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THEORETICAL & EXPERIMENTAL STUDIES

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The Validation of a Permeation Cell for Testing Chemical Protective Clothing

The performance of a simple rugged permeation cell for testing chemical protective clothing was compared with the reference cell suggested by the American Society for Testing and Materials and using their validation protocol. The new cell overcomes some of the limitations of the reference cell including ruggedness, low dead space, ease and speed of use, and small sample size. The testing of the new cell was performed under standard conditions using acetone against reference neoprene with an automated test system incorporating a photoionization detector. The performance of the new cell was found to be within the acceptance criteria for normalized breakthrough time and steady state permeation rate. The normalized breakthrough time index was a major impediment to the automated testing of more than one cell at a time, as it required a very low degree of cross contamination between cells, if a shared detector was used. It is suggested that lag times rather than normalized breakthrough times form part of the basis for comparison of permeation cells. The pretreatment of test samples to remove volatile contaminants requires consideration.

Keywords: chemical protective clothing, permeation, testing, validation

There is wide recognition of the standard permeation cell published by the American Society for Testing and Materials (ASTM) in ASTM F739[1,2] for chemical permeation testing of chemical protective clothing (CPC) materials used to manufacture garments like chemical suits and gloves. The cell is fragile as it is made of glass, and it does not specifically direct the flow of the incoming collecting medium to disrupt any boundary layer of permeant that may form on the collection side of the test sample. It is designed for fluids and cannot test solid chemicals, but it requires about 60 mL of challenge chemical. It is also slow and tedious to use. Though the ASTM cell was designed to test finished items, it is often used to test the samples of CPC materials. However, it is large and uses a test sample of 68-mm diameter, preventing the taking of samples from the fingers of gloves, and the use of multiple bolts prevents the testing of intact garments. Despite these difficulties and drawbacks, the ASTM cell is still the benchmark that other cells need to meet. A smaller version exists,[3] but does not appear to be in common use. Some published cell designs overcome specific shortcomings or limitations of the ASTM cell, but no single design is likely to be ideal.

To demonstrate equivalence between an alternative new test cell and the ASTM cell, ASTM F739 1996 requires that the test materials be documented and the tests be reported in a certain manner. It is implied that if the test results are within the ASTM acceptance limits, then the alternate cell can be said to be equivalent to the ASTM cell.

Acceptance data for reference neoprene is also published in ASTM F739 1996 and ASTM Committee F-23 has had much foresight in making this material available for testing cells. When the test material and challenge chemical are identical, the requirement for demonstrating equivalence is that the results, in triplicate, are within the acceptance limits for reproducibility (variation between laboratories) and repeatability (variation within a laboratory) published in the standard. However, there is no statistical rationale for testing in triplicate.

In 1988 Patton[4] attempted to validate the proprietary Radian Microcell against the ASTM cell and found a 1985 draft of an ASTM *Standard Practice for Determining Equivalency of*

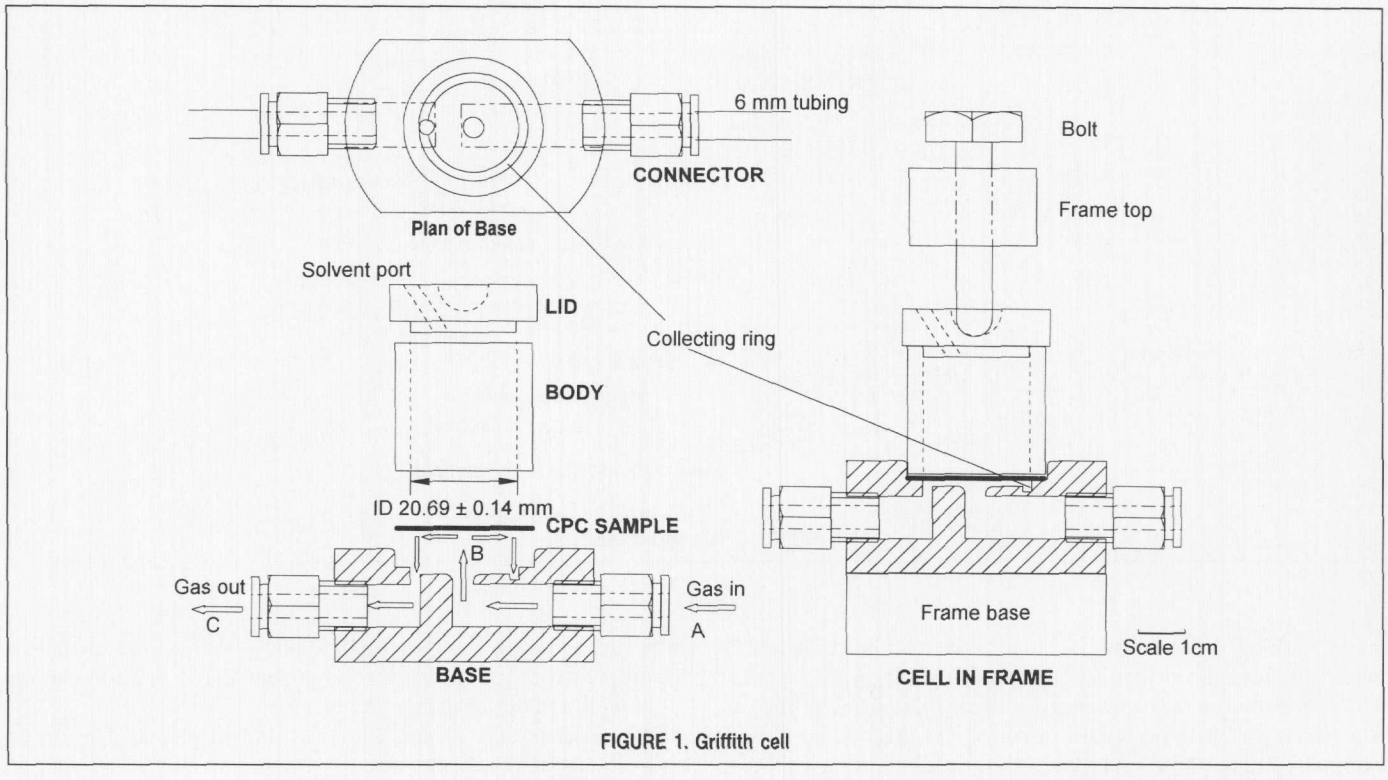

FIGURE 1. Griffith cell

Optional Chemical Permeation Cells to That of the ASTM Cell was inadequate to determine equivalency. Where some equivalence to a reference cell has been demonstrated[5,6] these cells do not appear to have gained wide acceptance, as indicated by either lack of adoption of the new design as the standard or by its lack of use by other researchers.

