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Whole Glove Permeation/ Penetration of Organic Liquids with a Dextrous Robot Hand 09/01/09-08/31/13

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LIST OF TERMS AND ABBREVIATIONS

Breakthrough time: The time when a challenge chemical is detected on the opposite side of the material

Degradation: The process by which a material is:chemically changed by a challenge chemical to allow mass transfer through the material

Dextrous: Capable of movement and flexibility

Diffusion: The movement of molecules within fluids such as air and liquids

Diffusion Coefficient: The area per unit time that molecules move within fluids

Dynamic Flow System: a continuously flowing system, here with a liquid that allows intermittent or continuous detection of the challenge chemical

Lag time: The extrapolated time for the start of the steady state.

Microhole: a hole of micron dimensions either originally in the material or created via degradation

Normalized Breakthrough Time: The time for a challenge chemical to reach the opposite side of the material for two specific configurations: open loop: 100 $ng/cm^2/min$; closed loop: 250 ng/cm^2.

Permeation: The movement of a chemical through a material without degrading the material

Permeation rate: The rate of movement of a chemical through a material relative to challenge area

Porosity: The volume of challenge chemical. contained per unit weight or area of material

Steady State: When time period when the permeation rate is constant

ABSTRACT

Original Achievements:

- **Development of a dynamic flow system for whole gloves on a dextrous robotic hand that is capable of continuous or intermittent sampling of water soluble chemicals that permeate through gloves**
- **Development of a whole glove dextrous robotic hand model, nonmoving and clenching, that was compared with the standard ASTM F739-99a permeation closed loop method for four different disposable glove nitrile materials using the nonvolatile solvent cyclohexanol**
- **Development of calibrated sensitive instrumentation to test for the presence of microholes**
- **Generation of the first porosity data for disposable gloves**
- **Measurement of normalized breakthrough times, lag times, steady state permeation rates, and diffusion coefficients of selected chemicals through 4 different disposable nitrile materials, the results showing that thicker gloves allowed greater protection than the thinnest gloves for a specific chemical**
- **Discovery that robotic hand clenching for whole glove permeation causes more permeation and earlier breakthrough for the thinnest glove but not for the thicker gloves. This is suggestive of a necessary balance between worker comfort/capability of manipulating objects and safety considerations**
- **The protection afforded by double gloving is more than double relative to both normalized breakthrough time and steady state permeation rate**

Section 1
Significant/Key Findings:

- Development of a dynamic flow system for whole gloves on a dextrous robotic hand that is capable of continuous or intermittent sampling of water soluble chemicals that permeate through gloves
- Development of a whole glove dextrous robotic hand model, nonmoving and clenching, that was compared with the standard ASTM F739-99a permeation closed loop method for four different disposable glove nitrile materials using the nonvolatile solvent cyclohexanol
- Development of calibrated sensitive instrumentation to test for the presence of microholes
- Generation of the first porosity data for disposable gloves
- Measurement of normalized breakthrough times, lag times, steady state permeation rates, and diffusion coefficients of selected chemicals through 4 different disposable nitrile materials, the results showing that thicker gloves allowed greater protection than the thinnest gloves for a specific chemical
- Discovery that robotic hand clenching for whole glove permeation causes more permeation and earlier breakthrough for the thinnest glove but not for the thicker gloves. This is suggestive of a necessary balance between worker comfort/capability of manipulating objects and safety considerations
- The protection afforded by double gloving is more than double relative to both normalized breakthrough time and steady state permeation rate

Translation of Findings
All the findings will be presented at national conferences and will be submitted for peer-reviewed publication. The research showed that the extra exposures involved in a moving hand rather than a still one occurred mainly for the thinnest glove, and that workers wearing these thin gloves need special attention. This needs to be emphasized in workplace safety discussions.

Outcomes/Impact:
The research results will allow as assessment of the exposure potential of worker based on performance-based criteria such as hoe thin a glove is , the type of glove, and the type of challenge chemical. More work needs to be done to assess the generality of the results to reduce morbidity and exposure potential.

Section 2.
There were 4 specific aims, each considered below.

Specific Aim 4. To develop a model to link ASTM Method F739-99a data for these chemicals and gloves with whole glove data generated from the robotic hand studies.

The compounds that do not have ASTM Method F739-99a closed-loop permeation data will have that data generated for them using a closed loop ASTM-type permeation cell to be able to assess if correlations and statistical differences exist between the corresponding parameters (normalized breakthrough time t_b, steady state permeation rate P_s, lag time t_l) for the optimized robotic hand system. The corresponding parameters for the same glove types will then be subjected to regression analysis and if necessary, multivariate analysis, to ascertain how data from ASTM Method F739-99a can be related to the corresponding data from the whole glove model.

a. Degradation and Closed Loop Permeation Cell Experiments

The research actually began with evaluation of the potential pure solvents by assessment of their degradation of the current Blue Safeskin glove of Kimberly-Clark/Kimtech and then measurement of the permeation parameters of those solvents that did not appreciably degrade the glove material in the ASTM F739-99a permeation closed-loop method to select the ultimate chemicals to test on the dextrous robot hand in its moving and non-moving modes. .

The initial list of 36 potential solvents with American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs) that boiled near or above 150C was, with boiling point in parentheses: amyl acetate (148), aniline (184), benzaldehyde (179), benzotrichloride (213), benzyl alcohol (206), benzyl chloride (179), butylcarbitol (231), butylcellosolve (170), butyrolactam (245), cellosolve acetate (156), chloronaphthalene (250), 2-chlorophenol (176), 2-chlorotoluene (159), 3-chlorotoluene (161), 4-chlorotoluene (164), cyclohexanol (161), cyclohexanone (157), 1,5-cyclooctadiene (151), diacetone alcohol (167), dibutylphthalate (340), dimethylacetamide (166), dimethylformamide (152), 2-ethoxyethanol or ethylglycolmonoethyl ether (135), ethylene glycol (198), ethyl glycolether (170), furfural (162), 1-heptanol (176), methyl amylketone (150), nitrobenzene (211), octanol (195), oleic acid (360), styrene (145), tricresyl phosphate (420), and triethanolamine (360). Of these solvents, benzyl alcohol, butylcellosolve, cyclohexanol, diacetone alcohol, ethylene glycol, tricresyl phosphate, and triethanolamine were candidates for permeation testing. Of these solvents, only cyclohexanol had a t_b greater than 10 minutes (29±6 minutes, good on the Kimberly-Clark rating scale) and less than 60 minutes and also a measurable P_s within 8 hours (2.19±0.6 µg/cm^2/min, very good/good on the Ansell/Kimberly Clark scales respectively). See **Draft Paper 1** for details. Ethylene glycol and triethanolamine had t_b greater than 8 hours, and while these solvents would be certainly protective over an entire 8-hour workshift, they were inconvenient chemicals to create a model to relate t_b, P_s, and t_l for the ASTM closed loop method relative to the robot hand models (non-moving and moving). Diacetone alcohol and benzyl alcohol had very high P_s and t_b shorter than 5 minutes, making them unsuitable robot hand candidate solvents.

Chemicals with TLVs were initially chosen since their properties, toxicity, and general personal protective equipment recommendations were known, and facilitated the safety of the research team. Cyclohexanol was also the only chemical of this list then known to have ASTM F739-99a open loop method data available for a disposable glove material.

Research on the ASTM closed loop permeation of cyclohexanol with a water collection solvent at 35C was then commenced on four different disposable glove materials from Kimberly Clark, original Blue Safeskin, current Blue, Purple, and Sterling, the only types then commercially available. See **Draft Paper 2** for details.

The major parameter that affected t_b, P_s, and t_l at 35C was glove thickness so that the thinner Sterling disposable material (0.078±0.003 mm) was always associated with shortest t_b (8±1 min) and t_l, and largest P_s (21±1 µg/cm^2/min) and Safeskin, the thickest glove at 0.124±0.005 mm, always had the longest t_b (29±2 min) and t_l and the lowest P_s (2.2±0.6 µg/cm^2/min). There was no difference in P_s (12±2 µg/cm^2/min) for the Purple (0.108±0.004 mm) and new Blue (0.101±0.003 mm) gloves, but Blue with a t_b of 26±1 min was more protective than Purple with t_b of 18±1 min. All the current Kimberly Clark gloves had the same acrylonitrile content (12%) in their inner surface, significantly higher than Safeskin (9.8±0.5%), but the acrylonitrile content of the outer surface for Safeskin and Blue (12-13%), and for Sterling and Purple (17%) were the same.

Double glove testing generated the following t_b/P_s average protection factors: Safeskin 4.3/36;Blue 3.4/7;Purple 5.5/2.8; and Sterling 6.5/4.4. Each glove protected better than double.

Toward the end of the grant period, a chemical with no TLV but with a American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Level (WEEL), d,l-limonene (boiling point 170C), was chosen as an acceptable second solvent for the robot hand model study. This aspect is incomplete but is ongoing.

Specific Aim 1: To continue developmental work to optimize a robotic hand system relative to accuracy and precision of permeation/penetration of reference chemicals through gloves.

The former robot hand system, the Yaeger Hand, is an inexpensive commercially available kit that the user has to assemble. Efforts were made to acquire and test robot hands that were better and less cumbersome to create. The hands that were tried were not strong enough to clench the doubly gloved fist, even though they could do that when ungloved or when only one glove was donned. The other robot hands that were suitable were prohibitively expensive.

Having chosen the Yaeger Hand, a dynamic sampling system had to be developed to allow determination of the permeation of the chemical. While continuous detection was optimal, the spectral properties of cyclohexanol in a water collection system did not allow the use of ultraviolet and infrared spectroscopies. Thus a dynamic flow system was designed that had a sampling point to allow intermittent sampling. The robot hand was first protected with a chemically protective medium size nitrile glove, and the test disposable glove of large size was slipped over it. A peristaltic pump and Viton tubing conveyed the water collection solvent in and out of the space between the gloves the tubing introducing the returning aqueous solution via holes in the tubing and the pump allowing a balanced in and out flow for the hand located in an incubator at 35C. The sampling point was at the highest point of the circuit and the flow was stopped to take 100 microliter aliquots for gas chromatography-mass spectrometry analysis. This system is a unique advance that allows a permeation curve to be quickly obtained.

To allow a comparison between whole glove (immersed vertically below the wrist) and the ASTM Method F739-99a exposed material area, the exposed area of the whole glove was estimated geometrically. The average glove thickness also had to be measured to be able to calculate diffusion coefficients from t_l data.

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The specific details are provided in **Draft Paper 3**.

The permeation parameters are provided for the 4 different disposable gloves for the nonmoving robot hand in **Table 1**.

Table 1: Summary of whole glove permeation data and glove safety ratings for cyclohexanol challenging a disposable Safeskin, Blue, Purple and Sterling Silver nitrile gloves at 35C. All measurements are in triplicate

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2/min$)	Diffusion Coefficient[c] (cm^2/min) x10^{-8}
Safeskin	20±3, good	10.0±0.7, good	60±20
Blue	22±5, good	9±1, very good	35±13
Purple	18±0, good	14±3, good	46±11
Sterling	12±0, good	18±2 good	35±5

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation
[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation
c:Underestimated because of swelling

The Safeskin and Blue gloves had non-statistically different t_b and P_s with Purple intermediate between them and Sterling, the latter having the shortest t_b and biggest P_s as expected.

Specific Aim 2: To compare the permeation/penetration of the selected compounds through the selected gloves with and without movement of the optimized robotic hand, and with and without press-on nails at temperatures of 25, 30, 32, 35, and 40 C. The inexpensive optimized robotic hand system selected in Specific Aim 1 will be used to evaluate single compounds for their permeation characteristics.

The optimized robotic hand model developed should result in the determination of what commercially available hand is practical (hand should mimic an average size human hand) but which is also inexpensive ($100), and what motions are to be investigated in depth as being most conservative (clenching and unclenching the fist or finger motions). It is expected that the clenching and unclenching fist model will be the most conservative whole glove model.

The permeation results for cyclohexanol for the nonmoving (**Table 1**) and clenching (**Table 2**) robot hand showed that permeation parameters for the Safeskin, Blue, and Purple gloves were generally statistically the same for the glove type investigated. The thinner Sterling glove did show much more permeation for the clenching glove than the other glove types, the t_b decreasing by about half and the P_s increasing by about 60%, as compared with no effect on t_b and P_s for the purple and blue gloves. The Safeskin glove showed a much smaller t_b for the clenching hand but no effect on P_s. There is a threshold for glove thickness for hand movement to affect permeation parameters. Other solvents need investigation. Since Kimberly Clark has

introduced its even thinner Lavender glove, the latter also needs evaluation in future research work. Because of time constraints, the effects of temperature and nails were not investigated.

See **Draft Paper 4** for details. The permeation parameters for the moving whole glove are provided in **Table 2**.

Table 2: Summary of whole glove (moving) permeation data and glove safety ratings for cyclohexanol challenging a disposable Safeskin, Blue, Purple and Silver nitrile gloves at 35C

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2/min$)	Diffusion Coefficient[c] (cm^2/min) x10^{-8}
Safeskin **n=3**	14±4, good	11.8±0.7, good	68±15
Blue **n=3**	18±5, good	7±1, very good	44±23
Purple **n=3**	18±0, good	11.4±0.6, good	47±9
Silver **n=3**	6±0, good	29±3 good	20±3

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation
[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation
c:Underestimated because of swelling

Essentially, the t_b values for the Safeskin, Blue and Purple gloves are not statistically different., all being longer than for the thinner Sterling glove. Surprisingly, the lowest P_s was shown by the Blue glove, with the Purple and Safeskin being equivalent, all much lower than the thinner Sterling glove.

Specific Aim 3: To determine the mechanism of glove failures in the robot hand experiments

The preliminary results raised the questions of whether movement alone was responsible for the results or whether chemical degradation had to occur before penetration, or if there was an interaction between chemical degradation and movement. Permeation was not much affected compared with penetration. The results of the experiments above should confirm if the preliminary results are general or not.

To attack this problem, it was necessary to develop a glove surveillance system that could detect microholes.   This was achieved by adapting the Frazier Air Permeability tester to detect microholes of defined sizes and using a water leak test. Each glove was examined before and after permeation for microholes both microscopically and by the new water leak test.   See **Draft Paper 5**. The technique can detect a leak from a 130 μm microhole. There was a linear relationship between water leak flow rate and tear length for both the palm area and the finger/fingertip, the latter producing about sixfold less leaking than the thinner palm area. The latter leak rate for whole gloves was about 500 times more than for isolated palm pieces typically used for the ASTM method. Microscopic examination showed that holes tended to

close more for cut pieces than for the whole glove situation because of the material surrounding the hole kept the hole open.

In addition, a porosity measurement of the conditioned gloves before and after permeation was undertaken using the Micromeritics Tristar II 3020 Surface Area and Porosity System that measures volumes of absorbed liquid nitrogen. These results are also contained in **Draft Papers 3-4**, and summarized in **Table 3**..

Table 3: Glove porosity for whole gloves before and after permeation. Triplicates were measured to provide the arithmetic means and standard deviations.

Glove Product	Porosity Pre-Permeation (m^2/g) n=3	Porosity Post-Permeation (m^2/g) n=3
Safeskin [a]	2.83±0.09	3.0±0.40
Blue Nitrile [b]	3.04±0.07	2.57±0.04
Purple Nitrile [b]	2.97±0.04	2.83±0.05
Sterling Nitrile [a]	5.12±0.03	4.5±0.50

[a]: Statistically different at $p \leq 0.05$

[b]: No statistical difference at $p \leq 0.05$

The porosity of the Blue (16%), Purple (4.7%) and Sterling (12%) gloves decreased, whereas that for Safeskin was not changed. These porosity measurements are the first reported for gloves.

Mass measurements revealed that cyclohexanol never dried out even after one month of drying, and infrared reflectance analysis did detect cyclohexanol at and below the glove surfaces. Thus mass is an unreliable and inconvenient parameter to ascertain porosity, but it does indicate that the decreased porosity may be due to cyclohexanol residual.

Other modes of testing the effect on the material before and after permeation using a penetrometer, a tensiometer, and the Frazier air permeability did not reveal significant differences.

Specific Aim 5. To develop a model to link ASTM Method F739-99a data for these chemicals and gloves with whole glove data generated from the robotic hand studies.
   The compounds that do not have ASTM Method F739-99a closed-loop permeation data will have that data generated for them using a closed loop ASTM-type permeation cell to be able to assess if correlations and statistical differences exist between the corresponding parameters (normalized breakthrough time t_b, steady state permeation rate P_s, lag time t_l) for the optimized robotic hand system. The corresponding parameters for the same glove types will then be subjected to regression analysis and if necessary, multivariate analysis, to ascertain how data from ASTM Method F739-99a can be related to the corresponding data from the whole glove model.

The modeling aspects for cyclohexanol were emphasized in **Draft Papers 3 and 4**. The t_b for the ASTM closed loop method was generally longer than for the moving whole glove (1.4 to 2.1 times) except for the Purple gloves where they were the same. This is not too surprising since there is more surface area exposed for whole gloves compared with cut pieces. The P_s

comparison resulted in the purple not being different unlike the Safeskin and Sterling where the moving whole glove method produced higher P_s . Blue showed lower P_s.

More data need to be generated to test the generality of the results.

DRAFT PAPER 1

PERMEATION OF SOME SEMIVOLATILE SOLVENTS THROUGH A DISPOSABLE NITRILE GLOVE

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Keywords: benzyl alcohol; cyclohexanol; diacetone alcohol; ethylene glycol; triethanolamine; hand protection

ABSTRACT

Semi-/non- volatile solvents are often used in manufacturing and formulating, but no permeation data by the closed loop method has been reported for them. In the present study, the permeation of 5 representative water miscible organic solvents (benzyl alcohol, cyclohexanol, diacetone alcohol, ethylene glycol, and triethanolamine) was each measured through a blue Safeskin glove using an ASTM-type-I-PTC-600 permeation cell with water collection solvent, and shaken at 8.53 ± 0.1 cm/sec in a $35.0\pm0.5^{\circ}$C water bath. Aliquots of 0.1 mL were sampled at regular time intervals to determine the normalized breakthrough time corresponding to 250 ng/cm^2 and any steady state permeation rate. Quantification was by the internal standard method after gas chromatography-electron impact mass spectrometry using a non-polar capillary column and measuring the separated analyte and the internal standard in helium carrier gas by selective ion mass spectrometry. In the case of triethanolamine the collection side solution at 8 hours was evaporated to 0.050 mL before being reacted with boric acid to produce the analyte of cyclohexanol borate (85 ± 7% recovery) for similar internal standard analysis with the borate ester. This type of disposable nitrile is not recommended to protect against benzyl alcohol or diacetone alcohol, partially protects against cyclohexanol for about 30 min, but is equivalent to CPC analogous materials for ethylene glycol and triethanolamine.

