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Permeation of Cyclohexanol Through Disposable Nitrile Gloves

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Permeation of Cyclohexanol Through Disposable Nitrile Gloves

A dissertation submitted in partial satisfaction of the
Requirements for the degree Doctor of Philosophy
in Environmental Health Sciences

by

Airek Royce Mathews

2013

ABSTRACT OF THE DISSERTATION

Permeation of Cyclohexanol Through Disposable Nitrile Gloves

By

Airek Royce Mathews
Doctor of Philosophy in Environmental Health Sciences
University of California, Los Angeles, 2013
Professor Shane Que Hee, Chair

This research was conducted to determine whether permeation of gloves on a robotic moving hand would produce shorter normalized breakthrough times (t_b) and faster steady state permeation rates (P_s) compared with a non-moving hand and the American Society of Testing and Materials (ASTM) F739-96 closed loop method. Cyclohexanol was used to complete this research because of its high boiling point and previous open loop data were available from glove manufacturers. A method was first developed to detect imperfections in glove material. Four glove products were selected for testing from one manufacturer. The ASTM closed loop method was used to generate new data for cyclohexanol. A dynamic whole glove permeation method was developed using a robotic hand, a water circulation system, and a sampling point to allow for interval sampling. This method was used to test still and moving hand configurations, and GC-MS analysis was used to analyze for cyclohexanol. The closed loop data for the Safeskin, Kimtech Science Blue, Purple, and Sterling nitrile gloves had t_b of 29±2, 26±1, 18±1, and 8±1 minutes, respectively. Open loop data for the Sterling glove had a t_b of 112 minutes. The respective P_s for the same gloves were 2.2±0.6, 12±1, 12±2, and 21±1 μg/cm^2/min. Compared to the ASTM closed loop method, whole glove permeation (still hand) for the Safeskin gloves produced a shorter t_b (20±3 minutes). The Safeskin gloves also produced a higher P_s (10.0±0.7 μg/cm^2/min). The most protective gloves for the whole glove still hand were the Blue nitrile gloves with a t_b of 22±5 minutes and P_s of 9±1 μg/cm^2/min. For moving hand whole glove experiments, the Safeskin and Blue nitrile gloves produced shorter t_b (14±4 and 18±5 minutes, respectively) compared to the ASTM closed loop method. For P_s the Safeskin and Sterling gloves were higher (11.8±0.7 and 29±3, respectively). Results for t_b and P_s were not consistent between the different types of gloves. The Safeskin and Kimtech Science Blue gloves were the best performing gloves overall. It is not recommended to wear the Sterling gloves when working with cyclohexanol.

The dissertation of Airek Royce Mathews is approved.

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2013

DEDICATION

This work is dedicated to my family and friends who have helped me along the way. Special appreciation goes to my mother Debra Singleton who always supported me throughout this process and my sister, Camille Mathews, who always added a little spice to my life.

To the loving memory of my grandmother, Edna Scarborough and grandfather John Singleton who I know would have been proud of my accomplishments.

To my aunt and cousins who always met me with nothing but love and support.

To the rest of my family and friends who always took the time to keep pushing me to finish.

It took a village to raise me. This is the fruit of your hard work and dedication.

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PRESENTATIONS

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CHAPTER 1

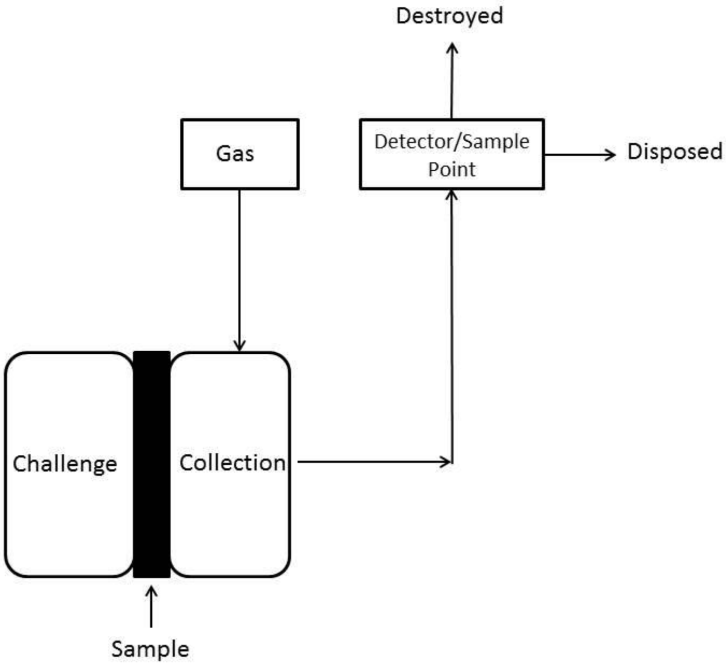
INTRODUCTION

1.1 Permeation

Permeation is the process by which a chemical moves through glove material at the molecular level.(1) Research in this field is limited and manufacturers are often relied upon to provide data on how protective their product is against different types of chemicals. This information comes in the form of a "Chemical Resistance Guide" and is typically provided for chemically protective clothing (CPC). Disposable nitrile gloves are inexpensive barriers used to protect wearers from skin exposures. However, there is often a lack of information on their chemical resistance. In 2011, 33,300 serious occupational illnesses/diseases were reported that were due to some type of skin exposure.(2) Considering that in 2011 there were 207,500 total cases reported (2), skin exposure plays a considerable role in occupational illnesses. Therefore, in order to effectively protect workers from dermal exposures, test methods are needed to provide the most accurate and precise information about how effective disposable nitrile gloves are in protecting the hands.

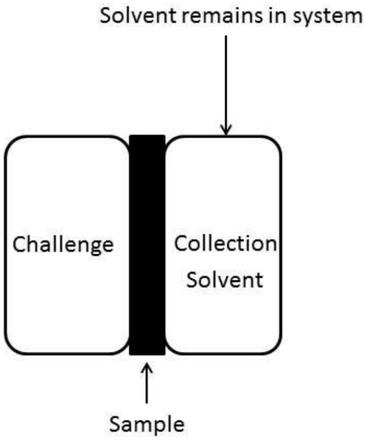
The American Society of Testing and Materials (ASTM) F739-96 "Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact" test method is one that measures personal protective equipment resistance toward a particular chemical. A flat portion of glove material is removed from the original glove and placed between two Polytetrafluoroethylene (PTFE) gaskets. This is then mounted tightly between a challenge and collection side. The challenge side contains the compound to be tested. The collection side can have two modes, open loop or closed loop. In the open loop mode, the collection side has a gas flowing through it to carry volatilized permeate to a detector or a sampling point. The gases that are often used for collection are nitrogen, air, or helium (1) and how effective the test is will depend on the chemical being tested and the carrier gas capacity for the chemical. (3) The gas may be recycled or not. Figure 1.1 is a schematic diagram of the open-loop mode. The drawback of the open loop method is that compounds with low vapor pressure may not volatilize completely to be carried to a detector or sample point; therefore there may a problem in achieving the normalized breakthrough time (t_b) at 0.100 µg/cm^2/min even when a large amount may have already permeated through the glove material. The (t_b) is a measure of how long it takes for the permeation to achieve a particular threshold. (1) In the case of the open loop test, the threshold is 0.100 µg/cm^2/min.

Figure 1.1: Diagram of open-loop system



The closed loop mode of the test method uses the same permeation cell as the open-loop method; however, the preferred solvent in the collection side is water and the volume is fixed. In this case the t_b is achieved when the collection side reaches 0.25 µg/cm^2. This test method has its drawbacks in that some compounds are not soluble in water and volatile chemicals may volatilize out of water. In order to use other solvents, further testing must be done to ensure that there is no degradation of the glove material, nor is there back permeation whereby the solvent can permeate between collection and challenge sides. Figure 1.2 below is a diagram of the closed-loop mode test set-up.

Figure 1.2: Diagram of closed loop system



There are two other permeation test methods besides the ASTM F739-96; the International Organization for Standardization (ISO) ISO6529 and the European Standard (EN)

EN 374-3 are test methods that differ from the ASTM test method. The ISO 6529 uses the ISO permeation cell to conduct permeation experiments and the EN 374-3 uses the ASTM permeation cell (4). Figure 1.3 contains images of the ASTM and ISO permeation cells.

The ISO cell provides permeation through gravity because the challenge chemical is on top, the protective equipment sample in the middle, and collection of any permeated chemical occurs on the bottom of the apparatus. Studies have compared the ISO and ASTM cells. For the permeation of benzene and 1,2-dichloroethane it was determined that the P_s was higher for the ISO cell by 1.3 times, while the t_b was unaffected (4). The ISO method was revised in 2001, and now specifies that the ASTM permeation cell design be used for testing. The ASTM permeation cell in Figure 1-3 prevents unnecessary force on the barrier material by removing the weight of the test chemical as a factor.

The various methods also have their own individual guidelines. The ASTM F739-96 calls for the reporting of the t_b and P_s depending on which test mode is being used. The P_s is the constant rate of permeation after breakthrough (1). For the open-loop mode the t_b threshold is at 0.100 $\mu g/cm^2/min$. (1) For the closed loop method the t_b threshold is 0.25 $\mu g/cm^2$.(1) The ISO 6529 calls for the reporting of both P_s and t_b. The t_b is at 0.1 or 1 $\mu g/cm^2/min$ for the open loop mode. (4) Lastly the EN-374-3 requires the reporting of only the t_b at 1.0 $\mu g/cm^2/min$. Figure 1.4 summarizes the test methods.

Figure 1.3: Diagrams of both cells. (Left) ASTM Type permeation cell (Right) ISO Type permeation cell

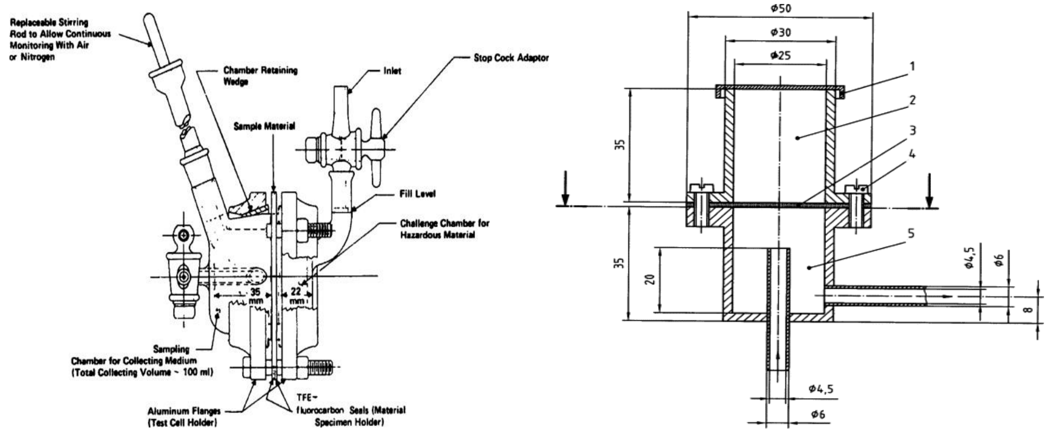


Figure 1.4: Summary of ASTM, ISO, and EN test methods

Test Method	Flow Rate of Collection Medium	Detection Limit	Results Reported
ISO 6529	5 vol. changes/min	0.1 or 1.0 µg/cm^2/min	P_s, t_b
EN 374-3	5 vol. changes/min	1.0 µg/cm^2/min	t_b
ASTM F739-96	50-150 mL/min	0.1 µg/cm^2/min (open) 0.25 µg/cm^2 (closed)	P_s, t_b

Many manufacturers use the open-loop mode of the test method to conduct their glove permeation experiments, including those chemicals that may be classified as semi/nonvolatile compounds. Semi/nonvolatile compounds are defined as any chemical that has a boiling point 150°C and above. Typically these compounds have low vapor pressures, and do not volatilize easily. Further experimentation is needed in order to determine which method is best suited for testing this class of chemicals for their t_b and P_s to better assess what is the most protective for workers. The t_b allows determination of how long a worker should wear personal protective equipment which is especially important for carcinogens or highly toxic compounds. The P_s aids in characterizing how much is permeating during the steady state period. The later helps determine the lag time t_l, the time at no mass permeated extrapolated from the steady state permeation period mass permeated versus time plot.(3) Diffusion coefficients (D) can be calculated using t_l and thickness (x) of the test material. D is in units of area divided by time. All this information is dictated by whether or not Fick's first law of diffusion (equation 1) holds true during permeation testing.

