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Development and Validation of an Alternative Chemical Permeation Test Cell

Citation

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ABSTRACT

A new chemical permeation test cell was developed. The new cell design focused on the flow path of the collection medium while incorporating important features of previous permeation test cell assemblies. Validation experiments were performed to compare the new cell with the unique test cells described in ASTM F739, *Standard Test Method for Permeation of Liquids and Gases Through Protective Clothing Materials Under Conditions of Continuous Contact*, and National Fire Protection Association (NFPA) 1994, *Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents*. In an evaluation of the permeation resistance of fluorinated ethylene propylene (FEP) film to toluene, the new design demonstrated results equivalent to the ASTM F739 cell combined with an overall reduction in variability. Larger cumulative permeation values were observed for all permeant-material pairs tested with the new cell when compared to the NFPA 1994 specified cell type. This difference was statistically significant at the 95 % confidence level, although levels of variation in intra-replicate and pooled data sets were found to be within accepted limits. The new cell was found to be a viable alternative for both cell types to which it was compared. The new design represents an evolution in permeation cell

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design not only by combining the functionality found in multiple cell types but also through the improved quality of chemical permeation test results.

Keywords
chemical protective equipment, permeation, permeation cell, validation, permeation rate

Introduction

Resistance to chemical permeation is a defining characteristic of chemical protective equipment (CPE). The protection provided by CPE is measured using standardized "swatch-level" test methods. At the most basic level, permeation testing evaluates the resistance to molecular transport of a challenge chemical through the matrix of the CPE material. The material is then characterized by two attributes: the magnitude of the transport and the rate at which it occurs. Assessment of these attributes provides the relevant information to identify afforded levels of protection. Consequently, the test cell assembly used for measuring chemical permeation has a pivotal role in the evaluation of CPE's performance.

Many permeation cells have emerged since the late 1970s [1–3]. A single design described by Henry and Schlatter in 1981 [4] has become the internationally recognized standard with its inclusion in the ASTM F739-12e1, *Standard Test Method for Permeation of Liquids and Gases Through Protective Clothing Materials Under Conditions of Continuous Contact* [5], and, more recently, ISO 6529:2013(E), *Determination of Resistance of Protective Clothing Materials to Permeation by Liquids and Gases* [6], test methods. Henry and Schlatter's design, henceforth referred to as the ASTM F739 cell, is smaller but remains fundamentally unchanged from its original inception [7].

The ASTM F739 cell is the most commonly used design for evaluating CPE against an infinite chemical exposure scenario. These testing methods require the material to be fully exposed and in constant contact with the challenge chemical, regardless of whether the challenge chemical is in a gaseous or liquid state. Although the volume of challenge is limited to that allowed by the cell design, a seemingly infinite mass of chemical is available for transport. Continuous exposure in this manner for extended periods of time is considered to be a worst-case scenario for the CPE end user [8].

When CPE is intended to be utilized within an environment in which constant contact with an undiluted chemical has been determined to not be a potential hazard, permeation testing is performed using an appropriate degree of chemical challenge [8,9]. Contrary to the aforementioned infinite exposure, the transport properties of materials evaluated in this manner are dependent upon the finite amount of challenge chemical available. Contemporary tests for reduced levels of exposure typically base their methodology on testing procedures originally intended for evaluating the protection of military CPE against chemical warfare agents (CWAs) [8]. For

example, a U.S. chemical, biological, radiological, and nuclear (CBRN) ensemble certification standard, National Fire Protection Association (NFPA) 1994:12, *Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents, 2012* [10], adopted a modified version of the "static diffusion" test method described by the U.S. military testing operating procedure (TOP) 08-2-501A [11].

To simulate a finite exposure scenario, these methods rely on the use of a challenge density or a mass of chemical per unit of surface area. Liquid chemicals are applied as discrete droplets in a uniform pattern across the material surface. To facilitate the application of challenge droplets [10], the permeation apparatus described in TOP 08-2-501A [11], or the liquid challenge/vapor permeation[4] (LC/VP) cell, henceforth referred to as the LC/VP cell, incorporated a large threaded cap into the challenge chamber. With the cap removed, the entire exposed surface area of the swatch is accessible. When testing against a gaseous and vapor-producing chemical, a concentration commensurate with the exposure situation is specified. A 1984 Chemical Research and Development Center report described the use of LC/VP cells in evaluating new air-permeable and semipermeable CPE technologies of the time [12]. As with the ASTM F739 cell, the LC/VP cell remained similar to the earliest found description.

The evolution of CPE technologies over the past 30 years has outpaced the advancement of the testing apparatus used to evaluate their protection. Additionally, the requirement of certifying CPE technologies to expected performance criteria has placed increased emphasis on permeation testing and the accuracy of the results obtained.

In an effort to augment permeation methods by increasing accuracy and reducing variability, a new chemical permeation test cell assembly has been developed. The new cell features a design with a focus on the collection medium flow path, inspired by the Griffith Mk2 permeation cell described by Bromwich [2]. Validation experiments were performed that compared the new assembly against the ASTM F739 and LC/VP cells within the environment of their respective testing methodologies. Materials that represent current CPE technologies and construction techniques were utilized in the validation experiments. A description of the new cell design along with the validation results are presented in the remainder of this paper.

Methods and Materials

NEW PERMEATION CELL

The new cell design incorporates the same collection medium flow path as Bromwich's Mk2 cell [2]. Due to the shared similarities with the Griffith cell family and for labeling simplicity, the new cell will be referred to as Mk3. It should be noted, however, that this work is independent of Bromwich's research.

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[4]The LC/VP cell is also referred to as the AVLAG cell due to its inclusion in the Aerosol Liquid Vapor Assessment Group test system found at the U.S. Army's Edgewood Chemical Biological Center.

