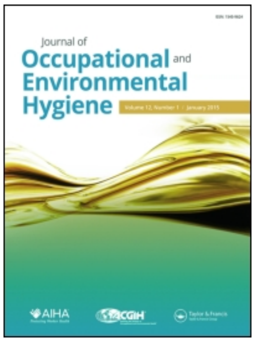

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Whole glove permeation of cyclohexanol through disposable nitrile gloves on a dextrous robot hand and comparison with the modified closed-loop ASTM F739 method 1. No fist clenching

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ABSTRACT

The aim was to develop a whole glove permeation method for cyclohexanol to generate permeation parameter data for a non-moving dextrous robot hand (normalized breakthrough time t_b, standardized breakthrough time t_s, steady state permeation rate P_s, and diffusion coefficient D). Four types of disposable powderless, unsupported, and unlined nitrile gloves from the same producer were investigated: Safeskin Blue and Kimtech Science Blue, Purple, and Sterling. The whole glove method developed involved a peristaltic pump for water circulation through chemically resistant Viton tubing to continually wash the inner surface of the test glove via holes in the tubing, a dextrous robot hand operated by a microprocessor, a chemically protective nitrile glove to protect the robot hand, an incubator to maintain 35°C temperature, and a hot plate to maintain 35°C at the sampling point of the circulating water. Aliquots of 1.0 mL were sampled at regular time intervals for the first 60 min followed by removal of 0.5 mL aliquots every hour to 8 hr. Quantification was by the internal standard method after gas chromatography-selective ion electron impact mass spectrometry using a non-polar capillary column. The individual glove values of t_b and t_s differed for the ASTM closed loop method except for Safeskin Blue, but did not for the whole glove method. Most of the kinetic parameters agreed within an order of magnitude for the two techniques. The order of most protective to least protective glove was Blue and Safeskin, then Purple followed by Sterling for the whole gloves. The analogous order for the modified F739 ASTM closed loop method was: Safeskin, Blue, Purple, and Sterling, almost the same as for the whole glove. The Sterling glove was "not recommended" from the modified ASTM data, and was "poor" from the whole glove data.

KEYWORDS
Cyclohexanol; gas chromatography-mass spectrometry; glove permeation; hand protection; infrared reflectance

Introduction

In the United States, the open loop ASTM F739 permeation test method at room temperature is used to generate the major permeation kinetic parameters for a chemical-material pair: the steady state permeation rate P_s, the normalized breakthrough time t_b,[1–3] and for the most recent ASTM F739-12 method, the standardized breakthrough time t_s.[2] The time at permeation rate of 100 ng/cm^2/min defines both t_b and t_s for the open loop system; t_b is defined at 250 ng/cm^2 and t_s at 100 ng/cm^2/min for the closed loop mode.

The open loop method has the disadvantage that compounds with low vapor pressure may not volatilize to meet t_b and t_s thresholds or not all the mass permeated evaporates.[3] The closed loop method involves a liquid collection medium facilitating sufficient solubility of the permeate without degrading the glove or allowing backpermeation. There is also concern about how well permeation through a small piece of glove from the palm or the opposite surface above the palm accounts for factors associated with wearing a whole glove like hand temperature, glove fit, glove movement, and glove stretching during workplace activities.[4] Whole glove permeation accounts for the effectiveness of the entire glove, including the finger tips and the areas between the fingers, these showing enhanced field permeation relative to the palm because of the forces operating there.[4]

Boeniger and Klingner reviewed a field sampling system to obtain real-time permeation measurements during work shifts.[5] An absorbent cotton/cotton-polyester/carbon cloth glove worn under the glove being tested (or two such gloves to indicate breakthrough of the first

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absorbent glove) integrated the permeated mass during wearing, assuming negligible permeate volatilization, no skin absorption loss, and no contamination from the skin or the donning/doffing/storing/transporting/laboratory handling. Qualitative colorimetric methods allowed visualization of absorbed glove residues or pads to indicate permeation. Quantitative methods involved extracting the absorbent glove/pads and determining the permeated mass by gas chromatography-mass spectrometry (GC-MS), or by spectroscopy.

Another approach is the dextrous robotic hand model.[6] A nylon absorbent inner glove between the exposed nitrile glove and the protected robot hand collected Captan permeate. Hand clenching did not increase the mass permeated at 8.0 hr at 35°C. However, some gloves tore when the hand clenched. Since Captan is a non-volatile solid[6] and the nylon and the nitrile gloves tight-fitting, the absorbent glove was an appropriate permeate collector. Acquiring kinetic parameter data is laborious since the nylon glove is extracted at different times using independent permeation setups.

