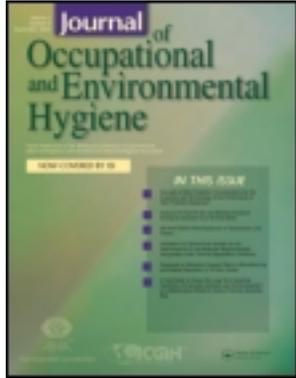


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Gerry O. Wood<sup>a</sup> & Jay L. Snyder<sup>b</sup>

<sup>a</sup> Consultant, Los Alamos, New Mexico

<sup>b</sup> National Institute for Occupational Safety and Health/Centers for Disease Control and Prevention/Department of Health and Human Services (NIOSH/CDC/DHHS), National Personal Protective Technology Laboratory, Pittsburgh, Pennsylvania

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# Estimating Reusability of Organic Air-Purifying Respirator Cartridges

Gerry O. Wood<sup>1</sup> and Jay L. Snyder<sup>2</sup>

<sup>1</sup>Consultant, Los Alamos, New Mexico

<sup>2</sup>National Institute for Occupational Safety and Health/Centers for Disease Control and Prevention/Department of Health and Human Services (NIOSH/CDC/DHHS), National Personal Protective Technology Laboratory, Pittsburgh, Pennsylvania

*Reuse of organic vapor air-purifying respirator cartridges after a job or shift can provide economy and energy savings. However, standards and manufacturers' guidance discourage reuse, presumably due to a lack of quantitative objective exposure and use information. Storage and simulated reuse laboratory studies and modeling have been done to provide such information. Two important parameters of breakthrough curves, midpoint time (related to adsorption capacity) and midpoint slope (related to adsorption rate), have been shown to be unchanged during storage for reuse. Extrapolations to smaller breakthrough concentrations and times can be made from this reference breakthrough and time. Significant step increases in breakthrough concentration upon cartridge reuse have been observed in some cases. Values of immediate breakthrough concentrations upon reuse (IBURs) have been measured and correlated. The Dubinin/Radushkevich adsorption isotherm equation has been used to estimate maximum IBURs, which depend on many factors, including conditions and duration of first use. An empirical equation describing rate of approach to maximum IBUR as a function of storage time has been developed to provide intermediate IBUR estimates, which are also very dependent on the vapor identity and extent of first-use loading. Using these equations, IBUR estimates with appropriate safety factors can be compared with the allowable breakthrough concentration to help the Industrial Hygienist make reusability decisions.*

**Keywords** air-purifying, cartridge, organic vapor, reusability, reuse

Correspondence to: Gerry Wood, 40 San Juan Street, Los Alamos, NM 87544.; e-mail: GerryConsulting@cs.com.

The findings and conclusions in this publication have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy.

## INTRODUCTION

After using an organic vapor (OV) air-purifying respirator (APR) cartridge for one job or shift, an obvious question

is, “Can I use it again?” Work practices or regulations may preclude reuse, but are these based on lack of knowledge or on objective information? As an extreme example, suppose a worker enters a workplace wearing a respirator with an APR cartridge whose service life for the measured workplace conditions is estimated to exceed 480 min. After 10 min he realizes he needs a tool that he cannot get until tomorrow and exits the contaminated environment. Must he throw away the barely used cartridge or can he continue to use it tomorrow?

Besides convenience, other benefits of reusing respirator cartridges, if demonstrated to be safe, are that it minimizes (1) waste disposal costs and environmental impact, (2) manufacturing costs and associated energy uses, and (3) purchasing costs and time.

## REGULATORY BACKGROUND

In the *Code of Federal Regulations* (29 CFR 1910.134) the Occupational Safety and Health Administration (OSHA) requires a cartridge/canister change schedule based on “objective information,” if the respirator does not have an end-of-service-life indicator.<sup>(1)</sup> This does not seem to preclude reuse; however, several of OSHA’s chemical specific standards go further. For example, with acrylonitrile (29 CFR 1910.1045) the change requirement is “end-of-service life or end of shift (whichever comes first).”<sup>(2)</sup> In a Compliance Directive (CPL 2-0.120)<sup>(3)</sup> OSHA states,

“... some contaminants have a tendency to migrate through cartridge/canister sorbent material during periods of storage or non-use. This is a characteristic of the contaminant-carbon bed interaction for organic chemicals with boiling points below 65 Centigrade and would predictably shorten breakthrough times. In cases where respirators are used for multiple days this could present an additional exposure to the respirator user. Where contaminant migration is possible, respirator cartridges/canisters should be changed after every workshift where exposure occurs unless the employer has specific objective data to

the contrary (desorption studies) showing the performance of the cartridge in the conditions and schedule of use/non-use found in the workplace.”

The British and European Standard (BS EN 14387:2004) allows reuse based on vapor boiling point (BP) or passing an adsorption test.<sup>(4)</sup> Gas filter (cartridge) Type A for organic gases and vapors with BP > 65°C are “not limited to single use.” Type AX for organic gases and vapors with BP ≤ 65°C are for “single use only.” Type SX developed for specific gases and vapors (organic or not) must pass a desorption test consisting of half loading, 3-day storage, and 2-hr clean airflow with no breakthrough.

The American National Standards Institute (ANSI Z88.2-1992) recommends desorption studies unless cartridges are changed daily.<sup>(5)</sup>

A major respirator manufacturer states, “Always use a new canister/cartridge(s). Do not re-use the canister/cartridge(s).” For powered APRs, “DO NOT reuse cartridges. Cartridges are intended for one time use only.”<sup>(6,7)</sup>

The goals of the work reported here have been (1) to obtain “objective information” to replace uncertainties, rules of thumb, and unknowns about reusability; (2) to understand how storage and reuse affect the protection of APR OV cartridges; and (3) to predict reusability and service life remaining upon reuse.

## TECHNICAL BACKGROUND

Wood and Kissane<sup>(8,9)</sup> carried out experimental studies of effects of storage between cartridge exposures at the Los Alamos National Laboratory (LANL) in the late 1990s. Ethyl acetate, methylene chloride, and hexane vapors of 1000 or 2000 ppm were loaded on MSA GMC-H and GME-H cartridges for times of 0.25 to 2 hr using a simulated breathing pump. These cartridges were then stored up to 35 days before rechallenging them at the same conditions. Effluent was monitored until cartridge bed saturation was reached.