There is still scope for the evolution of new permeation cells that show equivalence of performance to the ASTM permeation cell, but take features from existing cells, add new features, or address the limitations of the ASTM cell design. However, without demonstrated equivalence, data for new cells are isolated from the existing large pool of test data produced using the ASTM cell.

A cell that is inexpensive, robust, easy to use, and can be used with solids, liquids, and gases both for the challenge chemical and the collection medium—and on excised samples from CPC or on intact garments—would be a marked improvement. This would approach the ideal cell for routine testing.

Modifications to existing cell size[7] or performance,[8] the challenge chemical or permeation detection side of the cell,[8-10] novel cells designs,[5,11] and special cells for field testing[12] have all been suggested, although usually without discussion of functional design criteria. Little has been published to rigorously demonstrate the equivalence of these various cells to the standard ASTM cell.[13] Also, no single cell gives the ability to test all chemicals, including solids, liquids, or gases.

A test cell for measuring the permeation of CPC was developed by Bromwich[13] as an inexpensive, robust alternative to the ASTM cell to demonstrate permeation through gloves in undergraduate occupational hygiene laboratory classes. Several hundred students, many with no technical background, have used the cell with minimal training to test CPC. This work describes this test cell, the Griffith cell, its features, and how it compares with the reference ASTM cell using published performance data.[2] The validation of the Griffith cell against the ASTM cell is described.

Open loop testing is the preferred test method, as it creates the greatest concentration gradient across the test material, and this approach has been used in this experiment. The two performance indices for demonstrating cell equivalence are the normalized breakthrough time (NBT) and the steady state permeation rate (SSPR).

METHODS AND MATERIALS

The validation of a cell requires the development of a system for reproducibly measuring the permeation of acetone though the neoprene reference sample, and a method of collecting the permeation data. The advent of inexpensive personal computers, data acquisition and control cards, and easy-to-use software, has enabled automation of much of the testing and allows a more rigorous approach. It has also permitted rapid and precise collection and analysis of test data. The developments in cell design need to match those in experiment automation.

Permeation Cell Design

The Griffith cell is rugged, simple for student use in large classes, and permits a large number of samples to be quickly taken from one glove with a wad punch. It connects to detectors (toluene stain tubes were used in teaching) and the collection gas supply without tools. The Griffith cell (see Figure 1) was designed to meet criteria of ruggedness and ease of use.

The carrier gas enters the cell in the base at A and is directed toward the CPC sample at B, where it collects any permeant and exits the cell at C, to a detector. Pressure-vacuum push fittings found in pneumatics allow rapid connection and disconnection, without tools, of the cell from the 6-mm pneumatic lines used in the test system. The connectors screw into the base with a one-eighth-inch British Standard Pipe (BSP) thread. To ensure the assembly does not leak, the cell is held together by a bolt in a

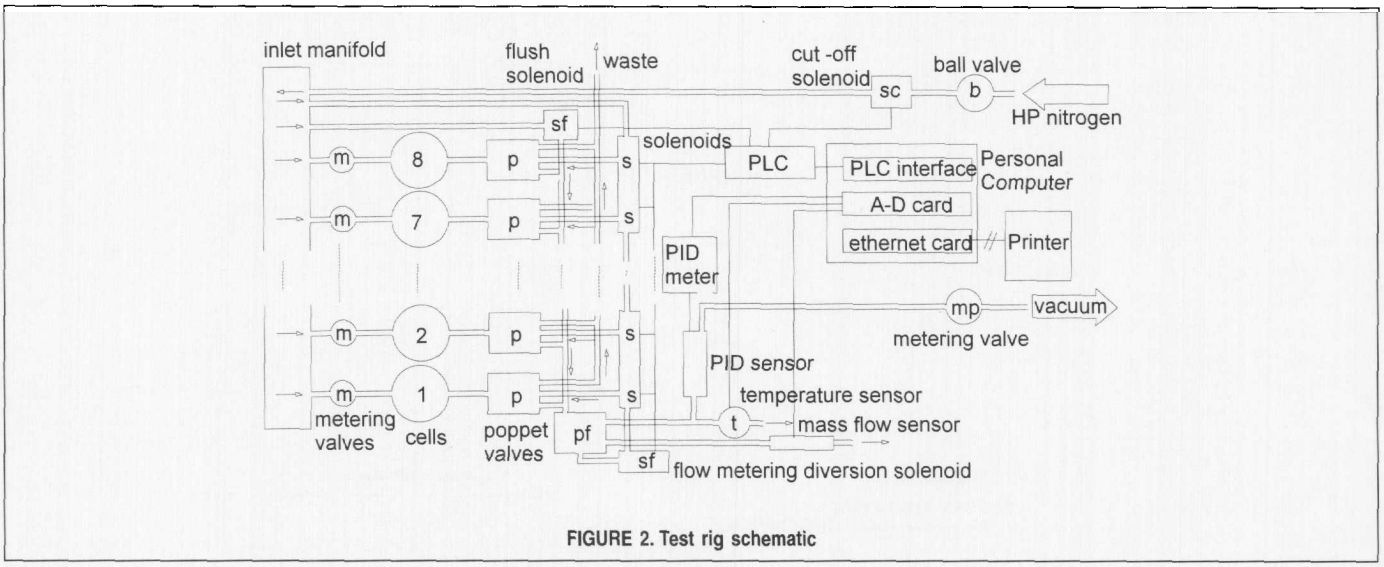

FIGURE 2. Test rig schematic

frame pushing down on the lid. The bolt may be tightened by hand with a handle welded to the top of the bolt, or by a spanner. A G clamp also proved a satisfactory clamp. The shape of the base is arbitrary and may be square or round. As the cell has a single external clamping bolt, it is possible to use it in situ on a glove or chemical suit without cutting the garment. The flat base makes the cell freestanding and easy to assemble.

