Journal of Occupational and Environmental Hygiene, 3: 153–160
ISSN: 1545-9624 print / 1545-9632 online

DOI: 10.1080/15459620500526560

Effect of Temperature on Permeation Through Air Supply Hoses

David Bromwich and Jwalitkumar Parikh

School of Environmental Engineering, Griffith University, Nathan, Queensland, Australia

Permeation of chemicals through the walls of air-supply hoses used with respirators is an underrecognized problem in industry. Transport of chemicals through the wall of a hose occurs in the same manner as through gloves and chemical suits, driven by the chemical concentration gradient, but for air-supply hoses the chemical evaporating inside the air-supply hose is inhaled. A simple method based on the mathematical equivalence of filling a homogeneous hose with a chemical, to immersing it in a chemical, has been developed. The method requires a short section of hose to be filled, plugged, and weighed at intervals to determine the breakthrough detection time and the cumulative permeation per meter. The method has been tested experimentally and calculations show that permeation of an air-line respirator hose could be a significant source of respiratory exposure, particularly for users of demand-type, supplied-air respirators.

Keywords air-supply hoses, chemicals, permeation, respiratory protection

Address correspondence to: David Bromwich, School of Environmental Engineering, Griffith University, Nathan, Queensland 4111, Australia; e-mail: d.bromwich@griffith.edu.au.

If a section of air-supply hose is immersed in a chemical, the chemical will tend to dissolve in the hose polymer and diffuse across the wall of the hose, driven by the chemical concentration gradient. The chemical then evaporates into the air inside the hose to be inhaled by the user.

The influence of temperature on permeation through gloves has been investigated,[1–3] and it is of interest to consider the same for air-supply hoses. An air-supply hose may be subject to much higher temperatures and any chemical exposure is more likely to be sustained rather than intermittent. For gloves, discomfort or pain could be expected to limit the exposure temperature, as they are thinner and in direct contact with the skin. Such a situation could occur during entry to a hot process vessel during the shutdown or by the air-supply hose trailing through a puddle of chemical in the sun. Sustained contact can also occur with chemicals that are not volatile but remain on the air line during storage. As for gloves, the breakthrough time would be expected to decrease with increasing temperature and the permeation rate to likewise increase.

METHODS AND MATERIALS

The theory and a new test method for determining the permeation of chemicals through air supply hoses is described by Bromwich and Braddock.[4] It was shown that chemical permeation through homogeneous hoses could be measured by filling a short sealed section of the hose with the chemical and weighing it at intervals as the chemical permeated the hose wall and evaporated. Lengths of Esdan PVC air supply hose (length 10 cm, diameter 18 mm, wall thickness 4 mm; Esdan Plastics, Melbourne, Australia) were filled with a challenge chemical, methyethyl ketone (MEK); the hose samples were sealed with steel ball bearings (7/16″, 11.11 mm).

In this experiment, the methodology was extended to measure the effect of temperature. An isothermal test rig was designed and constructed (Figure 1) to permit testing of hose samples at temperatures above ambient. A ventilated isothermal tube was immersed in a heated water bath such that a warmed airflow introduced at the bottom of the tube removed permeant from the hose sample suspended in the tube. This ensured the chemical concentration gradient across the hose wall was maximized. A loose-fitting stopper on the tube allowed the warmed air and permeant to escape. The sealed hose sample was removed at intervals with a bent metal strip (lifter) so it could be weighed (Mercury AMD model 202, capacity 120 g, sensitivity 0.1 mg) to determine the amount of permeant that had evaporated. The thermometers T1 and T2 were used to demonstrate that the test rig was isothermal.

A precision water bath temperature controller controlled a water bath heater-stirrer and maintained the water bath within 1°C for temperatures above room temperature. A layer of bubble wrap on the surface of the water bath reduced evaporation and aided temperature control.

Replicate testing was performed at 19, 30, 40, 50, 60, and 70°C, to represent temperatures that could be found in the workplace. Drift in the room air-conditioning control meant room temperature was 19°C ± 1°C rather than 20°C ± 1°C. A test tube of MEK and the unsealed hose samples were warmed in the water bath before permeation testing began to ensure isothermal conditions from the outset. The intervals between weighing were increased approximately geometrically