A major observation was breakthrough concentration step increases immediately (within 30 s) upon cartridge simulated reuse from what existed before storage. (Hereafter, a value of the breakthrough concentration after such a step increase will be referred to as an Immediate Breakthrough Upon Reuse, IBUR, with units of concentration, ppm. IBUR can also be unitless as in fraction of challenge concentration.) Often, there were subsequent plateaus of breakthrough concentration until the breakthrough curve resumed. These IBURs increased with storage time to apparently approach maximum values. The type of vapor and extent of initial vapor loading, but not so much loading concentration, affected the rates of increases and magnitudes of IBURs. At similar conditions, IBURs were largest for methylene chloride (BP = 40°C), intermediate for ethyl acetate (BP = 77°C), and least for hexane (BP = 69°C). Water vapor pre-adsorption and co-adsorption (high relative humidity, RH) with hexane resulted in even greater IBURs. In one case, a cartridge loaded with ethyl acetate and stored

under refrigeration (3°C) for 2 weeks showed half the IBUR of one stored at room temperature.

Wood<sup>(9)</sup> explained and modeled these observations as no-flow vapor phase migration of vapors during storage from vapor-loaded carbon at the cartridge inlet to fresh carbon nearer the outlet of the cartridge carbon sorbent bed.

Balieu<sup>(10)</sup> first defined low boiling OVs as those with BP lower than 65°C to include methanol (BP = 64°C), which had breakthrough times about one-fifth of those for tetrachloromethane (BP = 77°C). Desorption tests with clean air showed methanol release after only 1 hr of storage, with effluent concentration depending on initial dose. These studies formed the basis for the European Standard desorption test requirements and conditions for vapors boiling below 65°C.<sup>(4)</sup>

Colton<sup>(11)</sup> published a review of the issues involved in OV cartridge reuse: adsorption, desorption, migration, volatility, mixtures of vapors, mechanisms, and change-out schedules. He questioned the adequacy of using BP > 65°C as the criterion for vapors nonvolatile enough for cartridge reuse, suggesting three or four levels of volatility criteria instead. Rules of thumb were proposed for chemicals of undefined “moderate volatility” (do not reuse after a few days) and “low volatility” (do not reuse after longer than 1 to 2 weeks). However, he concluded that in the absence of desorption data, “prudent practice” should prohibit organic vapor cartridges’ use for more than one shift.

Maggs and Smith<sup>(12)</sup> observed significant desorption of methyl bromide adsorbed in APR canisters (without the triethylenediamine (TEDA)-impregnated activated carbon placed in some canisters today for organic halides). This led them to recommend against intermittent canister use (unless initial dose is “low”) due to desorption, vapor redistribution, and possible resulting hazardous effluent concentrations. This would be expected for such a volatile, low BP (3.5°C) compound.

At the other extreme, Dharmarajan et al.<sup>(13)</sup> reported that hexamethylene diisocyanate (HDI) monomer was not detected in cartridge effluent air after six 7-hr HDI challenges, each followed by 17 hr of storage. This was true even in the presence of other organic vapors and water vapor (80% RH). They concluded that migration of HDI was insignificant and APR OV cartridges could be used for 40 hr of HDI protection. This would be expected for a BP of about 288°C (extrapolated).

Aitken et al.<sup>(14)</sup> reported on effects of discontinuous and intermittent exposures of OV cartridges to isopropanol (BP = 82.3°C) and cyclohexane (BP = 80.7°C). Intermittent (2 hr air/vapor flow, 2 hr no air or vapor flow, repeated) breakthrough curves with nonexposure times subtracted were indistinguishable from continuous flow ones within experimental variations. One long-term (1-week) storage experiment after 362 min exposure of an A1P2 filter to 200 ppm isopropanol showed a sudden and significant increase (~35% of challenge concentration) in breakthrough upon restart. A larger cartridge (A2P3) showed no such increase even though the initial exposure was for 1107 min. Smaller increases (~5%) in breakthrough concentrations immediately following exposure breaks were

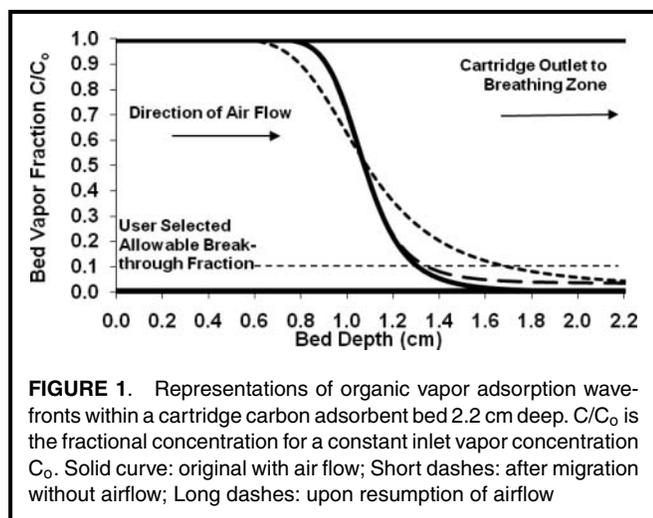
observed in two other AIP2 cases: an overnight break with isopropanol and a 1-week break with cyclohexane.

These results with chemicals of BP intermediate to those of the previous two references and both above the BP = 65°C criterion show failure of the latter in predicting reusability. The two chemicals have very similar BPs but showed much different storage effects. Also, at least three other parameters were significant: carbon bed size, period of first exposure, and period of nonexposure.