Cell construction is of brass except for the body. The body is made of thick-walled stainless steel tubing with an inside diameter of 20.69±0.14 mm, to contain liquid challenge chemicals. Its outside diameter of 26 mm determined the diameter of the test sample. The only critical dimension is the inside diameter of the body, which determined the corresponding collection area in the base.

The central inlet port at B directs the carrier gas toward the CPC sample and is designed to eliminate stagnant gas flows near the sample and to ensure good removal of the permeant to the outlet port, with a collecting ring to enhance this flow. At very low flows the degree of stagnation will vary between cell designs. Tests with this cell using water rather than nitrogen, with the collecting flow scaled down by 15 to give a similar Reynolds number, indicated that for a nitrogen flow of 500 mL/min there was no stagnation and that the flow was turbulent. At 100 mL/min the flow took less than 1 sec to clear the collecting surface of the test sample to the collecting ring. There was some initial asymmetry toward the outlet port, after which the remains of the bolus moved evenly toward the collecting ring and then along the collecting ring to the outlet port. The flow was probably not turbulent. Diffusion of the vapor near the test sample surface in the 1-mm gap between test sample and cell base into this radial flow would ensure that no pockets of vapor would persist. Tests with nitrogen flow rates between 400 and 7000 mL/min had no effect on steady state permeation rate when reference neoprene was challenged with acetone.

The major features of the cell are that:

- it is very quickly assembled and disassembled;
- it is small—1 mL of (toxic) challenge chemical is used;
- it is capable of being used on intact garments;
- samples are quickly prepared using a wad punch;
- samples may be taken from most areas of a garment, including the fingers of gloves;
- it has a fast response time from lower dead volumes (3.7 mL, compared with 60 mL for the ASTM cell);
- it can be adapted for use with solids[9] and gaseous challenge chemicals (with a sealed lid, though the ASTM cell too can be used with gaseous challenge chemicals);
- it is mechanically robust, as it was undamaged by 1-m drops onto the laboratory floor;
- it can be easily made in a small workshop on a metalworking lathe; and
- it is less bulky than the ASTM cell and ideal for use if a number need to run together.

Experimental Setup

A testing rig was developed[14] and is shown schematically in Figure 2. Electrical connections are shown as single lines and gas flows as double lines. The main feature of the test rig is a high degree of automation while testing eight cells in sequence in a 1-min cycle, with no intervention once the challenge solvent is placed in each cell. The test rig is also capable of rapid reconfiguration though software changes and quick connect fittings between most elements.

The test rig is designed to sequentially measure the chemical permeating each cell by diverting flow through each cell to an HNU P101 photoionization detector (HNU Systems, Newton, Mass.) with a 10.2 eV lamp (PID) sensor. Carrier gas (high purity nitrogen) enters the test rig from a gas regulator. The nitrogen flow can be stopped with a cut-off solenoid valve sc or manual ball valve b to conserve nitrogen. The nitrogen pressurizes the inlet manifold and then flows to the cells via metering valves m (Swagelok NUPRO B244, Brisbane Valve & Fitting, Brisbane, Australia). The nitrogen supply pressure (90 kPa) is sufficient to ensure that flow though one cell does not affect the flow through another. Cells 1 to 8 are clamped in a rigid steel frame, in a row, each with its own metering valve.

The exhaust from each cell is normally directed to waste by the poppet valves p operated pneumatically by solenoid valves s. These poppet valves are switched in sequence to allow the carrier gas from each cell to be tested by the PID sensor. The flow to the PID sensor is diverted just before each measurement by the flow metering diversion solenoid and poppet valves, sf and pf respectively, to a mass flow sensor (Honeywell AW5000, Honeywell Sensing & Control, Sydney, Australia), to measure the flow though the cell. This delay is not wasted as it still allows the line

from the cell to the poppet valve pf to be flushed and greatly reduces chemical exposure to the flow sensor. The whole collecting line from solenoid valve sf to the PID sensor and temperature sensor t is flushed with 5 L/min nitrogen by solenoid sf before the start of a run and then as required.

Temperature of the carrier gas is measured by a temperature sensor t (LM335Z, National Semiconductor, Santa Clara, Calif.) in the gas flowing past the PID sensor, and the flow through the PID sensor is controlled by the metering valve mp connected to the laboratory vacuum. All cells are treated the same, except that flow rates through the cells are in approximate proportion to the exposed sample areas in each cell, to present the PID sensor with the same range of challenge chemical concentrations.

The control solenoids are actuated by an inexpensive programmable logic control (PLC) card (Procon, Melbourne). The cards and software were initially driven by a generic 486SX IBM® compatible personal computer (PC), but later a Dell® 133 MHz Pentium® PC was used. Signals from the temperature sensor, mass flow sensor, and PID are digitized by a generic 16-channel, 12-bit, analogue to digital converter card inside the PC.

A control program was written in Microsoft Visual Basic® 3.0 Professional and run under Microsoft Windows for Workgroups® V3.11. The control program regulated the sequencing of the flow through the cells past the PID; measured the flow, temperature, and solvent concentration in the collection medium through each cell in a cycle; linearized the response of the sensors; and displayed all the data graphically and stored it as computer files for calculation of breakthrough times, steady state permeation rates, and any other permeation indices programmed into the code.