Development of a real-time dextrous robot hand system to allow timed sampling would allow generation of whole glove permeation parameter data. Comparison with the results from the ASTM method would be illuminating on a specific glove and relative ranking basis. These were the goals of the present study with cyclohexanol and different disposable nitrile gloves.

Methods

Gloves and chemicals

Gloves

The gloves used were Kimberly Clark Safeskin Blue, and Kimtech Science Purple, Blue, and Sterling nitrile disposable gloves, all unlined, unsupported, and powderless, of unspecified thickness, 24 cm in length, and of medium size, from Kimberly Clark Worldwide (Fisher Scientific, Pittsburgh, PA). An Ansell Solvex nitrile CPC glove (Fisher Scientific) was used to protect the robot hand during permeation testing.

Chemical chosen for permeation

The test chemical had to be sufficiently water soluble and of high enough boiling point that evaporation was negligible but allowed detection by GC-MS. Cyclohexanol has[7] a boiling point of 161.84°C; a water solubility at 30°C of 4.3%; and a melting point of 25.93°C. The cyclohexanol (Reagentplus-99%) challenge chemical was from Sigma Aldrich, St Louis, MO.

Other chemicals used

The 4-bromophenol (99%) internal standard (IS) for GC-MS was from Aldrich, St Louis, MO.

The following were from Fisher Scientific (Pittsburgh PA): Optima nitric acid for a 10% (v/v) nitric acid solution for container cleaning, Optima acetone for the cleaning of containers and permeation cells, and neutral liquid detergent; sodium dichromate (99%) was used for an aqueous saturated salt solution to generate a $(55 \pm 4)\%$ relative humidity (RH) atmosphere inside a pyrex vacuum desiccator.

Water for aqueous solutions was obtained from a Millipore Milli-Q Water System (Temecula, CA) and Millipore Simplicity Water Purification final polishing system (Temecula, CA). Helium (99.9999%) and nitrogen (99.9999%) were purchased from Air Liquide (El Segundo, CA).

Equipment

A Marathon digital micrometer from Fisher Scientific, Pittsburgh PA, measured glove material thickness at specific locations. A calibrated Fisher Scientific traceable printing hygrometer/thermometer allowed measurement of RH and temperature.

The GC-MS system was a Hewlett-Packard (Santa Clara, CA) 5890 with a 60 m × 0.32 mm DB-1701 chemically bonded (1-μm thick film) fused silica capillary column before a quadrupole mass spectrometer (Hewlett Packard 5988A), operated at 70 eV electron impact energy at an ion source temperature of 260°C, 150°C quadrupole temperature, and 280°C transfer line temperature.

Infrared (IR) reflectance spectra were obtained on an Avatar 360 Fourier transform (FT) spectrometer system (ThermoNicolet, Madison, WI), a single-beam FT-IR spectrophotometer using the reflectance mode and operated with OMNIC 6.0a software controlled by Windows 98. The crystal was diamond in the single-reflection horizontal attenuated total reflectance mode.

The spectral range was 600–4000 cm^{-1}. The number of scans was 128.

For the detection of micro holes and tears in glove materials a Frazier air permeability tester linked to a 5.0-L polypropylene Bel-Art vacuum desiccator and a computer controller were used.[8] The vacuum desiccator was modified by drilling two holes in the top and bottom that were 2.75 in outer diameter (OD). The holes were smoothed with a file and a 2.0 in polyvinyl chloride (PVC) flexible rubber coupler 1.0 in tall was cut to fit around the holes to avoid damage to the glove material. A 2.0 in solid PVC reducer bushing was used inside the glove to hold it in place during testing. For glove pieces, the Frazier air permeability tester was set to 7–8 in of water vacuum pressure and water was added to the glove piece compartment and held for 90 sec to check for any leaks before and after permeation. Similarly for the whole glove, the tester was set to 11–12 in, water was added to fill the glove to just below the wrist area, and then held for 90 sec at that pressure. For the Sterling glove the vacuum pressure was reduced to 8–9 in of water because higher vacuum caused glove inflation inside the test dome. Microscope examination of the glove surfaces was also used to determine microholes or tears.

Robot hand

The robot hand was built to the same reference man anthropogenic specifications for whole glove permeation in Phalen and Que Hee[6] with the following modifications.

1. Two 2.75 in holes were drilled into the gear and motor housing, directly across from each other above the gears. A flat-head Phillips machine screw, #4–40 × 1"(Home Depot, Los Angeles, CA), was added above the gears to prevent them slipping out of place.
2. The AC adapter used to power the R7-11D1-5 DPDT toggle switch was changed to an Enercell 1.4–12 V 300 mA adapter set to 4.5 V. The adapter was fitted with a 9.0 V snap connector.
3. The mechanical stirrer was omitted.

