough; however, this is often a good approximation. Capacity (g/g carbon) is calculated by the equation:

$$W_e = C_o \, Q \, t_{sto} / W \qquad (2)$$

where C_o is the challenge concentration in gravimetric units (g/m^3), Q (m^3/min) is the airflow rate, W (g) is the weight of carbon, and t_{sto} is in minutes.

An example of this is the calculation of capacities of 6 vapors on a 3M 7251 cartridge from breakthrough curve midpoints (Wood and Snyder, 2007). The resulting D-R plot is Figure 6 with parameters shown on the graph and listed in Table I.

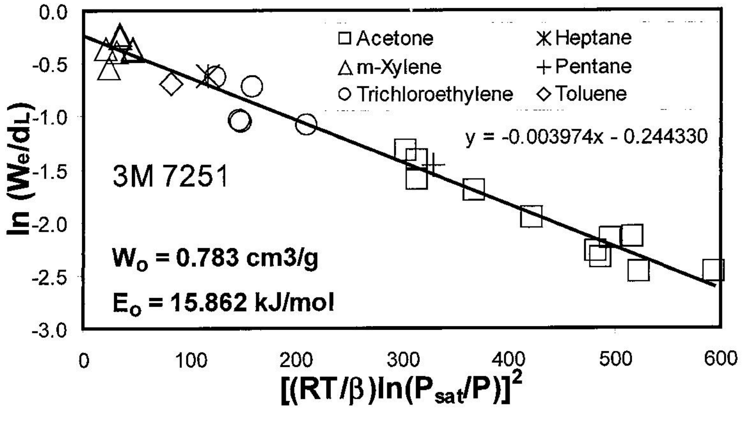

Figure 6. D-R plot for 3M 7251 cartridge.

Earlier Breakthrough Time

The least desirable, but most common, measurement is of the time to reach a selected breakthrough concentration or fraction of the challenge concentration below 50%. When this is all the information available, the stoichiometric time must be obtained by extrapolating from the earlier time (Figure 7). An adsorption rate model or equation must be chosen to do this.

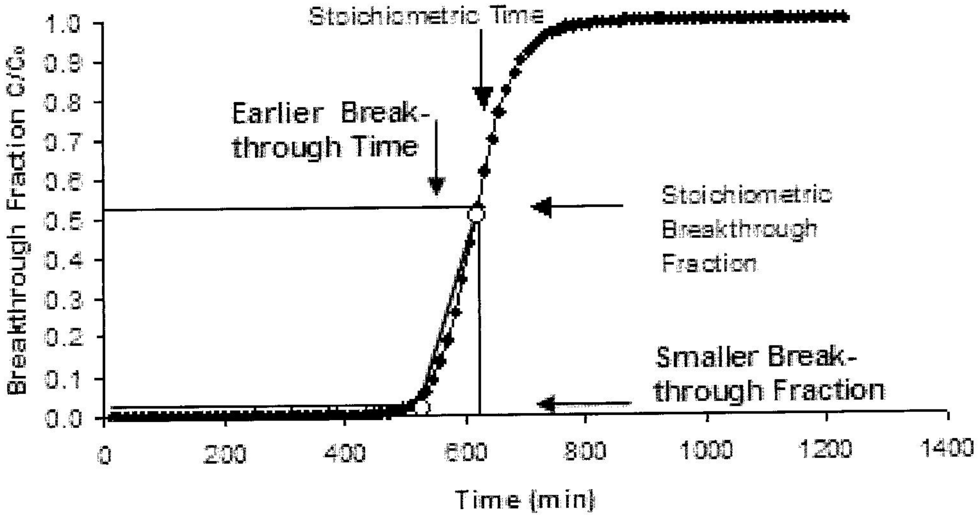

Figure 7. Breakthrough curve characteristics and extrapolation.

This is the least desirable method because it depends on uncertain kinetics. The further the extrapolation is, the more the possible error. For this reason, breakthrough times for breakthrough fractions less than 1% should not be used for this purpose.

