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Los Angeles

Impacts of Gunshot Cleaner Components and Glove Material on the Permeation of Gunshot
Residues

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

by

Travis Donald Cribbs

2024

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ABSTRACT OF THE DISSERTATION

Impacts of Gunshot Cleaner Components and Glove Material on the Permeation of Gunshot
Residues

by

Travis Donald Cribbs

Doctor of Philosophy in Environmental Health Sciences

University of California, Los Angeles, 2024

Professor Shane S. Que Hee, Chair

Human exposure to organic gunshot residues is a largely under researched topic in environmental and occupational health. This study aimed to examine how the components of a complex liquid blend affect the permeation behavior of its constituents. In the initial study, Hoppes No. 9 Gun Bore Cleaner, a firearm cleaning solvent, was chosen to test two types of disposable nitrile gloves from Kimberly-Clark's Kimtech Science: the thinnest (Lavender) and thickest (Blue). Testing was conducted using the 1-inch diameter closed-loop ASTM F739 cell at 35°C without recirculation with n-decane collection, and subsequent analysis via capillary gas chromatography-mass spectrometry to quantify the permeated compounds. Results showed that the thicker Blue glove resisted Hoppe's permeation more than the thinner Lavender glove. The Lavender glove permeated 3.2 times more mass at 60 minutes despite having the same standardized breakthrough times (7.5 ± 2.5 min). Unexpectedly, the kerosene fraction permeated at a much higher rate than anticipated, appearing at the standardized breakthrough time for Hoppe's, contrary to the Kimberly-Clark chemical resistance guide's listing for Sterling

disposable nitrile glove material. Notably, components reported by the glove manufacturer to quickly permeate nitrile material, like ethanol, did not permeate slower than expected, hinting at a possible carrier function. A semiquantitative risk assessment confirmed the inadequacy of both gloves, suggesting that individuals using personal protective equipment may not receive the anticipated resistance to chemical permeation when dealing with complex mixtures, thus heightening exposure risk. Further research is necessary to develop improved glove testing measures to ensure worker safety and health.

Additionally, this research examined how methyl centralite and ethyl centralite, two major gunshot residue components, simulated gunshot residues when permeating disposable nitrile glove material in three different solvents: Hoppe's Gun Cleaning Solvent, n-decane, and an n-decane/ethanol 7:3 v/v mixture. The objective was to determine whether ethanol plays a key role in a carrier effect. Permeation testing followed a modified ASTM F739-20 standard method at 35.0 ± 0.1 °C with sample quantification conducted via GC-MS analysis. The findings indicate significant variations in permeation behavior across solvents. Hoppe's solvent caused a type D permeation behavior characterized by a notable increase in permeation rate to a maximum post-standardized breakthrough time then followed by a lower SSPR. This was attributed to ethanol and other polar components. Conversely, the n-decane/ethanol mixture displayed a type A behavior with the SSPR being the maximum permeation rate, with markedly reduced permeation rates and total permeated analyte mass, indicating ethanol's likely pivotal role in the carrier effect. The study results emphasize the importance of considering the complete chemical composition of mixtures when assessing their interactions with protective equipment, and are suggestive of the need for comprehensive testing protocols in PPE selection. Limitations include the lack of prior research on firearm cleaning solvents' permeation through PPE and challenges

in comparing study findings with manufacturer-reported glove effectiveness for individual components. The study suggests adjusting concentrations of analytes and solvent groups for future investigations. Overall, this research offers insights into the permeation behavior of complex chemical mixtures through disposable nitrile gloves, aiding in better protective equipment selection and testing methodologies, and thereby improving worker safety and health.

Finally, this research examines how different glove materials affect the permeation of gunshot residue components compared to when these materials are used individually. Simulated gunshot residues containing methyl centralite and ethyl centralite dissolved in a 7:3 v/v mixture of n-decane and ethanol, mimicking gun cleaning solvent, were used to challenge two types of disposable glove materials: nitrile rubber and polyvinylchloride (PVC). Testing was again conducted using the closed-loop ASTM F739 cell without recirculation and n-decane collection at 35.0 ± 0.1 °C, followed by quantification of permeated compounds through capillary gas chromatography-mass spectrometry. Results showed that the combination of nitrile gloves alone exhibited the highest reduction in permeation. The next best reduction was observed with a combination of nitrile and vinyl gloves, with the vinyl side specifically facing the challenge solution. However, for Hoppe's solvent, the kerosene components appeared at the standardized breakthrough time. Moreover, using vinyl-only glove material led to increased permeation of ethyl centralite compared to methyl centralite, while all other material combinations resulted in decreased permeation of ethyl centralite compared to methyl centralite. This suggests that the specific combination or orientation of glove materials used affected the expected resistance to chemical permeation and needs to be confirmed with different challenge chemicals and glove material combinations. Further research is necessary to develop improved glove testing measures

to ensure worker safety and health, particularly when utilizing gloves with multiple types of materials such as laminated gloves.

The dissertation of Travis Donald Cribbs is approved.

Wendie A. Robbins

Su-Jung Tsai

Yifang Zhu

Shane S. Que Hee, Committee Chair

University of California, Los Angeles

2024

“Such I hold to be the genuine use of Gunpowder: that it makes all men alike tall.”

Thomas Carlyle

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I love you.

VITA

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Selected Publications

Cribbs T, and Que Hee SS. 2024. Permeation of gun cleaning solvents through disposable nitrile gloves. *J. Occup. Environ. Hyg.* doi: 10.1080/15459624.2024.2345815

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2. Cribbs, Travis; Que Hee, Shane. Permeation of gun cleaning solvents through disposable nitrile gloves. 2020 American Industrial Hygiene Conference and Exposition. June 2020, virtual (Oral)
3. Cribbs, Travis; Que Hee, Shane. Permeation of firearm fouling through disposable nitrile gloves. 2021 Southern California American Industrial Hygiene Association/Orange County American Industrial Hygiene Association Section Award Dinner. April 2021, Virtual (Oral)
4. Cribbs, Travis; Que Hee, Shane. Effects of polar and non-polar solvent components on simulated organic gunshot residue permeation characteristics through disposable nitrile gloves. 2021 American Industrial Hygiene Conference and Exposition. May 2021, virtual (Poster)

5. Cribbs, Travis; Que Hee, Shane. Permeation through disposable nitrile gloves: gun cleaning solvents and gunshot residue. 2021 American Industrial Hygiene Conference and Exposition. August 2021, virtual (Oral)
6. Cribbs, Travis; Que Hee, Shane. Permeation of inorganic gunshot residues dissolved in commercial gun cleaning solvent through disposable nitrile gloves. 2022 American Industrial Hygiene Conference and Exposition. May 2022, Nashville, TN (Poster)

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3. National Institute for Occupational Safety and Health – Southern California Education and Research Center Student Pilot Project Grant, 2020
4. Southern California American Industrial Hygiene Association/Orange County American Industrial Hygiene Association Section Scholarship Award, 2021

1. OVERVIEW

Firearms are a ubiquitous part of American life. Approximately one third of all adults in the United States own a firearm, and approximately 40 percent of all households in the country reportedly have a firearm within (Schaeffer 2023). In fact, there are more firearms owned in the United States than there are people, with roughly 120.5 firearms owned per 100 people (Black 2022). Despite some variation in the exact distribution of firearm ownership between different demographic groups, firearms have reportedly been owned by men and women of every race and creed listed in the United States Census.



Figure 1.1. Average American enjoying legal firearm ownership.

While there is very little information as to whether these numbers reflect recreational only, occupational only, or a mixture of both occupational and recreational firearm ownership, it is still safe to claim that many Americans have, at some point in their lives, interacted with a firearm. Despite this vast pool of interactions between the people and their firearms, a simple trip to a firing range would show that common hygienic practices needed to reduce the exposure to harmful associated chemicals, are woefully underutilized. If there is a discrepancy in recreational hygienic practices in regards to firearms, there is little wonder in how this translates to occupational exposures to those same chemicals.



Figure 1.2. Firearm and case of ammunition utilized in this research, mid-ejection.

Firearms are the most unseen and unstudied cause of occupational lead exposure in the United States and in the world (Ozonoff, 1994).

Lead on the Range - “The perils of firearms exist at both ends of the barrel”: Evidence gathered over decades has shown that workers in occupations that regularly utilize firearms have higher blood lead levels than the average member of their country of residence. While much research has been performed to measure blood lead levels in cross-sectional type studies, very little attention has been paid to baseline pre-shooting blood lead levels compared to post shooting levels. There have also been very few studies utilizing other bodily media, such as urine or stool, to measure biological lead levels in shooters. Despite this lack of data, there is even less information regarding the exposure to organic gunshot residues. With hundreds of known organic gunshot residues known to exist, very few studies address organic gunshot residues in populations (Manganelli et al. 2019) or the environment (Maitre et al. 2018). Furthermore, not one study was located that addressed the permeation of any gunshot residue through personal protective glove material. This research gap serves as the impetus for the following body of research.

In Chapter 2, the objective was to study the interaction of the components of a complex liquid mixture on the permeation parameters of its constituents. A firearm cleaning solvent, Hoppe’s no. 9 Gun Bore Cleaner, was selected to challenge two varieties of powderless, unsupported-unlined disposable nitrile gloves, the thinnest (Kimberly-Clark Lavender) and thickest (Kimberly-Clark Blue), using the 1-inch diameter ASTM F739 permeation cell with closed-loop n-decane collection without recirculation, followed by capillary gas chromatography-mass spectrometric quantitation of the permeated compounds. This was to establish a preliminary framework for organic gunshot residue permeation testing that would be

the basis of further research. Chapter 3 involved the permeation behavior of methyl centralite and ethyl centralite, simulating gunshot residues, through disposable nitrile glove material when exposed to three different solvents: Hoppe's Gun Cleaning Solvent, n-decane only, and a n-decane/ethanol 7:3 mixture. The aim was to identify if ethanol was the key driver of a carrier effect. A modified ASTM F739-20 standard method was employed for permeation testing, and GC-MS analysis was conducted for sample quantification. In Chapter 4, the objective was to study the effects of differing glove materials on the permeation of gunshot residues compared to each material as a single layer. Simulated gunshot residues of methyl centralite and ethyl centralite dissolved in a simulated gun cleaning solvent mixture of 7:3 n-decane/ethanol was utilized to challenge two varieties of disposable gloves materials, nitrile rubber and polyvinylchloride, using the above permeation cell, conditions, and analysis.

Overall, this study sought to quantitate many key aspects of organic gun cleaning solvent and gunshot residue permeation primarily through disposable nitrile gloves. The results of this study are, on their own, important indicators for a need of new research regarding these exposures, and also help shed light on incomplete information afforded to workers regarding the performance of personal protective equipment commonly utilized in the workplace. Finally, this research serves as the preliminary foundation for a new branch of occupational and environmental health research focused on the exposure to organic gunshot residues, one of the most underdeveloped bodies of knowledge in the field.

2. PERMEATION OF GUN CLEANING SOLVENTS THROUGH DISPOSABLE NITRILE GLOVES

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2.1. ABSTRACT

The objective was to study the interaction of the components of a complex liquid mixture on the permeation parameters of its constituents. A firearm cleaning solvent, Hoppes no. 9 Gun Bore Cleaner, was selected to challenge two varieties of disposable nitrile gloves, the thinnest (Kimberly-Clark Lavender) and thickest (Kimberly-Clark Blue), using the closed-loop ASTM F739 cell without recirculation and n-decane collection followed by capillary gas chromatography-mass spectrometric quantitation of the permeated compounds. The thicker Blue glove resisted the permeation of Hoppe's relative to the thinner Lavender glove as shown by 3.2 times more mass permeated by the Lavender glove at 60 min in spite of the same standardized breakthrough times, (7.5 ± 2.5 min). The kerosene fraction permeated faster at a much higher rate than expected. The Kimberly-Clark disposable nitrile glove chemical resistance guide lists a breakthrough time for kerosene to be 82 min for Sterling disposable nitrile glove material. However, for Hoppe's the kerosene components appeared at the standardized breakthrough time. Mixture components that were reported by the glove manufacture to quickly permeate the disposable nitrile material, such as ethanol, did not permeate at a rate slower than expected indicative of a possible carrier function. A semiquantitative risk assessment confirmed the unacceptability of both gloves. Persons utilizing personal protective equipment, such as gloves, may not be afforded the expected resistance to chemical permeation when chemicals are in a

suitable mixture hence enhancing the risk of exposure. More research is needed to produce better glove testing measures to assure the safety of workers.