INTRODUCTION

In 2011 there were 33,300 illness/diseases reported across all industries in the United States as a result of skin exposure.[1] OSHA recordable skin exposures were almost double those for inhalation.[2] Many exposures occurred with semi-/non- volatile chemicals (with boiling points (BPs) greater than 150°C).[2] These chemicals are used widely and frequently. Chemically resistant gloves should be worn for optimum personal protection. Often disposable gloves may be the only ones available because of cost, in emergencies, and the preference to use gloves that allow manipulation of work pieces. To assess how well gloves perform as barriers, permeation and penetration tests are done. Limited permeation data exist for organic semi-/non- volatile chemicals for disposable gloves.

Most researchers and glove companies in the United States use the open loop mode of the ASTM F739-96 method to generate permeation data, the major parameters being the steady state permeation rate P_s and the normalized breakthrough time t_b.[3] Open loop testing involves the permeated analyte being volatilized in a gas stream, typically nitrogen or air,[3] and quantified by an appropriate calibrated detector. However, compounds with low vapor pressure may not volatilize completely.[4] If the chemical does not volatilize completely, then any normalized breakthrough time and steady state permeation rate obtained at room temperature may not be accurate. The alternative closed loop method uses a set volume of liquid as a collection solvent. The analyte has to be soluble enough to allow quantification. The collection solvent also must not degrade or back-permeate the glove material. Water is usually the preferred collection solvent.[3]

Of the semi-/non- volatile pure organic chemicals for which glove manufacturer data were available, cyclohexanol (BP 161.84°C)[5] had open-loop permeation data for disposable and chemically protective nitrile gloves. Cyclohexanol had a first detection breakthrough time of >360 min for CPC nitrile (Ansell Solvex)[6,7] in the Open Loop ASTM Method F739-99a. Ansell did not report any open–loop ASTM Method F739-99a data for cyclohexanol for its disposable nitrile and neither did Kimberly-Clark Professional for its original Safeskin Blue glove, but Best Manufacturing disposable nitrile showed breakthrough in 80 minutes in the open-loop method.[8] Ethylene glycol was also tested in the open loop mode on Ansell Touch N Tuff disposable nitrile (4 mil) with t_b of 38 min and P_s, 9-90 μg/cm^2/min,[9] compared with >360 min and 0.9-9 μg/cm^2/min respectively for Solvex CPC nitrile.[6,7] Kimberley-Clark Professional now markets its Safeskin brand disposable laboratory gloves under the Kimtech Science brand name as Blue, Lavender, Purple and Sterling gloves, and its chemically resistant gloves under the Kleenguard brand name as G80 gloves through its Jackson Safety affiliate.[10] There were no closed loop data for any semi-/non- volatile pure chemicals in the glove manufacturer permeation chemical battery.

Therefore a set of semi-/non- volatile pure organic solvents that had appreciable water solubility was chosen to investigate the permeation of one type of disposable glove- the original Kimberly Clark Safeskin. The chemicals were: benzyl alcohol (BP, 204.7°C;[5] AIHA WEEL 10 ppm),[11] cyclohexanol (BP 161°C;[5] OSHA PEL,[12] NIOSH REL,[12] ACGIH TLV-TWA,[13] 50 ppm); diacetone alcohol (BP,167.9°C;[5] OSHA PEL,[12] NIOSH REL,[12] ACGIH TLV-TWA,[13] 50 ppm; ethylene glycol, (BP, 197.6°C;[5] ACGIH Ceiling 100 mg/m^3 [13]), and triethanolamine (BP 335.4 °C;[5] ACGIH TLV-TWA, 5 mg/m^3 [13]). Benzyl alcohol is an antimicrobial pharmaceutic aid; a flavor industry precursor to make its esters; a precursor in industrial manufacturing to make benzyl derivatives; a solvent for gelatin, casein, cellulose acetate, and shellac; a perfume ingredient; and an embedding material in microscopy.[5] Cyclohexanol is used

in soaps, synthetic detergents, and polishes like lacquers; a solvent for alkyd resins, phenolic resins, and ethylcellulose; and to make celluloid.[5] Diacetone alcohol is used in the manufacturing of artificial silk and leather; in hydraulic fluids and antifreeze as a solvent for cellulose acetate, nitrocellulose, celluloid, fats, oil, waxes,and resins.[5] Ethylene glycol, the major ingredient in antifreeze, is also in hydraulic brake fluids, electrolytic condensers, and a solvent in the paint and plastic industries, printer's inks, inks, softening agent for cellophane, stabilizer in some fire extinguishers, and a precursor of many chemicals.[5] Triethanolamine has uses in the cosmetic industry as an additive in cuticle removers; cosmetics such as lotions and chelating agents; and in surfactants; as a resin solvent; and lubricant.[5]

METHODS
Gloves and Chemicals

The gloves used were Kimberly Clark Safeskin blue nitrile disposable gloves, unlined, unsupported, and powderless, of unspecified thickness, but 24 cm in length (Fisher Scientific, Pittsburgh, PA).

The following challenge chemicals were purchased from Sigma Aldrich, St Louis, MO: benzyl alcohol (99%); cyclohexanol (Reagentplus-99%);diacetone alcohol (99%); ethylene glycol (99%); and triethanolamine (97%). The internal standards for gas chromatography-mass spectrometry (GC-MS) from Aldrich, St Louis, MO were: 4-bromophenol (99%) for benzyl alcohol and cyclohexane; 4-methoxyphenol (99%) for diacetone alcohol; 1,3-propanediol (99%) for ethylene glycol; and 1,2-dichloroethane (99%) for triethanolamine

Sodium dichromate (99%) from Fisher Scientific Pittsburgh PA was used for a saturated salt solution prepared in water to generate a (55 ± 4)% relative humidity atmosphere inside of a pyrex vacuum desiccators from Fisher Scientific.

All 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 random locations of the palm region. Vernier calipers measured the large dimensions of big pieces of glove. ASTM-type-I-PTC-600 permeation cells from Pesce Lab Sales (Kennett Square, PA) were used for permeation testing. A Thermo Scientific reciprocal shaking bath and Fisher Scientific shaking water bath, from Fisher Scientific (Pittsburgh, PA), were used for temperature control and mixing for the immersed permeation cells. Erlenmeyer flask clamps for a 250 mL flask were modified to conform to the shape of the permeation cells to hold them in the Thermo Scientific reciprocal shaking bath. The Fisher scientific shaking water bath was modified with support tubing bars to support clamps to hold the permeation cells in position. A torque wrench was used to tighten permeation cell nuts uniformly.
A calibrated Fisher Scientific traceable printing hygrometer/thermometer was used for the measurement of relative humidity and temperature.

The GC-MS system used for analysis was a Hewlett-Packard (Santa Clara, CA) 5890 with a 30 m x 0.25 mm HP-5ms chemically bonded (0.25 μm thick film) fused silica capillary column with attached quadrupole mass spectrometer, the Hewlett Packard 5988A, operated at 70 eV electron impact energy at an ion source temperature of 260°C. The GC-MS transfer line

temperature was 250^oC. Helium was the carrier gas. There was a 3 minute solvent delay. For cyclohexanol and the normalized breakthrough time elucidation, a 60 m $\times$ 0.32 mm DB-1701 capillary column (1-μm thick film) was used to achieve the desired sensitivity.

Infrared reflectance spectra were obtained on an Avatar 360 Fourier transform (FT) spectrometer system (ThermoNicolet, Madison, WI), a single-beam 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 4000–600 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 glove examination chamber (a 5-L polypropylene vacuum dessicator) and a computer controller were used. With glove pieces the Frazier air permeability tester was set to 7-8 in H_2O vacuum pressure and water was added to the glove piece compartment and held for 90 seconds to check for any leaks before and after permeation. Microscopic magnification of the glove surface was also used to determine whether micro holes or tears were present.

For the triethanolamine experiments, a SP Temp-Blok Module Heater (American Scientific Products, McGaw Park, IL) was used in conjunction with a 8 mm $\times$ 20 mm heating block (Thomas Scientific, Swedesboro,NJ) to evaporate aqueous collection samples to concentrate them for derivatization.

Procedures
GC-MS Analysis

Aliquots injected for GC-MS were 2.0 μL in volume unless indicated otherwise. All GC-MS quantitations used the internal standard (IS) method whereby the area response of analyte injected divided by the area of the IS was interpolated on a linear plot of area of analyte standard divided by area of the IS versus mass of analyte injected. The only exception was for triethanolamine that required derivatization to the borate ester that was then used as the analyte. The linear portions of the plots were characterized by their slopes, intercepts, their associated standard deviations, the correlation coefficients, and p-values.

The GC-MS conditions now follow:

Benzyl alcohol: After a solvent delay of 4.0 min at 50^oC, the column was held at 50ºC for 6 min, then 120 ºC/min to 250 ºC, holding for 6 min at flow rate of (2.0±0.1) mL/min with the injector at 250^oC. The ions monitored were m/z 79 for benzyl alcohol and m/z 172 for 4-bromophenol, the internal standard. The latter was at 20 μg/mL concentration in all injected samples.

Cyclohexanol: After injecting 3.0 μL with a solvent delay of 3.0 min at 45^oC, the HP-5ms column temperature was at 45^oC for 5 min, increased to 250^oC at 70^oC/min at flow rate (1.0±0.1) mL/min with the injector at 250^oC. The ions monitored were m/z 57 and 81 for cyclohexanol and m/z 172 for 4-bromophenol, the internal standard. The latter was 10 μg/mL concentration in all injected samples. For the DB-1701 column, after a solvent delay of 6 min, the program began at 90^oC to 250^oC at 80^oC/min at flow rate 2.5 mL/min.

Diacetone alcohol: After a solvent delay of 3.0 min at 70^oC, the program started at 70 ºC for 5.5 min, then 60 ºC/min to 250 ºC, holding for 6 min at flow rate of (1±0.1) mL/min with the injector at 250^oC. The ions monitored were m/z 43 and 59 for diacetone alcohol and m/z 109 and 124 for 4-methoxyphenol, the internal standard. The latter was 100 μg/L concentration in all injected samples.

<u>Ethylene glycol</u>: After a solvent delay of 3.0 min at 45°C, the column was ramped at 6°C/min to 55°C, 1°C/min to 65°C, 120°C/min to 275°C holding for 1 min at flow rate (1.0±0.1) mL/min with the injector at 225°C. The ions monitored were m/z 31 for ethylene glycol and m/z 57 for 1,3-propanediol, the internal standard. The latter was 25 mg/L concentration in all injected samples.

<u>Triethanolamine</u>: For triethanolamine, a 10 mL sample from the permeation cell collection side was first evaporated to 0.050 mL at 50°C under nitrogen, 5 µg boric acid in 0.050 mL acetonitrile added, and the reaction allowed to proceed in the 2-mL vial capped at 50°C for 1 hour before injection of the weighed cooled sample. For analyses after a solvent delay of 3.0 min at 50°C, the column was at 50 ℃ for 5 min and then at 120 ℃/min to 300℃, holding for 5 min at flow rate of (5±0.1) mL/min with the injector at 250°C. The ions monitored were m/z 126 for triethanolamine borate and m/z 62 and 98 for 1,2-dichloroethane, the internal standard. The latter was at 21 µg/L concentration in all injected samples. To generate the internal standard standardizations, the appropriate triethanolamine borate concentrations were used instead of triethanolamine.

For all analyses, dilution into a working linear range was performed when necessary.

Permeation

The ASTM test protocol was followed with some modifications. Test specimens were cut out from the palm or back of hand areas of the glove material. The test pieces were checked for microholes (Frazier physical and microscopic examination). The gloves were then conditioned at 56±1% relative humidity at 25 ± 1°C for 24 hours. After conditioning the glove specimens were removed and their thickness (micrometer), mass (electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

The test pieces were then mounted between the PTFE gaskets of the permeation cell and sealed by the stainless steel flanges of the permeation cells, tightening the nuts to a uniform torque of 16 ft lb. The assembled cells were placed in modified clamps and inserted into the water bath. The water bath was maintained at 35.0 ± 0.5^{o}C and a shaking speed of 8.36±0.09 cm/sec to eliminate concentration gradients in the collection solvent. The permeation cells were allowed to equilibrate to the temperature for 30 minutes. At the start of the 30 minutes equilibration period, 10 mL of triply deionized water was added as the collection solvent on the collection side of the permeation cell. The test chemical was added to the challenge side of the cell and the testing proceeded. Permeation testing occurred over 8-hours and 100 µL samples were taken at regular times into pre-chilled 2 mL vials that varied in sampling time depending on whether the steady state or the normalized breakthrough time was to be measured. The samples were weighed at room temperature to ascertain the exact mass of the sample that was taken. The glove samples were reconditioned at the original conditions before re-measuring all of the parameters. All samples were done at least in triplicate and accompanied by blanks (air challenge).

The mass in the collection side during permeations was calculated by multiplying the injected sample mass by collection side volume in µL at time t obtained by assuming linear collection side evaporation between volume at zero time and the volume at 480 min, all divided by 2, the volume in µL injected. The total mass collected in the collection side (corrected for previous mass removed by collection) divided by the exposed surface area were then plotted versus sampling time in minutes to generate the permeation curves. The time period of steepest slope was identified as the steady state permeation period and its slope and standard deviation obtained as in the standardization measurements above. The lag time t_l was calculated from the

linear regression equation for the time when the injected mass divided by exposed area was zero. The diffusion coefficient D was then calculated from equation 1:[4]

$$D = l^2/6t_1 \tag{1}$$

where l is the initial thickness in cm, t_1 is the lag time in minutes, and D has the dimensions cm^2/min.

The sampling time interval where the permeation rate was <250 ng/cm^2 was determined to be the normalized breakthrough time.

RESULTS
Benzyl Alcohol.

The linear working range for GC-MS of injected benzyl alcohol was 1 to 200 ng with lower quantifiable limit (LQL) of 1 ng. The retention times of analyte and IS were 7.5 min and 8.6 min respectively. The material swelled during the permeation relative to the blank but returned to its initial thickness at p ≤0.05 (Student *t* test) on reconditioning at the original conditions. Weight changes were within 10% of the original weight. Degradation resulting in hole formation occurred in 35-45 minutes of challenge. Therefore the calculated D are apparent rather than real even if the mean t_1 were 14.95±0.71 min. The reflectance infrared spectra did not indicate large spectral changes in reconditioned intact material but the outside surface still retained traces of benzyl alcohol unlike the collection side surface. The outside surface reflectance at 1400-1500 cm^{-1} decreased after permeation.

Cyclohexanol.

The working linear range for GC-MS of injected cyclohexanol was 0.3 to 330 ng, with LQL of 0.15 ng. The retention times for analyte and IS were 8 and 11.5 minutes, respectively. Cyclohexanol had a t_b of 29.3±2 min, a P_s of 2.19±0.6 µg/cm^2/min, and a D of 1.84x10^{-7}± 2.4x10^{-8} cm^2/min. The material swelled slightly during the permeation but reverted to the original thickness after reconditioning. The infrared reflectance of the challenge surface usually showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but there was no change for the collection surface.

Diacetone Alcohol.

The working linear range for GC-MS of injected diacetone alcohol was 50 to 1000 ng, with LQL of 39 ng. The retention times for analyte and IS were 7.0 min and 9.5 min, respectively. Diacetone alcohol had a t_b <5 min, a P_s of 1012±79 µg/cm^2/min, and a D of 5.2x10^{-6}±4x10^{-6} cm^2/min. The material swelled greatly during permeation but reverted to the original dimensions after reconditioning. There were no IR spectral changes for the challenge or collection sides of the glove material relative to the blanks.

Ethylene Glycol.

The linear dynamic range for GC-MS of injected ethylene glycol was 65 to 1000 pg with LQL of 65 pg. The retention times for analyte and IS were 5.5 min and 6.0 min, respectively. There was no swelling or shrinking of material even during the permeation (0.117 ± 0.001 mm). The weight change was 8±6 mg. There were no detected microholes. The infrared reflectance of the challenge surface showed more intensity at 1200 cm^{-1} relative to the blank with a broad weak OH-stretch region centered at 3400 cm^{-1} indicative of retained ethylene glycol. There were no IR spectral changes for the inner collection surface relative to the blank. Permeation at 325-450 ng over 8 hours and 128-177 ng/cm^2 were noted but the rate never exceeded 250 ng/cm^2.

Triethanolamine.

The recovery for derivatization of triethanolamine to triethanolamine borate was 85±7%. The working linear range for GC-MS of injected triethanolamine borate was 20 to 200 ng, and the LQL was 10 ng. There were no significant weight or thickness changes. There were no microholes. The glove challenge surface showed triethanolamine presence with enhanced broad OH stretches centered at 3350 cm^{-1} and a new absorption at 1050 cm^{-1}. There was no spectral difference for the collection surface relative to the blank. The permeation was <106 ng/cm^2 at 8 hours. The t_b was greater than 8 hours.

The D values for benzyl alcohol and diacetone alcohol are underestimates because of the observed swelling of the material during the permeation, even though this was completely reversible on reconditioning.

DISCUSSION

The permeation results are summarized in Table I. These are the first closed loop permeation data for these chemicals for this glove type.

There are two industry criteria to adjudge glove safety, one based on first detected breakthrough time from Kimberly Clark Professional and the other based on steady state permeation rate from both Ansell and Kimberly Clark Professional. The t_b ratings of Kimberly Clark Professional for these disposable nitrile materials are:[14] <1 min, not recommended; 1-9 min, poor; 10-59 min, good; and 60-480 min, excellent. For open loop testing, t_b is defined as the time when the permeation rate reaches 0.1 µg/cm^2/min.[3] The Kimberly Clark steady state permeation rate classification for CPC nitrile in µg/cm^2/min is <1, excellent;1-100, good; 100-10,000, poor; >10,000, not recommended.[15] The analogous Ansell steady state rate classification in µg/cm^2/min is:[6] <0.9, excellent; 0.9-9, very good; 9-90, good; 90-900, fair; 900-9,000, poor; >9,000, not recommended. We recommend that glove manufacturers have uniform criteria, and to tabulate t_b data as recommended by ASTM Method F739-99a rather than 1st detected breakthrough time data.

As can be seen from Table 1, this type of disposable nitrile is not recommended to protect against benzyl alcohol or diacetone alcohol, partially protects against cyclohexanol for about 30 min, and is equivalent to CPC analogous materials for ethylene glycol and triethanolamine. Protection against cyclohexanol was "very good" by the Ansell system relative to steady state permeation rate and "good" by the Kimberly Clark system.

The closed loop t_b data for ethylene glycol, triethanolamine, and benzyl alcohol agree with the open loop t_b data for Sterling disposable nitrile (3.5 mil) tabulated by Kimberly-Clark Professional.[14] The cyclohexanol t_b of 112 min in the latter disagreed with the present closed loop data. The closed loop t_b was much shorter than the open loop t_b. There were no comparable data for diacetone alcohol. There are no analogous data for the original Safeskin Blue gloves nor for the Kimtech lavender (2.8 mil) and purple nitrile gloves (6.0 mil).

There is a clear need to compare the permeations of the same chemicals against the different disposable nitrile gloves in view of the differing data for different disposable nitrile gloves from different manufacturers and manufacturer use of different breakthrough time definitions that also differ from ASTM Method F739-99a recommendations. The breakthrough time based on first detection is technique dependent but could be important for permeated carcinogens and sensitizers where no exposure may be desired. None of the chemicals of the present study are carcinogens or sensitizers.