Viton 2.79 mm inner diameter extension and three-stop tubing (Cole Parmer, Vernon Hill, IL) were used for the water delivery system to the robot hand. This tubing provided the best resistance towards cyclohexanol, was also flexible, and handled high flows. PTFE tubing (3.0 mm OD; 1.48 mm ID) and polypropylene T-connectors (4.0 mm) (Cole Parmer, Vernon Hill, IL) joined the Viton tubing together at the pump and around the robot hand. An Ismatec Compact Analog pump (Cole Parmer, Vernon Hill, IL) was connected to the tubing to transport water throughout the system and to provide pressure to irrigate the collection side surfaces of the disposable glove. An 18-gauge Hamilton needle tip (Fisher Scientific) was used to puncture holes in the Viton tubing, and the plastic tips of Fisherbrand Enviro Swabs were used as seals. A Corning Hot Plate/Stirrer (Fisher Scientific) maintained a water bath temperature of 35.0 ± 0.5°C for the circulating water in a 40-mL vial with cap (modified with two 3.0 mm holes drilled into the cap) and with a 0.5 in Fisher Scientific magnetic stir bar. Parafilm created seals around the robotic hand and over the 40-mL vial cap.

A Precision Econotherm Laboratory Oven (Fisher Scientific) maintained a temperature of 35.0°C for the 6-L of cyclohexanol in a Pyrex vacuum desiccator and to contain the robotic hand.

Procedures

GC-MS analysis

All quantitations used the IS method. The area response of analyte injected divided by the area of the IS was plotted vs. analyte mass injected. The linear portions of the plots were characterized by their slopes, intercepts, their associated standard deviations, the correlation coefficient, and p-value. Sample injection ratios were interpolated with the linear regression lines. Dilution was sometimes necessary into the linear regions.

The GC-MS conditions follow. The DB-1701 column analysis began at 90°C for 6 min, and increased to 280°C at 120°C/min at helium flow rate (2.5 ± 0.1) mL/min with the injector at 280°C. There was a 6.0-min solvent delay. The ions monitored were m/z 57 and 81 for cyclohexanol and m/z 172 for 4-bromophenol. The latter was 10.0 μg/mL in all injected samples. 3.0 μL aliquots were injected.

Modified ASTM F739 closed loop permeation procedure

The ASTM F739 closed-loop test protocol was followed with some modifications (closed loop). Test specimens were cut from the palm or back of hand areas of the glove. The test pieces were checked for micro-holes (Frazier physical and microscopic examination). The gloves were conditioned at 56 ± 1% RH at 25 ± 1°C for 24 hr as per the F739 ASTM method The glove specimens were then removed and their thicknesses (micrometer using five random positions), masses (electronic balance), and infrared reflectance spectra (Avatar 360) obtained.

The test pieces were then mounted between the PTFE gaskets of the permeation cell and sealed by its flanges, tightening the nuts to a torque of 16 ft lb (21.7 Joules). The assembled cells in triplicate were placed in modified clamps and inserted into the water bath. The water bath was maintained at 35.0 ± 0.5°C and a shaking speed of 8.36 ± 0.09 cm/sec. At the start of the 30-min equilibration, 10.0 mL of water was added to the permeation cell collection side. Cyclohexanol (10.0 mL) was added to the challenge side at zero time. Sampling into prechilled 2.0 mL vials occurred over 8-hr and 100 μL samples were taken at times that varied depending on whether the steady state permeation or the breakthrough times was being measured. The sampled volume was not replaced with an equal volume of water. The samples were weighed at room temperature. The glove samples were reconditioned at the original conditions before re-measuring all parameters. At least triplicate samples and blanks (air challenge) were evaluated.

Whole glove permeation procedure

Whole gloves were tested for microholes/tears by the Frazier method.[8] The gloves were conditioned at 56 ± 1% RH at 25 ± 1°C for 24 hr. The gloves were then removed and their thickness (micrometer-see later), mass (electronic balance), and IR reflectance spectra (Avatar 360) obtained.

A chemically resistant Ansell Solvex nitrile glove (medium, unsupported, unlined, and powderless) was placed over the clamped inverted robot hand in the flat neutral position, and left in the Precision Econotherm Laboratory oven at 35°C for 1 hr. Next, 100 mL of water and a water bath were heated to 35°C on the Corning Hot Plate/Stirrer. The 40.0-mL vial was capped (modified cap), and attached to a ring stand and clamp holding the vial in the water bath.