$$J = -D\frac{\delta C}{\delta x} \quad (1)$$

Fick's first law describes the rate of transfer per unit area. In this case J is the rate of transfer per unit area, c is the concentration of the substance that is diffusing, x is the distance traveled through the material, and D is the diffusion coefficient. (3) In order to apply Fick's law to determine relationships of mass permeated and permeation rates the following assumptions must hold true:

- At time zero, there is no permeated chemical in the polymer
- The exposed polymer immediately equilibrates with the chemical

- The concentration of the chemical on the collection side of surface is maintained at essentially zero
- The diffusion coefficient remains constant
- The thickness of the polymer remains constant

If all the assumptions hold then equation 1 can be re-written to determine the lag time t_l as shown in equation 2 below.

$$t_l = \frac{x^2}{6*D} \quad (2)$$

The effect the test chemical has on the glove material will dictate whether Fick's first law can be used to calculate D (equation 3).

$$D = \frac{x^2}{6*t_l} \quad (3)$$

Glove permeation research is limited in regards to semi/non-volatile neat chemicals and disposable gloves using ASTM method F739-96 in the closed loop mode. Previous research has included mixtures in many instances. Metal working fluids (which are complex mixtures of organics with boiling points over 150°C), were studied using the ASTM F739-96 test method in the closed loop mode across several disposable glove materials, ultimately determining nitrile to be the most resistant.(5) Neat chemicals were not tested. Other studies with high boiling chemical mixtures have been reported for many pesticide formulations. (3)

Often, glove permeation research is conducted using the ASTM F739-96 test method in the open loop mode, regardless of the chemical properties. For example, 2-ethoxyethyl acetate, which has a boiling point of 156.4°C (6), was tested against a chemically protective butyl rubber glove, and determined not to have breakthrough for four hours (7). 2-Ethoxyethyl acetate has a vapor pressure of 2.0 mm Hg at 20°C (8), relative to acetone with a vapor pressure of 231 mm Hg at 25^{o}C (9). There are no research data that validate whether the open loop method and closed loop method produce equivalent results. In order to show this, both closed loop and open loop data need to be generated.

The ASTM F739-96 test method currently does not take potential external factors into account during permeation testing. For glove permeation a flat piece of glove is removed from the palm or forehand area and placed into the permeation cell, and the glove material is tested. A study conducted by Springle et al, presented data that suggested the temperature of a human hand at rest is about 32^{o}C. (10) The conclusion can be drawn that any worn tight-fitting glove would acclimate to this hand temperature as well. However, all glove supplier permeation data is at room temperature or about 25^{o}C. The temperature increase of the glove material due to the hand should affect P_s and t_b, since it has been shown that temperature affects permeation rates (11).

Within the permeation cell, concentration gradients are also a concern when samples are being removed for analysis or if emulsions are present on the challenge side as with pesticide formulations in water. In order to have adequate mixing, a shaker was used in a study by Phalen and Que Hee (12). This study also addressed the concern of heat playing a role in glove permeation by placing the ASTM type permeation cells in a shaking water bath at 35^{o}C to simulate the heat generated by a working individual. (12) If these factors are not taken into consideration then permeation data that have been, and will be generated, does not accurately represent the environment in which the gloves are being used.

A major question to resolve, however, is how representative of whole glove permeation is the ASTM method?

1.2 Whole Glove Permeation

If there is a research need for closed loop data to validate any differences with the open loop mode of the permeation test method, it should also be determined how well glove samples used in these modes predict P_s and t_b of the whole gloves actually worn in the field.

Whole glove permeation accounts for the entire glove including regions of concern such as the finger tips and the areas between the fingers, areas that commonly have failures. (13) From the data generated with this type of experimentation it can be determined how viable the ASTM glove permeation method is, and whether new methodology needs to be developed to better predict P_s and t_b. Furthermore, after the development of a whole glove permeation system capable of measuring P_s and t_b, testing can be conducted on gloves to determine how much of an effect, if any, hand movement has. Previous research has addressed both these topics in part.

There have been previous ideas of how to best conduct whole glove permeation testing. (14,15) Boeniger and Klingner reviewed an in-use field sampling system to obtain real time measurements of permeation during work shifts.(15) 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 analyte 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. Only a few published studies have reported on qualitative colorimetric methods either to visualize absorbent glove analyte residues directly or indirectly using commercially available chromophore impregnated pads affixed to the 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 liquid chromatography-ultraviolet-visible spectrophotometry. Very few investigators have provided analyte recoveries.

A way to simulate potential human exposure and reduce contamination is through the use of a dextrous robotic hand. Phalen and Que Hee developed a whole glove robotic hand permeation method for an aqueous pesticide emulsion containing Captan(14). There was no t_b threshold reached in 8 hours in regards to hand movement of a robotic hand and the mass permeated was the same, movement or not. (14) There was more penetration observed due to glove tearing during movement, however. Since Captan is a solid (14), examination of pure semi/non-volatile liquids is a logical next step.

The robotic hand has its pitfalls as well. Robotic hands range in price from fifty to five hundred thousand dollars (prosthetic hands). Hands in the lower end of the price range typically are very limited in movement and are not automated. Some wriggle fingers or are walking hands, but most do not move. Hands in the higher end of the price range have excellent ranges of motion and can complete difficult tasks when required, but they are not very economical. Robotic hands do not simulate the temperature of human hands, and depending on the components that are involved the robotic hand can overheat and raise the temperature beyond that desired. Robotic hands require maintenance and repair after use in order to keep them in optimal working condition. Sometimes the robot hands are not strong enough to allow the fist to clench when a glove is donned but may be adequate without the glove. Thus, the properties of gloves that bear on such behavior need to be considered too.

1.3 Glove Manufacturing and Glove Parameters

In order to understand the properties of gloves, their manufacturing processes need to be discussed. Disposable nitrile gloves are made from acrylonitrile butadiene rubber (NBR) (16,17). This is produced from a polymerization reaction between acrylonitrile and butadiene as co-monomers (17). There are additional ingredients to the mix that vary with the intended use of the item that is being made. The ingredients that can vary include reinforcement fillers, plasticizers, protectants, flame retardants, and vulcanization agents (18). The typical mix may include water, emulsifier/soap, the monomers (acrylonitrile and butadiene), radical generating activator, and other ingredients (depending on what the intended use is). (18) The result is a crumb rubber that can be further processed to make a host of items by heating and pouring the crumbs in a mold to confer homogeneity and shape.

Acrylonitrile and butadiene ratios can be varied to have different barrier resistances and varying the temperature of the process factors into this as well. (17) Varying the acrylonitrile content can change the properties of the item being developed. Lower NBR content provides greater flexibility and resilience but causes less oil and fuel resistance. (18) Higher NBR content will provide greater resistance to oils, fuels, and greater abrasion resistance and tensile strength. (17) There are two types of NBR -- cold NBR and hot NBR. Cold NBR is the polymerization of acrylonitrile and butadiene between the temperatures of 5-15^{o}C (18) which allows for more flexibility (19) in the rubber while hot polymerization (between the temperatures of 30-40^{o}C (18)) provide a tougher rubber. (19) Porcelain hand forms are then used to shape the rubber into the gloves. The porcelain hands are dipped into the rubber mixture, removed, and allowed to dry. The number of times the hand is dipped dictates how thick the glove material will be (17). After the dipping process, the coated hand forms are cured (usually patent protected), where additives and coatings may be applied, and the coated hand finally dried. (18) The glove is then peeled carefully off the hand form.

Since acrylonitrile is the basis for many disposable gloves and it has the ability to increase oil/chemical resistance, there have been previous studies that have explored determining the acrylonitrile content of a glove and concluding whether for target chemicals a higher acrylonitrile content is protective. Phalen and Que Hee used attenuated total reflectance/Fourier transform infrared (ATR-FTIR) spectrophotometry at 2237±5 cm^{-1} to determine the acrylonitrile content of glove materials. Acrylonitrile rubbers of varying percentages (10, 19-22, 30-35, and 37-39) were used as reference materials to generate a standard curve. (19) From this curve glove materials were measured and their acrylonitrile contents were obtained. The observed acrylonitrile peak was analyzed for changes in peak intensity before and after chemical permeation of the glove. It was ultimately noted that increasing the acrylonitrile content in gloves decreased the steady state permeation rate (P_s) for Captan, a pesticide. The acrylonitrile content is therefore a quality assurance/quality control parameter that could be used to compare nitrile gloves, and to assess whether changes occur to the glove material over time and after permeation.

Another variable that has not been researched for gloves is porosity. Porosity is the measure of empty space in materials. All materials have this type of space. Previous research on latex gloves has suggested that these types of gloves have 0.03372 cm^3/g of empty pore volume. (20) The research was conducted using the mercury intrusion test. Essentially mercury is used to fill the empty spaces (or gaps) within the material. (21) Pressure is then applied to a testing tube with the sample and mercury inside. The reduction in mercury is attributed to the filling of the gaps in the material. The measurement was used to assess why latex gloves have minimal resistance to chemicals, especially ones used in the field of medicine. There is no information as to the porosity of nitrile gloves and whether this changes after prolonged exposure to a chemical. This is, therefore, a research need.

Another glove parameter to be evaluated before permeation testing is the presence of any micro holes or microtears that may lead to erroneous data where both permeation and penetration are measured together. If glove materials have an existing hole or tear then this will allow penetration through the hole or tear. Penetration is the free flow of chemical through a protective barrier due to deformity in the material and not on the molecular level (1). There are standard tests that exist for the detection of holes and tears such as the 1-liter water leak test (22), air burst test (23), microscope examination, or surface electrical conductivity (24). Various methods have their advantages, but each method has no quantitative detection limit. In order to reliably use a method, there needs to be a process of experimentation that outlines the abilities and limitations of that method. Therefore there needs to be a standard sensitive method for the detection of holes and tears prior to permeation test being conducted. This was also addressed during the present research.

In summary, glove permeation research faces many barriers that must be overcome to produce data that is accurate and precise. From production of acrylonitrile-butadiene rubber to wearing the glove as a barrier there are many factors that come into play. Currently the ASTM F739-96 method tests protective materials for barrier effectiveness without considering hand temperature, finger and fist-clenching movement, or other human factors such as fingernails.

Also this method does not account for other areas of the glove material such as the fingers and finger tips. . The two modes within this test both have their strengths and weaknesses.

Currently the open loop mode is the most popular of the two, but is not always applicable to all chemicals being tested. Each test should be used appropriately based on the properties of the chemical being tested. Whole glove permeation testing is the next logical step, which is moving from testing subsamples of glove material to testing the whole glove. However, methodology for the latter needs to be developed to accommodate all challenge phases -solid, liquid, and gas. More quality assurance and control techniques need to be developed to determine whether chemicals are causing glove degradation upon exposure, since this is sometimes not visible to the naked eye. Technology such as ATR-FTIR, porosimetry, and microscopy may be appropriate. More research needs to be done in order to advance our understanding of how to best test gloves for effectiveness, and develop ways of doing so that are reliable and practical.

1.4 Choice of Test Chemical for Permeation Experiments

Cyclohexanol was chosen because it was the sole organic pure chemical that had ASTM F739-96 open loop data for both disposable and CPC gloves. There was no closed loop or whole glove permeation data in the research or company literature. Since open loop testing is common among glove manufacturing companies, chemical resistance guides are developed using the ASTM open loop testing method. Breakthrough times and steady state permeation rates are reported along with criteria of what is considered “Good”, “Fair”, or “Poor”. For cyclohexanol the Ansell guide (25) has criteria for chemically protective material and Kimberly Clark has a chemical selection guide for its disposable nitrile gloves (26).

Cyclohexanol is an organic compound with a boiling point of 161.84°C (27) and molecular weight of 100.16 g/mol (27). This is a semi volatile chemical as the vapor pressure is 0.657 mm Hg at 25°C (28), and does not volatilize as fast as other compounds such as acetone. The water solubility of cyclohexanol is adequate for closed loop mode permeation testing, being 4.3 grams/100 grams of water at 30°C (29).

The main routes of exposure for cyclohexanol are inhalation and skin absorption. Cyclohexanol is a skin, eye and throat irritant if someone is exposed to 100 ppm in air (30). Exposure to high concentrations of cyclohexanol can lead to more severe reactions such as dizziness, vomiting, headache and nausea (31). Prolonged exposure to cyclohexanol will begin to cause dermatitis, liver, kidney, and lung damage (31). In a study by Fasano et al, cadaver skin was used to determine that cyclohexanol had a skin flux of 0.22 μg/cm^2/h, (32) which is not extremely fast. Most of the cyclohexanol was recovered from the skin surface (32).

