Title

Permeation of Limonene through Disposable Nitrile Gloves in the Robot Hand Whole Glove and ASTM Closed Loop Models

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

by

Sean Banaee

2015

ABSTRACT OF THE DISSERTATION

Permeation of Limonene through Disposable Nitrile Gloves in the Robot Hand Whole Glove and ASTM Closed Loop Models

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Sean Banaee

Doctor of Philosophy in Environmental Health Sciences

University of California, Los Angeles, 2015

Professor Shane S. Que Hee, Chair

The ultimate purpose was to assess if a whole glove dextrous robotic hand model provided results that differed from the reference modified closed-loop ASTM F739-99/12 glove permeation technique. The candidate compounds were low volatile solvents to minimize the influence of volatilization as a confounding factor. After preliminary closed-loop studies with 2-ethoxyethanol and 2-butoxyethanol showed the breakthrough times for purple nitrile disposable gloves were too short to be compared in the dextrous robotic hand model, limonene was selected to compare the permeation parameters of different disposable nitrile exam gloves (blue, purple, sterling, and lavender) In the modified closed-loop ASTM permeation model four 1-inch diameter standard permeation cells (3 cells with solvent as challenge and one air blank) were used with water as the collection solvent at 35°C. Samples were analyzed by capillary gas chromatography-mass spectrometry and the internal standard method (4-bromophenol). For the static and moving whole glove model, a Yeager robotic hand and assembled. A circulating water system transferred water from between the outer test glove and the inner chemically protective glove of the doubly gloved robot hand in an incubator at 35.0 ± 0.5 °C. The observed scheduled breakthrough time (SBRT) for blue, purple, sterling, and lavender glove specimens in the ASTM system was 70 ± 10 min, 30 ± 10 min, 15 ± 5 min, and 5 ± 5 min respectively. The two robot hand models showed similar SBRTs: 5 ± 5 min for lavender, 15 ± 5 min for sterling and purple, and 30 ± 10 min for blue gloves. The SBRTs for the blue and purple gloves for the robotic hand were significantly shorter than for the ASTM technique ($P \leq 0.05$). The average post-permeation thicknesses (before re-conditioning) for all glove materials for the moving and still robotic hand were more than 10% of the pre-permeation ones ($P \leq 0.05$) except for the blue gloves, although this was not so on reconditioning. The average steady state permeation rate (SSPR) for lavender glove for the static robotic hand was 0.423 ± 0.031 $\mu g/cm^2/min$ significantly higher (1.43 times) than for the ASTM method (0.295 ± 0.028 $\mu g/cm^2/min$ [$P \leq 0.05$]). Lavender gloves showed a significantly higher SSPR when the moving robotic hand was used (0.490 ± 0.031) compared to a non-moving one ($P \leq 0.05$). Although the respective SSPR for other gloves samples (blue, purple, and sterling) with the moving hand experiment appeared more than the static hand, the difference was not significant ($P \leq 0.05$). Here the exposed surface area was held constant as was temperature to assess if motion alone caused differences in permeation parameters. This suggests a thickness threshold for hand motion differences. The lavender, sterling, and purple gloves failed the Kimberly Clark Professional permeation breakthrough time criteria and Ansell's criteria for use, and therefore they should not be used as personal protective equipment for exposure to limonene, even for short exposure periods. Although blue gloves provided the highest performance against limonene compared to other gloves, they are safe for less than 20 minutes. Compared to the ASTM F739-99/12 model, the robotic hand permeation model is more sensitive and stringent in defining gloves' efficacy since it better simulates grip motions in the workplace.

The dissertation of Sean Banaee is approved.

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2015

DEDICATION

This dissertation is dedicated to my son, Pourya. Thank you for your support and company during all the late nights, when I was busy in the lab and it was often too late to buy pizza for you.

With my deepest gratitude and warmest affection, I dedicate this thesis to my advisor, Professor Que Hee who has been a constant source of knowledge and inspiration.

I would like to dedicate this thesis to my wife who encouraged me throughout this journey.

I also dedicate this dissertation to my father and mother for all their support during this long path and of course to my sister Shahnaz, who was always behind me during all tough times.

Your task is not to seek for love, but merely to seek
and find all the barriers within yourself that you
have built against it. Rumi

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Despite technological advances on controlling and minimizing workplace exposure to chemicals, protective clothing and gloves are still counted as the primary means of dermal protection in the work environment.(1,2) The hierarchy of control measures emphasizes engineering, elimination, substitution and source-oriented rather than employee-oriented measures such as protective clothing, which are regarded as the last line of defense.(3) However, at many work activities and industrial situations, personal protective equipment (PPE) is counted as the primary response along with emergency and rescue operations, non-feasible/cost effective engineering controls, short/frequent exposures, and medical measures.(3) Therefore, careful consideration should be taken on providing clothing with reliable protection.(12)

Exposure to chemicals has always been a major safety concern in process industries. In occupational health the emphasis has always been on inhalation as the major entry route for chemicals. As a result, most of the research studies have been focused on developing risk assessment and defining standards and work practices to address risks related to inhalation rather than dermal exposure, despite the fact that for a large number of occupations, hands are the first target directly exposed to chemical and mechanical hazards.(4, 34) The shortage of studies and assessment methods on skin exposure is understandable(4) given that the PELs, TLVs, RELs and WEELs relate to inhalation exposure and that respirators have assigned protection factors based on these inhalation guidelines, while such a standard has not been developed for protective clothes including gloves because there are no quantitative skin regulations. (5)

Nevertheless, dermal exposure to chemicals is a major workplace health concern and hands are the primary routes of exposure organ at risk.(6) Skin absorption for a chemical in the current regulations and guidelines is notated as “skin”. NIOSH has also developed a set of dermal guidelines (4) that also incorporates skin irritation in addition to skin absorption as well as a skin permeation estimation model.(53) It is estimated that more than 10 % of working population in the US risk potential exposure to chemicals via skin contact in 2013.(4) BLS reported 34,400 cases of occupational dermal diseases in 2012, which is a significant number comparing to 19,300 cases of respiratory diseases in the same period. (54, 55) The annual volume of chemicals used in the US is enormous. According to the Toxic Substances Control Act (TSCA) database, in 2002 about 15 trillion pounds of chemicals were imported or produced in the US.(7) In 2005 that number soared to 27 trillion pounds of 6,200 chemicals indicating a growth in daily chemical use.(7)

Given the magnitude of the above figures and the millions of employees who are potentially at risk to even a fraction of these chemicals in industry, service, research, and agricultural sectors, it is imperative to study and develop risk assessment methods on PPE (including gloves) to be able to define whether or not a specific PPE is safe enough to be worn while exposure to a specific chemical and if so, for how long? In order to address such questions and make decisions about workers’ protection, it is crucial to determine permeation parameters such as breakthrough detection time and steady state permeation rate for the target chemicals.(2)

1.2 GLOVE PERMEATION

1.2.1 Definitions

The performance of chemically protective clothing can be assessed by the study of degradation, penetration, and permeation.(10) Degradation is the reaction of challenge chemical with glove material that causes changes in physical or chemical properties of the glove. Some common observable impacts of degradation on fabrics include: swelling, shrinkage; color change; becoming harder or softer, stiffer, or brittle; and texture deterioration and weakness. Penetration is defined as the flow of bulk liquid through seams, gaps, holes, zippers, openings or closures.(8, 43) No Chemical, molecular, or mechanical change in the protective material are required for penetration.(8) Permeation by contrast, is defined as the process by which a chemical moves through protective clothing material at the molecular level.(2,8,9) It consists of three consecutive phases: absorption of the permeant into the external portion of the glove material, diffusion of the permeant through the glove, and desorption of migrated molecules from the inside portion to the collection side.(8,11)

In protective clothing studies, diffusion is known as one of the determinants used to define required efficacy and performance. Fick's first law is the basic mathematical model for permeation studies. Equation 1-1 presents Fick's first law:

$$J = -D \times \frac{dc}{dx} \qquad (1-1)$$

Where J is the transfer rate per unit area of the membrane (µg/cm^2/min), c is the permeant concentration (µg/cm^3), x is polymer thickness (cm), and D is the diffusion coefficient (cm^2/min).(10)

Equation (1-1) can be simplified as the following:

$$J = -D \times \frac{C_1 - C_2}{L} \qquad (1-2)$$

Where C_1 and C_2 are analyte concentrations or masses in the challenge cell at times 1 and 2 and where D is independent of the concentration gradient and thickness.(10) Most permeation studies apply equation (1-3) for defining the diffusion coefficient via lag time (t_i) when no material swelling or shrinking occur. Lag time is measured by the extension of the steady state section of the permeation curve to the horizontal time axis. (In the cumulative permeation curve, the permeated mass or mass/area of analyte is plotted on the *y*-axis versus time on the *x*-axis*)*.(20)

$$D = \frac{L^2}{6t_i} \qquad (1-3)$$

Equation (1-3) is extracted from Fick's first law of diffusion and is more popular in permeation studies. In order to apply equation (1-3) for calculating the diffusion coefficient, some critical points should be considered including: a) the diffusion coefficient is applicable if no change in glove thickness is observed after permeation, b) on the cumulative permeation mass curve no permeation happens at the zero reference time (no detectable concentration of the permeant at inner side of the protective clothing at the starting time), c) instant equilibrium between the solvent and protective clothing upon contact, d) the permeant is in liquid or gas phase.(20)

The present study is focused on a permeation model for evaluating the reliability of disposable protective gloves, and representativeness of the current permeation testing procedures. Standard permeation models are the primary method to define protective gloves' efficacy and assuring their safety.(12) In many instances permeation may occur without any observable effects on glove materials or the skin and cause little dermal exposure.(13) For a given glove material, permeation for different chemicals varies and it may occur efficiently and rapidly (13) or over a long period of time.

1.2.2 Permeation Standards

Over the last 35 years, several standard institutions developed methods and procedures on protective clothing permeation. The American Society of Testing and Materials (ASTM) developed the first version of the ASTM F739 standard on chemical permeation resistance as "ASTM F739, Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases under Conditions of Continuous Contact" in 1981. Since then it was revised multiple times in 1985, 1991, 1996, 1999, and 2012.(14, 15) The title for the latest version changed to "Standard Test Method for Permeation of Liquids and Gases through Protective Clothing Materials under Conditions of Continuous Contact".(16)

The ASTM F739 standard has been known as the most frequently applied standard method in the U.S. for evaluating permeation resistance of protective clothing, especially gloves.(17) The test method consists of a cell with two glass chambers, one as the permeant chamber, which contains challenge analyte, and is in direct contact with the outer surface of the glove specimen.(16, 17, 19)

The other side, the collection chamber (collection medium), is in direct contact with the inner side of the glove material and permeated analyte is collected or analyzed directly.(16, 17, 19) Two Polytetrafluoroethylene (PTFE) gaskets hold the glove specimen between the challenge and collection chambers in an upright position.(10, 16, 19) Fig 1.1 shows a standard ASTM permeation cell. The mass of permeated chemical through the protective clothing from challenge side to collection medium depends on several parameters such as: texture of the glove material, permeant molecular size, solubility effects of the permeant in the glove specimen, permeation method, cell size, thickness of the glove specimen, area of the glove exposed to permeant, mechanical stretching, temperature, flow rate, duration and pattern of exposure, analytical sensitivity, single or mixture of chemicals, and chemical natures of the permeant and gloves. Such parameters are also critical for the breakthrough detection time.

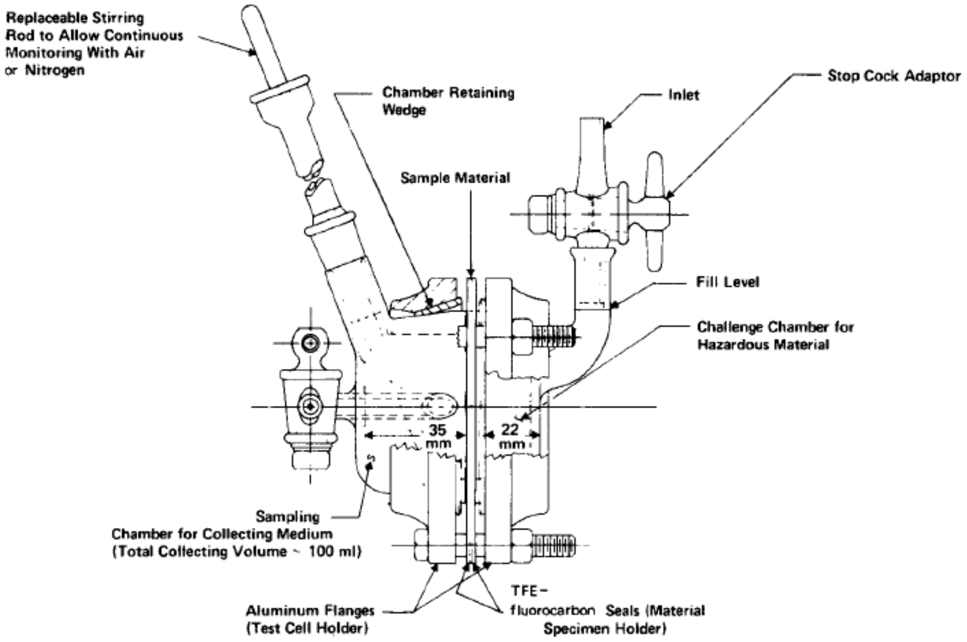


Fig. 1.1, ASTM F739-2012 Permeation Test Cell (16)

The ASTM F739-99/12 standard defines the permeation process in open loop and closed loop modules. The open loop and closed loop models are characterized by gaseous and liquid collection media respectively.(10, 16)

The open loop system utilizes a dynamic collection medium using air, nitrogen, and helium as the preferred collection media (Fig 1.2).(16) In the event that the collection medium interferes with the analytical method, an alternative gas needs to be used.(16, 19) The capability of the carried gas in the collection medium of capturing the permeated analyte is counted as a determinant that impacts the sensitivity of the method.(19, 20)

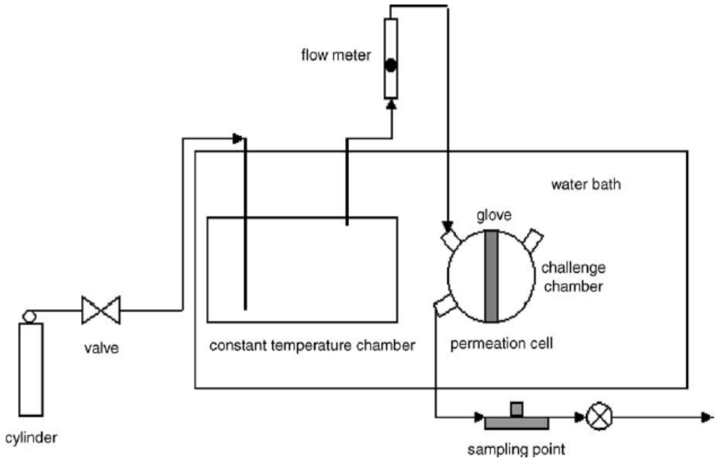


Fig. 1.2, Open loop permeation cell. (12)

A fresh gaseous collection medium with high purity flows continuously through the collection chamber with a constant flow rate capturing the potential permeant and sending it to the analyzer.(16) ASTM recommends that the collection medium follow rate should cover the minimum 5 chamber volume changes per min. (16) A second constraint on the flow rate for the collection medium in an ASTM open loop chamber of 25 mm diameter is keeping the flow rate at a minimum of 100 cm^3/min. (16) The analytical method may be designed in a sequential or continuous monitoring. (10) Such analytical methods should be capable of detecting at least 0.1µg/cm^2/min, which is the ASTM minimum required sensitivity. (10)

To analyze a given chemical, several analytical techniques exist with different sensitivities and it will be difficult to detect the analyte upon the permeation on inner face of the protective clothing, if the permeant is low volatile. (22) ASTM F739-12 addressed this challenge by standardizing breakthrough time for detection of different analytes whether in open or closed loop systems.

ASTM F739-12 defines some measures for evaluating the efficacy of protective clothing, such as: breakthrough detection time (BRDT), standardized breakthrough time (SBRT), steady state permeation rate (SSPR), and cumulative permeation during the permeation time.(10)

The breakthrough detection time is the time to detect the challenge chemical at the inner surface of the test sample or in a collection medium.(10, 18) The standardized breakthrough time (normalized breakthrough detection time, NBDT, in ASTM F739-99 for the open loop system) is defined as the time when a permeation of 0.1 µg/cm^2/min is reached. Steady state permeation rate is the point at which the rate of permeation becomes constant.(10) The ASTM F739-12 adds another measure for defining SSPR in an open loop system thus: when measured values for collected samples with a minimum of 5 minutes intervals show less than 5% relative standard deviation, then the average of 4 measurements will be counted as SSPR.(10)

The ASTM open loop module is essentially designed for high volatile compounds with low boiling points. (21) In other words, the gaseous collection medium used in the open loop system is not able to capture and carry highly non-volatile permeated compounds efficiently because of the low vapor pressure of non-volatile chemicals.(19, 20) This may cause a non-realistic breakthrough detection time and standardized breakthrough time even if an analytical method with high sensitivity is used.(19, 20)

Another drawback of the open loop system is that all samples taken before reaching breakthrough detection time are not counted in calculations and the permeated mass from time zero to breakthrough time will be missed.(20) Such a problem does not exist in the closed loop system, because the volume of the collection solvent is almost constant and the maximum volume of samples taken during the whole permeation process at different time intervals usually does not exceed 10% of the initial collection chamber volume, ensuring permeation conditions in terms of area exposed on the collection side stay almost constant.

The closed loop permeation system is very similar to the open loop module. The challenge chamber in the permeation cell is the same as in the open loop system. However, in the collection, the collection medium always holds a liquid solvent such as water. This makes the closed loop system superior for conducting permeation tests on non-volatile and semi-volatile compounds.

However, glove manufacturers use the open loop method as the default standard for defining their products' permeability and breakthrough time and all catalogs and data provided by glove manufactures cite the open loop method regardless of the volatility and physical properties of chemicals.

In some closed loop systems the collection solvent circulates in a loop, but the total solvent volume remains constant (with ±10% for taking samples) during the whole permeation process (Fig 1.3).(12) Open loop systems are also usually recirculating. The closed loop collection chamber can be only attached to one inlet with no outlet so that adding collection medium and taking samples over different time intervals are conducted via the same opening (Fig. 1.4).

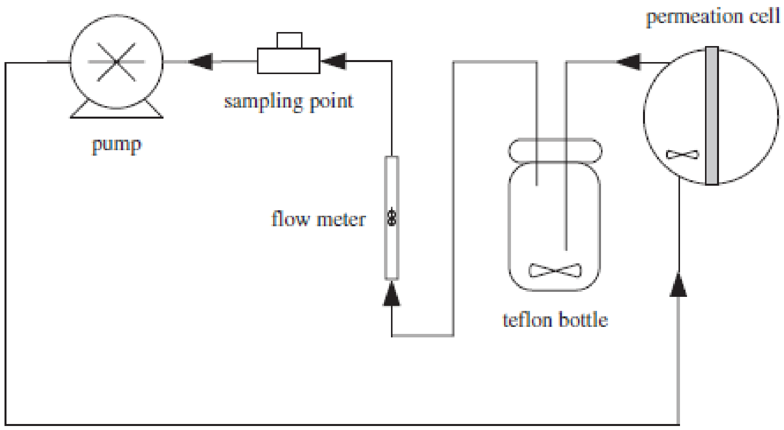


Fig. 1.3, ASTM Closed loop with circulating liquid collection medium (12)

For the closed loop system, ASTM F739-12 applies the same definitions and measures used in the open loop module to evaluate the efficacy of protective clothing such as BRDT, SBRT, SSPR, and cumulative permeation during the permeation time. Schwope et al,(20) compared open loop and closed loop permeation models based on Fick's law analysis and found no correlation in breakthrough detection time between the two methods.

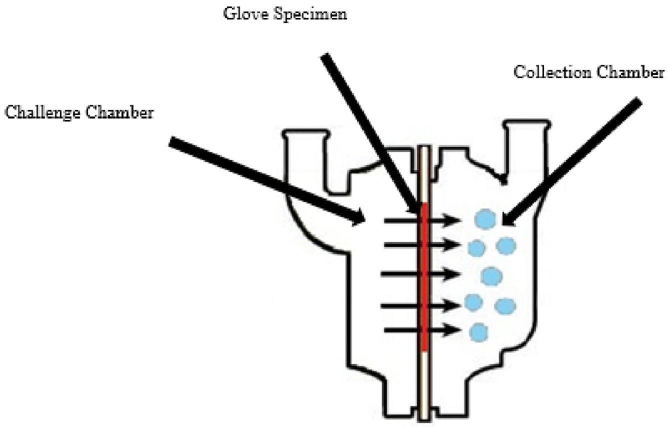


Fig. 1.4, ASTM Closed loop with static liquid collection medium

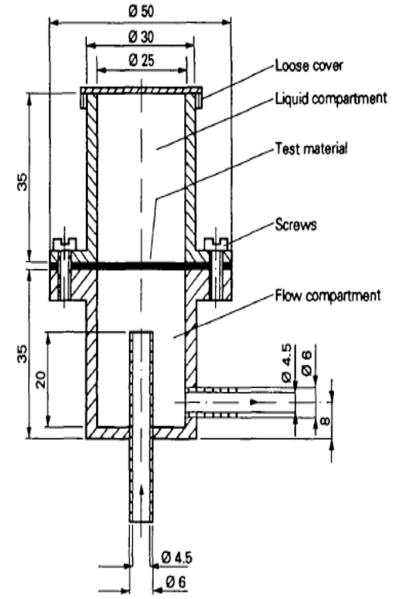
The minimum sensitivity criteria (0.1 μg/cm^2/min) is the same in the closed loop system, but it should be achieved within 5 minutes sampling time. (10) In the closed loop module also a constant increase in permeant concentration is required to be able to define the SSPR. (10)

The International Organization for Standardization (ISO) developed a standard on protective clothing permeation as ISO 6529-2013-2; "Protective clothing-Protection against chemicals-Determination of resistance of protective clothing materials to permeation by liquids and gases on permeation". (23) Another permeation standard developed by the European Union (EN) is EN 374-3:2003 "Protective gloves against chemicals and microorganisms. Part 3: Determination of resistance to permeation by chemicals". (11)

Both ISO 6529 and EN 374-3 use two-chamber permeation cells with a 51 mm diameter for challenge and collection solutions, similar to ASTM 739 cells. The initial ISO 6529 permeation cell (ISO 6529-1990), utilized gravity in the permeation process; analyte permeates vertically through the protective clothing, which is clamped horizontally between two cells with a challenge chamber on the top and collection chamber on the bottom. This followed the procedure used in the Franz cell used in the European pharmaceutical industry. (56, 57) However, in the next revision, ISO 6529-2001 adopted a cell configurations similar to the ASTM F739 and denoted the initial vertical permeation cells as alternative cells. (12)

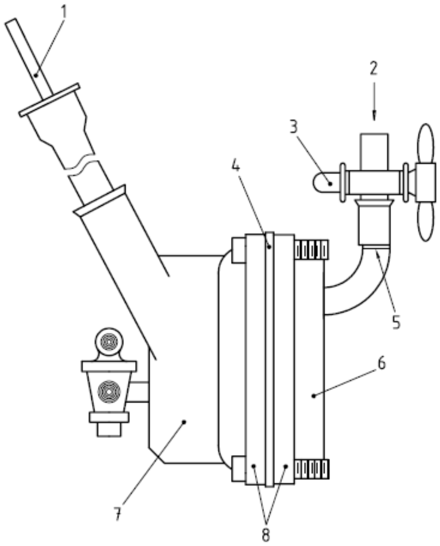
The ISO permeation cells with the gravity mechanism are not popular and the updated version (primary cells) are used most. (17) Fig. 1.5 and 1.6 show the primary and alternative cells in ISO 6529-2001. The permeation cells developed by EN 374-3:2003 also have similar features to the ASTM F739 cells. The ASTM F739-12 recommends 5 chamber volumes per minute as the minimum required flow rate for all permeation sets with a dynamic liquid flowing collection medium such as open loop systems (with a gaseous collection media) and closed loop systems (with a dynamic liquid collection media). ISO 6529-2001 and EN 374-3:2003 both emphasize the same flow rate as the minimum requirement for any permeation cell with a dynamic collection solvent as liquid or gaseous state.

ISO 6529-2001 and EN 374-3:2003 use terms similar to ASTM F739-99, such as normalized breakthrough detection time and steady-state permeation rate for measuring permeation. EN 374-3:2003 defines the normalized breakthrough detection time as reaching a permeation of 1.0 μg/cm^2/min whereas ISO 6529-2001 also allows for two permeation rates as 0.10 μg/cm^2/min and 1.0 μg/cm^2/min for defining the normalized breakthrough time. Comparing the normalized breakthrough detection time in EN 374-3:2003 and standardized breakthrough time in ASTM 739-12 suggests that the ASTM method provides a higher sensitivity with a factor of 10 (Table 1.1).



Exposed area of test material: 4.91 cm^2
Volume of flow compartment: 17.2 cm^3

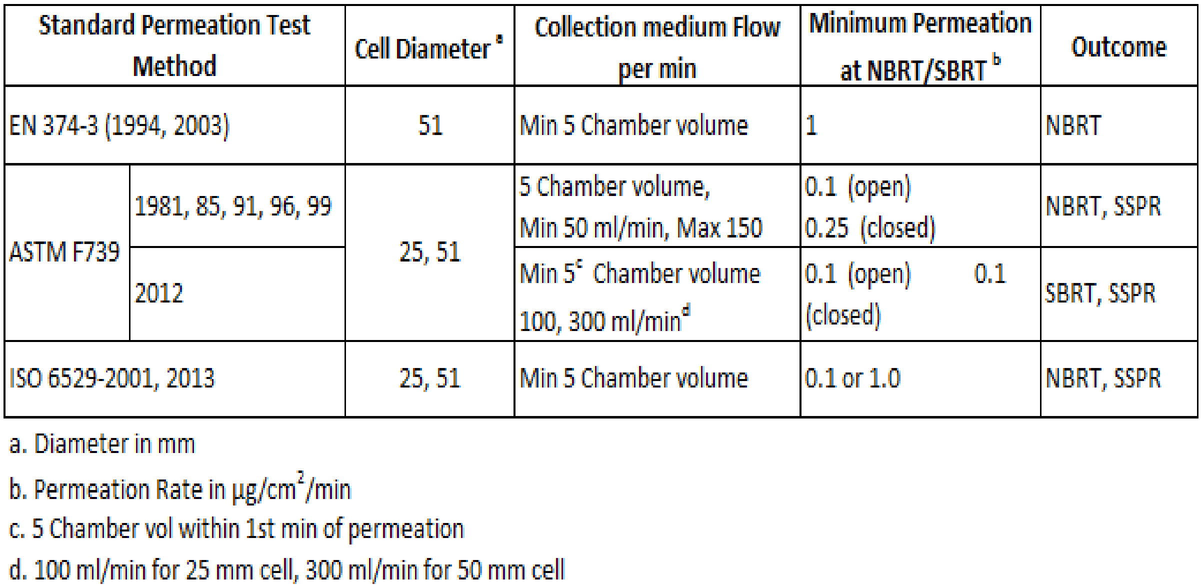
Fig. 1.5, ISO 6529-2001 alternative permeation cell. *Dimensions in millimeters



Key

1	Replaceable stirring rod	5	Fill level
2	Challenge chemical inlet	6	Challenge side for test chemical
3	Stop cock adapter	7	Sampling side for collection medium
4	Gasket	8	Aluminium flanges

Fig. 1.6, ISO 6529-2001 permeation cell for liquid compounds.



Standard Permeation Test Method		Cell Diameter [a]	Collection medium Flow per min	Minimum Permeation at NBRT/SBRT [b]	Outcome
EN 374-3 (1994, 2003)		51	Min 5 Chamber volume	1	NBRT
ASTM F739	1981, 85, 91, 96, 99	25, 51	5 Chamber volume, Min 50 ml/min, Max 150	0.1 (open) 0.25 (closed)	NBRT, SSPR
	2012		Min 5[c] Chamber volume 100, 300 ml/min[d]	0.1 (open) 0.1 (closed)	SBRT, SSPR
ISO 6529-2001, 2013		25, 51	Min 5 Chamber volume	0.1 or 1.0	NBRT, SSPR

a. Diameter in mm

b. Permeation Rate in μg/cm^2/min

c. 5 Chamber vol within 1st min of permeation

d. 100 ml/min for 25 mm cell, 300 ml/min for 50 mm cell

Table 1.1, Determinant features in ASTM, ISO, and EN Permeation Standards

Groce(25), Chao et al (12, 17), IPCS (24), Makela et al.(13, 18, 22) and Mellstorm (25) studied the permeation standards and compared the ASTM, EN, and ISO standards. Mellstorm (25) conducted a study on the permeation of toluene and 1,1,1,-tricholorethane on three neoprene gloves using both ASTM F739 and ISO 6529 standards. The results indicated a significant difference in SSPR from ASTM and ISO standards for two of the gloves. Chao et al(12) studied the permeation of 1,2-dichloroethane and benzene on two chemically protective gloves (nitrile and neoprene) using ISO 6529 and ASTM F739 permeation cells. The results showed higher SSPR for ISO cells than with ASTM cells.

A study on the permeation of 70% isopropyl alcohol through different surgical glove brands using ASTM F739 and EN 374 methods indicated longer breakthrough detection time in EN standard cells compared with the ASTM cells test method (18).

An overall comparison between ASTM F739 and EN 374 standard permeation methods suggests that ASTM F739 is 10 times more sensitive than the EN 374 standard permeation method. The challenge is that even with the ISO and ASTM conservative definition of NBRT (0.1.0 µg/cm^2/min), this limit is not necessarily a comprehensive criterion for all toxic chemicals as a safe threshold value, for example, carcinogens. ASTM and ISO apply this limit for all chemicals regardless of toxicity. As a result, dermal exposure less than 0.10 µg/cm^2/min for many toxic chemicals could be unsafe and a different scale may be needed for highly toxic chemicals.

The ASTM designed cell consists of a 100 mL collection chamber with 32 mm diameter and a challenge chamber with 22 mm diameter. The effective surface area between the challenge chamber and collection chamber in a nominal cell is equivalent to an exposed diameter of 50-mm. Pesce Lab modified ASTM F739-12 closed loop permeation cell and developed I-PTC-600 cells containing challenge chamber, collection chamber, Teflon gaskets, aluminum and stainless steel flanges and bolts with 1-inch effective diameter or 5.07 cm^2 effective operational area.

In a typical I-PTC-600 cell, each circular glove cut is held between the Teflon gaskets and the Pyrex chambers and tightened using three bolts tightened with a 16 ft-lb torque wrench with the inner surface of the glove facing the collection chamber and the outer side facing the challenge chamber.(59, 60)

The nominal volume for both challenge and collection chambers is 10 mL. The Pesce Lab I-PTC-600 cells are conventionally used in closed loop permeation studies as modified ASTM cells. In order to assure a homogenous distribution of the challenge compound in the collection chamber and prevented concentration gradients, Que Hee et al (58) developed a moving-tray water bath in which permeation cells are submerged in water holding temperature at $35.0 \pm 0.5\ ^{o}$C and agitates with different RPMs in a horizontal level.