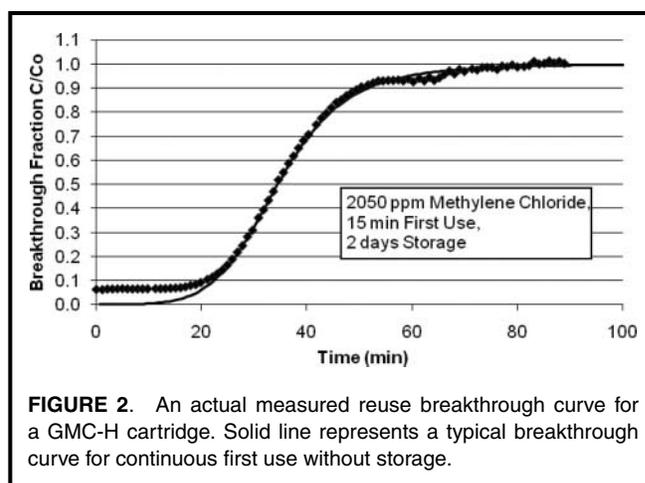
## THEORETICAL BACKGROUND

As vapors are adsorbed from air flowing through an activated carbon bed, whether by cyclic breathing or steady pumped flow, a vapor wavefront is formed in equilibrium with adsorbed vapor (solid curve in Figure 1). Faster rate of adsorption yields a steeper wavefront; first-order adsorption rate yields the sigmoidal shape shown. Rapid vapor removal prevents significant vapor from exiting a cartridge bed for a practical use period. As more vapor is removed and the inlet of the carbon bed is saturated at the challenge concentration, the wavefront moves toward the outlet and the effluent concentration increases. A breakthrough curve, which is a plot of effluent concentration vs. time, is the mirror reflection of the adsorption wave. When the allowable breakthrough concentration (or fraction) is reached at the outlet, cartridge service life has been reached.

When flow is stopped before service life is reached, the adsorption wave is initially frozen into place as equilibrium continues between vapor in air and vapor adsorbed on carbon. However, the vapor in air is free to diffuse toward the outlet of the bed, where vapor concentration is lower, and be adsorbed on less vapor-loaded carbon. This vapor migration results in flattening of the vapor distribution (short-dashed curve in Figure 1) and in increases in the vapor concentration at the bed outlet.



**FIGURE 1.** Representations of organic vapor adsorption wavefronts within a cartridge carbon adsorbent bed 2.2 cm deep.  $C/C_0$  is the fractional concentration for a constant inlet vapor concentration  $C_0$ . Solid curve: original with air flow; Short dashes: after migration without airflow; Long dashes: upon resumption of airflow



**FIGURE 2.** An actual measured reuse breakthrough curve for a GMC-H cartridge. Solid line represents a typical breakthrough curve for continuous first use without storage.

Upon resumption of airflow (as in cartridge reuse) the vapor at the bed outlet will be released into the user's breathing zone. The wavefront will sharpen (long-dashed curve in Figure 1) as flow-enhanced adsorption rate returns, but carbon already loaded with vapor near the outlet will continue to release vapor to flowing air.

If sufficient migration has occurred during cartridge storage, the breakthrough curve upon simulated reuse may look something like the actual measured breakthrough curve shown in Figure 2. The sigmoidal shape is retained; however, there may also be an IBUR and then a plateau (steady-state) of effluent vapor. If the IBUR and plateau exceed the allowable breakthrough concentration, the cartridge must not be reused; if it doesn't, the remaining service life can be estimated if the reuse breakthrough curve can be measured or predicted.

Equation-based models for estimating service lives of OV cartridges<sup>(15,16)</sup> are often based on the reaction kinetic form of the Wheeler-Jonas equation:<sup>(17)</sup>

$$t_b = \frac{W_e W}{C_0 Q} - \frac{W_e \rho_B}{k_v C_0} \ln \left( \frac{C_0 - C}{C} \right) \quad (1)$$

which includes (1) carbon bed parameters of bed weight  $W$  (g) and packed density  $\rho_B$  (g/cm<sup>3</sup>); (2) use parameters of challenge vapor concentration  $C_0$  (g/cm<sup>3</sup>), breakthrough concentration  $C$  (g/cm<sup>3</sup>), and airflow rate  $Q$  (cm<sup>3</sup>/min); and (3) vapor/carbon interaction parameters of adsorption rate coefficient  $k_v$  (min<sup>-1</sup>) and adsorption capacity  $W_e$  (g/g carbon) at  $C_0$ . With these units, breakthrough time  $t_b$  is in minutes.

If the breakthrough curve midpoint (first term of Eq. 1) and adsorption rate (represented by the rate coefficient  $k_v$ ) can be known, breakthrough at another concentration ( $C$ ) can be estimated. At the midpoint of the breakthrough curve, which for current purposes is taken as the time  $t_{50\%}$  at which  $C/C_0 = 0.5$ , the midpoint capacity  $W_e = C_0 t_{50\%} (Q/W)$ . The flow rate-normalized and bed mass-normalized capacity is  $W_e W/Q = C_0 t_{50\%}$ , which is expressed in units of parts-per-million-minutes (ppm-min). These are the units used here for capacity comparisons.

Prior to this work it was not known whether the midpoint (50%) times and slopes at midpoints (Figure 1) of the original,

migration, and reuse wavefronts coincide or are shifted by migration during storage between uses. One of the objectives of this work was to determine which is the case.

## EXPERIMENTAL

Measurements of continuous and reuse breakthrough curves have been done at NIOSH to supplement those done at LANL.<sup>(8,9)</sup> The vapors, cartridges, and average conditions used at both places are shown in Table I. This article is an evaluation of both sets of data together.

The experimental apparatus used at NIOSH, modified from that reported previously,<sup>(16)</sup> is shown in Figure 3. The experimental procedure consisted of using a cartridge model 3M Number 7251. It has simple cylindrical geometry for which it was easy to construct an aluminum gastight holder for testing. Cartridges were used as-received, one at a time. Carbon bed dimensions were reported by the manufacturer to be 7.6 cm diameter and 2.25 cm deep for 44.5 g of adsorbent. These are the parameters used in the model. The carbon granules were

reported by the manufacturer to be 12–16 mesh, so an average diameter of 0.14 cm was used in the model. Chemicals used were ACS-certified reagents or better.