There is little information as regards the metabolites of cyclohexanol in the body. Once inside the body, cyclohexanol undergoes biotransformation to different derivatives. The major urinary metabolites for cyclohexanol are 1,2-/1,4-cyclohexanediol, and cyclohexanol β-glucuronide. The most abundant metabolite formed is 1,2-cyclohexanediol at 19.1±3.8 % of the original dose(33); unchanged cyclohexanol comprised 1.1±0.3% and 1,4-cyclohexanediol constituted 8.4±1.4% in humans (33). Other studies have shown that cyclohexanol β-glucuronide was the dominant metabolite (about 60% of cyclohexanol from the original dose). (34) Cyclohexanol has also been observed to oxidize to cyclohexanone. (33) Some literature exists to show that there is a high affinity of cyclohexanol for alcohol dehydrogenase (ADH) which would oxidize cyclohexanol to the ketone, cyclohexanone (35,36). Cytochrome P450 also plays some role in the biotransformation of cyclohexanol to 1,2-and 1,4-cyclohexanediols (37), but this is not the most important transformation. More research is needed in order to determine what happens to cyclohexanol in the body, since there are conflicting conclusions. In animal studies, the rat oral LD_{50} for cyclohexanol is 2060 mg/kg (38), which suggests that cyclohexanol is not very acutely toxic. The potential for exposure to cyclohexanol can come in the forms of liquid, vapor, or aerosol.

Cyclohexanol is a commonly used chemical in many industries. In the United States between 500 million - 1 billion pounds of cyclohexanol are manufactured in a year. (39,40) The dominant use of cyclohexanol is the manufacturing of adipic acid which is used is the production of Nylon 66 (41). Cyclohexanol is also used in a formulation to produce caprolactam which is used in the manufacturing process of Nylon 6 polymer. (41) Cyclohexanol is also used in paints, lacquers, varnishes, and finish removers. (42) Since cyclohexanol use spans multiple industries, the potential for employee exposure is broad. The occupational regulatory levels for cyclohexanol are 50 ppm Permissible Exposure Limit (PEL) and Recommended Exposure Limit (REL) for both Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH), respectively (43). The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) is 50 ppm as well (44). For all cases, this level was set because of the effect that cyclohexanol has on the skin, eyes, nose, throat and the narcosis that may arise from exposure (43,44).

The analytical method used for quantifying cyclohexanol is important in order to determine the amount a person has been exposed to, or to determine protective equipment's ability to resist different chemicals. Gas chromatography with flame ionization detection is the method used by OSHA and NIOSH for the quantification of cyclohexanol. (45, 46, 47). OSHA includes cyclohexanol with cyclohexanone for sampling and analysis, and NIOSH samples and analyzes multiple similar alcohols. The gas chromatograph mass spectrometer (GC-MS) is another viable instrument that can be used for the detection of cyclohexanol because of its capacity to detect a wide range of chemicals, separate them, and have the ability to detect very low concentrations, typically between 0.25-100 pg (48). It is essential to have such a versatile instrument in order to analyze a wide variety of compounds but to also ensure detection of the normalized breakthrough time concentration.

1.5 Hypothesis and Specific Aims

The major hypothesis was that the moving robotic hand would generate higher P_s and t_b when compared to a still hand robot hand and to the ASTM F739-99 closed loop test.

The research at hand aims to generate original ASTM F739-96 closed loop mode data for cyclohexanol and to compare these data with those for existing open loop mode permeation data to determine which test method best suits permeation of semi/non-volatile compounds. Development of a dynamic whole glove permeation method using a dextrous robot hand is required to ascertain whether the ASTM closed loop method generated similar data to the whole glove P_s and t_b. Once a whole glove permeation method was developed, it was possible to determine whether hand movement generates statistically different P_s and t_b of various glove materials compared to a non-moving hand. Lastly a quantitative method was to be developed for the detection of micro-holes/tears in glove materials.

The glove materials tested were the Kimberly Clark Safeskin, Kimtech Science Blue, Purple, and Sterling disposable nitrile gloves, all being unlined, unsupported, and powderless disposable gloves from the same producer. Each glove has its own characteristics in regards to amount of acrylonitrile (%), thickness, porosity and mass which may play a role in their abilities to resistant chemical exposures.

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CHAPTER 2

PERMEATION OF SOME SEMIVOLATILE SOLVENTS THROUGH A DISPOSABLE NITRILE GLOVE

[This chapter has been submitted for publication]

2.1 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±0.5^{o}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.

2.2 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, 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^{o}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^{o}C;(5) AIHA WEEL 10 ppm),(11) cyclohexanol (BP 161^{o}C;(5) OSHA PEL,(12) NIOSH REL,(12) ACGIH TLV-TWA,(13) 50 ppm); diacetone alcohol (BP,167.9^{o}C;(5) OSHA PEL,(12) NIOSH REL,(12) ACGIH TLV-TWA,(13) 50 ppm; ethylene glycol, (BP, 197.6^{o}C;(5) ACGIH Ceiling 100 mg/m^3 (13)), and triethanolamine (BP 335.4 ^{o}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 ethyl cellulose; 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)

2.3 METHODS

2.3.1 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 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).

2.3.2 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^{o}C. The GC-MS transfer line temperature was 250^{o}C. Helium was the carrier gas. There was a 3 minute solvent delay. For cyclohexanol and the normalized breakthrough time elucidation, a 60 m × 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 desiccator) 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 × 20 mm heating block (Thomas Scientific, Swedesboro,NJ) to evaporate aqueous collection samples to concentrate them for derivatization.

2.3.3 Procedures

GC-MS Analysis

Aliquots injected were 2.0 µL in volume unless indicated otherwise. All quantitation's 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^{o}C, 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^{o}C. 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^{o}C, the HP-5ms column temperature was at 45^{o}C for 5 min, increased to 250^{o}C at 70^{o}C/min at flow rate (1.0±0.1) mL/min with the injector at 250^{o}C. 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 ^{o}C to 250^{o}C at 80^{o}C/min at flow rate 2.5 mL/min.

Diacetone alcohol: After a solvent delay of 3.0 min at 70°C, the program started at 70 °C for 5.5 min, then 60 °C/min to 250 °C, holding for 6 min at flow rate of (1±0.1) mL/min with the injector at 250°C. 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.

Ethylene glycol: 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.

Triethanolamine: 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 °C for 5 min and then at 120 °C/min to 300°C, 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.

2.3.4 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^{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±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)

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

where l is the initial thickness in cm, t_l is the lag time in minutes, and D has the 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.

Statistical Analysis

Each permeation experiment was conducted at least in triplicate, depending on if the coefficient of variation (CV) was less than 10%. The latter is based on the NIOSH and EPA CV criterion for precision. For CVs above 10%, a power *Student* t-test was used to determine how many replicates, n, were needed. Linear regression was used to characterize linear relationships, including standard deviations of the slope and intercept as well as defining the correlation coefficient r, and p-values. Analysis of variance was used to assess independent variable interactions. The *Student* t-test was used to test the statistical significance of different means.

2.4 RESULTS

2.4.1 Benzyl Alcohol

The linear working range for GC-MS of injected benzyl alcohol was 100 to 200 ng with lower quantifiable limit (LQL) of 2 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 $p \leq 0.05$ (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_l 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.

2.4.2 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 $\mu g/cm^2/min$, and a D of $1.84 \times 10^{-7} \pm 2.4 \times 10^{-8}$ cm^2/min. The material swelled slightly during the permeation but reverted to the original thickness after reconditioning. 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.

2.4.3 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 $5.2\times10^{-6}\pm4\times10^{-6}$ 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.

2.4.4 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.

2.4.5 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.

2.5 DISCUSSION

The permeation results are summarized in Table 2.1. These are the first closed loop permeation data for these chemicals for this glove type.

Table 2.1: 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] ($\mu g/cm^2/min$)**	**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

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 2.1, 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.

In the case of cyclohexanol there is a large discrepancy between the data obtained from the closed loop method and the manufacturer's data obtained using open loop methodology. This might be due to the different temperature exposure conditions, room temperature for the open loop method and 35^{o}C for the closed loop method since the melting point of cyclohexanol is 23-25^{o}C. (5) Since there was an 83 minute difference between these two tests more research needs to be conducted at the same temperature conditions to ensure this is a real change. There also needs to be wearer education as to how often to change gloves at the prevailing ambient conditions.

2.6 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.

2.7 ACKNOWLEDGEMENTS

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CHAPTER 3

PERMEATION OF CYCLOHEXANOL THROUGH DISPOSABLE NITRILE GLOVES

3.1 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^{o}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.

3.2 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 ethyl cellulose; 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).

3.3 METHODS

3.3.1 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±4)% 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).

3.3.2 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^{o}C. The GC-MS transfer line temperature was 250^{o}C. Helium was the carrier gas. The injector port temperature was 250^{o}C. There was a 3 minute solvent delay at 45^{o}C. The temperature program was 45^{o}C for 5 min, increasing to 250^{o}C at

70^{o}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 × 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^{o}C, the program began at 90 ^{o}C to 250^{o}C at 80^{o}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 desiccator) 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.

3.3.3 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±1% relative humidity at 25±1^{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±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 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_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:$^{(5)}$

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

where l is the initial thickness in cm, t_l is the lag time in minutes, and D has the 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)

Statistical Analysis

Each permeation experiment was conducted at least in triplicate, depending on if the coefficient of variation (CV) was less than 10%. The latter is based on the NIOSH and EPA CV criterion for precision. For CVs above 10%, a power *Student* t-test was used to determine how many replicates, n, were needed. Linear regression was used to characterize linear relationships, including standard deviations of the slope and intercept as well as defining the correlation coefficient r, and p-values. Analysis of variance was used to assess independent variable interactions. The *Student* t-test was used to test the statistical significance of different means.

3.4 RESULTS

The linear range for GC-MS of injected cyclohexanol was 0.15 to 330 µg/mL for the DB 1701 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. Averaged permeation curves for all gloves can be found in Appendix A.

3.4.1 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 $(1.8 \pm 0.2) \times 10^{-7}$ 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.

3.4.2 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 $\mu g/cm^2/min$, 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 were (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.

3.4.3 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 $\mu g/cm^2/min$, 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.

3.4.4 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.

3.5 DISCUSSION

The permeation results for all four glove types are summarized in Table 3.1. This is the first closed-loop glove permeation data to compare these disposable nitrile glove types relative to permeation for any chemical.

Table 3.1: 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

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 μg/cm^2/min.(4) The Kimberly Clark steady state permeation rate classification in its KleenGuard G80 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:(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 3.1 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 µg/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 µg/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 µg/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 µg/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±1.0 µg/cm^2/min.

From the physical characteristics in Table 3.2, 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.

Table 3.2: 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

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. Development of a whole glove permeation method for liquids should be the next step to determine how well current standard methods predict steady state permeation rate and normalized breakthrough time for glove materials.

There is 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. Semi/non-volatile compounds will take more time to volatilize into the gas stream using the open loop method creating a false breakthrough time that is longer than it should be, if the closed loop method had been used for testing. If, with further research, the trend continues that the open loop method is over estimating the breakthrough times of semi/non-volatile chemicals then it creates a false sense of how long gloves can be worn.

3.6 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.

3.7 ACKNOWLEDGEMENTS

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CHAPTER 4

WHOLE GLOVE PERMEATION OF CYCLOHEXANOL THROUGH DISPOSABLE NITRILE GLOVES

4.1 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 $\mu g/cm^2/min$. 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.

4.2 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 in needed 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 published studies on whole glove permeation testing, 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) by using a dextrous robotic hand model. Phalen and Que Hee(5) used a robotic hand 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.

4.3 METHODS

4.3.1 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.

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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 (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).

4.3.2 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 4.1) 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.

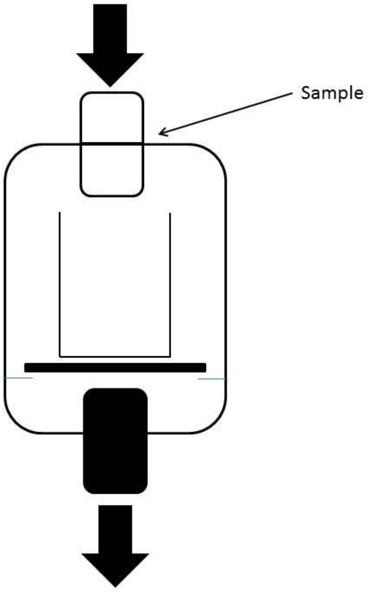

Figure 4.1: Diagram of the Frazier Air permeability testing of glove samples. The glove sample is loaded into the coupler and the vacuum is pulled on the sample. Any water that penetrates/permeates the glove material is captured in a container inside the testing dome.

4.3.3 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.

4.3.4 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^{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 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^{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^{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 4.2 shows a schematic of the entire set-up of the whole glove permeation process.