2.2. INTRODUCTION

In 2020, the United States full-time equivalent worker incidence rate for non-fatal skin diseases or disorders was 1.8 per 10,000 for 19,800 cases, the second largest non-fatal injury (Bureau of Labor and Statistics 2020). A common cause for these injuries is exposure to organic chemicals. Personal protective equipment (PPE) is often the first and last line of defense against chemical exposure, especially gloves, to protect hand skin from liquids. The most common glove type used to reduce exposure to aqueous solutions is a disposable nitrile glove (Anna 2003; Grand View Research 2022). These gloves are also preferred because of their comfort, ergonomics, affordability, and convenience of use (Anna 2003). However, disposable nitrile gloves do not resist permeation of all types of chemicals (Anna 2003). They are predicted to have the largest global compound annual growth rate (5.8%) of any non-powdered disposable glove type from 2022 to 2030 (Grand View Research 2022).

Glove manufacturers commonly use the ASTM F739-99 standard (ASTM 1999) and the ASTM F739-12 standard (ASTM 2012) to conduct permeation testing for gloves. Temperature requirements for these tests are user-defined ± 1 °C for the 1999 standard, or at 27 ± 1 °C for the 2012 standard. Only the ASTM D6978-05 standard, a similar permeation testing standard specifically for chemotherapy drugs, specifies a testing temperature of 35 ± 2 °C, a temperature expected of human skin (Nadel et al. 1971). The most recent ASTM F739 standard at the time of this publication is the ASTM F739-20 standard (ASTM 2020).

Hoppe's no 9 gun bore cleaner is a complex mixture of multiple polar and non-polar components used to aid in the cleaning of firearms during maintenance. No research has

previously been conducted on the permeation of this gun bore cleaner through any glove material and no study was identified that measured its permeation through skin. No study of the permeation of components of Hoppe's in combination was found. Furthermore, there is little information or research available that identify the interactions that occur among the components of complex liquid mixtures that challenge gloves. Chemical permeation resistance parameters reported by disposable nitrile glove manufacturers are limited and focus usually on pure chemicals (Kimberly-Clark 2015; Ansell 2019), as is also true even for chemically protective gloves (Ansell 2016). It is likely that the permeation parameters of components will differ from those when alone (Banaee and Que Hee 2020).

This research sought to characterize the permeation of Hoppe's no. 9 gun bore cleaner, and to compare those permeation characteristics to known single-chemical permeation data.

2.3. METHODS

2.3.1. Materials

Commercially available disposable nitrile gloves (Kimberly-Clark XL powder-free disposable Blue and Lavender nitrile exam gloves, unlined and unsupported, No. 53104) were selected due to their wide use and popularity (Grand View Research 2022), along with published data regarding resistance to chemical permeation from key mixture components (Kimberly-Clark 2015). Glove pieces of 1.50 in. (3.76 cm) in diameter were cut from the palm and conditioned overnight at room temperature and 54% relative humidity as described elsewhere (ASTM 2012) before their initial thicknesses were measured in triplicate with an Electronic Digital Micrometer Model CO-030025 (0-25mm, 0.001 resolution) and with a Mettler AE260 Analytical Balance (Hightstown, NJ, USA).

Hoppe's no. 9 gun bore cleaner was purchased from Amazon (Seattle, WA); Its most recent 2022 safety data sheet lists the components as kerosene [petroleum] (30-60%), ethanol (10-30%), propan-2-ol (5-10%), amyl acetate (1-5%), 2-methylbutyl acetate (1-5%), methanol (1-5%), ammonium hydroxide (<1%), (R)-p-mentha-1,8-diene (<1%), 1,8-cinole (<1%), 4-methylpentan-2-one (<1%), geraniol (<1%), naphthalene (<1%), nerol (<1%), citronellol (<1%), p-cymene (0.121%), and diammonium peroxodisulphate (<1%) (Bushnell Holdings 2022). When this study began, the then current 2016 Safety Data Sheet indicated the following composition: ethyl alcohol, 15-40%; kerosene, 15-40%; oleic acid, not available; amyl acetate, 5-10%; and ammonium hydroxide, 1-5%. The PPE guidance was to use protective clothing impervious to its ingredients, practically the same as in the most recent Safety Data Sheet with the added precautions that the glove supplier/manufacturer should be consulted, that the chosen glove must also resist degradation as well as permeation, and that it comply with OSHA 1910.138.

The n-Decane (99%) used for collection of permeates and the sodium dichromate (99%) used to produce 55% relative humidity to condition gloves at room temperature were secured from Fisher Scientific (Chino, CA, USA). Methyl salicylate (99%), analytical grade ethanol (99.5%), lauric acid (99.9%) and isosafrole originated from Sigma Aldrich (St Louis, MO, USA). Helium (99.9999%) was purchased from Air Liquide (El Segundo, CA). Water was sourced from a Millipore Milli-Q Water System and Millipore Simplicity Water Purification final polishing system (Temecula, CA).

An ASTM F739-12 compliant 1-inch internal diameter permeation cells model I-PTC-600, including aluminum flanges, Teflon gaskets, bolts, and nuts were purchased from Pesce Lab (Kennett Square, PA, USA), which is a non-recirculating closed-loop system. Temperature

control was achieved by dipping the cell up to its stems in a Fisher Shaking Bath Model 2870 held at 35.0 ± 0.1 °C (Chino, CA, USA).

An Agilent 6890N Network GC System and 5973 Network Mass Selective (MS) Detector equipped with an Agilent fused silica capillary column 60 m x 0.320 mm x 1.0- μ m DB-1701 film, part number 123-0763 (Santa Clara, CA, USA) were used for analysis.

A Fisher Scientific Centrifric Model 228 was used to centrifuge samples. A Bransonic Ultrasonicator Model B2200R-1 mixed samples. An American Optical MicroStar hand-held microscope (Buffalo, NY, USA) allowed examination of materials. Hamilton Micro-syringes, 0-10 μ L (Reno, NV, USA) facilitated GC-MS sample injections.

Standards were produced using Eppendorf pipets/tips and Pyrex volumetric flasks, and permeation collection samples were stored in 2-ml borosilicate glass vials, all from Fisher Scientific, Chino, CA, USA.

2.3.2. Calculations

All calculations were performed on Microsoft Excel 365 version 2212. These included linear regressions for the method of internal standards where slopes, intercepts, standard deviations, correlation coefficients, and p-values were calculated.

The cumulative mass for each challenge cell was calculated by multiplying the observed concentration by the volume in the test cell corrected for mass already sampled at the time of sampling.

Analyte permeation rates were calculated by dividing the differences of the collection side analyte mass between adjacent sampling times in mg or μ g by the glove exposed area in cm^2 , and by the sampling time interval in minutes (min).

The diffusion coefficient D in cm^2/min of a challenge chemical was calculated using the following equation:

$$D = \frac{l^2}{6 * L_t} \quad (\text{Equation 1})$$

where l is the glove thickness in cm , and L_T is lag time in min from the time intercept at zero permeation of a component mass/area versus sampling time plot.

Statistical differences between representative values and their standard deviations involved Student t testing at the $p \leq 0.05$ level (Rosner 2016).

2.3.3. Testing for Permeation Cell Collection Solvent

The candidates for collection solvents were carbon disulfide, cyclohexane, decane, hexane, perfluorohexane, and water. A 1.0-mL volume of Hoppe's was added slowly to 1.0 mL of candidate solvent in a 15-mL centrifuge tube with shaking. The mixture was ultrasonicated for 5 min and left for 24 hours to assess phase separation visually.

2.3.4. Identification and Quantitation of Gun Bore Cleaner Components

A 150 mg/mL concentration of Hoppe's in decane was serially diluted to 1.0 mg/mL. A volume of 2.0 μL of this solution was injected into the GC-MS in the total ion current (TIC) mode (m/z 30-550 at 70 eV). The initial temperature program was 80 $^\circ\text{C}$ for 4 min, ramped at 10 $^\circ\text{C}/\text{min}$ up to 250 $^\circ\text{C}$ for 10 min, and finally increased at 10 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$ and held for ten min at helium flow rate of 2.5 mL/min. The injector, column-mass spectrometer link, and quadrupole temperatures were respectively 280 $^\circ\text{C}$, 230 $^\circ\text{C}$, and 150 $^\circ\text{C}$.

The temperature program was further optimized by being started at 80 °C, held for 4 min, ramped to 280 °C at 1 °C/min, and then held for 20 min, other temperatures being the same as just above.

For quantitation by the internal standard (IS) method for Lavender gloves with the selected ion monitoring mass spectrometry mode, 100- μ L triplicate standards of Hoppe's in μ g/mL of 0.0, 0.10, 0.20, 0.50, 1.0, 2.0, 2.5, 5.0, 10. to determine analyte standardized breakthrough time, and of 10,000, 20,000, 40,000, 50,000, 60,000, 80,000, 100,000 and 200,000 for the steady state period. A 10- μ L volume of 1,000 μ g/mL lauric acid was added to each as IS with thorough mixing, thus reducing the Hoppe's concentrations by 9.1%. The GC-MS ions of specific m/z were: ethanol, 27, 29, 31, and 45; methyl-butyl acetate, 43, 55, 61, and 70; 1,2,3-tetrahydro-6-methyl-naphthalene, methyl salicylate, and β -isosafrole, 92, 104, 118, 120, 131, 146, 152, and 162; lauric acid, 43, 60, and 73; and oleic acid, 41, 55, and 69. The standards were analyzed by GC-MS and the linear regions of analyte peak area divided by IS peak area average versus analyte concentration subjected to linear regression analysis.

For the Blue gloves, a new internal standard, 1,2-dibromopropane, allowed less interference with the permeated Hoppes components. For the optimized temperature program, the initial temperature was set to 74 °C, ramped up to 250 °C at 100 °C/min, then immediately ramped down to 140 °C at 100°C/min and held there for 10 min. After this, the temperature was ramped back up to 250 °C at 80 °C/min and held there for 0.75 min, completing run data acquisition. Post-run column cleaning ensued at 250 °C for 55 min. Data collection time was 20 min, and total run time including post-run cleaning of the column was 75 min. Five selected ion monitoring detection groups were chosen: Group 1, the alcohol group, began detection at 3.00 min with m/z 27.0, 29.0, 31.0, and 45.0. Group 2, the 1,2-dibromopropane group, began at 6.00

min with m/z 121.0 and 123.0. Group 3, the methyl salicylate group, started at 15.50 min with m/z 92.0, 120.0, and 152.0. Group 4, the 6-methyltetralin group, initiated at 17.50 min with m/z 118.0, 131.0, and 146.0 m/z. Group 5, the β -isosafole group, began detection at 18.50 min with m/z 104.0, 131.0, and 162.0. The solvent delay was from 8.50 to 15.50 min.

Internal standard curves were produced with 0, 1, 10, 25, 50, 100, 1000, 10000, 25000, 50000, and 100000 $\mu\text{g/mL}$ of the combined equal concentration standards in n-decane in triplicate.

2.3.5. Permeation Cell Preparation

The ASTM F739-12 standard test method for permeation of liquids and gases through protective clothing materials under conditions of continuous contact was used for permeation testing (ASTM 2012) with four permeation cells. Glove swatches 45 mm in diameter were cut from the palm areas. The swatches were examined with the hand-held microscope to detect deficiencies, holes, abrasions, or other defects. The test materials were then conditioned in a desiccator (Fisher Scientific, Chino, CA, USA) at $55 \pm 1\%$ relative humidity, maintained by a saturated aqueous solution of sodium dichromate, and 27 ± 2 °C for 24 hours. After removal from the desiccator, glove thicknesses were measured (micrometer) and their weights (balance). The swatches were then placed in the test cells between their gaskets, and the locking bolts tightened to 5.0 ft·lb by torque wrench. Water was placed on the collection side of each cell and the cells placed on top of brown paper towels to check for leaks. After one hour of no leaks, the water was drained, the cells disassembled, cleaned with neutral liquid detergent and water, rinsed with deionized water, and then air-dried. The swatches were returned to the desiccator for an additional 24 hours of conditioning.

2.3.6. Sample Collection

The collection sides of the assembled cells were filled with 10 mL of decane (technical decane for Lavender gloves; n-decane for the Blue gloves). After visual inspection that no leaks immediately occurred, the cells were placed in the shaker water bath. Hoppe's (10 mL) was then introduced into three of the four cells. A 100- μ L sample was immediately taken from each collection side and deposited into separate 1-mL vials precooled to -15 °C. The bath was set to shake at 75 ± 1 rpm. A sample of the bath water was also taken for analysis. All samples were stored in a freezer at -15 °C. Additional sampling occurred at 5, 10, 30, 60, 120, 180, 240, 360, and 480 min for the Lavender gloves and 5, 10, 15, 20, 30, 40, 60, 120, and 240 min for the Blue gloves, the shaker being stopped temporarily. After 480 min, the fluids from the collection sides were retained in 10-mL graduated cylinders. Another sample of the bath water was taken for analysis to confirm no leaks. Samples were stored in a freezer at -15 °C.