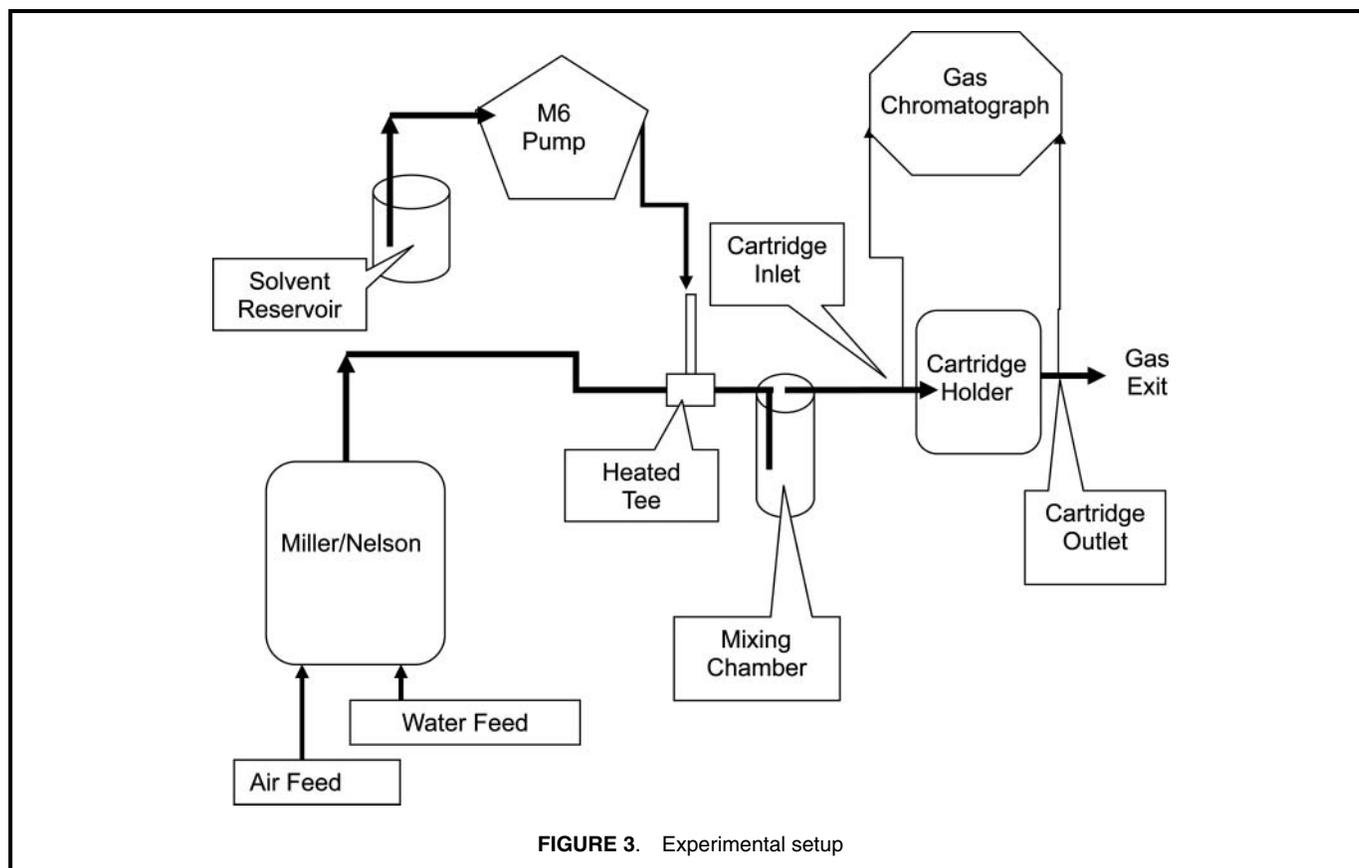
A Miller/Nelson number HCS-401 (Assay Technology, Livermore, Calif.) Flow-Temperature-Humidity Control System was used to generate a constant air source of known temperature and relative humidity. Compressed air filtered for organics and particles fed the Miller/Nelson unit as well as distilled water for humidification purposes. The output from the Miller/Nelson was connected to a heated brass block via a tee. This permitted conditioned air from the Miller/Nelson to enter and exit. The third leg of the tee contained a Peek tubing line delivering solvent from a Valco M6 pump (Valco Instruments, Inc., Houston, Texas). The brass block was heated using a tube heater (Omega Engineering, Stamford, Conn). Effluent stream from the block was transferred via polyethylene tubing to a 10-L stainless steel container (Campbell Hausfeld, South Pasadena, Calif.) for mixing before entering the cartridge holder. The incoming gas stream to the cartridge holder was tapped with a one-eighth-inch Teflon tube connected to a gas

**TABLE I. Vapors, Cartridges, Average Experimental Conditions, and Fit Results for Data Groups**

| Vapor              | Cartridge | Average Co (ppm) | Average RH (%) | Average First Use Time (min) | Maximum Storage (hr) | n <sup>A</sup> | Experimental Best Fit    |                     |                             |                             |                              |
|--------------------|-----------|------------------|----------------|------------------------------|----------------------|----------------|--------------------------|---------------------|-----------------------------|-----------------------------|------------------------------|
|                    |           |                  |                |                              |                      |                | k <sub>Stor</sub> (1/hr) | IBURmax (ppm)       | Relative Standard Deviation | D/R Estimated IBURmax (ppm) | Ratio Estimated/Experimental |
| Methylene Chloride | GMC-H     | 994              | 20             | 30                           | 336                  | 9              | 0.031                    | 175                 | 0.09                        | 424                         | 2.42                         |
| Methylene Chloride | GMC-H     | 2044             | 20             | 15                           | 360                  | 6              | 0.0098                   | 325                 | 0.17                        | 47                          | 0.14                         |
| Methylene Chloride | GMC-H     | 2037             | 20             | 30                           | 24                   | 4              | 0.097                    | 797                 | 0.01                        | 179                         | 0.22                         |
| Hexane             | GMC-H     | 978              | 20             | 60                           | 336                  | 8              | 0.0077                   | 21                  | 0.13                        | 4.7                         | 0.22                         |
| Ethyl Acetate      | GMC-H     | 997              | 20             | 120                          | 63                   | 24             | 0.047                    | 277                 | 0.37                        | 168                         | 0.61                         |
| Ethyl Acetate      | GME-H     | 999              | 20             | 90                           | 842                  | 11             | 0.0041                   | 74                  | 0.23                        | 43.9                        | 0.59                         |
| Ethyl Acetate      | GME-H     | 1004             | 20             | 60                           | 845                  | 4              | 0.0012                   | 42                  | 0.41                        | 40.6                        | 0.97                         |
| Ethyl Acetate      | GMC-H     | 1018             | 20             | 60                           | 145                  | 6              | 0.005                    | 59                  | 0.24                        | 16.6                        | 0.28                         |
| Methylene Chloride | 3M        | 977              | 20             | 30                           | 168                  | 8              | 0.043                    | 415                 | 0.06                        | 424                         | 1.02                         |
| Pentane            | 3M        | 484              | 20             | 105                          | 355                  | 4              | 0.0205                   | 79                  | 0.17                        | 330                         | 4.18                         |
| Chloroform         | 3M        | 996              | 20             | 30                           | 168                  | 5              |                          | NA(39) <sup>B</sup> |                             |                             |                              |
| Toluene            | 3M        | 508              | 33             | 233                          | 67                   | 3              |                          | NA(2) <sup>B</sup>  |                             |                             |                              |
| Toluene            | 3M        | 525              | 74             | 160                          | 69                   | 3              |                          | NA(2) <sup>B</sup>  |                             |                             |                              |
| MIBK               | 3M        | 497              | 25             | 184                          | 663                  | 8              |                          | NA(1) <sup>B</sup>  |                             |                             |                              |
| MIBK               | 3M        | 495              | 80             | 115                          | 667                  | 6              |                          | NA(0) <sup>B</sup>  |                             |                             |                              |

<sup>A</sup>n = Number of data in a set.