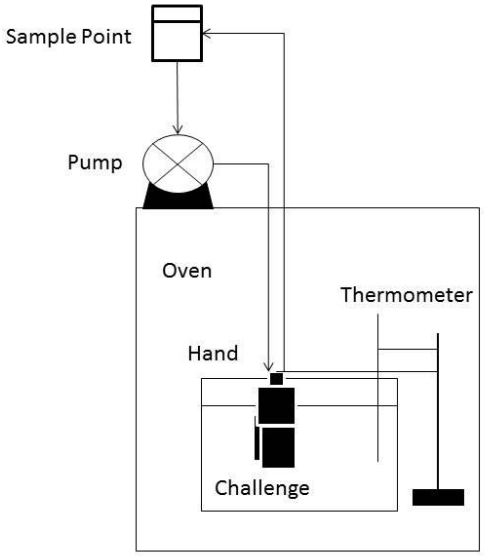

Figure 4.2: Schematic of whole glove permeation set-up

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)

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

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.

Statistical Analysis

Each permeation experiment was conducted at least in triplicate, depending on if the coefficient of variation (CV) was less than 10%. The latter is based on the NIOSH and EPA CV criterion for precision. For CVs above 10%, a power *Student* t-test was used to determine how many replicates, n, were needed. Linear regression was used to characterize linear relationships, including standard deviations of the slope and intercept as well as defining the correlation coefficient r, and p-values. Analysis of variance was used to assess independent variable interactions. The *Student* t-test was used to test the statistical significance of different means.

4.4 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. Permeation curves for the ASTM closed loop method can be found in Appendix A and whole glove permeation curves can be found in Appendix B.

ASTM Permeation Testing

4.4.1 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.

4.4.2 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.

4.4.3 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.

4.4.4 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 4.1 summarizes the whole glove permeation results, and the comparison between the ASTM closed loop method and whole glove permeation data are summarized in Table 4.2. Table 4.3 shows the average thickness and acrylonitrile content of unexposed glove materials, and Table 4.4 shows the porosity of the materials before and after permeation.

Table 4.1: 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 **n=3**	20±3, good	10.0±0.7, good	60±20
Blue **n=5**	22±5, good	9±1, very good	35±13
Purple **n=3**	18±0, good	14±3, good	46±11
Sterling **n=3**	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 4.2: 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 $p \leq 0.05$ (comparison of whole glove and ASTM closed loop data under each glove)

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

Table 4.3: 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 for inside and outside acrylonitrile %)

[b]: No statistical difference at $p \leq 0.05$ (Comparison completed for inside and outside acrylonitrile %)

[c]: Statistically different at $p \leq 0.05$ (Comparison completed for pre and post thickness)

[d]: No Statistical difference at $p \leq 0.05$ (Comparison completed for pre and post thickness)

Table 4.4: 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 $p \leq 0.05$

4.4.5 Whole 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.

4.4.6 Whole 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.

4.4.7 Whole 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.

4.4.8 Whole 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.

4.4.9 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 4.3 shows the thickness differences for the whole gloves tested. Table 4.5 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 4.6. Each glove’s total area is practically the same and this is expected since all gloves were the same size, medium.

Table 4.5: 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

As shown in Table 4.3, 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.

4.4.10 Area

Table 4.6 is a breakdown of glove area by region. The areas were measured in order to determine the equivalent normalized breakthrough time concentration.

Table 4.6: Whole glove average areas by region (and their standard deviations) for the 10 gloves of Table 4.5

	Safeskin (cm^2) n=3	**Blue (cm^2) n=3**	**Purple (cm^2) n=3**	**Sterling (cm^2) n=3**
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

4.4.11 Weight

The weights before and after whole glove permeation are shown in Table 4.7, 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 $p \leq 0.05$.

Table 4.7: Whole Glove mass before and after permeation

Glove	Pre-Permeation Mass (g)	Post Permeation Mass (g)
Safeskin **n=3**	6.58±0.06	7.88±0.19
Blue **n=5**	7.28±0.32	7.66±0.46
Purple **n=3**	6.01±0.32	6.99±0.44
Sterling **n=3**	3.96±0.01	4.67±0.13

4.4.12 Porosity

Table 4.4 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 $p \leq 0.05$.

4.5 DISCUSSION

These are the first dynamic data (Table 4.1) generated for whole glove permeation testing of a semi/non-volatile compound and the first comparison with its closed loop ASTM analog method (Table 4.2). 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 $p \leq 0.05$ level. The P_s and t_b were not statistically different for the Purple nitrile glove; however, the t_b was statistically the same for the Blue nitrile glove at $p \leq 0.05$.

As can be seen from Table 4.1 the Blue and Safeskin nitrile gloves provided the best overall whole glove protection from cyclohexanol. The P_s for both gloves was not statistically different; however, the t_b were statistically different between the two gloves. For the gloves their thickness and porosity data (Table 4.3 and 4.4) were not statistically different at $p \leq 0.05$. Finally, the two gloves share a statistically similar outside acrylonitrile content but a statistically different inside acrylonitrile content (Table 4.3) at $p \leq 0.05$.

The worst performing disposable glove was the Sterling exam glove. The t_b and P_s were 12±0 min and 18±2 $\mu g/cm^2/min$, 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), however they share some similarity with their acrylonitrile content at $p \leq 0.05$ (Table 4.3).

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 $\mu g/cm^2/min$ P_s. The Sterling exam glove was still the lowest performing glove with 8±1 min t_b and 21±1 $\mu g/cm^2/min$ 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 acrylonitrile content (outside) but similar in terms of their thickness, acrylonitrile content (inside), and t_b at $p \leq 0.05$ (Table 4.3 and 4.8). 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 4.8: 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

Table 4.2 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±0.6 µg/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±1 µg/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 not statistically different at $p \leq 0.05$. The Purple nitrile glove showed no significant 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.

From the data presented the whole glove Safeskin, Blue, and Sterling gloves produced results that were less protective than the ASTM closed loop method. With this decrease in protectiveness a false sense of security could be created with open loop breakthrough times. More research needs to be conducted to determine which test method to use for semi/non-volatile chemicals. This research could lay the foundation for a larger study to investigate which chemicals should be used with the appropriate test method, and to determine if the ASTM method over or under estimates permeation results.

4.6 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.

4.7 ACKNOWLEDGEMENTS

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CHAPTER 5

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

5.1 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. Aliquots of 1.0 mL 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. The Safeskin and Sterling whole glove moving hand(whole glove M) data show less protection for whole glove (M) in terms of Ps compared to whole glove still hand (whole glove S) and ASTM closed loop method. For the

Sterling gloves the whole glove (M) was less protective in terms of t_b as well when compared to whole glove (S). Whole glove (M) was less protective compared to the ASTM closed loop method in terms of t_b for the Safeskin and Blue nitrile gloves. Results in the effectiveness of the glove material were not consistent. .

5.2 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.

5.3 METHODS

5.3.1 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±4)% 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).

5.3.2 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 5.1) 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.

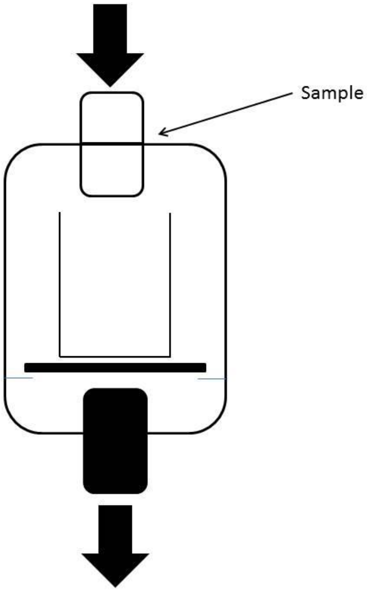

Figure 5.1: Diagram of the Frazier Air permeability testing of glove samples. The glove sample is loaded into the coupler and the vacuum is pulled on the sample. Any water that penetrates the glove material is captured in a container inside the testing dome.

5.3.3 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 ± 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.

5.3.4 Procedures

GC-MS Analysis

Aliquots injected were 3.0 µL in volume. 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 DB-1701 GC 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 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°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°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^{o}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^{o}C for 1 hour. Next, 100 mL of water and a water bath were then heated to 35^{o}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 5.2 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.

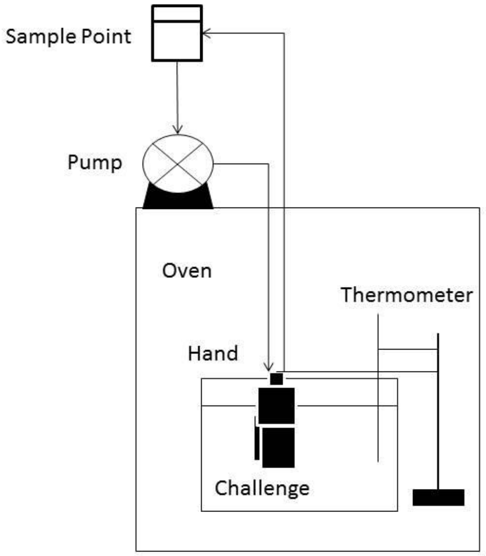

Figure 5.2: Schematic of whole glove permeation set-up

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: $^{(2)}$

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

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.

Statistical Analysis

Each permeation experiment was conducted at least in triplicate, depending on if the coefficient of variation (CV) was less than 10%. The latter is based on the NIOSH and EPA CV criterion for precision. For CVs above 10%, a power *Student* t-test was used to determine how many replicates, n, were needed. Linear regression was used to characterize linear relationships, including standard deviations of the slope and intercept as well as defining the correlation coefficient r, and p-values. Analysis of variance was used to assess independent variable interactions. The *Student* t-test was used to test the statistical significance of different means.

5.4 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. Permeation curves for the ASTM closed loop method can be found in Appendix A, whole glove (S) permeation curves can be found in Appendix B, and whole glove (M) permeation curves can be found in Appendix C.

ASTM Permeation Testing

5.4.1 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.

5.4.2 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.

5.4.3 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.

5.4.4 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 5.1 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 5.2. Table 5.3 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.

Table 5.1: Summary of whole glove (moving) permeation data and glove safety ratings for cyclohexanol challenging a disposable Safeskin, Blue, Purple and Silver nitrile gloves

Glove n=3	**Breakthrough Time^{a} (min)**	**Steady State Permeation Rate^{b} (μg/cm^{2}/min)**	**Diffusion Coefficient^{c} (cm^{2}/min) x10^{-8}**
Safeskin	14±4, good	11.8±0.7, good	68±15
Blue	18±5, good	7±1, very good	44±23
Purple	18±0, good	11.4±0.6, good	47±9
Sterling	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 5.2: 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=5	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 $p \leq 0.05$ (comparison of whole glove (M) and ASTM closed loop data under each glove)

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

Table 5.3: Comparison between Whole Glove (S) and Whole Glove (M) permeation data

Glove Name	Breakthrough Time[a] (min)	Steady State Permeation Rate[b] (μg/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 $p \leq 0.05$ (comparison of whole glove (S) and whole glove (M) data under each glove)
[e]: No statistical difference at $p \leq 0.05$ (comparison of whole glove (S) and whole glove (M) data under each glove)

5.4.5 Whole 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. The IR spectrum for the whole glove (M) showed no difference from that of the whole glove (S).

5.4.6 Whole 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. The IR spectrum for the whole glove (M) showed no difference from that of the whole glove (S).

5.4.7 Whole 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 IR spectrum for the whole glove (M) showed no difference from that of the whole glove (S).

5.4.8 Whole 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 IR spectrum for the whole glove (M) showed no difference from that of the whole glove (S).

5.4.9 Thickness & Area

It should be noted that all glove materials swelled slightly (<10%) during the permeation experiment but reverted to the original thickness after reconditioning. Table 5.4 shows the thickness differences for the whole gloves tested. Table 5.5 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 5.6 and broken down by regions. Each glove's total area is practically the same and this is expected since all gloves were the same size, medium.

As shown in Table 5.4, 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.

Table 5.4: 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 $p \leq 0.05$ (Comparison completed for inside and outside acrylonitrile %)
[b]: No statistical difference at $p \leq 0.05$ (Comparison completed for inside and outside acrylonitrile %)
[c]: Statistically different at $p \leq 0.05$ (Comparison completed for pre and post thickness)
[d]: No Statistical difference at $p \leq 0.05$ (Comparison completed for pre and post thickness)

Table 5.5: 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 5.6: Whole Glove areas by region

	Safeskin (cm^2) n=3	**Blue (cm^2) n=3**	**Purple (cm^2) n=3**	**Sterling (cm^2) n=3**
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

5.4.10 Weight

The weights before and after whole glove permeation are shown in Table 5.7, 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 $p \leq 0.05$.