CONCLUSIONS

This type of disposable nitrile is not recommended to protect against benzyl alcohol or diacetone alcohol, partially protects against cyclohexanol for about 30 min, and is equivalent to CPC analogous materials for ethylene glycol and triethanolamine.

ACKNOWLEDGMENTS

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Table I

Summary of permeation parameters and glove safety ratings for the test chemicals challenging a disposable Safeskin nitrile glove

Chemical Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] (µg/cm^2/min)	Diffusion Coefficient (cm^2/min) x10^8
Benzyl Alcohol	<5, poor	3,430±650, poor/poor	196±19[c]
Cyclohexanol	29±6, good	2.19±0.6, very good/good	18.4±2.4
Diacetone Alcohol	<5, poor	1012±79, poor/poor	520±400[c]
Ethylene Glycol	>480, excellent	Not applicable	Not applicable
Triethanolamine	>480, excellent	Not applicable	Not applicable

[a]:Kimberly Clark safety rating follows the arithmetic mean and standard deviation

[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation

[c]:Underestimated because of swelling

DRAFT PAPER 2:

PERMEATION OF CYCLOHEXANOL THROUGH DISPOSABLE NITRILE GLOVES

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ABSTRACT

The aim was to compare the cyclohexanol permeation characteristics of four types of disposable nitrile gloves marketed by the same producer. The gloves that were tested were Safeskin Blue, and Kimtech Blue, Purple, and Sterling nitrile exam gloves. The ASTM-type-I-PTC 600 permeation cell with water as the collection solvent in the closed loop mode was shaken at 8.5±0.1 cm/sec in a 35.0±0.5°C water bath. Aliquots of 0.1 mL were sampled at regular time intervals to determine the normalized breakthrough time t_b corresponding to 250 ng/cm^2 and the steady state permeation rate P_s. Quantification was by the internal standard method after gas chromatography-electron impact mass spectrometry using a non-polar capillary column and measuring the separated analyte and the 4-bromophenol internal standard by selective ion mass spectrometry. The most protective glove was the original Safeskin Blue nitrile exam glove followed by the Kimtech Science Blue nitrile, Kimtech Purple nitrile exam gloves, and then the Kimtech Science Sterling nitrile exam glove. The closed loop method is much more sensitive for cyclohexanol than the open-loop technique. The manufacturer's open loop t_b was 112 min and the P_s was 1.18 pg/cm^2/min for the Sterling glove whereas the closed-loop t_b was (8±1) min and the P_s was 21±1 μg/cm^2/min.

INTRODUCTION

Disposable nitrile gloves are inexpensive barriers to protect the skin.[1] Therefore, they are commonly used to guard against chemical exposure, even though they are not designed to do that. . Though chemically resistant gloves should be worn for optimum personal protection against chemicals, disposable gloves may be the only ones available because of cost, in emergencies, and the worker preference to use gloves that allow best manipulation of work pieces. There are many makers of disposable gloves, and even within one maker there may be multiple brands (purposes) and lines.(glove types) Usually, limited chemical permeation and degradation data are provided for disposable gloves.

Physical characteristics often differ for each line and among different lots of the same line. Thickness can differ for every glove material tested, thinner materials allowing more permeation than thicker ones of the same material.[1] Increasing acrylonitrile content is thought to confer more resistance to oil, fuel, and other non-polar chemicals.[1] These two parameters are a function of the quality assurance/quality control of the gloves. Increasing temperature also enhances permeation, necessitating temperature control.[3]

Typically in the United States, glove manufacturers use the ASTM F739-96 permeation method to generate data about their products. The open loop mode of the test method is most commonly used by glove manufacturers, the critical parameters being the steady state permeation rate P_s, and the normalized breakthrough time t_b.[4] The drawback is that compounds with low vapor pressure may not volatilize enough.[5] The t_b parameter, being more dependent on sensitivity than P_s, may not be accurate, especially if the flow through the collection side is not high enough at the surface exposed to air. In contrast, the ASTM closed loop method uses a set volume of liquid as a collection solvent and this allows for a more accurate assessment of the

permeation of semi/non-volatile chemicals because analyte volatilization is not key. The closed loop method may not be suitable for compounds with high Henry Law constants if volatilization is favored over solubilization in the collection solvent. The other disadvantage of the closed loop method is that the collection solvent must not degrade the test material or back permeate. For these reasons, water is the preferred collection solvent if analyte solubility in water is adequate.

In 2011 there were 33,300 illness/diseases reported across all industries in the United States from skin exposure.[6] OSHA recordable dermal exposures were almost double those for inhalation.[7] Many cases involve semi-/non- volatile chemicals (boiling points (BPs) greater than 150°C).[7] These chemicals are used widely and frequently, but little permeation data are available on them even for chemically protective gloves.

Cyclohexanol, a semi-volatile chemical of boiling point of 161°C [8] and OSHA PEL ,[9] NIOSH REL,[9] and ACGIH TLV-TWA[10] value of 50 ppm, is used in soaps, synthetic detergents, polishes, lacquers; as a solvent for alkyd resins, phenolic resins, and ethylcellulose; and to make celluloid. [7] Overexposure causes central nervous system impairment and eye irritation. Cyclohexanol was selected in the present study for testing because it has appreciable water solubility of about 4% at 25°C, [9] and some previous open loop data from glove manufacturers. In the latter, chemically protective Ansell vinyl gloves had a breakthrough time of 60 min and a P_s between 0.9-9 µg/cm^2/min; Ansell Natural Rubber gloves had a breakthrough time of <10 min with a P_s between 90-900 µg/cm^2/min.[11] Best nitrile N-Dex 7005 had a breakthrough time of 80 min and a P_s of 209 µg/cm^2/min.[12] Kimberly Clark, during the course of this study, published data for disposable Kimtech Science Sterling nitrile glove with t_b of 112 min and a P_s of 1.18 pg/cm^2/min.[13]

The purpose of this research was to assess differences in P_s and t_b of gloves of one brand and of the same line. The gloves tested were the Kimberly Clark original Safeskin Blue nitrile exam glove, and the Kimtech Science Blue, Purple, and Sterling nitrile exam gloves. Kimberly Clark now markets its Safeskin brand of disposable gloves under the Kimtech Science brand as Blue, Lavender, Purple, and Sterling disposable exam gloves [14].

METHODS

Gloves and Chemicals

The gloves were Kimberly Clark Safeskin blue (old), and Kimtech Science purple, blue, and Sterling nitrile disposable gloves, all unlined, unsupported, and powderless, of unspecified thickness, but 24 cm in length (Fisher Scientific, Pittsburgh, PA).

The challenge chemical was cyclohexanol (Reagentplus-99%), purchased from Sigma Aldrich, St Louis, MO. The 4-bromophenol (99%) internal standard for gas chromatography-mass spectrometry (GC-MS) was from Aldrich, St Louis, MO.

The following were from Fisher Scientific, Pittsburgh PA: Optima nitric acid used to make a 10 % (v/v) nitric acid solution for cleaning of all glassware and plasticware; Optima acetone utilized in the cleaning of all glassware and permeation cells; a neutral liquid detergent for cleaning purposes; and sodium dichromate (99%) used for a saturated salt solution prepared in Milli Q water to generate a $(55\pm4)\%$ relative humidity (RH) atmosphere inside of a pyrex vacuum desiccator also from Fisher Scientific.

All water for aqueous solutions was from a Milli-Q Water System (Millipore, Temecula, CA), polished with a Simplicity Water Purification system (Millipore, 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 random locations of the palm region. Vernier calipers measured the large dimensions of big pieces of glove. ASTM-type-I-PTC-600 permeation cells from Pesce Lab Sales (Kennett Square, PA) were used for permeation testing. A Thermo Scientific reciprocal shaking bath and Fisher Scientific shaking water bath, from Fisher Scientific (Pittsburgh, PA), were used for temperature control and mixing of the contents of the immersed permeation cells. The.250 mL Erlenmeyer flask clamps of the Thermo Scientific reciprocal shaking bath were modified to conform to the shape of the permeation cells. The Fisher scientific shaking water bath was modified with copper support tubing bars to support clamps to hold the permeation cells in position. A torque wrench was used to tighten permeation cell nuts uniformly. A calibrated Fisher Scientific traceable printing hygrometer/thermometer was used for the measurement of RH and temperature.

The GC-MS system was a Hewlett-Packard (Santa Clara, CA) 5890 with a fused silica HP-5ms chemically bonded capillary column, 30 m x 0.25 mm, and 0.25 μm thick film, linked to the Hewlett Packard 5988A quadrupole mass spectrometer operated at 70 eV electron impact energy at an ion source temperature of 260°C. The GC-MS transfer line temperature was 250°C. Helium was the carrier gas. The injector port temperature was 250°C. There was a 3 minute solvent delay at 45°C. The temperature program was 45°C for 5 min, increasing to 250°C at 70°C/min at flow rate (1.0±0.1) mL/min. Aliquots injected were 3.0 μL in volume. For normalized breakthrough time elucidation, a 30 m $\times$ 0.25 mm DB-1701 capillary column (1-μm

thick film) was obtained from Agilent Technologies, Santa Clara, CA. After a solvent delay of 6 min at 90°C, the program began at 90 ^{o}C to 250°C at 80°C/min at flow rate 2.5 mL/min. For both columns, the ions monitored were m/z 57 and 81 for cyclohexanol and m/z 172 for 4-bromophenol, the internal standard. The latter was 10 µg/mL concentration in all injected samples.

Infrared reflectance spectra were obtained on an Avatar 360 Fourier transform (FT) spectrometer system (ThermoNicolet, Madison, WI), a single-beam 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 4000–600 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 glove examination chamber (a 5-L polypropylene vacuum dessicator) and a computer controller were used. With glove pieces the Frazier air permeability tester was set to 7-8 in H$_2$O vacuum pressure and water was added to the glove piece compartment and held for 90 seconds to check for any leaks before and after permeation. Microscopic magnification of the glove surface was also used to determine whether micro holes or tears were present.

Procedures

GC-MS Analysis

All quantitations used the internal standard (IS) method whereby the area response of analyte injected divided by the area of the IS versus mass of analyte injected for the standard curve was used to interpolate unknown analyte mass. The linear portions of the plots were

characterized by their slopes, intercepts, their associated standard deviations, the correlation coefficient, and p-values. For all analyses, dilution into a working linear range was performed when necessary.

Permeation

The ASTM test protocol was followed with some modifications. Test specimens were cut out from the palm or back of hand areas of the glove material. The test pieces were checked for microholes (Frazier physical and microscopic examination). The gloves were then conditioned at $56\pm1\%$ relative humidity at $25\pm1^{o}C$ for 24 hours. After conditioning the glove specimens were removed and their thickness (micrometer), mass (electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

The test pieces were then mounted between the PTFE gaskets of the permeation cell and sealed by the stainless steel flanges of the permeation cells, tightening the nuts to a uniform torque of 16 ft lb. The assembled cells were placed in modified clamps and inserted into the water bath. The water bath was maintained at $35.0\pm0.5^{o}C$ and a shaking speed of 8.36 ± 0.09 cm/sec to eliminate concentration gradients in the collection solvent. The permeation cells were allowed to equilibrate to the temperature for 30 minutes. At the start of the 30 minutes equilibration period, 10 mL of triply deionized water was added as the collection solvent on the collection side of the permeation cell. The test chemical was added to the challenge side of the cell at the end of the equilibration period and the testing proceeded. Permeation testing occurred over 8-hours and 100 µL samples were taken at regular times into pre-chilled 2-mL vials that varied in sampling time depending on whether the steady state or the normalized breakthrough time was to be measured. The samples were weighed at room temperature. The glove samples

were reconditioned at the original conditions before re-measuring all of the parameters. All samples were done at least in triplicate and accompanied by blanks (air challenge).

The process to determine the mass in the collection side at any time during permeations was initiated by obtaining the mass of analyte in the aliquot injected after interpolation on the internal standard curve via substitution of sample area (corrected for any background) in the linear regression equation. This aliquot mass was multiplied by the collection side volume in µL at time t corrected for evaporation and volume of previous samples removed divided by the injection volume.

The total mass collected in the collection side (corrected for previous mass removed by collection) divided by the exposed surface area were then plotted versus sampling time in minutes to generate the permeation curves. The time period of steepest slope was identified as the steady state permeation period and its slope and standard deviation obtained as in the standardization measurements above. The lag time t_1 was calculated from the linear regression equation for the time when the injected mass divided by exposed area was zero. The diffusion coefficient D was then calculated from equation 1:[5]

$$D = l^2/6t_1 \text{---(1)}$$

where l is the initial thickness in cm, t_1 is the lag time in minutes, and D has the dimensions cm^2/min.

The sampling time interval where the permeation rate was <250 ng/cm^2 was determined to be the normalized breakthrough time, as defined in the ASTM F739-96 closed loop method permeation method.[4]

RESULTS

The linear range for GC-MS of injected cyclohexanol was 0.15 to 330 µg/mL for the DB1701 column. The retention times for analyte and IS were 8 and 11.5 minutes, respectively. All materials swelled slightly (about 5-8%) during the permeation but reverted to the original thickness after reconditioning. No microholes were detected in permeated nitrile material.

Safeskin Blue Nitrile Exam Glove

The original Safeskin blue nitrile exam glove had a t_b of 29.3±2.0 min, a P_s of 2.2±0.6 µg/cm^2/min, and a D of (1.8± 0.2) x10^{-7} cm^2/min. The glove had an average thickness of 0.1241±0.0048 mm and acrylonitrile contents of outside/inside of (13± 2/9.8±0.5)%. In most cases the FTIR reflectance of the challenge surface showed a more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol. For the collection surface there were no IR spectral changes relative to the blanks.

Kimtech Science Blue Nitrile Exam Glove

The Kimtech Science Blue nitrile exam glove had a t_b of 26±1 min, a P_s of 12±1 µg/cm^2/min, and a D of (3.69±0.21) x10^{-7} cm^2/min. The original average thickness was 0.1011±0.0025 mm and acrylonitrile contents of outside/inside was (12.2±1.0/11.7±1.0)%. In some cases the FTIR reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for some challenge surfaces and all collection surfaces there were no IR spectral changes relative to the blanks.

Kimtech Science Purple Nitrile Exam Glove

The Kimtech Science Purple nitrile exam glove had a t_b of 18±1 min, a P_s of 12±2 µg/cm^2/min, and a D of (5.3±0.7) x10^{-7} cm^2/min. The original glove had an average thickness of 0.1075±0.0039 mm and acrylonitrile contents of outside/inside of (17.2±0.7/12.1±0.7)%. The FTIR reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of hydrophobic coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Kimtech Science Sterling Nitrile Exam Glove

The Kimtech Science Sterling nitrile exam glove had a t_b of 8±1 min, a P_s of 21±1 µg/cm^2/min, and a D of (3.0±0.2) x10^{-7} cm^2/min. The glove had an average thickness of 0.0779±0.0025 mm and acrylonitrile contents of outside/inside of (17.1±0.8/12±1)%. The infrared reflectance of the challenge side showed decreased intensity in the C-H stretching region at 2900 cm^{-1}. This may indicate a loss of hydrophobic coating on the outside surface of the glove material. The reflectance of the collection side surface showed a more intense broad weak OH-stretch at 3400 cm^{-1} after permeation indicative of cyclohexanol presence.

DISCUSSION

The permeation results for all four glove types are summarized in Table 1. This is the first closed-loop glove permeation data to compare these disposable nitrile glove types relative to permeation for any chemical.

There are two industry criteria to adjudge glove safety, one based on first detected breakthrough time from Ansell and the other based on steady state permeation rate from both Ansell and Kimberly Clark Professional. The t_b ratings of Kimberly Clark Professional for these

disposable nitrile materials are:[13] <1 min, not recommended; 1-9 min, poor; 10-59 min, good; and 60-480 min, excellent. For open loop testing, t_b is defined as the time when the permeation flux rate reaches 0.1 $\mu g/cm^2/min$.[4] The Kimberly Clark steady state permeation rate classification in its KleenGuard G80 CPC nitrile in $\mu g/cm^2/min$ is <1, excellent; 1-100, good; 100-10,000, poor; >10,000, not recommended.[15] 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. We recommend that glove manufacturers have uniform criteria, and to tabulate t_b data as recommended by ASTM Method F739-99a rather than as 1st detected breakthrough time.

From Table 1 it can be seen that the original Safeskin blue nitrile exam glove was the most protective against cyclohexanol, followed by the Kimtech Science Blue nitrile exam glove, then the Purple nitrile exam glove, and finally the Sterling nitrile exam glove. The maximum time of protection is about 30 minutes with the original Safeskin nitrile exam glove, with a normalized breakthrough time of 29±2 min, "good" by the Kimberly Clark chemical resistance guide. The P_s was 2.2±0.6 $\mu g/cm^2/min$, "very good" by the Ansell chemical resistance guide. The Kimtech Science Blue nitrile exam glove had a normalized breakthrough time of 26±1, which is "good", and a steady state permeation rate of 12±1 $\mu g/cm^2/min$ that is also "good". The Purple nitrile exam glove was observed to have a t_b of 18±1 minutes, "good" (Kimberly Clark) and a P_s of 12±2 $\mu g/cm^2/min$, "good" (Ansell). Finally, the Sterling nitrile exam glove had a t_b of 8±1 minutes ("poor" by Kimberly Clark), and a P_s of 21±1 $\mu g/cm^2/min$, "good" (Ansell). For the Sterling nitrile exam gloves Kimberly Clark reported open loop data in their "Kimberly Clark Nitrile Gloves Chemical Resistance Guide".[13] Their t_b was 112 min and their P_s was 1.18

$pg/cm^2/min$. Compared to the obtained closed loop data for the same glove the t_b is much longer than 8 ± 1 minutes and P_s much lower than $21.4\pm1.0\,\mu g/cm^2/min$.

From the physical characteristics in Table 2, it can be seen that the original Safeskin blue nitrile exam glove was the thickest and had the smallest acrylonitrile content on the collection side of the glove material. The Purple and Sterling exam gloves had the most acrylonitrile content in both the challenge and collection sides of the glove material. The Sterling nitrile glove was thinnest of all these tested gloves and attempts to compensate by increasing nitrile content only can go only so far. Further research needs to be done to confirm this with other chemicals, and if the new Kimtech Science Lavender disposable nitrile glove, which is thinner than the Sterling glove, will show the same trend.

There is also a clear need to conduct further research on the ASTM F739-96 test method to determine which modes are best suited for more volatility classes. Further permeation testing needs to be conducted to determine if the ASTM closed loop method is also a good predictor of whole glove permeation results. Therefore more research also needs to be done on a whole glove permeation method.

CONCLUSIONS

The original Safeskin blue nitrile exam glove provided the best protection against cyclohexanol. The Kimtech Science Blue and Purple nitrile exam gloves provided "good" resistance toward cyclohexanol but the Sterling glove is not recommended. The closed loop mode is much more sensitive than its open loop counterpart in regards to semi/non-volatile compounds, based on Kimberly Clark open loop data for cyclohexanol.