<sup>B</sup>NA = Not enough data to establish an IBURmax plateau. The concentration shown in parentheses is the largest observed value of IBUR.



chromatograph. A similar connection was made to the stream exiting the holder. This provided a means to monitor the vapor concentrations entering and exiting the cartridge being tested.

The vapor monitor consisted of an SRI model 8610 dual column, dual flame detector gas chromatograph (GC; SRI Inc., Torrance, Calif.). It was equipped with two ten-port automated valves with 1-mL sample loops and used PeakSimple software provided by SRI. The GC could be programmed to automatically sample the two (cartridge input and output) gas streams, quantify the concentrations, and store the values in an Excel spreadsheet (Microsoft, Inc., Redmond, Wash.) for future use. The columns, RTX-5, 30 m long  $\times$  0.053 mm ID and 1.0  $\mu$  film thickness (Restek, Bellefonte, Pa.) were operated at 120°C and 5 mL/min hydrogen carrier flows. All components could be eluted in under 3 min. This permitted simultaneous monitoring of the input and exhaust of the cartridge at 3-min intervals.

The gas chromatograph responses for each chemical vapor were calibrated by using standards produced in the laboratory. A 10-L gas bag (SKC, Inc, Eighty Four, Pa.) was filled with 6 L of air. An appropriate amount of solvent was injected using a microliter liquid syringe (Valco VICI precision syringe). The vapor and air were mixed by kneading the gas bag. A sample of the standard was injected into the gas sampling loop of the gas sampling valve. Thus the same plumbing was used for calibration and analysis of unknowns. This was done at a frequency of once or twice a day depending on the length

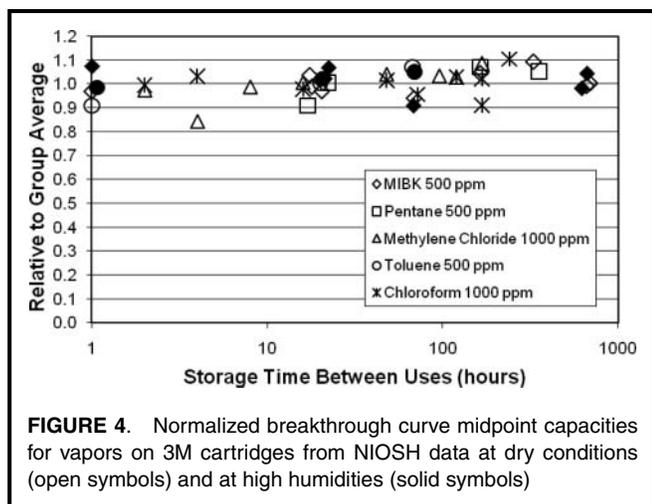
of analysis time. In all cases, the GC was found to hold calibration very well. The lower detection limits for these organic vapors was on the order of 1.0 ppm as determined by the first detectable peaks above baseline noise.

Airflows into the cartridge were calibrated by using a dry gas meter manufactured by American Meter Co. (Horsham, Pa.). Ambient temperature and atmospheric pressure were recorded. The M6 liquid chromatograph (LC) pump and air source (breathing pump or compressed air) in Figure 3 were operated until a steady-state condition existed, typically 1 to 2 hr, so that consistent concentrations could be generated before introducing the test cartridge. Once the concentration reached steady-state, the solvents in the LC pump reservoirs were weighed. Knowing the weight of solvent used and the concentration going into and out of the cartridge, a mass balance could be done as a check on calibrations. The cartridge was then placed in the holder so that vapors in the airstream could be forced through it as the GC software was started. Cartridge pressure drop did not significantly affect airflow. Data collection by the GC was usually continued until total breakthrough occurred.

## RESULTS AND DISCUSSION

### Breakthrough Curve Midpoint Comparisons

Breakthrough curve midpoints ( $C/C_0 = 0.5$  at  $t_{50\%}$ ) were obtained for storage and non-storage experiments. Both  $t_{50\%}$



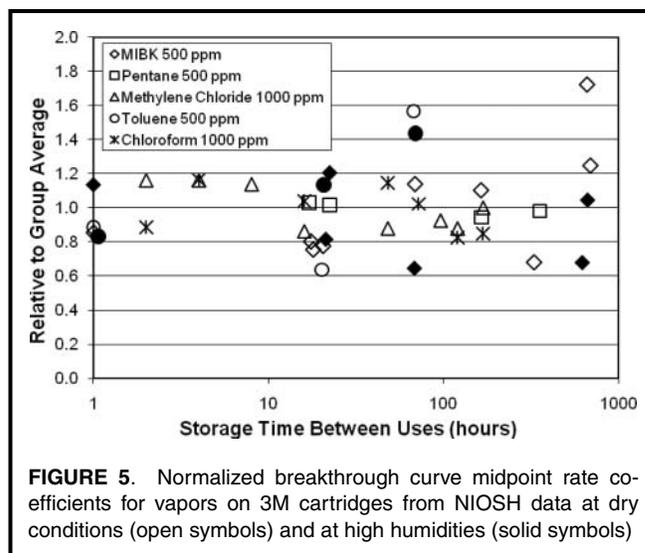
**FIGURE 4.** Normalized breakthrough curve midpoint capacities for vapors on 3M cartridges from NIOSH data at dry conditions (open symbols) and at high humidities (solid symbols)

( $= W_e W/C_o Q$ ) and rate coefficient  $k_v$  were obtained from Eq. 1 by least mean squared difference curve fitting of experimental breakthrough curve data near the midpoints.<sup>(18)</sup> The flow rate- and bed mass-normalized capacities ( $C_o t_{50\%}$  in ppm-min) for each group of  $n$  experiments (listed in Table I, each group for the same cartridge and vapor and nearly the same concentration, flow rate, humidity, and first vapor loading) were normalized by dividing by the average of the  $n$  capacities for all in the group. This was necessary to be able to combine the data from all such groups to show all the observations on the same graph and scale. Rate coefficients were similarly normalized for comparisons on the same scale and to look for trends.