Viton tubing was cut to the following quantities and lengths: 1 × 29 in; 1 × 25 in; 2 × 21 in; and 2 × 12 in. Two channels were connected on the Ismatec pump with Viton three-stop tubing. One three-stop tube was fitted with the 29-in tube on the left side, which led into the oven through the top vent hole. The right side of this same tubing (a 21-in Viton piece) was attached to lead to the 40-mL vial. For the second three-stop tube the left side was fitted with the other 21-in tubing which also led to the 40-mL vial, with the right side attached to the 25-in Viton tubing. The 25-in piece of Viton tubing was used as a part of the water delivery system inside the glove. Holes were punctured into the tubing every 0.5 in over 9 in from the end of the tube using an 18-gauge needle. The end where the holes started was plugged with the plastic tip of a Fisherbrand Enviro Swab of length 0.125 in.

After 1 hr acclimation, the test glove was slid over the Solvex glove protected hand. The two 12-in pieces of Viton tubing were inserted between the test glove and the chemically protective nitrile glove. One piece was led down the side of the thumb and draped around the hand top and the other was led down the pinky finger and brought to the front of the palm area. These two tubings were joined with a polypropylene T-connector. The third connection was made to the 29-in tubing leading to the Ismatec pump. The 25-in tubing was wrapped around the robot hand 1 in (2.54 cm) below the cuff of the glove to be tested, with the holes inside of the glove. The only open end was attached to the last free connection of the three-stop tubing.

A volume of 20.0 mL of preequilibrated water was added to the 40-mL vial; and 80.0 mL then added between the test glove and the chemically resistant nitrile glove. The cuff of the test glove was then wrapped with parafilm, and the pump activated to ensure water flow without test glove distention. The hand was then placed into the desiccator with cyclohexanol and attached to a ring stand. The glove was submerged from the tip of the middle finger to 7.5 in down the glove during permeation testing. Figures 1 and 2 show a schematic and a photograph, respectively, of the entire set-up.

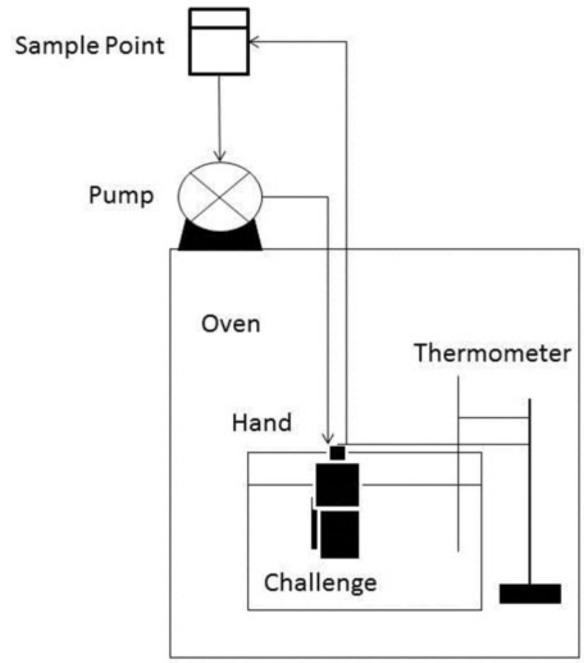

Figure 1. Schematic of whole-glove permeation set-up. The sample point has a hotplate underneath it.

For the first 30 min 1.0 mL samples were taken every 6.0 min from the 40-mL vial for t_b and t_s determination. After this, 0.50-mL samples were obtained every hour during the steady state period. The volume removed for analysis was 10.0 mL, 10% of the total. Preliminary testing showed that equivalent results were obtained with sample volumes replaced with the same volume of water. Permeation testing was completed with the robotic hand being still.

Permeation curve production

The mass in the collection stream at time t during permeations was calculated by multiplying the injected sample mass by the inverse of the volume fraction injected, assuming linear evaporation between zero time and the volume at 480 min (verified experimentally at the conditions of constant room temperature of 25 ± 1 °C, an oven and sampling point temperature of 35.0 ± 0.5 °C, constant room ventilation, and the same geometry), and correcting for volume and mass removed by prior sampling. The total mass collected at each sampling time divided by the exposed surface area was then plotted vs. sampling time in min to generate the permeation curves. The time period of steepest slope was the steady state period and its slope and standard deviation obtained. The lag time t_l was calculated from the linear regression equation for the

Figure 2. Photograph of the whole-glove permeation set-up showing from the top left of the opened incubator the peristaltic pump, the microprocessor (center top) to control the clenching of the double-gloved robot hand (incubator center, held by a clamp, but with cyclohexanol container that the hand dips into absent for clarity), with the clamped sampling point on top of the incubator right side standing on its magnetic stirrer-hotplate and connected to the hand and peristaltic pump with black Viton tubing. A multi-strip is at the bottom left. The vent to the nearby fumehood from the center of the top of the incubator is also not shown for clarity.

time when the mass divided by exposed area was zero. The diffusion coefficient D was then calculated from Equation (1):[1]

$$D = l^2/6t_l, \quad (1)$$

where l is the initial thickness in cm, t_l is the lag time in minutes, and D has the units of cm^2/min.