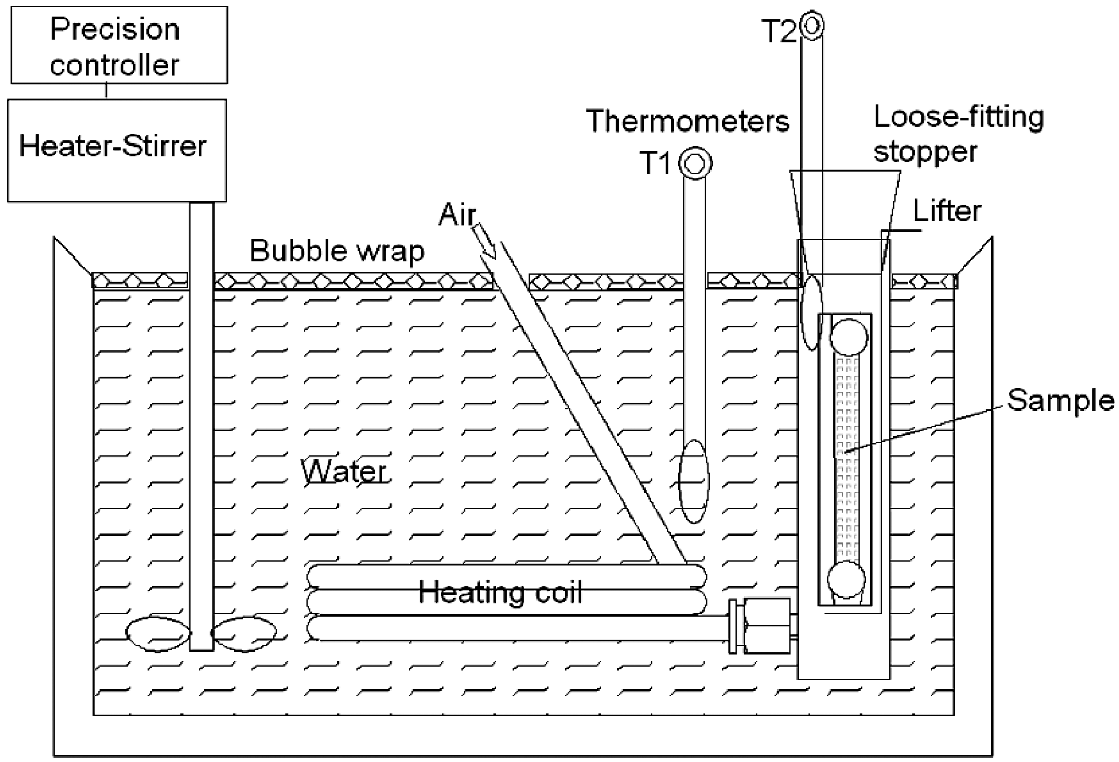

FIGURE 1. Isothermal permeation test rig

to measure early detail like breakthrough, but to minimize the number of weighings required. This was important, as the trials were typically performed for 100 hours (range 25 to 360 hours).

The cumulative permeation (CP) was calculated as weight loss in milligrams per meter of hose. These units permit an estimate of chemical permeating the hose for a given temperature and length of hose in full contact with the chemical. If the volume of air inhaled is known, the average concentration (mg/m^{-3}) can be compared directly with the exposure limit. The duration of the exposure would also have to be taken into account in assessing the risk.

The steady-state permeation rate (SSPR) is calculated from the slope of the CP curve before the permeant is depleted. A 5.6 mm end correction for the actual exposed length between the ball bearings of the Esdan hose samples was used in calculating the permeation per meter of hose.[4] BT is defined here as the time before permeation appears to proceed rapidly, in contrast with the approach taken in the companion article[4] where the breakthrough detection time (BDT) was based on the analytic limit of detection. The reason for this change in approach is explained in Results. The lag time (LT) for each permeation curve was calculated from the time intercept of the section of the permeation curve used to calculate the SSPR. Note that these lag times do not have the same simple relationship to the diffusion coefficient and membrane thickness for hose as they would with gloves[4] (see Results) and estimates of the diffusion coefficient were not possible at this stage.

RESULTS

The effect of temperature on the permeation of MEK through Esdan hose is shown in Figure 2, with duplicate trials shown as open circles and filled triangles. As the temperature increases, the SSPR also increases and breakthrough is evident earlier. When the liquid MEK is depleted, the CP curve begins to level. This depletion of the solvent was observed visually at the end of trials.[4]

The estimate of the BT depends not only on the sensitivity of the balance and the degree of care taken during the filling and sealing the hose samples, as residual chemical can evaporate from the ends of the hose sample for several minutes but also on the method of defining breakthrough. Permeation can be detected within the first hour in all cases, but the process initially proceeds at a slower rate as the solvent front moves through the hose wall. This initial process is more apparent in Figure 3.