Such normalized capacities were plotted against storage times (hours) before challenge vapor restarts. Figure 4 shows results from data obtained at NIOSH with the 3M cartridge and five chemicals at dry conditions (up to 28 days), at high relative humidities (71–80% for toluene and 75–89% for MIBK), and at about 500 or 1,000 ppm vapor concentration for storage periods up to 28 days. The concentrations given in these graphs are the target concentrations for each group; actual concentrations varied slightly for each experiment and were individually considered in the calculations of capacity. Continuous exposure (zero storage time) experiments were included in the averages for normalization but are not plotted on the graphs due to the logarithmic scale.

The scatter of 56 normalized capacity data around 1.0 is represented by a standard deviation of 0.053. The same analysis of LANL data ( $n = 76$ ) for MSA GMC-H (up to 2.5 days storage) and GME-H cartridges (up to 85 days storage) and three vapors gave a standard deviation of 0.056. In neither case were trends of capacity with storage time observed.

Similarly, Figure 5 shows normalized adsorption rate coefficients ( $\text{min}^{-1}$ ) at breakthrough curve midpoints (as described above) from the NIOSH data plotted against storage times for groups of vapors, target concentrations, and relative humidities. These are from the same groups of reuse breakthrough curves from which capacities were extracted. The standard deviations for the normalized rate coefficients were 0.27 ( $n =$



**FIGURE 5.** Normalized breakthrough curve midpoint rate coefficients for vapors on 3M cartridges from NIOSH data at dry conditions (open symbols) and at high humidities (solid symbols)

54) for the NIOSH tests and 0.15 ( $n = 72$ ) for the Los Alamos tests. No trends of rate coefficients with storage time were observed.

An important observation from Figures 4 and 5 is that within these experimental variabilities, adsorption capacities and rate coefficients are essentially unchanged by storage and simulated cartridge reuse. These parameters reflect the breakthrough curve time and slope, respectively, at 50% breakthrough of a fixed challenge concentration. The observed experimental variabilities are not surprising considering the variabilities observed in commercial cartridges.<sup>(19)</sup> Also,  $k_v$  is calculated from small differences in breakthrough times (curve slopes), rather than absolute values, as is the case with capacities.

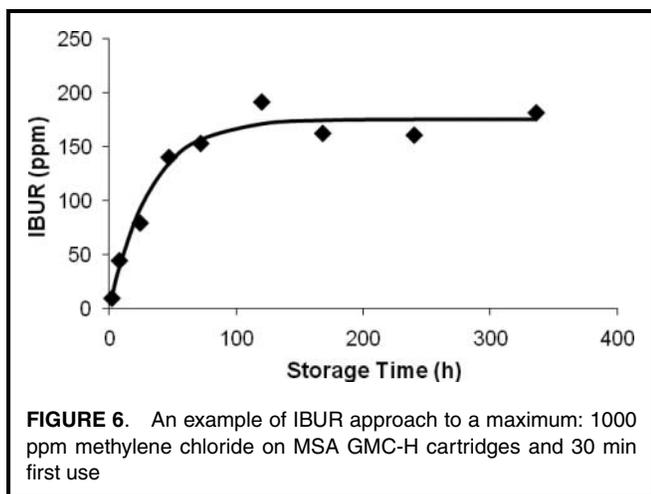
The implication of these observations is that measured or estimated values of these parameters for first-use breakthrough curves can be used for reuse breakthrough curves as well. Service life estimation models and computer programs, such as MultiVapor version 2.2.3<sup>(20)</sup> from NIOSH, can be used to estimate such parameters for reuse breakthrough curves.

### Immediate Breakthroughs Upon Reuse

IBURs, such as illustrated in Figure 2 and explained in Figure 1, were obtained from reuse breakthrough curves. Often, there were subsequent plateaus of breakthrough concentration until the breakthrough curve resumed. However, it is the immediate effluent concentration upon reuse (first breath) that is of concern here. Figure 6 shows an example of measured IBURs approaching an apparent maximum, IBUR<sub>max</sub>, with increasing storage duration ( $t_{\text{stor}}$  in hours). For the 10 sets of data in Table I with sufficiently long storage times to define an IBUR<sub>max</sub>, data were fit by least mean squared difference analysis to:

$$\text{IBUR} = \text{IBUR}_{\text{max}}(1 - \exp[-k_{\text{stor}} t_{\text{stor}}]) \quad (2)$$

to extract first-order approach-to-IBUR<sub>max</sub> storage rate coefficients  $k_{\text{stor}}$  (units of reciprocal hours) and experimental



IBURmax values shown in Table I. Relative standard deviations of experimental IBUR/IBURmax ratios from best-fit IBUR/IBURmax ratios are also given in Table I. Equation 2 can be used to obtain intermediate values of IBUR from values of IBURmax and  $k_{\text{stor}}$  obtained independently (discussed below).

### IBUR Modeling

Admittedly, these experimental values of  $k_{\text{stor}}$  and IBURmax can only be approximate due to the paucity of data, especially at long storage times. However, the following empirical prediction equation based on the four listed input factors has been developed for the storage rate parameter  $k_{\text{stor}}$  with units of reciprocal hours:

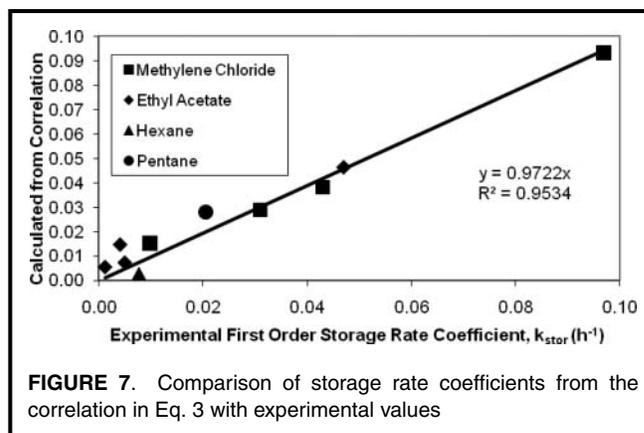
$$k_{\text{stor}} = (\varepsilon/\beta)^2 \exp[-12.1 + 0.168(W_L/V_B)(\varepsilon/\beta)^2] \quad (3)$$

where

- $\varepsilon$  = vapor adsorption potential (kJ/mol) =  $RT \ln(P_{\text{sat}}/P)$
- $\beta$  = vapor affinity coefficient (relative to benzene)
- $W_L$  = first-use bed loading of vapor (g)
- $V_B$  = carbon bed volume ( $\text{cm}^3$ )