2.3.7. Sample Analysis

Analysis of the samples involved GC-MS using the appropriate IS method and SIM parameters. Samples were processed from the earliest to the latest sampling time in the sequence cell blank, 1, 2, and then 3. Manual integration was used for all sampling times.

Concentrations for ethanol, methyl salicylate, and β -isosafrrole were calculated for each cell using the internal standard linear regression equations. Aggregate concentrations were calculated by averaging the individual component concentrations from cells 1, 2 and 3, corrected by values for the blank cell.

The ratios of the analytes were also calculated at each sampling time point to provide an indication on whether the permeation was differential or concerted and thus to determine if an aggregate permeation rate could be calculated for Hoppe's rather than individual component rates.

2.4. RESULTS

2.4.1. Initial Testing

2.4.1.1 Collection Solvent

Water was determined to be an unsuitable collection medium due to gelatinization of Hoppe's upon mixing. Carbon disulfide was initially considered as a collection solvent due to its miscibility with Hoppe's. However, due to its ability to degrade nitrile, carbon disulfide was not chosen. Perfluorohexane, while suitable for complex hydrophobic mixtures like cutting oils, was immiscible with Hoppe's as were hexane and cyclohexane. Decane was miscible with Hoppe's and did not appear to degrade the Lavender glove nitrile.

2.4.1.2 GC-MS Analysis

All the standards met their purity specifications except for isosafrole which contained $97.2 \pm 0.1\%$ isosafrole and $2.8 \pm 0.1\%$ β -isosafrole, assuming the same response factor for these isomers.

Analysis of Hoppe's using the total ion current GC-MS mode revealed one prominent peak at approximately 3.0 min, whose mass spectrum fit ethanol. At approximately 7.0 min, a large peak was confirmed to be the solvent. At approximately 9.0 min, the decane peak subsided and was followed by a field of large, asymmetric peaks with shoulders, representing the kerosene fraction (Bushnell Holdings 2022). Three prominent peaks with retention times of 16, 18, and 19 min were selected within this kerosene field for future analysis. At approximately 21 min, a short broad peak eluted, of mass spectrum consistent with oleic acid. At approximately 27 min,

another short broad peak eluted that appeared to be ethyl oleate. Overall, the mixture consisted of at least 250 compounds, most being unsuitable for sensitive quantitation purposes.

Lauric acid was initially chosen as an IS due to its molecular weight (200.32 g/mol) and boiling point (300 °C). Temperature program optimization resulted in lauric acid being detected between the kerosene and the oleic acid peaks. The resolution was adequate for the early permeation period but not for the later periods when concentrations of Hoppe's components increased. Trial and error with various high-boiling point solvents allowed 1,2-dibromoethane to be selected instead as the optimal IS.

Three major resolved candidate peaks in the kerosene field were identified from TIC mass spectra to most likely be 1,2,3,4-tetrahydro-6-methyl-naphthalene, methyl salicylate, and β -isosafrole. Analytical grade methyl salicylate, analytical grade ethanol, and a mixture of isosafrole and β -isosafrole had relative retention times that were the same as the mixture constituents, and generated similar mass spectra, thus confirming their identities. Subsequent testing showed the estimated ethanol concentration in the Hoppe's mixture to be $29.7\% \pm 5.9\%$. This is within the range of ethanol listed in the 2019 Hoppe's data sheet of between 10-30 % (Bushnell Holdings 2019; Bushnell Holdings 2022), and well within the expected concentration of the 2016 Hoppe's data sheet of between 15-45% (Bushnell Holdings 2016). The estimated concentration of methyl salicylate in Hoppe's was determined experimentally to be $(0.59 \pm 0.13\%)$. The Hoppe's data sheets did not list methyl salicylate as a component (Bushnell Holdings 2016; Bushnell Holdings 2019; Bushnell Holdings 2022), and the kerosene mixture standard that was tested produced a completely different chromatogram, albeit with a similar relative retention time span as the observed kerosene field in Hoppe's.

2.4.2. Lavender Nitrile Glove Permeation

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 2.1. Post-test thicknesses and masses of gloves 1, 2, and 3 are reported as their true values minus the blank difference, and their standard deviations pooled with the standard deviation of the blank. All differences between pre- and post-test glove characteristics were significant at the $p \leq 0.05$ level with four degrees of freedom. Specifically, all glove samples showed increases in both thickness and mass after the permeation experiment at the $p \leq 0.05$ level with four degrees of freedom.

Pre-permeation test gloves were not significantly different in thickness than the glove blank but were significantly thicker post-permeation at the $p \leq 0.05$ level with four degrees of freedom. However, the significantly thicker blank glove post-permeation test raises the concern of collection fluid back-permeation.

The standardized breakthrough time (SBT), the time in min at which the permeation rate reaches $0.1 \mu\text{g}/\text{cm}^2/\text{min}$, occurred between 5 and 10 min, that is, 7.5 ± 2.5 minutes. Collection side concentrations then increased rapidly. After 60 min, the calculated concentrations in the permeation cell were inaccurate because of IS resolution problems as the components of Hoppe's increased in concentration. The aggregate permeation rates up to 60 min are shown in Figure 2.1. The estimated cumulative mass of Hoppe's in the collection cell was calculated to be 1.07 ± 0.17 g at 60 minutes.

2.4.3. Blue Nitrile Glove Permeation

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 2.2. All glove pieces, excluding blanks, showed statistically significant increases in mass and thickness at the $p \leq 0.05$ level. Swelling of the glove material was observed to be $10 \pm 0.4\%$ for the challenge glove material compared to $4.9 \pm 0.4\%$ for the blank glove material. As

all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The standardized breakthrough time occurred between 5 and 10 min, that is, 7.5 ± 2.5 min. Tests for linearity using a Student's *t*-distribution showed that the increases in concentration for ethanol, methyl salicylate, and Hoppe's were linear at the $p \leq 0.05$ level during the steady state between 30 and 240 min. The differences between mass ratios of components in the Hoppe's mixture when compared to their ratios in the collection solvent were less than 30%. The results implied that all the components of the mixture permeated together and that an aggregate permeation rate for the mixture could be calculated from the fraction of each analyzed component. The aggregate permeation rates are shown in Figure 2.2. The steady state permeation rate was calculated to be $1642 \pm 350 \mu\text{g}/\text{cm}^2/\text{min}$. The lag breakthrough time was 17.3 ± 2.1 min and using eqn. 1, the diffusion coefficient was $22.5 \pm 2.7 \times 10^{-7} \text{ cm}^2/\text{min}$. The equation is valid for no significant swelling or shrinking. The estimated cumulative mass of Hoppe's in the collection cell was calculated to be 0.337 ± 0.034 mg at 60 minutes and 4.66 ± 0.55 mg at 480 minutes.

There was an increase in the signal area ratio of kerosene components compared to ethanol (Figures 2.3.-2.5.). The methyl salicylate/ethanol signal area ratio was found to be 0.45 ± 0.7 as sampled, compared with 0.12 ± 0.1 in the Hoppe's standard. The 1,2,3,4-tetrahydro-6-methyl-naphthalene/ethanol signal area ratio was 0.091 ± 0.016 as sampled, compared with 0.038 ± 0.007 in the Hoppe's standard. The β -isosafrol/ethanol signal area ratio was found to be 0.084 ± 0.010 as sampled, compared to 0.024 ± 0.003 in the Hoppe's standard. Each kerosene component to ethanol signal ratio was approximately 3 to 4 times larger compared to the signal

ratio found in the Hoppe's standard. When these signal area ratio data were translated into mass ratios through linear regression, there were no statistically significantly different mass ratios relative to the original Hoppe's mass ratios at $p \leq 0.05$ because of the greater imprecision of the mass ratio data.

2.5. DISCUSSION

The analytes had been selected on the basis of being the most sensitive surrogates for the polar and nonpolar fractions of Hoppe's. The consistency of the mass ratios of the collected analytes relative to the original Hoppe's mixture showed that the permeation involved all analytes together rather than differentially, allowing a Hoppe's mixture permeation rate to be calculated for Figures 1 and 2. This behavior is consistent with a "carrier effect" (Perron et al. 2002; Banaee and Que Hee 2020) of a dominant constituent that provides the same result as a penetration mechanism involving bulk liquid transfer rather than a permeation mechanism where differential permeation is more likely. The penetration type permeation mechanism is shown with dimethyl sulfoxide solvent that carries other solution components with it through membranes (Kurihara-Bergstrom et al. 1986).

The thicker Blue glove slowed the permeation of Hoppe's when compared to the thinner Lavender glove as shown by 3.2 times more mass permeated by the Lavender glove at 60 min relative to the Blue in spite of the standardized breakthrough times being the same, (7.5 ± 2.5 min). This breakthrough time is unacceptable by Kimberly-Clark sole breakthrough time criteria. A peak permeation rate of 10.3 ± 2.9 mg/cm²/min occurred for the Lavender glove at 30 minutes, compared with 2.16 ± 0.15 mg/cm²/min at 120 minutes for the Blue glove. There appears to be a trend amongst the major glove producers to emphasize breakthrough or detection times rather than steady state permeation rates (Kimberly-Clark 2015; Ansell 2016; Ansell 2019). This lone

criterion is not acceptable for the present data since the Blue glove is more resistant than the Lavender one.

Figure 2 shows that a Type D permeation (ASTM 2012) scenario has occurred, involving an initial spike in the permeation rate after which the rate slows and stabilizes. This can occur on ‘heavy’ swelling of the gloves (ASTM 2012). Heavy swelling is not itself defined in the ASTM standard. However, as the percent difference in thickness between the pre-and post-test measurements were less than 10% for all glove pieces, it is unknown if swelling was the primary driver. It is unlikely that actual penetration occurred as the gloves were examined under a hand-held microscope for physical defects, such as pinholes or breaks, both before and after permeation testing.

The breakthroughs of kerosene components were also significantly faster than expected. The Kimberly-Clark disposable nitrile glove chemical resistance guide lists a breakthrough time for kerosene to be 82 min for Sterling disposable nitrile glove material (Kimberly-Clark 2015). However, kerosene components in the Hoppe’s mixture broke through the Blue and Lavender disposable nitrile material in 7.5 min. The stated permeation time for ethanol was 7 min for Sterling gloves. Furthermore, a Kimtech chemical permeation table for Kimtech Blue nitrile gloves provides a permeation time of 28 min for ethanol using the EN 16523-1 permeation standard with 61% degradation per the EN 374-4 degradation standard (Kimberly-Clark 2022). Unfortunately, this particular chemical permeation table did not have information on kerosene or other fuel oils.

The increase in permeation of the Hoppe’s components may have been affected by the selection of n-decane as an alternative collection fluid. A previous study (Xu and Que Hee 2008) showed that increased back-permeation of a collection fluid may increase the detection

breakthrough time, normalized breakthrough time, and permeated mass. Furthermore, the less rapid increase in permeation rate when compared to the Lavender nitrile gloves would lead to the conclusion that penetration did not occur for the Blue glove. It is likely that other components of the mixture, probably ethanol, facilitate the accelerated co-permeation of other Hoppe's components. This also supports the probability that other constituents in the Hoppe's mixture would be co-permeated at an accelerated rate as well.

Risk assessment of the allowed permeation through the gloves depends not only on time worn before doffing, work activities, temperature, and doses of permeated/penetrated exposure chemicals, but also on what permeation mechanism occurs. Here the penetration-like permeation implies that toxicology characteristics of Hoppe's itself should be used rather than the toxicology of its components. The most recent Hoppe's Safety Data Sheet of 2022 (Bushnell Holding 2022) indicates that apart from contact toxicity with the skin and mucous membranes and causing allergies/sensitization for these endpoints, Hoppe's is a central nervous system toxicant and an IARC Group 1 carcinogen, the latter because of the presence of polyaromatic hydrocarbons in the kerosene fraction. ASTDR does not have any non-cancer or cancer risk values associated with fuel oils but has a minimum risk level for kerosene inhalation of 0.01 mg/m^3 based on decreased blood glucose levels observed in male rats. IARC lists fuel oils as possible human carcinogens but does not have a risk value associated with oral or inhalation routes of exposure. Neither ASTM or IARC have determined risks associated with dermal exposure to kerosene due to lack of data and studies. ASTDR has no minimum risk level associated with oral kerosene exposure due to 'unsuitable' data. In contrast, ACGIH recommends a kerosene TLV (A3 carcinogen and sensitizer) of 200 mg/m^3 based on vapor exposures causing irritation and central nervous system effects (ACGIH 2023). The NIOSH REL is 100 mg/m^3 (NIOSH 2023). There is

no OSHA PEL. The risk assessment situation for kerosene and therefore Hoppe's is muddled, inhalation guidelines being from as low as technologically possible for a human carcinogen to 200 mg kerosene equivalent/m³. If the kerosene content is about the same as for ethanol (30%), 200 mg kerosene equivalent/m³ is 667 mg Hoppe's/m³ assuming no other contributions to toxicity. Thus the 667 mg Hoppe's/m³ is the equivalent air concentration Time Weighted Average over 8 hours. For a moderate workload, the 8-hour air volume inspired is about 10 m³ (Que Hee 1993), thus leading to a maximum absorbed dose of 6.7 g of Hoppe's to elicit systemic central nervous system effects. Because of breath expiration, the real absorbed dose is probably about 70% of this, or about 4.7 g (Que Hee 1993).