At least three gloves were exposed to cyclohexanol and three blanks (no cyclohexanol exposure with the water collection system running for the whole glove or an air challenge for the modified ASTM system) for each disposable glove type.

The lower ends of the sampling time ranges were averaged to represent the t_x parameters to provide the most conservative estimation. The t_b was determined at 250 ng/cm^2 and t_s at 100 $ng/cm^2/min$.

Other glove measurements

To calculate the t_b and t_s for the whole glove, the exposed surface area needed to be measured. The glove was sectioned by the 5 finger and 2 palm regions. First, measuring 2.0 in from the edge of the glove cuff defined the wrist region that was not included in the calculation because it was not challenged. Another measurement was made 5.75 in down the glove and a horizontal line was drawn to separate the fingers from the palm. A vertical line was drawn from between the index finger and thumb, and designated as the thumb area. Representative shapes were used to calculate the area. The tips of all the fingers were treated as half-spheres, and for all fingers except the thumb below the tips of fingers the areas were found using the equation for the Frustum of a Right Circular cone.[9] The thumb was treated as three separate areas—a half sphere for the tip, below that a Frustum of Right Circular cone,[9] and a triangle for the bottom portion. The areas were found for each glove type.

Glove thicknesses were measured in the above eight areas. First the wrist was measured, followed by the lower palm region, then the upper palm region. Each finger's thickness was measured as well. Ten measurements for each area were averaged.

Acrylonitrile content was measured by reflectance infrared spectroscopy at the analytical wavelength of 2237 $\pm$ 5 cm^{-1} and using the acrylonitrile standards and technique published elsewhere.[10] Porosity measurements were made to determine degradation of inner glove material from exposure to cyclohexanol. Reflectance FTIR or thickness measurements do not detect this. Samples were cut using a PaperPro hole puncher (Office Depot Los Angeles, CA) to produce consistent size circles of 0.125 in (3.18 mm) diameter. The samples were placed in a 10.0 mL quartz sample tube, weighed, and degassed for 24 hr under a nitrogen stream at 80°C using a Micromeritics Degassing unit. The porosity was measured with a Micromeritics Tristar II 3020 Surface Area and Porosity System. The configuration of the system was for nitrogen gas, and analysis was conducted using liquid nitrogen as recommended.

Results

GC-MS

There were two working linear ranges for cyclohexanol GC-MS: 0.3–30 ng; and 30–330 ng. The lower range allowed t_b and t_s determinations. The upper range covered the rest. The retention times for analyte and IS were 8.0 and 11.5 min, respectively.

Permeation parameters and infrared characteristics

Table 1 summarizes the closed loop and whole glove permeation parameter data. Table 2 shows the physical characteristics for the gloves.

While most of the t_b and t_s differed at $p \leq 0.05$ for the same glove for the closed loop method except for Safeskin, they were statistically the same for all gloves for the whole glove method. For the latter, the P_s values for the same

Table 1. Modified ASTM closed loop and whole glove permeation data for Safeskin Blue and Kimtech Blue, Purple, and Sterling disposable nitrile gloves.

Glove	Breakthrough time[a], t_b/t_s[b] (min)	Steady state permeation rate[a,c] (μg/cm^2/min)	Diffusion coefficient[a,d] (cm^2/min) $\times 10^{-8}$
Safeskin			
Whole Glove n = 3	20 ± 3/20 ± 4	10.0 ± 0.7, good	60 ± 20
Closed Loop n = 9	29 ± 2[e]/40 ± 15[e]	2.2 ± 0.6[e], very good	18 ± 2[e]
Blue			
Whole Glove n = 4	22 ± 5/20 ± 4	9 ± 1, very good	35 ± 13
Closed Loop n = 9	26 ± 1/17 ± 5[f]	12 ± 1[e], good	37 ± 2
Purple			
Whole Glove n = 3	18 ± 0/20 ± 4	14 ± 3, good	46 ± 11
Closed Loop n = 9	18 ± 1/15 ± 0[e,f]	12 ± 2, good	53 ± 7
Sterling			
Whole Glove n = 3	12 ± 0/12 ± 0	18 ± 2 good	35 ± 5
Closed Loop n = 9	8 ± 1[e]/15 ± 0[e,f]	21 ± 1[e], good	30 ± 2

[a]The data are expressed as the arithmetic mean and standard deviation of n glove replicates. [b]t_b is normalized and t_s is standardized breakthrough time. [c]Ansell ratings follow the arithmetic mean and standard deviation. [d]Apparent because of slight swelling during the experiment but no statistical difference at $p \le 0.05$ on reconditioning. [e]Statistically different at $p \le 0.05$ (comparison of closed loop data with whole glove data for the same glove parameter). [f]t_b and t_s for the same method are statistically different at $p \le 0.05$.

glove differed between the closed loop and whole glove methods for all gloves except for Purple. For Safeskin, the P_s was lowest for the whole glove method unlike for Blue or Sterling gloves where the whole glove method was higher. All the values for D were about the same except for Safeskin where it was about three times lower than for the ASTM closed loop.