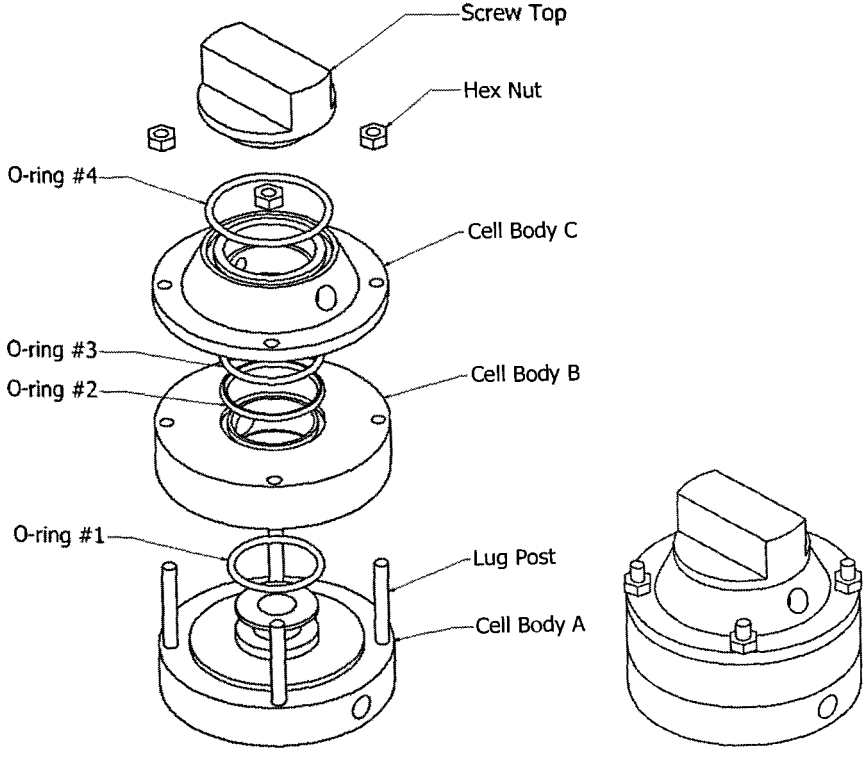
DESIGN AND ASSEMBLY

The Mk3 test cell assembly is shown in **Fig. 1**. The cell consists of three distinct cell bodies, which are depicted as A, B, and C in the figure. The material specimen is placed between bodies B and C, sandwiched between O-ring #2 and O-ring #3. Liquid challenge chemicals can be applied via removal of the screw cap. Vapor or gaseous chemicals enter and exit the cell through the two opposing ports in cell body C. The entire cell assembly is fastened with hex nuts on the four lug posts threaded into body A.

The cell body may be constructed using a variety of chemically resistant materials. Aluminum or stainless steel construction typically would be preferred for durability, but another material may be used if, for example, the challenge chemical is reactive with metal. In such situations, other materials, such as fluoropolymers, would be considered. When using polymer construction materials, lug posts should be threaded into an external metal flange placed anterior to cell body A rather than the soft polymer body in order to avoid deformation.

The design uses four O-rings for sealing within the cell. O-ring materials should be chosen based on chemical compatibility and the ability to seal around the test specimen.

FIG. 1 New chemical permeation test cell assembly.



Because O-ring #1 does not come in contact with the challenge chemical, materials that provide the best seal between cell bodies should be used. Consequently, the choice of O-ring material would be dependent upon the material used in cell body construction.

Dimensional drawings for the Mk3 cell design are shown in **Fig. 2**. All dimensions are shown in millimeters. Ordinate dimensions originate from the datum on their respective axis, and are labeled as 0.00. Threads in cell body and lug posts are not described because they are locality- and end use-specific. However, in order to maintain functionality with existing LC/VP cell components, the screw top threads must be "1 ½ in. square thread, 45° chamfer on leading and trailing thread, 0.5 in. deep" as detailed in NFPA 1994:12 [10]. Additional mechanical drawings can be requested by contacting the corresponding author.

COLLECTION CHAMBER FLOW PATH COMPARISON

New Cell Design

The collection medium enters the cell through the inlet located in cell body B and revolves around the central spindle created by the elevated portion of body A. The

FIG. 2 Dimensional drawings of Mk3 permeation cell in mm.

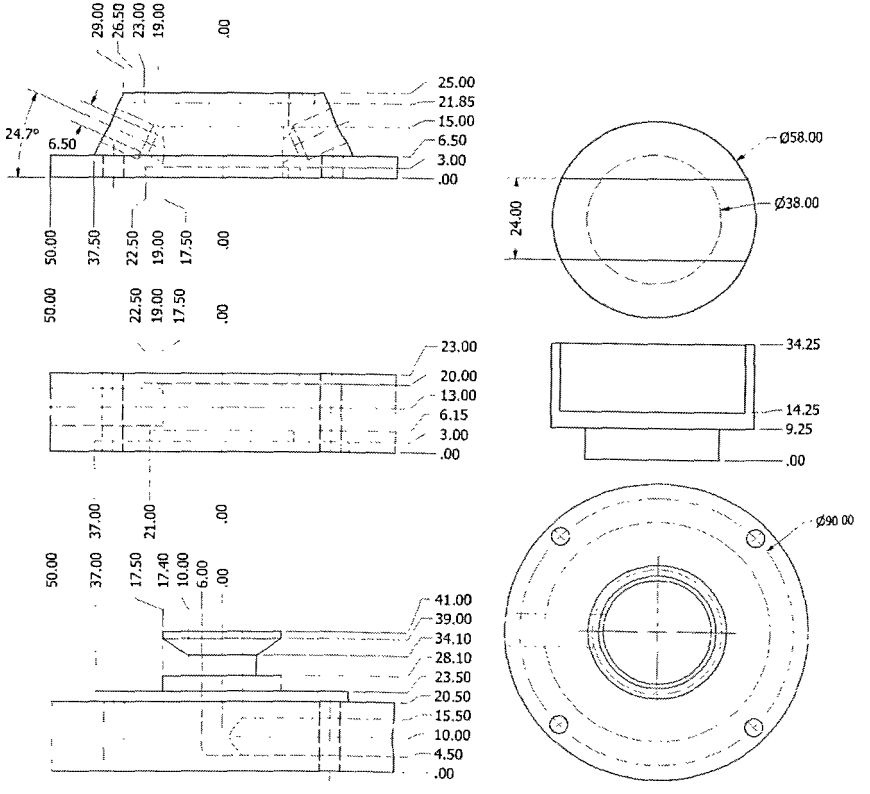
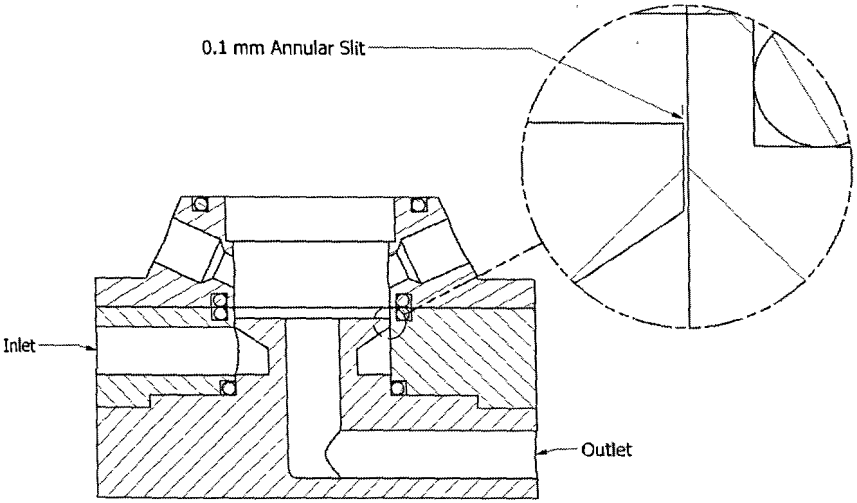