Table 5.7: Whole Glove (M) mass before and after permeation

	Pre-Permeation Mass (g)	Post Permeation Mass (g)
Safeskin n=3	6.47±0.10	7.01±0.43
Blue n=3	7.41±0.25	7.82±0.10
Purple n=3	5.93±0.08	6.69±0.12
Sterling n=3	3.97±0.02	4.79±0.06

5.4.11 Porosity

Table 5.8 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 $p \leq 0.05$.

Table 5.8: 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 $p \leq 0.05$

5.5 DISCUSSION

This is the first permeation kinetic data (Table 5.1) 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 5.2). This is also the first use of a dynamic system with comparison between a still and moving robotic hand (Table 5.3). 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 not statistically different for the Purple nitrile gloves and for t_b were statistically the same for the Sterling nitrile glove at $p \leq 0.05$.

Only for the Safeskin and Sterling nitrile gloves was the steady state permeation rate higher for whole glove (M) higher than the ASTM closed loop method. The Blue nitrile glove steady state permeation rate for the whole glove (M) method was slower than that of the ASTM closed loop method. In regards to the steady state permeation rate there's no consistent trend where the whole glove (M) was higher than the ASTM closed loop method. Only for the Safeskin and Sterling gloves was the whole glove (M) method shown to be less protective than the ASTM closed loop method. For normalized breakthrough time the only two gloves that have statically significant differences were the Safeskin and Blue gloves and in both cases the normalized breakthrough time of the whole glove (M) method was shorter than that of the ASTM closed loop method. In terms of these two gloves the moving hand method demonstrated less protection than the ASTM closed loop method in regards to the normalized breakthrough time.

As can be seen from Table 5.1 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 $\mu g/cm^2/min$ respectively). The second best performing glove was the Safeskin. Between the two the P_s are statistically different, but the t_b were not statistically different (Table

5.1). 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 5.4).

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 5.2 & 5.4). The two gloves have some similarity in terms of their inside and outside acrylonitrile percentage at $p \leq 0.05$ (Table 5.4).

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 acrylonitrile content (outside) but similar in terms of their thickness, acrylonitrile content (inside), and t_b at $p \leq 0.05$ (Table 5.2 and 5.4). 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 not statistically different while the t_b were statistically different at $p \leq 0.05$.

The Safeskin, and Sterling gloves shoed statically significant differences in steady state permeation rate between whole glove (M) and whole glove (S). In both cases the steady state permeation rate was faster than the whole glove (S) method. Therefore, in regards to the steady state permeation rate for these two gloves the whole glove (M) method was less protective than the whole glove (S). For the normalized breakthrough time the only glove that has statically different normalized breakthrough times between the whole glove (S) and whole glove (M) was the Sterling nitrile glove. For the Sterling glove the whole glove (M) was less protective than the whole glove (S) method. For the rest of the gloves there was not a consistent trend of the whole glove (M) being less protective that the whole glove (S) method.

Table 5.2 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 $\mu g/cm^2/min$. 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 2 min longer than the whole glove method at 8±1 min, and a lower P_s of 21±1 $\mu g/cm^2/min$ 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 $p \leq 0.05$. The Blue nitrile whole glove (M) P_s were not statistically different from the ASTM closed loop method, as well as the t_b at $p \leq 0.05$. The Purple nitrile glove showed no differences between the ASTM closed loop and whole glove permeation (M) 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 (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 $\mu g/cm^2/min$.(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.(10) The analogous Ansell steady state rate classification in $\mu g/cm^2/min$ 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.

The Safeskin, Blue, and Sterling gloves whole glove (M) data suggest that the moving hand model was less protective. Gloves should be exposed to movement in order to account for this factor and determine effectiveness in resisting chemical permeation. Compared to the ASTM closed loop method there was a decrease that could make the difference between exposure and no exposure. Adding external conditions during glove permeation testing gives the ability to disseminate normalized breakthrough times that are more protective. A method needs further research, and accepted in industry, that will account for external factors of the workplace in order to better estimate how long gloves should be worn to minimize exposure to chemicals.

5.6 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.

5.7 ACKNOWLEDGEMENTS

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CHAPTER 6
DETECTION OF MICRO HOLES AND TEARS IN DISPOSABLE NITRILE GLOVE MATERIAL

6.1 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.

6.2 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 is 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 (6) 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.

6.3 METHODS

6.3.1 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. The measurements are made after calibration of the software with the microscope and ruler. The Calibration process is expanded in the procedures section.

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

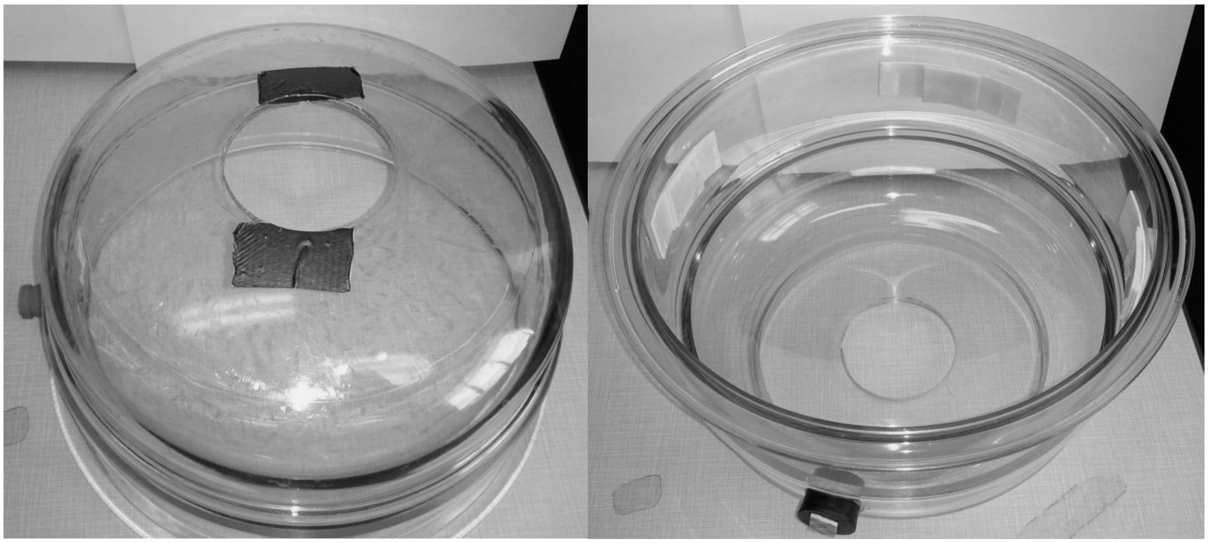
Hamilton company metal hub sharp non-coring needles were used for tearing glove materials. The gauges used were 21, 22, 24, 26s, 30, and 33.

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 that were 2.75 in. diameter (OD) (Figure 6.1 a & b).

Figure 6.1: (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.



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 6.2).

Figure 6.2: (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

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 6.3). 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 6.4).

Figure 6.3: PVC reducer bushing placed in the cuff of gloves to hold it in place during whole glove testing.

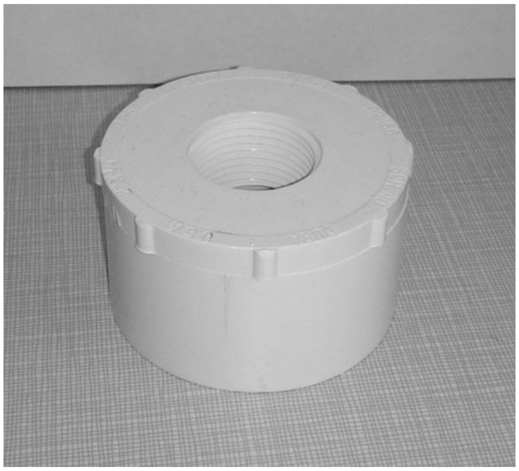
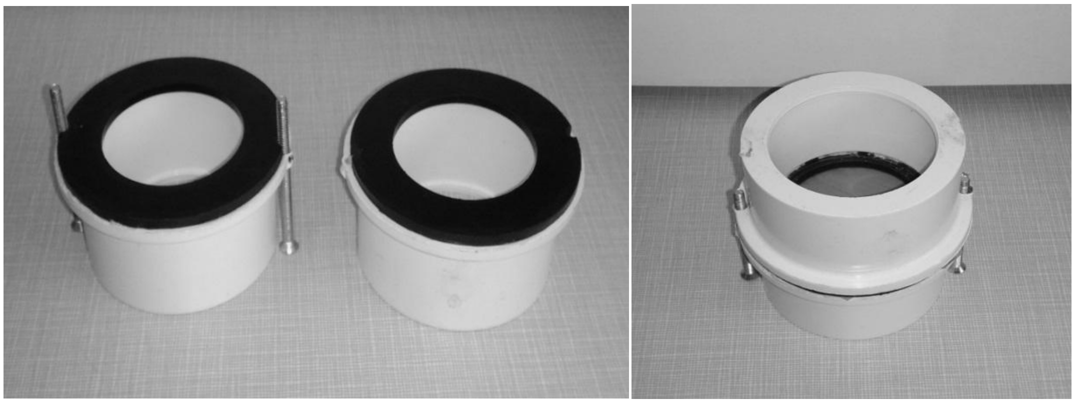


Figure 6.4: PVC bushings modified with rubber gaskets to hold glove pieces in place during hole detection testing.



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.

6.3.2 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.

Microscope Measurement Calibration

The Microviewer software is capable of measuring items that are under the microscope. Under the options screen of the program there is a measurement function. First information about the computer screen has to be loaded into the program. The monitor size and H/V ratio is loaded into the program. A reference unit has to be used in order for the program to make measurements, so a ruler with the mm side was focused under the microscope. One mm in length was used as the reference for the software. A line is drawn 1 mm in length on the image showing in the computer screen. A snapshot was taken; the program saved the information and was calibrated.

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 6.4). 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. Figure 6.5 is the entire system completed and Figure 6.6 is the dome in the adaptor and whole glove testing modes.

Figure 6.5: The final product, the whole system with the dome interface.

Figure 6.6: The test dome in the adaptor mode (Left) and whole glove (Right) testing modes

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.

6.4 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.

6.5 DISCUSSION

Table 6.1 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 6.2 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 6.1: 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 6.2: Flow rate for each tear produced by various needle 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 6.3 is a breakdown of whole glove testing between the palm and finger/fingertip area. The palm area produced much larger flow rates than the finger/fingertip 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 6.3) 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 $p \leq 0.05$. 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 $p \leq 0.05$.

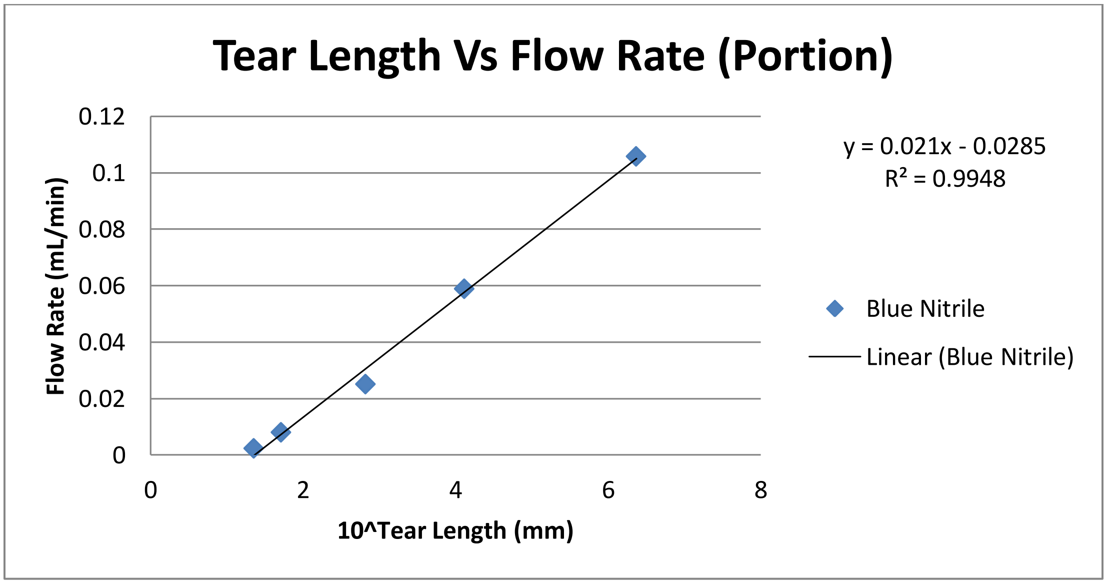
Table 6.3: Whole glove flow rates in the finger and palm by gauge size