Temperature, Flow, and Solvent Concentration

The temperature transducer was calibrated with a certified thermometer. The mass flow sensor was indirectly calibrated by a bubble tube (Gilian 800268 meter, Gilian Instrument Corp., Wayne, N.J.) with a D800286 20–6000 mL/min certified flow sensor) placed before the PID sensor and alternating the carrier gas flow between the bubble tube and mass flow sensor. The mass flow sensor's calibration curve was programmed into the test software to read in milliliters per minute.

A flow rate of between 50 and 150 mL/min for the collecting gas is recommended for the ASTM cell,[2] with adequacy of mixing of the collection media in the cell as the rationale for the lower flow rate. No rationale is given for the upper flow rate. In this experiment a nitrogen flow rate of at least 2000 mL/min, or dilution of the effluent flow, was required to match the acetone concentrations from the ASTM cell to the PID detector. It was found that the steady state permeation rate for the Griffith cell was essentially unaffected (<0.15%) for nitrogen flows between 400 to 7000 mL/min. At a flow rate below 400 mL/min, the PID was off-scale, and at 7000 mL/min the neoprene sample vibrated so violently that the acetone was sprayed from the filling hole in the cell lid. Flow rates of 2000 mL/min for the ASTM cell and 500 to 1000 mL/min for the Griffith cell were chosen. Perkins[17] used 5000 to 9000 mL/min with an ASTM cell modified to allow larger flow rates through the ASTM cell's stopcocks and found that breakthrough time (BT) was decreased with pressure in the cell due to flow though the cell. The association was weak (correlation coefficient $r^2=0.2$; that is, only 20% of the change in BT could be attributed to changes in flow rate).

The fan inside the PID detector head was sealed and overridden and its flow controlled at 50 mL/min by a precision metering valve attached to the laboratory vacuum. The PID was calibrated with 0 to 11 μL of acetone using a 10-μL micro-syringe (SGE International, Ringwood, Australia) in 4 liters of nitrogen in a 5-liter Tedlar® sampling bag (SKC Inc., Eighty Four, Pa.).

Liquid test chemical was introduced into the cell with a pipette through the lid, wetting the upper surface of the CPC sample that had been cut from a glove or other CPC with a 26-mm wad punch. The CPC sample formed an adequate seal between the body and the base without any gaskets. The liquid test chemical, usually an organic solvent, then began to permeate the CPC sample by diffusion and was removed from the lower surface of the CPC sample cell by a carrier gas.

Decontamination of the cells between runs was done for 15 minutes at 60°C in a vacuum oven made from a circular electric frying pan with a lid of 13-mm polycarbonate sheet. The low decontamination temperature was necessitated by the 60°C temperature rating of the seals in the connectors.

Normalized BT

As most measurements of permeation are performed at intervals using instruments like gas chromatographs, BT has been defined in ASTM F739 1996[2] as "the elapsed time measured from the start of the test to the sampling time that immediately precedes the sampling time at which the test chemical is first detected." This is a conservative estimate of the time at which material is first detected on the inside of the CPC. However, the nature of the diffusion process is such that almost the instant a chemical is placed on one side of a polymer membrane, molecules will appear at undetectable concentrations on the other side. Therefore, BTs are very dependent on the sensitivity of the chemical detector. To allow data to be compared between laboratories, the time that a permeation rate of 0.1 μg/cm²/min of the chemical is detected is defined by the ASTM F739 standard as the NBT. While this does allow comparison of data, it must be treated with caution as significant amounts of very toxic chemicals may permeate before this rate is reached; the data may be highly variable between batches of CPC,[15] and the chemical may be an impure mixture that permeates at different rates than the pure test chemical. Other factors such as sample thickness and workplace temperature may also affect permeation.

ASTM suggests that the BT be based on analytic detection limits, and an NBT based on detecting 0.1 μg/cm²/min be recorded. This does require that the analytic detection limit be known, particularly if NBT is to be used to compare cells with the ASTM cell.

Detection Limits

The method of determining the detection of 0.1 μg/cm²/min to estimate the NBT in ASTM F739 1996 is stated as "twice the baseline noise level of the system with the blank cell in place." This is open to interpretation, as the method of determining the noise level is not defined. Appendix X2 of the standard outlines a method of slowly injecting solvent into a cell with an aluminum blank as a test sample. This appears to be based on a paper by Verschoor,[16] who used a semiquantitative estimate of the noise level from a chart recording of the permeation rate, and dilution of the test chemical with an undetectable chemical to achieve low injection rates. The method does not directly relate to the detection of breakthrough under test conditions, as the test sample is substituted by an aluminum blank. If the sample itself produces any volatile contamination, then this would adversely affect the detection limit.

The International Union of Pure and Applied Chemists and

the American Chemical Society Subcommittee on Environmental and Analytical Chemistry[17] both suggest a statistically based detection limit. A detection limit of three standard deviations (SD) above the blank is suggested, particularly if the scatter of measurements of the blank is not normally distributed. In this experiment it was found that the distribution of the noise signal about the blank signal approximated a normal distribution, so two rather than three SD above the blank would give a confidence level of 97.7% that a nonzero permeation rate was detected. This compares with a lower 89% confidence level when the blank distribution is not known, requiring that three SD rather than two SD to be used.

For a given test cell, sample, and challenge chemical, the system detection limit depends on the range setting of the PID, the degree of decontamination of the system prior to a test, and the nitrogen flow rate. For acetone in nitrogen for normal runs (using the highest range of the PID of 5000, and 500 mL/min nitrogen) with multiple cells, this was 0.1 $\mu g/cm^2/min$ with the Griffith cell, determined as two SD of the signal above background. With careful decontamination of the PID, reduced flow rates (100 mL/min), and the lowest range setting on the PID (of 50 rather than 5000), the detection limit could be reduced to less than 0.004 ± 0.001 $\mu g/cm^2/min$, if only a single cell was monitored. The design of the experiments was then dictated by the required detection limits.