Utilizing three separate models for dermal permeation, the estimated maximum dermal permeation in $\mu\text{g Hoppe's cm}^{-2} \text{ min}^{-1}$ was 8.47 ± 5.1 and 15.4 ± 2.0 (Fiserova-Bergerova et al. 1990), 1.34 ± 0.80 and 0.671 ± 0.087 (Guy and Potts 1993), and 6383 ± 3800 and 231.4 ± 0.1 (Wilschut et al. 1995) for ethanol and methyl salicylate, respectively (Figures 2.6. and 2.7.), at 8 hours of exposure, for intact skin. Assuming an average human hand of 186 cm² area, the total dose absorbed after 8 hours in g would be 0.37 ± 0.22 and 0.069 ± 0.009 (Fiserova-Bergerova et al. 1990), 0.058 ± 0.35 and 0.030 ± 0.004 (Guy and Potts 1993), and 276.6 ± 166.5 and 10.7 ± 1.4 (Wilschut et al. 1995) for ethanol and methyl salicylate, respectively (Figures 2.8. and 2.9.). All three models are unable to estimate the dermal permeation of kerosene as there is no set molecular weight for such mixtures. However, since ethanol appears to act as a carrier for the kerosene fraction, ethanol alone largely determines the permeation kinetics. but the toxicity is more related to that of kerosene rather than to ethanol alone. Since ethanol is about 30% of the mass of Hoppe's, the absorbed dose of Hoppe's could be between 0.2 g (Guy and Potts 1993)

and 923 g (Wilschut et al. 1995). This range includes the 6.7 g maximum threshold based on the TLV.

2.6. LIMITATIONS

No previous studies have been conducted on the permeation of firearm cleaning solvents through personal protective equipment, such as nitrile gloves. Furthermore, while the ASTM provides standard methods for testing the permeation of chemicals through glove materials, no known chemical resistance chart for the gloves used in this study provide additional information that would allow this study to fully recreate the conditions which generated their reported results, especially the collection solvent, open- or closed-loop sampling design, testing temperatures, or the analytical instrument and method used. Because of this lack of information, it is not entirely possible to compare the stated effectiveness as published by the glove manufacturer to the results found in this study.

It is a primary goal of this study to not only explore the permeation characteristics of a commercial grate complex mixture through a ubiquitous glove material, but also to establish a reproducible method that reflect the conditions of materials as used by workers.

2.7. CONCLUSIONS

Hoppe's gun cleaning solvent readily permeates through disposable nitrile gloves. As the vast majority of gun cleaning solvents contain a similar mixture of a non-polar petroleum fraction and a highly polar alcohol fraction as its primary mixture, it is likely that these results are generalizable to other gun cleaning solvents, and any other mixture that comprises of a polar/non-polar solvent mixture. More testing is needed to confirm similar increased permeation of non-polar components through nitrile gloves with other gun cleaning solvent brands, or other polar/non-polar mixtures. A thicker glove, such as a chemically protective glove, would likely

perform better than disposable gloves. It is also possible that double gloving with an outer glove more resistant to ethanol, such as Viton (Anna 2003), with a disposable nitrile glove under would fare much better due to possible decreased co-permeation occurring. Further testing should be performed to confirm this. It is not recommended that single disposable nitrile gloves, even of the thickest variety, be used when continually handling Hoppe's, or equipment saturated or covered with Hoppe's.

Hoppe's readily permeates through both gloves with the Blue glove more resistant in terms of mass permeated after breakthrough. It is unknown what exact methods and materials were used for permeation testing by the glove manufacturer, which may explain some differences in the permeation parameters of the material. However, because it is unfeasible to test all permeation conditions with all possible variables accounted for, the method proposed in this study represents the closest conditions for a human hand wearing a glove possible given the equipment used, and thus show a risk of exposure to gun cleaning solvents permeating through disposable nitrile glove material.

A different analytical analysis technique, such as utilizing an open-loop collection method with a nitrogen gas carrier to an FID detector, would offer some benefits for future testing for the ethanol component of Hoppe's No. 9 Gun Bore Cleaner. However, the inability to easily determine the diffusion coefficient is a disadvantage of this method. Further testing should focus on more resistant configurations and materials while maintaining the advantages of disposable gloves.

2.8. FIGURES

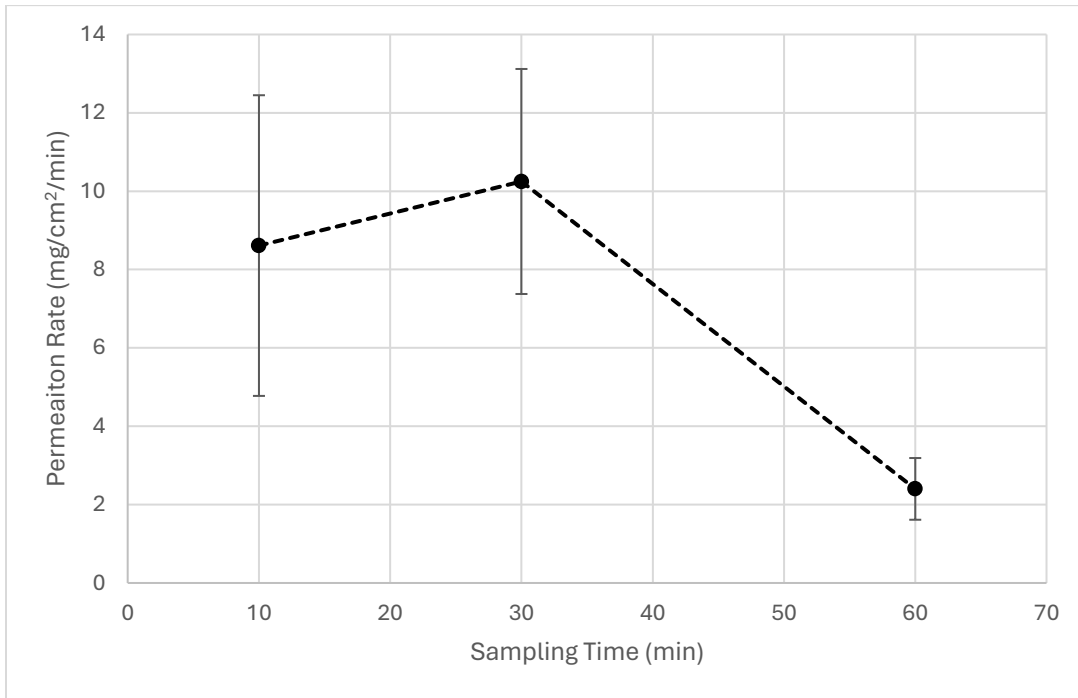


Figure 2.1. Aggregate Hoppe's permeation rate through three Lavender nitrile gloves.

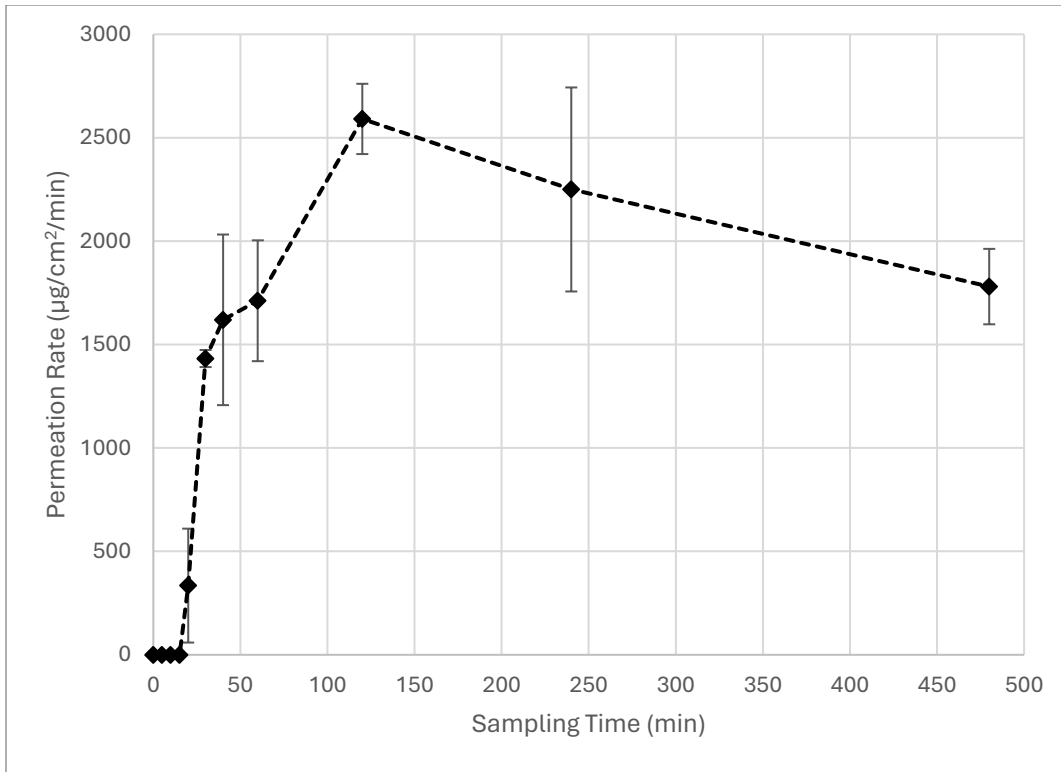


Figure 2.2. Aggregate Hoppe's permeation rate through three Blue nitrile gloves.

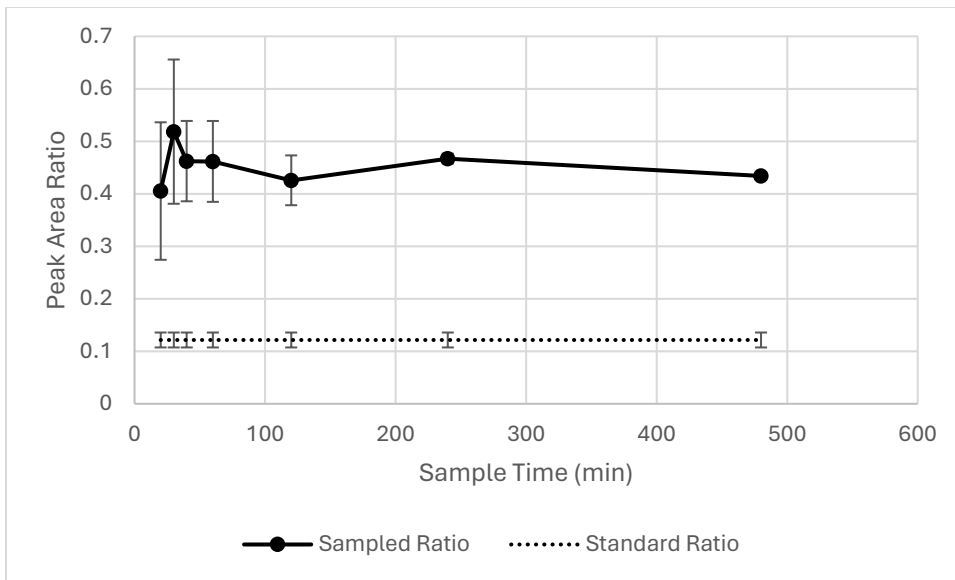


Figure 2.3. Peak area ratios for methyl salicylate and ethanol.