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

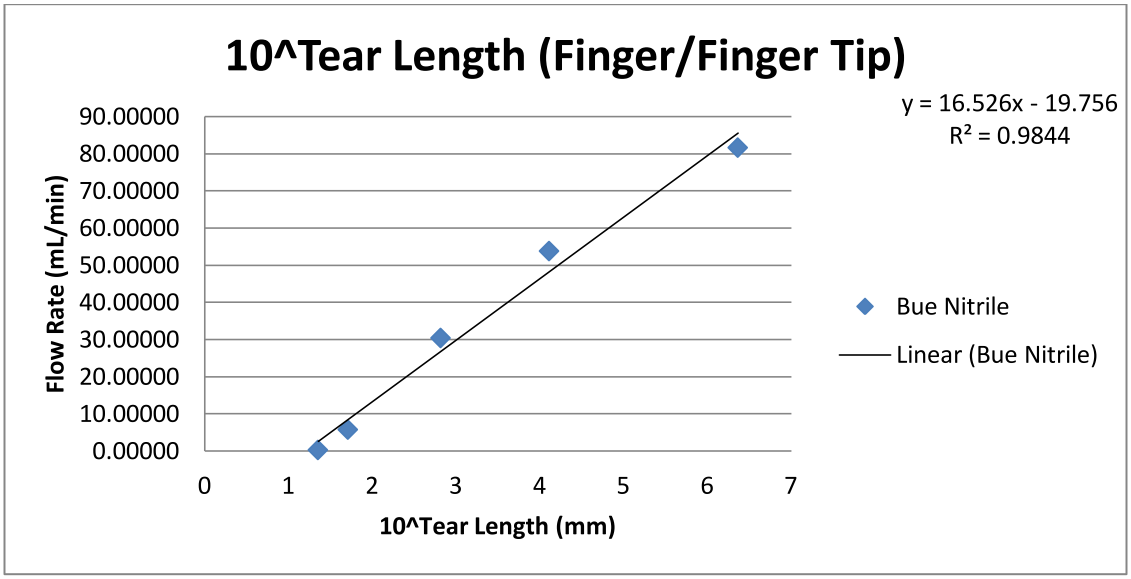
Figure 6.7 is a transformed graph of flow rate (mL/min) versus the power of ten raised to the length of the tear for the glove cut outs that were tested. This was done in order to develop a linear trend between flow rate and length of tear. Figures 6.8 and 6.9 are of the same concept except Figure 6.8 is for the finger/finger tips and Figure 6.9 is a graph for the palm area. All three plots are significant and have p-values ≤ 0.05.

Figure 6.7: Flow rate vs. transformed tear length for glove pieces [a]



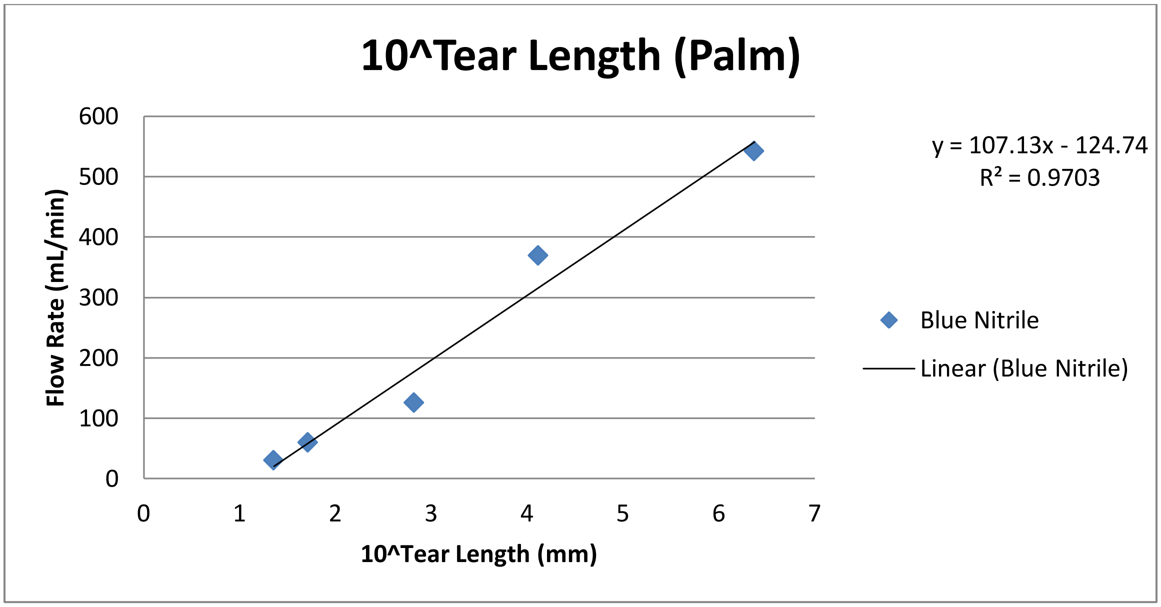
a: Linear regression shows slope at $p \leq 0.05$

Figure 6.8: Flow rate vs. Transformed Tear Length for whole glove finger area [a]



a: Linear regression shows slope at $p \leq 0.05$

Figure 6.9: Flow rate vs. Transformed Tear Length for whole glove palm area [a]



a: Linear regression shows slope at $p \leq 0.05$

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.

6.6 CONCLUSIONS

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.

6.7 ACKNOWLEDGEMENTS

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CHAPTER 7

CONCLUSIONS

The hypothesis was that the moving robot hand would produce a higher P_s and shorter t_b than the ASTM F739-96 and whole glove still permeation methods. Permeation testing of four different types of gloves showed that the P_s and t_b of the moving robot hand was not consistently different from the analogs of the ASTM F739-96 and whole glove still robotic hand methods. Since various nitrile gloves were tested it was determined that the best performing gloves were the Safeskin and Blue nitrile gloves overall, and worst was Sterling. More research needs to be completed in order to determine properties of glove materials that have the largest effect on glove permeation.

Currently the ASTM F739-96 test method open loop mode is the prime method used to determine P_s and t_b. Closed loop data was generated for benzyl alcohol, cyclohexanol, diacetone alcohol, ethylene glycol, and triethanolamine. This was the first closed loop data obtained for these chemicals. While for benzyl alcohol, ethylene glycol, and triethanolamine the open and close loop data agreed, it did not for cyclohexanol. Based on the Kimberly Clark Kimtech Science Chemical resistance guide, cyclohexanol has an open loop breakthrough time of 112 min, while the data obtained from the closed loop modified method was 8±1 minutes. From this information it would appear that semi/non-volatile compounds will show differences in breakthrough times between the open and closed loop methods. The key factor may be temperature since cyclohexanol is a solid at room temperature for the open loop method and a liquid at 35^oC for the closed loop method.

Cyclohexanol was the compound of choice because it had existing open loop data provided by the manufacturer of the gloves. This chemical, while it is not extremely toxic, also has a high boiling point of 160^{o}C making it a suitable semivolatile compound for testing. The solubility in water allows for closed loop testing and was suitable for GC-MS analysis. Cyclohexanol is used in industry for the production of many products, and may expose workers in the production of Nylons.

Permeation testing of four different types of gloves; Safeskin, Kimtech Science Blue, Purple and Sterling was conducted using the closed loop method. All results obtained provided t_b less than 30 minutes. The “Kimberly Clark Nitrile Gloves: Chemical Resistance Guide” was generated using the Sterling gloves, and comparing the Sterling glove in both experimental cases shows that the closed loop method was much more sensitive than the open loop method of the ASTM F739-96 test method. The Sterling gloves in the open loop testing produced a 112 min t_b while the closed loop modified method produced an 8±1 minute t_b. The P_s values also differed for the open and closed loop, being 1.18 pg/cm^2/min and 21±1 µg/cm^2/min respectively. It is differences such as these that call for more research in the area of whether there needs to be more consideration of chemical properties when selecting the test method best suited for permeation experimentation.

Since the ASTM method is widely used there are other concerns about whether this method is a good surrogate for a whole glove. There are many factors that come into play. Stretching of the glove material while wearing, and the pressure the glove material experiences from the finger tips are all factors that are not captured within ASTM methodology. A dynamic whole glove permeation system was developed for liquids to determine P_s and t_b. The system allows for sampling at various time intervals which is an advance on previous whole glove permeation research that used an inner glove for the capture of permeated compound.

It was determined that of the four gloves tested, there were some cases where a nonmoving robotic hand had higher P_s and lower t_b when compared to the ASTM F739-96 test method. It was shown that the Safeskin, Blue, Purple, and Sterling gloves all performed "Good" based on Kimberly Clark standards for their disposable gloves. The best performing gloves were the Safeskin and Blue nitrile gloves, the thickest gloves, with t_b of 20±3 and 22±5 min respectively. The P_s values for the Safeskin and Blue nitrile gloves were 10.0±0.7 and 9±1 $\mu g/cm^2/min$, respectively, not statistically different at $p \leq 0.05$. The gloves that had t_b shorter for the whole glove system than the ASTM closed loop test method were the Safeskin and Blue Gloves. The purple gloves showed no differences between the two test methods, and the Sterling gloves performed better under whole glove testing conditions.

More advanced whole glove permeation testing incorporated hand movement into the permeation testing. This produced data that, in some cases, differed statistically at $p \leq 0.05$ from the ASTM closed loop and the still whole glove permeation methods. When comparing the whole glove moving hand permeation data to the ASTM closed loop data the Safeskin, Blue, and Sterling gloves produced t_b that were less than the ASTM closed loop method data. The t_b times for the whole glove moving hand for the Safeskin, Blue, and Sterling gloves were 14±4, 18±5 and 6±0 min as opposed to the ASTM t_b of 29±2, 26±1, and 8±1 min respectively. The t_b for the Purple nitrile gloves was 18 min for both. P_s values for the whole glove moving hand were greater than the ASTM method P_s for the Sterling and Safeskin nitrile gloves; however for the remaining gloves the P_s were lower than for the ASTM closed loop method.

Each glove has its own characteristics and this information was incorporated to determine glove degradation or integrity. Infrared analysis of gloves before and after permeation testing revealed that cyclohexanol does not cause permanent degradation of the glove material. This information is coupled with other parameters such as thickness, mass, and porosity of glove material. The data obtained suggest that there are no large differences in the glove material after exposure to cyclohexanol. Glove integrity is another key factor since out of the box testing must be conducted to ensure there are no physical imperfections in the glove material such as holes or tears. This was conducted using the developed method with the Frazier air permeability tester. This method has a detection limit of 0.13±0.01 mm tears and is a good tool for quantitative assessment of whether a tear or holes are present or not. It might be noted that about 20% of the Kimtech Science Blue gloves in a standard box contained microholes, and wearers in the field usually do not test for glove integrity—unless tears occur during donning.

The developed dynamic whole glove permeation system is a new method to test for the testing of glove materials. This method is more realistic relative to working conditions than the current ASTM method, since it allows systematic investigation of factors such as stretching of the material by moving fingers and hand heat, and should provide more representative P_s and t_b that may be more protective than from the ASTM open loop method. All glove manufacturers need standardized methodology that will be as protective as possible yet is still easy and inexpensive enough to implement in their quality assurance and quality control procedures.

If glove manufacturers could apply the proper test method for the type of chemical that is being tested then fewer people would experience unnoticed skin exposure. If the cyclohexanol data collected hold true for other semi/non-volatile chemicals, then there are a number of people who have been exposed to chemicals that were handled because the breakthrough times were not representative of the ambient conditions. This could potentially be a large public health issue because wearers rely on these gloves to act as a barrier between themselves and what they are working with. To reduce skin exposure to chemicals, all glove manufacturers need to have a standardized way of testing chemicals. Reporting of a breakthrough time is limited since it relies on the detection limit of the analytical method being used. A t_b forces all to achieve the same minimum level of detection.

Glove manufacturers must take into account working conditions because the external stressors will affect the glove's ability to resist chemical permeation. Temperature must be controlled because the human hand warms up during work, which in turn heats up the glove barrier being worn. Increasing temperature is known to increase permeation. Temperature needs to set preferably for a worst case scenario greater than the actual skin temperature of 32.0^{o}C to account for workplaces with hot processes or working in the sun.

Overall, the most protective gloves for cyclohexanol liquid spills were the Safeskin and Kimtech Science Blue nitrile gloves. In terms of the t_b and P_s values, the Sterling gloves are not recommended. The Purple nitrile glove was in the middle, not performing extremely well, but not bad either. In some cases the whole glove moving hand had a reduced t_b and had an increase in the P_s, but this was not consistent when compared to the still hand and ASTM test data.