FIG. 3 Cross-sectional view of Mk3 permeation cell.

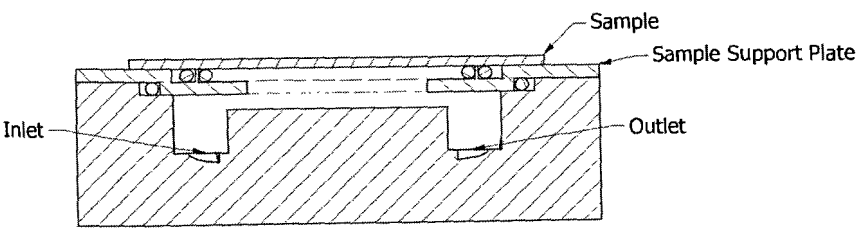


collection medium is then forced up through a 0.1-mm annular slit depicted in Fig. 3. This creates a radial collection flow across the surface of the specimen that culminates in the large outlet in the middle of the central spindle. The collection medium, along with any collected permeant, exits through cell body A. According to Bromwich, "The flow accelerates as it moves inwards towards the center of the cell. This ensures better scrubbing of permeant from the entire surface of the sample and increasing turbulence, reducing the possibility of stagnation at the center of the test sample" [2].

LC/VP Cell Design

A cross-sectional view of the LC/VP test cell, Fig. 4, provides insight into its collection medium flow path. Following the assembly procedure described in NFPA 1994:12, the design of the sample support plate creates a cavity beneath the

FIG. 4 Cross-sectional view of the LC/VP cell collection chamber.



specimen approximately 5 mm deep [10]. The collection medium must turn 90° in order to make contact with the surface of the test material before returning to the main collection stream. With the assumption that the collection flow will follow a path of least resistance, it is likely that contact between the collection medium and the specimen's surface is limited.

ASTM F739 Cell Design

A cross-sectional view of the ASTM F739 cell collection chamber as viewed from the top is shown in **Fig. 5**. Collection medium entering the cell is directed toward the face of the material being tested. In order to exit the chamber, the collection medium must flow toward a single outlet depicted on the right side of the figure. Due to the design, the areas within the collection chamber opposite of the outlet and near the top stir port (not shown) represent possible regions of stagnant flow.

Flow Visualization

To visualize the collection chamber flow, computational fluid dynamics (CFD) analysis was performed on exact models of all three cell designs. An in-depth discussion of CFD analysis is beyond the scope of this work. As such, the findings presented are meant to provide a general comparison among cell designs. The CFD analysis was performed using turbulent air at 1.0 L/min for the Mk3 and LC/VP cells and 160 mL/min for the ASTM F739 cell. The trace paths predicted by the analysis are depicted in **Fig. 6**. The design of the Mk3 cell (**Fig. 6a**) resulted in all collection flow traces contacting the material (not shown) prior to exiting the cell body. The cavity found beneath the material surface on the LC/VP model (**Fig. 6b**) was completely devoid of trace paths, highlighting a potential region of stagnation.

FIG. 5 Cross-sectional view of ASTM F739 cell collection chamber.

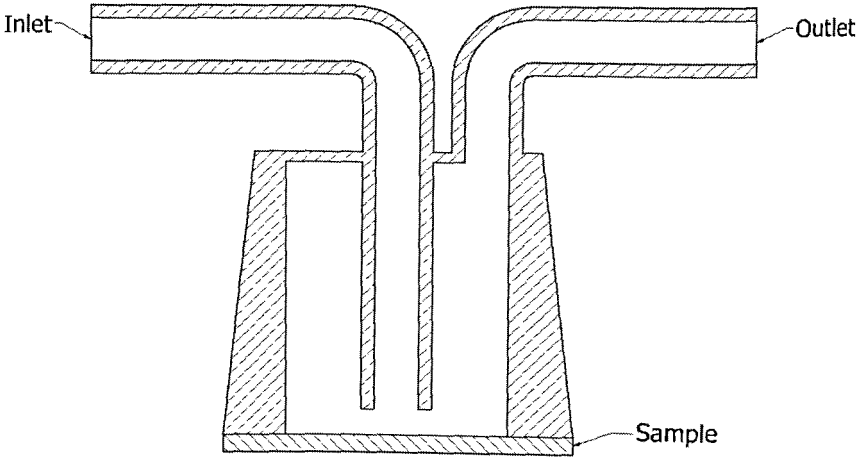
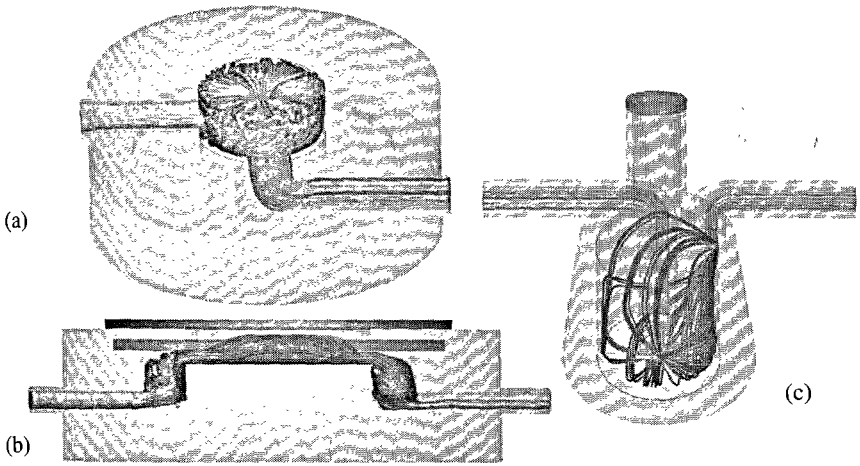