During this initial period, the hose becomes softer as the solvent acts as a plasticizer. Under these conditions, holes in the polymer are opened, permitting greater diffusion by the solvent.[5] This process would occur more readily as temperatures increase. Once the solvent front has moved through the hose wall and changed its diffusion properties, the permeation rate increases rapidly. This increase occurs sooner and more rapidly as the temperature increases. Clearly, a different thermodynamic process is occurring initially, when permeation

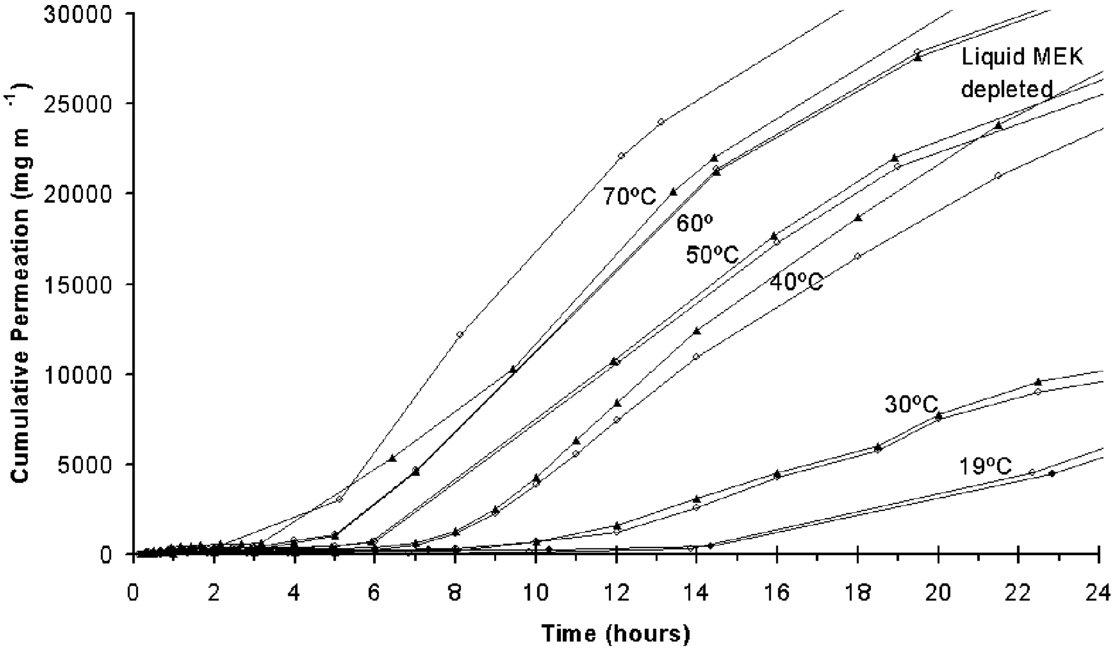

FIGURE 2. MEK permeation with temperature through Esdan hose in 24 hours

is first detected, compared to when the permeation begins to increase more rapidly. If the SSPR is estimated in this period of rapid permeation, then the associated BT would be best estimated when this rapid permeation is first evident—approximated by the diagonal line in Figure 3. This permits changes in BT and SSPR with temperature to be more directly compared. The BT typically occurs when less than 0.05% of the added MEK has permeated.

Early permeation data from the companion study[4] are shown in Figure 4 with the 19°C data from this study but on log-log scales to show both early and late data. The cumulative permeation has been normalized as mg/m^{-1} to remove