1.2.3 Whole Glove Permeation Studies

Although all the above standards were developed to define the right breakthrough time and the efficacy of the gloves in protecting workers from chemical exposure, such standards may not necessarily represent on-site working conditions and the way a glove behaves in the workplace and on a worker. Both the US and international standards study glove permeation under static conditions in which the glove specimen is held between two chambers. By contrast, in the workplace using gloves requires donning and doffing as well as frequent flexion and extensions throughout the work shift. Mechanical movement is a basic defined function for hands, As a result gloves will be under same dynamic forces as hands. This has been overlooked in the standards. Moreover, glove resistance and texture are affected not only by movement, flexion and extension, but also by other mechanical and physical motions such as pushing, pulling, lifting and pressing objects as well as stretching hands while conducting individual or multiple tasks, all of which add a tremendous stress on the gloves.

Boeniger et al (28) discussed the limitations of permeation standards with regard to chemicals with low vapor pressure and asserted that ASTM is not an appropriate permeation test method for over 80% of the of the chemicals in threshold limit value (TLV) list with skin notation because they are categorized as low vapor pressure (≤5 mm Hg). Klingner et al (29) also emphasized the lack of standard methods for testing and evaluating NBRT and SSPR of low volatility compounds with low vapor pressure. To address the above concerns, a few studies have been conducted on different gloves using alternative methods such as flexed permeation methods, on-site permeation testing, and a whole glove permeation model.

Berardinelli et al(48) studied the permeation of acetone through a chemically protective glove using portable direct reading instruments, with a photoionization detector (PID) detection system, and compared results with ASTM F739 cell and an alternative smaller permeation cell. Results indicated no significant difference in breakthrough detection times between the PID detector and both permeation cells. However, the respective SSPR was different.

Gunderson et al(27) studied the permeation of meta-phenylenediamine (MPDA) through chemically protective gloves, conducted an on-site testing method via stain sampling, and compared the results with laboratory testing methods. The results indicated that the breakthrough time for on-site samples was significantly less than for laboratory testing.

Ceballos et al (2) discussed the limitations of the ASTM standard for evaluating the permeation of polymerizing materials through disposable latex gloves in spray coatings operations and developed a permeation panel. The panel used colorimetric SWYPE pads for defining breakthrough time and solid collection media for the permeation rate. Results indicated a 30 min breakthrough time and a 2.9 ng/min/cm^2 for 1,6-hexamethylene diisocyanate and isophorone diisocyanate through the disposable latex glove materials.

A permeation study on permeation of chemotherapeutic drugs through surgical latex and polyvinyl chloride (PVC) gloves was conducted using a modified permeation cell with a pneumatic shocking feature. Results showed no significant difference in NBRTs between flexed and static permeation cells; however, the diffusion coefficient was significantly different. (30)

Perkins et al(42) studied the effects of glove flexure on permeation using chemically protective gloves as a whole glove model. The model utilized a high volatile compound (acetone) as a permeant and used air flow inside the glove as collection media, weighing gloves in different time intervals as an indicator of permeation. Although the method in general did not provide enough precision, permeation results did indicate a significant difference between gloves in static and flexed positions.

A dynamic robotic hand was developed to study the permeability of disposable nitrile gloves when exposed to captan using cotton glove solid collection plus inner nitrile surface wiping.(31) No significant difference on permeated mass was observed between static and dynamic hands.

Mathews (32) studied the permeation of cyclohexanol through different nitrile gloves using a whole glove moving hand ~~(~~with circulating water as the collection media inside an enclosing outer larger glove~~)~~ and the closed loop ASTM method. The results indicated a significant difference in NBRT and SSPR between ASTM cells and the moving hand for blue and sterling gloves. However, no significant difference was found between moving and non-moving hands with blue and purple gloves, but differed for Sterling gloves, the latter being the thinnest glove.

Phalen et al(33) developed a whole glove permeation test attached to a pneumatic system as a whole glove shocker to evaluate the permeation of ethanol, as a high volatile solvent, through different disposable nitrile gloves. Air flow was used as collection media connected to a photoionization detector (PID) as an online direct monitoring system. Findings on the stressed whole glove model revealed that pneumatic movement resulted in earlier NBRT and a higher rate in SSPR than the static hand.

1.3 GLOVE MANUFACTURING

Standards, references, and manufacturers use different criteria to classify gloves, such as: thickness, material, texture and structure, weight, chemical content, cut protection performance level, voltage protection, heat and cold protection, mechanical protection, and chemical protection.

One of the most common classifications is based on the thickness of the gloves, in which gloves are placed into 4 groups: disposable, household, industrial, and special gloves with the thicknesses of 0.007 to 0.25 mm, 0.20 to 0.40 mm, and 0.36 to 0.85 mm respectively.(34) No thickness range has been defined for specific gloves and it varies based on the purpose and application. The other major classification is based on the gloves' materials: rubber and plastic, leather, textile, and any combination of these.(34) The US Department of Energy uses a 6-way classificatory system for gloves: disposable, fabric, metal, leather, aluminized, and chemical-resistant gloves.(37)

Acrylonitrile butadiene or nitrile butadiene rubber (NBR) has unique features such as a high resistance to oil, acids, fuels, and solvents and also considerable strength and flexibility. NBR is known as a copolymer from acrylonitrile and butadiene. The acrylonitrile and butadiene content of NBR are 35-45% and 65-55% respectively. NBR's nitrile content is an important factor that contributes to its properties as: high resistance to sharps and penetration. Higher nitrile content increases oil resistance and reduces flexibility. (33, 35, 44) Moreover, because NBR has a high tolerance of a wide range of temperatures it has many applications in industry and service sectors. (35, 36) Such features have made NBR a major ingredient of disposable nitrile gloves. (19, 33, 34, 35)

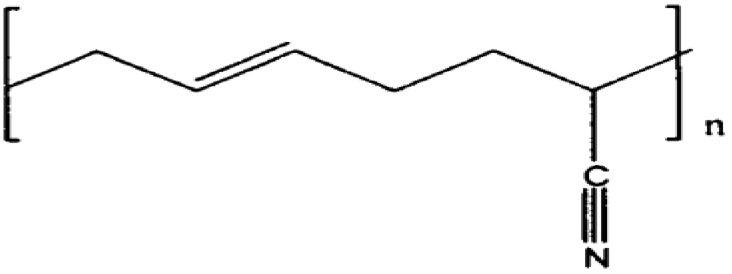


Fig. 1.7, NBR Chemical Structure (62)

Natural rubber gloves contain 90-95% natural latex plus 5-10% mix of other chemical ingredients, which are reported to cause irritations and allergic symptoms in some cases.(34) Figure 1.7 shows the NBR chemical structure.

Glove manufactures use a variety of methods in making the gloves, such as dipping, punching and welding, and sewing, depending on the material used and the expected features of the product.(34) Disposable gloves manufacturing process consists of multiple steps, starting with designing formers or molds which are generally made from ceramic or stainless steel in varying sizes, shapes, and dimensions. The next step is online cleaning, where molds are washed with water, acid (for organic residuals), and alkaline (for non-organic materials); rinsed; and brushed; (40) followed by a coagulation process. At this stage molds are dipped in a coagulant solution containing lubricants to make a coating over the mold surface that eases polymer detachment from the mold by preventing it from sticking.(34, 39) Molds are then gently immersed into a suspension containing latex. This process can be repeated until reaching the expected glove thickness.(34) The next step is leaching in which water soluble elements are removed through washing with water. This is important for medical products due to hypersensitivity concerns. Formers coated with NBR are then guided to an oven for the vulcanization process which causes polymer cross-linking and creates strength between polymer chains in a coherent and unique texture.(34) The oven conditions are critical and parameters such as temperature, humidity, air flow, and time duration should be monitored carefully. The final steps are cooling, stripping, testing and packing. After the gloves cool, they are removed from the molds and respective standard tests such as ASTM/USFDA are conducted. (40) For gloves with specific features such extra protection against toxic chemicals and more elasticity, non-polymer materials such as carbon black, plasticizers, stabilizers, and antioxidants may be included in the suspension.(39) The pigment added to the suspension defines the expected glove color.

Disposable gloves are being used widely in many industrial, medical, laboratory, chemical, manufacturing, food, and service sectors. They have several advantages such as low cost, availability, accessibility, and are needless to clean. Their flexibility is a unique feature with several applications in medical and high tech industries. Workers prefer to wear them. The worldwide consumption of disposable gloves is soaring; global investment in the gloves industry increases 20% every year. In 2007, 100 billion disposable gloves were used which if sorted back to back, would reach from the earth to the moon and back 30 times.(41)

Disposable gloves, also known as single-use gloves, are classified in 4 major classes: nitrile, latex, Neoprene, and vinyl gloves. They have some similarities, but different thicknesses and color coding which help distinguish them. Latex gloves have been used for years with many applications, but they have drawbacks, such as allergic reactions with symptoms such as skin rash, Itchy; red eyes, runny nose, asthma, and shortness of breath. (61)

The amount of exposure needed to sensitize an individual to natural rubber latex is not known, but when exposures are reduced, sensitization decreases. Individuals with known latex allergies should never wear latex gloves and may not be able to work in areas where latex gloves are used. Persons with known latex allergies should follow their organization's procedures to ensure that they are not exposed. NBR disposable gloves have minimized the allergic reactions and compared to latex provide higher puncture resistance and better protection against oils and acids.

Glove manufacturers conduct permeation tests on their products and provide information about NBRT and SSPR for different chemicals and solvents. A quick overview of such datasheets will help one to determine whether the selected glove is protective enough during exposure to a specific chemical. The criteria for defining the effectiveness of a given glove for each chemical are usually noted. Moreover, all permeation studies by glove manufacturers apply ASTM F739 and EN 374 permeation standards as reference. Some European glove manufactures are using both ASTM F739 and EN 374 standard tests for their products and the guideline contains NBDT and steady state permeation rate for both standards. For example, DuPont-Europe and Respirex, (45, 46) worldwide manufacturers for a variety of personal protective equipment including gloves, provide datasheets on glove selection containing SSPR and two NBRTs as 0.10 μg/cm^2/min and 1.0 μg/cm^2/min for ASTM F739 and EN 374 standards respectively. However, both DuPont-Europe and Respirex use EN performance classification as efficacy criteria in which gloves are categorized into 6 classes, from 1 to 6, based on NBRT. Class 1 and 6 are represent the poorest and highest performance with a NBRT of more than 10 min and 480 min, respectively.

Ansell and Kimberly Clark Professional (KCP) are known as major disposable and chemically protective gloves manufacturing corporations in the US and both apply the ASTM F739 permeation model for testing their products. They provide two different scales for evaluating the protectiveness of their products.

KCP defines dual criteria for the chemical resistance rating of disposable nitrile gloves. (49) The major criteria for rating is based on normalized breakthrough time (as indicated in Table 1.2) and volatility. The ASTM defines standardized breakthrough detection time as the time when the permeation rate reaches 0.10 μg/cm^2/min.(8) KCP categorizes normalized breakthrough time as <1 min, not recommended (NR); 1-9 min, poor; 10-59 min, good; and 60-480 min as excellent. (49, 50)

Rating	Permeation breakthrough time (min)
Excellent (E)	60-480
Good (G)	10--59
Poor (P)	1--9
Not Recommended (NR)	< 1

Table 1.2, Kimberly Clark Professional (46) permeation breakthrough time criteria for chemical resistance rating of disposable nitrile gloves.

KCP has also developed an internal definition for low and high volatile compounds using a 25 ° C boiling point as a reference temperature. In this model, chemicals with a boiling point higher than 25 ° C are considered low volatile and lower than 25 ° C are considered high volatile. KCP defines a chemically protective glove safe with a green coding, if a high volatile compound has an excellent (60-480 min) or good (10-59 min) permeation breakthrough time, or if a low volatile compound has an excellent permeation breakthrough time (60-480 min). Such criteria are not compatible with the definition for semi/nonvolatile compounds in other references with a large margin. However, it is used along with NBDT for glove selection. Semi/non-volatile chemicals are characterized with a boiling point of 150 ° or higher. (19, 52)

Ansell indicates that a chemically protective glove can be safe if either combination of the following criteria are met. (51)

a- The degradation rating is excellent and permeation breakthrough time is 30 min or greater, and permeation rate is excellent (less than 0.9 μg/cm^2/min.), very good (less than 9 μg/cm^2/min), or good (less than 90 μg/cm^2/min).

b- Permeation rate is not available and permeation breakthrough time is 240 min or more, and degradation is excellent, good, or very good. The latter triple criteria are even harder to meet than the first one, because it requires a 240 minutes or greater breakthrough time. A color code rating system is used to simplify the selection process as for KCP.

Most of permeation studies by glove suppliers are focused on chemically protective gloves and only in a few cases are charts for disposable gloves available. Moreover, the open loop permeation method has been used as the default standard method by glove manufacturers for all volatile and semi-nonvolatile chemicals. As a result, all guidelines, booklets, and datasheets on breakthrough time and steady state permeation are extracted under open loop conditions regardless of permeant volatility.

The gaseous collection medium used in an open loop system is not able to capture and carry non-volatile permeated compounds efficiently because of low vapor pressure of non-volatile chemicals. (19, 20) This can result in a non-realistic breakthrough detection time and standardized breakthrough time even if an analytical method with high sensitivity is used. (19, 20) This indicates a major inconsistency and concern on all permeation data provided by glove manufacturers for glove exposure to semi-nonvolatile chemicals.

Considering all pros and cons for open loop and closed loop permeation standards as well as alternative experimental glove permeation methods, a moving robotic hand is the model for addressing all of the short comings discussed for ASTM, ISO, EN, and other alternative permeation methods. The whole glove moving hand model utilizes flexion and extension features, which makes it close to on-site working conditions. Moreover, the model exposes the whole glove to the chemical, which is another advantage of the model compared to glove cuts used in the open loop and closed loop systems. Lastly, the model takes advantage of a circulating closed loop collection method, which makes it compatible for studying the permeation kinetics of semi-volatile and low volatile chemicals. In order to understand the consistency and applicability of the model for a wide range of chemicals as a universal method, multiple studies on different low volatile solvents with disposable gloves with range of thickness need to be performed.

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CHAPTER 2

RESEARCH HYPOTHESIS AND SELECTED COMPOUND

2.1 RESEARCH HYPOTHESIS

The primary hypothesis of this research is that a moving robotic hand will allow for more permeation through a disposable glove than a static hand at the same temperature, thickness, and type. It was also hypothesized that permeation through a disposable glove will be consistent in both the modified closed loop and the static whole glove permeation methods.

Chapter 1 discussed the disadvantages and advantages of the various permeation systems, and it was concluded that the closed loop mode was most suitable for nonvolatile solvents rather than the open loop method, the standard one used by glove manufacturers. The question was which solvents would be candidates.

The criteria for the non-volatile solvent candidates in the modified closed loop system were that they did not degrade the glove and the collection solvent did not also degrade the glove and did not backpermeate. The best collection solvent was hence chosen to be water. Thus the candidate challenge solvents had also to be adequately soluble in water. Another criterion was that the solvent have a guideline like a threshold limit value, recommended exposure limit, permissible exposure limit, or workplace environmental exposure limit, with preference to the first three guidelines to be able to interpret the health risk of any permeated material. The challenge chemical should also be preferably a member of the ASTM solvent battery and also have data for chemical protective gloves. Since Mathews (1) studied cyclohexanol in his robotic hand PhD study, this suggested other nonvolatile alcohols. Preliminary studies by Mathews et al showed that ethylene glycol (boiling point (BP) 198° C) did not permeate disposable Blue nitrile at all and so was unsuitable whereas diacetone alcohol (BP 167° C) and benzyl alcohol (BP 206° C) permeated within 5 minutes and also were unsuitable. To test whether gloves permeated for normalized breakthrough times at least greater than 20 minutes in the modified close-loop test for the disposable gloves was therefore the starting point to choose a challenge solvent for the robotic hand experiments.

The present research study initially started with conducting the modified closed loop permeation technique on two semi-volatile glycol ethers, 2-ethoxyethanol (2-EE, BP 135° C) and 2-butoxyethanol (2-BE, BP 170° C). 2-EE and 2-BE have solubilities of 63 g/L and 1000 g/L at 25° C, respectively. There were no previous permeation studies for disposable gloves on 2-BE and 2-EE using the ASTM closed loop method. However, the SBRT was observed within the first sampling interval as 10±10 min. Thus, such a short breakthrough time was not long enough to prove the hypotheses.

At the next step, limonene was chosen as a challenge solvent because limonene has physical characteristics as a boiling point of 175 °C, a solubility of 13.8 mg/L in water (at 25 °C) . Moreover there are no previously published studies on limonene permeation through disposable gloves and very few reports have focused on chemically protective gloves permeation using the ASTM F739-99 open loop method. Also, limonene is counted as essential solvent with many applications in several industries (150 million pounds per year in U.S.).(2,3) The capability of instrumental methods in detecting and analyzing limonene at SBRT concentration criteria were also considered during the analyte selection process. There exists no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for limonene. The American Industrial Hygiene Association (AIHA) adopted a workplace environmental exposure level (WEEL) of 30 ppm 8-hr time weighted average (TWA) for limonene.(4)

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CHAPTER 3

PERMEATION OF LOW VOLATILE SOLVENTS THROUGH DISPOSABLE NITRILE GLOVES

3.1 ABSTRACT

The purpose of this study was to investigate the permeations of the low volatile solvents 2-butoxyethanol (2-BE) and 2-ethoxyethanol (2-EE) through disposable, unlined, unsupported, purple nitrile exam glove materials from Kimberly Clark. This study utilized the American Society for Testing and Materials (ASTM) F739-99a and 2012 closed-loop permeation method. For each set, four 1-inch diameter standard permeation cells (3 cells with solvent as challenge and one air blank) were used with water as the collection solvent. Aliquots of 0.1 mL were taken at permeation time intervals of 1.0 and 10 min, 1.0, 2.0, 4.0, 6.0, and 8.0 h. The analytical method was based on gas chromatography-mass spectrometry (GC-MS). The percent differences of the thickness and weight for both analytes before and after permeation experiment on conditioning were less than 10 %. The ASTM normalized breakthrough time (NBRT) corresponding to 0.25 $\mu g/cm^2$ occurred at <20 minutes for both solvents and the average steady state permeation rate (SSPR) was 1.27 ± 0.11 $\mu g/cm^2$ for 2-BE and 4.83 ± 0.45 $\mu g/cm^2$ for 2-EE. This reflects that the SSPR for 2-EE permeation test on disposable purple nitrile gloves is nearly 4 times higher than for 2-BE ($P \leq 0.05$). 2-EE showed a diffusion coefficient of $(1.6 \pm 0.21) \times 10^6$ which was significantly more ($P \leq 0.05$) than the respected diffusion coefficient for 2BE $(3.88 \pm 1.1) \times 10^6$. Both solvents exceeded the ASTM threshold NBRT after exposure and are categorized as “not recommended” by Kimberly Clark Professional permeation breakthrough time criteria and did not comply with Ansell’s criteria

either. These gloves should not be used as personal protective equipment for exposure to 2-butoxyethanol or 2-ethoxyethanol, even for very short period exposures.

3.2 INTRUDUCTION

Personal protection equipment such as chemical-resistant gloves is the first line of defense against potential skin exposure to toxic chemicals in the workplace.(1) The National Institute for Occupational Safety and Health (NIOSH) emphasizes the selection of the most appropriate glove for exposure to chemicals and defines the time limit it can be worn and whether it can be reused.(1) It is estimated that more than 10% of the working population in the U.S. risk potential exposure to chemicals via skin contact.(2) Considering that dermatitis is one of the top 3 occupational disorders, the direct and indirect costs of medical compensation are on the billion dollar scale.(3)

Many chemicals, whether absorbed through the skin upon contact or inhaled, cause health problems.(4) In fact, research has revealed that skin absorption for a large number of chemicals can occur without the workers noticing.(4)

Although the major routes of entry for chemicals are inhalation, ingestion, and skin absorption, for many chemicals skin contact is crucial. The risks of skin absorption are particularly important when it comes to exposure to low-volatile compounds. Because of low vapor pressure, such chemicals can remain in the work environment for extended periods of time.(4) One of the physical features used in categorizing chemical volatility is boiling point. In general volatility is used to classify chemicals with boiling points below 150 °C. Compounds that boil at or over 150 °C are categorized as semi/nonvolatile compounds.(9)

The American Society for Testing and Materials (ASTM) F739-99/12 standard addressed permeation process in open loop and closed loop forms. The open loop and closed loop models utilize gaseous and liquid collection media respectively. (5, 6)

The major criterion for choosing between these two methods is the volatility of the challenge solvent. For compounds of high volatility, the open loop model is recommended. The open loop testing model consists of a dynamic collection medium in which a carrier gas is constantly flowing across the challenge side and carries the vapor of the permeated analyte to a detector. However, compounds with low volatility or high boiling points are not readily vaporized, and this method is not recommended for such compounds.(7, 8)

ASTM F739-99/12 recommends the closed loop method for low volatile solvents. In this method a liquid in the collection side is in direct contact with the permeated solvent, and at defined intervals samples are taken from the collection side for analysis. The collection solvent must not attack the material to be tested and must also solubilize the challenge compound.

A handful of glove permeation studies have been conducted using the closed loop method and to date most research on glove permeation is focused on chemically protective gloves using the open loop model. The permeation data in catalogs provided by glove manufacturers are all based on the open loop model.

Xu et al.(10) studied permeation of various disposable gloves as nitrile, chloroprene, vinyl and latex gloves challenged by complex non-volatile water-insoluble straight oil metalworking fluids (MWF) using the ASTM F739-99a closed loop method. The results indicated that disposable nitrile gloves are safe and protective enough to be worn during exposure to metalworking fluids.(10)

In another study Xu et al.(42) compared the permeation of MWF through disposable nitrile gloves (SafeSkin) and chemically protective nitrile glove (Sol-Vex) in a closed loop system. Although the Ansell guideline categorized the disposable glove in the “very good” class, the breakthrough time was less than 30 min. It was therefore suggested that chemically protective gloves be used as a safety measure during exposure to MWFs.

Phalen et al (11) conducted a study on the permeation of the pesticide captan through disposable blue nitrile gloves using the ASTM closed loop method. The results showed a breakthrough time within two hours of exposure. Such gloves should be used only for a single occasion with no reuse option.

2-Butoxyethanol is a non-volatile glycol ether with an ether-like odor and a boiling point of 171 °C.(12) Exposure routes are through the major routes of chemical entry to the body including inhalation, skin absorption, ingestion, and eye contact. The target organs for 2-butoxyethanol include kidney, liver, eyes, skin, respiratory system, central nervous system (CNS), and blood system.(12, 18, 28) The primary toxic impact caused by 2-butoxyethanol and its metabolite (2-butoxyacetic acid) is hematotoxicity.(12, 43) Current OSHA PEL,(14) NIOSH REL,(15) and ACGIH (20) TLV-TWA for 2-butoxyethanol are 50 ppm, 5 ppm, and 20 ppm respectively.

NIOSH and OSHA defined skin notation for 2-BE as “potential for dermal absorption”.(44) The recommended immediately dangerous to life or health concentration (IDLH) for 2-BE is 700 ppm. 2-Butoxyethanol has many applications in various industries as a solvent in latex paints, surface protective coatings, and varnishes. (7) The market demand in the US for 2-butoxyethanol was 320 million pounds (9, 16) in 2003, of which 75% was for paints and coatings.

There is no previous permeation study on 2-BE and 2-EE using the ASTM closed loop method for disposable gloves, and therefore such research is presently being proposed. Glove manufacturers conducted permeation study on chemically protective nitrile gloves using ASTM open loop method for 2-BE (BP 171 °C).(11) Ansell reported a 470 min NBRT and less than a 9 μg/cm^2/min steady state permeation rate for Chemical Protective Clothing (CPC) nitrile gloves (Ansell Sol-Vex) exposed to 2-BE in the Open Loop ASTM Method F739-99a.(24) Similar experiments conducted by Kimberly Clark Professional (47) indicate more than a 480 min NBRT and a 6 μg/cm^2/min steady state permeation rate for G80 CPC nitrile gloves. The normalized breakthrough detection times for 2-butoxyethanol with other CPC gloves are reported as 180 min, 120 min, 45 min, 60 min, and >480 min for unsupported Neoprene, supported Polyvinyl Alcohol, natural Rubber, Polyvinyl Chloride, and unsupported Viton, respectively. (24)

Ansell classified the steady state permeation rate (SSPR) for all above glove materials, except unsupported Viton, in the G (Good) category, which represents less than 90 μg/cm^2/min. Forsberg et al (46) reported 2-BE NBRTs for CPC nitrile glove manufactures Mapa (Pioneer A-14 and AF-18), Anselledmont (37-155), and North (LA-102G) as: >480 min, 420 min, and >420 min, respectively.

2-Ethoxyethanol is a moderately non-volatile organic solvent with no odor and a boiling point of 135 °C.(13, 17) It has similar applications in the varnish industry as 2-butoxyethanol plus several other uses in finishing leather, dye solutions, and printing inks, as well as being an anti-icing agent in hydraulic fluids and jet fuel.(17, 18, 19)

The current OSHA PEL, (14) NIOSH REL,(25) and ACGIH (15) TLV-TWA for 2-ethoxyethanol are 200 ppm, 0.5 ppm, and 5 ppm respectively, all with skin notations. The defined IDLH for 2-EE is 500 ppm. The annual production of 2-ethoxyethanol in the US was 45 million kilograms in 2002. (17) It affects the male reproductive system and causes embryo and fetal damage.(45)

Ansell reported a 293 min NBRT and less than 90 μg/cm^2/min steady state permeation rate for Chemical Protective Clothing (CPC) nitrile gloves (Ansell Sol-Vex) exposed to 2-EE in the open loop ASTM method F739-99a.(24) The respective experiments conducted by Kimberly Clark

Professional(47) indicate more than 240 min NBRT and 5 μg/cm^2/min steady state permeation rate for G80 nitrile chemical resistant gauntlets. The normalized breakthrough detection time for 2-EE with other CPC gloves are reported as 128 min, 75 min, 25 min, 38 min, and 465 min for unsupported Neoprene, supported Polyvinyl Alcohol, natural Rubber, Polyvinyl Chloride, and unsupported Viton respectively. (24)

Ansell classified SSPR for unsupported Neoprene, supported Polyvinyl Alcohol, and Polyvinyl Chloride in the G (good) category (less than 90 μg/cm^2/min), natural Rubber in the VG (very good) category (less than 9 μg/cm^2/min), and unsupported Viton in the E (Excellent) category (less than 0.9 μg/cm^2/min). Forsberg et al (46) reported 2-EE NBRTs for CPC nitrile glove manufactures Mapa (Pioneer A-14), Anselledmont (37-155), Best (22R), and Magrigold (Blue) as: 416 min, 92 min, 420 min, and 281 min respectively. Comparing all NBRTs for 2-EE and 2-BE reported by Ansell, Kimberly Clark, and Forsberg shows a shorter NBRT for 2-EE.

No permeation studies are available for 2-butoxyethanol and 2-ethoxyethanol with disposable nitrile gloves by glove manufacturers such as Ansell or Kimberly-Clark.

The present research focused on Kimberly Clark disposable powderless, unsupported, unlined purple nitrile exam gloves and determined the permeation parameters for the ASTM F739-1999/2012 closed loop method with 2-BE and of *2- butoxyethanol and 2- ethoxyethanol as* non-volatile solvents.

3.3 EXPERIMENTAL

3.3.1 Chemicals, solvents, and glove samples

The gloves used were disposable, powder-free, unsupported, unlined, purple nitrile exam gloves (24.2 cm length; 0.12 mm thickness, Kimberly Clark No. 55082-M), ordered from Fisher Scientific, Pittsburgh, PA.

The analytes, 2-ethoxyethanol (99%) and 2-butoxyethanol (99%), were obtained from Acros Organics. 4-bromophenol (99%) was selected as the internal standard (IS) for the analytical method, gas chromatography-mass spectrometry (GC-MS). Helium (99.999%) from Air Products (Long Beach, CA) was used as carrier gas for gas chromatography-mass spectrometry (GC-MS) operation. The water utilized for all aqueous solutions was produced from two filtration systems, Millipore Milli-Q Water System and Millipore Simplicity portable ultrapure water purification system (Temecula, CA).

3.3.2 Equipment

Glove material thickness was measured at the palm region using an Electronic Digital Micrometer Model CO-030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific. A Mettler analytical balance AE260 Scale (Mettler, Hightstown, NJ) weighed the glove cuts. Modified ASTM F739-12 closed loop permeation cells model I-PTC-600 containing challenge chamber, collection chamber, Teflon gaskets, aluminum and stainless steel flanges and bolts were obtained from Pesce Lab (Kennett Square, PA).

The GC–MS system consisted of two components: an Agilent 6890N Gas Chromatograph with a non-polar, HP-5MS fused silica capillary column, 60 m length x 0.42 mm (external diameter), 0.32 mm internal diameter, 1 μm internal film thickness operated in the splitless mode and a Mass Selective Detector (MSD), Agilent 5973 Mass Selective Detector (MSD) (Agilent Technologies). Agilent 6890N Gas Chromatograph contains an oven with 28 × 31 × 16 cm dimensions.

A Thermo Nicolet Avatar 360 Fourier Transform (FT) Infrared Spectrometer was used for the acquisition of Infrared Reflectance (IR) spectra. The infrared spectra ranged from 4000 to 400 cm^{-1}, with 124 scans for higher resolution and spectra uploaded with OMNIC 6.0a software. The Avatar 360 Fourier-transform (FT) spectrophotometer system (Thermo Nicolet, Madison, WI) operated in the transmission mode and was equipped with a DTGS detector with KBr beam splitter. In the reflectance mode, a diamond cell was used.

3.3.3 Permeation procedure

The glove samples were checked to be within expiration date. In order to fit into the permeation cells, the glove materials were cut from the palm area in two inch diameter circular pieces, and were conditioned in a desiccator at 52±1% and 23 ^{o}C for 24 h before the permeation test under an atmosphere generated by saturated potassium dichromate at room temperature (23 ^{o}C). In the next step, the glove cuts' average thickness (micrometer) at marked spots within 1 cm radius of circular area and mass (balance) were measured from triplicate measurements. The infrared reflectance spectra (Avatar 360) were also obtained for the challenge and collection surfaces of each glove piece using the clamp accessory.

Each circular glove cut was held in an ASTM type permeation cell between the Teflon gaskets and the Pyrex chambers and tightened using three bolts tightened with a 16 ft-lb torque wrench with the inner surface of the glove facing the collection chamber (water) and the outer side facing the challenge chamber.(31, 32) The effective surface area between the challenge chamber and collection chamber was equivalent to an exposed diameter of 25.4 mm and was 507 mm^2 (5.07 cm^2).

Four 1-inch diameter permeation cells (3 experimental cells with challenge solvent and one air blank) were used with water as the collection fluid in a protocol based on the ASTM F 739-99/12 closed-loop permeation method. A 10 mL volume of the analyte (2-butoxyethanol, 2-ethoxyethanol) was added to the challenge chamber and 10 mL of collection solvent (water) pipetted into the collection chamber. (31, 32) All cells were clamped to a shaking water bath and submerged with the water holding temperature at 35.0 ± 0.5 °C and agitated with a horizontal movement of 7.0 ± 0.5 cm/s which represents a 100 RPM cycle. This created a homogenous distribution of the permeant in the collection chamber and prevented concentration gradients.