FIG. 6 CFD model of flow within the collection chambers of the (a) Mk3, (b) LC/VP, and (c) ASTM F739 cell designs.



Trace paths seen within the ASTM F739 collection chamber (**Fig. 6c**) depicted a similar lack of flow in the chamber opposite of the outlet as reported previously [2,13].

IMPORTANT FEATURES

The new hybrid design incorporates the essential elements found in previous test cells along with additional improvements:

- A radial collection flow path ensures permeant is efficiently removed from the surface of the test material and discharged from the cell by reducing the potential for stagnant flow.
- The rugged cell assembly can be manufactured utilizing a variety of chemically resistant materials by a basic machine shop.[5] This eliminates the need to use a specialty glass company for fabrication.
- A large threaded cap allows for the easy and safe introduction of liquid challenge chemicals.
- The vertical assembly holds test specimens horizontally, allowing for the use of minimal challenge chemical. Less than 2 mL is sufficient for full material coverage.
- The exposure surface area and challenge free volume remain identical to the LC/VP cell. These characteristics were incorporated to ensure the new cell design retains functionality in test methods that specify the use of the LC/VP cell.

[5]The Mk3 cell assemblies utilized for the validation experiments were manufactured by the in-house machine shop at the Morgantown, WV, campus of the National Personal Protective Technology Laboratory.

Experimental Design

To test for differences between the new cell and existing designs, validation experiments were performed utilizing materials that were representative of current CPE technologies and construction techniques. Comparisons of cell designs were conducted using statistical methods to assess whether the results among cell types were significantly different. Equivalency among permeation cells historically has been evaluated by comparing results obtained from a standard reference permeant-material pair to the results published in the interlaboratory study section of ASTM F739 [2,5,7,14–16]. This method of validation was not chosen because previous research found it be an ineffective means of determining equivalency [14,16]. Additionally, the permeation resistance exhibited by the ASTM F739 neoprene reference material did not accurately represent the performance expected of CPE as specified by contemporary ensemble certification standards [5,10,17].

The ASTM F739 and LC/VP cell types are intended for use in permeation test methods that represent fundamentally different chemical permeation scenarios [5,8,10]. Therefore, two separate experiments were performed to compare the performance of the new cell design to those of the ASTM F739 and LC/VP cells independently within the confines of their respective methodologies.

To minimize potential temperature fluctuations, an environmental chamber was constructed to house permeation cells throughout the test duration. The chamber was constructed out of polycarbonate. A thermostatically controlled heater maintained the required testing temperature. Multiple fans ensured a uniform temperature throughout the chamber. Collection flow rate was controlled using four mass flow controllers. Upon entering the environmental chamber, a coil of stainless steel tubing brought the collection medium up to testing temperature prior to entering the permeation cell.

ASTM F739 COMPARISON EXPERIMENT

To compare the new cell design to the ASTM F739 cell, the permeation resistance of fluorinated ethylene propylene (FEP) film against toluene was evaluated per ASTM F739-12 [13]. Testing was performed in an open-loop configuration.

Materials and Setup

Glass, 2.54-cm (1.0-in.) ASTM F739 permeation cells were purchased (Pesce Lab Sales, Inc., Kennett Square, PA). Reagent grade toluene (99.8 % purity) and n-hexane (95 % purity) were used (Fisher Scientific LLC, Pittsburgh, PA). FEP film with a thickness of 0.00254 cm (1 mil) was chosen to represent a thin chemical barrier film common in laminated CPE technologies. Individual specimens were randomly cut from the roll of sample material.

Where contact with the challenge chemical was possible, FEP-encapsulated Viton[6] O-rings were used in the Mk3 cell assembly. Additionally, both Mk3 and

[6]Viton is a registered trademark of E. I. du Pont de Nemours and Co.

ASTM F739 cells required supplemental sealing. All test cells were sealed using an ethylene vinyl acetate-based adhesive (LM-44; Power Adhesives, Charlotte, NC). The additional adhesive was placed around the outside of the O-rings on the Mk3 assembly to ensure a precise surface area was maintained. Care was taken when applying additional sealing to the ASTM F739 cell assemblies to maintain expected surface area.

Analysis

OI Analytical (Pelham, AL) series 3500 MINICAMS[7] and a companion continuous sampling system (CSS) were used for analysis. A portion of the collection medium stream was sampled at 100 mL/min for 6 min. The cumulative mass of permeant was then determined for each sampling period. The CSS module collected the sampled permeant on one of two sorbent tubes. At the end of the designated sampling period, the CSS module switched the collection stream to the second tube. Simultaneously, the collected permeant on the first tube was thermally desorbed and transferred to the MINICAMS system for analysis by a flame ionization detector. The use of the CSS module ensured all changes in the permeation rate were captured, which limited analyses to one cell at a time.