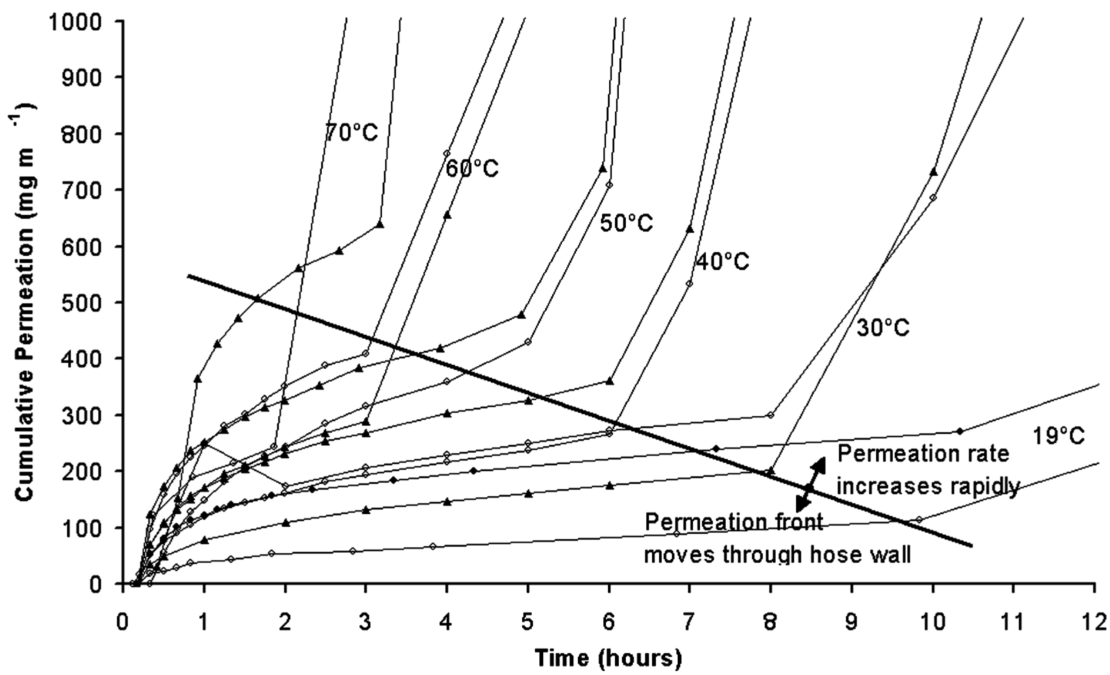

FIGURE 3. Initial MEK permeation through Esdan hose

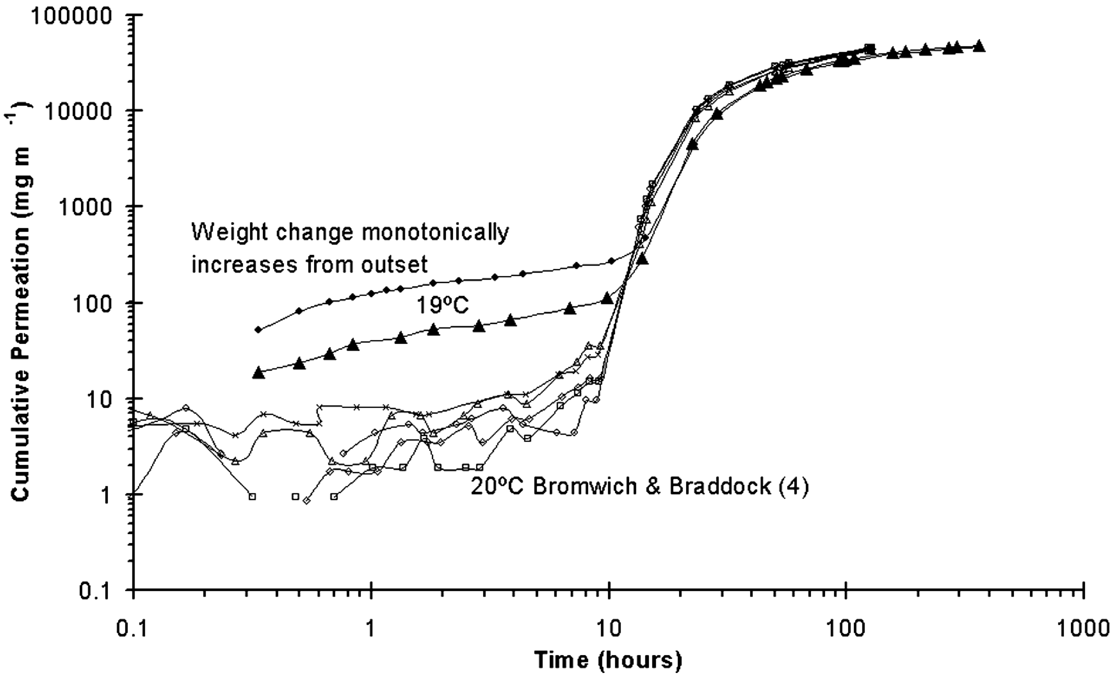

FIGURE 4. Cumulative permeation at 19°C

the scaling from different sample lengths. Though the hose samples were from the same batch and the experiments were performed in the same laboratory, the experimenter (JP) was different and the 20°C experiment temperature was closer to 19°C ± 1°C through a drift in the temperature control of the laboratory, as at this temperature, the isothermal apparatus was not used.

The differences in the data sets in Figure 4 indicate the type of interlaboratory differences that could be expected. However, the CP at 19°C in this investigation (Figure 4) slowly increases from time zero, making estimates of a nonzero BDT based on the method analytic limit of detection not possible. The unknown uncertainties associated with the use of the isothermal apparatus at elevated temperatures would require that the analytic detection limit be established at each temperature. This was not done. Consequently, the BDT as reported in the companion article[4] were not calculated.