In the following examples the adsorption kinetics and affinity coefficient correlation inherent in the Breakthrough (Wood, 2004) and MultiVapor (Wood, 2007) models and service life computer programs have been assumed. The procedure is this: After all other parameters have been entered into the MultiVapor program (NIOSH, 2009) and a tentative breakthrough time calculated, the micropore volume input value is varied until the experimental breakthrough time is reproduced. The breakthrough concentration is changed to half the challenge and the corresponding $t_{50\%}$ (approximate t_{sto}) is calculated by the program. The model output is compared to the experimental data to see if it still matches or is close. Then Equation (2) is used to obtain the capacity and one point on the D-R plot. (This is a tedious process that is planned to be made simpler in a future version of the MultiVapor software.)

The first example of this procedure is with data reported for a multigas, impregnated-carbon canister, ABC-SF90 containing PLW K 14x35 T carbon (Lavanchy 2005). One percent breakthrough (10 ppm) times were given for 39 vapors at 1000 ppm and 70% relative humidity. Other cartridge and test condition parameters were helpfully reported. Figure 8 shows the D-R plot obtained for 35 of these vapors. Not shown are the data for formic acid, acetic acid, propionic acid, and methanol, which were very significant outliers for unknown reasons.

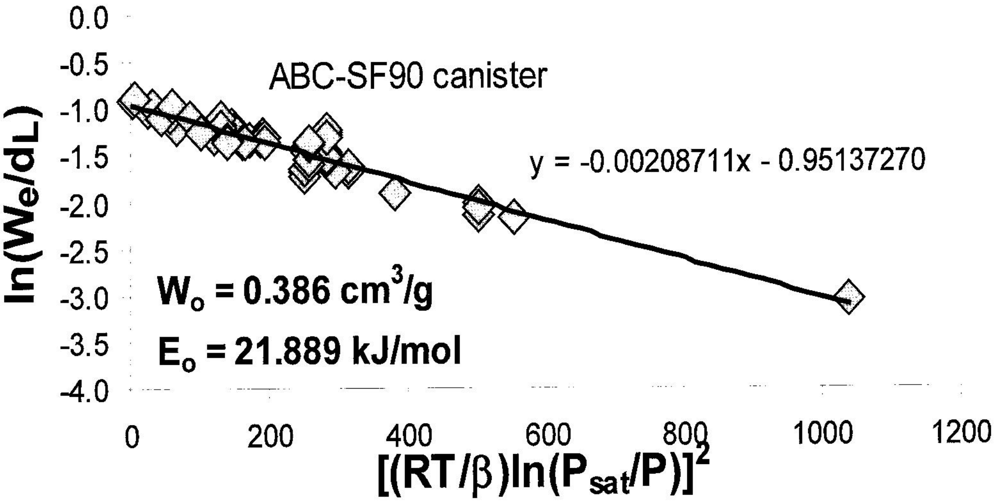

Figure 8. D-R plot for the ABC-SF90 canister.

The final example uses breakthrough time data from tests with ASZM-TEDA carbon, which is impregnated to remove reactive gases as well as nonreactive organic vapors. U.S. Army Dugway Proving Ground studies (Woolery, 2008) used Freon-12 (dichlorodifluoromethane) as the test gas with C2A1 CBRN canisters containing ASZM-TEDA carbon. Temperature, concentration, flow rate, and humidity were varied. Reported times for 10% breakthrough at only the driest conditions (21.6-23.9% RH) were used here. Extrapolations to 50% breakthrough times for calculations of capacities were done using the MultiVapor program.

Figure 9 shows the D-R plot for ASZM-TEDA carbon using this data source plus the Los Alamos National Laboratory results (Wood, 1997) discussed above. They are in good agreement, together covering a wide range and giving the D-R parameters in Table II.