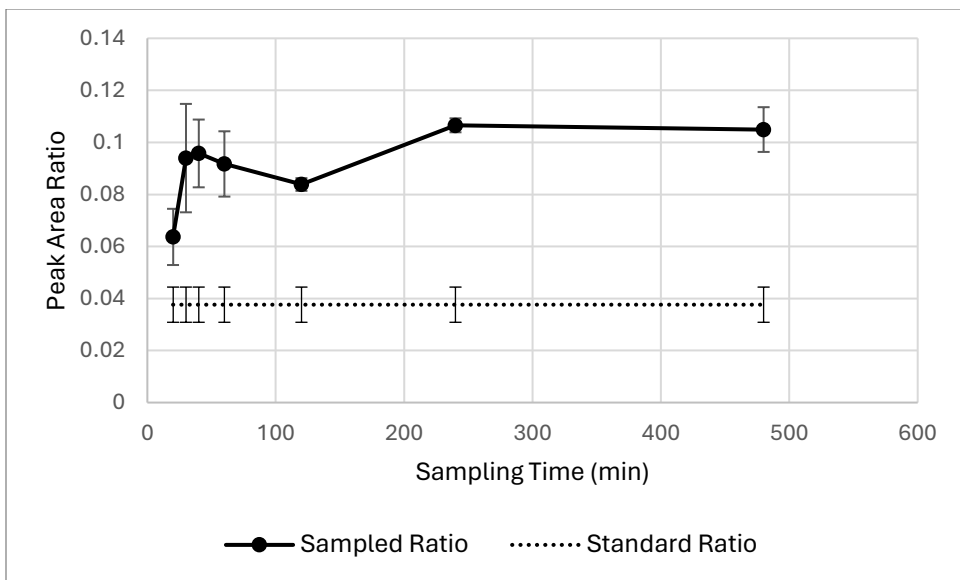


Figure 2.4. Peak area ratios for 1,2,3,4-tetrahydro-6-methyl-naphthalene and ethanol.

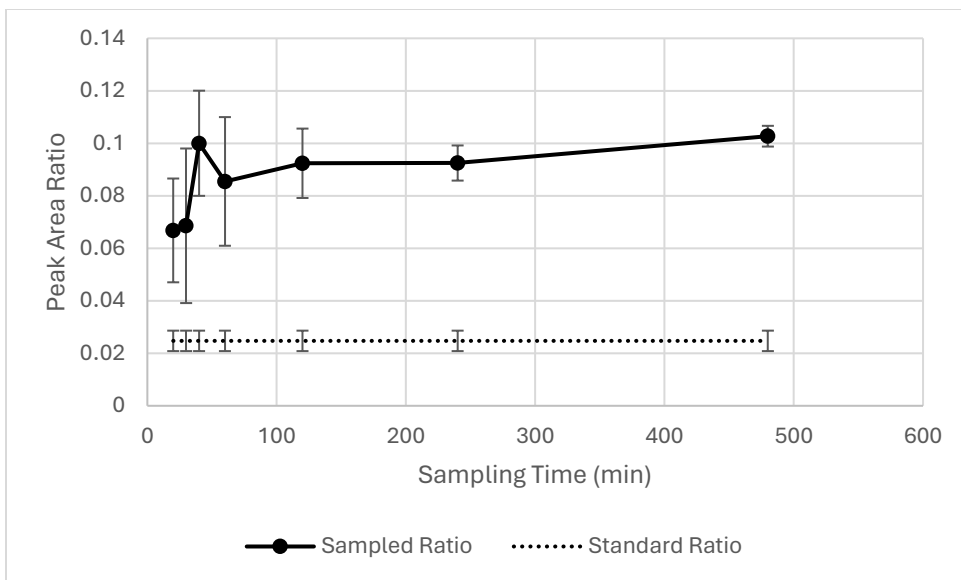


Figure 2.5. Peak area ratios for β -isosafrole and ethanol.

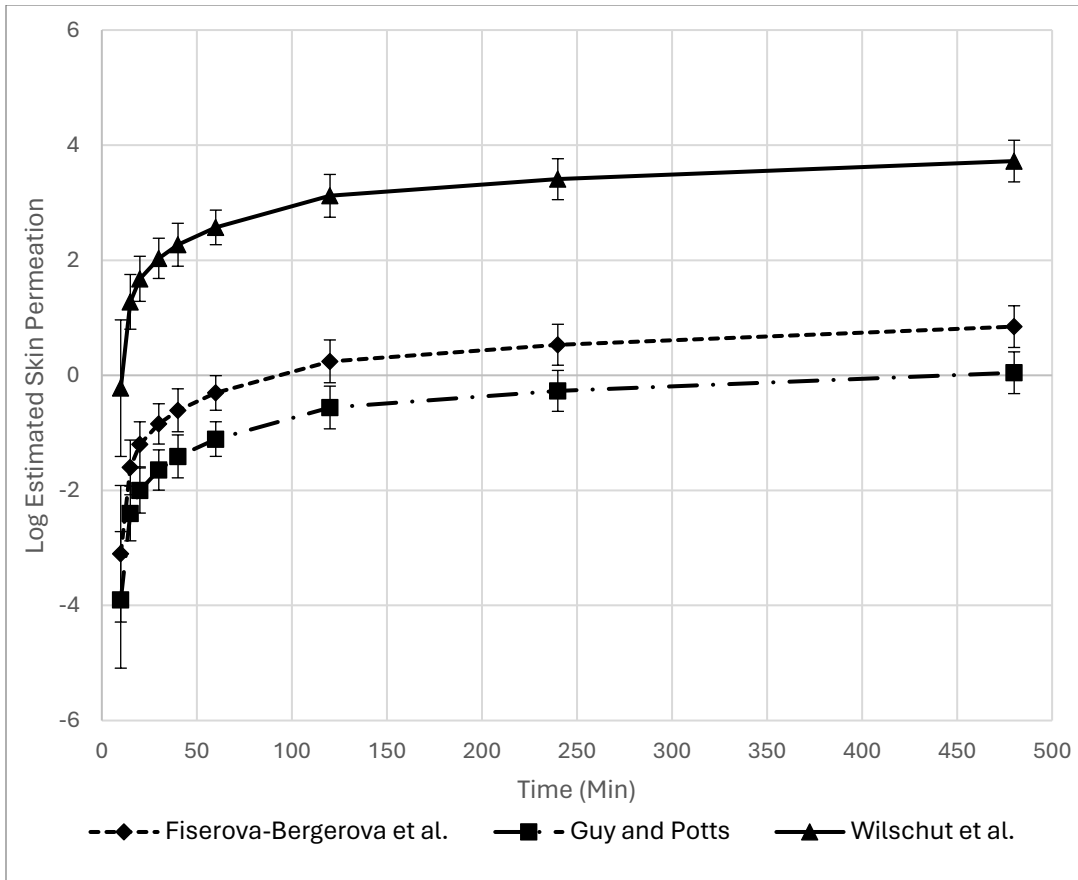


Figure 2.6. Estimated log skin permeation rate for ethanol.

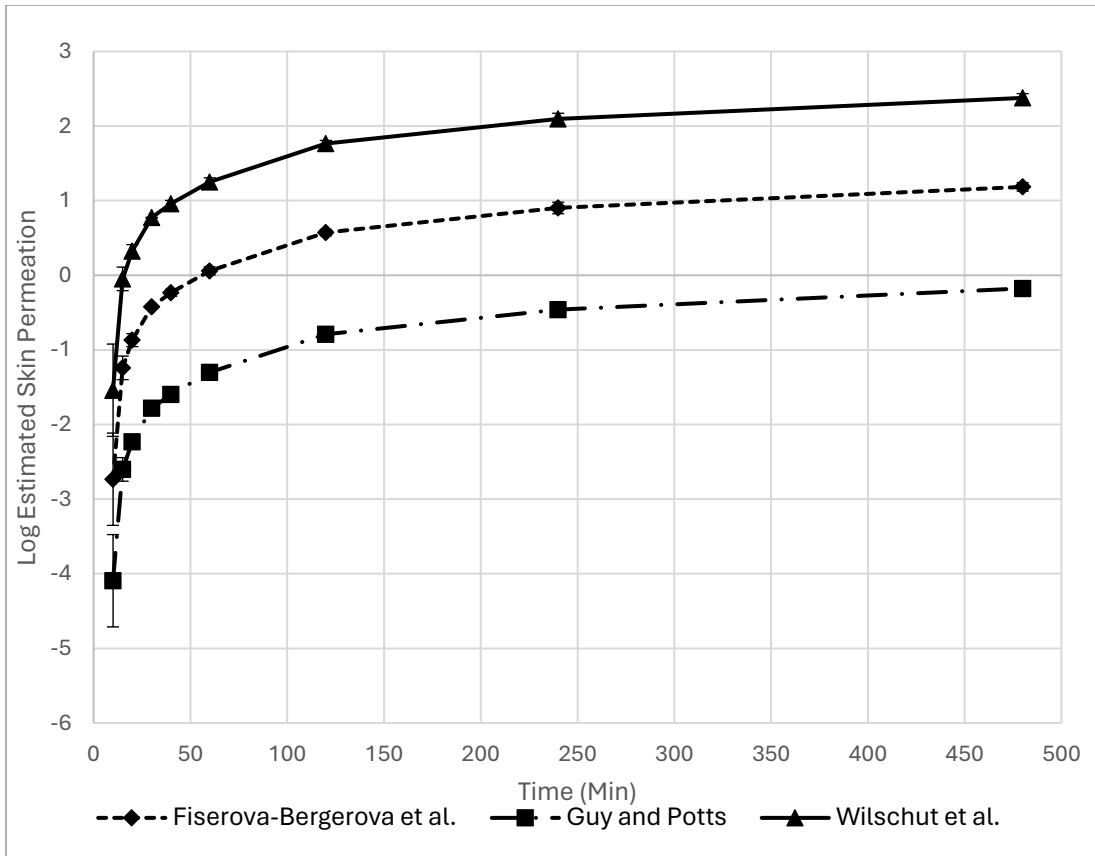


Figure 2.7. Estimated log skin permeation rate for methyl salicylate.

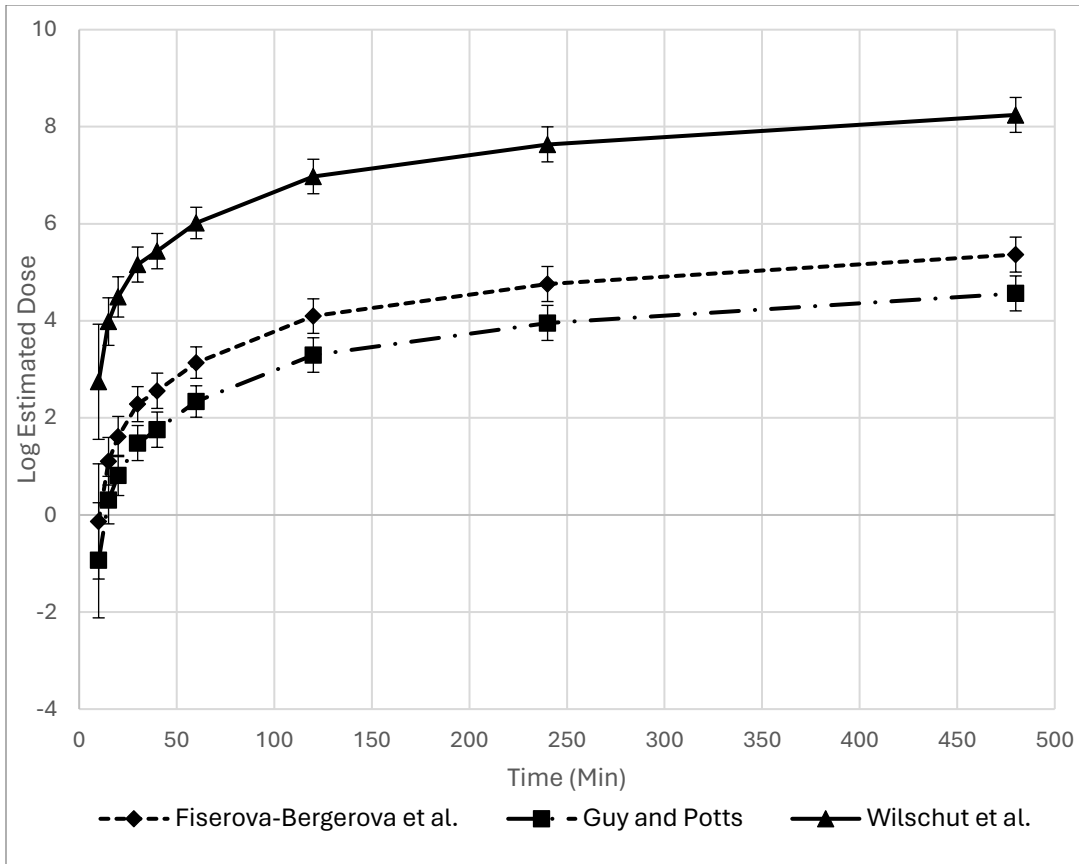


Figure 2.8. Estimated log dose for ethanol.