Figure 5 shows data from a 30°C trial, to illustrate the method of deriving SSPR, BT, and LT. The permeation rate (PR) is calculated by differentiating the CP data. The BT is the time on the PR curve just before the permeation rate increases. This approach to estimating BT is more satisfactory than estimates from the CP curve where small changes in permeation are not as obvious. The figure also shows four data points (open circles) used to calculate the SSPR. The time intercept of a best fit line with the time axis of the CP curve is used to estimate the equivalent of an LT with gloves (using the Intercept function in Microsoft Excel).

The BT index used in this study is less rigorous than the BDT index defined in terms of the analytic detection limit but should relate better to thermodynamic predictions of SSPR, which is calculated when the hose has also softened with permeant. The BT, LT, and SSPR for the duplicate trials over the temperature range 19–70°C are given in Table I.

DISCUSSION

By determining the pattern of change of permeation with temperature, it is possible to predict permeation outside a measured range[3] to a limited extent. In Figure 6, the natural logarithms of the SSPR estimates are plotted against the inverse of the absolute temperature. Similar plots are given in Figure 7 for BT and LT. An exponential fit of SSPR, BT, and LT with the inverse of absolute temperature can been justified[2] as these parameters can be expected to follow an Arrhenius relationship with the absolute temperature over a limited temperature range.

TABLE I. Effect of Temperature on BT, LT, and SSPR

Temperature (°C)	BT (Hour)	LT (Hour)	SSPR ($mg/m^{-1}/Hour^{-1}$)
19	10.3, 9.8	15.0, 13.9	614, 611
30	8.0, 6.0	10.1, 10.7	749, 777
40	6.0, 6.0	7.8, 7.0	1748, 1437
50	5.0, 3.9	5.6, 5.0	1659, 1594
60	3.0, 3.0	4.3, 4.9	2220, 2235
70	2.7, 1.9	4.2, 3.8	2149, 2614

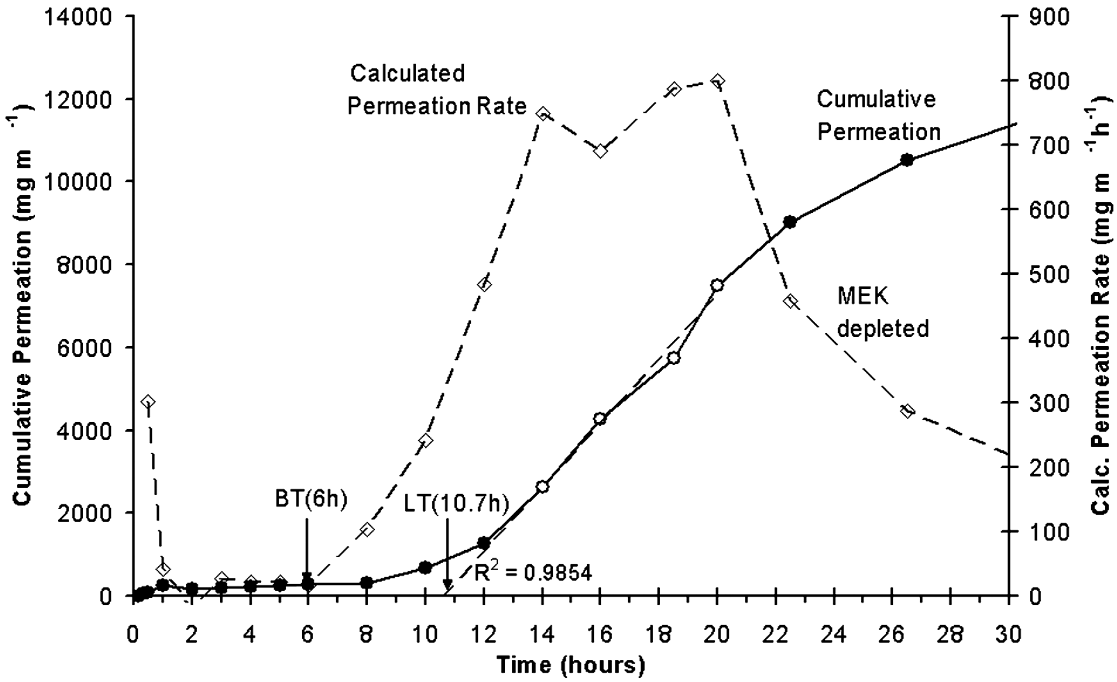

FIGURE 5. CP and calculated PR at 30°C for estimating LT and BT, respectively

For a person using new Esdan hose and breathing 10 m^{-3} of permeant-laden air in 8 hours with 1 meter of hose exposed to MEK, the average inhaled dose at different temperatures is shown in Figure 8. The CP at 8 hours was estimated using the Forecast function in Microsoft Excel when a measurement was not made at exactly at 8 hours. The error bars in Figure 8 are the exposure estimates from the replicate trials. At 57°C, an inhaled dose equivalent to exposure at the threshold limit