Table II. D-R Parameters for Multigas Cartridges and Canisters

Cartridge	Micropore Volume W_o (cm^3/g)	Adsorption Potential E_o (kJ/mol)
CBRN (ASZM-TEDA Carbon)	0.409	20.366
ABC-SF90 (PLW K 14x35 Carbon)	0.386	21.889
MSA GME-H	0.430	21.099

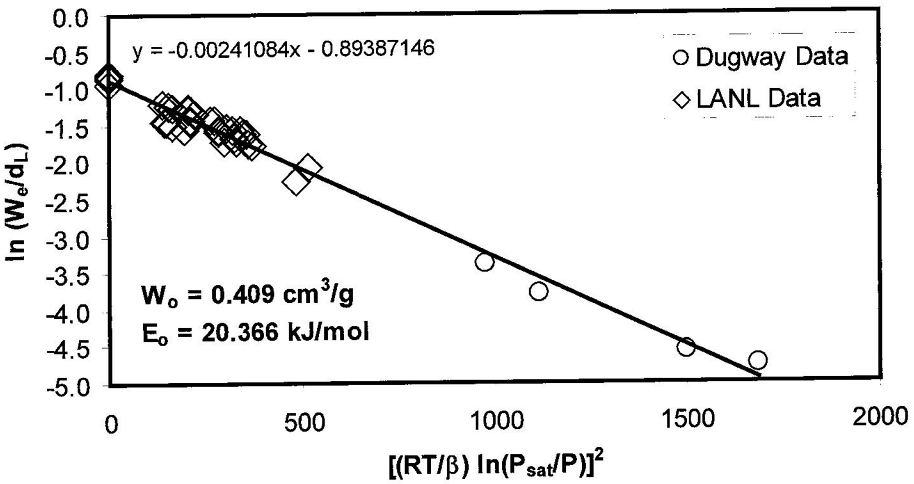

Figure 9. D-R plot for ASZM-TEDA carbon.

Typical OV Cartridge Parameters

There are times when the D-R and physical parameters for a particular OV cartridge or canister are not readily available, but are needed for a purpose such as rough service life estimation to decide on applicability. It would be useful to have available "typical" parameters for an approximate calculation. Table III shows the carbon bed parameters measured for 6 brands of OV cartridges (Cossement et al., 2008) and typical values derived from their averages.

Table III. Carbon Bed Parameters for Six OV Cartridges

Cartridge	Bed Diameter (cm)	Depth (cm)	Average Carbon Weight (g)
Willson T01	7.7	2.6	58.9
North N7500	7.5	2.3	44.1
Scott 642-OV	8.0	2.3	49.6
MSA GMA-OV	7.3	2.3	42.2
3M 6001	9.0	1.8	46.4
Survivair 100100	8.2	2.2	45.9
Typical (Average):	**8.0**	**2.2**	**47.8**

When the dynamic saturation data for all six cartridges and ten vapors are combined in a D-R plot (Figure 10) the resulting typical D-R parameters are: W_o = 0.533 cm^3/g and E_o = 18.666 kJ/mol.

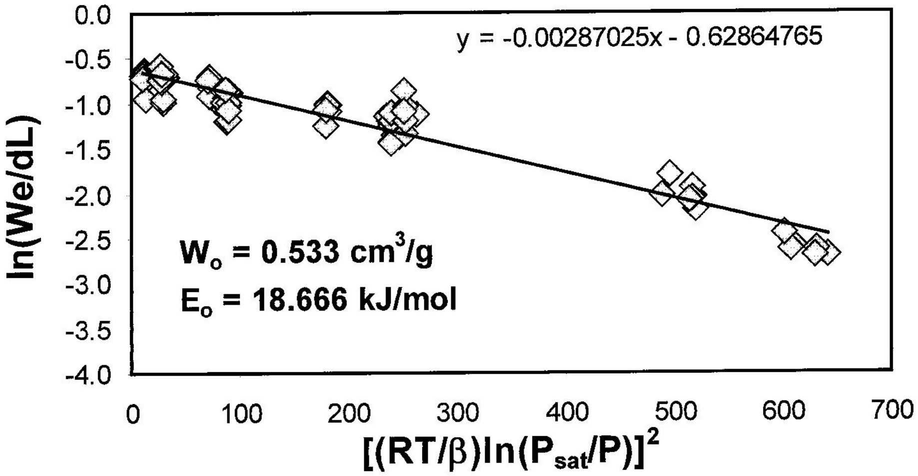

Figure 10. Combined D-R plot for 6 OV cartridges.