SSPR

Once a chemical has permeated a sample of CPC, there is a tendency for a constant permeation rate to develop, driven by the chemical concentration gradient across the test sample, the diffusivity of the material to the chemical, and the thickness of the sample. This is the SSPR.

Experiment and room temperature were 21 ± 1°C at all times, and relative humidity was usually between 45 and 69%. The sample storage conditions required by ASTM F739 1996 are 21 ± 5°C with a relative humidity of 30 to 80%, but no standard experimental test temperature is given. The test temperature has not yet been standardized by ASTM F739 1996, but the SSPR could be expected to increase with temperature, making comparisons difficult.

Reference Cell

Although not needed for the comparison of the Griffith cell to published ASTM cell data, an ASTM cell was constructed by a local scientific glass company (Labglass, Brisbane, Australia) with drawings from ASTM F739 1985.[1] This allowed the shape of an ASTM cell permeation curve to be qualitatively compared with the Griffith cell permeation curves. Rather than a metal clamp with three bolts to hold the cell, a PVC clamp with six bolts was made to hold the cell together. This had some "give" and proved to be satisfactory. The cell was used without gaskets as it was found to seal well with the neoprene sample material, if carefully tightened. The actual diameter of the wetted sample area of the ASTM cell was 42.92 ± 2.96 mm compared with the 51 mm specified in ASTM F739 1996. This size disparity was of some concern, but the main objective of this experiment was to compare the Griffith cell with the published ASTM data, and a miniature 25-mm version of the ASTM cell was said to be comparable[13] to the standard ASTM cell.

Test Materials

The 400 μm reference neoprene used in this experiment came from the same stock as material used for the published figures in ASTM F739 1996. Acetone (analytic reagent grade, Ajax Chemicals, Sydney, Australia) was used as the challenge chemical as suggested by ASTM, and for calibrating the PID sensor.

Sample thickness was measured with a dial gauge (2109F, Mitutoyo Corp., Kawasaki-Shi, Japan) readable to 1 μm and a stated accuracy of 3 μm with a 5-mm flat circular foot on the gauge and a flat surface on the stand. Engineering check strips with an apparent precision of 10 μm indicated measurements were well within the ± 20 μm accuracy specified by ASTM F739 1996. Thickness measurements on the neoprene stock showed a variation of 32 μm over the surface, averaging 405 ± 5.6 μm ($n=280$). This was comparable with the ASTM data (range 390 to 430 μm, $n=8$), which was not unexpected as the material came from the same batch. The dial gauge was shown to compress the neoprene by 2.1 ± 0.7 μm, but this correction was not large and so was not applied to this data. A calibrated top pan microbalance (Sartorius M5, Sartorius AG, Goettingen, Germany) readable to 1 μg was used to weigh the cut samples, but this had no relevance to the cell validation outcomes as no comparable density data for the standard material was available.

Experiments

Two experiments were performed, the first to determine the SSPR and the second to determine the NBT.

In the first experiment, six runs of eight cells were performed with the Griffith cells challenging standard neoprene with acetone with a cycle time of 54 sec. Two runs were also made with only the ASTM cell and had a cycle time of 7.2 sec. A nitrogen flow rate (controlled to 1%) of 500 mL/min through the Griffith cells and 2000 mL/min through the ASTM cell was used.

Prior to each run, residual contamination was removed from the cells. The three Griffith cells were baked in the vacuum oven at 60°C, and the ASTM cell was baked in a hot air oven at 45°C, as it was too bulky to fit in the vacuum oven. Approximately 1 mL of acetone was introduced into each Griffith cell on a computer prompt and a start timer for each cell was triggered in the computer. As the ASTM challenge cell volume was nominally 60 mL, the cell was tilted from its vertical orientation during the first couple of seconds to wet the entire exposed sample with acetone. Filling of the cell could then proceed in a less hurried manner. Once the cells were loaded and the experiment started, the experiment continued for a predetermined 60 min.

The second experiment required a more thorough decontamination of the test rig prior to each use. An hour-long flushing with high-purity nitrogen of the system, PID, and cell with sample in place, achieved a stable, low background signal from the PID. To maintain the required low detection limits, only one Griffith cell at a time was tested, to eliminate the possibility of carry-over between cells. However, this did enable over 1000 measurements to be made on each run as there was no need to wait for a new equilibrium between measurements. During this experiment it was noted that there was a small but immediate response from the PID on addition of the acetone. Several runs were performed with neoprene samples that had been baked in the vacuum oven at 60°C for 15 minutes to determine whether the sample was the source of immediate response.

An NBT for the ASTM cells is required to be reported, and this implies that the time at which a permeation rate of 0.1 $\mu g/cm^2/min$ occurs is measured. To measure this permeation rate, a lower, zero permeation rate must be demonstrated and a detection

TABLE I. Replicability of Data

Index	ASTM F739 1996 Acceptance Data			Experimental Results			
				Griffith Cell		ASTM Cell	
	Mean	Lower Limit	Upper Limit	Mean	Standard Deviation	Mean	Standard Deviation
SSPR (μg/cm²/min)	245	152	397	201.9	7.48	203.3	3.77
NBT (minutes)	7.2	4.8	9.6	9.5	0.48		

limit calculated, based on the noise in this zero signal. This very low level must be achieved before the acetone is added to the neoprene test sample. For a sequence of tests, the levels in the system must be cleared from 200 μg/cm²/min to a stable figure near 0.01 μg/cm²/min, a factor of 20,000. This was achieved, but was time-consuming. With multiple cells switching to the one detector, it was not possible to reliably ensure than the residual levels in the system (mainly in the PID) were below the NBT permeation rate. Thus, to measure the NBT only one cell could be tested in each run unless separate detectors were used for each cell.

To allow the second experiment to continue to steady state conditions and demonstrate equivalence between the two experiments, the PID scale had to be changed from 50 to 5000 and the flow rate increased from 100 to 500 mL/min, once breakthrough was evident.