Nevertheless, the developed dynamic whole glove permeation system aided by a systematic method of ascertaining microholes is the basis for a universal test method that is much more representative of actual working conditions than the current ASTM Standard method.

CHAPTER 8

FUTURE WORK

More chemicals need to be tested using the ASTM closed loop method and the dynamic whole glove testing system at the same temperature conditions to determine if the t_b and P_s will continue to reveal how well the ASTM method is a surrogate for whole glove permeation.

There needs to be further research and development into the dynamic whole glove permeation system to make improvements and make it more robust.

More research needs to investigate the idea of porosity being a factor in how well a glove can resist a chemical and determine if increases in porosity correlate with increases in P_s or decreases in t_b.

Thickness changes need to be researched, and perhaps the expansion of Fick's Law virial expression tested. It is difficult to know the thickness change that occurs while permeation testing is occurring. A system should be devised to measure thickness during testing. The major assumption for Fick's law at a given temperature is constant thickness. However, there were some glove materials whose thickness changed during exposure, and reverted back to their original thickness after the exposure was over and after reconditioning.

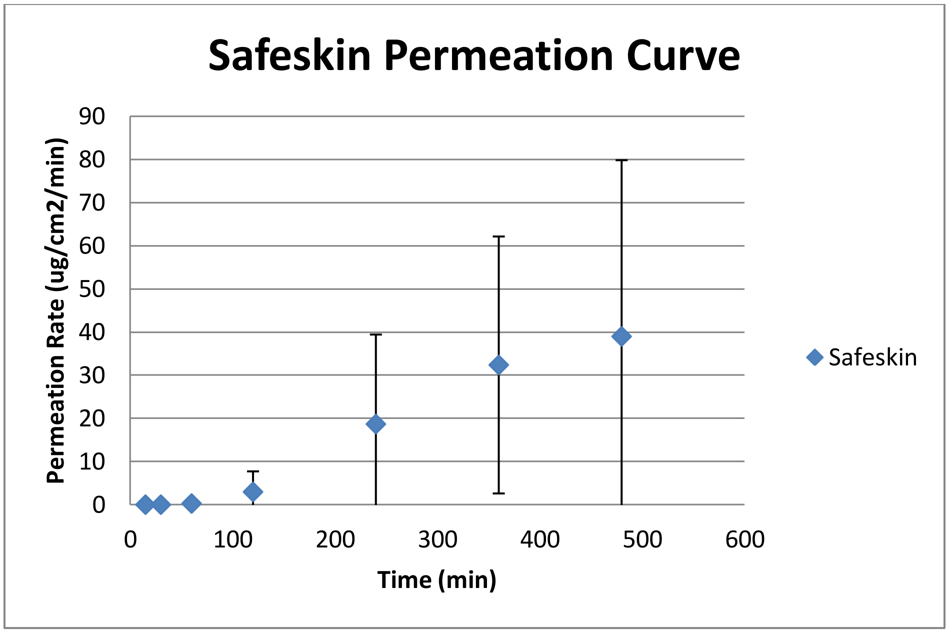
Since mass changes take so long to become constant for whole gloves, mass change is not a practical measurement parameter that can be interpreted readily.

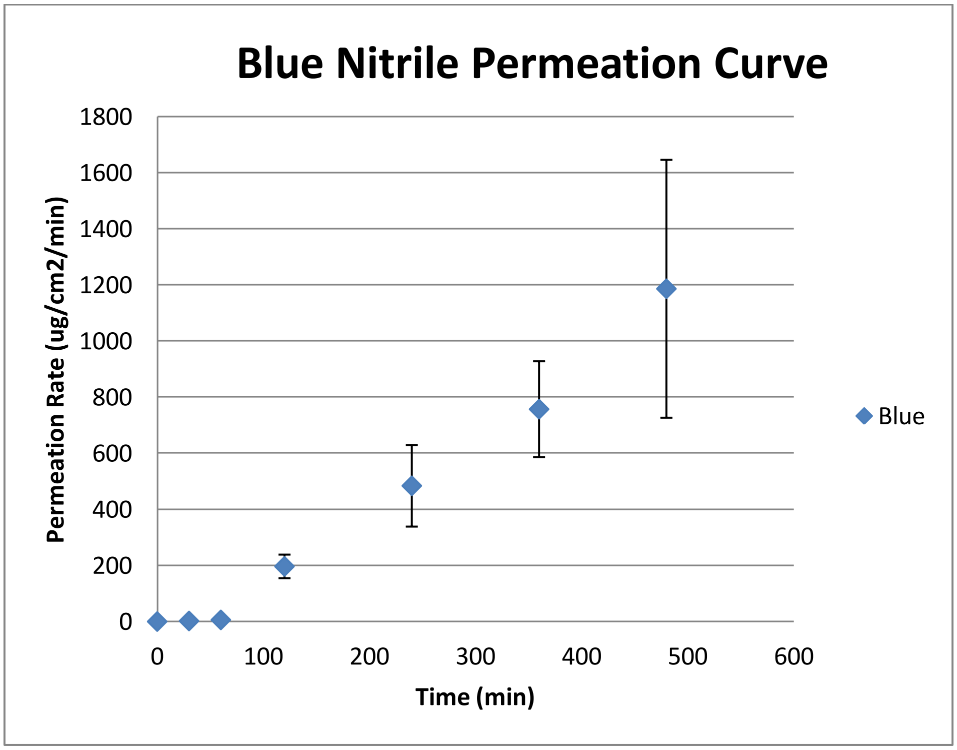
More replicates will need to be tested in order to increase the statistical power and determine trends in the data observed.

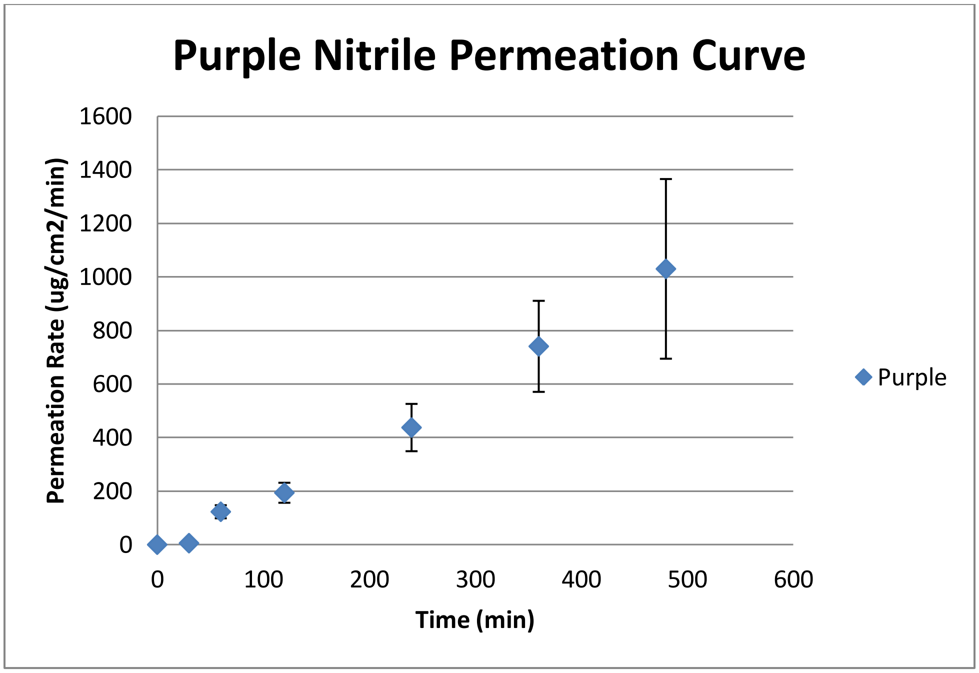
This project could also be expanded to other glove material types such as disposable neoprene gloves and chemically protective glove materials to determine how well the ASTM closed loop method compares with the open loop method and with the whole glove permeation methods.

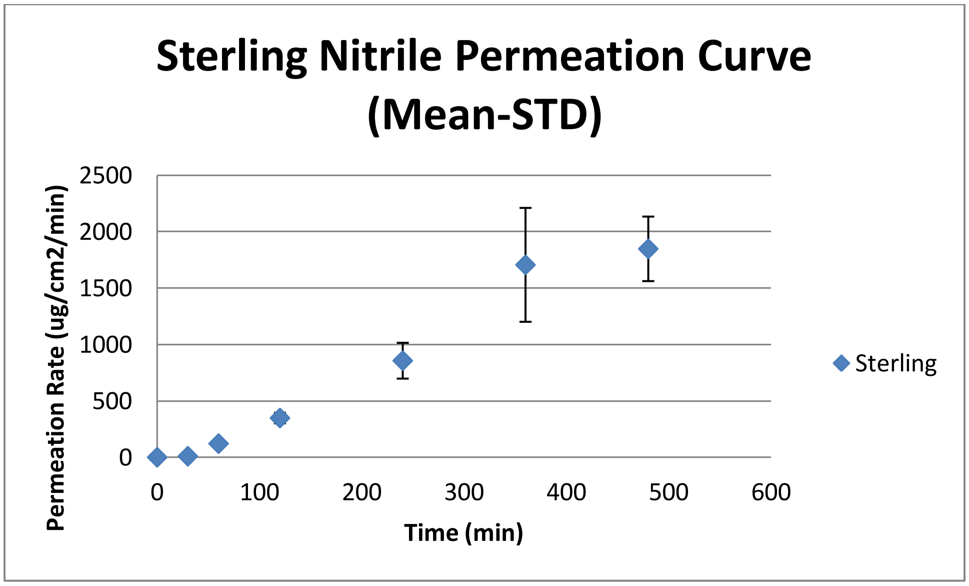
APPENDIX A: AVERAGE PERMEATION CURVES OF ASTM CLOSED LOOP METHOD

NOTE: Standard deviations are shown



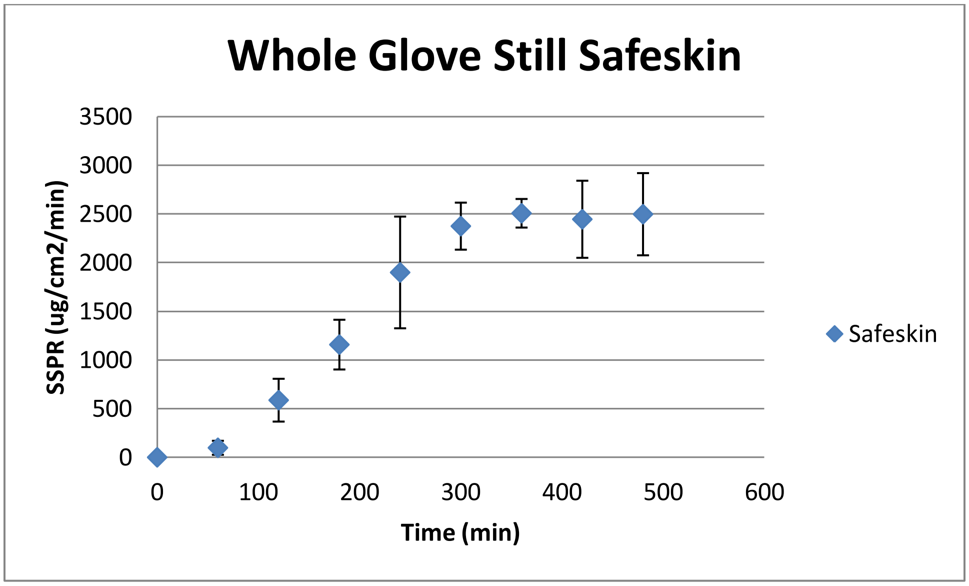


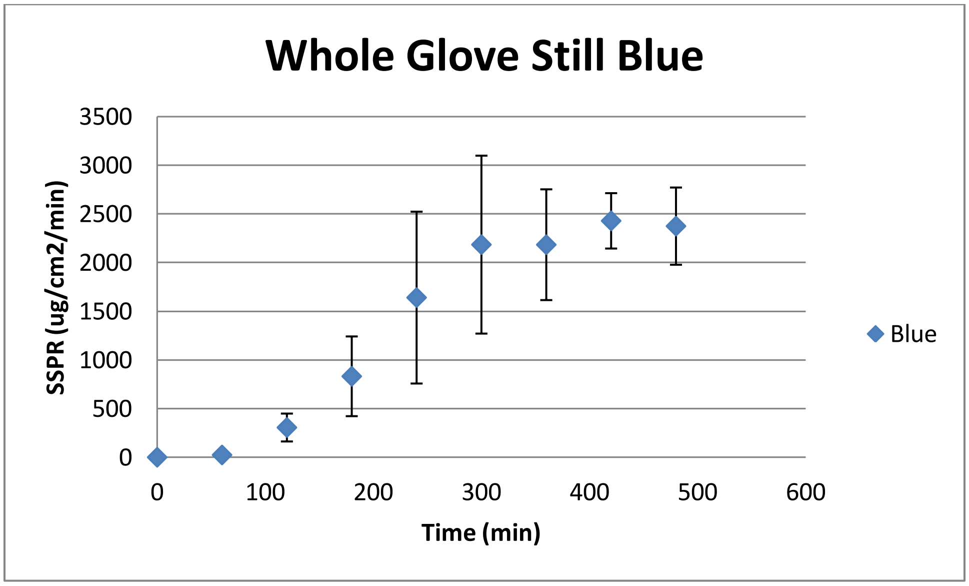

Purple Nitrile Permeation Curve
Permeation Rate (ug/cm2/min)
1600
1400
1200
1000
800
600
400
200
0
0
100
200
300
400
500
600
Time (min)
Purple