ACKNOWLEDGMENTS

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Table 1: Summary of normalized breakthrough times,steady state permeation rates, and diffusion coefficients for Kimberly Clark Safeskin, and Kimtech Science blue, purple, and Sterling nitrile gloves. There were 9 gloves of each type. The data are expressed as arithmetic mean±standard deviation

Glove Product	Normalized Breakthrough Time (min)	Steady State Permeation Rate (µg/cm^2/min)	Diffusion Coefficient (cm^2/min) x 10^7
Safeskin	29±2	2.2±0.6	1.8± 0.2
Kimtech Science Blue	26±1	12±1	3.7±0.2
Kimtech Science Purple	18±1	12±2	5.3±0.7
Kimtech Science Sterling	8±1	21±1	3.0±0.2

Table 2: Average physical characteristics of disposable glove material before permeation. The data are expressed as arithmetic mean±standard deviation for n gloves.

Glove Product	Thickness (mm) n=50	Acrylonitrile % Outside n=20	Acrylonitrile % Inside n=20
Safeskin	0.124±0.005	13± 2	9.8±0.5
Kimtech Science Blue	0.101±0.003	12±1	12±1
Kimtech Science Purple	0.108±0.004	17.2±0.7	12.1±0.7
Kimtech Science Sterling	0.078±0.003	17.1±0.8	12±1

DRAFT PAPER 3

WHOLE GLOVE PERMEATION OF CYCLOHEXANOL THROUGH DISPOSABLE NITRILE GLOVES

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ABSTRACT

The aim was to develop a whole glove permeation method for cyclohexanol capable of generating enough data to produce permeation curves and to determine normalized breakthrough times t_b. The permeation characteristics of four types of disposable nitrile gloves marketed by the same producer were determined from the developed method. The gloves that were tested were the Safeskin Blue, and Kimtech Science Blue, Purple, and Sterling nitrile exam gloves. The whole glove method developed involved a pump for water circulation, chemically resistant Viton tubing for transport of water and to continually wash the inner surface of the test glove via holes in the tubing, a dextrous robot hand, a chemically protective nitrile glove to protect the robot hand, an oven to maintain 35^oC temperature, and a hot plate to maintain 35^oC at the sampling point of the circulating water. Aliquots of 1.0 mL were sampled at regular time intervals for the first 30 min followed by removal of 0.5 mL aliquots every hour for 8 h. The 1.0 mL aliquots were used to determine the t_b corresponding to 250 ng/cm^2 and the 0.5 mL aliquots used to determine the steady state permeation rate P_s. Quantification was by the internal standard method after gas chromatography-electron impact mass spectrometry using a non-polar capillary column and measuring the separated analyte and the internal standard by selective ion mass spectrometry. The Kimtech Science blue glove had a t_b of 22±5 min and P_s of 8.8±1.0 µg/cm^2/min. The Safeskin gloves had a t_b of 20±3 minutes and P_s of 10.0±0.7 1µg/cm^2/min. The Kimtech Science Purple and Sterling gloves had t_b of 18±0 and 12±0 min respectively, as well as respective P_s of 14±3 and 18±2 µg/cm^2/min. The order of most protective to least protective disposable nitrile glove was Kimtech Science Blue=Safeskin glove, Kimtech Science Purple, and then Kimtech Science Sterling, the last being not recommended to wear. The protectiveness was related to glove thickness rather than acrylonitrile content.

INTRODUCTION

Disposable gloves are a common staple in hand protection across many industries, and are also less expensive than chemically protective gloves (CPC). Furthermore, disposable gloves provide superior tactile sensation, this allowing better manipulation of work pieces than their CPC analogs. Disposable gloves are not designed to protect against chemicals, but are used anyway in emergencies and in situations when they are the only glove available. There are many makers of disposable gloves, and even within one maker there may be multiple brands (purposes) and lines.(glove types) Usually, limited chemical permeation and degradation data are provided for disposable gloves[1]. Even less data are available for whole-glove permeation.

In the United States, the ASTM F739-96 permeation method is typically used to generate data using the open loop mode. The critical parameters are the steady state permeation rate P_s, and the normalized breakthrough time t_b[1]. The time at permeation rate of 100 ng/cm^2/min defines the t_b. These criteria may be inadequate relative to risk analysis since they do not address the toxic effects of the compound on the body or the skin. Nevertheless, the criteria are still useful to compare the permeation potential of chemicals through glove materials. Another drawback is that compounds with low vapor pressure may not volatilize enough.[2] The t_b parameter, being more dependent on sensitivity than P_s, may not be accurate if the air flow at the surface exposed to collection air is not high enough to completely volatilize the permeated molecules. In contrast, the ASTM closed loop method uses a set volume of liquid as collection solvent and this allows for a more accurate assessment of the permeation of semi/non-volatile chemicals because analyte volatilization is not key if the challenge molecule is adequately soluble in the collection solvent.. The closed loop method may not be suitable for compounds with high Henry Law constants when volatilization is favored over solubilization in the

collection solvent; if the collection solvent degrades the glove; or back permeation of the collection solvent occurs through the material. For these reasons, water is the preferred collection solvent if analyte solubility in water is adequate.

Another concern about the ASTM F739-96 test method is how well permeation through a small piece of glove material from the palm or the opposite surface above the palm accounts for other factors associated with wearing a whole glove such as hand temperature, glove fit, glove movement, and glove stretching during workplace operations.[3] This suggests research on whole glove validation under work place conditions or to simulate those conditions. Whole glove permeation accounts for the effectiveness of the entire glove including areas of concern such as the finger tips and the areas between the fingers, often the areas that commonly have shown enhanced field permeation relative to the palm area. [3]

There have been previous ideas of how to best conduct whole glove permeation testing. Boeniger and Klingner reviewed an in-use field sampling system to obtain real time measurements of permeation during work shifts.[4] An absorbent cotton/cotton-polyester/carbon cloth glove worn under the glove being tested (or 2 such gloves to indicate breakthrough of the 1st absorbent glove) integrates the permeated mass during wearing assuming negligible analyte volatilization loss, no skin absorption loss, and no contamination either from the skin or during donning/doffing/storing/transporting/laboratory handling. Another important variable not mentioned in that review is efficient absorbent glove/protective glove contact. In the few literature studies, qualitative colorimetric methods have been used, either to visualize absorbent glove analyte residues directly or by using commercially available chromophore impregnated pads affixed to the protective glove's inner collection surface. More quantitative methods involve extracting the absorbent glove or pads and determining the permeated mass by such

techniques as gas chromatography-mass spectrometry (GC-MS), or ultraviolet-visible spectrophotometry. Very few investigators have provided analyte recoveries.

Another approach is to eliminate the human contamination variable (and human subjects concerns) and to use a dextrous robotic hand model such as used by Phalen and Que Hee[5] to determine the permeation of the pesticide Captan through nitrile gloves with a cotton absorbent inner glove to assess the protectiveness of the nitrile glove. There was no difference between mass permeated after 8.0 h in regards to robot hand clenching and no clenching at 35°C. However, some gloves developed tears for the moving hand. Since Captan was a solid[6] and non-volatile, and the cotton glove and the nitrile glove were tight-fitting, the cotton absorbent glove was appropriate as a collection device. However, acquiring kinetic data for such a system is laborious since the cotton glove must be extracted at different times in independent permeation experiments to assemble a permeation curve to determine P_s and t_b. Development of a real time system that allows for sampling for the dextrous robot hand model would be helpful to generate whole glove permeation data to provide insight into how simulated human factors affect permeation, and that would also be suitable for laboratory testing for whole glove permeation.

The goals of the present research were to develop a dynamic whole disposable nitrile glove permeation method for non-volatile, water soluble compounds to generate whole glove permeation P_s and t_b data, and to compare these permeation parameters for different disposable nitrile gloves using cyclohexanol as model compound. This is the first report of such whole glove permeation data.

METHODS
Gloves and Chemicals

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, but 24 cm in length (Fisher Scientific, Pittsburgh, PA). An Ansell Solvex nitrile CPC glove (Fisher Scientific) was used to protect the robotic hand during permeation testing.

The cyclohexanol (Reagentplus-99%) challenge chemical was purchased from Sigma Aldrich, St Louis, MO. 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 used to make a 10 % (v/v) nitric acid solution for cleaning all glassware and plasticware; Optima acetone utilized in the cleaning of all glassware, and a neutral liquid detergent for cleaning purposes.

The following were from Fisher Scientific, Pittsburgh PA: Optima nitric acid used to make a 10 % (v/v) nitric acid solution for cleaning of all glassware; Optima acetone utilized in the cleaning of all glassware and permeation cells, and neutral liquid detergent for cleaning purposes.

Sodium dichromate (99%) from Fisher Scientific Pittsburgh PA was used for a saturated salt solution prepared in water to generate a $(55\pm4)\%$ relative humidity (RH) atmosphere inside of a pyrex vacuum desiccator from Fisher Scientific.

All 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 was used for the measurement of RH and temperature.

The GC-MS system used for analysis was a Hewlett-Packard (Santa Clara, CA) 5890 with a 60 m x 0.32 mm DB-1701 chemically bonded (1-µm thick film) fused silica capillary column with attached quadrupole mass spectrometer (Hewlett Packard 5988A), operated at 70 eV electron impact energy at an ion source temperature of $260^{o}C$. The quadrupole temperature was $150^{o}C$. The GC-MS transfer line temperature was $280^{o}C$. Helium was the carrier gas. There was a 6.0 minute solvent delay. Aliquots injected were 3.0 µL in volume.

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 4000–600 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 glove examination chamber (a 5.0-L polypropylene Bel-Art vacuum desiccator) (Figure 1) and a computer controller were used. 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. With the whole glove, the Frazier air permeability tester was set to 11-12 in. of water vacuum pressure, water was added to the glove, and then held for 90 sec at that pressure to check for any leaks before and after permeation. For the Sterling glove the vacuum pressure was reduced to 8-9 in. of water because higher vacuum caused inflation of the glove inside the test dome. Microscopic magnification of the glove surfaces was also used to determine whether micro holes or tears were present.

Robotic Hand

The robotic hand was built to the same specifications presented for whole glove permeation in Phalen and Que Hee[5] 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 x 1"(Home Depot, Los Angeles, CA), was added above the gears to prevent them slipping out of place during experiments

2. The AC adapter used to power the R7-11D1-5 DPDT toggle switch was changed to an Enercell 1.4-12V 300 mA adapter set to 4.5 V. The adapter was fitted with a 9.0 V snap connector.

3. The mechanical stirrer used in the Phalen paper was omitted.

Viton 2.79 mm extension and three-stop tubing (Cole Parmer, Vernon Hill, IL) were used for the water delivery system to the robotic hand. This tubing provided the best resistance towards cyclohexanol and was also fairly flexible and capable of handling pressure. PTFE tubing (3.0 mm OD; 1.48 mm ID) and polypropylene T-connectors (4.0 mm) (Cole Parmer, Vernon

Hill, IL) were used to connect 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) was used to maintain a water bath

temperature of 35.0 ± 0.5^{o}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 inch Fisher Scientific magnetic stir bar.

Parafilm was used to create seals around the robotic hand and over the 40-mL vial cap.

A Precision Econotherm Laboratory Oven (Fisher Scientific) was used to maintain a

temperature of 35.0^{o}C for the 6-L of cyclohexanol in a Pyrex vacuum desiccator and to contain

the robotic hand.

Procedures

GC-MS Analysis

Aliquots injected were 3.0 μL in volume unless indicated otherwise. All quantitation's

used the IS method whereby the area response of analyte injected divided by the area of the IS

was interpolated on a linear plot of area of analyte standard divided by area of the IS versus mass

of analyte injected. The linear portions of the plots were characterized by their slopes, intercepts,

their associated standard deviations, the correlation coefficients, and p-values.

The GC-MS conditions follow:

The DB-1701 column analysis began at 90°C for 6 min, increased to 280°C at 120°C/min at flow

rate (2.5 ± 0.1) mL/min with the injector at 280°C. The ions monitored were m/z 57 and 81 for

cyclohexanol and m/z 172 for the 4-bromophenol IS. The latter was 10 μg/mL concentration in

all injected samples. For all analyses, dilution into a working linear range was performed when necessary.

Permeation Procedures

Closed Loop Procedure. The ASTM test protocol was followed with some modifications. Test specimens were cut out from the palm or back of hand areas of the glove material. The test pieces were checked for micro-holes (Frazier physical and microscopic examination). The gloves were then conditioned at 56±1% RH at 25±1°C for 24 hours. After conditioning, the glove specimens were removed and their thickness (micrometer using 5 random positions), mass (electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

The test pieces were then mounted between the PTFE gaskets of the permeation cell and sealed by the stainless steel flanges of the permeation cells, tightening the nuts to a uniform torque of 16 ft lb. 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^{o}C and a shaking speed of 8.36±0.09 cm/sec to eliminate concentration gradients in the collection solvent. The permeation cells were allowed to equilibrate to the temperature for 30 min. At the start of the 30 min equilibration period, 10 mL of triply deionized water was also added as the collection solvent on the collection side of the permeation cell. The test chemical was added to the challenge side of the cell to constitute zero time and sampling proceeded. Sampling occurred over 8-hours and 100 µL samples were taken at regular times into pre-chilled 2.0 mL vials that varied in sampling time depending on whether the steady state or the normalized breakthrough time was to be measured. The samples were weighed at room temperature to ascertain the exact mass of the sample that was taken. The glove samples were reconditioned at the original conditions before

re-measuring all of the parameters. At least triplicate samples and blanks (air challenge) were evaluated.

Whole Glove Procedure. Whole gloves were tested for micro holes/tears by the Frazier detection method. The gloves were then conditioned at 56±1% RH at 25±1°C for 24 h. After conditioning, the glove specimens were removed and their thickness (micrometer-see later), mass (electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

A chemically resistant Ansell Solvex nitrile glove (unsupported, unlined and powderless) was placed over the clamped inverted robot hand in a flat neutral position, and left in the Precision Econotherm Laboratory oven set at 35°C for 1 hour. Next, 100 mL of water and a water bath were then heated to 35°C on the Corning Hot Plate/Stirrer. The 40 mL vial was capped (with the 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: 1x 29 in.; 1x 25 in.; 2x 21 in.; and 2x 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. tube which also led to the 40 mL vial, and the right side was 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 were plugged with the plastic tip of a Fisherbrand Enviro Swab, the lengths used to plug the tubing was 0.125 inch.

After one hour of acclimation of the robotic hand the test glove was slid over the 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 to the top hand, and the other was led down the pinky and brought to the front of the palm area. These two pieces of tubing were attached using a polypropylene T-connector; the third connection was made to the 29 inch tubing leading to the Ismatec pump. The 25 in. piece of tubing was wrapped around the robot hand 1 in. 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 connection free of the three-stop tubing.

A volume of 20 mL of preequilibrated water was added to the 40 mL vial, and the remaining 80 mL added directly in-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 the system was flowing properly. If so, the hand was placed into the desiccator with cyclohexanol and attached to a ring stand to be held in place. Measuring from the tip of the middle finger to 7.5 in. down the glove is the portion of the glove that was submerged during permeation testing. Figure 2 shows a schematic of the entire set-up of the whole glove permeation process.

For the first 30 min 1.0 mL samples were taken every 6 min from the 40 mL vial to determine t_b. After which 0.500 mL samples were taken every hour over 8 hours to cover the steady state permeation period to generate permeation curves for the whole glove. The total volume removed for analysis was 10.0 mL which is 10% of the total volume in the system. Permeation testing was completed with the robotic hand being still.

The mass in the collection stream during permeations was calculated by multiplying the injected sample mass by collection side volume in μL at time t obtained by assuming linear

collection side evaporation between volume at zero time and the volume at 480 min, all divided by 3, the volume in μL injected. The total mass collected in the collection side (corrected for previous mass removed by collection) divided by the exposed surface area were then plotted versus sampling time in min to generate the permeation curves. The time period of steepest slope was identified as the steady state permeation period and its slope and standard deviation obtained as in the standardization measurements above. The lag time t_l was calculated from the linear regression equation for the time when the injected mass divided by exposed area was zero. The diffusion coefficient D was then calculated from equation 1:[1]

$$D = \frac{l^2}{6t_l} \quad \text{----------------------------------- (1)}$$

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

At least three gloves were exposed to cyclohexanol and three blanks (no cyclohexanol exposure with the water collection system running) for each disposable glove type.

Glove Area Measurements

To ascertain the t_b concentration for the whole glove, the area had to be measured. The glove was sectioned off for all the fingers and the palm region. First, measuring down the glove 2.0 in., this was the wrist region that was not included in the calculation because it was not exposed to the chemical during testing. Another measurement was made 5.75 in. down the glove and a horizontal line drawn to separate the fingers from the palm. A vertical line was drawn down from between the index finger and thumb, to be measured as the area of the thumb. 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 Frustim of Right Circular cone equation [7]. The thumb was treated as three separate areas being a half sphere for the tip of the finger, below the Frustim of Right Circular cone [7], and a triangle for the bottom most portion of the thumb. The areas were found for each glove type used.

Glove Thickness Measurements

To understand in greater detail differences between the palm region and the finger regions glove samples thicknesses were measured in 8 areas mentioned above. 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 taken and averaged.

Glove Porosity Measurements

Porosity measurements were made in order to determine any degradation of glove material from exposure to cyclohexanol. This ensured there was no inner glove degradation that other methods such as reflectance FTIR or thickness measurements missed. Samples were cut using a PaperPro hole puncher (Office Depot Los Angeles, CA) to ensure consistent size circular pieces of 0.125 in. in diameter. The samples were placed in a 10 mL quartz sample tube, weighed, and degassed for 24 h under a nitrogen stream at $80^{o}C$. The instrument used for degassing was 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

There were two working linear ranges for the GC-MS and injected cyclohexanol. The first was 0.3 to 30 ng, with LQL of 0.15 ng. The second was from 30 ng to 330 ng. The first linear range was used to determine the normalized breakthrough concentration and the second was used

to determine the rest of the permeation curve. The retention times for analyte and IS were 8.0 and 11.5 minutes, respectively.

ASTM Permeation Testing

Safeskin Blue Nitrile Exam Glove

The Safeskin blue nitrile exam glove had a t_b of 29±2 min, a P_s of 2.2±0.6 µg/cm^2/min, and a D of (1.8± 0.2) x10^{-7} cm^2/min. The Safeskin exam glove had an average thickness of 0.1241±0.0048 mm and acrylonitrile contents of outside and inside of (13± 2)% and (9.8±0.5)% respectively. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes relative to blanks.

Blue Nitrile Exam Glove

The Blue nitrile exam glove had a t_b of 26±1 min, a P_s of 12±1µg/cm^2/min, and a D of (3.7±0.2) x10^{-7} cm^2/min. The blue exam glove had an average thickness of 0.1011±0.0025 mm and acrylonitrile contents of outside and inside of (12±1)% and (12±1)% respectively. In some cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but most challenge and collection surfaces showed no IR spectral changes relative to the blanks.