RESULTS

Summary of Results

The replicability of the data to the interlaboratory published data in ASTM F739 1996 is shown in Table I. The SSPR results are for the first experiment (n=48) with Griffith cells and the ASTM cell (n=2). The NBT results are from the second experiment (n=4).

The reproducibility of the data within this laboratory is shown in Table II. The SSPR data is from the first experiment (n=48) and the NBT data is from the second experiment (n=4). The reproducibility acceptance limits are 2.8 (or 1.96 $\sqrt{2}$) times the coefficient of variation within the ASTM laboratories.

Steady State Permeation Experiment

A graphical view of the data indicates the closeness of the permeation curves. Rather than present all 48 curves, the results from a typical run of 8 Griffith cells, plus 2 runs with the ASTM cell are shown in Figure 3. The raw permeation data was transformed to units of micrograms per square centimeter per minute including adjustments for average flow rate through the cell and wetted area of the cell.

There was little variation within runs, between runs, or between cells. The ASTM cell deviated slightly from the Griffith cell around breakthrough, but merged with the Griffith cells before steady state conditions occurred.

TABLE II. Reproducibility of Data

Index	Coefficient of Variation (%)			
	ASTM F739 1996 data		Griffith Cell	
	Value	Acceptance Limit	Within Runs	Pooled Data
SSPR	22	62	2.1	3.7
NBT	12	33		4.7

NBT Experiment

The time of breakthrough is shown in Figure 4, and it is evident that all the cells show significant permeation by 9 minutes. The NBT permeation rate is reached between 9 and 10 minutes.

The permeation curves in Figure 4 are on a logarithmic scale to emphasize the noise in the signal before breakthrough is detected and the nature of the diffusion process that predicts an immediate but undetectable breakthrough. The permeation rate zero just prior to the addition of the acetone was set to a slightly positive value of 0.003 μg/cm²/min rather than straddling zero, to allow the data to be shown on a logarithmic scale. This small offset has no significant effect on the determination of either the NBT or the SSPR.

The immediate detection of an unknown volatile chemical from the samples is much less evident in the neoprene samples that were pretreated with heating to 60°C in a vacuum for 15 minutes prior to the test. The untreated samples did quite return to the pretest levels before breakthrough.

DISCUSSION

Validation Criteria

ASTM F739 1996 has tabulated performance criteria for the ASTM cell based on interlaboratory trials involving six laboratories using three polymers challenged with acetone. (Thirty laboratories would have been statistically desirable, or a more conservative application of Student's t statistic may have been desirable to estimate acceptance limits.) For neoprene, three replicates were used, and it appears neoprene was chosen for validating cells as it gave the most reliable data. Twelve measurements, from four of the laboratories, appear to have been pooled to produce the acceptance statistics with a 95% confidence interval.

On this basis, the replicability of the ASTM data and repeatability of the data for the two experiments were all well within the acceptance limits recommended by ASTM. The Griffith cell can be said to be equivalent to the ASTM cell.

SSPR

The coefficient of variation for the 48 Griffith cell SSPR estimates was less than a third of that for the laboratories in the ASTM trials. The reason for this higher degree of replicability is not known as limited details were given for the ASTM interlaboratory trials. Figure 5 shows the curves from Figure 4 on an expanded scale for the period 30 to 60 min. The degree of correlation of the permeation curves is more obvious in this figure as there is more variation between cell types than between cells. The greater

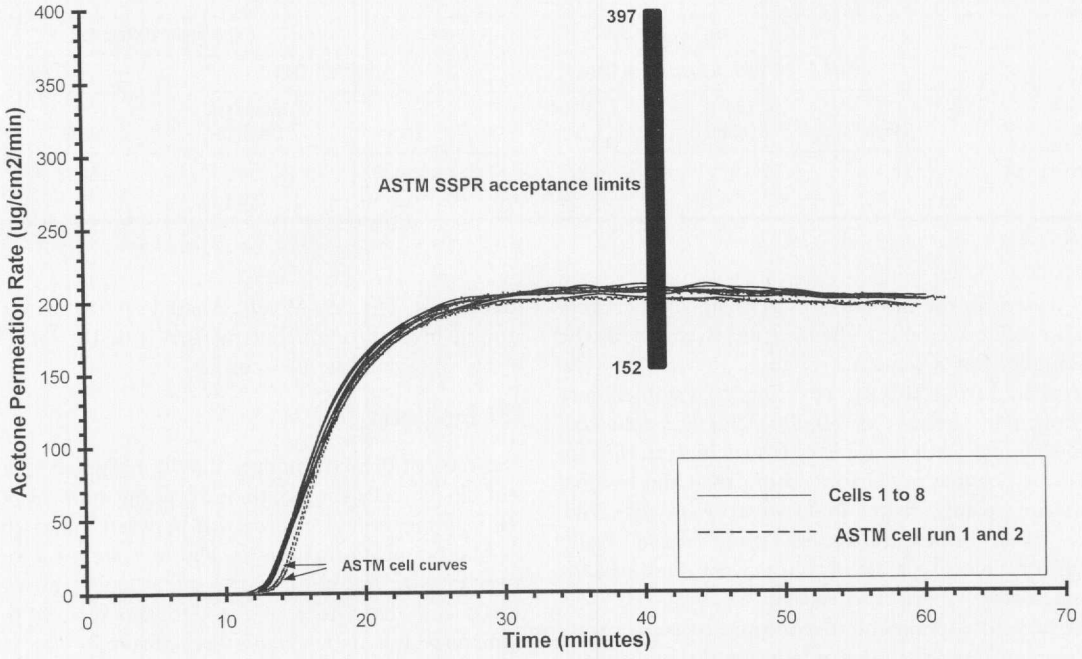

FIGURE 3. Cell permeation curves, run B and two ASTM runs

number (165 versus 16) measurements were made on the ASTM cells in this period as only one cell was monitored. A slight downward trend after 40 min is evident in all the curves.

This downward trend may be attributed to swelling of the polymer by the acetone rather than drying of the test sample, since separate tests with various depths of solvent (3 to 15 mm) in the Griffith cell produced the same result.