Aliquots of 0.1 mL were taken at permeation time intervals of 1.0, 20 min, 1, 2, 4, 5, 6, and 8 h and deposited into 1.5-mL vials plus 2 µL of internal standard (4-bromophenol) with 0.1 ug/uL concentration. Because of the small volume of the sample size (0.1 mL), care was taken to insert the tip of the needle containing the internal standard as close as possible to the sample to make sure it merged with collection solution before side-to-side mixing. The sum of all samples taken did not exceed 10% of the initial collection solvent volume. The analytical method was based on gas chromatography-mass spectrometry (GC-MS) and internal standard method (4-bromophenol).

After the permeation test, glove specimens were blotted dry, and reconditioned in desiccator for reflectance IR analysis as well as measured for thickness and mass.

3.3.4 GC-MS analysis

The MS was initially used in the total ion current mode (TIC) to extract intensities of all mass spectral peaks over the mass to charge ratio (m/z) range of 50–500. Thus, the purities of the analytes, solvents, and internal standard were examined. The injected volume for all samples was 2.5 µL. In the next quantification phase, to define breakthrough times, the selected ion monitoring mode (SIM) was used to enhance sensitivity and selectivity for the compounds of interest (at m/z 57 for 2-butoxyethanol, m/z 59 for 2-ethoxyethanol, and m/z 172 for the 4-bromophenol internal standard).

For 2-butoxyethanol, the GC column temperature started at 120 °C for 2 min and ramped at 40 ° C/min to 280 ° and then kept at 280 ° C for 4 min at a helium rate of 2.0 mL/min. The set point temperature for inlet, ion source, and MS quadrupole were 250 ° C, 230 ° C, and 150 ° C respectively. The solvent delay and SIM dwell time were set for 2 min. The selection of the internal standard was based on not interfering with the analyte and stable response in a sensitive linear range at which the normalized breakthrough time could be detected.

For 2-EE, the GC column temperature ramp started at 50 °C for 4 min and ramped up at 120 ° C /min to 280 ° and kept at 280 ° C for 6 min at a helium flow rate of 2.0 mL/min. The set point temperature for inlet, ion source, and MS quadrupole were 250 ° C, 230 ° C, and 150 ° C respectively. The solvent delay and SIM dwell time were set for 2 min. Selection of the internal standard was based on not interfering with the analyte as well as sensitive and consistent response from MS detector and to allow detection of the normalized breakthrough time.

1.00 mL of standard solutions of the analytes in water with concentrations of 0.00, 0.1, 0.3, 0.5, 1, 5, 10 and 100 ng/µL were made in the presence of 1 µg/µL of the internal standard (aliquots of 2 µL from internal standard with the concentration of 0.1 µg/µL was added to each 0.100 mL standard and sample solution). After injection, the area under peak for the analyte and internal standard was extracted using RTE manual integration. The area under the curve ratio of standard solutions (2-butoxyethanol and 2-ethoxyethanol standards) over the internal standard was plotted versus the corresponding standard solution concentration.

To define the linear relationship features for standards such as slopes, intercepts, standard deviations, standard deviations of the slope and intercept, correlation coefficient, slope, and p-values, the linear regression model was used. The independent samples *Student* t-test was used to determine whether the average of two samples were significantly different and to define the p-values of r.

3.4 RESULTS AND DISCUSSION

3.4.1 GC-MS Analytical Features

The GC-MS linear dynamic range for 2-butoxyethanol was 0.2 ng to 10.0 ng with 0.2 ng detection limit and regression equation as $y = 1.3991x - 0.123$ and a coefficient of determination as $R^2=0.994$. The retention time for 2-BE and the internal standard were 4.3 min and 7.5 min, respectively. The total run time for each injection was 11.00 min.

The GC-MS linear dynamic range for 2-ethoxyethanol was 0.2 ng to 10.0 ng with 0.2 ng detection limit and regression equation as $y = 7.3611x - 0.1314$ and a coefficient of determination as $R^2=0.991$. The retention time for 2-EE and the internal standard were 7.00 min and 9.5 min, respectively. The total run time for each injection was 11.92 min.

GC-MS provided the minimum sensitivity required by ASTM criteria for analyzing 0.127 ng/uL of 2-butoxyethanol and 2-ethoxyethanol. Based on the ASTM closed loop method normalized breakthrough time criteria (5), the analytical method should provide a minimum sensitivity of 0.25 $\mu g/cm^2$ of the permeant, which is equal to 0.127 ng/μL of 2-BE. (The area of the glove specimen with a diameter of 25.4 mm was 5.07 cm^2. 0.25 μg x 5.07 cm^2 =1.27 μg/10 mL analyte, which is equal to 0.127 ng/μL).

3.4.2 Thickness

The thickness measurements are reported in Table 3.1. The average post-permeation glove materials thicknesses for 2-butoxyethanol and 2-ethoxyethanol were 107 ± 1 μm and 108 ± 1 μm, respectively. Glove specimens swelled less than 10% for experiments using both 2-BE and 2-EE. Initial observations indicated swelling and discoloration after the permeation test on analytes. Thickness measurements on some glove specimens after reconditioning revealed a significance difference in thicknesses (paired *student* t-test) before and after challenging (Table 3.1). For the 2-BE permeation experiment, one of the gloves appeared to shrank, but on average the glove specimens swelled 1.9% which was not significant at $P \leq 0.05$. Reconditioning after permeation experiments was a critical step before continuing other measurements or studies on glove materials. While it is clear that materials swelled during the permeation period itself, this was also reversible on reconditioning.

3. 4.3 Weight

The weights of conditioned glove specimens before and after permeation tests are reported in Table 3.1. The average glove weights before and after exposure to 2-EE were 0.299 ±0.004 gr, and 0.311± 0.010 gr, respectively. The corresponding weights for 2-BE were 0.268 ± 0.006 gr and 0.280 ±0.012 gr. All reconditioned samples, including blanks, showed some degree of weight increase after challenging with 2-BE and 2-EE. Glove cuts exposed to 2-BE gained an average of 3.8% weight after permeation versus 3.2% for 2-EE, which are all below 10% and none of the changes were significant ($P \leq 0.05$). However, using the paired *student* t-test for analyzing and comparing each glove specimen before and after exposure as pair indicates significant differences ($P \leq 0.05$) in all glove specimens (Table 3.1).

	Thickness before challenging	Thickness after challenging	Weight before challenging	Weight after challenging
2-EE				
Sample A	105 ± 2	108 ± 2	0.305± 1	0.313± 1*
Sample B	107 ± 2	109 ± 1	0.299± 1	0.314± 1*
Sample C	104 ± 1	108 ± 1 *	0.295± 1	0.302± 1*
Blank (D)	104 ± 2	106 ± 2	0.301± 1	0.306± 1*
2-BE				
Sample A	105 ± 2	108 ± 2 *	0.261± 1	0.266 ± 1*
Sample B	103 ± 1	108 ± 1 *	0.272± 1	0.288 ± 1*
Sample C	106 ± 1	104 ± 1	0.268± 1	0.279 ± 1*
Blank (D)	105 ± 1	106 ± 1	0.270± 1	0.273 ± 1*

* Significantly different, $P \leq 0.05$

Table 3.1, Glove sample average thickness (μm) and weight (gr) before and after permeation for 2-EE and 2-BE.

3.4.4 Infrared reflectance analysis

The strongest absorption for the inner and outer side of blank and challenged gloves with 2-EE was located at 900 and 1500 cm^{-1}. An increase in C-H bends at 1400–1500 cm^{-1} was observed at outer side of the gloves exposed to 2-EE comparing to inner side. After subtracting of exposed gloves from unexposed ones, traces of 2-BE and 2-EE were observed on outer side of the glove surfaces. The spectra before and after the permeation test with 2-EE and 2-BE were similar with minimal changes.(33, 34) This suggests that 2-BE and 2-EE did not make a major impact on the glove surfaces.

3.4.5 Permeation

3.4.5.1 Breakthrough Time

Permeation curves for 2-BE and 2-EE are shown in Fig. 3.1 and 3.2. The normalized breakthrough times for both 2-BE and 2-EE were achieved within the first 20 minutes of the experiment. In fact, the collection chamber reached the ASTM (5) 0.25 µg/cm^2 criterion for NBRT upon 2-BE coming into contact with the glove materials. Fig. 3.1 and 3.2 and Table 3.2 show that reaching NBRT was quicker for 2-EE. This is consistent with the study conducted by Ansell on Neoprene, Polyvinyl alcohol, Natural rubber, and other CPCs and confirms a shorter detection breakthrough time for 2-EE as compared to 2-BE.(23, 24)

The permeation curves also illustrate that steady state permeation rate occurred within the time region of 20 and 120 minutes for 2-BE and 2-EE. The time frame for SSPR varies for chemicals and it can be impacted by solubility in the collection solvent as well. 2-BE and 2-EE both have ether and alcohol groups which promotes hydrophilic solubility of the solvents and classifies their solubility in water as miscible. The solubility of 2-EE and 2BE in water is 8.4 mmol/L (1000 mg/L) and 5.5 mmol/L (500 mg/L), respectively, and the permeation rate did not reach this limit. The observed standardized breakthrough time (SBRT) for both solvents was at 10±10 min.

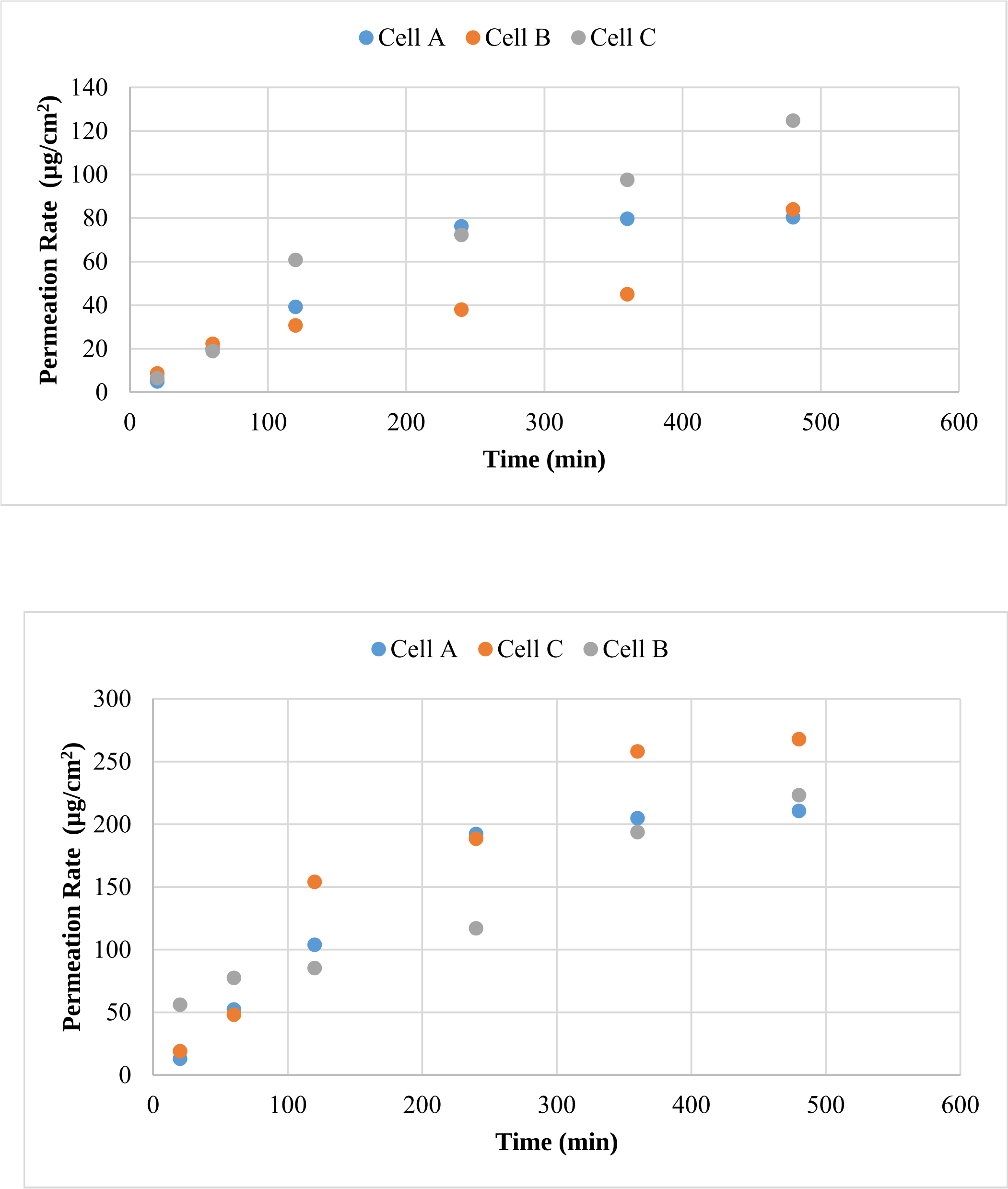

Fig. 3.2, Permeation of 2-ethoxyethanol through disposable nitrile gloves

3.4.5.2 Permeation Rate

The permeation parameters of 2-EE and 2-BE are indicated in Table 3.2. Analysis of samples taken from the 2-EE and 2-BE permeation cell experiments showed an average steady state permeation rate of 1.27±0.11 µg/cm^2/min for 2-BE and 4.83 ±0.45 µg/cm^2/min for 2-EE. This reflects that the SSPR for the 2-EE permeation test on disposable purple nitrile gloves is over 4 times higher than for 2-BE ($P \leq 0.05$).

Permeant	Replicate	SBRT ^{A} (min)	SSPR ^{B} (µg/cm^2/min)	D ^{C} x10^{-6} (cm^2/min)	20 min Permeated Mass (µg/cm^2)	Total Permeation Rate^{D} (µg/cm^2)
2-BE						
	1	10 ±10	0.9	1.6	5	80
	2	10 ±10	1.2	1.3	9	84
	3	10 ±10	1.4	1.8	6	125
	Avg		1.2 ±0.25	1.6 ±0.2	6.6± 2.1	96±24
2-EE	1	10 ±10	3.9	5.6	19	211
	2	10 ±10	5.1	3.5	26	268
	3	10 ±10	5.5	2.3	43	262
	Avg		4.8 ±0.8	3.8 ±1.2	29± 12	247± 31

A., Standardized Breakthrough Time, B., Steady State Permeation Rate
C., Fick's Coefficient Diffusion (D) , calculated using the equation: $D = \frac{L^2}{6ti}$ in which L: glove thickness (cm) and t_i lag time (min) D., Permeation rate after 8 hours

Table 3.2, Permeation elements of 2-EE and 2-BE through disposable purple nitrile gloves

The regression analysis between 2-EE's SSPR and 2-BE's SSPR indicates an equation as $Y = 3.2632X + 1.0263$ with $r^2 = 0.97$ and $P \leq 0.05$. The average diffusion coefficient for 2-EE was $(3.8 \pm 1.1) \times 10^6$, which higher that respected diffusion coefficient for 2-BE with a factor of 2.4. The 20 min and 8 h 2-EE permeation mass per area unit of the glove was measured as 29±12 and 247±31 µg/cm^2 respectively, whereas the 20 min and 8 h measurements for 2-BE were 6.6± 2.1 and 96± 24 µg/cm^2. This suggests that mass permeation ratio for 2-EE was higher than 2-BE with a factor of 4.4 at the end of initial 20 min permeation period and at the end of 8 h the 2-EE was still higher by a factor of 2.6 ($P \leq 0.05$). However, for both analytes no linear regression was found between the 20 min and 8 h permeated mass ratio ($P \leq 0.05$).

Both solvents are known as glycol ethers with similar ether and alcohol groups; the latter group promotes their hydrophilic solubility. Moreover, 2-EE is more water soluble than 2-BE by a factor of 1.53, which the molar solubility ratio between the two solvents. (2-EE water solubility is 1000 mg/L which is 8.4 mmol/L and 2-BE water solubility is 500 mg/L which is 5.5 mmol/L). Comparing the molecular weight of the two solvents indicates that 2-BE's molecular weight is 30 % more than 2-EE (118 gr vs 90 gr). This suggests an inverse ratio between the molecular weight of the two solvents and their respective diffusion coefficients and permeation rates. The Hildebrand solubility parameters for 2-BE and 2-EE are 20.2 and 21.9 respectively. The regression analysis on 2-EE/2-BE ratio of parameters as Hildebrand solubility (1.08), diffusion coefficient (2.38), and SSPR (4.0) indicates a linear equation as $y = 1.4579x - 0.4295$ with $r^2 = 0.995$ ($P \leq 0.05$). Defining the efficiency of the gloves using the permeation data such as the ASTM standardized breakthrough detection time (6) (at 0.1 $\mu g/cm^2/min$) and mass permeated during the first 20 min permeation test reveals that the gloves are not protective enough.

However, Kimberly Clark Professional and Ansell provide two other criteria for evaluating the effectiveness of the gloves. Kimberly Clark Professional, one of the largest manufacturers of disposable and chemical protective gloves, defines a dual criteria for chemical resistance rating of disposable nitrile gloves. (21) The major criteria for rating is based on normalized breakthrough time as indicated in Table 3.3. Based on this classification, the gloves are not recommended or at most, poor. Kimberly Clark categorizes NBRT as: <1 min, not recommended (NR); 1-9 min, poor; 10-59 min, good; and 60-480 min as excellent. (21, 38)

Rating	Permeation breakthrough time (min)
Excellent (E)	60-480
Good (G)	10--59
Poor (P)	1--9
Not Recommended (NR)	< 1

Table 3.3 Kimberly Clark Professional (46) permeation breakthrough time criteria for chemical resistance rating of disposable nitrile gloves.

The second embedded criterion is boiling point. Solvents with boiling points of less than 24 ^{o} C are defined as high volatile and higher than 24 ^{o} C defined as low volatile.(46) Using the Kimberly Clark Professional scale, since the permeation breakthrough time for exposure of disposable purple nitrile *gloves to 2-BE and 2-EE* occurred momentarily upon contact, such gloves will be categorized as either not recommended (given breakthrough times within 1 min) or poor (given breakthrough times within 1-9 min). Although the challenge solvents (2-BE and 2-EE) used are low volatile, the breakthrough time was not excellent. These combined criteria also suggest that such gloves are not protective enough. The ASTM defines standardized breakthrough detection time as the time when the permeation rate reaches 0.1 μg/cm^2/min.(5, 6)

Ansell provides a triple criteria scale for defining the efficiency of chemically protective gloves which includes: degradation resistance rating, permeation breakthrough time, and permeation rate.(11,12)

Ansell defines six different categories for the permeation rate as: Excellent with a permeation rate of <0.9 μg/cm^2/min; Very Good, 0.9-9; Good, 9-90; Fair, 90-900; Poor, 900-9000; and Not Recommended (NR), >9,000 μg/cm^2/min. Table 3.4 shows this categories. .(23, 24, ,38)

Rating	Permeation Rate ($\mu g/cm^2/min$)
Excellent (E)	<0.9
Very Good	0.9-9
Good	9--90
Fair	90-900
Poor	900--9000
Not Recommended (NR)	>9,000

Table 3.4. Ansell permeation rate criteria for Chemical Resistant Gloves. (23)

As can be seen from Tables 3.2 and 3.4, the steady state permeation rates for both 2-BE and 2-EE are located within the very good rating (0.9-9 $\mu g/cm^2/min$) based on Ansell's categorization. However Ansell indicates that a chemically protective glove can be safe if all of the following criteria are met: the degradation rating is excellent; permeation breakthrough time is 30 minutes or greater; and permeation rate is excellent, very good, or good. (23, 24) A color code rating system is used to simplify the selection process as for Kimberly-Clark.

Though the glove samples meet the Ansell SSPR criteria, this study indicated an immediate breakthrough time of 10 ±10 min for disposable nitrile gloves during exposure to both solvents and it is concluded that such gloves will receive a red label and are not suitable for exposure to 2-BE and 2-EE. Ansell provides another triple criteria for a glove to be approved with a green label as: the permeation rating is not specified, the permeation breakthrough time is 240 minutes or greater, and the degradation rating is excellent. This option is even harder to meet than previous one, because it requires a 240 minutes or greater breakthrough time.

3.5 CONCLUSIONS

Disposable purple nitrile exam gloves showed a higher permeability to 2-thoxyethanol comparing to 2-butoxyethanol. Since the permeation of 2-butoxyethanol and 2-ethoxyethanol exceeded the ASTM threshold normalized breakthrough detection time upon exposure, were categorized as not recommended with Kimberly Clark Professional permeation breakthrough time criteria, and could not comply with Ansell's triple criteria, the disposable purple nitrile exam gloves should not be used as personal protective equipment for exposure to 2-butoxyethanol or 2-ethoxyethanol even for very short period exposures.

3.6 ACKNOWLEDGEMENTS

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CHAPTER 4

PERMEATION OF LIMONENE THROUGH DISPOSABLE NITRILE GLOVES

4.1 ABSTRACT

The purpose of this study was to investigate the permeation of limonene through different disposable, unlined, unsupported, nitrile exam glove materials (blue, purple, sterling, and lavender) from Kimberly Clark. This study utilized the modified American Society for Testing and Materials (ASTM) F739-99a/2012 closed-loop permeation method. For each glove set, four 1-inch diameter standard permeation cells (3 cells with limonene as challenge and one air blank) were used with water as the collection solvent. Aliquots of 0.1 mL were taken at permeation time intervals of 1.0, 10, 20, 40, 60, and 80 min, 2.0, 4.0, 6.0, and 8.0 h. The analytical method was based on gas chromatography-mass spectrometry (GC-MS). The percent differences of the thickness and weight for the analytes before and after permeation on conditioning were less than 10 %. The ASTM normalized breakthrough time (NBRT) corresponding to 0.25 µg/cm² occurred at <10 minutes for lavender, <20 minutes for sterling, <40 minutes for purple, *and* <80 minutes for blue gloves. The average steady state permeation rate (SSPR) for blue, purple, sterling, and lavender was 0.013 ± 0.002 µg/cm^2/min, 0.069 ± 0.006 µg/cm^2/min, 0.077 ±0.010 µg/cm^2/min, and 0.295 ± 0.028 µg/cm^2/min respectively. The lavender gloves showed a significantly higher SSPR than all other glove samples ($P \leq 0.05$). The lavender, sterling, and purple gloves were categorized as "not recommended" by Kimberly Clark Professional permeation breakthrough time criteria and did not

comply with Ansell's criteria either. The lavender and sterling gloves should not be used as personal protective equipment for exposure to limonene, even for short period exposures. The blue gloves showed the best performance and met all requirements for "Excellent" for the Kimberly Clark and Ansell criteria.

4.2 INTRODUCTION

Personal protection equipment such as chemical-resistant gloves is the first line of defense against potential skin exposure to toxic chemicals in the workplace.(1) The National Institute for Occupational Safety and Health (NIOSH) emphasizes the selection of the most appropriate glove for exposure to chemicals and defines the time limit it can be worn and whether it can be reused.(1) It is estimated that more than 10% of the working population in the U.S. risk potential exposure to chemicals via skin contact.(2) Considering that dermatitis is one of the top 3 occupational disorders, the direct and indirect costs of medical compensation are on the billion dollar scale.(3)

Many chemicals, whether absorbed through the skin upon contact or inhaled, cause health problems.(4) In fact, research has revealed that skin absorption for a large number of chemicals can occur without the workers noticing.(4)

Although the major routes of entry for chemicals are inhalation, ingestion, and skin absorption, for many chemicals skin contact is crucial. The risks of skin absorption are particularly important for exposure to low-volatile compounds. Because of low vapor pressure, such chemicals can remain in the work environment for extended periods of time.(4) One of the physical features used in categorizing chemical volatility is boiling point. In general volatility is used to classify chemicals with boiling points below 150 ° C. Compounds that boil at or over 150 ° C are categorized as semi/nonvolatile compounds.(7)

The American Society for Testing and Materials (ASTM) F739-99/12 standard addresses the permeation process in open loop and closed loop forms. The open loop and closed loop models utilize gaseous and liquid collection media respectively. (5, 6)

The major criterion for choosing between these two methods is the volatility of the challenge solvent. The ASTM open loop module is essentially designed for highly volatile compounds with low boiling points. (8) The open loop testing model consists of a dynamic collection medium in which a carrier gas constantly flows across the challenge side and carries the vapor of the permeated analyte to a detector in a recycled system. However, compounds with low volatility are not readily vaporized (9) and the gaseous collection medium used in the open loop system may not capture and carry semi/non-volatile permeated compounds efficiently because of their low vapor pressure.(10, 11) This will result in reaching a unrealistic breakthrough times even if an analytical method with high sensitivity is used.(10, 11)

ASTM F739-99/12 recommends the closed loop method for low volatile solvents. In this method a liquid in the collection side is in direct contact with the permeated solvent, and at defined intervals samples are taken from the collection side for analysis. The collection solvent must not attack the material to be tested and must also solubilize the challenge compound sufficiently.

A handful of glove permeation studies have been conducted using the closed loop method and to date most research on glove permeation is focused on chemically protective gloves using the open loop model. The permeation data in catalogs provided by glove manufacturers are all based on the open loop model.

Mikatavage et al. (37) studied permeation of nitrile and Viton gloves in ASTM closed loop module challenged by chlorinated aromatic compounds. The results showed a 4 h breakthrough time for Viton gloves compared to less than 1 h for nitrile gloves. It was concluded that breakthrough time is a more reliable criteria for defining the performance of the gloves than the steady state permeation rate.

Xu et al.(12) studied permeation of various disposable gloves as nitrile, chloroprene, vinyl and latex gloves challenged by complex non-volatile water-insoluble straight oil metalworking fluids (MWF) using the ASTM F739-99a closed loop method. The results indicated that disposable nitrile gloves are safe and protective enough to be worn during exposure to metalworking fluids. In another study Xu et al.(13) compared the permeation of MWF through disposable nitrile gloves (SafeSkin) and chemically protective nitrile glove (Sol-Vex) in a closed loop system. Although the Ansell guideline categorized the disposable glove in the "very good" class, the breakthrough time was less than 30 min. It was therefore suggested that chemically protective gloves be used during exposure to MWFs.

Phalen et al (14) conducted a study on the permeation of the pesticide captan through disposable blue nitrile gloves using the ASTM closed loop method. The results showed a breakthrough time within two hours of exposure. Such gloves should be used only for a single occasion with no reuse option.

Limonene was chosen as challenge solvent because of its extensive use in industry and previously published studies that are all focused on the ASTM F739-99 open loop method. Other parameters such as low vapor pressure (1.5 mm Hg at 25 °C) and capability of instrumental methods in detecting and analyzing limonene at standardized breakthrough time (SBRT) concentration criteria were also considered during the selection process. Measured water solubility for limonene is 13.8 mg/L at 25 °C.(15, 38)

The worldwide annual production of Limonene in 2004 was over 150 million pounds (75,000 metric tons) and it is rising fast.(15, 16) The US Environmental Protection Agency (EPA) reported that every year in North America over 1 million tons of limonene is released into the air through natural sources and in globally some 23 million tons is emitted.(17) Some of limonene's physical properties include: boiling point; 175 °C, melting point; -74.35 °C, specific gravity; 0.841, flash point; 50 °C, and is used as a solvent component for many chemical formulations. (18) Limonene is a liquid solvent with a pale yellow color and a molar mass of 136 g/mol.

Limonene is used widely as solvent in resin manufacturing, lubricant, wetting and dispersing agents. It was recommended as replacement for chlorinated hydrocarbons such as dichloroethene and trichloroethane which are highly toxic and carcinogenic.(19) Limonene is used as an flavor and fragrance additive, in air-fresheners, hygienic products, hand cleaners and deodorants, and as an ingredient in pesticides, insect repellents, antimicrobial and antifungal solutions. It has also many applications in industrial procedures as a degreasing agent in the aircraft and textile industries, an adhesive agent, tank cleaning, paper softening, printing ink, paint, and polishing. Limonene has been used in pharmaceutical, microbiological, sweets, baked goods, gelatins and puddings, chewing gums, food beverages, ice cream and furniture industries.(20, 21, 22, 23)

Limonene can be absorbed through skin contact, inhalation, and ingestion. The absorption is very slow through the gastrointestinal system. Liver, kidneys, and blood system are counted as the main destinations for limonene. Studies on limonene shows it is metabolized to perillic acid and observed in plasma and urine. (24, 25, 26) The major portion of ingested limonene is found in urine in

48 h. (25, 27) Dermal exposure to limonene is quick and within 2 h symptoms as burning and itching have been reported.

Falk et al, (28) reported painful reflexes as itching and burning as well as skin swelling in less than 30 minutes from dermal exposure to limonene. A purpuric eruption started 6 h after exposure with itching symptoms, which continued for two days and rashes were noticeable for several weeks.

The American Conference of Governmental Industrial Hygienists (ACGIH), International Agency for Research on Cancer (IARC), and Occupational Safety and Health Administration (OSHA) have not classified limonene with respect to carcinogenicity to human. Developing renal and bladder tumors as well as liver enlargement in rats exposed to limonene have been reported.(19)

There exists no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for limonene. The American Industrial Hygiene Association (AIHA) adopted a workplace environmental exposure level (WEEL) of 30 ppm 8-hr time weighted average (TWA) for limonene.(29)

There is no previously published study using the ASTM closed loop permeation method for limonene, and its use is proposed in the present research. Chemically protective gloves including nitrile have been evaluated for limonene challenge by the ASTM open loop method. Forsberg reported a 65 minutes NBRT and 102 $mg/m^2/min$ SSPR for chemically protective gloves (neoprene) with 0.43 mm thickness. (30) The breakthrough time for other chemically protective gloves such as polyvinyl alcohol and Viton gloves exposed to limonene were 480 min.

The American Conference of Industrial Hygienists (ACGIH) has cited 68 min breakthrough time for Chemical Protective clothing for the Selection of Chemical Protective Clothing.(31) Kimberly Clark (32) indicated that the NBRT for the disposable nitrile gloves (silver and sterling) exposed to limonene as 105 min using the ASTM F739 open loop method. The corresponding SSPR was 0.157 pg/cm^2/min.

Computer-Aided Management of Emergency Operations chemicals (33) (a database of hazardous chemicals that emergency responders use to get response recommendations and predict hazards, such as explosions or chemical fires) reported 480 minutes breakthrough time for chemically protective gloves such as Polyvinyl alcohol gloves (0.23 mm), Nitrile Edmont (0.38 mm), and Viton (0.23 mm) for limonene. The breakthrough time for Neoprene Edmont gloves (0.43 mm) was reported 60 min.

The present research focused on permeation of limonene as a low volatile solvent through 4 different disposable powderless, unsupported, unlined nitrile exam gloves as *blue, purple, sterling, and lavender from* Kimberly Clark and determined the permeation parameters for the ASTM F739-1999/2012 closed loop method. The results will also be compare with those of the moving robotic hand permeation experiment.