The Sterling glove in both testing modes always had the lowest t_b, t_s (coequal lowest with the Purple glove for the closed loop method), and the highest P_s. The Safeskin closed loop testing showed a t_b 9.0 min longer than for the whole glove, and a t_s that was 20 min longer, as well as a nearly fivefold lowering of P_s compared with the whole glove. The D values were also statistically different at $p \le 0.05$ with the whole glove D being higher.

The Sterling glove had a closed loop t_b 4 min shorter than the whole glove, a closed loop t_s 3 min shorter than for the whole glove, and a slightly higher P_s for the closed loop. The D values were about the same. The whole glove Blue P_s was lower than that from the closed loop, but the t_b, t_s and D values for both were statistically the same at $p \le 0.05$. The Purple glove showed no differences at $p \le 0.05$ for t_b, P_s, or D but the closed loop t_s was lower than for the whole glove.

Table 2. Modified ASTM Closed loop glove physical parameters for unexposed, conditioned Safeskin Blue, and Kimtech Science Blue, Purple, and Sterling gloves.

Glove	Thickness (mm) n = 50	Acrylonitrile % outside n = 20	Acrylonitrile % inside n = 20
Safeskin	0.124 ± 0.005[a]	13 ± 2	9.8 ± 0.5[a,b]
Blue	0.101 ± 0.003	12 ± 1	12 ± 1
Purple	0.108 ± 0.004	17.2 ± 0.7[a]	12.1 ± 0.7
Sterling	0.078 ± 0.003[a]	17.1 ± 0.8[a]	12 ± 1

[a]Statistically different from Blue value at $p \le 0.05$ for the same parameter. [b]Statistically different from acrylonitrile outside value at $p \le 0.05$.

For the modified ASTM closed loop method, the infrared reflectance of the challenge surface showed a moderately intense broad OH-stretch at 3400 cm^{-1} indicative of cyclohexanol. The infrared reflectance of the challenge side for the Purple and Sterling gloves also showed decreases of the strong C-H stretches at 2900 cm^{-1}. The collection surface exhibited no IR spectral changes for all gloves relative to the blank except for the Sterling glove which showed the characteristic cyclohexanol absorption at 3400 cm^{-1}.

For all the whole gloves, the infrared reflectance of the challenge surface showed a moderately more intense broad OH-stretch at 3400 cm^{-1} indicative of cyclohexanol. Furthermore, the collection surface of all the whole gloves had no IR spectral changes relative to the blank. The infrared reflectance of the challenge surface of the Sterling glove also showed decreases of the strong C-H stretch region at 2900 cm^{-1}. Both methods agreed that cyclohexanol had permeated the Sterling glove.

Thickness and Acrylonitrile Content

All glove materials swelled slightly (but <10%) during the permeation experiment but reverted to the original thickness after reconditioning. Table 3 shows the average thickness differences for the unexposed and exposed whole gloves. Each glove's average thickness is different, with the unexposed Sterling glove being the thinnest by 38% relative to both the Safeskin and Blue, with the Purple being just 7.7% thinner. The Purple and Sterling gloves have similar inner and outer average acrylonitrile contents as have the Safeskin and Blue gloves. Only the Blue glove has the same outer and inner surface acrylonitrile content, all the rest having higher content in their outer surfaces.

Table 4 presents average thickness by hand region. Thickness varies from the wrist down to the fingers, and

Table 3. Average physical characteristics of the disposable nitrile whole gloves.

Glove	Acrylonitrile % Outside n = 20	Acrylonitrile % Inside n = 20	Glove area (cm^2) n = 3	Thickness pre-permeation (mm) n = 30	Thickness post-permeation (mm) n = 30
Safeskin	13 ± 2	9.8 ± 0.5[a,b]	1125 ± 9[b]	0.13 ± 0.01	0.14 ± 0.01
Blue	12 ± 1	12 ± 1	1242 ± 10	0.13 ± 0.01	0.14 ± 0.02
Purple	17.2 ± 0.7[b]	12.1 ± 0.7[a]	1129 ± 51[b]	0.12 ± 0.01	0.13 ± 0.01
Sterling	17.1 ± 0.8[b]	12 ± 1[a]	1067 ± 10[b]	0.081 ± 0.008[b]	0.092 ± 0.008[b]

[a]Statistically different acrylonitrile content of inside versus outside for the same glove at $p \leq 0.05$. [b] Statistically different for the same parameter relative to Blue at $p \leq 0.05$.