When these typical physical and typical D-R parameters are used in the MultiVapor (NIOSH 2009) model to estimate breakthrough times (service lives) for the original experimental conditions (Cossemant et al., 2008), the good agreement shown in Figure 11 results. Other assumptions were water affinity coefficient β_{H2O} = 0.06, carbon granule diameter = 0.11 cm, and carbon preconditioned at 20% RH.

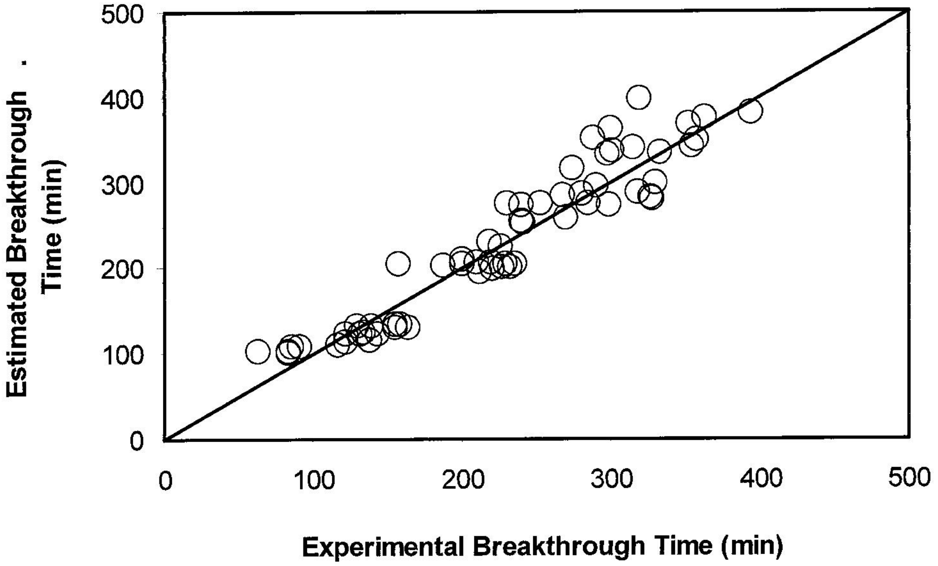

Figure 11. Comparison of estimated and experimental breakthrough times for 6 OV cartridges and 10 vapors calculated using typical cartridge bed and typical D-R parameters.

Typical Multigas Canister Parameters

Table IV shows the carbon bed parameters reported for two canisters with impregnated carbons and typical values derived from their averages. Water affinity coefficients (β_{H2O}) were calculated by this author. The data used to plot Figures 3, 8, and 9 for three impregnated carbons were combined in Figure 12 to obtain typical D-R parameters for impregnated (multigas) cartridges and canisters: W_o = 0.404 cm^3/g and E_o = 20.784 kJ/mol.