4.3 EXPERIMENTAL

4.3.1 Chemicals, solvents, and glove samples

The gloves used were Kimberly Clark blue, purple, sterling, and lavender disposable gloves, all powder-free, unsupported, unlined, nitrile exam gloves, ordered from Fisher Scientific, Pittsburgh, PA.

The analyte, limonene (96%), was obtained from Acros Organics. 4-bromophenol (99%) was selected as the internal standard (IS) for the analytical method, gas chromatography-mass spectrometry (GC-MS). Helium (99.999%) from Air Products (Long Beach, CA) was used as carrier gas for gas chromatography-mass spectrometry (GC-MS) operation. The water utilized for all aqueous solutions was produced from two filtration systems, Millipore Milli-Q Water System and Millipore Simplicity portable ultrapure water purification system (Temecula, CA).

4.3.2 Equipment

Glove material thickness was measured at the palm region using an Electronic Digital Micrometer Model CO-030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific. A Mettler analytical balance AE260 Scale (Mettler, Hightstown, NJ) weighed the glove cuts. Modified ASTM F739-12 closed loop permeation cells model I-PTC-600 containing challenge chamber, collection chamber, Teflon gaskets, aluminum and stainless steel flanges and bolts were obtained from Pesce Lab (Kennett Square, PA).

The GC–MS system consisted of two components. One was an Agilent 6890N Gas Chromatograph with a non-polar, fused silica capillary column, 60 m length x 0.42 mm (external diameter), 0.32 mm internal diameter, 1-µm internal film thickness operated in the splitless mode contained in an 28 x 31 x 16 cm oven. The second component was an Agilent 5973 Mass Selective Detector (MSD) (Agilent Technologies).

A Thermo Nicolet Avatar 360 Fourier Transform (FT) Infrared Spectrometer was used for the acquisition of Infrared Reflectance (IR) spectra. The infrared spectra ranged from 4000 to 400 cm^{-1}, with 124 scans for higher resolution and spectra uploaded with OMNIC 6.0a software. The Avatar 360 Fourier-transform (FT) spectrophotometer system (Thermo Nicolet, Madison, WI) operated in the transmission mode and was equipped with a DTGS detector with KBr beam splitter. In the reflectance mode, a diamond cell was used.

4.3.3 Permeation procedure

Each set of glove samples were checked to be within expiration date. In order to fit into the permeation cells, the glove materials were cut from the palm area in two inch diameter circular pieces, and were conditioned in a desiccator at 52±1% and 23 ^{o}C for 24 h before the permeation test under an atmosphere generated by saturated potassium dichromate at room temperature (23 ^{o}C). In the next step, the glove cuts' average thickness (micrometer) at marked spots within 1 cm radius of circular area and mass (balance) were measured from triplicate measurements. The infrared reflectance spectra (Avatar 360) were also obtained for the challenge and collection surfaces of each glove piece using the clamp accessory.

Each circular glove cut was held in an ASTM type permeation cell between the Teflon gaskets and the Pyrex chambers and tightened using three bolts tightened with a 16 ft-lb torque wrench with the inner side of the glove facing the collection chamber (water) and the outer side facing the challenge chamber (limonene).(58, 59) The effective surface area between the challenge chamber and collection chamber was equivalent to an exposed diameter of 25.4 mm and was 507 mm^2 (5.07 cm^2).

Four 1-inch diameter permeation cells (3 experimental cells with challenge solvent and one air blank) were used with water as the collection fluid in a protocol based on the ASTM F 739-99/12 closed-loop permeation method. A 10 mL volume of the analyte (limonene) was added to the challenge chamber and 10 mL of collection solvent (water) pipetted into the collection chamber.

(31, 32) All cells were clamped to a shaking water bath and submerged with the water holding temperature at 35.0±0.5 °C and agitated with a horizontal movement of 7.0±0.5 cm/s which represents a 100 RPM cycle. This created a homogenous distribution of the permeant in the collection chamber and prevented concentration gradients. All above steps were repeated for each selected glove materials.

Aliquots of 0.1 mL were taken at permeation time intervals of *1.0, 10, 20, 40, 60, and 80 min, 2.0, 4.0, 6.0, and 8.0 h.* and deposited into 1.5-mL vials plus 2 µL of internal standard (4-bromophenol) at 0.1 ug/uL final concentration. Because of the small volume of the sample size (0.1 mL), care was taken to insert the tip of the needle containing the internal standard as close as possible to the sample to make sure it merged with the collection solution before side-to-side mixing. The sum of all samples taken did not exceed 10% of the initial collection solvent volume. The analytical method was based on gas chromatography-mass spectrometry (GC-MS) and internal standard method (4-bromophenol).

After the permeation test, glove specimens were blotted dry, and reconditioned in desiccator for reflectance IR analysis as well as thickness and mass measurement.

4.3.4 GC-MS analysis

The MS was initially used in the total ion current mode (TIC) to extract intensities of all mass spectral peaks over the mass to charge ratio (m/z) range of 50–500. Thus, the purities of the analytes, solvents, and internal standard were examined. The injected volume for all samples was 2.5 µL. In the next quantification phase, to define breakthrough times, the selected ion monitoring mode (SIM) was used to enhance sensitivity and selectivity for the compounds of interest (at m/z 68, 93 for limonene and m/z 172 for the 4-bromophenol internal standard).

The GC temperature program for limonene, the injector temperature was 250 ° C and the column temperature started at 120 ° C for 2 min and ramped at 25 ° C /min to 200 ° C, held for 2 min, and ramped at 100 ° C/min up to 280 ° C with a final hold 3.6 min at a helium flow rate of 1.0 mL/min. The set point temperature for inlet, ion source, and MS quadrupole were 250 ° C, 230 ° C, and 150 ° C respectively. The solvent delay and SIM dwell time were set at 2 min. The selection of the internal standard was based on not interfering with the analyte and stable response in a sensitive linear range at which the normalized breakthrough time could be detected.

1.00 mL of standard solutions of the analytes in water with concentrations of 0.00, 0.1, 0.3, 0.5, 1, 5, 10 and 100 ng/µL were made in the presence of 1.0 µg/µL of the internal standard (aliquots of 2.0 µL from internal standard with of 0.1 µg/µL was added to each 0.100 mL standard and sample solution). After injection, the areas under the peaks for the analyte and internal standard were extracted using RTE manual integration. The area under the curve ratio of the limonene standard solutions over the internal standard was plotted versus the corresponding standard solution concentration.

To define the linear relationship features for standards such as slopes, intercepts, standard deviations, standard deviations of the slope and intercept, correlation coefficient, slope, and p-values, the linear regression model was used. The independent samples *Student* t-test was used to determine whether the average of two samples were significantly different and to define the p-values of r.

4.4 RESULTS

4.4.1 GC-MS Analytical Features

The GC-MS linear dynamic range for limonene was 0.1 ng to 10.0 ng with 0.1 ng detection limit and regression equation as $y = 0.4306x + 0.8795$ and a coefficient of determination as $R^2=0.992$. The retention times for the limonene and the internal standard were 5.4 min and 9.5 min, respectively. The total run time for each injection was 11.6 min.

GC-MS provided the minimum sensitivity required by ASTM criteria for analyzing 0.127 ng/uL of limonene. Based on the ASTM closed loop method normalized breakthrough time criteria (5), the analytical method should provide a minimum sensitivity of 0.25 μg/cm^2 of the permeant, which is equal to 0.127 ng/μL. (The area of the glove specimen with a diameter of 25.4 mm was 5.07 cm^2. 0.25 μg x 5.07 cm^2 =1.27 μg/10 mL analyte, which is equal to 0.127 ng/μL).

The water solubility for limonene is 0.0138 μg/mL at 25 °C. (15, 38) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with the solubility of limonene at 35 °C (0.028 μg/mL) in the collection volume assuming a doubling of solubility every 10 °C increase in temperature. Results confirmed that the collection medium provided adequate solubility for the permeant and the system did not reach to saturation point at 120 min in moving and still robotic hand experiments with blue gloves.

4.4.2 Blue Nitrile Gloves

The disposable blue nitrile gloves showed a standardized breakthrough time of 70 ±10 min, a normalized breakthrough time of 80 min, and a steady state permeation rate of 0.013 ±0.002 µg/cm^2/min. The average thickness of glove specimens before and after challenging were 128 ± 3 µm and 130 ± 2 µm respectively (not statistically significant $P \leq 0.05$). Table 4.1 indicates the standardized breakthrough time, steady state permeation rate, and diffusion coefficient for all glove samples. Also, the steady state permeation curves for all challenged glove materials are presented in Appendix A.1, A.2, and A.3. The average glove weights before and after exposure to limonene were 299 ± 5 mg and 307 ± 7 mg respectively (not statistically significant $P \leq 0.05$, Table 4-1).

Infrared reflectance analysis showed a higher absorbance in outer surface of the glove materials with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-300 cm^{-1}, which is a good indicator for limonene residuals on the glove surface. The same analysis on conducted for the inner side of the sample specimens, blank specimens, and conditioned specimens and no changes in the spectra was observed before and after the permeation test.

4.4.3 Purple Nitrile Gloves

The permeation parameters for purple gloves revealed a standardized breakthrough time of 30 ± 10 min a normalized breakthrough time of 40 min, and a steady state permeation rate of 0.069 ± 0.006 µg/cm^2/min. The average thickness of glove specimens before and after challenging were

104 ± 2 µm and 109 ± 3 µm respectively (statistically significant P ≤0.05). The average glove weights before and after exposure to limonene were 269 ± 4 mg and 276 ± 9 mg respectively (not statistically significant P ≤0.05, Table 4-1).

Infrared reflectance analysis on purple glove specimens showed an increase in absorbance on the outer surface of the glove materials with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-300 cm^{-1}, which is due to the limonene. Subtracting the exposed glove specimen’s spectra from unexposed ones confirmed the limonene on the outer side of the glove surfaces. Comparing the rest of the IR spectra between the challenged gloves and the blank indicates that the absorption is weaker in intensity after the permeation. This is due to loss of hydrophobic coatings on the challenge side of the glove during direct contact with limonene. However, such reductions were not observed for the inner side of the glove pieces.

4.4.4 Sterling Nitrile Gloves

The permeation parameters for sterling gloves revealed a standardized breakthrough time of 15 ± 5 min, a normalized breakthrough time of 20 min, and a steady state permeation rate of 0.077 ± 0.010 µg/cm^2/min. The average thickness of glove specimens before and after challenging were 73 ± 2 µm and 76 ± 3 µm respectively (not statistically significant P ≤0.05). The average glove weights before and after exposure to limonene were 193 ± 4 mg and 201 ± 6 mg respectively (statistically significant P ≤0.05, Table 4-1).

Infrared reflectance analysis on sterling glove specimens showed an intense increase in absorbance on both outer and inner surface of the glove at 888 cm^{-1} and 2800-300 cm^{-1} with the C-H bend and stretch. After subtracting the spectrum of the exposed gloves from unexposed ones, traces of limonene were observed on the outer and inner sides of the glove surfaces.

Infrared reflectance analysis on sterling glove specimens showed an intense reduction in absorbance on both outer and inner surfaces of the glove materials through the whole spectra. This is due to loss of hydrophobic coatings on the challenge side of the glove during direct contact with limonene.

4.4.5 Lavender Nitrile Gloves

The permeation parameters for lavender gloves revealed a standardized breakthrough time of 5 ± 5 min, a normalized breakthrough time of 10 min, and a steady state permeation rate of 0.295 ± 0.028 µg/cm^2/min. The average thickness of glove specimens before and after challenging were 59 ± 3 µm and 62 ± 4 µm respectively (not statistically significant $P \leq 0.05$). The average glove weights before and after exposure to limonene were 151 ± 3 mg and 155 ± 6 mg respectively (not statistically significant $P \leq 0.05$, Table 4-1).

Infrared reflectance analysis on lavender glove specimens showed an intense increase in absorbance on both outer and inner surfaces of the glove with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-300 cm^{-1}. After subtracting exposed gloves from unexposed ones, traces of limonene were observed on the outer and inner sides of the glove surfaces. The lavender infrared spectra also indicated an intense reduction in absorbance on both outer and inner surfaces of the glove materials through the whole wavelength range. This is due to loss of hydrophobic coatings on the challenge side of the glove during direct contact with limonene.

4.5 DISCUSSION

The average post-permeation thicknesses for all glove materials were 3.1% more than pre-permeation ones. Initial observations indicated swelling and discoloration after the permeation test on limonene. The discoloration was most vivid in purple gloves. Thickness measurements on purple glove specimens after reconditioning revealed a significant difference in thicknesses (P ≤ 0.05). However, such difference in thickness was not observed with other glove specimens (P ≤ 0.05). Plus, the thickness differential for all glove samples was less than 10%.

Glove Material	Thickness before challenging (µm)	Thickness after challenging (µm)	Weight before challenging (mg)	Weight after challenging (mg)
Blue	128 ± 3	130 ± 2 ^{NS}	299 ± 5	307± 7 ^{NS}
Purple	104 ± 2	109 ± 4 ^{S}	269 ± 4	276 ± 9 ^{NS}
Sterling	73 ± 2	76 ± 3 ^{NS}	193 ± 4	201 ± 6 ^{S}
Lavender	59 ± 3	62 ± 4 ^{NS}	151 ± 3	155 ± 6 ^{NS}

S: Significantly different
NS: Not Significant

Table 4.1, Average thicknesses for blue, purple, sterling, and lavender glove specimens before and after permeation.

Reconditioning after permeation experiments was a critical step before continuing other measurements or studies on glove materials. While it is clear that materials swelled during the permeation period itself, this was also reversible on reconditioning except for the purple gloves. All reconditioned samples, including blanks, showed some degree of weight increase after challenging with limonene. However the weight change was below 10 % for all glove samples. The sterling glove cuts weight before and after permeation was 193 ± 4 g and 201 ± 6 g respectively. This showed an average 4.1 % weight gain, which was significant (P ≤0.05).

The permeation parameters of limonene for the glove specimens are indicated in Table 4.2. The normalized breakthrough times for the lavender gloves were achieved within the first 10 minutes of the experiment. In fact, the collection chamber reached the *ASTM F739-99a/2012* (5, 6) 0.25 μg/cm^2 and 0.1 μg/cm^2 criterion for NBRT and SBRT upon limonene coming into contact with the glove materials. The observed NBRTs for the sterling, purple, and blue gloves was 15 ±5 min, 30 ±10 min, and 70 ±10 min respectively. This suggests that blue gloves are more protective than the other gloves.

Lavender gloves showed the highest permeation rate compared to the other glove samples ($P \leq 0.05$). The sterling gloves were second in permeation rate. Although the permeation rates for the sterling gloves was more than the purple, the difference was not significant ($P \leq 0.05$).

Defining the efficiency of the gloves using the ASTM standardized breakthrough detection time criterion(6) (0.1 μg/cm^2/min) revealed that the lavender gloves are not protective enough during exposure to limonene. However, Kimberly Clark Professional (KCP) and Ansell provide two different set of criteria for evaluating the effectiveness of the gloves. Kimberly Clark Professional, one of the largest manufacturers of disposable and chemical protective gloves, defines a dual criteria for chemical resistance rating of disposable nitrile gloves.(32) The major criteria for rating

Glove Material	Standardized Breakthrough Time (min)	Steady State Permeation Rate (μg/cm^2/min)	Diffusion Coefficient (cm^2/min) × 10^5
Blue	70 ± 10	0.013 ± 0.002	1.39 ± 0.24
Purple	30 ± 10	0.069 ± 0.006	7.2 ± 2.29
Sterling	15 ± 5	0.077 ±0.010	4.3 ± 1.11
Lavender	5 ± 5	0.295 ± 0.028	3.52 ± 0.75

Table 4.2, Permeation elements of limonene through Kimberly Clark blue, purple, sterling, and lavender disposable nitrile gloves

is based on normalized breakthrough time as indicated in Table 4.3. Based on this classification, lavender gloves are located in the "not recommended" category, sterling and purple gloves are in the "good" category, and blue gloves are in the "excellent" category. Kimberly Clark categorizes NBRT as: <1 min, not recommended (NR); 1-9 min, poor; 10-59 min, good; and 60-480 min as excellent. (32, 34)

Rating	**Permeation breakthrough time (min)**
Excellent (E)	60-480
Good (G)	10--59
Poor (P)	1--9
Not Recommended (NR)	< 1

Table 4.3 Kimberly Clark Professional (46) permeation breakthrough time criteria for chemical resistance rating of disposable nitrile gloves.

The second embedded criterion is boiling point. Solvents with boiling points of less than 24 ^{o} C are defined as high volatile and higher than 24 ^{o}C defined as low volatile.(32) However, other definitions abound in references characterize semi/non-volatile chemicals are characterized with a boiling point of 150 ^{o}C or higher. (7, 10, 39)

KCP defines a glove for exposure to low volatile compounds safe (green) if the permeation rating is excellent. Using the Kimberly Clark Professional scale, since limonene is a low volatile solvent and the permeation breakthrough time for exposure of disposable lavender nitrile *gloves to limonene* occurred upon contact, such gloves are categorized as either "not recommended" (given breakthrough times within 1 min) or "poor" (given breakthrough times within 1-9 min).

The purple and sterling gloves also are not safe, because their permeation breakthrough time is not "excellent". Only the blue gloves with excellent permeation breakthrough time rating are counted as safe for exposure to limonene. The ASTM defines standardized breakthrough detection time as the time when the permeation rate reaches 0.1 µg/cm^2/min.(5, 6)

Ansell provides a triple criteria scale for defining the efficiency of chemically protective gloves which includes: degradation resistance rating, permeation breakthrough time, and permeation rate.(35, 36)

Ansell defines six different categories for the permeation rate as: Excellent with a permeation rate of <0.9 µg/cm^2/min; Very Good, 0.9-9; Good, 9-90; Fair, 90-900; Poor, 900-9000; and Not Recommended (NR), >9,000 µg/cm^2/min. Table 4.4 shows this categories. .(35, 36)

As can be seen from Tables 4.2 and 4.4, the steady state permeation rates for all glove specimens are located within the "excellent" rating (<0.9 µg/cm^2/min) based on Ansell's categorization.

However Ansell indicates that a chemically protective glove can be safe if all of the following criteria are met: the degradation rating is "excellent"; permeation breakthrough time is 30 minutes or greater; and permeation rate is "excellent", "very good", or "good". (35, 36) A color code rating system is used to simplify the selection process as for Kimberly-Clark.

Rating	Permeation Rate (µg/cm^2/min)
Excellent (E)	<0.9
Very Good	0.9-9
Good	9--90
Fair	90-900
Poor	900--9000
Not Recommended (NR)	>9,000

Table 4.4. Ansell permeation rate criteria for Chemical Resistant Gloves. (35)

Though the glove samples met the Ansell SSPR criteria, this study indicated an immediate breakthrough time of 5 ±5 min for lavender disposable nitrile gloves during exposure to limonene and it is concluded that such gloves will receive a red label and are not suitable for exposure to limonene. The same conclusion can be made for the sterling and purple gloves. Although they passed the SSPR requirement, they both have breakthrough times less than 30 min (lavender; 15 ± 5 min, purple; 30 ± 10 min) which disqualifies them to pass the requirements as a safe glove. Only the blue gloves passed all three requirements and can be categorized as safe for exposure to limonene. Ansell provides another triple criteria for a glove to be approved with a green label when: the permeation rating is not specified, the permeation breakthrough time is 240 minutes or greater, and the degradation rating is "excellent". This option is even harder to meet than the previous one, because it requires a 240 minutes or greater breakthrough time. Thus even the blue disposable glove would not meet this criterion.

4.6 CONCLUSIONS

Disposable lavender, sterling, and purple nitrile exam gloves showed a high permeability to limonene. Since the permeation of limonene through lavender and sterling nitrile exam gloves exceeded the ASTM threshold normalized breakthrough detection time, such gloves were categorized as "not recommended" with Kimberly Clark Professional permeation breakthrough time criteria, and could not comply with Ansell's triple criteria. The disposable lavender and sterling nitrile exam gloves should not be used as personal protective equipment for exposure to limonene even for very short period exposures.

The blue gloves showed the highest performance for limonene and met all requirements in Kimberly Clark and Ansell grading system as "excellent". The Purple gloves are not as safe as blue ones, however they may be safe to be used for very short exposures less than 20 minutes.

4.7 ACKNOWLEDGEMENTS

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CHAPTER 5

PERMEATION OF LIMONENE THROUGH DISPOSABLE NITRILE GLOVES USING A DYNAMIC AND STATIC ROBOTIC HAND

5.1 ABSTRACT

The purpose of this study was to investigate the permeation of limonene, a low volatile solvent through different disposable, unlined, unsupported, nitrile exam glove materials (blue, purple, sterling, and lavender, from Kimberly Clark). This study utilized a robotic hand in a whole glove permeation model with moving and non-moving features. A Yeager robotic hand with enough strength for flexion and extension was chosen and assembled to fit the gloves. A circulating water system using Viton tubing was used to transfer water at 35.0±0.5 °C from the glove to the sampling point. The temperature of the gloved robot hand was also held at 35.0±0.5 °C in an incubator. A lab controller was used to control the robotic moving hand's flexion-extension cycle at 20 second intervals.

Aliquots of 1.0 mL were taken at permeation time intervals of 0, 10, 20, 40, 60, and 80 min, then 2.0, 4.0, 6.0, and 8.0 h., and deposited into 1.5-mL vials plus 2.0 μL of internal standard (4-bromophenol) at 1 μg/μL concentration. The sum of all samples taken did not exceed 10% of the initial collection solvent volume. The analytical method was based on gas chromatography-mass spectrometry (GC-MS) and internal standard method (4-bromophenol).

The average post-permeation thicknesses (before re-conditioning) for all glove materials in dynamic and static modules were more than 10% of the pre-permeation ones ($P \leq 0.05$), although this was not so on reconditioning. The static and dynamic robotic hands showed similar SBRTs: 5 ± 5 min for lavender, 15 ± 5 min for sterling and purple, and 30 ± 10 min for blue gloves. The SBRT for the blue and purple gloves in robotic hand was significantly shorter than the ASTM modified closed loop technique ($P \leq 0.05$). Lavender gloves showed a significantly higher SSPR when the moving robotic hand was used (0.490 ± 0.031) compared to a non-moving hand ($P \leq 0.05$). Although the respective SSPR for other gloves samples (blue, purple, and sterling) with the moving hand experiment appeared more than the static hand, the difference was not significant ($P \leq 0.05$).

The lavender, sterling, and purple gloves failed the Kimberly Clark Professional permeation breakthrough time criteria and Ansell's criteria for use, and therefore they should not be used as personal protective equipment for exposure to limonene, even for short exposure periods. Although blue gloves provided the highest performance against limonene compared to other gloves, they could not pass the criteria defined by KCP and Ansell as safe for occupational exposure to limonene. However, they may be safe for use with very short exposures to limonene (less than 20 minutes). Compared to the ASTM F739-99/12 model, the robotic hand permeation model is more sensitive and stringent in defining gloves' efficacy.

5.2 INTRODUCTION

Personal protection equipment such as chemical-resistant gloves is the first line of defense against potential skin exposure to toxic chemicals in the workplace.(1) The National Institute for

Occupational Safety and Health (NIOSH) emphasizes the importance of selecting the most appropriate glove for exposure to chemicals and defines the time limit it can be worn and whether it can be reused.(1) It is estimated that more than 10% of the working population in the U.S. risks potential exposure to chemicals via skin contact.(2) Considering that dermatitis is one of the top 3 occupational disorders, the direct and indirect costs of medical compensation are on the billion dollar scale.(3)

Many chemicals, whether absorbed through the skin upon contact or inhaled, cause health problems.(4) In fact, research has revealed that skin absorption for a large number of chemicals can occur without the workers noticing.(4)

Although major routes of entry for chemicals also include inhalation and ingestion, for many chemicals skin contact is crucial. The risks of skin absorption are particularly important when it comes to exposure to low-volatile compounds. Because of low vapor pressure, such chemicals can remain in the work environment for extended periods of time.(4) One of the physical parameters used in categorizing chemical volatility is boiling point. In general volatility is used to classify chemicals with boiling points below 150 ° C. Compounds that boil at or over 150 ° C are categorized as semi/nonvolatile compounds.(7)

The American Society for Testing and Materials (ASTM) F739-99/12 standard addressed the permeation process in both open loop and closed loop forms. The open loop and closed loop models utilize gaseous and liquid collection media respectively. (5, 6)

The major criterion for choosing between these two methods is the volatility of the challenge solvent. For compounds of high volatility, the open loop model is recommended. The ASTM open loop module is essentially designed for high volatile compounds with low boiling points. (8) The open loop testing model consists of a dynamic collection medium in which a carrier gas is constantly flowing across the challenge side and carries the vapor of the permeated analyte to a detector. However, compounds with low volatility are not readily vaporized, (9) and the gaseous collection medium used in the open loop system is not able to capture and carry semi/non-volatile permeated compounds efficiently because of the low vapor pressure of such chemicals.(10, 11) This will result in reaching an unrealistic breakthrough detection time and standardized breakthrough time even if an analytical method with high sensitivity is used.(10, 11)

ASTM F739-99/12 recommends the closed loop method for low volatile solvents. In this method a liquid in the collection side is in direct contact with the permeated solvent, and at defined intervals samples are taken from the collection side for analysis. The collection solvent must not attack the material to be tested, not backpermeate, and must also adequately solubilize the challenge compound.

A handful of glove permeation studies have been conducted using the closed loop method and to date most research on glove permeation is focused on chemically protective gloves using the open loop model. See Chapters 1 and 4 for more information on these studies.

The permeation data in catalogs provided by glove manufacturers are all based on the open loop model.

Although the ASTM closed loop model addresses the concern of non-volatile compounds in the collection chamber and provides more accurate breakthrough time and permeation rates, it may not necessarily represent on-site working conditions and the way a glove behaves in the workplace and on a worker.

Current research methods in both open loop and closed loop systems fail to take into account many other factors that may contribute to the permeation of chemicals through the protective glove barrier. For example, disposable glove thickness is not the same across different areas: finger tips are thicker and the wrist is thinner than the palm area. In existing testing methods the permeation experiment relies on a small portion of glove surface in the palm area, which may not be representative of the overall glove thickness. Moreover, the ASTM and other international standards study glove permeation under static conditions in which the glove specimen is held between two chambers at room temperature.

By contrast, in the workplace using gloves requires donning and doffing as well as frequent flexion and extensions throughout the work shift. Mechanical movement is a basic defined function for hands; as a result gloves will be under same dynamic forces as hands. This has been overlooked in the standards. Such short-comings in existing methods can result in non-realistic standardized breakthrough times (SBRT) and steady state permeation rates (SSPR) even if an analytical method with high sensitivity is used.(10, 11)

Boeniger et al(12) discussed the limitations of permeation standards with regard to chemicals with low vapor pressure and asserted that the ASTM permeation test method is not appropriate for over 80% of the chemicals in the threshold limit value (TLV) list with skin notation because they are categorized as low vapor pressure (≤defined here as <5 mm Hg).

To address the above concerns, a few studies have been conducted on different gloves using alternative methods such as flexed permeation methods, on-site permeation testing, and a whole glove permeation model.

Berardinelli et al(13) studied the permeation of acetone through a chemically protective glove using portable direct reading instruments, with a photoionization detector (PID, model PI-101, 10.2 eV) detection system, and compared the results with those of an ASTM F739 cell and an alternative smaller permeation cell. Results indicated no significant difference in breakthrough detection times between the PID detector and both permeation cells. However, the respective SSPR was differed.

Gunderson et al(14) studied the permeation of meta-phenylenediamine (MPDA) through chemically protective gloves, conducted an on-site testing method via stain sampling, and compared the results with laboratory testing methods. The results indicated that the breakthrough time for on-site samples was significantly lower than for laboratory testing.

Ceballos et al(37) discussed the limitations of the ASTM standard for evaluating the permeation of polymerizing materials through disposable latex gloves in spray coatings operations and developed a permeation panel. The panel used colorimetric SWYPE pads for defining breakthrough time and solid collection media for the permeation rate. Results indicated a 30-min breakthrough time and a rate of 2.9 ng/cm^2/min for 1,6-hexamethylene diisocyanate and isophorone diisocyanate through the disposable latex glove materials.

A study on permeation of chemotherapeutic drugs through surgical latex and polyvinyl chloride (PVC) gloves was conducted using a modified permeation cell with a pneumatic shocking feature. Results showed no significant difference in NBRTs between flexed and static permeation cells; however, the diffusion coefficient was significantly different. (38)

Perkins et al(39) studied the effects of glove flexure on permeation using chemically protective gloves as a whole glove model. The model utilized a high volatile compound (acetone) as a permeant and used air flow inside the glove as collection media, weighing gloves in different time intervals as an indicator of permeation. Although the method in general did not provide enough precision, permeation results did indicate a significant difference between gloves in static and flexed positions.

Mathews (40) studied the permeation of cyclohexanol through different nitrile gloves using a whole glove moving hand with circulating water as the collection media inside an enclosing outer larger glove and the results compared with a modified closed loop ASTM method. The results indicated a significant difference in NBRT and SSPR between ASTM cells and the moving hand for sterling gloves. While no significant difference was found between moving and non-moving hands with blue and purple gloves, the sterling gloves differed, the latter being the thinnest glove. This was suggestive of a glove thickness threshold for cyclohexanol-nitrile.

Phalen et al(41) developed a whole glove permeation test attached to a pneumatic system as a whole glove shocker to evaluate the permeation of ethanol, a high volatile solvent, through different disposable nitrile gloves. Air flow was used as collection media connected to a photoionization detector (PID) as an online direct monitoring system. Findings on the stressed whole glove model revealed that pneumatic movement resulted in earlier NBRT and a higher rate in SSPR than the static hand.

The worldwide annual production of limonene in 2004 was over 150 million pounds (75,000 metric tons) and it is rising fast.(15, 16) The U.S. Environmental Protection Agency (EPA) reported that every year in North America over 1 million tons of limonene is released into the air through natural sources. The respective value on a global scale is 23 million tons.(17) Some of limonene's physical properties include: boiling point, 175 °C; melting point, -74.35 °C; specific gravity, 0.841; flash point, 50 °C.(18) Measured water solubility for limonene is 13.8 mg/L at 25 °C.(15, 47)

A liquid solvent with a pale yellow color and a molar mass of 136 g/mol, limonene is used as a solvent component for many chemical formulations.

Limonene is used widely as a solvent in resin manufacturing, lubricants, and wetting and dispersing agents. It has been recommended as a replacement for chlorinated hydrocarbons such as dichloroethene, and trichloroethane which are highly toxic and suspected human carcinogens.(19) Limonene is also used as flavor and fragrance additive, in air-fresheners, hygienic products, hand cleaners and deodorants, and as an ingredient in pesticides, insect repellents, and antimicrobial and antifungal solutions. It also has many applications in industrial procedures as a degreasing agent in the aircraft industry, in textiles, as an adhesive agent, and in tank cleaning, paper softening, printing ink, paint, and polishing. Limonene has been used in pharmaceuticals, microbiological products, sweets, baked goods, gelatins and puddings, chewing gums, food beverages, ice cream and furniture industries. (17, 21, 22, 23)

Limonene can be absorbed through skin contact, inhalation, and ingestion. Absorption through the gastrointestinal system is very slow. The liver, kidneys, and blood system are the main target organs for limonene. Studies on limonene show that it is metabolized to perillic acid in plasma and urine. (24, 25, 26) The major portion of ingested limonene is found in urine within 48 h. (25, 27) By contrast, dermal exposure to limonene is quick; within 2 h symptoms such as burning and itching have been reported.