Table 4. Whole glove thickness by region as expressed through arithmetic mean and standard deviation parameters.

Region	Safeskin (mm) n = 10	Blue (mm) n = 10	Purple (mm) n = 10	Sterling (mm) n = 10
Wrist	0.096 ± 0.007[a]	0.111 ± 0.006	0.092 ± 0.004[a]	0.059 ± 0.003[a]
Palm-Low	0.119 ± 0.008	0.119 ± 0.004	0.108 ± 0.007[a]	0.069 ± 0.002[a]
Palm-High	0.132 ± 0.011	0.132 ± 0.005	0.113 ± 0.007[a]	0.075 ± 0.002[a]
Thumb	0.138 ± 0.012	0.129 ± 0.003	0.118 ± 0.007[a]	0.079 ± 0.004[a]
Index	0.147 ± 0.010[a]	0.135 ± 0.004	0.124 ± 0.008[a]	0.082 ± 0.004[a]
Middle	0.140 ± 0.009	0.140 ± 0.004	0.121 ± 0.006[a]	0.082 ± 0.003[a]
Ring	0.139 ± 0.007	0.136 ± 0.008	0.122 ± 0.006[a]	0.082 ± 0.002[a]
Pinky	0.146 ± 0.015[a]	0.131 ± 0.004	0.126 ± 0.011[a]	0.083 ± 0.004[a]

[a]Statistically different at $p \leq 0.05$ from the Blue value for the same region.

there are differences among the fingers. The Safeskin and Blue gloves are very similar compared with the other gloves that are all thinner, with the Safeskin being thicker than the Blue for the index and pinky fingers and thinner for the wrist. The low Palm was always the thinnest region apart from the wrist. The thicknesses of the Safeskin and Blue gloves in the whole glove experiments were similar unlike for the closed loop experiments.

Area

The total average area of each glove in Table 3 reveals that the Sterling glove was about 14% smaller than the largest glove, the Blue, with the Safeskin and Purple gloves both being about 9.4% smaller. An analysis of the areas of the hand regions (Table 5) shows that the Blue had the largest area for all regions except for the pinky.

Weight

The weights before and after whole glove permeation are shown in Table 6, where the Blue glove shows no significant difference before and after permeation at $p \leq 0.05$.

Table 5. Whole glove average areas by region (and their standard deviations) for the 10 gloves of Table 4.

Region	Safeskin (cm^2)	Blue (cm^2)	Purple (cm^2)	Sterling (cm^2)
Thumb	113 ± 5[a]	131 ± 4	113 ± 1[a]	110 ± 2[a]
Index	116 ± 2[a]	133 ± 12	126 ± 4	117 ± 3[a]
Middle	150 ± 7[a]	167 ± 7	146 ± 7[a]	148 ± 8[a]
Ring	119 ± 3[a]	137 ± 4	132 ± 10	121 ± 6[a]
Pinky	77 ± 2	70 ± 4	85 ± 8[a]	75 ± 4
Palm	550 ± 6[a]	606 ± 18	527 ± 42[a]	535 ± 32[a]

[a]Statistically different at $p \leq 0.05$ from the Blue value for the same region.

Table 6. Whole glove mass before and after permeation for triplicates.

Glove	Pre-permeation mass (g)	Post-permeation mass (g)
Safeskin	6.58 ± 0.06	7.88 ± 0.19[a]
Blue	7.28 ± 0.32	7.66 ± 0.46
Purple	6.01 ± 0.32	6.99 ± 0.44[a]
Sterling	3.96 ± 0.01	4.67 ± 0.13[a]

[a]Statistically different at $p \leq 0.05$ from pre-permeation value.

The remaining gloves exhibited weight increases after permeation at $p \leq 0.05$ after reconditioning.

Porosity

Table 7 shows the measured porosity of the unexposed and exposed gloves. The Safeskin and Sterling gloves showed no statistical difference for unexposed and exposed at $p \leq 0.05$. The Purple (4.7%) and Blue (15%) gloves both decreased in porosity after exposure. The unexposed Sterling glove had by far the highest porosity,

Table 7. Glove porosity for whole gloves before and after permeation. Triplicates were measured to provide the arithmetic means and standard deviations.