The instrument was calibrated daily. Toluene calibration standards of a known mass were prepared in hexane. Standards were injected into the CSS at the start of the sampling period. The instrument manufacturer listed the limit of detection (LOD) for toluene as 19 ng. The LOD was assessed experimentally by measuring the average background response for the toluene peak for 78 min or 13 sampling periods. According to Harris, the LOD is equal to three times the standard deviation (SD) plus the blank response [18]. The calculation resulted in an LOD of 25.7 ng. The minimum detectable permeant for the ASTM F739 and Mk3 cells were calculated as 0.005 $\mu g/cm^2$ and 0.003 $\mu g/cm^2$, respectively.

Procedure

Six individual tests were performed with each of the two test cell assemblies. All ASTM F739 validation testing was performed at 27°C for 480 min. The collection medium was filtered, dry air with a total flow rate of 160 mL/min. The surface area of each specimen was saturated with challenge chemical throughout the duration of the test.

Permeation Indexes

A number of indexes exist for use in evaluating chemical permeation resistance including breakthrough time (BT), permeation rate (PR), steady-state permeation rate (SSPR), and cumulative permeation (CP) [5,19]. Excluding BT, all applicable indexes were utilized during the ASTM F739 comparison.

[7]MINICAMS is a registered trademark of O. I. Corporation/OI Analytical, CMS Field Products.

The CP, total mass of permeant per surface area unit, between time i-1 and i was calculated using Eq 1:

$$CP_i = \frac{m_p}{A} + CP_{i-1} \tag{1}$$

where:

CP_i = cumulative permeation per sample period i, μg/cm^2,
m_p = mass of permeant per sample period i, μg, and
A = exposed surface area, cm^2.

The average PR was calculated for each CSS sampling period using Eq 2:

$$\bar{P} = \frac{(CP_i - CP_{i-1})F_t}{t_s F_s} \tag{2}$$

where:

$\bar{P}$ = average permeation rate per sample period, μg/cm^2/min,
CP_i = cumulative permeation per sample period i, μg/cm^2,
t_s = duration of sample period, min,
F_t = total flow rate of collection medium, L/min, and
F_s = flow rate of sampling stream, L/min.

ASTM F2815:10, *Standard Practice for Chemical Permeation through Protective Clothing Materials: Testing Data Analysis by Use of a Computer Program* [19], described the calculation of the SSPR by averaging the three data points of highest permeant concentration located within the steady-state region of the PR curve [20]. Similarly, SSPR was measured for this work with the number of data points increased from three to ten.

The steady-state region was characterized by the use of lag time (LT). According to Crank, permeation reaches a steady state after a period of three lag times [21]. For this study, the steady-state region was designated after a period of four LTs to ensure SSPR was achieved. LT is equal to the intercept of the linear portion of the CP curve with the time axis as depicted in **Fig. 7** [21]. The linear region of the CP curve was established by a simple linear regression in the form of the square of the Pearson product moment correlation coefficient (r^2). Linearity was defined as $r^2 \geq 99.999$ % for eleven data points centered on CP_i.

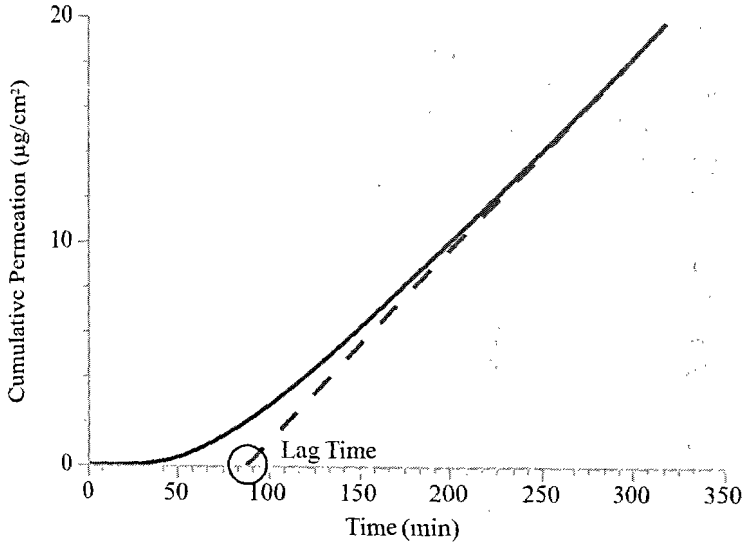
LC/VP COMPARISON EXPERIMENT

To compare the new cell design to the LC/VP cell, permeation testing was performed per NFPA 1994:12. Acrylonitrile and dimethyl sulfate were chosen as challenge chemicals.

Materials and Setup

Aluminum LC/VP cells were manufactured from the technical drawings included in NFPA 1994:12 [10]. Viton O-rings were used in both Mk3 and LC/VP cell assemblies. Supplemental sealing was not used. Acetone, acrylonitrile (VCN),

FIG. 7 Determination of lag time from cumulative permeation graph.



carbon disulfide (CS_2), and dimethyl sulfate (DMS) were purchased through Fisher Scientific (Pittsburgh, PA). High-performance liquid chromatography-grade acetone (99.99 % purity) was used. All other chemicals had a purity of 99 % or greater.

A moisture barrier (MB) intended for use in emergency medical service (EMS) products was chosen to compare the Mk3 and LC/VP cells. The EMS MB was constructed of a two-layer laminate with a poly(tetrafluoroethylene) membrane. The thickness of the material was approximately 0.2 cm. The MB material was not originally intended to provide permeation resistance. Its use was due in part to the significant CP demonstrated under the limited challenge density and time specified in the test method. Furthermore, the EMS MB was representative of a type of material utilized in the construction of NFPA 1994 Class 2 ensembles.

Permeation testing in NFPA 1994:12 specified a collection medium of filtered air at 32 ± 2°C and 80 % ± 5 % RH [10]. The collection medium was conditioned to the required relative humidity by the use of an MH-070-24 humidifier tube (PermaPure, LLC, Lakewood, NJ). The collection medium flowed through the tube prior to entering the environmental chamber. Relative humidity of the collection medium was controlled by adjusting the water temperature inside the humidifier.

Cumulative Sampling

The collection medium stream was cumulatively sampled throughout the test duration. Upon exiting the permeation cell, the collection medium flowed through a

sampling tube that contained an appropriate sorbent bed for the permeant being collected. Solvent extraction removed the permeant from the sorbent. Sorbent tubes were purchased from SKC Inc. (Eighty Four, PA). All samples were filtered with 0.22-μm poly(vinylidene fluoride) syringe filters prior to analysis. Chemical sampling and analysis methods published by the National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) were used to determine appropriate sampling and extraction techniques for each challenge chemical.