Falk et al(28) reported painful reflexes as itching and burning as well as skin swelling, in less than 30 minutes from dermal exposure to limonene. A purpuric eruption started 6 h after exposure with itching symptoms, which continued for two days, and rashes were noticeable for several weeks.

The American Conference of Governmental Industrial Hygienists (ACGIH), International Agency for Research on Cancer (IARC), and Occupational Safety and Health Administration (OSHA) have not classified limonene with respect to carcinogenicity in humans. However, rats exposed to limonene produced renal and bladder tumors as well as liver enlargement.(19)

There exists no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for limonene. The American Industrial Hygiene Association (AIHA) adopted a workplace environmental exposure level (WEEL) of 30 ppm 8-hr time weighted average (TWA) for limonene.(29) The maximum allowable workplace concentration (MAK) is 20 ppm based on skin sensitization and pregnancy risk.(48) There is no previously published study using the ASTM closed loop permeation method for limonene. Chapter 4 introduced the first permeation study on limonene using the ASTM closed loop method. See Chapter 4 for the other open loop studies with chemical protective gloves.

Limonene was chosen as challenge solvent because of its extensive use in industry and because previously published permeation data for it were are all focused on the ASTM F739-99 open loop method. Other parameters, such as low vapor pressure (1.5 mm Hg at 25°C) and capability of instrumental methods in detecting and analyzing limonene at standardized breakthrough time (SBRT) concentration criteria, were also considered during selection process. The experimental study started with the permeation of limonene using a whole glove hand in static position. The findings were used to address the second hypothesis of this study and compare the ASTM closed loop permeation model with that of the static robotic hand. To support the first hypothesis, a moving robotic hand was used to study the permeation of limonene through disposable nitrile gloves.

5.3 EXPERIMENTAL

5.3.1 Chemicals, solvents, and glove samples

The gloves used were Kimberly Clark blue, purple, sterling, and lavender disposable gloves, all powder-free, unsupported, unlined, nitrile exam gloves, ordered from Fisher Scientific, Pittsburgh, PA. The analyte, limonene (96%), was obtained from Acros Organics. 4-bromophenol (99%) was selected as the internal standard (IS) for the analytical method, gas chromatography-mass spectrometry (GC-MS) from Aldrich. Helium (99.999%) from Air Products (Long Beach, CA) was used as the carrier gas for the gas chromatography-mass spectrometry (GC-MS) operation. The water utilized for all aqueous solutions was produced from two filtration systems: Millipore Milli-Q Water System and Millipore Simplicity portable ultrapure water purification system (Temecula, CA).

5.3.2 Equipment

Glove material thickness was measured at the palm region using an Electronic Digital Micrometer Model CO-030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific. A Mettler analytical balance AE260 Scale (Mettler, Hightstown, NJ) weighed the glove specimens. A bionic robotic hand kit was ordered from Scientifics Direct, Inc., Tonawanda, NY. In order to be customized as a whole hand with moving option for permeation purposes, the kit required assembly and some modifications such as soldering, drilling, and adding parts and electronic features. Viton tubes (2.79 mm) were used for transferring and circulating the collection medium (water) from the glove to the sampling vial. Viton tubes were connected using PTFE (Polytetrafluorethylene) tubing; 1.48 mm as well as polypropylene T-connectors (Cole Parmer, Court Vernon Hill, IL). The power for continuous water circulating from the inner side of the glove samples to the sampling point was provided through a peristaltic Reglo 2-channel Var-Speed Analog pump (Cole Parmer, Court Vernon Hills, IL). The collection medium's temperature was stabilized at $35.0 \pm 0.5\ ^{o}C$ using a Corning Steering Hot Plate (Fisher Scientific). The analyte's temperature was also stabilized at

35.0 ± 0.5 °C using a Precision Laboratory Oven-Econotherm from Fisher Scientific. A Traceable Lab Controller was used to control the robotic moving hand's flexion-extension cycle at 20 second intervals (Fisher Scientific).

The GC–MS system consisted of two components: an Agilent 6890N Gas Chromatograph with a non-polar, HP-5MS fused silica capillary column, 60 m length x 0.42 mm (external diameter), 0.32 mm internal diameter, 1 µm internal film thickness operated in the splitless mode and a Mass Selective Detector (MSD), Agilent 5973 Mass Selective Detector (MSD) (Agilent Technologies). The Agilent 6890N Gas Chromatograph contains an oven with 28 × 31 × 16 cm dimensions.

A Thermo Nicolet Avatar 360 Fourier Transform (FT) Infrared Spectrometer was used for the acquisition of Infrared Reflectance (IR) spectra. The infrared spectra ranged from 4000 to 400 cm^{-1}, with 124 scans for higher resolution and spectra uploaded with OMNIC 6.0a software. The Avatar 360 Fourier-transform (FT) spectrophotometer system (Thermo Nicolet, Madison, WI) operated in the transmission mode and was equipped with a DTGS detector with KBr beam splitter. In the reflectance mode, a diamond cell was used.

5.3.3 Procedure

5.3.3.1 GC-MS

The MS was initially used in the total ion current mode (TIC) to extract intensities of all mass spectral peaks over the mass to charge ratio (m/z) range of 50–500. Thus, the purities of the analytes, solvents, and internal standard were examined. The injected volume for all samples was 2.5 µL. In the next quantification phase, to define breakthrough times, the selected ion monitoring mode (SIM) was used to enhance sensitivity and selectivity for the compounds of interest (at m/z 68, 93 for limonene and m/z 172 for the 4-bromophenol internal standard).

To set up the GC temperature programing for limonene, the column temperature started at 120° C for 2 min and ramped at 25° C /min to 200° C, held for 2 min, ramped at 100° C/min up to 280° C, and then held 3.6 min at a helium rate of 1.0 mL/min. The set point temperature for inlet, ion source, and MS quadrupole were 250° C, 230° C, and 150° C, respectively. The solvent delay and SIM dwell time were set for 2 min. The selection of the internal standard was based on not interfering with the analyte and stable response in a sensitive linear range at which the normalized breakthrough time could be detected.

1.00 mL of standard solutions of the analytes in water with concentrations of 0.00, 0.1, 0.3, 0.5, 1, 5, 10 and 100 ng/µL were made in the presence of 1.0 µg/µL of the internal standard (aliquots of 2.0 µL from internal standard with the concentration of 1.0 µg/µL was added to each 1.0 mL standard and sample solution). After injection, the areas under peak for the analyte and internal standard were extracted using RTE manual integration. The area under the curve ratios of the limonene over the internal standard were plotted versus the corresponding standard solution concentrations or mass injected.

To define the linear relationship features for standards such as slopes, intercepts, standard deviations, standard deviations of the slope and intercept, correlation coefficient, slope, and p-values, the linear regression model was used. The Student t-test was used to determine whether the average of two samples were significantly different and to define the p-values of r. To define relation between dependent and independent variables, the analysis of variance was used.

5.3.3.2 Whole Glove Permeation

Each set of glove samples was checked to be within expiration date. The gloves were conditioned in a desiccator at 52±1% and 23 ^{o} C for 24 h before the permeation test under an atmosphere generated by saturated potassium dichromate at room temperature (23 ^{o} C). The selected glove average thicknesses (micrometer) at marked spots of the palm were measured from triplicate measurements. The thicknesses and weights were measured before and after permeation (before re-conditioning). The infrared reflectance spectra (Avatar 360) were also obtained for the challenge and collection surfaces of each glove using the clamp accessory.

At the next step the robotic hand was covered with a chemically protective Solvex nitrile glove as a primary barrier against the analyte and collection solvents. A beaker holding 100 mL of water was conditioned at 35^{o} C in the hot plate/stirrer, acting as a water bath for the collection solvent. Then a modified 40 mL vial with two holes (one each for supply and return water) was attached to a clamp and held in the water bath.

The Viton tubing was cut in duplicate to 3 different dimensions as 2 pieces in 29”, 2 piece 21” and 2 piece in 12” for circulating water through the system. Two Viton tubes were inserted in the peristaltic pump with one Viton 3-stop tubing in each tube (channel). Each 3-stop tubing had supply and return ends. One of the 21” Viton tubes connected to the supply end of the first 3-stop tubing at the first channel and the other one connected to the return section of 3-stop tubing at the second channel. The other end of both 21” Viton tubes connected to the 40 mL vial through the separate holes made in the cap. An 18 gauge needle was used to make holes over every 0.5” at the first 9” of one of the 29” Viton tubes, and the punctured end of the tube was heated with a burner and sealed. The holes acted as water suppliers for the glove. The 29” Viton tubes were used as water supply and return connections from the peristaltic pump to the whole glove set in the oven with an optimized flow rate of 16 mL/min. The sealed punctured side of the 29” Viton tube was wrapped around the glove (Robotic hand) within 1” from the cuff and the other side fitted to the supply end of the second 3-stop tubing. The 12” Viton tubes were placed at pronation and supination of the hand and collected water from both sides of the glove. The front side of the 12” Viton tubes jointed with a T-connector which directly attached to the second 29” Viton tube and led to the return end of the first 3-stop tubing. The supply end of the first 3-stop tubing led to the 40 mL vial.(40)

Aliquots of 80 mL from the purified water were added to the space between the disposable nitrile glove and the chemical protective glove, and 20 mL of the water added to the sampling point, 40 mL vial. To avoid spilling of the water, parafilm tape was wrapped over the cuff of the glove. Finally, the robotic hand was held into a desiccator containing the analyte (limonene) with 7.5” of the glove from the tip of the middle finger immersed in limonene.

A jacket shield was made and covered around the toggle switch to protect the connections from overheating and prevent physical damage during the permeation. The robotic hand fingers were covered with clear duct tape to cover and remove sharp edges, protect the chemically protective glove from physical damage, and facilitate donning and doffing procedures. An overview schematic model of the whole glove permeation is shown in Figure 5.1.

Aliquots of 1.0 mL were taken at permeation time intervals of 0, 10, 20, 40, 60, and 80 min, 2.0, 4.0, 6.0, and 8.0 h., and deposited into 1.5-mL vials plus 2.0 µL of internal standard (4-bromophenol) with 1.0 µg/uL concentration. The sum of all samples taken did not exceed 10% of the initial collection solvent volume. The analytical method was based on gas chromatography-mass spectrometry (GC-MS) and internal standard method (4-bromophenol). After the permeation test, glove specimens were blotted dry and reconditioned in the desiccator for reflectance IR analysis as well as measured for thickness and mass.

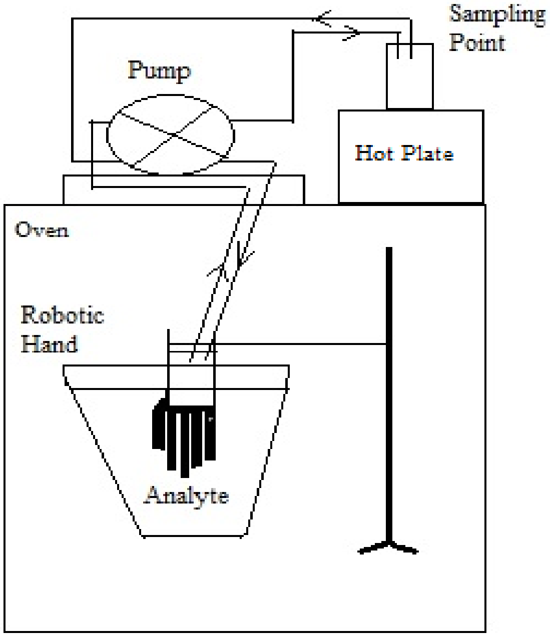

Figure 5.1: Robotic hand permeation model

The first phase of the whole glove permeation test started with a still hand and continued with the moving hand feature. The total permeated mass of the analyte was calculated for each time interval, and the mass taken during each sampling time was included in the total mass. The commutative permeation curve was plotted by permeated mass/area of the analyte on the *y* axis versus time on the *x*-axis. The steady state permeation rate was defined as the area of the permeation curve with the steepest slope.

Lag time (t_l) was measured by the extension of the steady state section of the permeation curve to the horizontal time axis, where mass/area reaches zero, and the diffusion coefficient was calculated using the equation 5-1.

$$D = \frac{L^2}{6t_i} \qquad (5-1)$$

5.4 RESULTS

5.4.1 GC-MS Analytical Features

The MS was initially used in the total ion current mode (TIC) to record intensities of all mass spectral peaks over the mass to charge ratio (m/z) range of 50–500. Thus, the purities of the analyte and internal standard were verified as 96% and 99%, respectively. The GC-MS working ranges were 0.1 ng to 1.0 ng and 1.0 ng to 10.0 ng with 0.1 ng as lower quantifiable limit. The retention times for limonene and the internal standard were 5.4 min and 9.5 min, respectively. The total run time for each injection was 11.6 min.

5.4.2 Glove Surface Area Measurements

Table 5.1 shows the glove area for the selected samples with medium size. The glove area was the key factor which impacted permeation parameters. The glove area for the blue, purple, and sterling gloves were extracted from the calculated values indicated in Mathew's study (40).

The surface area for lavender gloves was measured with the breaking the glove surface into wrist, palm, and fingers. The presented glove surface area in Table 5.1 includes the whole glove area. However, since the first two inches of the wrist area was not directly exposed to the analyte, this region was not included in calculating permeation parameters. The blue gloves are holding the maximum surface area with an average area of 1242 ± 10 cm^2 and calculated surface area for lavender gloves showed an average area of 910 ± 15 cm^2, which was the lowest surface area among all glove specimens.

Glove Model	Area (cm^2)
Blue	1242±10
Purple	1129±51
Sterling	1067±10
Lavender	910 ±15

Table 5.1, calculated glove area for selected glove samples. (40)

5.4.3 Blue Nitrile Gloves

Table 5.2 and 5.3 present permeation parameters for individual permeations in whole glove dynamic and static robotic hand models respectively. Also other glove characteristic such as weight and thickness before and after permeation experiments for moving and still robotic hand models are indicated in Table 5.4 and 5.5 respectively. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry. Table 5.6 compares average permeation parameters for the blue gloves between static robotic hand and ASTM permeation models with standard deviation for triplicate experiments. Table 5.7 compares average permeation parameters for the blue gloves between still and moving robotic hand models with standard deviation for triplicate experiments. The average steady state permeation curves for the challenged blue glove materials in still and moving robotic hand models are provided in Appendix A.2 and A.3 respectively.

Glove Material	Replicate	SBRT (min)	SSPR (µg/cm^2/min)	$D_f \times 10^{-5}$ (cm^2/min)	SSPP (min)
Blue Moving Robotic Hand	A	30 ± 10	0.0103	0.00008	40 - 80
	B	30 ± 10	0.0094	0.00012	40 - 80
	C	30 ± 10	0.0113	0.00009	40 - 80
Average		5 ± 5	0.0103	0.00010	40 - 80
Purple Moving Robotic Hand	A	15 ± 5	0.0620	0.00006	20 - 60
	B	15 ± 5	0.0680	0.00007	20 - 60
	C	15 ± 5	0.0710	0.00010	20 - 60
Average		15 ± 5	0.0670	0.00008	20 - 60
Sterling Moving Robotic Hand	A	15 ± 5	0.0950	0.00012	20 - 60
	B	15 ± 5	0.1050	0.00011	20 - 60
	C	15 ± 5	0.1000	0.00008	20 - 60
Average		5 ± 5	0.1000	0.00010	20 - 60
Lavender Moving Robotic Hand	A	5 ± 5	0.4380	0.00015	10 - 40
	B	5 ± 5	0.3960	0.00032	10 - 40
	C	5 ± 5	0.4350	0.00017	10 - 40
Average		5 ± 5	0.4230	0.00021	10 - 40

Table 5.2, Permeation parameters for blue, purple, sterling, and lavender nitrile gloves in whole glove moving hand permeation model.

Glove Material	Replicate	SBRT (min)	SSPR (μg/cm^2/min)	$D_f \times 10^{-5}$ (cm^2/min)	SSPP (min)
Blue Still Robotic Hand	A	30 ± 10	0.0103	1.10	40 - 80
	B	30 ± 10	0.0094	1.04	40 - 80
	C	30 ± 10	0.0113	0.61	40 - 80
Average		30 ± 10	0.0103	0.92	40 - 80
Purple Still Robotic Hand	A	15 ± 5	0.0620	8.85	20 - 60
	B	15 ± 5	0.0680	10.9	20 - 60
	C	15 ± 5	0.0710	13.1	20 - 60
Average		15 ± 5	0.0670	11.05	20 - 60
Sterling Still Robotic Hand	A	15 ± 5	0.0950	7.51	20 - 60
	B	15 ± 5	0.1050	6.10	20 - 60
	C	15 ± 5	0.1000	5.46	20 - 60
Average		15 ± 5	0.1000	6.36	20 - 60
Lavender Still Robotic Hand	A	5 ± 5	0.4380	33	10 - 40
	B	5 ± 5	0.3960	12	10 - 40
	C	5 ± 5	0.4350	11	10 - 40
Average		5 ± 5	0.4230	19	10 - 40

Table 5.3, Permeation parameters for blue, purple, sterling, and lavender nitrile gloves in whole glove still hand permeation model.

Glove Material	Thickness before challenging (μm)	Thickness after challenging (μm)	Weight before challenging (g)	Weight after challenging (g)
Blue	121 ± 3	135 ± 2	6.66 ± 0.05	7.02 ± 0.10
Purple	106 ± 3	124 ± 3	5.96 ± 0.20	6.84 ± 0.40
Sterling	74 ± 4	86 ± 5	3.94 ± 0.01	4.76 ± 0.06
Lavender	59 ± 3	73 ± 3	3.17 ± 0.02	4.11 ± 0.20

Table 5.4, Average thicknesses and weight for blue, purple, sterling, and lavender gloves in moving robotic hand module before and just after permeation.

Glove Material	Thickness before challenging (μm)	Thickness after challenging (μm)	Weight before challenging (g)	Weight after challenging (g)
Blue	122 ± 3	136 ± 2	6.56 ± 0.03	7.07± 0.20
Purple	105 ± 2	122 ± 4	5.94 ± 0.10	6.71 ± 0.50
Sterling	74 ± 3	85 ± 5	3.93 ± 0.05	4.65 ± 0.15
Lavender	58 ± 2	72 ± 4	3.17 ± 0.02	4.20 ± 0.40

Table 5.5, Average thicknesses and weight for blue, purple, sterling, and lavender gloves in still robotic hand module before and just after permeation.

The water solubility for limonene is 0.0138 μg/mL at 25 °C. (15, 47) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with the solubility of limonene at 35 °C (0.028 μg/mL) in the collection volume assuming a doubling of solubility every 10 °C increase in temperature. Results confirmed that the collection medium provided adequate solubility for the permeant and the system did not reach to saturation point at 120 min in moving and still robotic hand experiments with blue gloves.

Glove Material	SBRT (min)	SSPR (µg/cm^2/min)	Df (cm^2/min) × 10^{-5}	SSPP (min)
Blue				
Static Robotic Hand	30 ± 10	0.010 ± 0.001	9.2 ± 2.7	40 – 80
ASTM Closed Loop	70 ± 10	0.013 ± 0.002	1.39 ± 0.24	240 – 480
Purple				
Static Robotic Hand	15 ± 5	0.067 ± 0.005	11 ± 2.2	20 – 60
ASTM Closed Loop	30 ± 10	0.069 ± 0.006	7.2 ± 2.29	40 – 80
Sterling				
Static Robotic Hand	15 ± 5	0.100 ±0.006	6.3 ± 1.10	20 – 60
ASTM Closed Loop	15 ± 5	0.077 ±0.010	4.3 ± 1.11	120 – 360
Lavender				
Static Robotic Hand	5 ± 5	0.423 ± 0.031	18 ± 12	10 – 40
ASTM Closed Loop	5 ± 5	0.284 ± 0.023	13.52 ± 2.75	20 – 60

Table 5.6, Permeation elements of limonene through Kimberly Clark blue, purple, sterling, and lavender disposable nitrile gloves in whole glove static hand and ASTM closed loop modules.

Glove Material	SBRT (min)	SSPR (µg/cm^2/min)	D_f (cm^2/min) × 10^{-5}	SSPP (min)
Blue				
Static Robotic Hand	30 ± 10	0.010 ± 0.001	9.2 ± 2.9	40 – 80
Moving Robotic Hand	30 ± 10	0.012 ± 0.001	9.9 ± 1.2	40 – 80
Purple				
Static Robotic Hand	15 ± 5	0.067 ± 0.005	11 ± 2.4	20 – 60
Moving Robotic Hand	15 ± 5	0.078 ± 0.007	7.9 ± 2.2	20 – 60
Sterling				
Static Robotic Hand	15 ± 5	0.100 ±0.006	6.3 ± 1.10	20 – 60
Moving Robotic Hand	15 ± 5	0.104±0.006	10.4 ± 2.7	20 – 60
Lavender				
Static Robotic Hand	5 ± 5	0.423 ± 0.031	18 ± 12	10 – 40
Moving Robotic Hand	5 ± 5	0.490 ± 0.029	21 ± 9.6	10 – 40

Table 5.7, Permeation elements of limonene through Kimberly Clark blue, purple, sterling, and lavender disposable nitrile gloves in whole glove still hand and moving hand modules.

5.4.3.1 Moving Hand

Table 5.2 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual blue glove permeation experiments in whole glove dynamic robotic hand model. Also, other blue gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.4. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 4.7 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The disposable blue nitrile gloves in moving hand experiment showed an average standardized breakthrough time of 30 ±10 min, an average steady state permeation rate of 0.012 ± 0.001 µg/cm^2/min, and an average apparent diffusion coefficient of 9.9 ± 1.2 cm^2/min. The steady state permeation period (SSPP) was ranged between 40 to 80 min.

The average thickness of glove specimens at the palm area before and after challenging (before reconditioning) were 121 ± 3 µm and 137 ± 2 µm respectively ($P \leq 0.05$). The average thickness after reconditioning was 124 ± 3 µm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and after exposure to limonene were 6.66 ± 0.05 g and 7.02 ± 0.10 g respectively This reflected a significant weight gain ($P \leq 0.05$). The average permeated concentration in collection solvent with the whole glove moving robotic hand at 120 min was calculated as 0.0035 µg/mL. Such permeated concentration confirmed that the dynamic robotic hand permeation set with blue gloves did not reach the saturation point of 0.0138 µg/mL at 25 °C on injection point or 0.028 µg/mL at 35 °C during the permeation experiment and water solubility was adequate to capture the permeated analyte.

Infrared reflectance analysis showed a stronger absorbance in the outer surface of the glove materials with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-3000 cm^{-1}, which is a good indicator for residual limonene on glove surfaces. However, such differences were not found in the inner surfaces of the glove specimens. The spectra for the moving hand permeation with blue gloves is provided in Appendix B.

5.4.3.2 Still Hand

Table 5.3 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual blue glove permeation experiments in whole glove static robotic hand model. Also, other blue gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.5. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 9.1 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The disposable blue nitrile gloves in the still the hand experiment showed an average standardized breakthrough time of 30 ± 10 min, an average steady state permeation rate of 0.010 ± 0.001 $\mu g/cm^2/min$, and an average apparent diffusion coefficient of 9.2 ± 2.9 cm^2/min. The steady state period range between 40 to 80 min. The average thickness of glove specimens before and after challenging were 122 ± 3 µm and 139 ± 2 µm respectively ($P \leq 0.05$). The average thickness after reconditioning was 125 ± 3 µm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$.

The average glove weights before and after exposure to limonene were 6.56 ± 0.03 g and 7.07 ± 0.20 g respectively. This reflected a significant weight gain ($P \leq 0.05$). The average permeated concentration in collection solvent with the whole glove still robotic hand at 120 min was calculated as 0.0028 µg/mL. Such permeated concentration confirmed that the dynamic robotic hand permeation set with blue gloves did not reach the saturation point of 0.0138 µg/mL at 25 °C on injection point or 0.028 µg/mL at 35 °C during the permeation experiment and water solubility was adequate to capture the permeated analyte.

Infrared reflectance analysis showed similar trends to the moving hand with a higher absorbance in outer surface of the glove materials with the C-H bend at 888 cm^{-1} and C-H stretch at 2800-300 cm^{-1}, which is a good indicator for residual limonene on the glove. However, such differences were not found in the inner surfaces of the glove specimens. The spectra for the still hand permeation with blue gloves is provided in Appendix B.

5.4.4 Purple Nitrile Gloves

Table 5.2 and 5.3 present permeation parameters for individual permeations in whole glove dynamic and static robotic hand models with purple gloves respectively. Also other glove characteristic such as weight and thickness before and after permeation experiments for moving and still robotic hand models are indicated in Table 5.4 and 5.5 respectively. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry. Table 5.6 compares average permeation parameters for the purple gloves between static robotic hand and ASTM permeation models with standard deviation for triplicate experiments. Table 5.7 compares average permeation parameters for the purple gloves between still and moving robotic hand models with standard deviation for triplicate experiments. The steady state permeation curves for all challenged purple glove materials in still and moving robotic hand models are provided in Appendix A.2 and A.3 respectively.

The water solubility for limonene is 0.0138 µg/mL at 25 °C. (15, 47) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with the solubility of limonene at 35 °C (0.028 µg/mL) in the collection volume assuming a doubling of solubility every 10 °C increase in temperature. Results confirmed that the collection medium provided adequate solubility for the permeant and the system did not reach to saturation point at 120 min in moving and still robotic hand experiments with blue gloves.

5.4.4.1 Moving Hand

Table 5.2 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual purple glove permeation experiments in whole glove dynamic robotic hand model. Also, other purple gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.4. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 8.3 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The disposable purple nitrile gloves in the moving hand experiment showed a standardized breakthrough time of 15 ±5 min, an average steady state permeation rate of 0.078 ± 0.007 µg/cm^2/min, and an average apparent diffusion coefficient of 7.9 ± 2.2 cm^2/min. The steady state period was observed ranged between 20 to 60 min. The average thicknesses of glove specimens before and just after challenging were 106 ± 3 µm and 124 ± 3 µm respectively ($P \leq 0.05$). The average thickness after reconditioning was 107 ± 2 µm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$.The average glove weights before and after exposure to limonene were 5.96 ± 0.2 g and 6.84 ± 0.5 g respectively. This reflected a significant weight gain ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove moving robotic hand at 120 min was calculated as 0.0092 µg/mL. Such permeated concentration confirmed that the dynamic robotic hand permeation set with blue gloves did not reach the saturation point of 0.0138 µg/mL at 25 °C on injection point or 0.028 µg/mL at 35 °C during the permeation experiment and water solubility was adequate to capture the permeated analyte.

Infrared reflectance analysis showed an increase in absorbance on the outer surface of the glove materials with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-300 cm^{-1}, due to excess limonene. Subtracting the exposed glove specimen's spectra from unexposed ones confirmed the limonene on the outer side of the glove surfaces. However such difference was negligible for inner side of the glove. The spectra for the moving hand permeation with purple gloves is provided in Appendix B.

5.4.4.2 Still Hand

Table 5.3 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual purple glove permeation experiments in whole glove static robotic hand model. Also, other purple gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.5. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 6.8 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The disposable purple nitrile gloves in the still hand experiment showed an average standardized breakthrough time of 15 ± 5 min, an average steady state permeation rate of 0.067 ± 0.005 $\mu g/cm^2/min$, and an average apparent diffusion coefficient of 11.0 ± 2.4 cm^2/min. The steady state period ranged between 20 to 60 min. The average thicknesses of glove specimens before and after challenging were 105 ± 2 µm and 122 ± 4 µm respectively ($P \leq 0.05$). The average thickness after reconditioning was 107 ± 3 µm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and after exposure to limonene were 5.94 ± 1 g and 6.71 ± 0.5 g respectively. This reflected a significant weight gain ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove moving robotic hand at 120 min was calculated as 0.0084 µg/mL. Such permeated concentration confirmed that the dynamic robotic hand permeation set with blue gloves did not reach the saturation point of

0.0138 μg/mL at 25 °C on injection point or 0.028 μg/mL at 35 °C during the permeation experiment and water solubility was adequate to capture the permeated analyte.

Infrared reflectances were similar to the moving hand spectra with an increase in absorbance on the outer surface of the glove materials with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-300 cm^{-1}, due to excess limonene. Subtracting the exposed glove specimen's spectra from unexposed ones confirmed the limonene on the outer side of the glove surfaces. However, such difference was not found in the inner surface of the glove specimens. The spectra for the still hand permeation with purple gloves is provided in Appendix B.

5.4.5 Sterling Nitrile Gloves

Table 5.2 and 5.3 present permeation parameters for individual permeations in whole glove dynamic and static robotic hand models with sterling gloves respectively. Also other glove characteristic such as weight and thickness before and after permeation experiments for moving and still robotic hand models are indicated in Table 5.4 and 5.5 respectively. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry. Table 5.6 compares average permeation parameters for the sterling gloves between static robotic hand and ASTM permeation models with standard deviation for triplicate experiments. Table 5.7 compares average permeation parameters for the sterling gloves between still and moving robotic hand models with standard deviation for triplicate experiments. The steady state permeation curves for all challenged sterling glove materials in still and moving robotic hand models are provided in Appendix A.2 and A.3 respectively.

The water solubility for limonene is 0.0138 µg/mL at 25 °C. (15, 47) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with the solubility of limonene at 35 °C (0.028 µg/mL) in the collection volume assuming a doubling of solubility every 10 °C increase in temperature. Results confirmed that the collection medium provided adequate solubility for the permeant and the system did not reach to saturation point at 120 min in moving and still robotic hand experiments with blue gloves.

5.4.5.1 Moving Hand

Table 5.2 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual sterling glove permeation experiments in whole glove dynamic robotic hand model. Also, other sterling gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.4. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 6.04 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The permeation parameters for the sterling nitrile gloves in the moving hand experiment revealed an average standardized breakthrough time of 15 ± 5 min, an average steady state permeation rate of 0.104±0.006 µg/cm^2/min, and an average apparent diffusion coefficient of 10.4 ± 2.7 cm^2/min. The steady state period ranged between 20 to 60 min. The average thicknesses of glove specimens before and after challenging were 74 ± 4 µm and 88 ± 5 µm respectively ($P \leq 0.05$). The average thickness after reconditioning was 75 ± 3 µm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and just after exposure to limonene were 3.94 ± 0.01 g and 4.76 ± 0.06 g respectively. This reflected a significant weight gain ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove moving robotic hand at 120 min was calculated as 0.0132 µg/mL. Water solubility was adequate to define the steady state permeation period.

Infrared reflectance analysis on sterling glove specimens showed an intense increase in absorbance on both the outer and inner surfaces of the glove the C-H bend at 888 cm^{-1} and the C-H stretch 2800-300 cm^{-1}. Traces of limonene were observed on the outer and inner sides of the glove after subtracting the exposed gloves absorbance from that of the unexposed ones.