The automation of this experiment gave acceptable values for

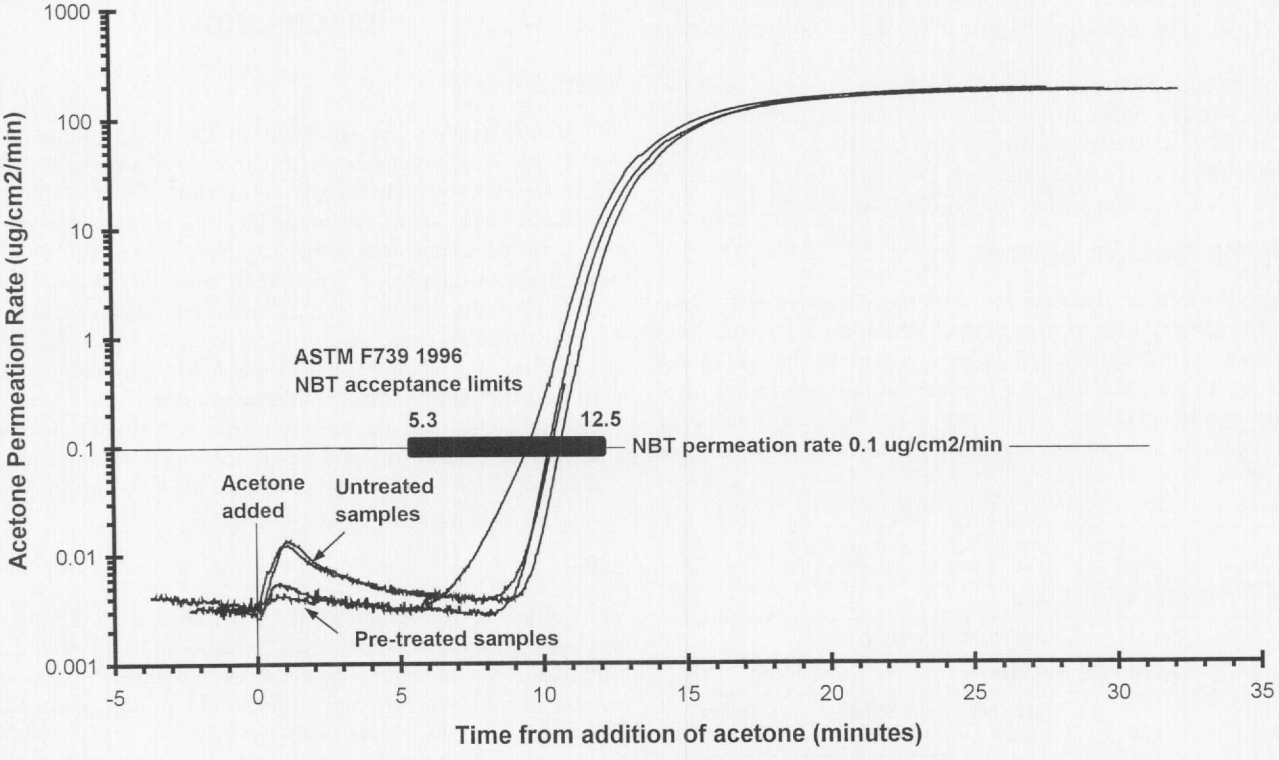

FIGURE 4. Breakthrough time and ASTM acceptance limits

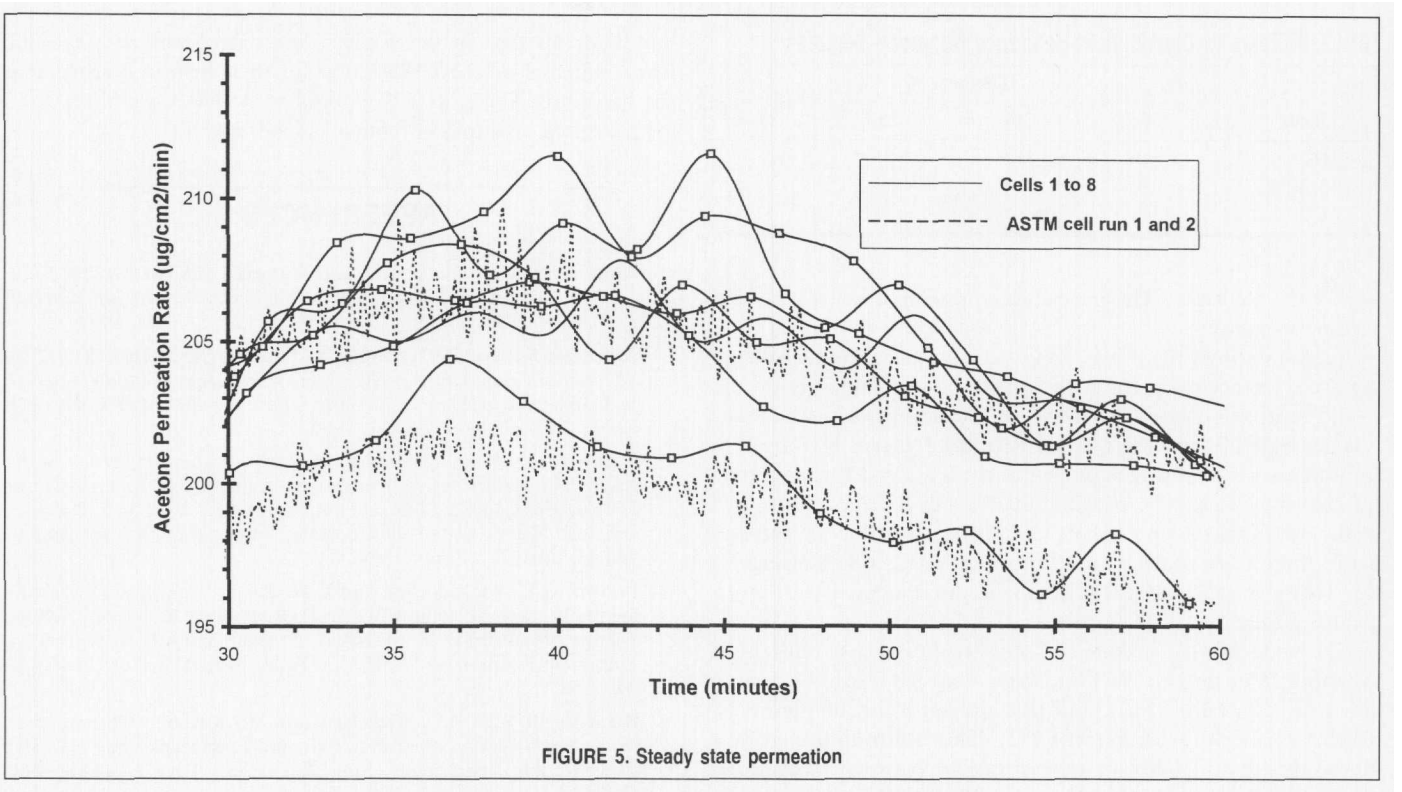

FIGURE 5. Steady state permeation

the SSPR, but the slight carry-over between cell measurements precluded the use of this data to directly estimate the NBT.

NBT

The NBT estimates for the four runs in the second experiment showed the degree of variation to be well within the ASTM acceptance limits, as shown in Table II. Indices other than the NBT exist, which would still assist the ranking of CPC for a particular chemical. The most popular one appears to be the lag time (LT), which is determined from the intercept of the integral of a permeation curve with the time axis. It is largely independent of the analytic detection limit that would allow multiple cells to be tested at once with some carry-over between cells, but less constrained by low detection limits. This would allow a sufficient number of measurements to give statistical validity to test results. The LT can also be directly used to determine the diffusion coefficient of the challenge chemical though the polymer and in turn allow the calculation of the solubility of the solvent in the polymer from the SSPR, which can be related to the product of diffusion and solubility.

Sample Preparation

On addition of the acetone, there was a hitherto unobserved, immediate fast response of the detector, peaking at about 1 min, followed by an exponential decay of at least 8 min. The source of the response appears to be the sample itself, as treating the sample in the vacuum oven for cell decontamination at 60°C for 15 min greatly reduced this initial response. A possible mechanism is that the acetone almost immediately sets up stresses in the exposed surface of the neoprene sample. These stresses may produce a slight stretching of the sample, releasing some absorbed air contaminants or other volatile material present in the sample. If the aim of the testing is to determine the permeation of the challenge chemical and minimize spurious effects, then a standard sample pretreatment may be worth considering.

This effect may have some application in the workplace. If the matrix of CPC is contaminated with a very toxic chemical, then there may be an immediate, low-level release of the chemical inside the CPC with the mechanical stresses of use or exposure to another chemical.

Test Criteria

In determining the number of tests to perform using the ASTM F739 1996 protocol, or to demonstrate equivalence, it appears that the choice of three replicates is an arbitrary choice with limited statistical basis. It is possible that the cost of testing a statistically significant number of samples is prohibitive, and closer to seven or eight replicates may be required to demonstrate real differences between sets of measurements on given samples. Schlatter,[18] in reporting the work of Mickelsen,[19] indicated that seven replicates were needed to be "statistically significant" in detecting differences in performance of samples.