The VCN sampling and analysis was based on the "NIOSH Manual of Analytical Methods (NMAM), Acrylonitrile: Method 1604" [22]. Permeant was collected on 200-/400-mg coconut shell charcoal (CSC) sorbent tubes. Each sorption tube was extracted with 4 mL of 2 % (volume/volume) acetone in CS_2. Extraction vials were left to stand for 30 min. An extraction of 10 μg of VCN spiked onto a CSC tube resulted in 94 % recovery.

DMS permeant was collected on 75-/150-mg Porapak-Q[8] sorbent tubes. Each tube was extracted with 4 mL of acetone and allowed to desorb for 30 min. Collection and extraction procedures were modified from "OSHA Sampling and Analytical Method: Dimethyl Sulfate" [23]. An extraction of 10 μg of DMS spiked onto a Porapak-Q tube resulted in 92 % recovery.

Analysis

Quantitative analysis for both VCN and DMS was performed using an Agilent Technologies (Santa Clara, CA) 7890N/5975 gas chromatograph/mass spectrometer. Calibration standards containing known concentrations of each analyte were prepared in their respective extractant solutions. Calibration was performed daily prior to analysis.

Procedure

All testing was performed per the specified permeation test procedure described in Section 8.7 of NFPA 1994:12 [10]. The new cell design was compared to the LC/VP cell at four distinct flow rates: 0.125, 0.5, 1.0, and 1.5 L/min. Challenge chemicals were evaluated separately. A series of two sorbent tubes were used when testing at a flow rate of 1.5 L/min in order to retain permeant completely.

The environmental chamber allowed four cells to be used simultaneously during the testing period. Two cells from each type were included in each run. A total of eight evaluations was completed for each cell type per challenge chemical at each of the specified flow rates. All testing was performed at 32°C for 60 min. At the start of the test, the challenge chemical was applied as seven individual 1-μL droplets. The CP after 60 min was measured for each test.

[8]Porapak is a registered trademark of Waters Associates, Inc.

Results

ASTM F739 COMPARISON EXPERIMENT

Toluene PR curves for all tests are shown in **Fig. 8**, which indicates a reduction in variability for the new cell design when compared to results obtained using the ASTM F739 cell. CP curves for all tests are shown in **Fig. 9**.

A summary of results for the ASTM F739 validation experiment are shown in **Table 1**. Average values consist of all runs ($n = 6$) for a cell type. Standard deviation (SD) and coefficient of variation (CV) of each permeation index are also included. Similar results were obtained from both cell types for all indexes.

A two-tailed Student's t-test was used to assess whether the average CPs from the two cell types were significantly different from each other at four measurement points (see **Table 2**). The results indicate that, at a 95 % confidence level, the new cell design results were not statistically significantly different from those of the ASTM F739 cell [18]. The absolute difference between the two cell designs is included in **Table 2**.

FIG. 8 Permeation rate of toluene through FEP film.

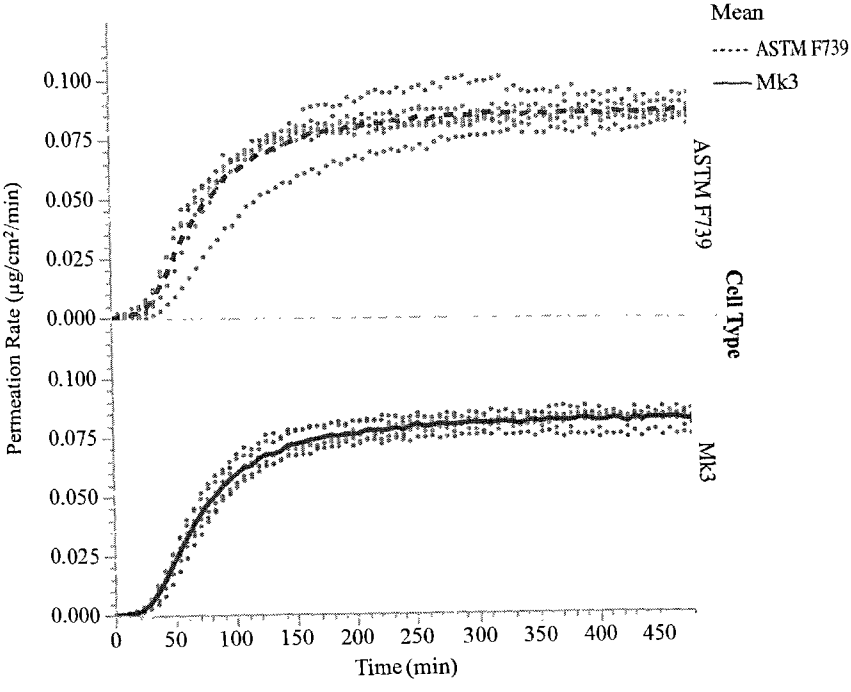
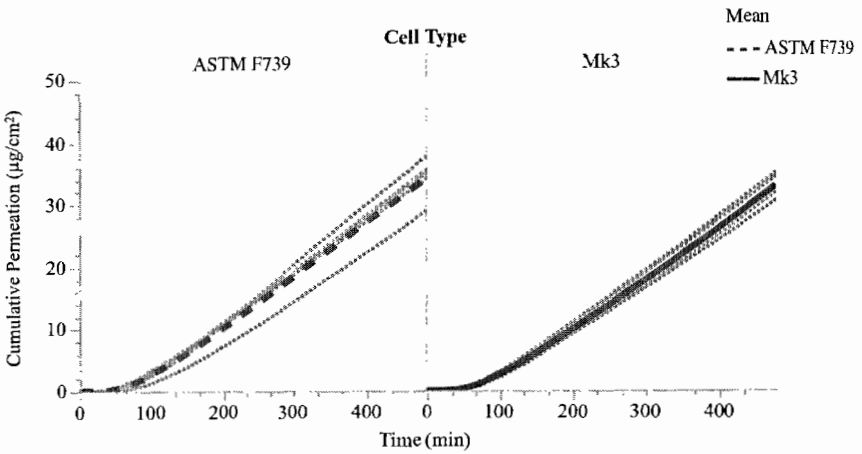


FIG. 9 Cumulative permeation of toluene though FEP film.