Purple Nitrile Exam Glove

The Purple nitrile exam glove had a t_b of 18±1 min, a P_s of 12±2 µg/cm^2/min, and a D of (5.3±0.7) x10^{-7} cm^2/min. The purple exam glove had an average thickness of 0.1075±0.0039 mm and acrylonitrile contents of outside and inside of (17.2±0.7)% and (12.1±0.7)% respectively. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of

coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Sterling Nitrile Exam Glove

The Sterling nitrile exam glove had a t_b of 8 ± 1 min, a P_s of 21 ± 1 µg/cm^2/min, and a D of (3.0 ± 0.2) x10^{-7} cm^2/min. The purple exam glove had an average thickness of 0.0779 ± 0.0025 mm and acrylonitrile contents of outside and inside of $(17.1\pm0.8)\%$ and $(12\pm1)\%$ respectively. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The infrared reflectance of the collection side surface showed a slightly more intense broad weak OH-stretch at 3400 cm^{-1} after permeation indicative of cyclohexanol.

Whole Glove Permeation Testing

Table I summarizes the whole glove permeation results, and the comparison between the ASTM closed loop method and whole glove permeation data are summarized in Table II. Table III shows the average thickness and acrylonitrile content of unexposed glove materials, and Table IV shows the porosity of the materials before and after permeation.

Safeskin Blue Nitrile Exam Glove

The Safeskin whole glove had a t_b of 20 ± 3 minutes, a P_s of 10.0 ± 0.7 µg/cm^2/min, and a D of (60 ± 20) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

Blue Nitrile Exam Glove

The Blue whole glove had a t_b of 22±5 minutes, a P_s of 9±1.0 µg/cm^2/min, and a D of (35± 13) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

Purple Nitrile Exam Glove

The Purple whole glove had a t_b of 18±0 minutes, a P_s of 13.8±3.0 µg/cm^2/min, and a D of (48± 11) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Sterling Nitrile Exam Glove

The Sterling whole glove had a t_b of 12±0 minutes, a P_s of 18±2 µg/cm^2/min, and a D of (35± 5) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Thickness

It should be noted that all glove materials swelled slightly (<10%) during the permeation experiment but reverted to the original thickness after reconditioning. Table IV shows the thickness differences for the whole gloves tested. Table V is a breakdown of whole glove thickness by region. Thickness in glove material varies from the wrist down to the fingers, and there is some difference in thickness between each finger. This varying thickness may play a

large role in the permeation of compounds. Therefore, depending on where the glove sample is obtained from for the ASTM closed loop method could lead to data that are not representative of the permeated region of the whole glove. The glove areas that were measured are also summarized in Table III. Each glove's total area are practically the same and this is expected since all gloves were the same size, medium.

As shown in Table III, each glove's average thickness is different, with the Sterling glove being the thinnest. The Purple and Sterling gloves have similar inner and outer acrylonitrile composition. The same can be said for the Safeskin and Blue nitrile gloves.

Weight

The weights before and after whole glove permeation are shown in Table VI, where the safeskin glove shows no significant difference before and after permeation at $p \leq 0.05$. The remaining gloves, Blue, Purple, and Sterling nitrile resulted in statistically different values before and after permeation at $p \leq 0.05$.

Porosity

Table IV shows the measured porosity of an unexposed and exposed glove to the test chemical. The Purple and Blue gloves were shown to have statistical differences in porosity measurements between the unexposed and exposed gloves; however, the Safeskin and Sterling gloves show no statistical difference between the unexposed and chemically exposed glove at $p \leq 0.05$.

DISCUSSION

These are the first dynamic data (Table I) generated for whole glove permeation testing of a semi/non-volatile compound and the first comparison with its closed loop ASTM analog

method (Table II). There were differences between the ASTM closed loop data and the whole glove data in terms of P_s and t_b for the Safeskin and Sterling gloves, as well as differences with the P_s for the Blue nitrile gloves at the p≤0.05 level. The P_s and t_b were statistically the same for the Purple nitrile glove and the t_b were statistically the same for the Blue nitrile glove at p≤0.05.

As can be seen from Table I the Blue and Safeskin nitrile gloves provided the best overall whole glove protection from cyclohexanol. The P_s for both gloves were statistically the same and t_b were statistically different between the two gloves. For the gloves their thickness and porosity data (Table III and IV) were statistically the same at p≤0.05. Finally, the two gloves share a statistically similar outside acrylonitrile content but a statistically different inside acrylonitrile content (Table III) at p≤0.05.

The worst performing disposable glove was the Sterling exam glove. The t_b and P_s were 12±0 min and 18±2 µg/cm^2/min, respectively, both statistically different at p≤0.05 from the corresponding Blue nitrile parameters. The Sterling gloves P_s and glove thickness are statistically different from the Purple nitrile (3rd lowest performing glove), however they share some similarity with their acrylonitrile content at p≤0.05 (Table II and III).

For the ASTM method in the closed loop mode the best performing glove was the Safeskin exam glove with 29±2 min t_b and 2.2±0.6 µg/cm^2/min P_s. The Sterling exam glove was still the lowest performing glove with 8±1 min t_b and 21±1 µg/cm^2/min P_s. Both parameters are statistically different at p≤0.05. The Safeskin and the second best performing glove, Blue nitrile, are statistically different in terms of P_s and acryolonitrile content (outside) but similar in terms of their thickness, acrylonitrile content (inside), and t_b at p≤0.05 (Table II and VIII). The Sterling nitrile glove and the third best performing glove, Purple nitrile, were statistically different in

terms of both P_s and t_b at $p \leq 0.05$. The two gloves are similar in acrylonitrile content inside and outside but are different in terms of thickness at $p \leq 0.05$.

Table II focuses on the closed loop and whole glove permeation data. The only gloves that show some difference between the ASTM closed loop method and the whole glove permeation method are the Safeskin and the Sterling nitrile disposable gloves. The Safeskin closed loop testing shows a t_b 9.0 minutes longer than the whole glove permeation method at 29 ± 2 minutes, as well as a much lower P_s at $2.19 \pm 0.6 \, \mu g/cm^2/min$. The diffusion coefficients were statistically different as well with the whole glove D being higher at $p \leq 0.05$. The Sterling glove had a closed loop t_b 4 min shorter than the whole glove method at 12 min, and a higher P_s of $21 \pm 1 \, \mu g/cm^2/min$ for the ASTM closed loop testing method. The diffusion coefficient for the whole glove was similar to the diffusion coefficient obtained using the ASTM closed loop testing method. The Blue nitrile P_s was different from that of the ASTM closed loop method, but the t_b for both were statistically the same at $p \leq 0.05$. The Purple nitrile glove showed no differences between the ASTM closed loop and whole glove permeation data obtained at $p \leq 0.05$.

There are two industry criteria to adjudge glove safety, one based on first detected breakthrough time from Ansell and the other based on steady state permeation rate from both Ansell and Kimberly Clark Professional. The t_b ratings of Kimberly Clark Professional for these disposable nitrile materials are:[8] <1 min, not recommended; 1-9 min, poor; 10-59 min, good; and 60-480 min, excellent. For open loop testing, t_b is defined as the time when the permeation rate reaches $0.1 \, \mu g/cm^2/min$.[1] The Kimberly Clark steady state permeation rate classification for CPC nitrile in $\mu g/cm^2/min$ is <1, excellent; 1-100, good; 100-10,000, poor; >10,000, not recommended.[9] The analogous Ansell steady state rate classification in $\mu g/cm^2/min$ is:[10] <0.9, excellent; 0.9-9, very good; 9-90, good; 90-900, fair; 900-9,000, poor; >9,000, not

recommended. We recommend that glove manufacturers have uniform criteria, and to tabulate t_b data as recommended by ASTM Method F739-99a rather than 1st detected breakthrough time data.

This is also the first report of microporosity data for gloves. There were statistical differences between exposed and unexposed materials in the whole glove method except for Safeskin Blue. This is probably caused by residual cyclohexanol since the gloves never attained constant weight even after two months of vacuum treatment. Thus any whole glove weight data are not useful for comparison purposes.

CONCLUSIONS

The most protective glove was the Safeskin glove followed by the Blue nitrile disposable glove in the closed loop ASTM test. Since the Safeskin brand is now marketed as the Kimtech Science Blue nitrile glove, the most protective commercially available disposable nitrile glove is the Blue Nitrile Disposable Glove. This glove also provides the best protection against cyclohexanol based on whole glove data.

ACKNOWLEDGMENTS

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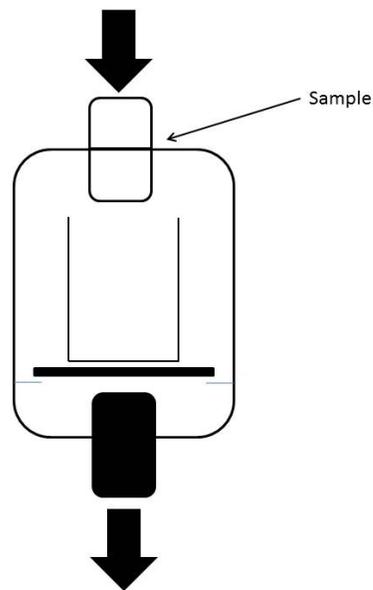
Figure 1: Diagram of the Frazier Air permeability testing of glove samples. The glove sample is loaded into the coupler and the vacuum is pulled on the sample. Any water that penetrates/permeates the glove material is captured in a container inside the testing dome.
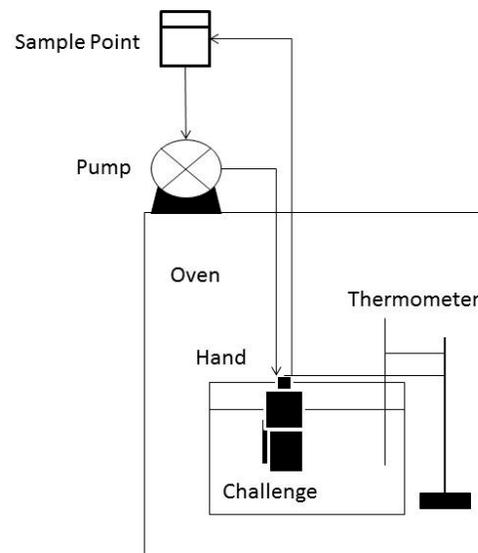
Figure 2: Schematic of whole glove permeation set-up

Table I: Summary of whole glove permeation data and glove safety ratings for cyclohexanol challenging a disposable Safeskin, Blue, Purple and Sterling Silver nitrile gloves. All measurements are in triplicate

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2/min$)	Diffusion Coefficient[c] (cm^2/min) $x10^{-8}$
Safeskin	20±3, good	10.0±0.7, good	60±20
Blue	22±5, good	9±1, very good	35±13
Purple	18±0, good	14±3, good	46±11
Silver	12±0, good	18±2 good	35±5

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation
[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation
c:Underestimated because of swelling

Table II: Comparison between ASTM Closed Loop and Whole Glove permeation data

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2/min$)	Diffusion Coefficient[c] (cm^2/min) x10^{-8}
Safeskin			
Whole Glove n=3	20±3, good[d]	10.0±0.7, good[d]	60±20
ASTM Closed Loop n=9	29±2, good[d]	2.2±0.6, very good[d]	18± 2
Blue			
Whole Glove n=4	22±5, good[e]	9±1, very good[d]	35±13
ASTM Closed Loop n=9	26±1, good[e]	12±1, good[d]	37±2
Purple			
Whole Glove n=3	18±0, good[e]	14±3, good[e]	46±11
ASTM Closed Loop n=9	18±1, good[e]	12±2, good[e]	53±7
Sterling			
Whole Glove n=3	12±0, good[d]	18±2 good[d]	35±5
ASTM Closed Loop n=9	8±1, poor[d]	21±1, good[d]	30±2

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation

[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation

[c]:Underestimated because of swelling

[d]: Statistically different at p ≤0.05 (comparison of whole glove and ASTM closed loop data under each glove)

[e]: No statistical difference at p ≤0.05 (comparison of whole glove and ASTM closed loop data under each glove)

Table III: Average physical characteristics of whole glove material

Glove Product	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 [a]	9.8±0.5 [a]	1125±9	0.13±0.01 [c]	0.14±0.01 [c]
Blue	12±1 [b]	12±1 [b]	1242±10	0.13±0.01 [c]	0.14±0.02 [c]
Purple	17.2±0.7 [a]	12.1±0.7 [a]	1129±51	0.12±0.01 [c]	0.13±0.01 [c]
Sterling	17.1±0.8 [a]	12±1 [a]	1067±10	0.081±0.008 [c]	0.092±0.008 [c]

[a]: Statistically different at $p \leq 0.05$ (Comparison completed within glove group, acrylonitrile)

[b]: No statistical difference at $p \leq 0.05$ (Comparison completed within glove group, acrylonitrile)

[c]: Statistically different at $p \leq 0.05$ (Comparison completed within glove group, thickness)

[d]: No Statistical difference at $p \leq 0.05$ (Comparison completed within glove group, thickness)

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

Glove Product	Porosity Pre-Permeation (m^2/g) n=3	Porosity Post-Permeation (m^2/g) n=3
Safeskin [a]	2.83±0.09	3.0±0.40
Blue Nitrile [b]	3.04±0.07	2.57±0.04
Purple Nitrile [b]	2.97±0.04	2.83±0.05
Sterling Nitrile [a]	5.12±0.03	4.5±0.50

[a]: Statistically different at $p \leq 0.05$

[b]: No statistical difference at $p \leq 0.05$

Table V: Whole glove thickness breakdown by region as expressed through arithmetic mean and standard deviation parameters

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

Table VI: Whole glove average areas by region (and their standard deviations) for the 10 gloves of Table V

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

Table VII: Whole Glove mass before and after permeation

	Pre-Permeation Mass (g)	**Post Permeation Mass (g)**
Safeskin	6.58±0.06	7.88±0.19
Blue	7.28±0.32	7.66±0.46
Purple	6.01±0.32	6.99±0.44
Sterling	3.96±0.01	4.67±0.13

Table VIII: ASTM Closed loop physical parameters

Glove Product	Thickness (mm) n=50	Acrylonitrile % Outside n=20	Acrylonitrile % Inside n=20
Safeskin	0.124±0.005	13± 2	9.8±0.5
Kimtech Science Blue	0.101±0.003	12±1	12±1
Kimtech Science Purple	0.108±0.004	17.2±0.7	12.1±0.7
Kimtech Science Sterling	0.078±0.003	17.1±0.8	12±1

DRAFT PAPER 4:

WHOLE GLOVE PERMEATION OF CYCLOHEXANOL THROUGH DISPOSABLE NITRILE GLOVES AND SIMULATED MOVEMENT

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ABSTRACT

Using a previously developed dynamic dextrous robotic whole glove permeation method, the permeation of cyclohexanol was investigated through Safeskin, and Kimtech Science Blue, Purple, and Sterling disposable nitrile exam gloves with simulated movement. The whole glove method developed involved a pump for water circulation, chemically resistant Viton tubing for transport of water and to continually wash the inner surface of the test glove via holes in the tubing, a dextrous robot hand, a chemically protective nitrile glove to protect the robot hand, an oven to maintain $35^{o}C$ temperature, and a hot plate to maintain $35^{o}C$ at the sampling point of the circulating water. The robot hand moved every 20 seconds, to prevent overheating of the relay switch. Aliquots of 1.0 mL were sampled at every 6 min for the first 30 min followed by removal of 0.5 mL aliquots every hour for 8 h. The 1.0 mL aliquots were used to determine the normalized breakthrough time t_b corresponding to 250 ng/cm^2 and the 0.5 mL aliquots used to determine the steady state permeation rate P_s. Quantification was by the internal standard method after gas chromatography-electron impact mass spectrometry using a non-polar capillary column and measuring the separated analyte and the internal standard by selective ion mass spectrometry. The non-moving Kimtech Science blue glove had a t_b of 18±5 min and P_s of 7±1.0 µg/cm^2/min. The Safeskin glove had a t_b of 14±4 minutes and P_s of 11.8±0.7 µg/cm^2/min. The Kimtech Science Purple and Sterling gloves had t_b of 18±0 and 6±0 min respectively, as well as respective P_s of 11.4±0.6 and 29±3 µg/cm^2/min.

INTRODUCTION

Whole glove permeation is the testing of an entire glove for its ability to resist a substance from permeating through the glove material. Since disposable nitrile gloves are inexpensive barriers not meant to protect hands from dermal chemical exposure, there is a need to ensure that current test methods are reflective of all the conditions that a glove encounters when being worn to accurately determine their effectiveness to resist chemical permeation. Disposable gloves are very popular because they provide increased tactile sensation compared to their chemically protective counterparts. Currently gloves are tested using the ASTM F739-96 test method in either the open loop or closed loop modes [1]. The mode that is most popular is the open loop but there are key factors that this mode does not take into account.

In the United States, the ASTM F739-96 permeation method is typically used to generate data using the open loop mode. The critical parameters are the steady state permeation rate P_s, and the normalized breakthrough time t_b[1]. The time at permeation rate of 100 ng/cm^2/min defines the t_b. These criteria may be inadequate relative to risk analysis since they do not address the toxic effects of the compound on the body or the skin. Nevertheless, the criteria are still useful to compare the permeation potential of chemicals through glove materials. Another drawback is that compounds with low vapor pressure may not volatilize enough.[2] The t_b parameter, being more dependent on sensitivity than P_s, may not be accurate if the air flow at the surface exposed to collection air is not high enough to completely volatilize the permeated molecules. In contrast, the ASTM closed loop method uses a set volume of liquid as collection solvent and this allows for a more accurate assessment of the permeation of semi/non-volatile chemicals because analyte volatilization is not key. The closed loop method may not be suitable for compounds with high Henry Law constants when volatilization is favored over solubilization in the collection solvent; if the collection solvent degrades the glove; or back permeation of the

collection solvent occurs through the material. For these reasons, water is the preferred collection solvent if analyte solubility in water is adequate.

There is continued concern for how well a small sample from the palm of glove material will represent the whole glove when work conditions may play a role in permeation through the entire glove [3]. Therefore this leads to the evaluation of whole glove permeation during work to be the optimal way to determine glove effectiveness. With this type of testing, data can be generated to compare whole glove permeation data with the ASTM F739-96 method to determine protectiveness, and to generate t_b that may be more protective then those provided by the open-loop method. .

Boeniger and Klinger reviewed glove sampling and analysis methodologies to use while a worker is completing their normal work tasks.[4] Doing this type of analysis takes into account hand temperature (temperature has been shown to affect permeation [5]), and hand movement that stretches the material so creating thinner material with a higher potential for permeation.[6] By using an absorbent liner or glove between the hand and the test glove any permeated mass absorbed by the inner glove/liner material can be extracted to determine permeated mass. The drawback to this system is not having a dynamic system that allows for sampling/analyzing at different times, and potential contamination from the skin of the user. Phalen and Que Hee eliminated the potential contamination from the human user and other human factors and used a dextrous robot hand to conduct whole glove permeation research.[7]

The robotic hand approach allows for the simulation of hand movement and no hand movement. However, the Phalen and Que Hee whole glove permeation methodology lacked a dynamic system that would allow for sampling/analysis at various time intervals. [6] This was also the case for the studies reviewed by Boeniger and Klinger.[4]

The aim of this research was to use a previously developed dynamic whole glove permeation system to generate data for whole glove permeation of a moving hand (whole glove (M)) and compare it to previously obtained whole glove permeation of a non-moving hand (whole glove (S)) and ASTM closed loop mode permeation data.