The logic for selecting these parameters was (1) larger affinity of the vapor for the carbon ( $\beta/\varepsilon$ ) would be expected to decrease the migration rate; (2) deeper beds (larger  $V_B$ ) would reduce the effect of migration at cartridge exit; and (3) more vapor adsorbed ( $W_L$ ) in first use duration ( $t_{\text{FU}}$ ) would be expected to increase migration rate. Equation 3 was selected from among several other candidates because it best described effects of these parameters. Parameters of the Dubinin/Radushkevich (D/R)<sup>(21)</sup> vapor adsorption isotherm ( $\varepsilon$  and  $\beta$ ), of the cartridge ( $V_B$ ), and of the use conditions ( $W_L$  and  $t_{\text{stor}}$ ) are easily obtained.<sup>(15,16,20)</sup> Affinity coefficients were calculated from a correlation with vapor polarizability,  $\beta = 0.0862 P_e^{0.75}$ .<sup>(15)</sup>

Figure 7 shows a comparison of values of  $k_{\text{stor}}$  calculated by Eq. 3 with experimental ones. The agreement is especially good at high values where migration is most significant but not so good at low values where IBURs are small and difficult to measure.



The D/R equation has been used successfully to correlate breakthrough adsorption capacities,  $W_e$  in g vapor/g carbon, for estimating organic vapor cartridge service lives:<sup>(15,21)</sup>

$$W_e = W_o d_L \exp[-(RT/\beta E_o)^2 \{\ln(P_{\text{sat}}/P)\}^2] \quad (4)$$

where

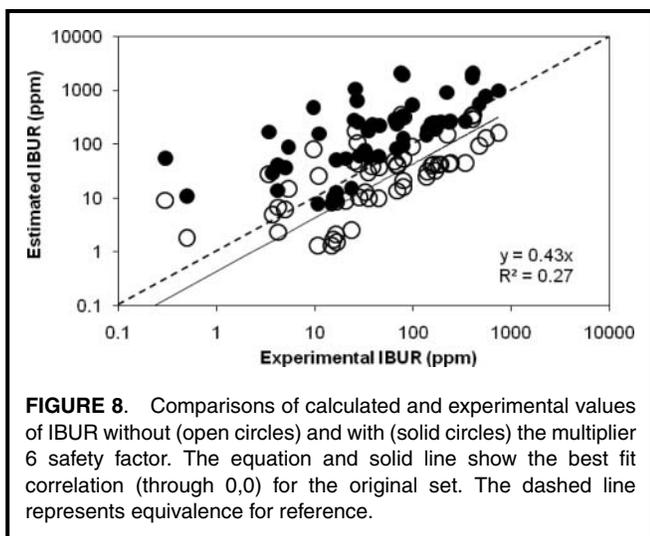
- $P_{\text{sat}}$  = saturation pressure of the vapor (torr)
- $E_o$  = adsorption potential of benzene ( $\beta = 1$ ) on the carbon (kJ/mol)
- $W_o$  = micropore volume of the carbon ( $\text{cm}^3/\text{g}$ )
- $d_L$  = liquid density of the vapor ( $\text{g}/\text{cm}^3$ )

Rearranging Eq. 4 to solve for vapor pressure  $P$ , converting to equivalent vapor concentrations ( $P$  becomes IBURmax and  $P_{\text{sat}}$  becomes  $C_{\text{sat}}$  in ppm), and setting  $W_L = W_e W$  allows prediction of vapor concentration in equilibrium with a given first-use loading of vapor  $W_L$  (g):

$$\text{IBURmax(ppm)} = C_{\text{sat}} \exp\{-(\beta E_o/RT) \times \text{sqrt}[\ln(W_o d_L W/W_L)]\} \quad (5)$$

Equating  $P$  with IBURmax assumes that (1) vapor is equally distributed throughout the bed at equilibrium, and (2) effluent concentrations measured upon reuse at the test flow rates are equivalent to equilibrium vapor concentrations. Table I shows a comparison of IBURmax values calculated by this equation with experimental ones from 10 sets of data. Overestimates might also be explained by leakages from cartridges during storage between uses. The various researchers involved in developing both the LANL and NIOSH sets of data used various (or no) methods of sealing the cartridges during storage periods. Underestimates might be due to incomplete (or pseudo-) equilibria attained without flow.

When Eqs. 2, 3, and 5 were used to estimate 60 intermediate IBURs (for experiments grouped in Table I) and these were compared with experimental ones, the open circles in Figure 8 were the results. There is a general trend agreement ( $y = 0.43x$ ), but with much scatter ( $R^2 = 0.27$ ) and many underestimates and overestimates. Applying a "safety factor" multiplier of 6 brings all the estimates (solid circles in Figure 8) near or above the dashed equivalence line. Such an adjustment usually results in a "conservative" estimate (often overestimate) of



**FIGURE 8.** Comparisons of calculated and experimental values of IBUR without (open circles) and with (solid circles) the multiplier 6 safety factor. The equation and solid line show the best fit correlation (through 0,0) for the original set. The dashed line represents equivalence for reference.

IBUR. Seven of the 60 data points (mostly for hexane) are still below the equivalence line; if risk assessment deems 12% too large, a higher safety factor should be used.