Glove	Porosity pre-permeation (m^2/g) n = 3	Porosity post-permeation (m^2/g) n = 3
Safeskin	2.83 ± 0.09[b]	3.00 ± 0.40[b]
Blue	3.04 ± 0.07	2.57 ± 0.04[a]
Purple	2.97 ± 0.04	2.83 ± 0.05[a,b]
Sterling	5.12 ± 0.03[b]	4.50 ± 0.50[b]

[a]Statistically different relative to pre-permeation at $p \leq 0.05$. [b]Statistically different relative to Blue for the same parameter at $p \leq 0.05$

being 1.8 times that of the Safeskin glove that had the lowest porosity although the latter was only about 7.0% lower than the Blue and Purple gloves. After exposure, the Sterling glove porosity decreased by 12%, but was not statistically significant at $p \leq 0.05$.

Discussion

This is the first report of the creation of a dynamic sampling dextrous robot hand permeation system. These are the first dynamic permeation data (Table 1) generated for whole glove permeation testing of a semi/non-volatile compound, the first comparison with the closed loop method, the first study to report porosities of disposable gloves (Table 7), and the first peer-reviewed journal study to report t_s data.

The Sterling glove in both test modes had the lowest t_b and t_s and the highest P_s. It also exhibited the lowest pre-permeation thickness (Tables 2 and 3), and the highest porosity (Table 7). The Sterling glove P_s, glove thickness, and porosity were statistically different at $p \leq 0.05$ from the respective values for the Purple nitrile glove, though they shared similar outside and inside acrylonitrile contents (Tables 1, 2, 3, and 7).

The Blue and Safeskin gloves provided the best overall protection from cyclohexanol with similar thicknesses (not for the modified ASTM closed loop method (Table 2)) and outside surface acrylonitrile contents (Tables 2 and 3). The order of decreasing protectiveness for the whole glove data was: Safeskin and Blue, then Purple followed by Sterling compared with Safeskin, Blue, Purple, Sterling for the ASTM closed loop method.

There are two industry criteria to adjudge glove safety, one based on steady state permeation rate from both Kimberly Clark Professional[11,12] and Ansell,[13] and another based on the first detected breakthrough time from Ansell.[13] The t_b ratings of Kimberly Clark Professional for these disposable nitrile materials are:[11] <1 min, not recommended; 1–9 min, poor; 10–59 min, good; and 60–480 min, excellent. There are no available t_s guidelines or data. The Kimberly Clark steady state permeation rate classification for CPC nitrile in $\mu g/cm^2/min$ is:(11) <1, excellent;1–100, good; 100–10,000, poor; >10,000, not recommended. The analogous Ansell steady state rate classification in $\mu g/cm^2/min$ is:(13) <0.9, excellent; 0.9–9, very good; 9–90, good; 90–900, fair; 900–9,000, poor; >9,000, not recommended. By these criteria, the Sterling glove is "not recommended" for the closed-loop method but "poor" for the whole glove methodrelative to t_b, and "good" relative to P_s, an apparently contradictory conclusion.

It is recommended that glove manufacturers have uniform criteria, and to tabulate t_s data as recommended by ASTM Method F739-12 rather than 1st detected breakthrough time data since the latter are technique dependent.

For the Sterling glove, Kimberly Clark reported open loop ASTM data.[11] Their t_b was 112 min and their P_s was 0.000001.18 $\mu g/cm^2/min$. Their t_b is much longer than our 8 ± 1 min (ASTM closed loop) or 12 min (whole glove); their P_s is much lower than 21 ± 1 $\mu g/cm^2/min$ (ASTM closed loop) or 18 ± 2 $\mu g/cm^2/min$ (whole glove). Our experiments were at 35°C, a temperature where cyclohexanol is a flowing liquid. The melting point of cyclohexanol is 25.93°C[7] so that the cyclohexanol at room temperature may have been solid, partially solid, or a viscous liquid.

Another disposable nitrile glove, Best N-Dex 7005, had a breakthrough time of 80 min and a P_s of 209 $\mu g/cm^2/min$.[14] The Ansell Barrier laminate, Solvex Nitrile, unsupported Neoprene, supported Polyvinyl Alcohol, and Polyvinyl Chloride gloves had breakthrough times of ≥360 min.[13] Natural Rubber gloves had a breakthrough time of 103 min with a P_s between 0.90–9 $\mu g/cm^2/min$. The Neoprene/Natural Rubber Blend glove had a breakthrough time of 47 min and a P_s of 9–90 $\mu g/cm^2/min$.

The permeation parameter relationships among thickness, acrylonitrile content, porosity, and the risk assessment for the clenching and non-clenching robot hand relative to the closed loop method are presented in the companion article.

Conclusions

The non-clenching robot hand model gave the same permeation kinetic data within an order of magnitude as the modified ASTM closed–loop method. Both methods agreed that the most protective gloves against cyclohexanol were the Safeskin and Blue gloves; both also agreed that the Sterling glove was the least protective, and the Purple glove intermediate. The biggest discrepancies appeared to be from glove thickness differences.

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