METHODS

Gloves and Chemicals

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, but 24 cm in length (Fisher Scientific, Pittsburgh, PA). An Ansell Solvex nitrile CPC glove (Fisher Scientific) was used to protect the robotic hand during permeation testing.

The cyclohexanol (Reagentplus-99%) challenge chemical was purchased from Sigma Aldrich, St Louis, MO. 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 used to make a 10 % (v/v) nitric acid solution for cleaning all glassware and plasticware; Optima acetone utilized in the cleaning of all glassware; and a neutral liquid detergent for cleaning purposes.

Sodium dichromate (99%) from Fisher Scientific Pittsburgh PA was used for a saturated salt solution prepared in water to generate a $(55\pm4)\%$ relative humidity (RH) atmosphere inside of a pyrex vacuum desiccator from Fisher Scientific.

All 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 was used for the measurement of RH and temperature.

The GC-MS system used for analysis was a Hewlett-Packard (Santa Clara, CA) 5890 with a 60 m x 0.32 mm DB-1701 chemically bonded (1-μm thick film) fused silica capillary column with attached quadrupole mass spectrometer (Hewlett Packard 5988A), operated at 70 eV electron impact energy at an ion source temperature of 260°C. The quadrupole temperature was 150°C. The GC-MS transfer line temperature was 280°C. Helium was the carrier gas. There was a 6.0 minute solvent delay. Aliquots injected were 3.0 μL in volume.

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 4000–600 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 glove examination chamber (a 5.0-L polypropylene Bel-Art vacuum desiccator) (Figure 1) and a computer controller were used. The vacuum desiccator was modified by drilling two holes in the top and bottom that were 2.75 in. outer diameter (OD)/2.0 in. inner diameter (ID). 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. With the whole glove, the Frazier air permeability tester was set to 11-12 in. of water vacuum pressure, water was added to the glove, and then held for 90 sec at that pressure to check for any leaks before and after permeation. For the Sterling glove the vacuum pressure was reduced to 8-9 in. of water because higher vacuum caused inflation of the glove inside the test dome. Microscopic magnification of the glove surfaces was also used to determine whether micro holes or tears were present.

Robotic Hand

The robotic hand was built to the same specifications presented for whole glove permeation in Phalen and Que Hee [7] with the following modifications.

4. 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 x 1"(Home Depot, Los Angeles, CA), was added above the gears to prevent them slipping out of place during experiments

5. The AC adapter used to power the R7-11D1-5 DPDT toggle switch was changed to an Enercell 1.4-12V 300 mA adapter set to 4.5 V. The adapter was fitted with a 9.0 V snap connector.

6. The mechanical stirrer used in the Phalen paper was omitted.

Viton 2.79 mm extension and three-stop tubing (Cole Parmer, Vernon Hill, IL) were used for the water delivery system to the robotic hand. This tubing provided the best resistance

towards cyclohexanol and was also fairly flexible and capable of handling pressure. PTFE tubing (3.0 mm OD; 1.48 mm ID) and polypropylene T-connectors (4.0 mm) (Cole Parmer, Vernon Hill, IL) were used to connect 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) was used to maintain a water bath temperature of $35.0\pm0.5^{o}C$ 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 inch Fisher Scientific magnetic stir bar. Parafilm was used to create seals around the robotic hand and over the 40-mL vial cap.

A Precision Econotherm Laboratory Oven (Fisher Scientific) was used to maintain a temperature of $35.0^{o}C$ for the 6-L of cyclohexanol in a Pyrex vacuum desiccator and to contain the robotic hand.

Procedures

GC-MS Analysis

Aliquots injected were 3.0 μL in volume. All quantitations used the IS method whereby the area response of analyte injected divided by the area of the IS was interpolated on a linear plot of area of analyte standard divided by area of the IS versus mass of analyte injected. The linear portions of the plots were characterized by their slopes, intercepts, their associated standard deviations, the correlation coefficients, and p-values.

The DB-1701 GC column analysis began at $90^{o}C$ for 6 min, increased to $280^{o}C$ at $120^{o}C$/min at flow rate (2.5 ± 0.1) mL/min with the injector at $280^{o}C$. The MS ions monitored were m/z 57 and

81 for cyclohexanol and m/z 172 for the 4-bromophenol IS. The latter was 10 µg/mL

concentration in all injected samples. For all analyses, dilution into a working linear range was

performed when necessary.

Permeation Procedures

Closed Loop Procedure. The ASTM test protocol was followed with some modifications. Test

specimens were cut out from the palm or back of hand areas of the glove material. The test

pieces were checked for micro-holes (Frazier physical and microscopic examination). The gloves

were then conditioned at 56±1% RH at 25±1$^{\rm o}$C for 24 hours. After conditioning, the glove

specimens were removed and their thickness (micrometer using 5 random positions), mass

(electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

The test pieces were then mounted between the PTFE gaskets of the permeation cell and

sealed by the stainless steel flanges of the permeation cells, tightening the nuts to a uniform

torque of 16 ft lb. 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$^{\rm o}$C and a shaking speed of

8.36±0.09 cm/sec to eliminate concentration gradients in the collection solvent. The permeation

cells were allowed to equilibrate to the temperature for 30 min. At the start of the 30 min

equilibration period, 10 mL of triply deionized water was also added as the collection solvent on

the collection side of the permeation cell. The test chemical was added to the challenge side of

the cell to constitute zero time and sampling proceeded. Sampling occurred over 8-hours and

100 µL samples were taken at regular times into pre-chilled 2.0 mL vials that varied in sampling

time depending on whether the steady state or the normalized breakthrough time was to be

measured. The samples were weighed at room temperature to ascertain the exact mass of the

sample that was taken. The glove samples were reconditioned at the original conditions before

re-measuring all of the parameters. At least triplicate samples and blanks (air challenge) were evaluated.

Whole Glove Procedure. Whole gloves were tested for micro holes/tears by the Frazier detection method. The gloves were then conditioned at 56±1% RH at 25±1°C for 24 h. After conditioning, the glove specimens were removed and their thickness (micrometer-see later), mass (electronic balance), and infrared reflectance spectra (Avatar 360) were obtained.

A chemically resistant Ansell Solvex nitrile glove (unsupported, unlined and powderless) was placed over the clamped inverted robot hand in a flat neutral position, and left in the Precision Econotherm Laboratory oven set at 35°C for 1 hour. Next, 100 mL of water and a water bath were then heated to 35°C on the Corning Hot Plate/Stirrer. The 40 mL vial was capped (with the 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: 1x 29 in.; 1x 25 in.; 2x 21 in.; and 2x 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. tube which also led to the 40 mL vial, and the right side was 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 were plugged with the plastic tip of a Fisherbrand Enviro Swab, the lengths used to plug the tubing was 0.125 inch.

After one hour of acclimation of the robotic hand the test glove was slid over the 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 to the top hand, and the other was led down the pinky and brought to the front of the palm area. These two pieces of tubing were attached using a polypropylene T-connector; the third connection was made to the 29 inch tubing leading to the Ismatec pump. The 25 in. piece of tubing was wrapped around the robot hand 1 in. 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 connection free of the three-stop tubing.

A volume of 20 mL of pre-equilibrated water was added to the 40 mL vial, and the remaining 80 mL added directly in-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 the system was flowing properly. If so, the hand was placed into the desiccator with cyclohexanol and attached to a ring stand to be held in place. Measuring from the tip of the middle finger to 7.5 in. down the glove is the portion of the glove that was submerged during permeation testing. Figure 2 shows a schematic of the entire set-up of the whole glove permeation process. For whole glove moving experimentation the same set up was followed for power cycling that was presented by Phalen and Que Hee [6]. The robot hand was set to move every 20 sec to prevent overheating of the relay switch.

For the first 30 min 1.0 mL samples were taken every 6 min from the 40 mL vial to determine t_b. After which 0.500 mL samples were taken every hour over 8 hours to cover the steady state permeation period to generate permeation curves for the whole glove. The total volume removed for analysis was 10.0 mL which is 10% of the total volume in the system. Permeation testing was completed with the robotic hand being still.

The mass in the collection stream during permeations was calculated by multiplying the injected sample mass by collection side volume in μL at time t obtained by assuming linear collection side evaporation between volume at zero time and the volume at 480 min, all divided by 3, the volume in μL injected. The total mass collected in the collection side (corrected for previous mass removed by collection) divided by the exposed surface area were then plotted versus sampling time in min to generate the permeation curves. The time period of steepest slope was identified as the steady state permeation period and its slope and standard deviation obtained as in the standardization measurements above. The lag time t_l was calculated from the linear regression equation for the time when the injected mass divided by exposed area was zero. The diffusion coefficient D was then calculated from equation 1:[2]

$$D = \frac{l^2}{6t_l} \quad \text{----------------------------------- (1)}$$

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

At least three gloves were exposed to cyclohexanol and three blanks (no cyclohexanol exposure with the water collection system running) for each disposable glove type.

Glove Area Measurements

To ascertain the t_b concentration for the whole glove, the area had to be measured. The glove was sectioned off for all the fingers and the palm region. First, measuring down the glove 2.0 in., this was the wrist region that was not included in the calculation because it was not exposed to the chemical during testing. Another measurement was made 5.75 in. down the glove and a horizontal line drawn to separate the fingers from the palm. A vertical line was drawn

down from between the index finger and thumb, to be measured as the area of the thumb.

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 Frustim of Right Circular cone equation [8]. The thumb was treated as three separate areas being a half sphere for the tip of the finger, below the Frustim of Right Circular cone [8], and a triangle for the bottom most portion of the thumb. The areas were found for each glove type used.

Glove Thickness Measurements

To understand in greater detail differences between the palm region and the finger regions glove samples thicknesses were measured in 8 areas mentioned above. 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 taken and averaged.

Glove Porosity Measurements

Porosity measurements were made in order to determine any degradation of glove material from exposure to cyclohexanol. This ensured there was no inner glove degradation that other methods such as reflectance FTIR or thickness measurements missed. Samples were cut using a PaperPro hole puncher (Office Depot Los Angeles, CA) to ensure consistent size circular pieces of 0.125 in. in diameter. The samples were placed in a 10 mL quartz sample tube, weighed, and degassed for 24 h under a nitrogen stream at $80^{o}C$. The instrument used for degassing was 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

There were two working linear ranges for the GC-MS and injected cyclohexanol. The first was 0.3 to 30 ng, with LQL of 0.15 ng. The second was from 30 ng to 330 ng. The first linear range was used to determine the normalized breakthrough concentration and the second was used to determine the rest of the permeation curve. The retention times for analyte and IS were 8.0 and 11.5 minutes, respectively.

ASTM Permeation Testing

Safeskin Blue Nitrile Exam Glove

The Safeskin blue nitrile exam glove had a t_b of 29±2 min, a P_s of 2.2±0.6 µg/cm^2/min, and a D of (1.8± 0.2) x10^{-7} cm^2/min. The Safeskin exam glove had an average thickness of 0.1241±0.0048 mm and acrylonitrile contents of outside and inside of (13± 2)% and (9.8±0.5)% respectively. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes relative to blanks.

Blue Nitrile Exam Glove

The Blue nitrile exam glove had a t_b of 26±1 min, a P_s of 12±1µg/cm^2/min, and a D of (3.7±0.2) x10^{-7} cm^2/min. The blue exam glove had an average thickness of 0.1011±0.0025 mm and acrylonitrile contents of outside and inside of (12±1)% and (12±1)% respectively. In some cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but most challenge and collection surfaces showed no IR spectral changes relative to the blanks.

Purple Nitrile Exam Glove

The Purple nitrile exam glove had a t_b of 18 ± 1 min, a P_s of 12 ± 2 µg/cm^2/min, and a D of (5.3 ± 0.7) x10^{-7} cm^2/min. The purple exam glove had an average thickness of 0.1075 ± 0.0039 mm and acrylonitrile contents of outside and inside of (17.2 ± 0.7)% and (12.1 ± 0.7)% respectively. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Sterling Nitrile Exam Glove

The Sterling nitrile exam glove had a t_b of 8 ± 1 min, a P_s of 21 ± 1 µg/cm^2/min, and a D of (3.0 ± 0.2) x10^{-7} cm^2/min. The purple exam glove had an average thickness of 0.0779 ± 0.0025 mm and acrylonitrile contents of outside and inside of (17.1 ± 0.8)% and (12 ± 1)% respectively. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The infrared reflectance of the collection side surface showed a slightly more intense broad weak OH-stretch at 3400 cm^{-1} after permeation indicative of cyclohexanol.

Whole Glove Permeation Testing

Table I summarizes the whole glove (M) permeation results, and the comparison between the ASTM closed loop method and whole glove permeation data are summarized in Table II. Table III is the comparison between whole glove (M) and whole glove (S). Table IV shows the average thickness and acrylonitrile content of unexposed glove materials, and Table V shows the porosity of the materials before and after permeation.

Safeskin Blue Nitrile Exam Glove

The nonmoving Safeskin whole glove had a t_b of 20±3 minutes, a P_s of 10.0±0.7 µg/cm^2/min, and a D of (60 ± 20) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

The moving Safeskin whole glove had a t_b of 14±4 minutes, a P_s of 11.8±0.7 µg/cm^2/min, and a D of (68 ± 15) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

Blue Nitrile Exam Glove

The non-moving Blue whole glove had a t_b of 22±5 minutes, a P_s of 9±1.0 µg/cm^2/min, and a D of (35 ± 13) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

The moving Blue whole glove had a t_b of 18±5 minutes, a P_s of 7±1.0 µg/cm^2/min, and a D of (44 ± 23) x10^{-8} cm^2/min. In most cases the infrared reflectance of the challenge surface showed a moderately more intense broad weak OH-stretch at 3400 cm^{-1} indicative of cyclohexanol, but for the collection surface there were no IR spectral changes for this side relative to the blanks.

Purple Nitrile Exam Glove

The non-moving Purple whole glove had a t_b of 18±0 minutes, a P_s of 13.8±3.0 µg/cm^2/min, and a D of (48± 11) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

The moving Purple whole glove had a t_b of 18±0 minutes, a P_s of 11.4±0.6 µg/cm^2/min, and a D of (47± 9) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Sterling Nitrile Exam Glove

The non-moving Sterling whole glove had a t_b of 12±0 minutes, a P_s of 18±2 µg/cm^2/min, and a D of (35± 5) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

The moving Sterling whole glove had a t_b of 6±0 minutes, a P_s of 29±3 µg/cm^2/min, and a D of (20± 3) x10^{-8} cm^2/min. The infrared reflectance of the challenge showed a noticeable reduction in intensity of the narrow strong C-C or C-H stretching region centered at 2900 cm^{-1}. This may be indicative of a loss of coating on the outside surface of the glove material. The collection side of the material had no change in IR spectrum relative to the blanks.

Thickness

It should be noted that all glove materials swelled slightly (<10%) during the permeation experiment but reverted to the original thickness after reconditioning. Table IV shows the thickness differences for the whole gloves tested. Table V is a breakdown of whole glove thickness by region. Thickness in glove material varies from the wrist down to the fingers, and there is some difference in thickness between each finger. This varying thickness may play a large role in the permeation of compounds. Therefore, depending on where the glove sample is obtained from for the ASTM closed loop method could lead to data that are not representative of the permeated region of the whole glove. The glove areas that were measured are also summarized in Table VII. Each glove's total area are practically the same and this is expected since all gloves were the same size, medium (Table IV).

As shown in Table IV, each glove's average thickness is different, with the Sterling glove being the thinnest. The Purple and Sterling gloves have similar inner and outer acrylonitrile composition. The same can be said for the Safeskin and Blue nitrile gloves.

Weight

The weights before and after whole glove permeation are shown in Table VIII, where the Safeskin glove shows no significant difference before and after permeation at $p \leq 0.05$. The remaining gloves, Kimtech Science Blue, Purple, and Sterling nitrile resulted in statistically different values before and after permeation at $p \leq 0.05$.

Porosity

Table V shows the measured porosity of an unexposed and exposed glove to the test chemical. The Purple and Sterling gloves were shown to have statistical differences in porosity measurements between the unexposed and exposed gloves while the robot hand was moving;

however, the Safeskin and Blue nitrile gloves show no statistical difference between the unexposed and chemically exposed moving glove at $p \leq 0.05$.

DISCUSSION

This is the first permeation kinetic data (Table I) generated for whole glove permeation testing with a moving and nonmoving robotic hand for a semi/non-volatile compound and the first comparison with its closed loop ASTM analog method (Table II). This is also the first use of a dynamic system with comparison between a still and moving robotic hand (Table III). There were differences between the ASTM closed loop data and the whole glove (M) data in terms of P_s and t_b for the Safeskin and Blue gloves, as well as differences with the P_s for the Sterling nitrile gloves at the $p \leq 0.05$ level. The P_s and t_b were statistically the same for the Purple nitrile gloves and the t_b were statistically the same for the Sterling nitrile glove at $p \leq 0.05$.

As can be seen from Table I the Blue nitrile gloves provided the best overall non-moving whole glove protection from cyclohexanol since it has the longest t_b and lowest P_s (18 ± 5 min and 7 ± 1 µg/cm^2/min respectively). The second best performing glove was the Safeskin. Between the two the P_s are statistically different, but the t_b are statistically the same (Table I). The glove thicknesses of the two gloves are statistically the same as well as the outside acrylonitrile percentage. Their difference was the inside acrylonitrile content at $p \leq 0.05$. (Table III).

The worst performing disposable glove was the Sterling exam glove. The t_b and P_s were 12 ± 0 min and 18 ± 2 µg/cm^2/min, respectively, both statistically different at $p \leq 0.05$ from the corresponding blue nitrile parameters. The Sterling gloves P_s and glove thickness are statistically different from the Purple nitrile (3rd lowest performing glove) (Table II & III). The

two gloves have some similarity in terms of their inside and outside acrylonitrile percentage at

$p \leq 0.05$ (Table II and Table III).

For the ASTM method in the closed loop mode the best performing glove was the Safeskin

exam glove with 29 ± 2 min t_b and 2.2 ± 0.6 µg/cm^2/min P_s. The Sterling exam glove was still the

lowest performing glove with 8 ± 1 min t_b and 21 ± 1 µg/cm^2/min P_s. Both parameters are

statistically different at $p \leq 0.05$. The Safeskin and the second best performing glove, Blue nitrile,

are statistically different in terms of P_s and acryolonitrile content (outside) but similar in terms of

their thickness, acrylonitrile content (inside), and t_b at $p \leq 0.05$ (Table II and VIII). The Sterling

nitrile glove and the third best performing glove, Purple nitrile, were statistically different in

terms of both P_s and t_b at $p \leq 0.05$. The two gloves are similar in acrylonitrile content inside and

outside but are different in terms of thickness at $p \leq 0.05$.