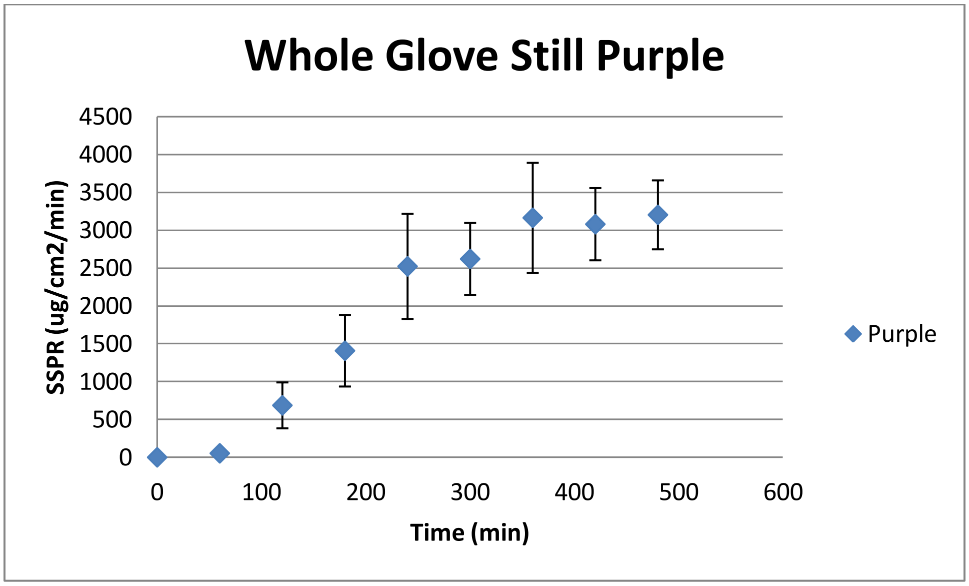

Sterling Nitrile Permeation Curve (Mean-STD)
Permeation Rate (ug/cm2/min)
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
Time (min)
Sterling

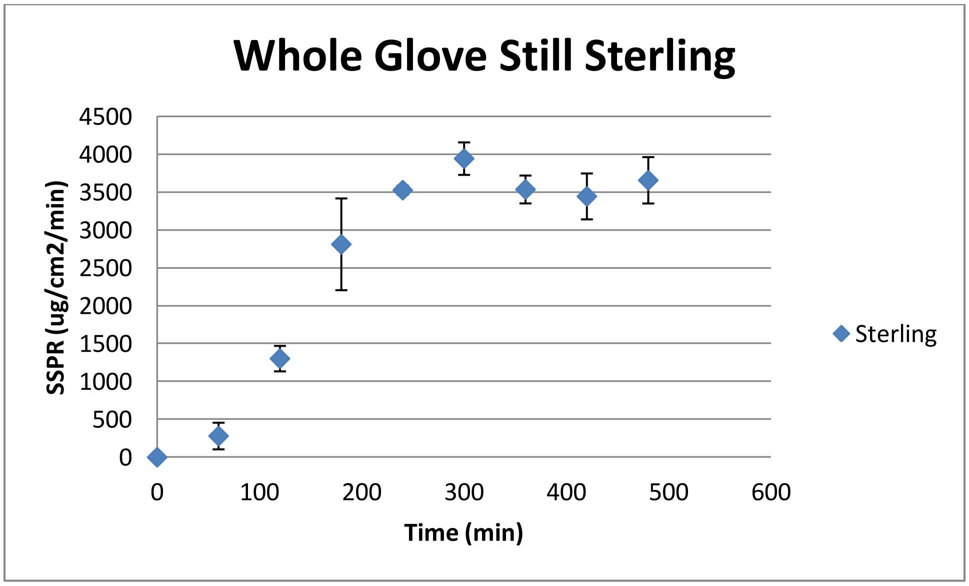
APPENDIX B: AVERAGE PERMEATION CURVES OF WHOLE GLOVE STILL HAND

NOTE: Standard deviations are shown



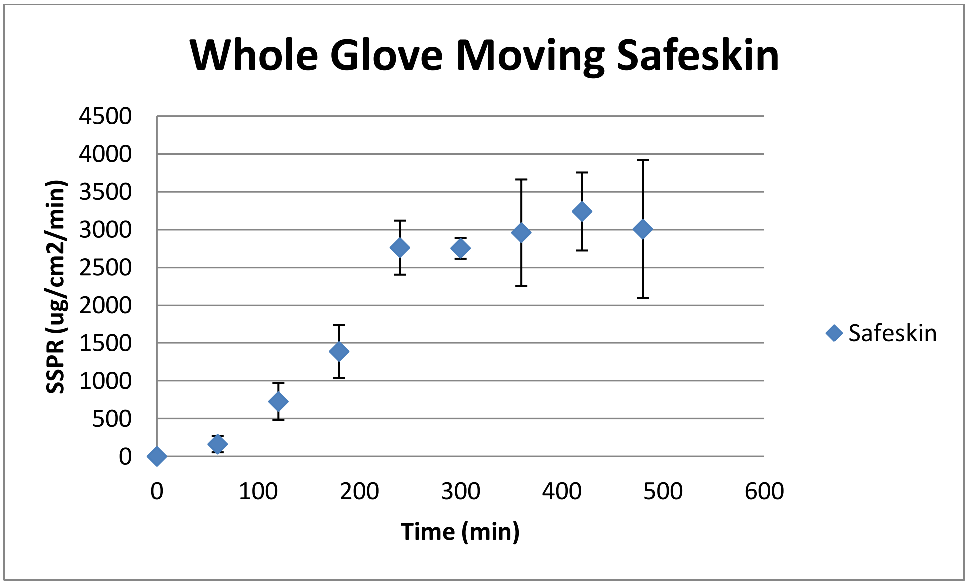


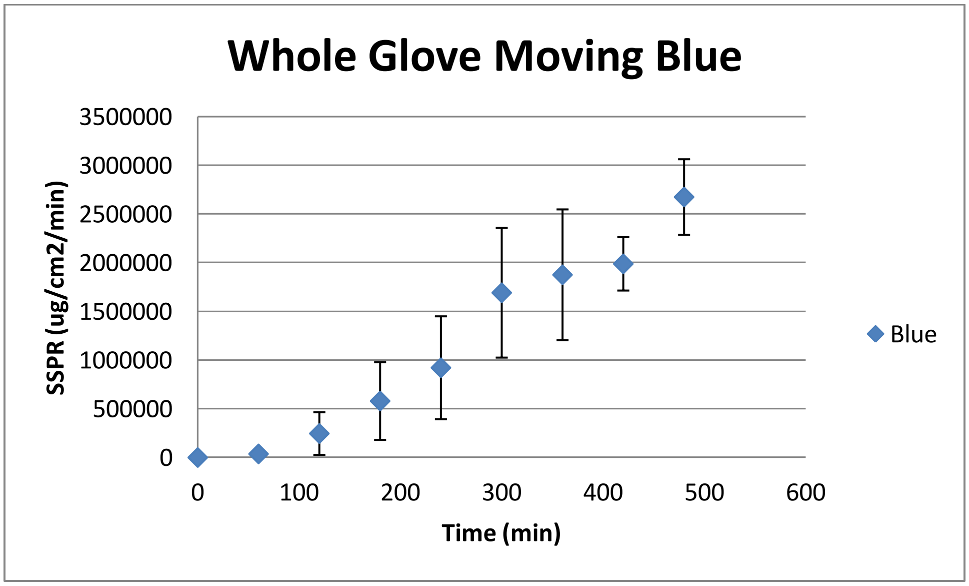

Whole Glove Still Purple
SSPR (ug/cm2/min)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
Time (min)
◆ Purple

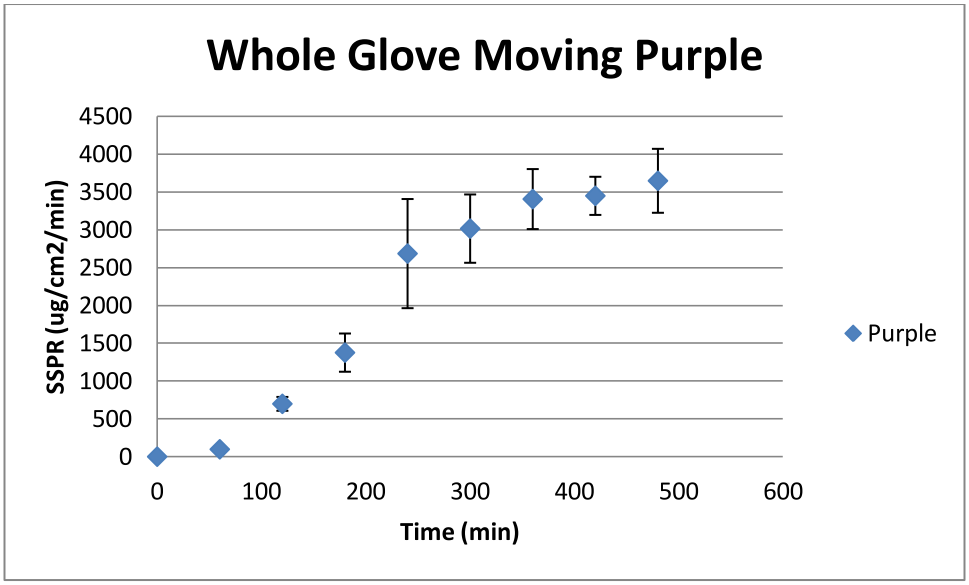

Whole Glove Still Sterling
SSPR (ug/cm2/min)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
Time (min)
◆ Sterling

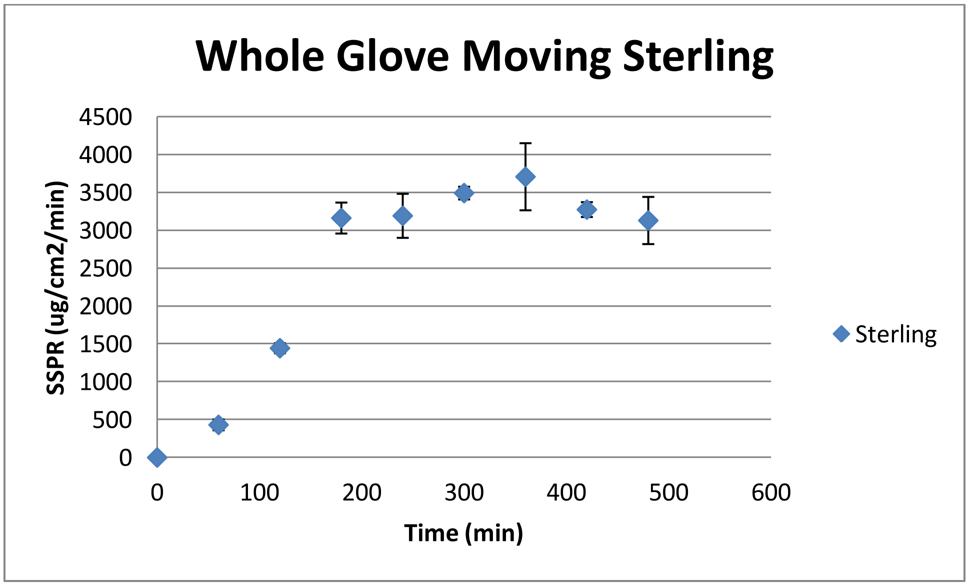
APPENDIX C: AVERAGE PERMEATION CURVES OF WHOLE GLOVE MOVING HAND

NOTE: Standard deviations are shown






Whole Glove Moving Purple
SSPR (ug/cm2/min)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
Time (min)
Purple


Whole Glove Moving Sterling
SSPR (ug/cm2/min)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
Time (min)
Sterling