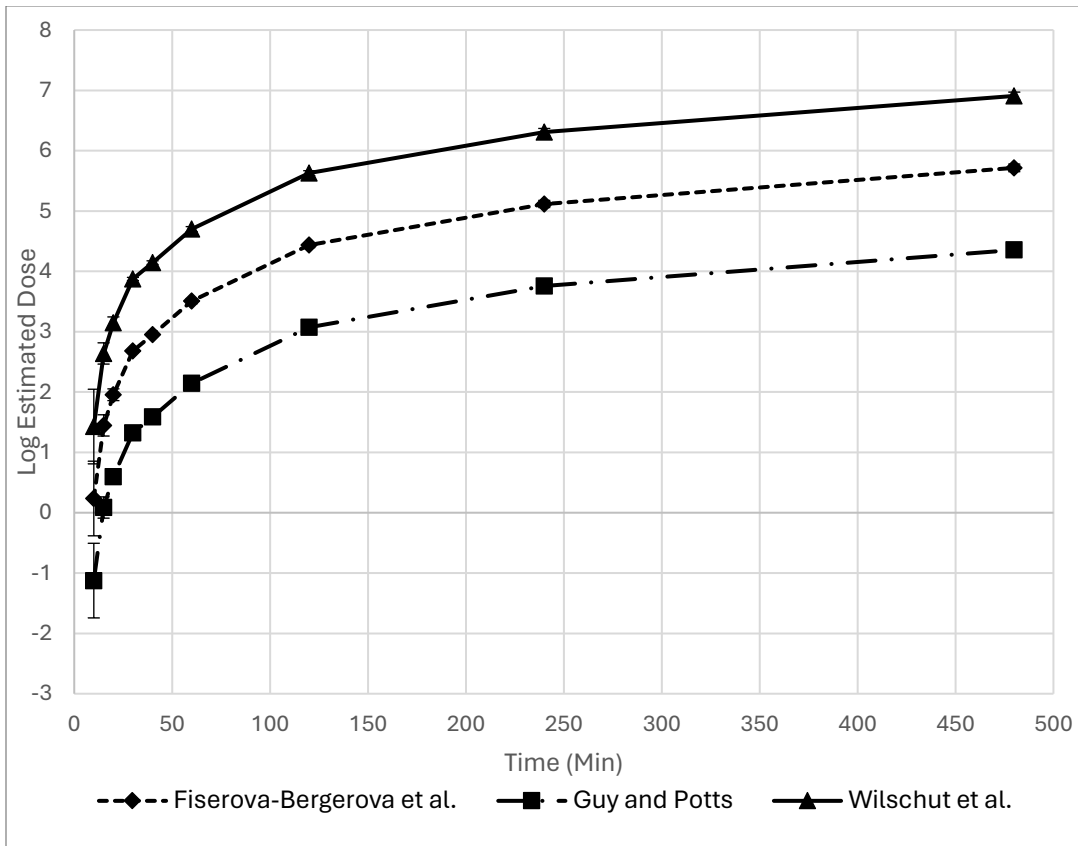


Figure 2.9. Estimated log dose for methyl salicylate.

2.9. TABLES

Table 2.1. Lavender nitrile glove physical data before and after permeation for three different gloves corrected for blank glove data.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
1	72 ± 2	78 ± 3	112.5 ± 0.1	114.0 ± 0.3
2	73 ± 2	78 ± 2	124.1 ± 0.1	128.1 ± 0.1
3	72 ± 1	79 ± 2	131.4 ± 0.1	132.5 ± 0.1

Table 2.2. Blue nitrile glove physical data before and after permeation for three different gloves corrected for blank data.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
1	153 ± 2	158 ± 3	196.5 ± 0.1	201.1 ± 0.1
2	153 ± 1	159 ± 3	212.9 ± 0.2	220.8 ± 0.1
3	152 ± 2	160 ± 1	217.5 ± 0.1	226.8 ± 0.1

3. EFFECTS OF POLAR AND NON-POLAR SOLVENT COMPONENTS ON SIMULATED ORGANIC GUNSHOT RESIDUE PERMEATION CHARACTERISTICS THROUGH DISPOSABLE NITRILE GLOVES

3.1. ABSTRACT

This study investigated the permeation behavior of methyl centralite and ethyl centralite, simulated gunshot residues, through disposable nitrile glove material when exposed to three different solvents: Hoppe's Gun Cleaning Solvent, n-decane only, and a n-decane/ethanol 7:3 mixture. The aim was to identify if ethanol is the key driver of a previously observed carrier effect. A modified ASTM F739-20 standard method was employed for permeation testing, and GC-MS analysis was conducted for sample quantification. Results reveal significant differences in glove physical characteristics and permeation behavior among solvents. Hoppe's solvent exhibited a type D permeation behavior with a substantial increase in permeation rate after a standardized breakthrough time, attributed to ethanol and other polar components. In contrast, the n-decane/ethanol mixture displayed a type A behavior. Substantially decreased permeation rates and total permeated analyte mass show that ethanol is likely the key driver of the carrier effect. The study underscores the importance of considering the complete chemical composition of mixtures in assessing their interactions with protective equipment and highlights the need for comprehensive testing protocols in PPE selection. Limitations include the lack of previous research on firearm cleaning solvents' permeation through PPE and challenges in comparing study results with manufacturer-reported glove effectiveness. Adjusted concentrations between analytes and solvent groups are recommended for future investigations. Overall, this research provides valuable insights into the permeation behavior of complex chemical mixtures through disposable nitrile gloves, informing better protective equipment selection and testing practices.

3.2. INTRODUCTION

In 2020, the United States full-time equivalent worker incidence rate for non-fatal skin diseases or disorders was 1.8 per 10,000 for 19,800 cases, the second largest non-fatal injury (Bureau of Labor and Statistics 2020). A common cause for these injuries is exposure to organic chemicals. Personal protective equipment (PPE) is often the first and last line of defense against chemical exposure, especially gloves, to protect hand skin from liquids. The most common glove type used to reduce exposure to aqueous solutions is a disposable nitrile glove (Anna 2003; Grand View Research 2022). These gloves are also preferred because of their comfort, ergonomics, affordability, and convenience of use (Anna 2003). However, disposable nitrile gloves do not resist permeation of all types of chemicals (Anna 2003). They are predicted to have the largest global compound annual growth rate (5.8%) of any non-powdered disposable glove type from 2022 to 2030 (Grand View Research 2022).

The most commonly used testing standards by glove manufactures are the ASTM F739-99 standard (ASTM 1999) and the ASTM F739-12 standard (ASTM 2012) to conduct permeation testing for gloves. There are varied testing temperature requirements between those standards; ± 1 °C for the 1999 standard, or at 27 ± 1 °C for the 2012 standard. Only the ASTM D6978-05 standard, a similar permeation testing standard specifically for chemotherapy drugs, specifies a testing temperature of 35 ± 2 °C, a temperature expected of human skin (Nadel et al. 1971). The most recent ASTM F739 standard at the time of this publication is the ASTM F739-20 standard (ASTM 2020).

Hoppe's no 9 gun bore cleaner is a complex mixture of multiple polar and non-polar components used to aid in the cleaning of firearms during maintenance. Previous research (Chapter 2) has shown that certain non-polar components in Hoppe's such as kerosene, permeate

much more quickly than expected through nitrile gloves. It was speculated in that research that the presence of dominant polar chemical components in the Hoppe's mixture, such as ethanol, were likely causing a carrier effect (Perron et al. 2002; Banaee and Que Hee 2020) that increased the non-polar component permeation. No study was found comparing the permeation observed with a common analyte between multiple solvent types. Furthermore, there is little information or research available that identify the interactions that occur among the components of complex liquid mixtures that challenge gloves.

This research sought to characterize the permeation of methyl centralite and ethyl centralite, simulated gunshot residues, through disposable nitrile glove material by three solvents, Hoppe's, n-decane only, and a n-decane/ethanol mixture, and to observe if ethanol is the likely driver of the previously observed carrier effect.

3.3. METHODS

3.3.1. Materials

Commercially available disposable nitrile gloves (Kimberly-Clark XL powder-free disposable Blue nitrile exam gloves, unlined and unsupported, No. 53104) were selected due to their wide use and popularity (Grand View Research 2022), along with published data regarding resistance to chemical permeation from key mixture components (Kimberly-Clark 2015). Glove pieces of 1.50 in. (3.76 cm) in diameter were cut from the palm and conditioned overnight at room temperature and 54% relative humidity as described elsewhere (ASTM 2012) before their initial thicknesses were measured in triplicate with an Electronic Digital Micrometer Model CO-030025 (0-25mm, 0.001 resolution), and their weights with a Mettler AE260 Analytical Balance (Hightstown, NJ, USA).

Hoppe's no. 9 gun bore cleaner was purchased from Amazon (Seattle, WA); Its most recent 2022 safety data sheet lists the components as kerosene [petroleum] (30-60%), ethanol (10-30%), propan-2-ol (5-10%), amyl acetate (1-5%), 2-methylbutyl acetate (1-5%), methanol (1-5%), ammonium hydroxide (<1%), (R)-p-mentha-1,8-diene (<1%), 1,8-cinole (<1%), 4-methylpentan-2-one (<1%), geraniol (<1%), naphthalene (<1%), nerol (<1%), citronellol (<1%), p-cymene (0.121%), and diammonium peroxodisulphate (<1%) (Bushnell Holdings 2022). When this study began, the then current 2016 Safety Data Sheet indicated the following composition: ethyl alcohol, 15-40%; kerosene, 15-40%; oleic acid, % not available; amyl acetate, 5-10%; and ammonium hydroxide, 1-5%. The PPE guidance in 2016 was to use protective clothing impervious to Hoppe's ingredients, practically the same as in the most recent Safety Data Sheet with the added precautions that the glove supplier/manufacturer should be consulted, that the chosen glove must also resist degradation as well as permeation, and that it complies with OSHA 1910.138.

The n-decane (99%) used for collection of permeates and the sodium dichromate (99%) used to produce 55% relative humidity to condition gloves at room temperature were secured from Fisher Scientific (Chino, CA, USA). Methyl centralite (99%), ethyl centralite (99%), diphenylamine (99%), and analytical grade ethanol (99.5%) originated from Sigma Aldrich (St. Louis, MO, USA). Helium (99.9999%) was purchased from Air Liquide (El Segundo, CA). Water was from a Millipore Milli-Q Water System and Millipore Simplicity Water Purification final polishing system (Temecula, CA).

No internal vendor was allowed to the researchers for firearms or ammunition. Thus, these materials were purchased from local public businesses. The Ruger Mini-14 used for generation of gunshot residue (GSR) was procured from Big 5 Sporting Goods (Santa Paula,

CA). The Federal 5.56 x 45mm NATO 55gr Full Metal Jacket ammunition was purchased from Turner's Outdoorsman (Oxnard, CA).

ASTM F739-12 compliant 1-inch internal diameter permeation cells model I-PTC-600, including aluminum flanges, Teflon gaskets, bolts, and nuts were purchased from Pesce Lab (Kennett Square, PA, USA), which is a non-recirculating closed-loop system. Temperature control was achieved by dipping the cell up to its stems in a Fisher Shaking Bath Model 2870 held at 35.0 ± 0.1 °C (Chino, CA, USA).

An Agilent 6890N Network GC System and 5973 Network Mass Selective (MS) Detector equipped with an Agilent fused silica capillary column 60 m x 0.320 mm x 1.0- μ m DB-1701 film, part number 123-0763 (Santa Clara, CA, USA) were used for analysis.

A Fisher Scientific Centrifuge Model 228 was used to centrifuge samples. A Branson Ultrasonicator Model B2200R-1 mixed samples. An American Optical MicroStar hand-held microscope (Buffalo, NY, USA) allowed examination of materials. Hamilton Micro-syringes, 0-10 μ L (Reno, NV, USA) facilitated GC-MS sample injections.

Standards were produced using Eppendorf pipets/tips and Pyrex volumetric flasks, and permeation collection samples were stored in 2-mL borosilicate glass vials, all from Fisher Scientific, Chino, CA, USA.

3.3.2. Calculations

All calculations were performed on Microsoft Excel 365 version 2402. These included linear regressions for the method of internal standards where slopes, intercepts, standard deviations, correlation coefficients, and p-values were calculated.

The cumulative mass for each challenge cell was calculated by multiplying the observed concentration by the volume in the test cell corrected for mass already sampled at the time of sampling.

Analyte permeation rates were calculated by dividing the differences of the collection side analyte mass between adjacent sampling times in mg or μg by the glove exposed area in cm^2 , and by the sampling time interval in minutes (min).

The diffusion coefficient D in cm^2/min of a challenge chemical was calculated using the following equation:

$$D = \frac{l^2}{6 \cdot L_T} \quad (\text{Equation 1})$$

where l is the glove thickness in cm, and L_T is lag time in min from the time intercept at zero permeation of a component mass/area versus sampling time plot.

Statistical differences between representative values and their standard deviations involved Student t testing at the $p \leq 0.05$ level (Rosner 2016).