For the comparison of whole glove (S) to whole glove (M) the physical comparisons of

thickness and acrylonitrile percentage remains the same as mentioned previously however there

are some differences in P_s and t_b. For the Safeskin glove it was determined that the P_s between

the whole glove (S) and whole glove (M) were statistically different while the t_b for both were

statistically the same at $p \leq 0.05$. The Blue and Purple nitrile gloves whole glove (S) and whole

glove (M) P_s and t_b were statistically the same at $p \leq 0.05$. Finally the Sterling nitrile gloves P_s

were statistically the same while the t_b were statistically different at $p \leq 0.05$.

Table II focuses on the closed loop and whole glove (M) permeation data. The gloves that

show some difference between the ASTM closed loop method and the whole glove (M)

permeation method are the Safeskin and Blue gloves for both the P_s and t_b, while the Sterling

nitrile disposable gloves P_s were statistically different at $p \leq 0.05$. The Safeskin closed loop

testing shows a t_b 15.0 minutes longer than the whole glove (M) permeation method at 29 ± 2 minutes, as well as a much lower P_s at 2.2 ± 0.6 µg/cm^2/min. The diffusion coefficients were statistically different as well with the whole glove D being higher at $p\le 0.05$. The Sterling glove had a closed loop t_b 2 min longer than the whole glove method at 8 ± 1 min, and a lower P_s of 21 ± 1 µg/cm^2/min for the ASTM closed loop testing method. The diffusion coefficient for the whole glove (M) was statistically different from the diffusion coefficient obtained using the ASTM closed loop testing method at $p\le0.05$. The Blue nitrile whole glove (M) P_s was statistically similar to the ASTM closed loop method, as well as the t_b at $p\le0.05$. The Purple nitrile glove showed no differences between the ASTM closed loop and whole glove permeation (M) data obtained at $p\le0.05$.

There are two industry criteria to adjudge glove safety, one based on first detected breakthrough time from Ansell and the other based on steady state permeation rate from both Ansell and Kimberly Clark Professional. The t_b ratings of Kimberly Clark Professional for these disposable nitrile materials are [9] : <1 min, not recommended; 1-9 min, poor; 10-59 min, good; and 60-480 min, excellent. For open loop testing, t_b is defined as the time when the permeation rate reaches 0.1 µg/cm^2/min.[1] The Kimberly Clark steady state permeation rate classification for CPC nitrile in µg/cm^2/min is <1, excellent;1-100, good; 100-10,000, poor; >10,000, not recommended.[10] The analogous Ansell steady state rate classification in µg/cm^2/min is:[11] <0.9, excellent; 0.9-9, very good; 9-90, good; 90-900, fair; 900-9,000, poor; >9,000, not recommended. We recommend that glove manufacturers have uniform criteria, and to tabulate t_b data as recommended by ASTM Method F739-99a rather than 1st detected breakthrough time data.

There were statistical differences between exposed and unexposed materials in the whole glove (M) method except for the Purple and Sterling nitrile gloves. This is probably caused by residual cyclohexanol since the gloves never attained constant weight even after two months of vacuum treatment. Thus any whole glove weight data are not useful for comparison purposes.

CONCLUSIONS

The most protective glove was the Safeskin glove followed by the Blue nitrile disposable glove in the closed loop ASTM test. For whole glove (S) and whole glove (M) the most protective glove was the Blue nitrile followed by the Safeskin glove. It is not recommended to wear the Sterling gloves when handling cyclohexanol.

ACKNOWLEDGMENTS

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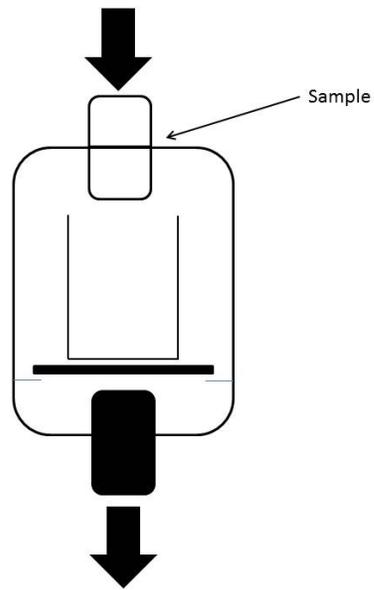
Sample

Figure 1: Diagram of the Frazier Air permeability testing of glove samples. The glove sample is loaded into the coupler and the vacuum is pulled on the sample. Any water that penetrates the glove material is captured in a container inside the testing dome.
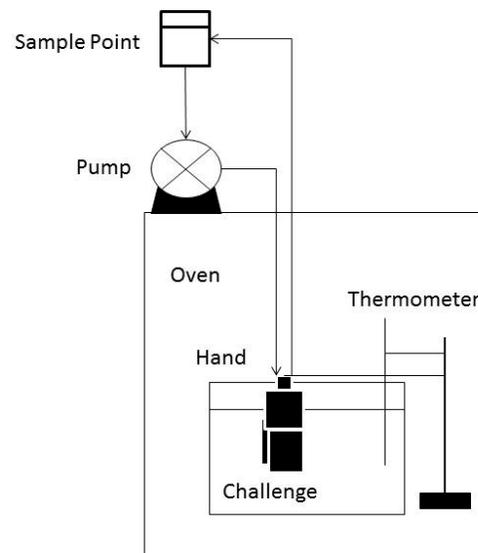
Figure 2: Schematic of whole glove permeation set-up

Table I: Summary of whole glove (moving) permeation data and glove safety ratings for cyclohexanol challenging a disposable Safeskin, Blue, Purple and Silver nitrile gloves

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] (μg/cm^2/min)	Diffusion Coefficient[c] (cm^2/min) x10^{-8}
Safeskin n=3	14±4, good	11.8±0.7, good	68±15
Blue n=3	18±5, good	7±1, very good	44±23
Purple n=3	18±0, good	11.4±0.6, good	47±9
Silver n=3	6±0, good	29±3 good	20±3

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation

[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation

c:Underestimated because of swelling

Table II: Comparison between ASTM Closed Loop and Whole Glove (M) permeation data

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2$/min)	Diffusion Coefficient[c] (cm^2/min) x10^{-8}
Safeskin			
Whole Glove (M) n=3	14±4, good [d]	11.8±0.7, good [d]	68±15
ASTM Closed Loop n=9	29±2, good [d]	2.2±0.6, very good [d]	18± 2
Blue			
Whole Glove (M) n=4	18±5, good [d]	7±1, very good [d]	44±23
ASTM Closed Loop n=9	26±1, good [d]	12±1, good [d]	37±2
Purple			
Whole Glove (M) n=3	18±0, good [e]	11.4±0.6, good [e]	47±9
ASTM Closed Loop n=9	18±1, good [e]	12±2, good [e]	53±7
Sterling			
Whole Glove (M) n=3	6±0, poor [e]	29±3 good [d]	20±3
ASTM Closed Loop n=9	8±1, poor [e]	21±1, good [d]	30±2

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation

[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation

[c]:Underestimated because of swelling

[d]: Statistically different at p ≤0.05 (comparison of whole glove (M) and ASTM closed loop data under each glove)

[e]: No statistical difference at p ≤0.05 (comparison of whole glove (M) and ASTM closed loop data under each glove)

Table III: Comparison between Whole Glove (S) and Whole Glove (M) permeation data

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] ($\mu g/cm^2/min$)	Diffusion Coefficient[c] (cm^2/min) $x10^{-8}$
Safeskin			
Whole Glove (S) n=3	20±3, good [e]	10±0.7, good [d]	60±20
Whole Glove (M) n=3	14±4, good [e]	11.8±0.7, good [d]	68±15
Blue			
Whole Glove (S) n=4	22±5, good [e]	9±1, very good [e]	35±13
Whole Glove (M) n=3	18±5, good [e]	7±1, very good [e]	44±23
Purple			
Whole Glove (S) n=3	18±0, good [e]	14±3, good [e]	46±11
Whole Glove (M) n=3	18±0, good [e]	11.4±0.6, good [e]	47±9
Sterling			
Whole Glove (S) n=3	12±0, good [d]	18±2 good [d]	35±5
Whole Glove (M) n=3	6±0, poor [d]	29±3 good [d]	20±3

[a]:Kimberly Clark   safety rating follows the arithmetic mean and standard deviation

[b]:Ansell/Kimberly Clark safety ratings follow the arithmetic mean and standard deviation

[c]:Underestimated because of swelling

[d]: Statistically different at p ≤0.05 (comparison of whole glove (S) and whole glove (M) data under each glove)

[e]: No statistical difference at p ≤0.05 (comparison of whole glove (S) and whole glove (M) data under each glove)

Table IV: Average physical characteristics of glove material for robotic moving hand

Glove Product	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 [a]	9.8±0.5 [a]	1125±9	0.13±0.01 [c]	0.14±0.01 [c]
Blue	12±1 [b]	12±1 [b]	1242±10	0.14±0.01 [c]	0.15±0.01 [c]
Purple	17.2±0.7 [a]	12.1±0.7 [a]	1129±51	0.12±0.01 [c]	0.13±0.01 [c]
Sterling	17.1±0.8 [a]	12±1 [a]	1067±10	0.082±0.010 [c]	0.093±0.010 [c]

[a]: Statistically different at p ≤0.05 (Comparison completed within glove group, acrylonitrile)

[b]: No statistical difference at p ≤0.05 (Comparison completed within glove group, acrylonitrile)

[c]: Statistically different at p ≤0.05 (Comparison completed within glove group, thickness)

[d]: No statistical difference at p ≤0.05 (Comparison completed within glove group, thickness)

Table V: Glove porosity for whole gloves (M) before and after permeation

Glove Product	Porosity Pre-Permeation (m^2/g)	Porosity Post-Permeation (m^2/g)
Safeskin (n=3) [b]	2.83±0.09	2.91±0.09
Blue Nitrile (n=3) [b]	3.04±0.07	2.88±0.07
Purple Nitrile (n=3) [a]	2.97±0.04	3.18±0.09
Sterling Nitrile (n=3) [a]	5.12±0.03	4.79±0.07

[a]: Statistically different at $p \leq 0.05$

[b]: No statistical difference at $p \leq 0.05$

Table VI: Whole glove thickness breakdown by region

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

Table VII: Whole Glove areas by region

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

Table VIII: Whole Glove (M) mass before and after permeation

	Pre-Permeation Mass (g)	**Post Permeation Mass (g)**
Safeskin	6.47±0.10	7.01±0.43
Blue	7.41±0.25	7.82±0.10
Purple	5.93±0.08	6.69±0.12
Sterling	3.97±0.02	4.79±0.06

Table IX: ASTM Closed loop physical parameters

Glove Product	Thickness (mm) n=50	Acrylonitrile % Outside n=20	Acrylonitrile % Inside n=20
Safeskin	0.124±0.005	13± 2	9.8±0.5
Kimtech Science Blue	0.101±0.003	12±1	12±1
Kimtech Science Purple	0.108±0.004	17.2±0.7	12.1±0.7
Kimtech Science Sterling	0.078±0.003	17.1±0.8	12±1

DRAFT PAPER 5:

DETECTION OF MICRO HOLES AND TEARS IN DISPOSABLE NITRILE GLOVE MATERIAL

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ABSTRACT

The developed method uses vacuum pressure to detect micro holes and tears in glove materials. It is capable of being used both quantitatively and qualitatively. A plastic Bel-Art vacuum desiccator was modified to interface with a Frazier air permeability tester in order to inflate the glove material. Water was added for testing of the glove material. If a glove cut out was being tested then 50 mL of water was added to a designed adapter. If the whole glove was being tested 600 mL of water was added to inside the glove. A vacuum was pulled between the pressures of 8-9 in. H_2O for glove pieces and between the pressures of 11-12 in. H_2O for whole gloves. For the design of this method Kimtech Blue nitrile gloves were used. Tears were pre-punctured into known areas of the gloves using 21, 22, 26s, 30, and 33 gauge needles. The size of tears varied from 0.80 ± 0.11 to 0.13 ± 0.01 mm in length. Flow rates of water escaping the tears were measured ranging from 106 ± 7 down to 2.5 ± 0.4 mL/min for glove pieces. For whole glove testing of the palm area the flow rates ranged from 543 ± 110 down to 31 ± 9 mL/min. For the finger/fingertip area flow rates ranged from 82 ± 18 down to 0.23 ± 0.06 mL/min. The detection limit of this method was 0.13 ± 0.01 mm due to constraints of available sturdy needle gauges smaller than 33 gauge. This is the first method developed that uses a Frazier air permeability tester for the detection of holes and tears in glove material.

INTRODUCTION

There are a number of methods used for the detection of holes/tears in glove materials. These methods range from electronic detection to more novel methods such as a leak test, however these methods do not have quantitative detection limits that have been investigated. A popular method for the detection of holes in glove materials is the ASTM D5151-06 1-Liter leak test. This test calls for the pouring of 1.0 liter of water at room temperature into a glove and with no excessive force observe for two minutes if any leaks occur in the glove material. [1] This test is used in industry and recommended to test medical gloves for defects by the FDA. [2] The 1-liter water leak test does not designate a detection limit; therefore this method may still overlook micro-size holes and tears which can lead to erroneous data when permeation testing of glove materials is involved.

Electronic methods do exist for the detection of holes and tears in glove materials. The Fluid Alarm System (FAS) is one that was tested to determine its effectiveness for the detection of holes in glove materials. The system works by generating a very small electrical current that allows for the detection of imperfections in glove materials. Latex gloves, when intact, act as insulators and will not conduct electricity; however as gloves are worn they may develop holes or tears and no longer act as insulators. The electrical current is allowed to pass through the glove material due to moisture, and the warning system is activated on the FAS device. [3] There are other electronic devices that work with the same logic; the Barrier Integrity Monitor (BIM) and the Surgic Alert Monitor (SAM) are two more devices that are capable of detecting holes and tears in glove materials [4]. These devices have the same principle as the FAS device, but the FAS system has a major drawback being unable to detect holes and tears in synthetic

rubbers. [3] Therefore devices such as these are limited to latex rubber gloves. The second limitation of these devices are that there is no reported detection limit of holes. It is possible to have a small hole in glove material that could go undetected by this system. Knowing the limits of a method can help one understand exactly what is being detected and know what size holes could be overlooked.

The airburst test is one that inflates a glove with air and observations are made to whether a hole is present or not [5] because the glove will partially deflate. This test may not work for smaller holes because the flow rate through the hole may be very low, allowing a glove to remain inflated even though a hole may be present.

The present research is a novel method to detect holes and tears using a Frazier air permeability tester and modified vacuum desiccator and pre-punctured glove material. The concept of pre-puncturing gloves has been used in research before by Kotilainen, H et al. where the 1-liter water leak test was tested by puncturing glove materials with a 30-gauge acupuncture needle. [6] Punctures of this size caused mixed results, some failing and some passing. There was no assessment of the minimum hole size detectable by this test method.

The research at hand developed a method for the detection of micro holes and tears in glove materials and has determined the method's limits.

METHODS

Equipment

Kimtech Science Blue nitrile gloves were used to develop and test this method. A laptop (Fujitsu Lifebook E series with Microsoft Windows 7 operating system) was used for processing the digital images captured from a microscope. .

The microscope was an electronic Aven Mighty Scope of 200X magnification power. Microviewer software was used for imaging and to measure samples. Is there a reticle scale?

Pure compressed air was used for the inflation of gloves. Tygon tubing was used to deliver the air inside the gloves for inflation.

Hamilton company metal hub sharp non-coring needles were used for tearing glove materials. The gauges used were 21, 22, 24, 26s, 30, and 33.

A room essentials plastic storage container was used to capture any water that may have flowed through the tear in glove material. A cork ring that was used had dimensions of 6 in (ID) x 8.3 in (OD) and supported the plastic container inside the dome for water capture.

The vacuum generated was pulled by a Frazier Air Permeability tester (FAP-HP-C) high pressure compact model from Frazier Instruments (Hagerstown, MD). This instrument is capable of pulling a vacuum between the ranges of 1-21 in. H_2O.

The testing dome was retrofitted from a Bel-Art Scienceware Transparent Vacuum Desiccator from Fisher Scientific. The vacuum desiccator was modified by drilling two holes in

the top and bottom opposite each other in the middle that were 2.75 in. diameter (OD) (Figure 1 a & b).

Dome hole linings were made using two Fernco 2.0 in. x 4 in. black polyvinyl chloride (PVC) flexible rubber couplers cut to be1.0 in. tall to fit around the holes to avoid damage to the glove material. The first was cut to be 1 in. tall for the top of the dome and the other was cut to be 3 in. tall for the bottom of the dome (Figure 2).

One Dura 2.0 in x 0.75 in. solid PVC reducer bushing was used inside the whole glove cuff area to hold it in place during testing (Figure 3). Two Dura 2.0 in. x 1.5 in. solid PVC bushings were used for glove cut outs. They were modified to create an adapter to hold a glove piece in place. Two holes were drilled in opposite ends of the bushings. Water gaskets were super-glued to the bottom of each reducer to prevent water leakage (Figure 4).

Two DANCO flush valve gaskets were cut and super-glued to the bottom of two reducer bushings to hold samples in place and to minimize water leakage.

An Everbilt 2 in. zinc plate was used with two 0.25 in.-20 x 2.5 in. zinc-plated flat-head Phillips Drive Machine Screw to tighten all parts together to ensure there was no leaking of water.

Procedures

Test Dome Manufacture

The vacuum desiccator was modified by drilling two holes in the top and bottom that were 2.75 in. outer diameter. 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. This was done for the top of the dome. For the bottom portion that interfaced with the Frazier Air Permeability tester another PVC coupler was cut to be 3 in. long and placed at the bottom of the dome. The exposed piece was then inserted into the Frazier air permeability tester to interface the two.

Adapter Manufacture

Figure 4 presents the adapter for glove portion testing. First, two flush valve gaskets were cut to fit around the top portion of two Dura solid PVC bushings. Gorilla superglue was used in order to make a lasting bond between the two items. After the adhesive dried, one bushing had 0.25 in. holes drilled into opposite ends of the extreme edge of the bushing. The same was done to the second. The bushings were placed on top of one another and 0.25 in. X 2 .5 in. screws were placed through the holes lining up the two bushings together. The screws were placed through the holes of an Everbilt 2 in. zinc plate and nuts were screwed on to tighten the assembly.

Glove Testing

The whole glove was inflated at 2.0±0.4 mL/min flow rate of air until first resistance. While maintaining this inflation (with a rubber band tightened around the glove and air tube, but still allowing some air to escape and the balloon to remain inflated) needle tips of varying gauges were used to puncture the glove material in predetermined areas. Inflating the glove past first resistance increased the tear length and became larger due to stretching of the glove material. The tear was located using the Aven microscope with the Microviewer software at 200X magnification. The microscope was calibrated before operation using the Microviewer software and recommended calibration techniques.