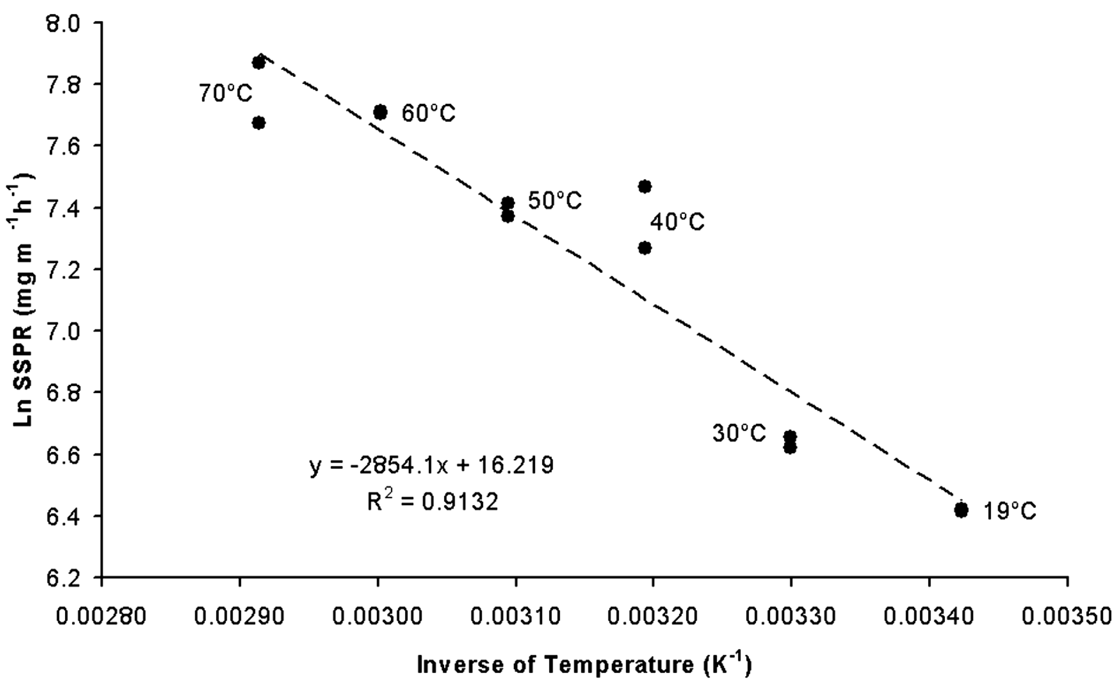

FIGURE 6. Ln(SSPR) for replicate data, with inverse of absolute temperature

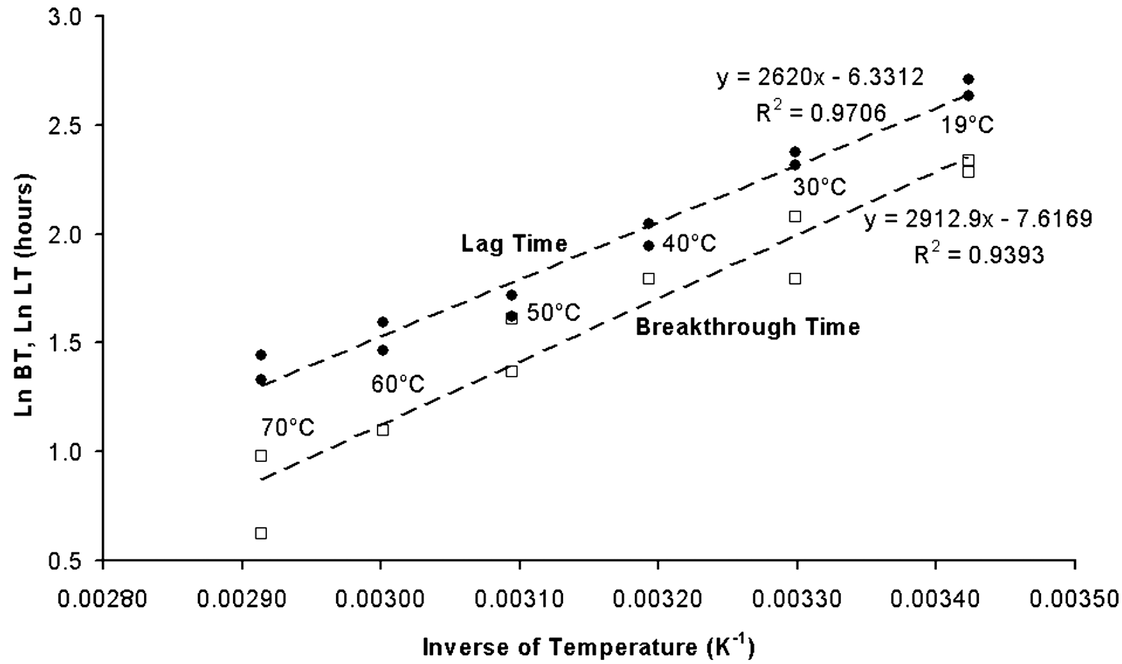

FIGURE 7. BT and LT with temperature, replicate data

value (TLV) (590 mg $m^{-3} \times$ 10 m^3 = 5900 mg) will be reached in the first 8 hours, and the respiratory dose will continue to climb with increasing temperature.

At slightly higher and lower temperatures, the SSPR and BT can be estimated. Cooler temperatures occur in many workplaces and elevated temperatures in excess of 90°C occur in solvent degreasing operations[(2)] and in any operation using steam or boiling water. Estimates of permeation indices at 15°C and 90°C using the exponential fits in Figure 7 are presented in Table II, with the measured data at 19°C. There is only a small

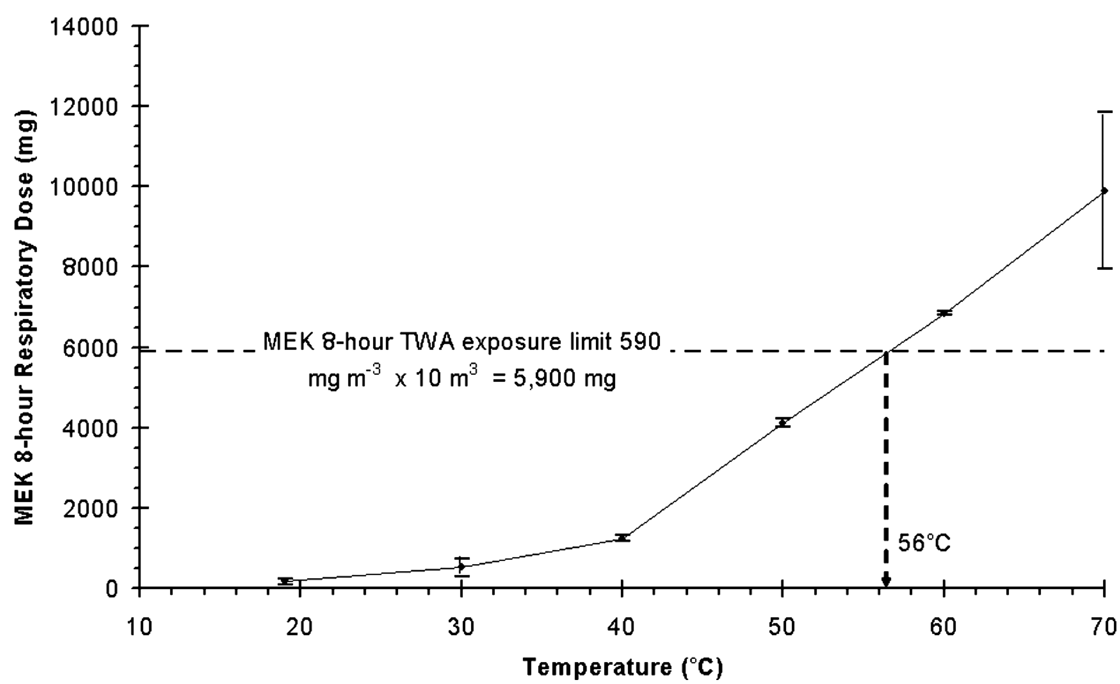

FIGURE 8. Respiratory dose in first 8 hours with 1 m of hose immersed in MEK

TABLE II. Predicted SSPR and BT at 15°C and 90°C

Temperature (°C)	15° Model	90° Model	19° Measured
SSPR (mg/m^{-1}/hour^{-1})	552	4270	613
BT (hour)	12.1	1.5	10.1
LT (hour)	15.8	2.4	14.5

change from 19°C to 15°C but a very large difference between 19°C and 90°C. There would be much greater uncertainties in the estimate of the permeation indices at 90°C than at 15°C, as the indices at 90°C require a greater degree of extrapolation and only limited linearity in the Arrhenius relationships can be expected.[3]

Activation Energies

A predictive model is useful in generalizing experimental findings. Perkins and You[3] demonstrated that permeation rate P through gloves follows an Arrhenius type relationship of the form

$$P = P_0 e^{-E_p/RT}$$

where

P is the steady-state permeation rate normalized for thickness (μg mm cm^{-2}min^{-1})