3.3.3. Selection of Analytes and Solvents

Gunshot residue (GSR) was initially generated with a Ruger Mini-14 rifle chambered in 5.56 x 45mm NATO by firing 1000 rounds of Federal 5.56 x 45mm NATO 55gr Full Metal Jacket ammunition with a firing rate of approximately 10 rounds per minute. The GSR generation occurred between 10am and 12pm at an outdoor location in southern California chosen for its seclusion and lack of animal and plant life. The weather was clear and without wind. All brass ejected from the firearm during the GSR generation was collected and accounted for. The GSR generated was removed from the firearm receiver and bolt with a nylon cleaning brush and removed from the barrel with a nylon bore brush. The GSR was collected into a pre-

weighed Teflon container and capped. The vial was placed into a cooler with ice packs and stored there until transported to the laboratory, where they were finally stored in a -15 ± 2 °C freezer until analysis.

The collected GSR was prepared for analysis by dissolving a known mass of 10.0 mg in n-decane. The solution was ultrasonicated for 10 minutes to ensure complete dissolution of the GSR. A volume of 2.0 μ L of this solution was injected into the GC-MS in the total ion current (TIC) mode (m/z 30-550 at 70 eV). The initial temperature program was 80 °C, held for 4 min, ramped to 280 °C at 1 °C/min, and then held for 20 min at helium flow rate of 2.5 mL/min. The injector, column-mass spectrometer link, and quadrupole temperatures were respectively 280 °C, 230 °C, and 150 °C. The most intense peaks of the over 200 peaks were found to be methyl centralite (1,3-dimethyl-1,3-diphenylurea; CAS RN 611-92-7) and ethyl centralite (1,3-diethyl-1,3-diphenylurea; CAS RN 85-98-3), and were thus selected as the simulated organic GSR for this experiment. The remaining dissolved GSR was retained for future GSR testing.

An internal standard of diphenylamine was chosen to allow for little interference with the permeated GSRs and for its solubility in n-decane, ethanol, n-decane, a mixture of both, and Hoppe's Gun Cleaning Solvent (GCS). For the optimized temperature program, the initial temperature was set to 200 °C, ramped up to 250 °C at 5 °C/min, then immediately ramped down to 200 °C at 100 °C/min and held there for 10 min. After this, the temperature was ramped back up to 250 °C at 80 °C/min and held there for 10 min, completing run data acquisition. Post-run column cleaning ensued at 250 °C for an additional 10 min. Data collection time was 20 min, and total run time including post-run cleaning of the column was 45 min. Two selected ion monitoring detection groups were chosen. Group 1, the diphenylamine group, began detection at

12.00 min with m/z 167.0, 168.0, 31.0, and 169.0. Group 2, the centralite group, began at 17.00 min with m/z 77.0, 106.0, 120.0, 134.0 and 148.0.

Internal standard curves were produced with 0, 1, 10, 25, 50, 100, 1000, 10000, 25000, 50000, and 100000 $\mu\text{g/mL}$ of the combined equal concentration standards in n-decane in triplicate.

Three solvents were selected testing: 1) n-decane only, 2) a 7:3 mixture of n-decane and ethanol, and 3) Hoppe's Gun Cleaning Solvent (GCS). These were chosen to explore the effects of polar solvent components when mixed with non-polar solvents. This 7:3 mixture of n-decane and ethanol closely matches ratio of Hoppe's GCS, and allows comparisons between the two. Initial concentration of analytes in the Hoppe's GCS solvent was 50.8 mg/ml methyl centralite and 50.2 mg/ml ethyl centralite. Due to issues with solubility in the n-decane only solvent, the concentrations for analytes in n-decane only and n-decane/ethanol mixture solvents were modified to be 1.1 mg/ml methyl centralite and 52.2 mg/ml ethyl centralite.

3.3.4. Permeation Cell Preparation

The ASTM F739-12 standard test method for permeation of liquids and gases through protective clothing materials under conditions of continuous contact was used for permeation testing (ASTM 2012) with four permeation cells. Glove swatches 45 mm in diameter were cut from the palm areas. The swatches were examined with the hand-held microscope to detect deficiencies, holes, abrasions, or other defects. The test materials were then conditioned in a desiccator (Fisher Scientific, Chino, CA, USA) at $55 \pm 1\%$ relative humidity, maintained by a saturated aqueous solution of sodium dichromate, and 27 ± 2 °C for 24 hours. After removal from the desiccator, glove thicknesses were measured (micrometer) and their weights (balance). The swatches were then placed in the test cells between their gaskets, and the locking bolts

tightened to 5.0 ft·lb by torque wrench. Water was placed on the collection side of each cell and the cells placed on top of brown paper towels to check for leaks. After one hour of no leaks, the water was drained, the cells disassembled, cleaned with neutral liquid detergent and water, rinsed with deionized water, and then air-dried. The swatches were returned to the desiccator for an additional 24 hours of conditioning.

3.3.5. Sample Collection

The collection sides of the assembled cells were filled with 10 mL of n-decane. After visual inspection that no leaks immediately occurred, the cells were placed in the shaker water bath. The experimental solution was then introduced into three of the four cells. A 100- μ L sample was immediately taken from each collection side and deposited into separate 1-mL vials precooled to $-15\text{ }^{\circ}\text{C}$. 10 μ L of 10.0 mg/mL diphenylamine internal standard was added to the vials after sample collection, for a total diphenylamine concentration of 0.909 mg/mL in each sample. The bath was set to shake at 75 ± 1 rpm. A sample of the bath water was also taken for analysis. All samples were stored in a freezer at $-15 \pm 2\text{ }^{\circ}\text{C}$. Additional sampling occurred at 5, 10, 15, 20, 30, 40, 60, 120, and 240 min, the shaker being stopped temporarily. After 480 min, the fluids from the collection sides were retained in 10-mL graduated cylinders. Another sample of the bath water was taken for analysis to confirm no leaks. Samples were stored in a freezer at $-15 \pm 2\text{ }^{\circ}\text{C}$.

3.3.6. Sample Analysis

Analysis of the samples involved GC-MS using the appropriate IS method and SIM parameters. Samples were processed from the earliest to the latest sampling time in the sequence cell blank, 1, 2, and then 3. Manual integration was used for all sampling times.

Concentrations for methyl centralite and ethyl centralite were calculated for each cell using the internal standard linear regression equations. Aggregate concentrations were calculated by averaging the individual component concentrations from cells 1, 2 and 3, corrected by values for the blank cell.

3.4. RESULTS

3.4.1 Hoppe's Gun Cleaning Solvent

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 3.1. All glove pieces, excluding blanks, showed statistically significant increases in mass and thickness at the $p \leq 0.05$ level. Swelling of the glove material was observed to be $3.7 \pm 1.7 \mu\text{m}$ when corrected for the blank glove material. The increase in glove mass post permeation testing was observed to be $11.7 \pm 0.6 \text{ mg}$ when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of Hoppe's GCS on the glove material.

The limit of quantitation was $0.1 \mu\text{g/mL}$ and limit of detection was $0.01 \mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.00058x - 0.00742$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.00074x - 0.001781$. The r value for both equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite in Hoppe's solvent are shown in Figures 3.1. and 3.2., respectively. The standardized breakthrough time (SBT) occurred at $12.5 \pm 2.5 \text{ min}$ for both methyl centralite and ethyl centralite. A substantial increase

in permeation rate was observed between the SBT and 120 minutes, with a maximum permeation rate of $35.9 \pm 3.2 \mu\text{g}/\text{cm}^2/\text{min}$ for methyl centralite and $27.4 \pm 2.4 \mu\text{g}/\text{cm}^2/\text{min}$ for ethyl centralite. The steady state permeation rate (SSPR) was calculated to be $19.9 \pm 3.6 \mu\text{g}/\text{cm}^2/\text{min}$ for methyl centralite and $19.8 \pm 6.0 \mu\text{g}/\text{cm}^2/\text{min}$ for ethyl centralite. The aggregate permeation rates are shown in Figure 1. The L_t was 9.7 ± 0.7 min for methyl centralite and 13.3 ± 1.0 for ethyl centralite. Using eqn. 1, the diffusion coefficient was found to be $38.4 \pm 2.8 \times 10^{-7} \text{ cm}^2/\text{min}$ for methyl centralite and $27.9 \pm 2.1 \times 10^{-7} \text{ cm}^2/\text{min}$. The equation is valid for no significant swelling or shrinking. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 5.9 ± 0.0 mg at 60 minutes and 57.0 ± 1.7 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0.5 ± 0.1 mg at 60 minutes and 52.3 ± 1.8 mg at 480 minutes.

3.4.2. n-Decane Only Solvent

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 3.2. No significant changes in thickness were observed for any glove piece. Swelling of the glove material was observed to be $0.1 \pm 1.0 \mu\text{m}$ when corrected for the blank glove material. The increase in glove mass post permeation testing was observed to be 1.4 ± 0.2 mg when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The limit of quantitation was $0.1 \mu\text{g}/\text{mL}$ and limit of detection was $0.01 \mu\text{g}/\text{ml}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.00058x - 0.00742$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.00074x - 0.001781$. The r value for both

equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900. The permeation rate curves for methyl centralite and ethyl centralite in a n-decane solvent are shown in Figure 3.3. and Figure 3.4., respectively. The SBT occurred at 360 ± 120 min for ethyl centralite but was not achieved with methyl centralite. No SSPR was achieved by the maximum test time of 480 minutes. The maximum permeation rate at that time was calculated to be $0.07 \pm 0.02 \mu\text{g}/\text{cm}^2/\text{min}$ for methyl centralite and $0.2 \pm 0.1 \mu\text{g}/\text{cm}^2/\text{min}$ for ethyl centralite. The aggregate permeation rates are shown in Figure 2. Because no steady state permeation rate was achieved, no L_t was able to be calculated. Consequently, the diffusion coefficient could not be calculated either. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 0 ± 0 mg at 60 minutes and 0.1 ± 0.1 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0 ± 0 mg at 60 minutes and 0.2 ± 0.1 mg at 480 minutes.

3.4.3 n-Decane/Ethanol 7:3 Mixture Solvent

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 3.3. All glove pieces, excluding blanks, showed statistically significant increases in mass and thickness at the $p \leq 0.05$ level. Swelling of the glove material was observed to be $8.3 \pm 1.5 \mu\text{m}$ when corrected for the blank glove material. The increase in glove mass post permeation testing was observed to be 11.1 ± 1.1 mg when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of Hoppe's GCS on the glove material.

The limit of quantitation was 0.1 $\mu\text{g/mL}$ and limit of detection was 0.01 $\mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.00058x - 0.00742$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.00074x - 0.001781$. The r value for both equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite in an n-decane/ethanol 7:3 mixture solvent are shown in Figure 3.5. and Figure 3.6., respectively. The SBT occurred at 17.5 ± 2.5 min for ethyl centralite and 25 ± 5 min for methyl centralite. No substantial increase in permeation rate was observed between the SBT and 120 minutes for either analyte and generally presented a normal A-type permeation curve, with a maximum permeation rate of 0.5 ± 0.1 $\mu\text{g/cm}^2/\text{min}$ for methyl centralite and 10.6 ± 2.2 $\mu\text{g/cm}^2/\text{min}$ for ethyl centralite. A SSPR was observed beginning at approximately 120 minutes for both methyl and ethyl centralite. The SSPR was calculated to be 0.4 ± 0.1 $\mu\text{g/cm}^2/\text{min}$ for methyl centralite and 8.6 ± 2.0 $\mu\text{g/cm}^2/\text{min}$ for ethyl centralite. The aggregate permeation rates are shown in Figure 3. The L_t was 39.2 ± 1.8 min for methyl centralite and 38.0 ± 1.2 min for ethyl centralite. Using eqn. 1, the diffusion coefficient was found to be $94.4 \pm 4.4 \times 10^{-7}$ cm^2/min for methyl centralite and $97.3 \pm 3.1 \times 10^{-7}$ cm^2/min . The equation is valid for no significant swelling or shrinking. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 0.005 ± 0.001 mg at 60 minutes and 0.5 ± 0.1 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0.8 ± 0.1 mg at 60 minutes and 4.0 ± 0.2 mg at 480 minutes.

3.5. Discussion

The results of this study validate the suspicion formulated in Chapter 2 that ethanol plays a key role in the increased permeation of non-polar chemicals through nitrile gloves. While there are many other chemicals in Hoppe's that may have the ability to increase the permeation of methyl centralite and ethyl centralite as well, the substantial relative abundance of ethanol in the Hoppe's mixture makes it likely to be the prime driver of that carrier effect (Perron et al. 2002; Banaee and Que Hee 2020). However, those other components do have a visible effect on the results. The absence of any of these polar components significantly reduce the permeation of non-polar gunshot residues at the $P \leq 0.05$ significance level.