If the test was for a glove cut out, then a 2 in. circular cut out was made around the area with the puncture and mounted into the bushing adapter (Figure 4). If the whole glove was being tested then the PVC reducer bushing was placed into the cuff of the glove, and both were loaded into the top of the test dome. Both the adapter and the reducer slip into the top of the dome's PVC black rubber lining.

For glove pieces, the Frazier air permeability tester was set to a vacuum pressure between 7-8 in. of H_2O and 50 mL of water was added to the glove piece adapter and held for 90 seconds to check for any leaks. With the whole glove, the Frazier air permeability tester was set to 11-12 in. of water vacuum pressure, 600 mL of water was added to the glove, and then held for 90 seconds at that pressure to check for any leaks. The water that leaks through the tears was collected in the plastic container inside the testing dome. Before each test, the weight of the dome is obtained. After each test, the dome is reweighed for the amount of water that penetrated the tear in the glove material. For the 33-gauge needle a Kimwipe was reweighed on a balance and was used to rub the surface of the glove material for any water around the test area and reweighed for the amount of water that penetrated. With this information flow rates were calculated for each tear length.

Results

The 21-gauge needle produced a tear of 0.80±0.11 mm in length, 22 gauge 0.61±0.10 mm, 26s-gauge 0.45±0.08 mm, 30-gauge 0.23±0.03 mm, and 33-gauge needle produced an average tear length of 0.13±0.01 mm. For the glove pieces the highest flow rate was 106±7 mL/min with the 21-gauge needle size. The 22-gauge needle produced a flow rate of 61±7 mL/min, followed by 26s-gauge with 25±3 mL/min. The 30-gauge needle produced a flow rate of 8.1±0.9 mL/min and the 33-gauge needle produced a flow rate of 2.5±0.4 mL/min.

For a whole glove the flow rates were separated into the palm and finger regions. For the palm area the flow rate for the 21-gauge needle was 543±110 mL/min. Following this was the 22-gauge needle at 370±82 mL/min and 26s-gauge needle with a 126±23 mL/min flow rate. The flow rate for the 30-gauge needle was 60±9 mL/min and 31±9 mL/min for the 33-gauge needle.

The finger flow rates started with the 21-gauge needle at 82±18 mL/min and the 22-gauge with 53±12 mL/min. The 26s had a flow rate of 30±5 mL/min and the 30 and 33 gauge needles had flow rates of 6±3 and 0.23±0.06 mL/min respectively.

Discussion
Table I summarizes the average tear size that each gauge needle produced. The 21 gauge needle produced the largest tear at 0.80±0.11 mm and the 33 gauge needle produced the smallest tear at 0.13±0.01 mm in length. These two are statistically different from each other. Each gauge needle produced tears that are statistically different from each other. Table II summarizes the flow rates that were obtained from testing of glove pieces. The 21-gauge needle produced the largest flow rate at 106±7 mL/min. In contrast the 33-gauge needle produced a flow rate of 2.5±0.4 mL/min. All the flow rates obtained are statistically different from each other at $p \leq 0.05$.

Table III is a breakdown of whole glove testing between the palm and finger/finger tip area. The palm area produced much larger flow rates than the finger/finger tip areas. The palm area with a tear produced by the 21-gauge needle had a flow rate of 543±110 mL/min. The lowest flow rate observed was the tear produced by the 33-gauge needle having a flow rate of 31±9 mL/min. The flow rates are all statistically different from each other at $p \leq 0.05$. For the whole glove finger breakdown (Table III) the highest flow rate produced by the 21-gauge needle was 82±18 mL/min and the lowest was produced by the 33-gauge needle at 0.23±0.06 mL/min. The flow rates between the palm area and glove piece were all statistically different at $p \leq 0.05$; however,

between the finger/finger tips and glove piece there are some similarities. The holes produced by the 21-, 30-, and 33-gauge needles produced flow rates that were statistically different from each other between the glove piece and finger/finger tips at p≤0.05. The holes produced by the 22- and 26s- gauge needles had flow rates that were statistically the same between the piece of glove and finger/finger tips at p≤0.05.

Figure 6 is a transformed graph of flow rate (mL/min) versus the power of ten raised to the length of the tear for the glove cut outs that were tested. This was done in order to develop a linear trend between flow rate and length of tear. Figures 7 and 8 are of the same concept except Figure 7 is for the finger/finger tips and Figure 8 is a graph for the palm area. All three plots are significant and have p-values ≤0.05.

The quantitative limit of this method was the detection of a 0.13±0.01 mm tear in the glove material. This constraint is due to the rigidity of needle gauges below 33-gauge. When the needles become more flexible it becomes difficult to tear the glove material since it cannot penetrate the glove. Therefore the smallest flow rate that can be detected is 2.5±0.4 mL/min for glove pieces and 31±9 and 0.23±0.06 mL/min for whole glove palms and finger/finger tips respectively.

The final product of the interface can be seen in Figure 5.

Conclusion

This method is the first to use a Frazier Air Permeability tester to detect imperfections in glove material. The detection limit of this method is detecting a tear length of 0.13±0.01 mm. The methodology uses less water than the 1-liter water leak test, and establishes a quantifiable limit, something other methods have not done. This method can be used quantitatively or qualitatively

to determine the presence or size of a tear in glove material. It is recommended that other methods be tested to determine the limits of hole detection to have assurance that small or medium sized holes are not being overlooked.

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Figure 1: (a) Left Side is top of dome with 2.75 in. hole cut out (b) Right side is the bottom of the dome with the 2.75 in. hole cut out.
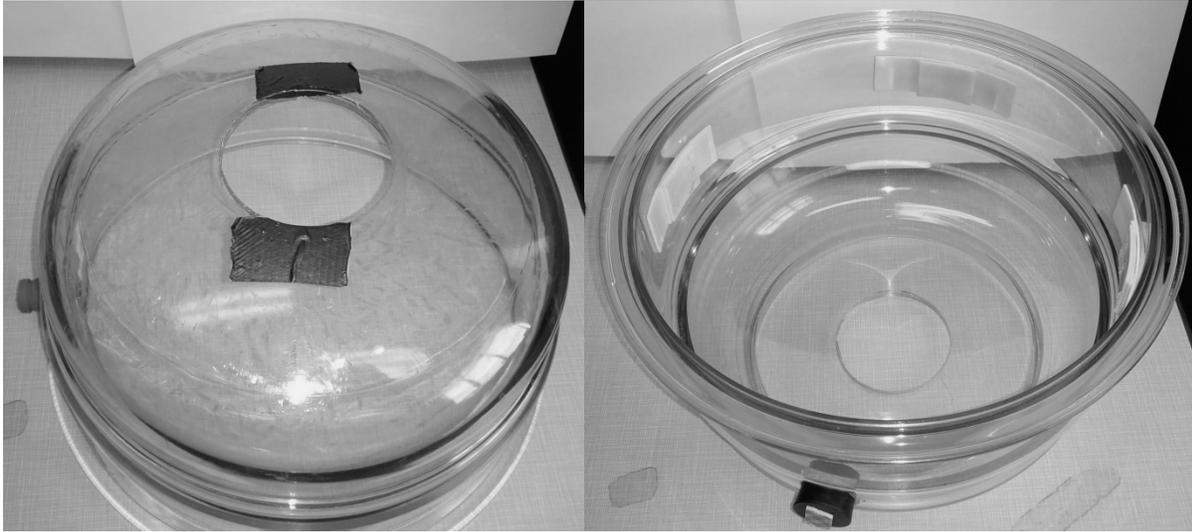
Figure 2: (Left) PVC flexible rubber coupler was cut to be 1.0 in. tall for the top of the dome (Right) PVC flexible rubber coupler was cut to be 3.0 in. tall for the bottom of the dome

Figure 3: PVC reducer bushing placed in the cuff of gloves to hold it in place during whole glove testing.

Figure 4: PVC bushings modified with rubber gaskets to hold glove pieces in place during hole detection testing.

Figure 5: The final product, the whole system with the dome interface.

Table I: Average tear length and gauge size

Gauge Size	Tear Length (mm) n=20
21	0.80±0.11
22	0.61±0.10
26s	0.45±0.08
30	0.23±0.03
33	0.13±0.01

Table II: Flow rate out of each tear produced by various gauge sizes

Gauge Size	Flow Rate (mL/min) n=9
21	106±7
22	61±7
26s	25±3
30	8.1±0.9
33	2.5±0.4

Table III: Whole glove flow rates in the finger and palm by gauge size

| Gauge Size	Palm Flow Rate (mL/min) n=18[a]	Finger/Finger Tip Flow Rate (mL/min) n=18 [a]
21	543±110	82±18
22	370±82	53±12
26s	126±23	30±5
30	60±9	6±3
33	31±9	0.23±0.06

a: Data is statically different between the two columns

Figure 6: Flow rate vs. transformed tear length for glove pieces [a]
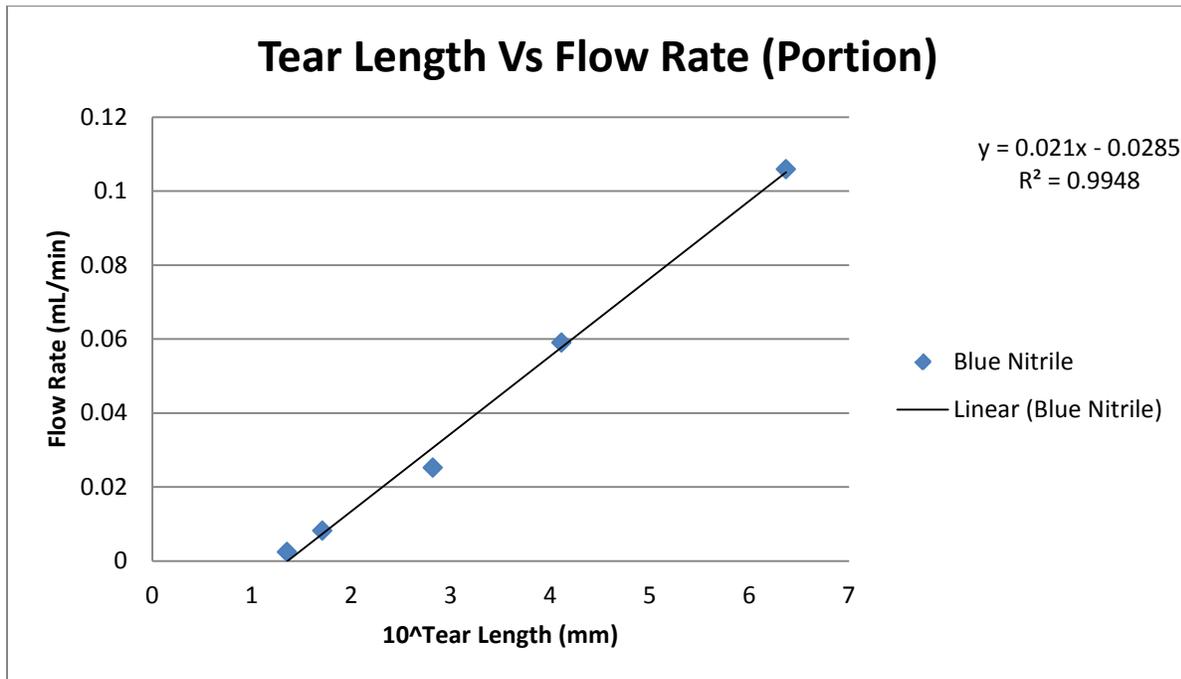
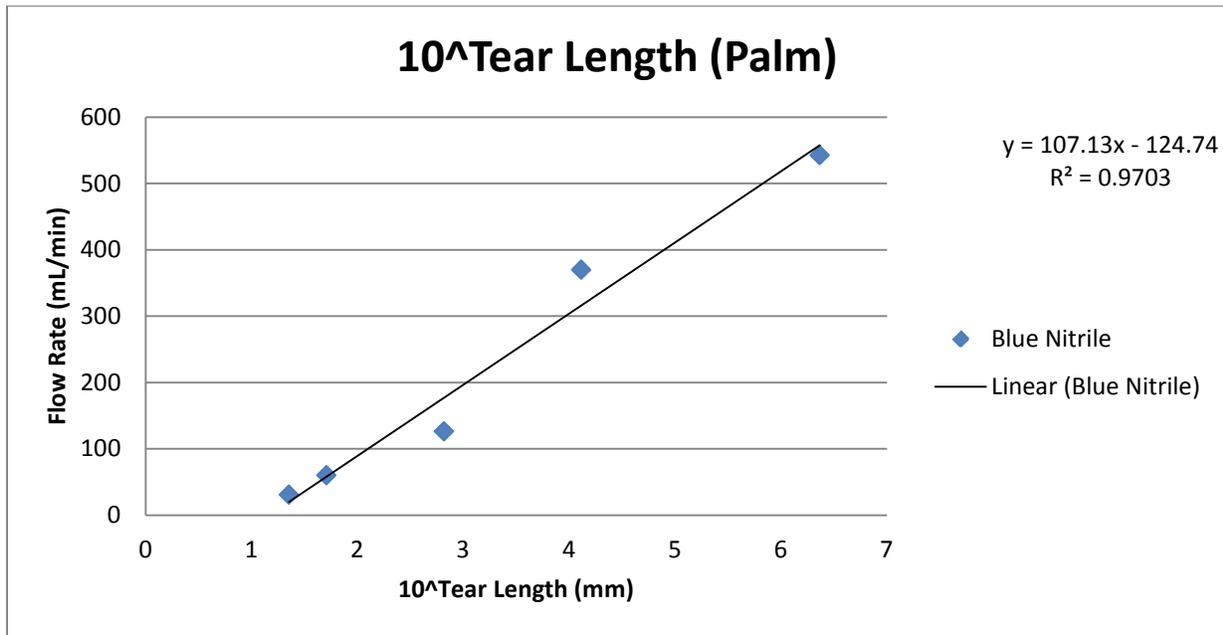a: Linear regression shows slope at p≤0.05

Figure 7: Flow rate vs. Transformed Tear Length for whole glove finger area [a]
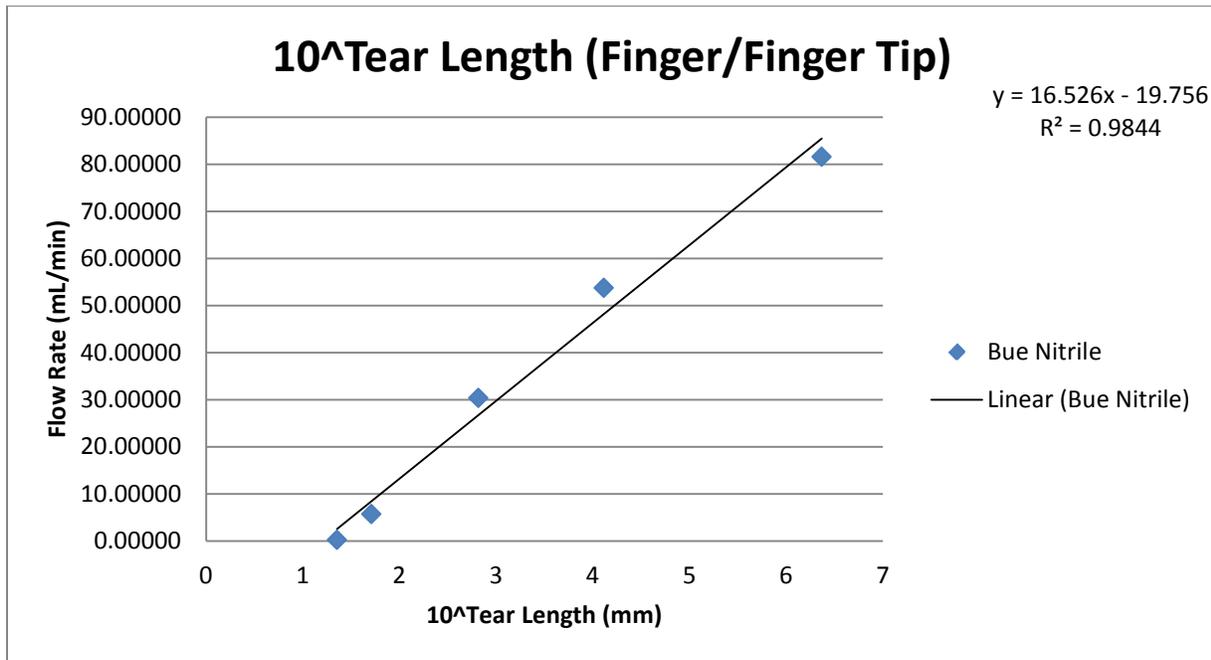
a: Linear regression shows slope at p≤0.05

Figure 8: Flow rate vs. Transformed Tear Length for whole glove palm area [a]

a: Linear regression shows slope at p≤0.05

Human Subjects: None. No Inclusion Enrollment Report is necessary

Child Subjects: None. No Public Policy Requirements and Objectives-Inclusion of Children as Subjects in Clinical Research filing is necessary.

Animals and Animal Data: None.

Genome Data: None.

Patents/Inventions: None filed.

Publications/Presentations from the Grant: No publications. Five draft publications are provided here as part of the current Final Report with probably 3-5 to come since work on d,l-limonene is still in progress. These will be reported when accepted.

The presentations at national/international scientific meetings from the grant (student is underlined) were:

1. Mathews, A. and Que Hee, S., "Triethanolamine Permeation through a Disposable Nitrile Glove." In: American Industrial Hygiene Conference and Exposition, May 14-May 19, 2011, Portland, Oregon. Abstract PO 114-1.

2. Zavala, J. and Que Hee, S., "Permeation of Efhylene Glycol through Disposable Nitrile Glove." In: American Industrial Hygiene Conference and Exposition, May 14-May 19, 2011, Portland, Oregon. Abstract PO 114-2.

3. Mathews, A. and Que Hee,S., "Detection of Micro-Holes and Tears in Disposable Nitrile Gloves". In: American Industrial Hygiene Conference and Exposition, June 16-June 21, 2012, Indianapolis, IN. Abstract SR-103-2.

4. Takaku-Pugh, S. and Que Hee, S., "Permeation of Benzyl Alcohol through Disposable Nitrile Gloves". In: American Industrial Hygiene Conference and Exposition, June 16-June 21, 2012, Indianapolis, IN. Abstract SR-103-4.

5. Mathews, A. and Que Hee, S., "Robotic Hand Whole Glove Permeation of Semi/Non-volatile Compounds through Disposable Nitrile Gloves". In: American Industrial Hygiene Conference and Exposition, May 18-May 23, 2013, Montreal, Que. Abstract SR-128-01.

6. Banaee, S. and Que Hee, S., "Permeation of 2-Ethoxyethanol through Purple Disposable Nitrile Gloves". In: American Industrial Hygiene Conference and Exposition, May 18-May 23, 2013, Montreal, Que. Abstract SR-128-02.

7. Banaee, S. and Que Hee, S., "Permeation of 2-Butoxyethanol through Purple Disposable Nitrile Gloves". In: American Industrial Hygiene Conference and Exposition, May 31-June 5, 2014, San Antonio, TX. Abstract SR-121-02.