LC/VP COMPARISON EXPERIMENTS

A summary of the results for the LC/VP validation experiments is shown in Table 3. Average CP values for both challenge chemicals were calculated for the two cell types at each individual flow rate ($n = 8$). SD and CV values were measured for these population sets.

Quartile box plots of the LC/VP comparison results are shown in Fig. 10. The population of each data set is depicted as a rectangle where the top and bottom lines define the seventy-fifth and twenty-fifth quartiles, respectively. The median sample value is displayed by a horizontal line within each rectangle.

TABLE 1 Summary of permeation results from ASTM F739 comparison experiment.

	Steady-State Permeation Rate (µg/cm²/min)			Lag Time (min)			Cumulative Permeation (µg/cm²)			
Cell Type	Avg	SD	CV (%)	Avg	SD	CV (%)	Time	Avg	SD	CV (%)
ASTM F739	0.0891	0.064	6.40	88.9	0.2	17.61	60	0.66	0.27	41.02
							120	3.97	0.83	20.93
							240	13.34	1.56	11.73
							480	34.04	2.65	7.77
Mk3	0.0836	0.040	3.95	85.6	0.1	10.49	60	0.68	0.14	20.16
							120	3.93	0.44	11.26
							240	12.89	0.86	6.70
							480	32.43	1.49	4.60

TABLE 2 Statistical comparison of permeation results from ASTM F739 comparison experiment.

Index	Time (min)	Absolute Difference	*t*-Stat[a]
CP, μg/cm^2	60	0.02	0.15
	120	0.04	0.08
	240	0.44	0.56
	480	1.61	1.19
LT, min		3.3	0.41
SSPR, μg/cm^2/min		0.0054	1.84

$\alpha = 0.05$.
t Critical two-tail: 2.23.
[a]If *t*-Stat < *t* Critical two-tail, population means not significantly different.

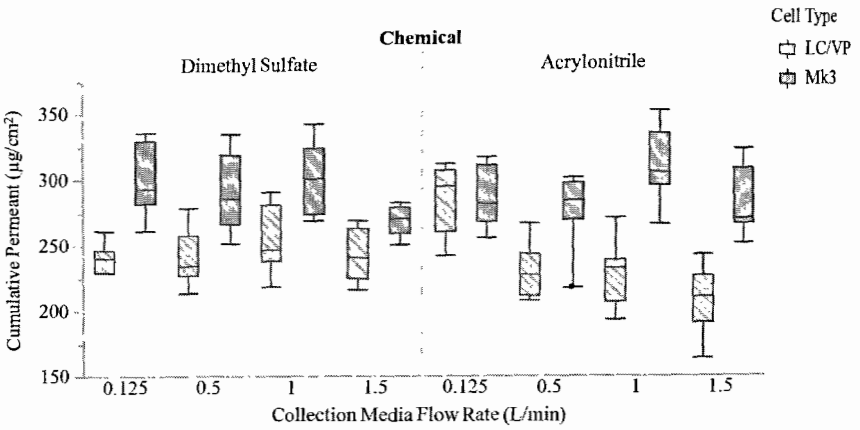
The range of the population is represented by capped vertical lines. Outliers are shown as filled circles.

Again, a two-tailed Student's *t*-test was used to assess whether the average CPs from the two cell types were significantly different from each other at each measurement point (see **Table 4**). With the exception of VCN at 0.125 L/min, the results indicate that, at a 95 % confidence level, the average CP measured using the new cell design is larger than that of the LC/VP cell [18]. The absolute difference between data sets is shown in **Table 4**.

TABLE 3 Summary of cumulative permeation results from LC/VP comparison experiments.

Challenge Chemical	Cell Type	Flow Rate (L/min)	Avg CP (μg/cm^2)	SD	CV (%)
Acrylonitrile	LC/VP	0.125	284.94	23.53	8.26
		0.5	228.92	18.58	8.12
		1.0	228.21	22.20	9.73
		1.5	206.76	22.81	11.03
	Mk3	0.125	286.98	21.11	7.35
		0.5	276.23	25.14	9.10
		1.0	308.98	24.99	8.09
		1.5	279.63	23.43	8.38
Dimethyl sulfate	LC/VP	0.125	240.62	10.34	4.30
		0.5	239.69	19.65	8.20
		1.0	254.47	23.36	9.18
		1.5	241.63	18.16	7.51
	Mk3	0.125	300.34	24.78	8.25
		0.5	291.54	27.38	9.39
		1.0	301.18	24.85	8.25
		1.5	268.64	10.37	3.86

FIG. 10 Box plots of cumulative permeation results from LC/VP comparison experiments.



Discussion

ASTM F739 VALIDATION

Several researchers have experimentally shown the ASTM F739 cell design to underrepresent SSPR values [13,24,25]. Anna, Zellers, and Sulewski suggested this effect may have been caused by "less than ideal" mixing in the collection chamber, resulting in stagnant regions [13]. The concentration gradient of challenge chemical across the material is the main driving force behind the permeation process [26]. Any permeant not removed from the collection surface of the test specimen

TABLE 4 Statistical comparison of LC/VP experiment results.

Challenge Chemical	Flow Rate (L/min)	Absolute Difference (μg/cm²)	*t*-Stat[a]
Acrylonitrile	0.125	2.04	0.17
	0.5	47.31	4.00
	1.0	80.77	6.39
	1.5	72.87	5.90
Dimethyl sulfate	0.125	59.72	5.89[b]
	0.5	51.86	4.07
	1.0	46.71	3.62
	1.5	27.00	3.42

$\alpha = 0.05$.
t Critical two-tail: 2.14.
[a]If *t*-Stat > *t* Critical two-tail, population means are considered statistically different.
[b]*t* Critical two-tail: 2.26 ($df = 9$).

decreases the magnitude of the gradient and may result in an overall reduction of permeation. Additionally, any permeant that is not removed from the collection chamber is not made available for analysis.