## CONCLUSIONS

A major conclusion of this article is that  $W_e$  and  $k_v$ , parameters determining  $t_{50\%}$  and earlier breakthrough times, are not changed during storage before reuse. The demonstrated lack of effects of storage between uses on breakthrough curve midpoint shape (time and slope) greatly simplifies the estimation of reuse curve breakthrough times (service lives). Except for IBUR, total use time (ignoring time between uses) can be considered the same as the estimated service life without storage and reuse. Models such as MultiVapor provide such estimates.<sup>(20)</sup>

The correlations and equations developed here allow conservative estimates of IBURs. As long as estimated IBUR does not exceed the allowable breakthrough concentration, reuse service life can be obtained from estimated service life without storage minus first use time. This assumes the same workplace conditions for both uses. For example, let us take (from measurements or model estimations) a breakthrough time of 173 minutes for 25 ppm methylene chloride (the OSHA permissible exposure limit) breakthrough in a challenge concentration of 500 ppm for a pair of typical OV cartridges.<sup>(22)</sup> Cartridge parameters, along with assumed environmental and use parameters, are listed in the Appendix. Reuse calculations using Eqs. 2, 3, and 5 are also shown in the Appendix.

**Reuse Case #1:** 30 min first use and 24 hr storage before reuse in the above equations give a prediction (Appendix) of 16 ppm IBUR and 143 min (173 min–30 min first use) remaining service life.

**Reuse Case #2:** 30 min first use and 72 hr storage before reuse in the above equations give a prediction of 41 ppm IBUR and no remaining service life, since 41 ppm is higher than the chosen allowable breakthrough concentration of 25 ppm. Note that under the OSHA rule of thumb (discussed above)

the 40°C boiling point of methylene chloride (below 65°C) would indicate significant migration and prohibit cartridge reuse beyond a work shift. The model presented here, even with a conservative factor of 6, indicates that a cartridge can be reused with methylene chloride under certain circumstances. Of course, professional judgment is essential in applying such guidance.

More extensive and better (more controlled storage conditions) experimental data should result in better agreement of model estimates with experimental values. The “conservative” safety factor might be eliminated and the goals of modeling for reusability (cost savings, and so on) could be better met.

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## APPENDIX

### Reuse Case #1 Assumed Conditions and Calculations

#### Typical Organic Cartridge and Carbon Properties

- Bed diameter = 8.0 cm
- Bed depth = 2.2 cm
- Bed weight W = 47.8 g each
- Micropore volume =  $W_o = 0.533 \text{ cm}^3/\text{g}$
- Adsorption potential (benzene)  $E_o = 18.666 \text{ kJ/mol}$

#### Vapor Properties

- Methylene chloride, CAS = 75-09-2
- Molecular weight Mw = 84.93 g/mol
- Liquid density  $d_L = 1.3266 \text{ g/cm}^3$
- Polarizability  $P_e = 16.343$
- Concentration  $C_o = 500 \text{ ppm}$
- Antoine vapor pressure parameters (torr),  
A = 16.3029, B = 2622.44, C = -41.7

#### Use and Reuse Parameters

- Temperature 23°C or T = 296.15°K
- Atmospheric pressure = 1 atm = 760 torr
- Total airflow Q = 30 L/min
- Two cartridges in parallel
- Allowable breakthrough concentration = 25 ppm
- First-use duration  $t_{FU} = 30 \text{ min}$
- Storage duration before reuse  $t_{stor} = 24 \text{ hr}$  for Reuse Case #1

#### Sample Calculations

Equation 2 is used to calculate IBUR (ppm) from  $k_{stor}$  and IBURmax obtained first from Eqs. 3 and 5, respectively. The

value for  $P_{sat}$  for the specific temperature of use (converted to ppm or other pressure unit) is obtained from Antoine's equation and Parameters A, B, and C:

$$P_{sat} = \exp\{16.3029 - [2622.44/(296.15 - 41.7)]\}$$

$$= 402.06 \text{ torr}$$

$$C_{sat} = (402.06)(10^6/760) = 529022 \text{ ppm}$$

Adsorption potential and affinity coefficient for Eqs. 3 and 5 are obtained from:

$$R = 0.0820254 \text{ L-atm/mol-deg} = 0.00831451 \text{ kJ/mol-deg}$$

$$\varepsilon = RT \ln(P_{sat}/P) = RT \ln(C_{sat}/C_o) = (0.00831451)(296.15) \times \ln(529022/500) = 17.1482 \text{ kJ/mol}$$

$$\beta = 0.0862 P_e^{0.75} = 0.7007 \text{ (no units)}$$

Total bed volume and first-use bed loading for Eq. 3 come from:

$$V_B = 2.2\pi(8.0)^2(2)/4 = 221.17 \text{ cm}^3 \text{ for two circular cartridges}$$

$$W_L = C_o Q t_{FU} = (500 \text{ ppm})(30 \text{ L/min})(30 \text{ min}) \times (10^{-6}/\text{ppm})(84.93 \text{ g/mol})(1 \text{ atm}) / (0.0820254 \text{ L-atm/mol-deg}) / 296.15^\circ \text{K} = 1.5733 \text{ g}$$

And the calculation of Eq. 3 becomes:

$$k_{stor} = (\varepsilon/\beta)^2 \exp[-12.1 + 0.168(W_L/V_B)(\varepsilon/\beta)^2]$$

$$= 0.0068118 \text{ h}^{-1}$$

For a total bed weight of W = (47.8 g)(2 cartridges) = 95.6 g, the calculation of Eq. 5 is:

$$\text{IBURmax (ppm)} = P_{sat} \exp\{-(\beta E_o/RT) \sqrt{\ln(W_o d_L W/W_L)}\} = 529022 \exp\{-((0.7007)(18.666)/((0.00831451)(296.15)) \sqrt{\ln((0.533)(1.3266)(95.6)/1.5733)}\} = 17.8 \text{ ppm}$$

Using the safety factor of 6 identified in the text, IBURmax(ppm) = 17.8 ppm \* 6 = 106.8 ppm

So that the result of Eq. 2 for Reuse Case #1 is:

$$\text{IBUR} = \text{IBURmax}(1 - \exp[-k_{stor} t_{stor}])$$

$$= 106.8(1 - \exp[-(0.0068118)(24)]) = 16 \text{ ppm}$$

Note that when the MultiVapor program<sup>(20)</sup> is used for these calculations at 50% reuse RH, the result is 18 ppm, since MultiVapor takes into account micropores filled with water during first use (in this case 0.040 cm<sup>3</sup>/g for a solubility factor of 0.0146 and a water affinity coefficient of 0.06).<sup>(15)</sup> Other MultiVapor carbon input parameters were 20% RH initial moisture and 0.11 average granule diameter. The micropore filling calculation is iterative and too complex to be shown here for the above example, but it is explained in Reference 15. At dry conditions, e.g., 20% RH, MultiVapor gives the same result as the above calculation, IBUR = 16 ppm.