Table IV. Carbon Bed Parameters for Two Multigas Cartridges and Canisters

Cartridge	Data Source	Bed Diameter (cm)	Depth (cm)	Average Carbon Weight (g)	Average Granule Diameter (cm)	β_{H20}
C2A1 CBRN	Woolery 2008	10.4	2.2	112.0	0.11	0.14
ABC-SF90	Lavanchy 2005	10.8	2.2	110.0	0.10	0.03
Typical (Average):		**10.6**	**2.2**	**111.0**	**0.11**	**0.09**

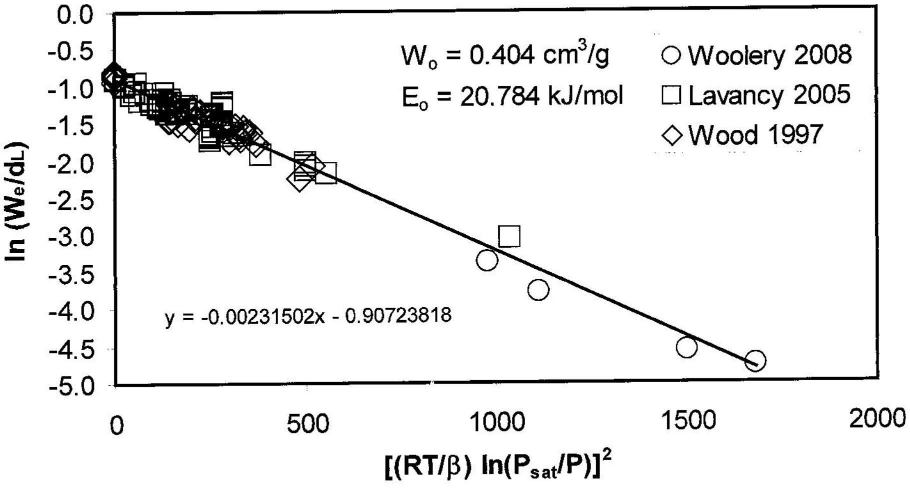

Figure 12. Combined D-R plot for three impregnated (multigas) carbons.

CONCLUSIONS

D-R plots can be derived from several types of data to produce parameters for estimating adsorption capacities of respirator carbons and cartridges for organic vapors. Typical parameters for OV cartridges and multigas canisters were derived by combining these data.

REFERENCES

3M Occupational Health & Environmental Safety Division (2008) 3M Service Life Software (Version 4.0) St. Paul, MN, USA. Available at http://csrv.3m.com/csrv/ .

Cossement D et al. (2008) Mise au point et validation d'un outil de calcul du temps de service des cartouches filtrantes pour vapeurs organiques, Rapport R-542, l'Institut de recherche Robert-Sauvé en santé et en sécurité du travail, Montreal, Quebec, Canada.

Lavanchy A et al. (2005) Prediction of Filter Performances against Organic Vapours: Statistical Analysis of Breakthrough Times as a Basis for a Simple Prediction Model. *JISRP* 22: 71-78.

NIOSH (2005) Breakthrough 2004. Publication No. 2005-125. CDC/National Institute for Occupational Safety and Health, Pittsburgh, PA. Available at http://www.cdc.gov/niosh/docs/2005-125/ .

NIOSH (2009) MultiVapor Version 2.1.3. CDC/NIOSH/National Personal Protective Technology Laboratory, Pittsburgh, PA. Available at http://www.cdc.gov/niosh/npptl/multivapor/multivapor.html .

Wood GO (1994) Estimating Service Lives of Organic Vapor Cartridges. *Am. Ind. Hyg. Assoc. J.* 55:11-15

Wood GO (1997) Unpublished data. Los Alamos National Laboratory, Los Alamos, NM, USA.

Wood GO (2001) Affinity Coefficients of the Polanyi/Dubinin Adsorption Isotherm Equations: A Review with Compilations and Correlations. *Carbon* 39:343-356.

Wood GO (2004) Estimating Service Lives of Organic Vapor Cartridges II: A Single Vapor at All Humidities. *J. Occup. Environ. Hyg.* 1:472-492.

Wood GO and Snyder JL. (2007) Estimating Service Lives of Organic Vapor Cartridges III: Multiple Vapors at All Humidities. *J. Occup. Environ. Hyg.* 1:472-492.

Woolery DO et al. (2008) Parameter Sensitivity of the C2A1 Filter and Data Comparisons with Four Filter Models. *JISRP* 25: 9-26.