The permeabilities of the material-permeant pairs explored by Anna, Zellers, and Sulewski were significantly larger than those measured in the ASTM F739 comparison experiment [13]. Permeants with greater mobility require removal from the material at an increased rate to avoid a reduction in the concentration gradient. Due to the relatively low permeability of toluene through FEP, it is unlikely that the SSPR values in this study were affected by inefficient mixing within the ASTM F739 cell. Although the ASTM F739 cell design may not have affected SSPR values, the lack of a defined collection medium flow path may have contributed to the increased variability among replicates.

Permeant lost into regions of stagnation combined with its delayed reintroduction into the collection medium stream may have artificially influenced the rate of permeation measured post-cell. Although similar results were observed for all permeation indexes, the new cell design demonstrated lower variability over all data sets. This decrease in variability may be due to the elimination of stagnant flow within the Mk3 collection chamber.

For all permeation indexes measured, the difference between the Mk3 design and the standard 2.54-cm ASTM F739 cell was not statistically different at the 95 % confidence level. Within the confines of this work, the Mk3 cell demonstrated the ability to provide results equal to those of the ASTM F739 cell design while reducing intrareplicate variability. Subsequently, the new cell design is a viable alternative to the ASTM F739 cell for CPE permeation testing.

LC/VP VALIDATION

The ASTM F739 and LC/VP cells were introduced in the early 1980s [4,12]. Until its recent specification in NFPA 1994:12 [10], the use of the LC/VP cell was largely limited to military applications. Consequently, studies of potential LC/VP alternates are not common. In a recent study, Rivin et al. described the use of an alternative "simple, screw top metal cell" alongside the LC/VP cell [27]. The authors reported "satisfactory" correlations between simulants evaluated with the alternative design and CWA tested with the LC/VP cell [27]. It should be noted, however, that the study did not report a direct comparison of cell designs. No publications describing a validation study comparing LC/VP and ASTM F739 cell designs were identified.

For both chemicals evaluated, the Mk3 cell exhibited larger CP results after 60 min across all flow rates. The difference between the CP values observed utilizing the Mk3 cell and the LC/VP cell design were significantly different at the 95 % confidence level. Much like the ASTM F739 comparison, the differences highlight the potential impact a test cell assembly may have on permeation testing results.

Due to the construction of the LC/VP cell, the majority of the collection medium may not make contact with the test material's surface. Similar to the decrease in

TABLE 5 Demonstrated variability within pooled data sets.

Pooled Data	Flow Rate (L/min)	CV (%)	
		Acrylonitrile	Dimethyl Sulfate
Per flow rate	0.125	8.08	13.51
	0.5	13.24	13.69
	1.0	17.99	12.48
	1.5	18.33	8.10
Total		15.66	12.26

SSPR reported by Anna et al., the lack of proper permeant removal may have resulted in the reduced CP values measured with the LC/VP cell. D'Onofrio reported that, when testing with low-volatility permeants, the LC/VP cell resulted in values 0.5 % of those measured by a direct contact method [28]. Although the reduction in CP was attributed to the physical properties of the challenge chemical, the results may have also been influenced by a failure to consistently remove the permeant from the material surface.

The variation between replicates was similar for both the LC/VP and Mk3 cells across all data sets. The similarity suggests cell design and collection flow rate were not the main source of variability. The acceptance criteria published in the ASTM F739-12 [5] interlaboratory study allow for variations of up to 30 % within a laboratory. Comparatively, ISO 6529:2013 [6] states intraspecimen variation may be as high as 20 %. The individual cell types displayed a level of variability between replicates below these accepted limits. To examine variability between cell designs, the LC/VP and Mk3 results were combined as shown in **Table 5**. Pooled data consisting of both cell types at each of the collection flow rates exhibited levels of variability less than 20 %. Further pooling the data to include values obtained from both cell types at all four flow rates resulted in CV values for VCN and DMS of 16 % and 12 %, respectively. Therefore, the significant difference in CP seen between cell designs fell within the accepted limits of variability associated with chemical permeation testing.

TEST APPARATUS-INDUCED BIAS

The performance demonstrated through permeation testing indicates the level of protection afforded to the CPE end user. Therefore, any biases introduced into permeation testing methods result in an inaccurate description of the CPE's actual protection. Based upon the outcome of the comparison studies, the design of a permeation test cell may have a significant impact on the accuracy of the results obtained using it.

Conclusion

The requirements surrounding chemical permeation resistance ultimately define the safety and functionality as well as the look and feel of CPE. Arguably, no other

specification or evaluation influences the materials and construction of CPE to the same degree. Contemporary certification requirements necessitate the continuous improvement of chemical permeation testing equipment and methodologies.

This paper described the development and characterization of a new chemical permeation test cell. The new design, the Mk3 cell, incorporates important features from previous designs and allows for its use with both infinite and finite permeation testing methodologies. Computational fluid dynamic modeling of the collection chambers found in standard permeation cell designs provided insight into potential regions of stagnant flow. CFD analysis may allow for predicting the performance of permeation cell designs.

Comparison experiments concluded that the Mk3 cell permeation results were not statistically different from the results using the test cell described in ASTM F739-12 [5]. The Mk3 cell produced test results with less variability than those from the ASTM F739 cell. The new cell exhibited larger cumulative permeation results when compared to the liquid challenge/vapor permeation apparatus specified in NFPA 1994-12 [10] and in TOP 08-2-501A [11]. The increase in CP was statistically different at the 95 % confidence level. The defined flow path of the collection chamber incorporated into the new design may have contributed to these differences. The variation observed in the results among replicates and within pooled data sets was within accepted limits.

Permeation test results may be influenced by the design of the testing apparatus. An increase in variability effectively limits the level of precision allowed for use in performance criteria. A reduction in permeation induced by the design of a test cell results in an inaccurate depiction of the tested material's performance. The new cell combines the functionality of both the ASTM F739 and LC/VP designs, resulting in an alternative that has the potential to reduce variability and improve the accuracy of chemical permeation testing results.

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