In work preceding these experiments[14] Ansell single- and double-dipped PVC gloves were challenged with toluene. A number of permeation indices, including BT (determined by a best fit time intercept of the permeation curve with the time axis), SSPR, and LT were calculated (see Table III). The number of measurements needed to discriminate between the gloves (power 80%, $p<0.05$)

TABLE III. Tests to Discriminate Ansell Single-Dipped and Double-Dipped PVC Gloves

Index	Number of Tests
BT	25525
SSPR	3
LT	36

TABLE IV. Tests to Discriminate Reference Neoprene Samples

	Difference %			
Index	5	10	20	30
BT	97	25	7	3
SSPR	15	4	1	1
LT	2	1	1	1

were also calculated. This probably represents a worst case, but realistic scenario.

Table IV shows the more precise measurements from challenging the reference neoprene with acetone gave a similar result, but would represent a best case scenario. The comparison set of data was generated by varying LT, SSPR, and LT means by 5 to 30%. In both cases the sensitivity of LT estimates was much greater than BT estimates. In the worst case scenario, only SSPR could be used with three tests to discriminate the gloves. In the best case scenario, three tests could be used to discriminate a 30% change in BT. However, LT and SSPR could be discriminated with much greater sensitivity.

The wide ASTM acceptance limits (replicability coefficient of variation 26%) for the NBT indicates that NBT may be a poor index of cell performance (and perhaps not a reliable figure on which to base the selection of CPC). This is also indicated by a much greater variability in reproducibility between laboratories than repeatability within a laboratory. The SSPR appears to be a more robust index (coefficient of variation 22%) as the index has greater reproducibility and a similar repeatability. The data from these experiments indicate the SSPR variability has the most potential for improvement. The choice of appropriate performance indices for comparison should eventually lead to more precise numbers being published by manufacturers to assist the CPC user to make the most appropriate choice of CPC.

As the SSPR for the Griffith cell was shown to be independent of the flow rates over a large range of flows, it appears that the only critical variable for the Griffith cell and the ASTM cell is the exposed area of the test sample, when the temperature is constant. The general ASTM flow requirements cannot be justified for cells, except indirectly as a requirement to ensure adequate removal of permeant from the test sample. This should be more a function of cell design than an operational requirement.

CONCLUSIONS

The Griffith cell with advantages over the standard ASTM cell, and possibly other similar cells, has been shown to be equivalent to the standard ASTM cell, using the ASTM F739 1996 criteria.

The difficulty in producing reliable NBT data at a low permeation rate impedes the automation of permeation testing and is overcome by the use of LT.

Pretreatment of test samples to remove residual volatile material may be warranted.

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