Infrared reflectance analysis on sterling glove specimens showed an intense reduction in absorbance on both the outer and inner surfaces of the glove materials through the whole spectra. The spectra for the moving hand permeation with sterling gloves is provided in Appendix B.

5.4.5.2 Still Hand

Table 5.3 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual sterling glove permeation experiments in whole glove static robotic hand model. Also, other sterling gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.5. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 5.0 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10 % coefficient variation in measurements as a quantitative criteria. ($P \leq 0.05$).

The permeation parameters for the sterling nitrile gloves revealed an average standardized breakthrough time of 15 ±5 min, an average steady state permeation rate of 0.100 ±0.007 μg/cm^2/min, and an average apparent diffusion coefficient of 6.3 ± 1.10 cm^2/min. The steady state period ranged between 20 to 60 min. The average thicknesses of glove specimens before and after challenging were 74 ± 3 μm and 88 ± 5 μm respectively ($P \leq 0.05$). The average thickness after reconditioning was 75 ± 4 μm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and after exposure to limonene were 3.93 ± 0.02 g and 4.65 ± 0.08 g respectively ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove still robotic hand at 120 min was calculated as 0.0118 μg/mL. Water solubility was adequate to define the steady state permeation period.

Observations on infrared reflectance analysis on the sterling still hand glove specimens were similar to those on the moving hand spectra; an intense increase in absorbance on both outer and inner surfaces of the glove with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-3000 cm^{-1}. Traces of limonene were observed on the outer and inner sides of the glove after subtracting the exposed gloves absorbance from unexposed ones. Infrared reflectance analysis on sterling glove specimens showed an intense reduction in absorbance on both outer and inner surfaces of the glove materials through the whole spectra. The spectra for the still hand permeation with sterling gloves is provided in Appendix B.

5.4.6 Lavender Nitrile Gloves

Table 5.2 and 5.3 present permeation parameters for individual permeations in whole glove dynamic and static robotic hand models respectively. Also other glove characteristic such as weight and thickness before and after permeation experiments for moving and still robotic hand models are indicated in Table 5.4 and 5.5 respectively. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry. Table 5.6 compares average permeation parameters for the lavender gloves between static robotic hand and ASTM permeation models with standard deviation for triplicate experiments. Table 5.7 compares average permeation parameters for the lavender gloves between still and moving robotic hand models with standard deviation for triplicate experiments. The steady state permeation curves for all challenged lavender glove materials in still and moving robotic hand models are provided in Appendix A.2 and A.3 respectively.

The water solubility for limonene is 0.0138 µg/mL at 25 °C. (15, 47) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with the solubility of limonene at 35 °C (0.028 µg/mL) in the collection volume assuming a doubling of solubility every 10 °C increase in temperature.

5.4.6.1 Moving Hand

Table 5.2 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual lavender glove permeation experiments in whole glove dynamic robotic hand model. Also, other lavender gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.4. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 6.8 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10% coefficient variation in measurements as a quantitative criteria.

The permeation parameters for the moving hand permeation experiment with lavender nitrile gloves revealed an average standardized breakthrough time of 5 ± 5 min, an average steady state permeation rate of 0.490 ± 0.031 μg/cm^2/min, and an average apparent diffusion coefficient of 21.0 ± 9.6 cm^2/min.

The steady state period ranged between 10 to 40 min. The average thicknesses of glove specimens before and just after challenging were 58 ± 4 μm and 71 ± 3 μm respectively. ($P \leq 0.05$). The average thickness after reconditioning was 57 ± 2 μm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and just after exposure to limonene were 3.17 ± 0.02 g and 4.11 ± 0.20 g respectively. This reflected a significant weight gain ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove moving robotic hand at 120 min was calculated as 0.0267 μg/mL. Water solubility was adequate to define the steady state permeation period.

Infrared reflectance analysis showed an intense increase in absorbance on both outer and inner surface of the glove with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-3000 cm^{-1}. After subtracting the absorbance of exposed gloves from that of the unexposed ones, traces of limonene were observed on the outer and inner sides of the glove surfaces. The lavender infrared spectra also indicated an intense reduction in absorbance on both outer and inner surface of the glove materials through the whole spectra. The spectra for the moving hand permeation with lavender gloves is provided in Appendix B.

5.4.6.2 Still Hand

Table 5.3 presents permeation parameters such as standardized breakthrough time, steady state permeation rate, and diffusion coefficients for individual lavender glove permeation experiments in whole glove static robotic hand model. Also, other lavender gloves permeation characteristics such as weight and thickness before and after permeation experiments for moving robotic hand model are indicated in Table 5.5. The average thickness and weight measurements were made just after permeation experiment, when glove specimens were blotted dry.

The coefficient variation (CV) value for steady state permeation rate were calculated as 5.5 %, which is in compliance with NIOSH and EPA coefficient variation criteria. NIOSH and EPA defined a maximum 10 % coefficient variation in measurements as a quantitative criteria.

The permeation parameters for the still hand permeation experiment with lavender nitrile gloves revealed an average standardized breakthrough time of 5 ± 5 min, an average steady state permeation rate of 0.423 ± 0.031 μg/cm^2/min, and an average apparent diffusion coefficient of 21.0 ± 9.6 cm^2/min. The steady state period ranged between 10 to 40 min. The average thicknesses of glove specimens before and just after challenging were 58 ± 2 μm and 70 ± 4 μm respectively ($P \leq 0.05$). The average thickness after reconditioning was 60 ± 4 μm. The reconditioned and initial thicknesses were not significantly different at $P \leq 0.05$. The average glove weights before and after exposure to limonene were 3.172 ± 2 g and 5.201 ± 0.180 g respectively ($P \leq 0.05$).

The average permeated concentration in collection solvent with the whole glove still robotic hand at 120 min was calculated as 0.0220 μg/mL. Water solubility was adequate to define the steady state permeation period.

Infrared reflectance analysis showed an intense increase in absorbance on both outer and inner surface of the glove with the C-H bend at 888 cm^{-1} and the C-H stretch at 2800-3000 cm^{-1}. After subtracting the absorbance of exposed gloves from that of the unexposed ones, traces of limonene were observed on the outer and inner side of the glove surfaces. The lavender infrared spectra also indicated an intense reduction in absorbance on both outer and inner surfaces of the glove materials through the whole spectra. The spectra for the still hand permeation with lavender gloves is provided in Appendix B.

5.5 DISCUSSION

5.5.1. Thickness and Weight Comparisons

The average thickness and weight measurements for the moving and still robotic hand experiments before and after permeation are reported in Table 5.4 and 5.5 respectively, and compared with the corresponding average measurements for the closed loop method for the same glove types.

The average post-permeation thicknesses (before re-conditioning) for all glove materials in dynamic and static modules were more than 10% of the pre-permeation ones. Initial observations indicated swelling and discoloration after the permeation test on limonene. The discoloration was most vivid in purple gloves. Post-permeation thickness measurements on all 4 glove specimens in the moving robotic hand experiments revealed a significant difference in thicknesses ($P \leq 0.05$). The same trend was also observed in the still hand permeation experiments. This is due to the accumulation of the non-volatile solvent (limonene) within glove. However, the swelling was reversible after reconditioning. The post-permeation measurements on blue, purple, sterling, and lavender gloves after reconditioning from dynamic and static whole glove experiments indicated no significant differences in glove thickness ($P \leq 0.05$).

The weight measurements on moving hand glove samples revealed an increasing trend. All blue, purple, sterling, and lavender glove samples in the still hand permeation experiments showed a statistically significant weight gain before reconditioning ($P \leq 0.05$). The weight gain for blue gloves was less than 10%. This was due to less swelling and change in thickness in blue gloves compared to all other glove samples. However, the weight gain for rest of the glove samples still hand experiments was more than 10%.

The weight measurement results are not surprising for a non-volatile solvent that is difficult to evaporate, and the weight data indicate limonene absorption and retention within the glove material even on reconditioning.

5.5.2 Comparison of the Permeation Parameters of the Modified ASTM Closed Loop versus Static Robot Hand Methods

The average permeated concentration in collection solvent with the whole glove still robotic hand at 120 min for blue, purple, sterling, and lavender gloves was calculated as 0.0028 µg/mL, 0.0084 µg/mL, 0.0118 µg/mL, and 0.0220 µg/mL respectively. These values confirmed that the static robotic hand permeation set with all selected glove samples did not reach to the saturation point of 0.0280 µg/mL and water solubility was adequate to capture the permeated analyte. The 120 min time was chosen was chosen because the permeation parameters such as SBRT and SSPR in all glove samples in still and moving robotic hand experiments located within the first hour of permeation experiment and this confirmed that collection solvent solubility doesn’t have any impact or overlap with permeation parameters. The average use of the disposable gloves in general is 15 min to 60 min, hence 120 min criteria was chosen as an extra safety measure to make sure about capability of the collection solvent in capturing the permeant during first 120 min of the experience.

The first hypothesis of this research was “The permeation of limonene through a disposable glove will be the same in the closed loop and the static whole glove permeation methods.”

Table 5-6 shows and compares the permeation parameters for limonene in whole glove still robotic hand and ASTM closed loop permeation cell methods. The ASTM closed loop experimental methods, procedures, and results have been discussed in Chapter 4 of this research. A general overview on SBRT with the static robotic hand and ASTM indicates that the robotic hand module is more sensitive to capturing the analyte than the ASTM method, especially in disposable nitrile gloves with higher thicknesses such as for the blue and purple gloves. This is confirmed by the earlier onset of the steady state permeation period for all the static and moving robotic hand experiments.

This results from the whole glove surface area compared with the ASTM surface area. In whole glove experiment method, the exposed surface area to the analyte is much higher than the ASTM cell, as in blue gloves, the surface area directly in contact with the analyte is 911 cm^2, whereas in ASTM permeation cell the efficient surface area in direct contact with the permeant is 5.07 cm^2. This suggests a ratio of 180 in the exposed surface area between the whole glove and ASTM cell. In other word, whole glove model provides a larger surface area for permeation, which results in earlier breakthrough time and steady state permeation period. It should also considered that the despite larger surface area in whole glove model, the volume of water collection medium is also more than ASTM permeation cell. The whole glove collection medium held 100 mL water versus 10 mL water in the ASTM cell; with a volume factor of 10 (Table 5.8). However, the surface area ratio of 180 is much larger than the volume ratio of 10. Overall area ratio holds an advantage of 18 (180/10) in providing more analyte permeation. This led to earlier observer SBRT and steady state permeation period in whole glove robotic hand experiments. The same explanation exists for the other glove experiments. Table 5.8 compares the area and water ratios between the whole glove robotic hand and ASTM models.

The standardized breakthrough times for the lavender gloves in whole glove static and dynamic hand modules as well as ASTM cells were achieved within the first 5 ±5 minutes of the experiment. In fact, breakthrough data passed both the ASTM F739-99a/2012 (5, 6) 0.25 μg/cm^2 and 0.1 μg/cm^2/min criteria for NBRT and SBRT upon limonene coming into contact with the glove materials. This indicates that lavender gloves are the most dysfunctional gloves for exposure to limonene. This is not surprising because they are the thinnest gloves of the nitrile gloves studied.

Since the acrylonitrile content for lavender gloves was similar to the sterling gloves, the thickness in lavender gloves is the key for such early breakthrough time.

Glove Specimen	Total Glove Area*(40)	Unexposed 2" Wrist Area*	Effective Glove Area*	ASTM Palm Area*	Area[I] Ratio	Solvent[II] Ratio
Blue	1242	331	911	5.07	180	10
Purple	1129	280	849	5.07	167	10
Sterling	1067	250	817	5.07	161	10
Lavender	910	230	680	5.07	134	10

* Units are in cm^2
I: Area Ratio= (Whole glove effective area) ÷ (ASTM palm area)
II: Solvent Ratio= (Whole glove collection solvent volume) ÷ (ASTM chamber volume)
III: Area Advantage = Area Ratio - Solvent Ratio

Table 5.8, Areas and water ratios between the Whole Glove Robotic Hand and ASTM Models

In static robotic hand experiments, blue and purple nitrile gloves showed a shorter NBRT compared to the ASTM closed loop method. Surface area is the key player for such earlier NBRTS, as it was discussed in previous page and Table 5.8. While the observed SBRT for sterling gloves in both ASTM permeation cells and still robotic hand was 15 ±5 min, the respective SBRT for purple gloves was 30 ±10 min in ASTM permeation cells and 15±10 min with the still robotic hand. This suggests that purple gloves should not be used even for a short period of exposure to limonene.

The best resistance to permeation performance in both the modified ASTM method and whole hand permeation experiments with limonene was observed in blue gloves. However, the recorded SBRT for the blue gloves in the still robotic hand was significantly shorter than the ASTM closed loop set ($P \leq 0.05$). This results from the large surface area in whole glove robotic hand compared with the ASTM surface area. In whole glove experiment method, the exposed surface area to the analyte is much higher than the ASTM cell, as in blue gloves, the surface area directly in contact with the analyte is 911 cm^2, whereas in ASTM permeation cell the efficient surface area in direct contact with the permeant is 5.07 cm^2. This suggests a ratio of 180 in the exposed surface area between the whole glove and ASTM cell (Table 5.8).

Lavender gloves showed the highest steady state permeation rate (SSPR) compared to all other glove samples in both whole glove still hand and ASTM cells ($P \leq 0.05$). The SSPR in lavender gloves (still hand) was more than in blue gloves by a factor of 42. This indicates the impact of thickness on permeation rate. The SSPR in lavender gloves was more than purple and sterling by factors of 4.2 and 6.3, respectively. The regression analysis on thickness and SSPR for blue, purple, and lavender gloves shows a reverse linear relationship ($r^2 = 0.97$ for non-moving hand). However, the correlation was not significant ($P \leq 0.05$).

Comparing the SSPR between the ASTM closed loop model and still robotic hand method suggests that the SSPR in lavender gloves with still robotic hand permeation method (0.423 ± 0.031 $\mu g/cm^2/min$) was significantly higher (1.43 times) than with the ASTM closed loop method (0.295 ± 0.028 $\mu g/cm^2/min$ [$P \leq 0.05$]). Surface area is the key player for such earlier SSPRs, as it was discussed 3 pages back. The only difference with lavender gloves is that the exposed surface area is 680 cm^2 (rather than 911 cm^2 in blue gloves), which provides a ratio of 134 compared with ASTM area (Table 5.8). Another noticeable difference between the ASTM permeation cells and still robotic hand in lavender glove specimens was in the time range for reaching steady state permeation period. The steady state permeation period for the robotic hand model occurred within 10-40 min, opposed to in 20-60 min for the ASTM method. Again, the surface area is the key player for such earlier steady state permeation periods. It was also found that although the SSPR gap between the two methods for blue gloves was less than for the lavender gloves, the whole glove static hand showed a significantly higher SSPR compared to the ASTM method ($P \leq 0.05$). In studying the permeation parameters in blue nitrile gloves, the most vivid difference between the static robotic hand and ASTM model was in SSPP. The SSPP was 40-80 min in the robotic hand versus 240-480 min in the closed loop model.

In order to apply equation (5-1) for calculating the diffusion coefficient, some critical points should be considered, including: a) the diffusion coefficient is applicable if no change in glove thickness is observed after permeation, b) on the cumulative permeation mass curve no permeation happens at the zero reference time (no detectable concentration of the permeant at inner side of the protective clothing at the starting time), c) instant equilibrium between the solvent and protective clothing upon contact, and d) the permeant is in liquid or gas phase.(11) Other models such as the Hildebrand model rely on dispersion as the single parameter to address the solubility which is not powerful enough.(45) In fact crucial parameters such as hydrogen bonding and polar solvents were overlooked since the theory was based on the behavior of hydrocarbon solvents. Vahdat's model also provides an estimate for diffusion coefficient (D_f); however, calculating the D_f requires solvent solubility in the glove texture and there exist several definitions for defining the solubility of solvents in the protective glove.(43)

Hansen Solubility Parameters (HSP) are also known as a 3D model which addresses solubility and diffusion features using three major parameters: dispersion, polarity, and hydrogen bonding. However, it performs poorly in solvent-polymer solubility because it lacks a harmonized method for converging the 3D parameters. (44)

In general, a good protective glove is expected to show low diffusion coefficients. (46) This suggests that the HSP parameters for the target chemical must be very low (with minimum swelling) to hold a negligible surface concentration, or the analyte molecular size must be very large to hardly be able to permeate through the polymer.

The calculated diffusion coefficient (D_f) using Fick's first law (equation 5-1) was not in the same harmony with the respective SSPR and SBRT. The significant swelling effect during permeation (Table 5-4, 5-5) made the D_f values mixed and non-harmonized with the respective SSPR. Mathews noticed similar concerns with D_f during a permeation study with cyclohexanol on blue, purple and sterling disposable nitrile gloves and indicated the impact of swelling on D_f.(40)

The regression analysis on D_f and SSPR for blue, purple, and lavender gloves in the whole glove still hand experiments (Figure 5.2) showed a linear relationship with a coefficient determination of $R^2 = 0.9923$ ($P \leq 0.05$).

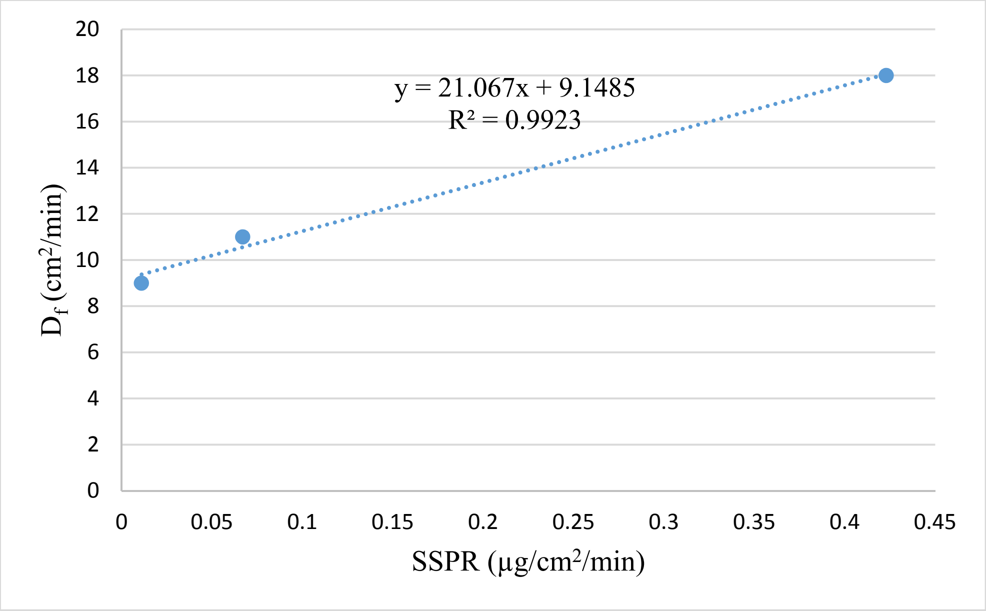

Figure 5.2: D_f vs SSPR in whole glove still robotic hand experiment (blue, purple, and lavender gloves)

The analysis suggests that in optimal permeation processes, thinner gloves are expected to show higher permeation rates and diffusion coefficients, assuming the same acetonitrile content. However, in this experiment sterling gloves were not included in this analysis because of the swelling effect and inconsistency with the respective permeation rate.

For the ASTM model, the same analysis was conducted for the blue, sterling, and lavender gloves, and the linear relationship was calculated as $Y = 42.727X + 0.9167$ and $R^2 = 0.9998$ ($P \leq 0.05$). The calculated D_f in purple gloves was not included in regression analysis.

The regression analysis on D_f and glove thickness before permeation for blue, purple, and lavender gloves in whole glove still hand experiments showed a reverse linear relationship with a coefficient determination of $R^2 = 0.9974$ and a liner equation of $Y = -0.1448X + 26.472$ ($P \leq 0.05$). The regression analysis on D_f and thickness with the same glove selections just after permeation (before reconditioning) shows the same reverse linear relationship as $Y = -0.1388X + 27.986$ and $R^2 = 0.9998$ ($P \leq 0.05$).

This confirms that glove materials with greater thickness and better protection are expected to show a lower D_f in ideal conditions. (46) The same reverse linear relationship exists with the ASTM corresponding thicknesses and D_f, $R^2 = 0.94$; however, it was not significant.

Studying post-permeation diffusion coefficients (before re-conditioning) on all glove materials in dynamic and static modules indicated more than 10% increase in D_f (ranged 15%-45%) compared with the pre-permeation ones ($P \leq 0.05$). This is a direct impact of swelling, which resulted in increasing thicknesses in all glove samples during dynamic and static permeation experiments ($R^2 = 0.99$, $P \leq 0.05$) as indicated in table 5.4 and 5.5.

5.5.3 Comparison of the Permeation Parameters for the Whole Glove Static Robotic Hand vs Dynamic Robotic Hand

The primary hypothesis of the current research was that a moving hand would produce more limonene permeation than a static hand for the same types of glove materials under the same conditions of temperature and pressure.

The other condition that was held constant here is the exposed surface area whereas the exposed surface area differed for the static robot hand and modified ASTM closed loop experiments.

Also it was considered that the collection solvent provides adequate solubility for the permeant captures the analyte during standardized breakthrough time window as well as steady state permeation rate. The water solubility for limonene is 13.8 mg/L at 25 °C. (15, 47) The average permeated concentration in collection solvent at 120 min was selected as reference and compared with maximum solubility of limonene at 35 °C (0.028 µg/mL) in the respective collection volume. Results confirmed that the collection medium provided adequate solubility for the permeant and the system did not reach to saturation point at 120 min in moving and still robotic hand experiments with blue gloves.

All blue, purple, sterling, and lavender glove samples in moving hand permeation experiments showed a statistically significant weight gain ($P \leq 0.05$). The weight gain for blue gloves in the dynamic hand system was less than 10%. This was due to less swelling and change in thickness in blue gloves compared to all other glove samples. However, the weight gain for the other glove samples in moving experiments was more than 10%.

The post-permeation measurements on blue, purple, sterling, and lavender gloves after reconditioning from both dynamic and static whole glove experiments indicated no significant differences in glove thickness ($P \leq 0.05$). This suggests that reconditioning is the key player on post permeation studies on glove specimens.

Table 5-7 indicates the permeation parameters for limonene in whole glove still and moving robotic hand methods. A general overview of SBRTs with the static and moving robotic hands indicates that both methods have similar sensitivity in detecting the analyte during permeation. This is confirmed by the respective SBRTs and SSPPs for the static and dynamic robotic hand models. As can be seen, in all still and moving robotic hand permeation experiments, the SSPPs are located in the same time ranges. This suggests that glove materials behave similarly during the permeation process whether moving or non-moving.

The standardized breakthrough times for the lavender gloves in whole glove static and moving modules were achieved within the first 5 ±5 minute of the experiment. In fact, the defined criterion for NBRT and SBRT were exceeded upon the analyte coming into contact with the glove materials. This indicates that lavender gloves are not protective enough against limonene even for very short exposures. Both methods showed that nitrile blue gloves provide the best performance with similar SBRTs. Lavender gloves showed the highest permeation rate compared to all other glove samples in both whole glove still and moving hand permeation experiments. Interestingly, the SSPR for the moving robotic hand with the lavender nitrile gloves was significantly higher than in the still hand method ($P \leq 0.05$) in spite of the area of exposure of the whole glove being identical. Comparing SSPR in moving robotic hand and the static hand for the other disposable nitrile glove specimens (blue, purple and sterling) revealed no significant differences between the two situations ($P \leq 0.05$).

However, in all glove specimens the SSPR for the moving hand was more than for the static robotic hand. This was confirmed when the SSPR mean with dynamic robotic hand module was significantly higher than for the static hand in only the lavender gloves experiment ($P \leq 0.05$). This is due the threshold thickness in lavender gloves compared with other glove samples. Since the acrylonitrile content (percentage) for lavender gloves was similar to the sterling gloves, the respective content in thinner gloves will be less than thicker ones. In other words, considering the thickness of lavender gloves, they are holding less acrylonitrile (acrylonitrile is providing strength in glove material against solvents) and this causes the glove texture more susceptible to physical stresses, as in moving robotic hand. Moreover, the lavender infrared spectra indicated an intense reduction in absorbance on both outer and inner surface of the glove materials through the whole spectra which are signs of degradation. This is due to loss of hydrophobic coatings on the challenge side of the glove during direct contact with limonene which will be aggregated with mechanical moving and causes increases increased permeation rate.

The SSPR differential between the moving and static robotic hands increased as the glove thickness decreased, as also observed for the sterling glove but not purple or blue gloves in the Mathews study with cyclohexanol.(40) A regression analysis on the initial glove thickness and SSPR gap (moving and still hand) for the blue, purple, and lavender gloves shows a reverse linear relationship ($Y = -0.0011x + 0.1306$, $R^2 = 0.9940$, $P \leq 0.05$). This suggests that as the glove materials get thinner, the effects of the moving robotic hand are more visible through increasing the corresponding SSPR.

5.5.4 Glove Resistance to Limonene

Evaluating the efficiency of the disposable nitrile gloves (by Kimberly Clark Professional and Ansell criterion) for exposure to limonene with the still and moving robotic hand models suggests that none of the gloves used in this study are safe enough. This is different than what was observed in Chapter 4 in evaluating the gloves for exposure to limonene based on the modified ASTM model. Kimberly Clark Professional (KCP) and Ansell provide two different sets of criteria for evaluating the effectiveness of the gloves.

Kimberly Clark Professional, one of the largest manufacturers of disposable and chemical protective gloves, defines a dual criteria for the chemical resistance rating of disposable nitrile gloves.(32) The major criteria for rating are based on normalized breakthrough times as indicated in Table 5.9. Kimberly Clark categorizes NBRT as: <1 min, not recommended (NR); 1-9 min, poor; 10-59 min, good; and 60-480 min, excellent. (32, 34)

Rating	Permeation breakthrough time (min)
Excellent (E)	60-480
Good (G)	10--59
Poor (P)	1--9
Not Recommended (NR)	< 1

Table 5.9 Kimberly Clark Professional (46) permeation breakthrough time criteria for chemical resistance rating of disposable nitrile gloves.

Based on this classification, lavender gloves are not recommended category, while sterling, purple, and blue gloves are in the good category. The second embedded criterion is boiling point. Solvents with boiling points of less than 24° C are defined as high volatile and higher than 24° C defined as low volatile.(32) KCP defines a glove safe (green) for exposure to low volatile compounds if the permeation rating is excellent. Using the Kimberly Clark Professional scale for limonene (as a low volatile solvent), only a glove with an excellent breakthrough time is considered safe for occupational exposure to limonene.

Since the permeation breakthrough time for disposable lavender nitrile gloves occurred momentarily upon contact, such gloves are either “not recommended” (given breakthrough times within 1 min) or “poor” (given breakthrough times within 1-9 min). The blue, purple and sterling gloves also are not safe, because their permeation breakthrough times are not excellent. The ASTM defines standardized breakthrough detection time as the time when the permeation rate reaches 0.1 µg/cm^2/min.(5, 6)

Ansell provides a triple criteria scale for defining the efficiency of chemically protective gloves: degradation resistance rating, permeation breakthrough time, and permeation rate.(35, 36) Ansell defines six different categories for the permeation rate as: excellent with a permeation rate of <0.9 µg/cm^2/min; very good, 0.9-9; good, 9-90; fair, 90-900; poor, 900-9000; and not recommended (NR), >9,000 µg/cm^2/min. Table 5.10 shows this categories.(35, 36)

As can be seen from Tables 5.3 and 5.4, the steady state permeation rates for all glove specimens are located within the excellent rating (<0.9 µg/cm^2/min) based on Ansell’s categorization.

Rating	Permeation Rate (µg/cm^2/min)
Excellent (E)	<0.9
Very Good	0.9-9
Good	9--90
Fair	90-900
Poor	900--9000
Not Recommended (NR)	>9,000

Table 5.10. Ansell permeation rate criteria for Chemical Resistant Gloves.(35)

However Ansell indicates that a chemically protective glove can be safe if all of the following criteria are met: the degradation rating is excellent; permeation breakthrough time is 30 minutes or greater; and permeation rate is excellent, very good, or good.(35, 36) As for Kimberly-Clark, a color code rating system is used to simplify the selection process.

Though the glove samples met the Ansell SSPR criteria, this study indicated an immediate breakthrough time of 5 ±5 min for lavender disposable nitrile gloves during exposure to limonene, and it is concluded that such gloves will receive a red label and are not suitable for exposure to limonene. The same conclusion can be made for the sterling, purple, and blue gloves. Although they passed the SSPR requirement, they all have breakthrough times of less than 30 min (sterling and purple; 15 ± 5 min, blue; 30 ± 10 min) which disqualifies them to pass the requirements of a safe glove. Ansell provides an alternative set of criteria for a glove to be approved with a green label as: the permeation rating is not specified, the permeation breakthrough time is 240 minutes or greater, and the degradation rating is excellent. This option is even harder to meet than previous one, because it requires a 240 minutes or greater breakthrough time.

While KCP and Ansell categorized blue gloves as safe for exposure to limonene, the moving and still robotic hand models disqualified all tested gloves (including blue) as safe protection during exposure to limonene. This suggests that robotic hand permeation model is more sensitive and stringent in defining gloves' efficacy compared to the ASTM model.

Because limonene is not a known human carcinogen (17, 31), some exposure to limonene may be allowable. Risk assessment based on the WEEL threshold value of 30 ppm (167 mg/m^3) shows that the maximum absorbed mass of limonene during an 8 hour work shift is 10 m^3 × 167 mg/m^3 = 1670 mg. The permeated mass in the whole glove moving robotic hand with lavender glove specimens (which have the highest permeability compared with other gloves) was 61 mg. This suggests that in worst case scenario, if all permeated mass through the glove absorbs into the body, it is still far below the threshold defined by WEEL and even the MAK 5 ppm equivalent to 278 mg. The NBRTs and SSPRs provided by glove manufacturers are devised by ASTM and do not include the toxicity of the chemicals in their guidelines and charts. In fact, the ASTM definition of SBRT (0.10 µg/cm^2/min) is not necessarily a comprehensive criterion for all toxic chemicals as a safe threshold value, for example, carcinogens. ASTM and ISO apply this limit for all chemicals regardless of toxicity. As a result, dermal exposure less than 0.10 µg/cm^2/min for many toxic chemicals could be unsafe and a different scale may be needed for highly toxic chemicals.

5.6 CONCLUSIONS

Disposable lavender, sterling, and purple nitrile exam gloves showed a high permeability to limonene in the robotic hand permeation experiment. Although blue gloves provided the highest performance during challenging with the limonene compared to other gloves, they still could not pass the criteria defined by KCP and Ansell as safe for occupational exposure to limonene. However, they may be safe to be used for very short exposures to limonene (less than 20 minutes). The robotic hand permeation model is more sensitive and stringent in defining gloves' efficacy compared to the ASTM F739-99/12 model.

5.7 ACKNOWLEDGEMENTS

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CHAPTER 6

FUTURE WORK

This research showed significant differences between a reference permeation method (ASTM) and the whole hand permeation model for a low volatile solvent. More chemicals need to be tested to confirm the findings on this study on how low volatile compounds behave in a robotic hand permeation model. The results may increase the data available showing the superiority of the whole glove model relative to the ASTM method.