P_0 is a pre-exponential factor with the same units as P

E_p is the activation energy (kJ mol^{-1})

R is the universal gas constant (0.001487 kJ mol^{-1}K^{-1})

Scaling SSPR by glove thickness as suggested by Perkins and You[3] is not necessary for the calculation of the activation energy associated with permeation because it makes no difference to the value of the activation energy. However, comparison between hose choices of different sizes is not so simple because the ratio of inner and outer diameters, as well as the wall thickness, appear in the expressions to calculate SSPR and LT.[4] By analogy with LT, a similar complexity of scaling could be expected with BT. An estimate of the activation energy for permeation (SSPR) is given in Table III. The activation energy for permeation of MEK through Esdan PVC hose is less than the values for other chemical through gloves but not unexpected as both MEK and PVC are polar.

For BT and LT, a similar Arrhenius-type relationship also exists (Figure 7), indicated by the fit of the linear regressions. The activation energies associated with these indices are 29.8 kJ mol^{-1} for BT and 41.1 kJ mol^{-1} for LT.

TABLE IV. Variability of Permeation Indices with Temperature

	Coefficient of Variation (%)		
Temperature (°C)	SSPR	BT	LT
19	0.28	2.48	3.76
30	1.81	14.29	3.03
40	9.79	0.00	5.27
50	2.02	12.15	4.99
60	0.33	0.00	6.38
70	9.76	17.65	5.63
Average	4.0	7.8	4.8

Repeatability

A measure of variability of the indices at different temperatures is the coefficient of variation (standard deviation/mean). For only replicate data this has limited use, particularly for BT, where coincidence of measurement times and intervals between measurements can produce a false impression of repeatability if the measurement times are far apart and identical. There was no distinct relationship between temperature and the variability of the data in Table IV.

Other Considerations

If pre-exposed hose is subject to elevated temperatures, this would be expected to significantly reduce BTs with subsequent uses or even show immediate breakthrough. In comparison with gloves, the greater thickness of the hose wall will not only make decontamination of the hose matrix more difficult but act as a larger reservoir for toxic chemicals on re-use.

As the permeation rate and breakthrough times increase with temperature, it becomes more important to flush the hose with clean air[4] before use or after breaks if any chemical contact with the hose has occurred. This would counter the more rapid pooling of permeant in the bore of the hose and the more rapid replacement of this pool with permeant from the walls, at elevated temperatures. Complete avoidance of chemical contact with the hose at elevated temperatures increases in importance as the temperature rises.

TABLE III. Comparison of Activation Energies (E_p) for Permeation

Study	Zellers	Perkins and You		This Study
Polymer/permeant	Natural rubbers and n-methylpyrrolidone	Butyl rubber and toluene	Neoprene rubber and benzene	Esdan PVC Hose and MEK
E_p (kJ mol^{-1})	11.38 to 14.1	45.9	13.2	5.7

CONCLUSIONS

CP increased significantly and BTs and LTs decreased significantly with temperature. At a temperature above 56°C, permeation of the hose wall can result in an inhaled dose within an 8-hour shift equivalent to the TLV for MEK, for continuous, complete immersion of a 1-m section of Esdan PVC hose.

A simple model can be used to predict SSPR, BT, and LT outside the measured ranges. At 90°C significant permeation can occur within 2 hours.

Avoidance of chemical contact with the hose becomes more important at elevated temperatures.

ACKNOWLEDGMENTS

The authors would like to thank Russell Saunders from the Griffith University mechanical workshops for the construction of the isothermal test rig, and Steven Beames from the Griffith University electronics workshop for the design and construction of the precision water bath controller.

REFERENCES

1. **Nelson, G.O., B.Y. Lum, G.J. Carlson, C.M. Wong, and J.S. Johnson:** Glove permeation by organic solvents. *Am. Ind. Hyg. Assoc. J. 42*:217–225 (1981).
2. **Zellers, E.T., and R. Sulewski:** Modeling the temperature dependence of n-methylpyrrolidone permeation through butyl- and natural- rubber gloves. *Am. Ind. Hyg. Assoc. J. 54*:465–479 (1993).
3. **Perkins, J.L., and M.-J. You:** Predicting temperature effects on chemical protective clothing permeation. *Am. Ind. Hyg. Assoc. J. 53*:77–83 (1992).
4. **Bromwich, D.W., and R. Braddock:** Chemical permeation testing of air-supply hoses. *J. Occup. Environ. Hyg. 3*:107–117 (2006).
5. **Perkins, J.L.:** Solvent-polymer interactions. In *Chemical Protective Clothing*, J.S. Johnson and K.J. Anderson (eds.). Fairfax, Va.: American Industrial Hygiene Association, 1990. pp. 37–50.