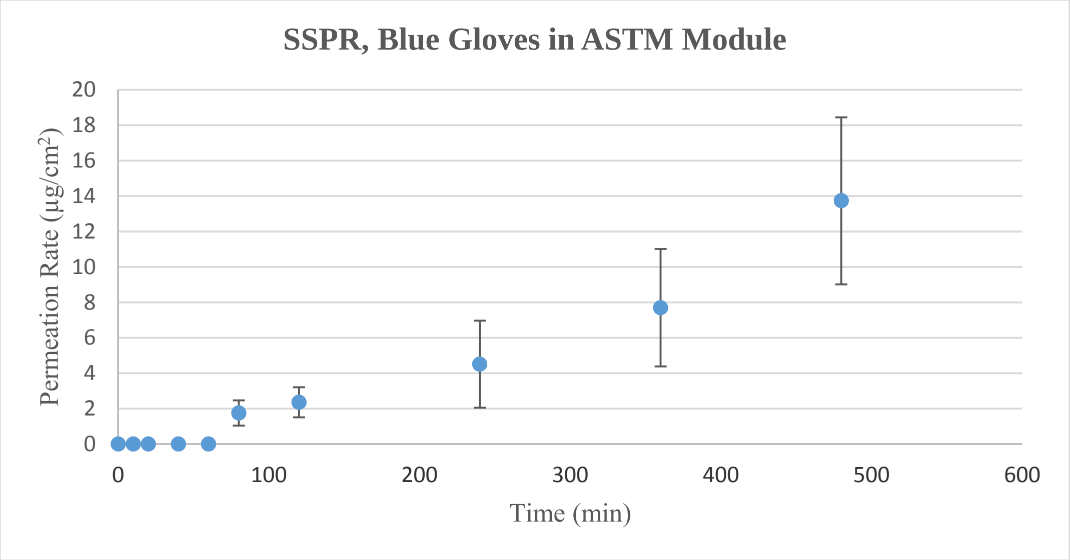
Also different robotic hands with more flexibility and features such as capability for gripping objects during the permeation process in a defined time interval will give even more realistic picture of contacting employees to chemicals in real world working conditions. The current robot hand grip force cannot be varied and other hands need to be investigated to assess how representative the current results are relative to the clench force.

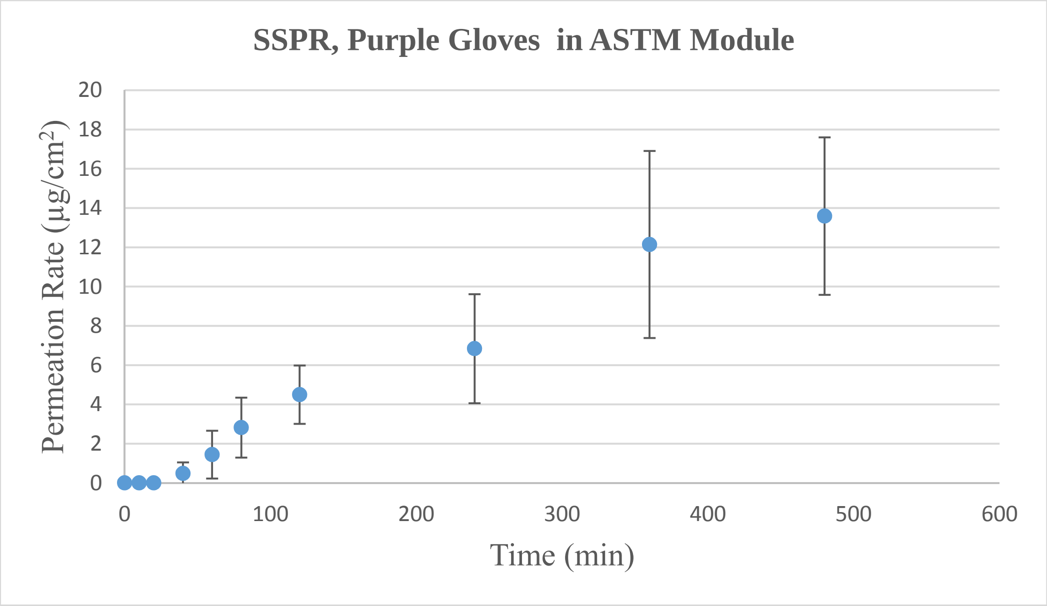
Whole glove permeation studies on other disposable gloves and chemically protective gloves such as neoprene, polyvinyl chloride, Viton, and latex are needed to see if other gloves with different thicknesses and glove polymer content will permeate significantly differently than the default permeation test model which is used by the glove manufacturers. This will also help to see whether the change in glove material thickness and swelling effect on diffusion coefficient is a general feature of whole glove permeation or not.

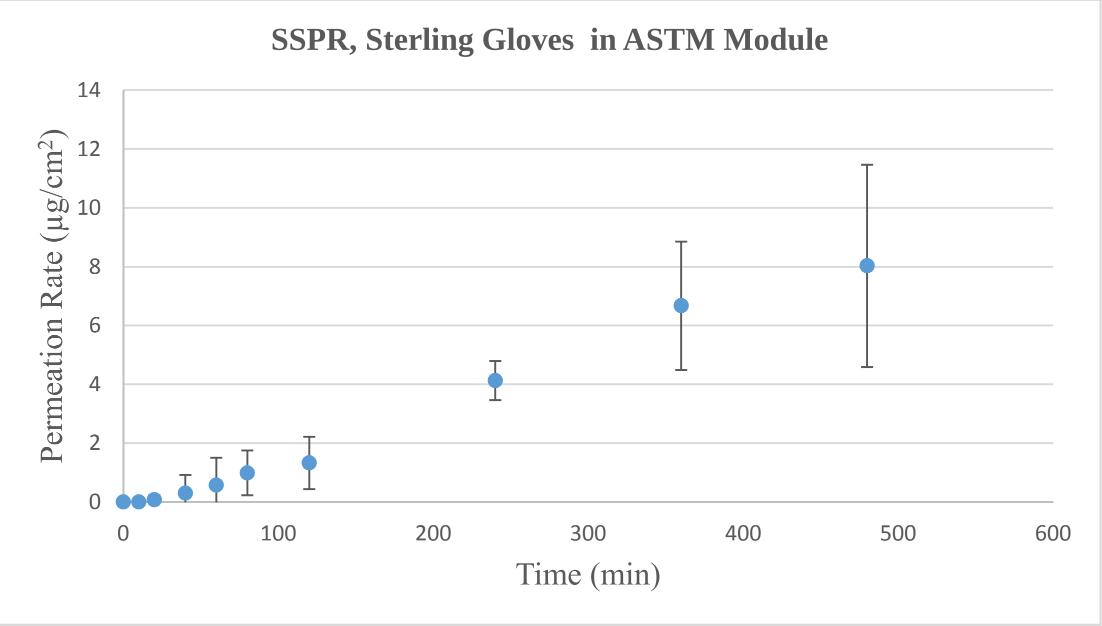
Study on whole glove permeation with mixtures of solvents will provide a new perspective on how the robotic hand model handles multiple analytes compared with the ASTM model and if the permeation rate will change with an additive, synergistic, or antagonistic trends.

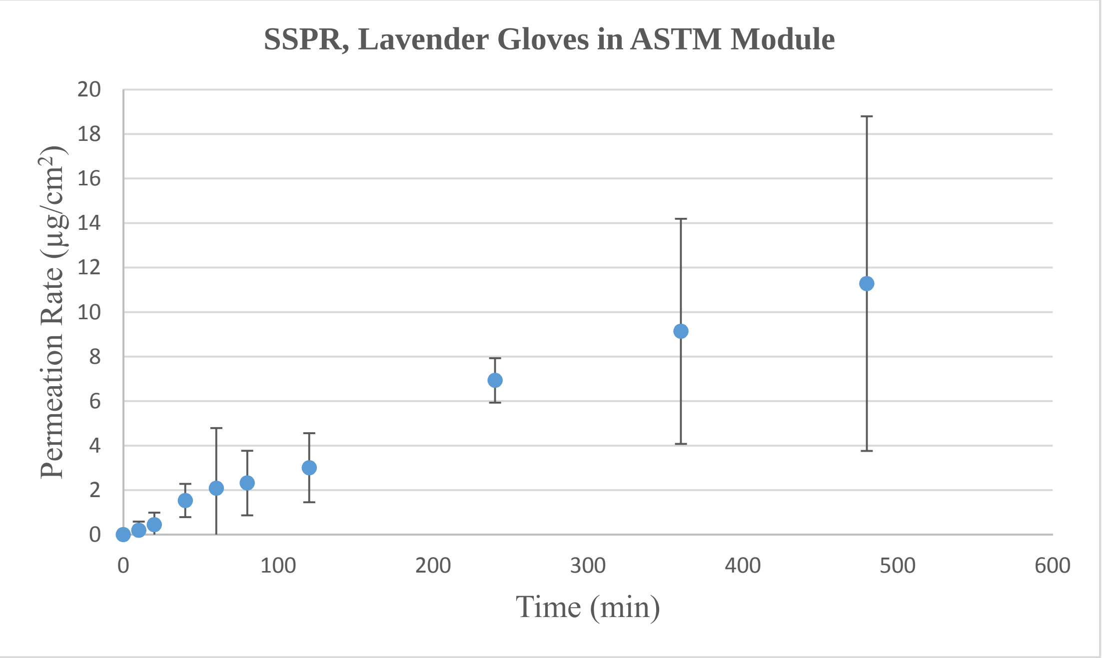
APPENDIX A: PERMEATION CURVES

A.1, AVERAGE PERMEATION THROUGH DISPOSABLE NITRILE GLOVES IN ASTM-F739 CLOSED LOOP SYSTEM

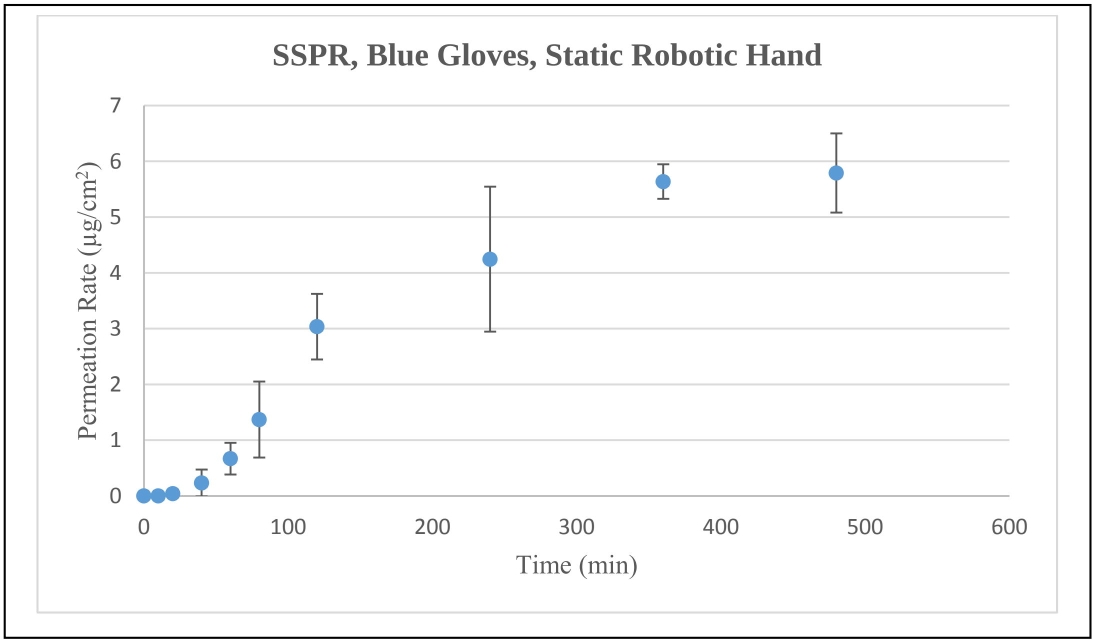


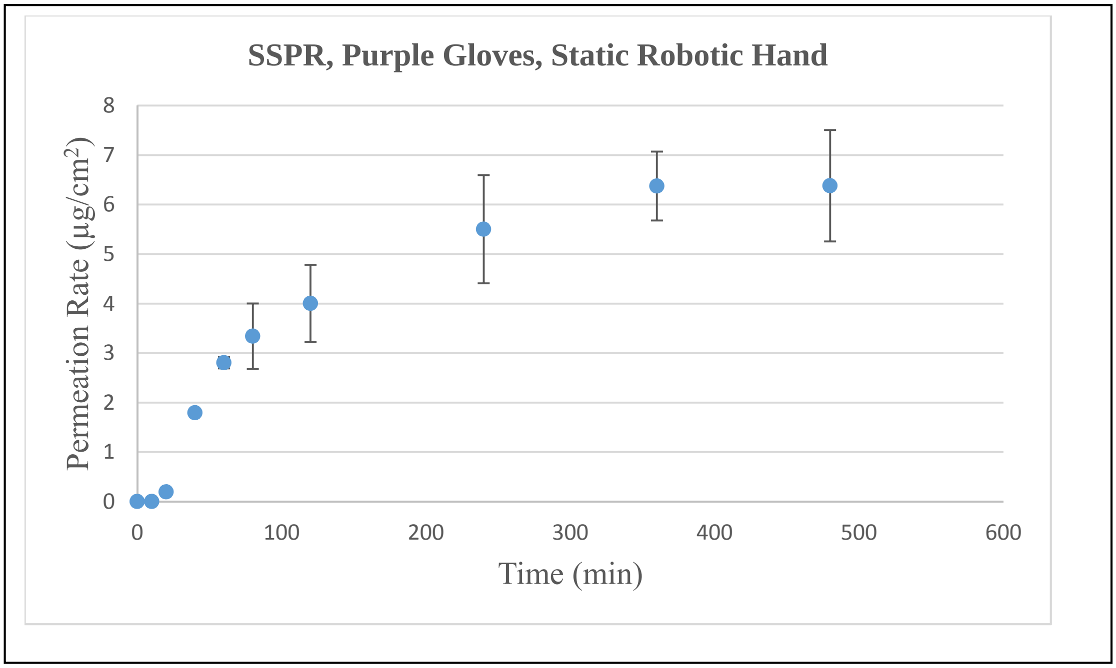


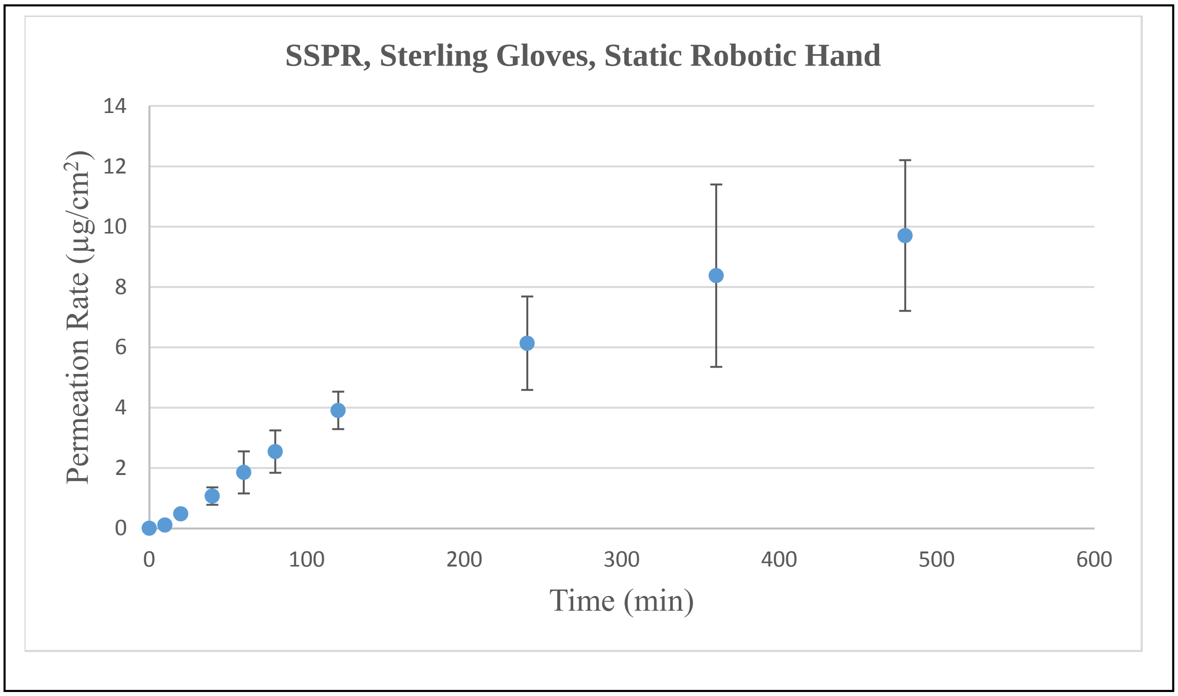

SSPR, Sterling Gloves in ASTM Module
Permeation Rate (µg/cm²)
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
Time (min)

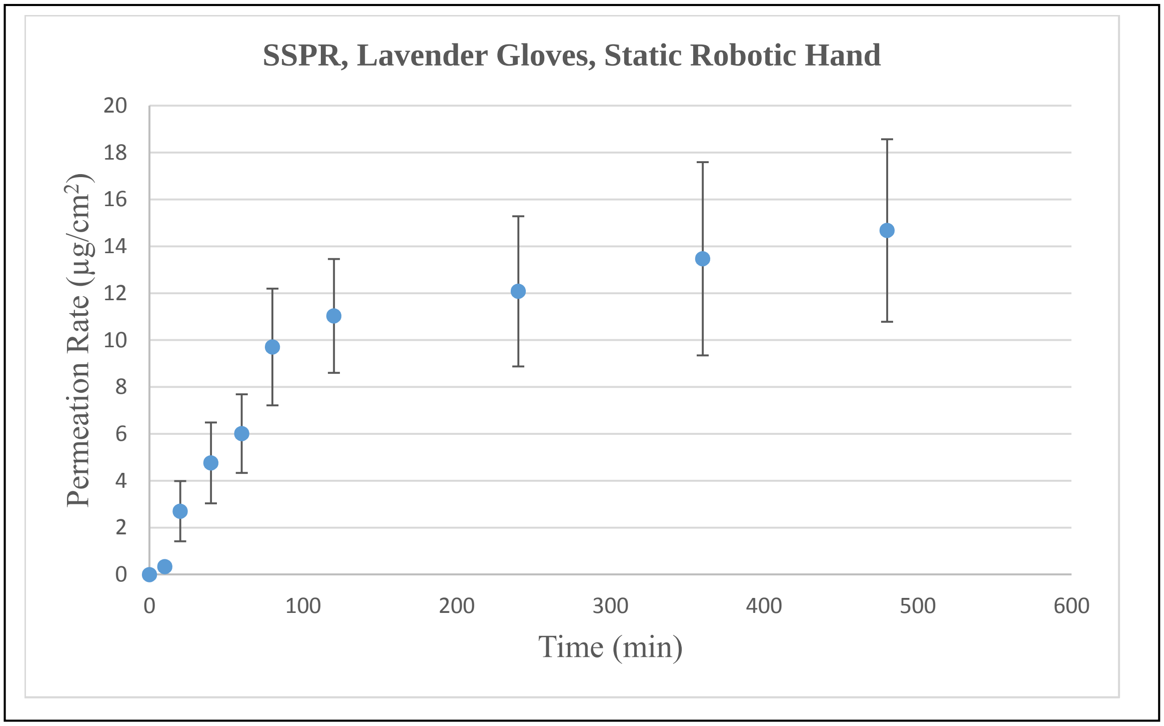

SSPR, Lavender Gloves in ASTM Module
Permeation Rate (µg/cm²)
20
18
16
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
Time (min)

A.2, AVERAGE PERMEATION THROUGH DISPOSABLE NITRILE GLOVES IN STATIC ROBOTIC HAND

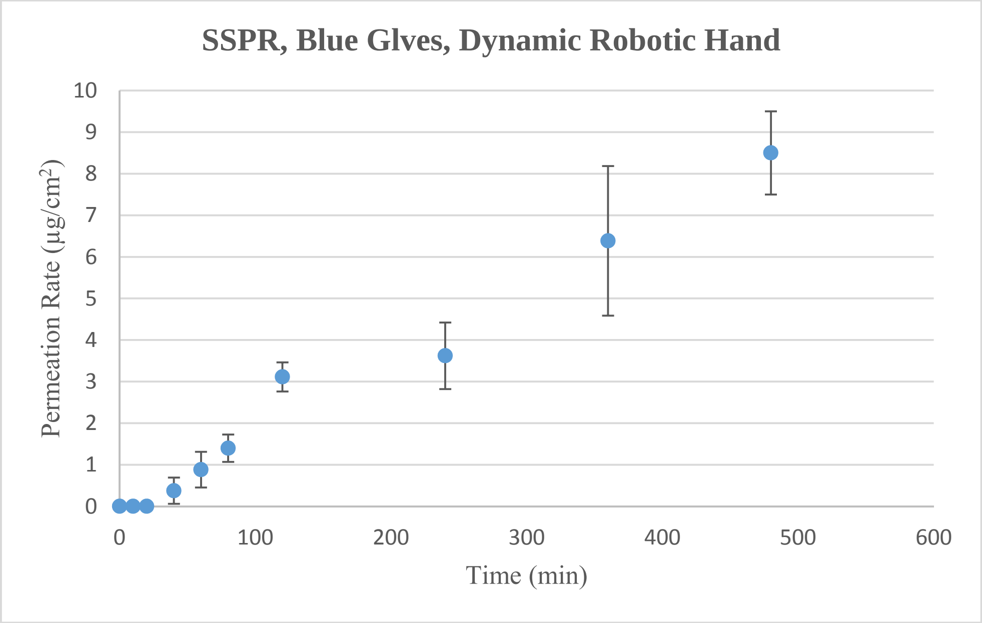


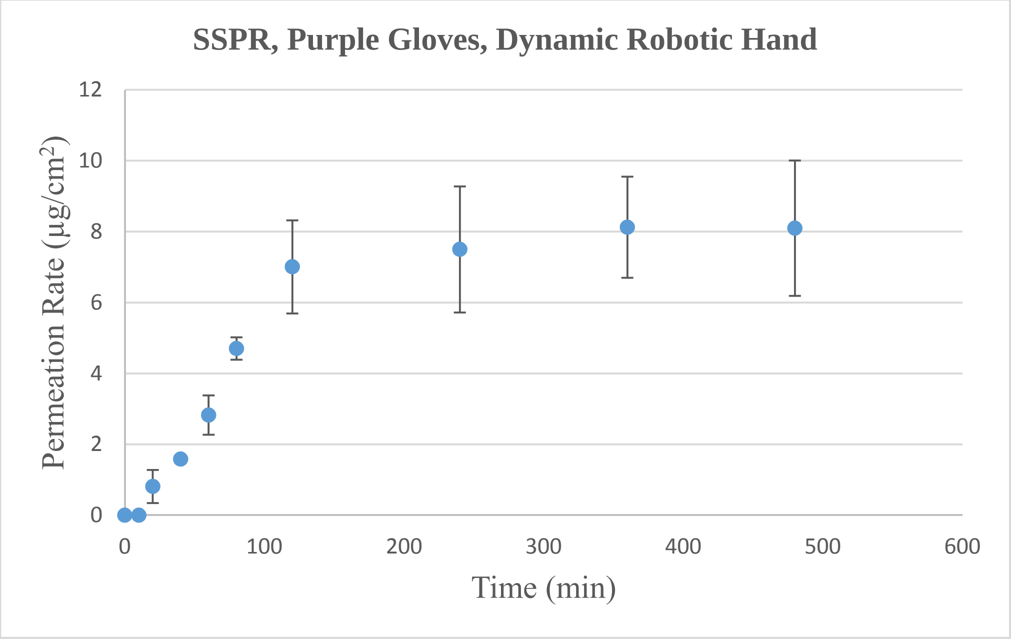


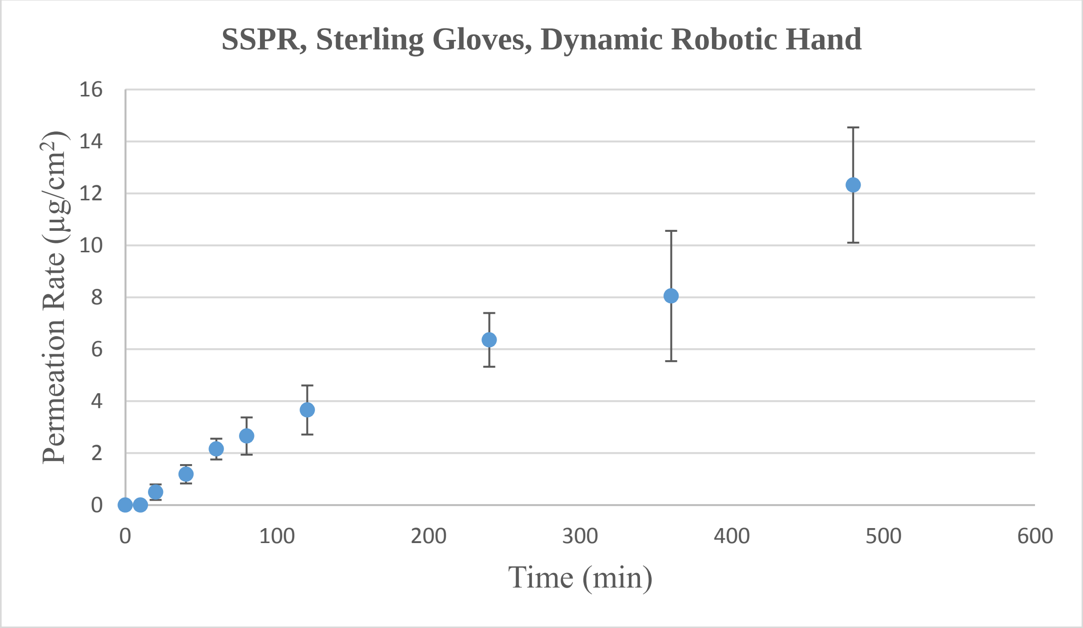

SSPR, Sterling Gloves, Static Robotic Hand
Permeation Rate (µg/cm²)
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
Time (min)

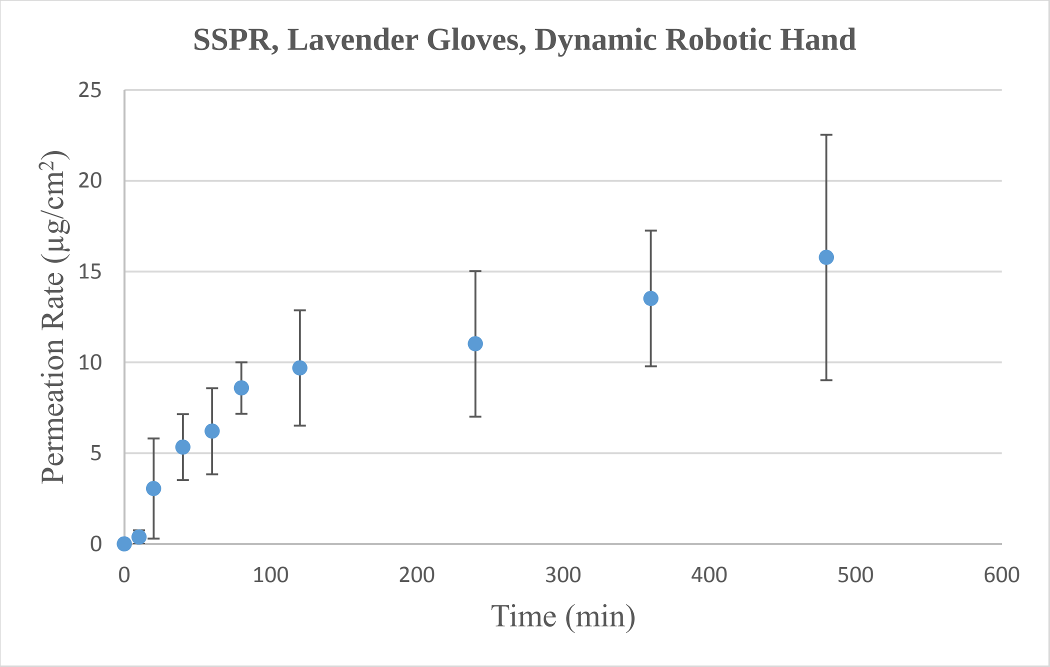

SSPR, Lavender Gloves, Static Robotic Hand
Permeation Rate (µg/cm²)
20
18
16
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
Time (min)

A.3, AVERAGE PERMEATION THROUGH DISPOSABLE NITRILE GLOVES IN DYNAMIC ROBOTIC HAND

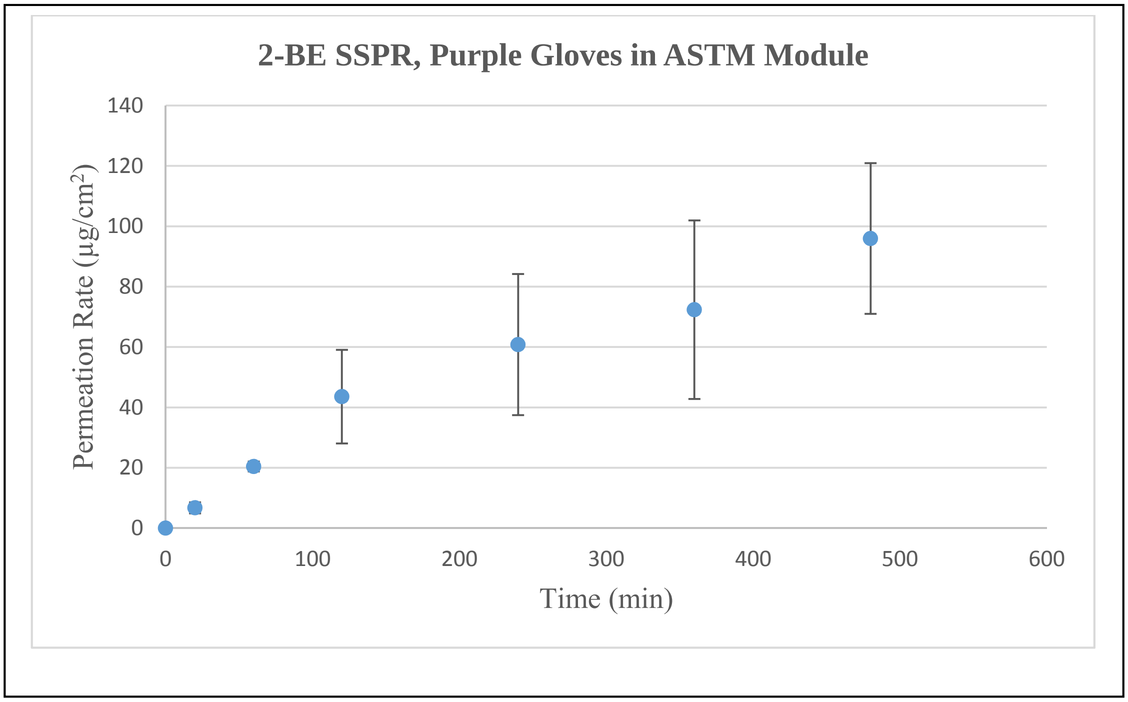


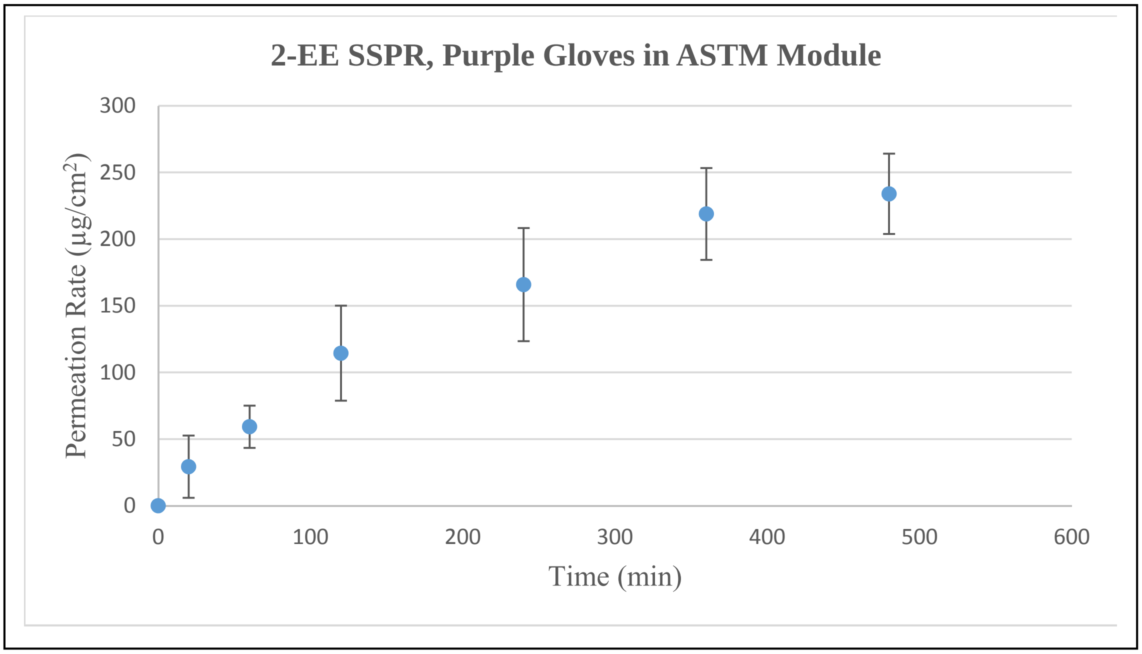



SSPR, Sterling Gloves, Dynamic Robotic Hand
Permeation Rate (µg/cm²)
16
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
Time (min)


SSPR, Lavender Gloves, Dynamic Robotic Hand
Permeation Rate (µg/cm²)
25
20
15
10
5
0
0
100
200
300
400
500
600
Time (min)

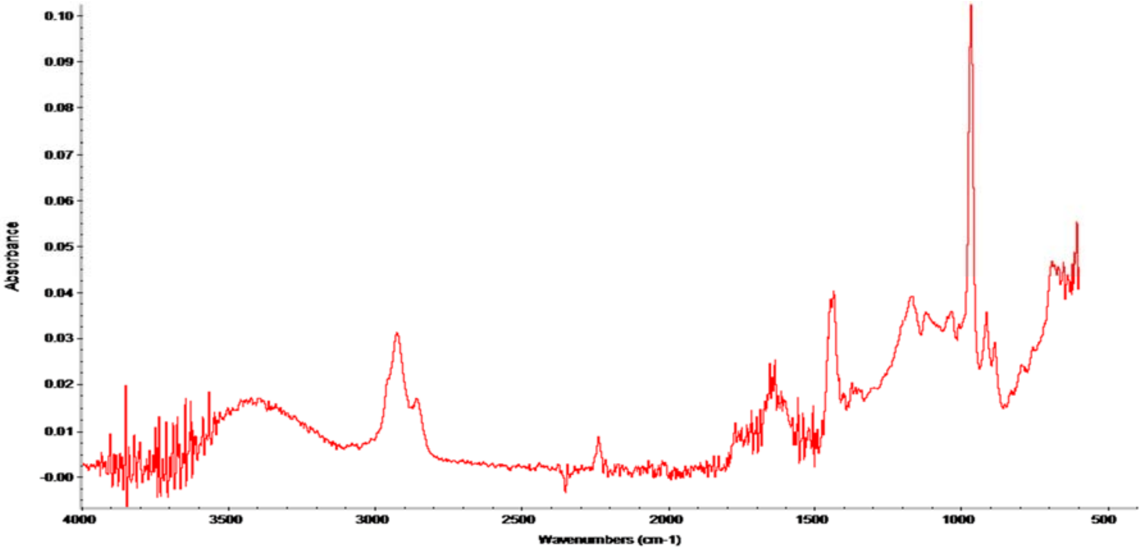
A.4, AVERAGE 2-EE and 2-BE PERMEATION THROUGH PURPLE GLOVES IN ASTM-F739 CLOSED LOOP SYSTEM



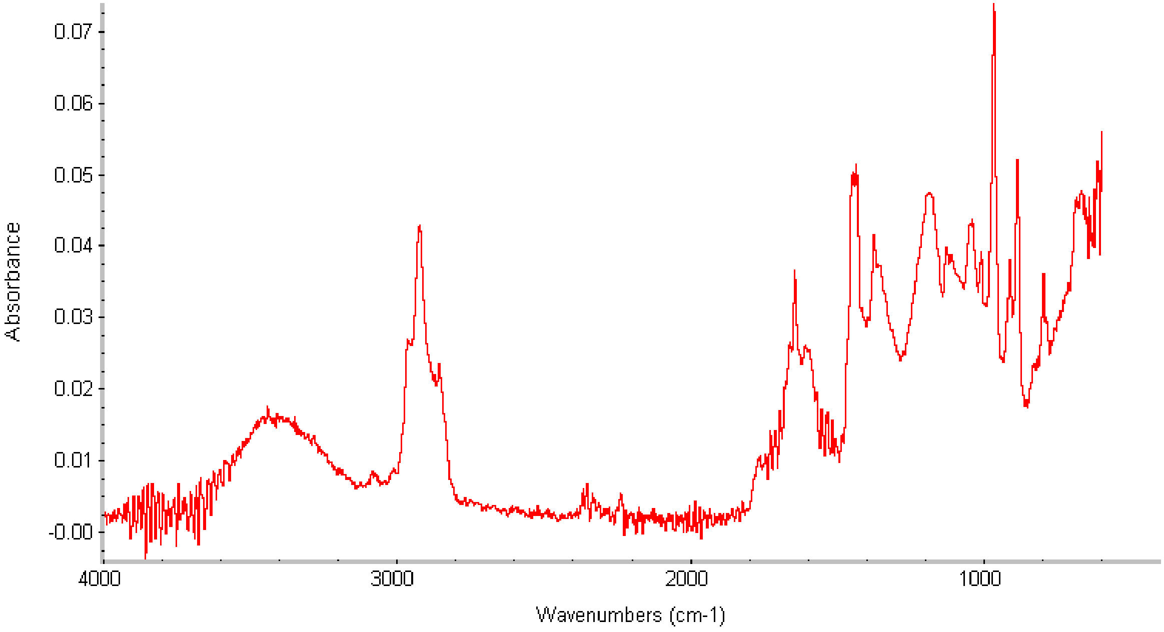


APPENDIX B: INFRARED SPECTRA

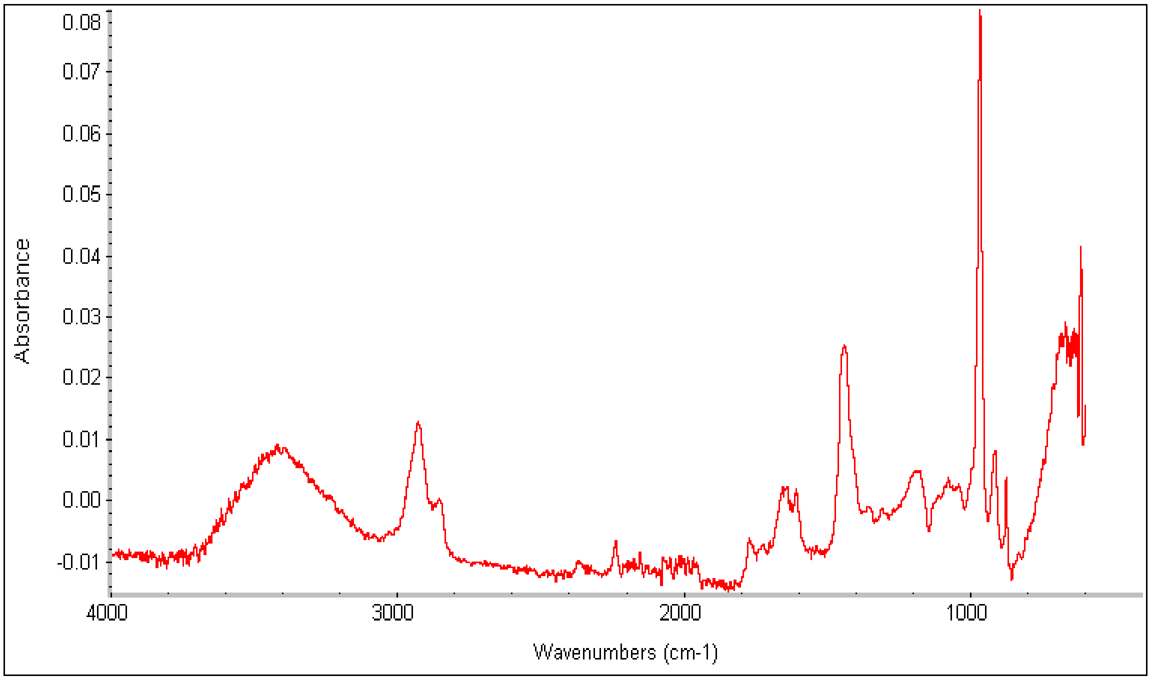
B.1, INFRARED SPECTRA FOR DSIPOSABLE NITRILE GLOVES IN WHOLE GLOVE DYNAMIC ROBOTIC HAND



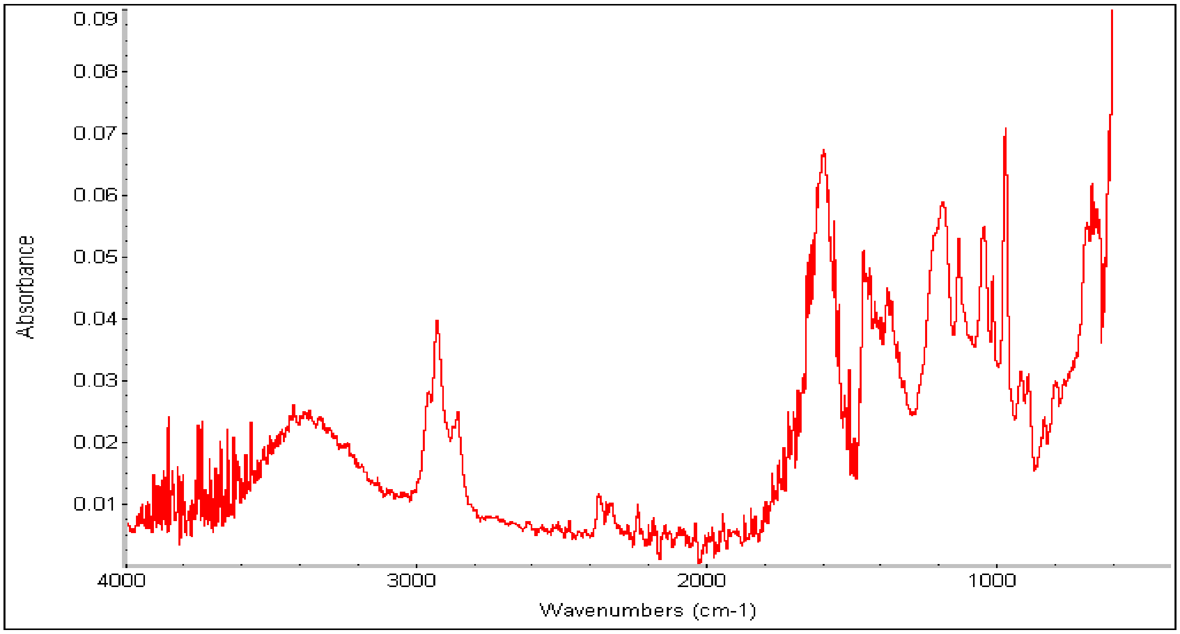
Infrared spectra for blue gloves in whole glove dynamic robotic hand.



Infrared spectra for purple gloves in whole glove dynamic robotic hand.

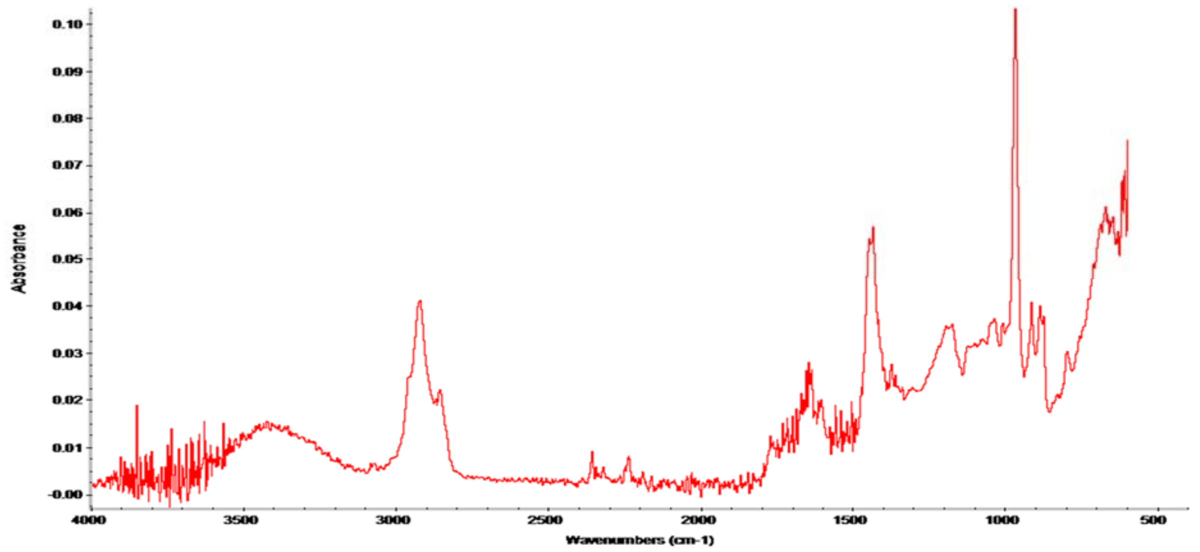


Infrared spectra for sterling gloves in whole glove dynamic robotic hand.

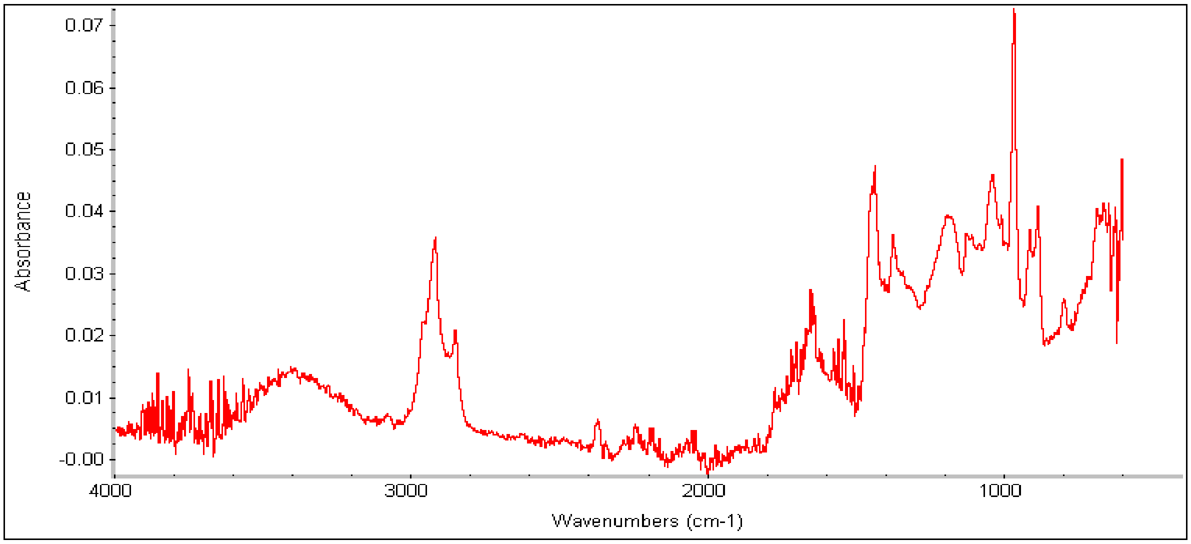


Infrared spectra for lavender gloves in whole glove dynamic robotic hand.

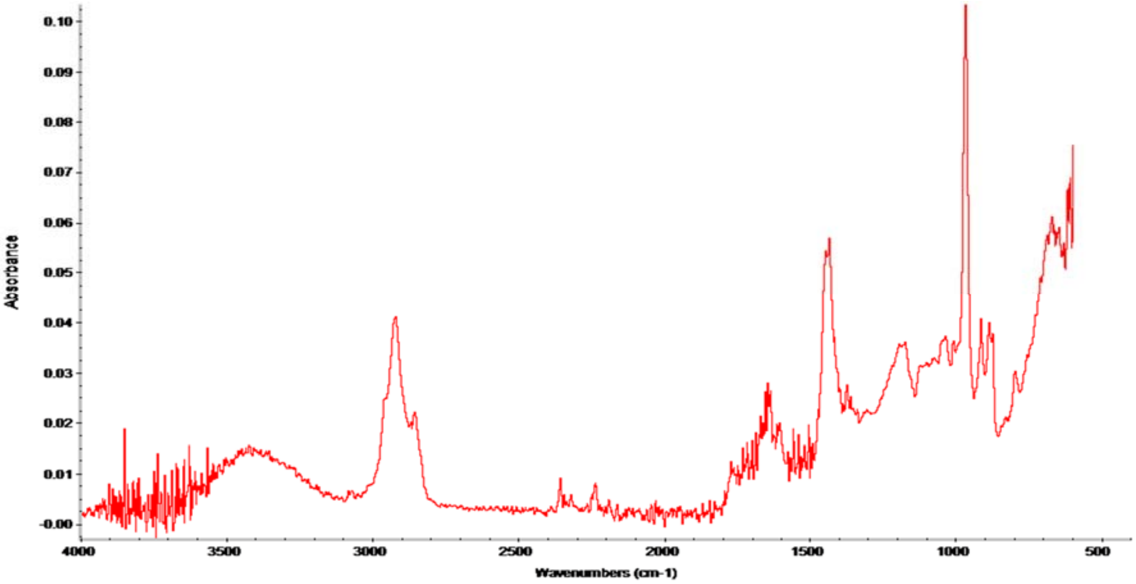
B.2, INFRARED SPECTRA FOR DSIPOSABLE NITRILE GLOVES IN WHOLE GLOVE STATIC ROBOTIC HAND



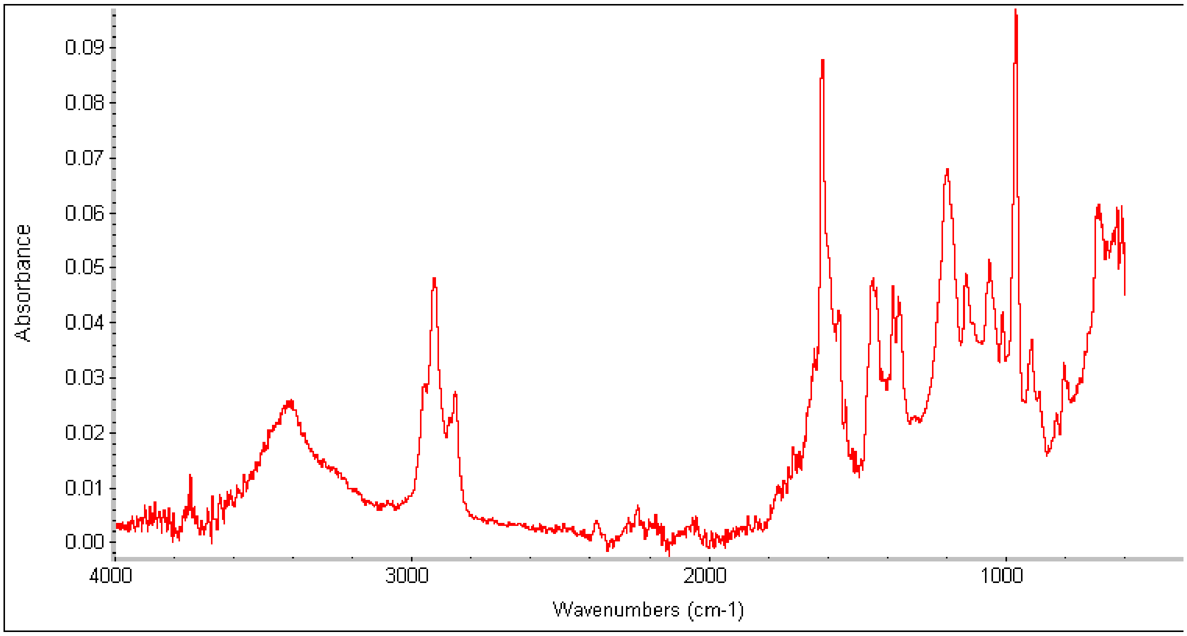
Infrared spectra for blue gloves in whole glove static robotic hand.



Infrared spectra for purple gloves in whole glove static robotic hand.

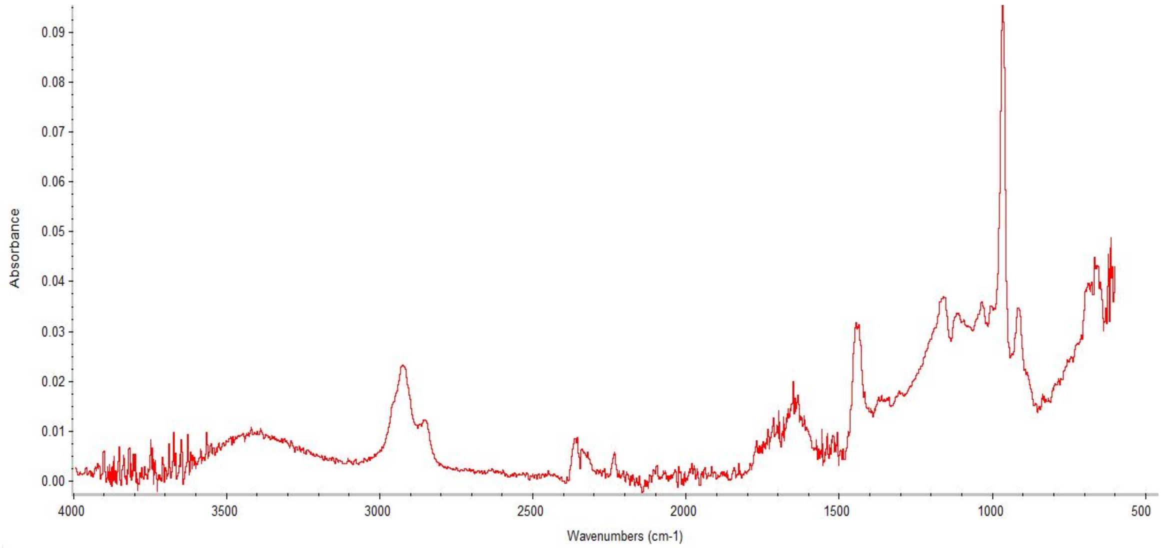


Infrared spectra for sterling gloves in whole glove static robotic hand.

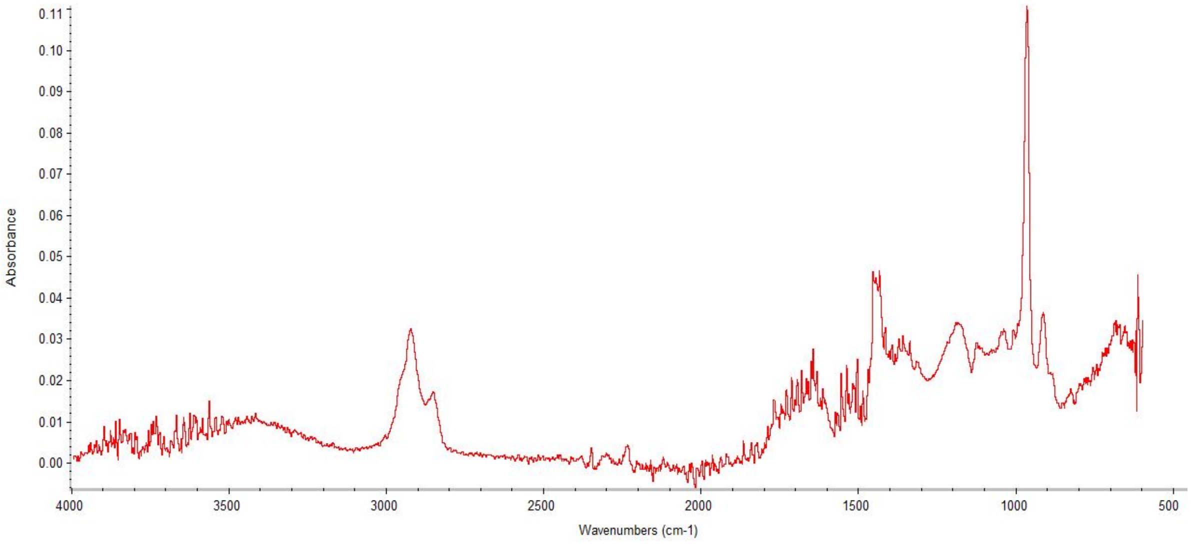


Infrared spectra for lavender gloves in whole glove static robotic hand.

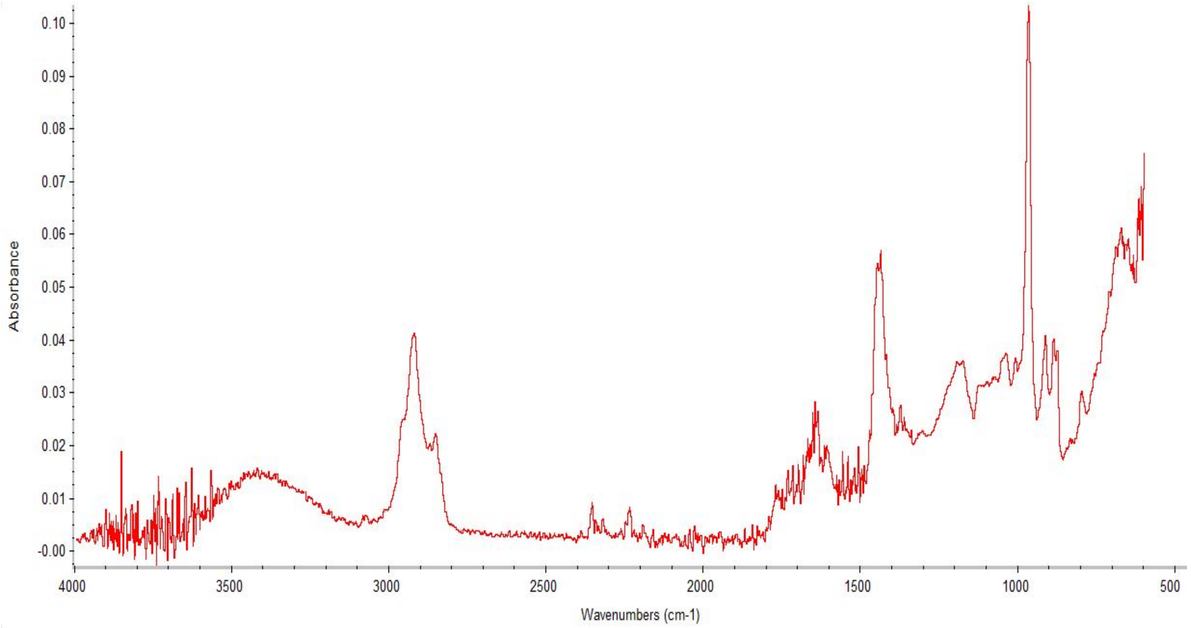
B.3, INFRARED SPECTRA FOR DSIPOSABLE NITRILE GLOVES IN ASTM CLOSED LOOP METHOD



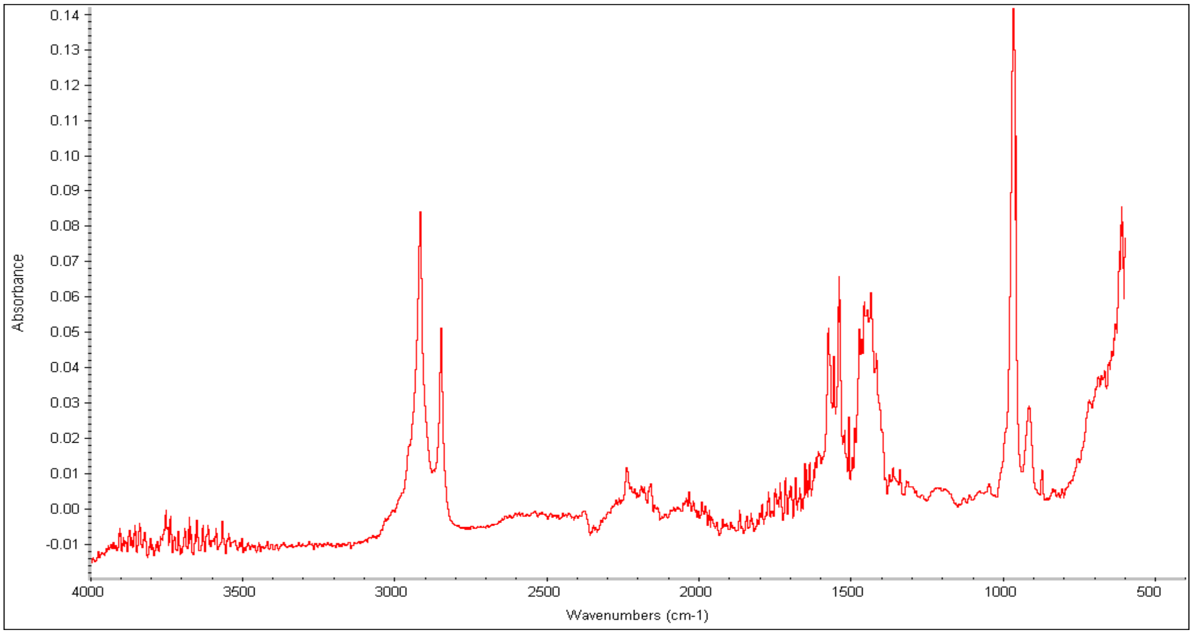
Infrared spectra for blue gloves in ASTM Closed loop method



Infrared spectra for purple gloves in ASTM Closed loop method



Infrared spectra for sterling gloves in ASTM Closed loop method



Infrared spectra for lavender gloves in ASTM Closed loop method