The most obvious difference in the results of this study is the difference in permeation rate behavior between Hoppe's and the n-decane/ethanol mixture. The permeation rate behavior exhibited with the Hoppe's challenge solvent is a pronounced type D permeation rate behavior, whereas the permeation rate behavior of the n-decane/ethanol challenge mixture is a type A permeation rate behavior. The presence of the type D permeation rate behavior causes an exponentially increased total analyte permeated mass compared to other permeation metrics. While the SSPR was doubled in the Hoppe's solvent test, the total permeated mass was more than five times that of the n-decane/ethanol mixture solvent for ethyl centralite. The likely key factor in these differences is the presence of other highly polar components in Hoppe's, such as methanol and isopropanol. As Hoppe's is a commercially sold chemical formulation, it is also likely that other 'trade secret' chemical components are present in the mixture that could have an even deeper effect on the differences in permeation parameters and behavior when compared to a n-decane/ethanol mixture. It must also be considered that n-decane was used as the non-polar base in lieu of kerosene for the simulated gun cleaning solvent mixture. This change was made

primarily to reduce noise and increase sensitivity for GC-MS analysis, as kerosene itself is a complex mixture of many petroleum compounds. There are likely some chemicals in the kerosene itself that may cause the observed changes in permeation between solvents of the present study.

3.6. LIMITATIONS

No previous studies have been conducted on the permeation of firearm cleaning solvents through personal protective equipment, such as nitrile gloves. Furthermore, while the ASTM provides standard methods for testing the permeation of chemicals through glove materials, no known chemical resistance chart for the gloves used in this study provide additional information that would allow this study to fully recreate the conditions which generated their reported results, especially the collection solvent, open- or closed-loop sampling design, testing temperatures, or the analytical instrument and method used. Because of this lack of information, it is not entirely possible to compare the stated effectiveness as published by the glove manufacturer with the results found in this study. Due to changes occurring in the concentration of methyl centralite and ethyl centralite between solvents due to solubility, this study should be repeated at a lowered common concentration.

3.7. CONCLUSIONS

This study investigated the cause of a carrier effect observed in a previous study where Hoppe's was used as challenge. The results indicate significant differences in glove physical characteristics and permeation characteristics between solvents with a common analyte. The results give evidence to show that the results of Chapter 2 are generalizable to other polar/non-polar mixtures. Permeation rate curves demonstrated a type D behavior for Hoppe's solvent, characterized by a substantial increase in permeation rate after a standardized breakthrough time

followed by a lower SSPR. In contrast, a type A behavior was observed for n-decane/ethanol mixtures. The presence of ethanol in Hoppe's was identified as a key driver for increased permeation of non-polar chemicals through nitrile gloves. However, other polar components in Hoppe's likely also contributed to this effect. The study also noted differences in permeation behavior and total permeated mass between Hoppe's and n-decane/ethanol mixtures, attributed to the presence of other highly polar components in Hoppe's.

These findings suggest that the presence of certain polar chemical components in complex mixtures like Hoppe's can significantly influence permeation parameters and behavior through nitrile gloves. The study highlighted the importance of considering the complete chemical composition of mixtures when evaluating their interactions with protective equipment. However, the study also acknowledged certain limitations, including the lack of previous research on firearm cleaning solvents' permeation through personal protective equipment and the challenges in comparing study results with manufacturer-reported glove effectiveness due to differences in testing conditions. Additionally, solubility concerns necessitate further investigation with adjusted concentrations between analytes and solvent groups. Overall, the study provides valuable insights into the permeation behavior of complex chemical mixtures through disposable nitrile gloves, emphasizing the need for comprehensive testing protocols and considerations in protective equipment selection.

3.8. FIGURES

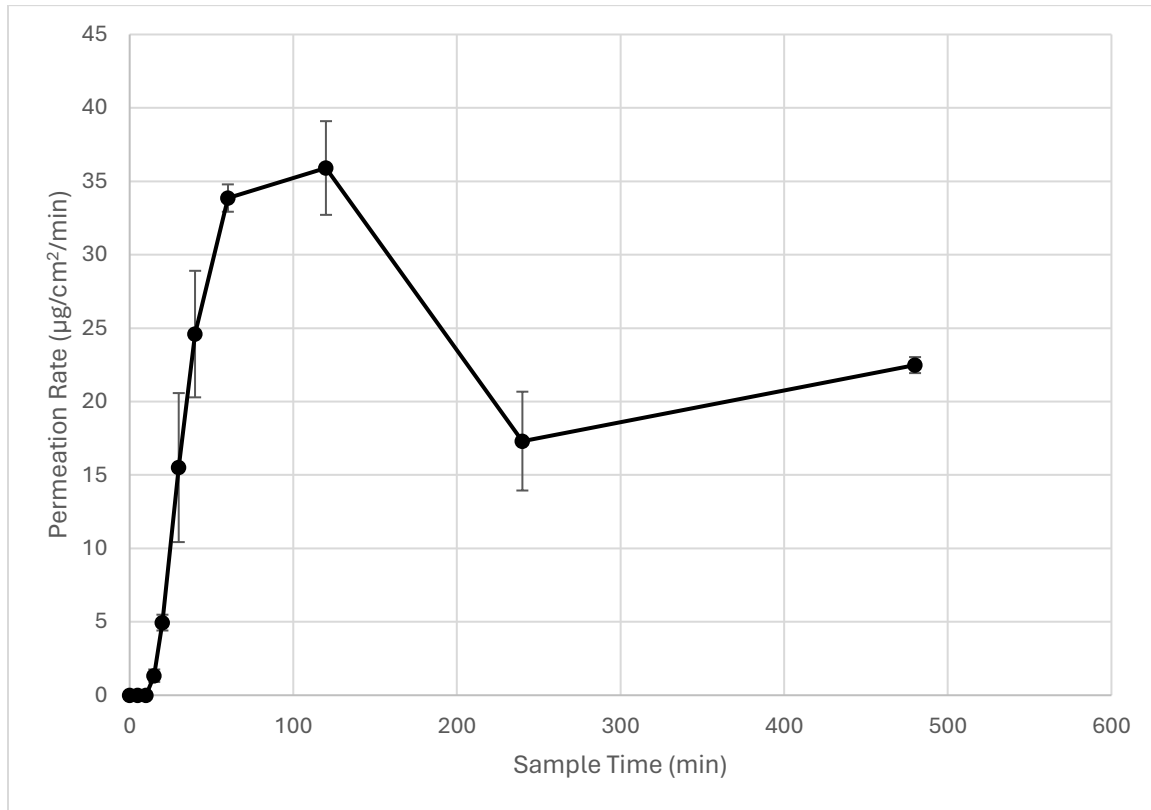


Figure 3.1. Methyl centralite average permeation rate in Hoppe's solvent

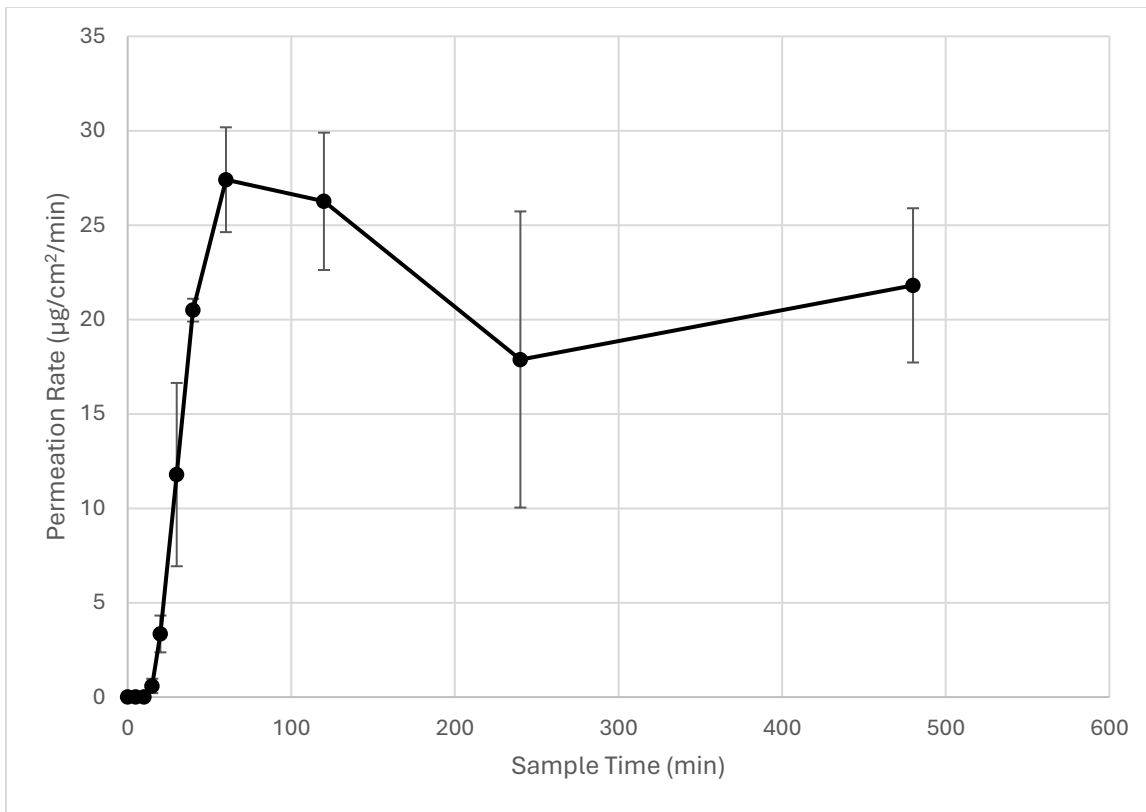


Figure 3.2. Ethyl centralite average permeation rate in Hoppe's solvent

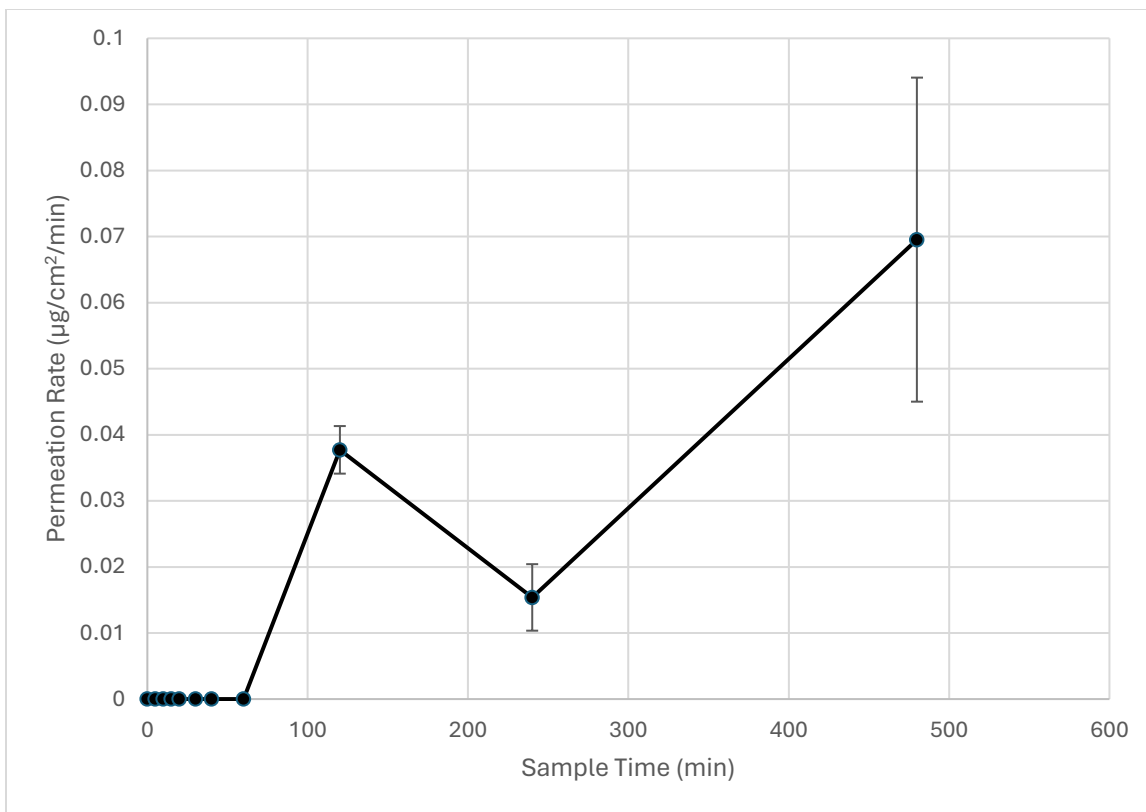


Figure 3.3. Methyl centralite average permeation rate in n-decane solvent

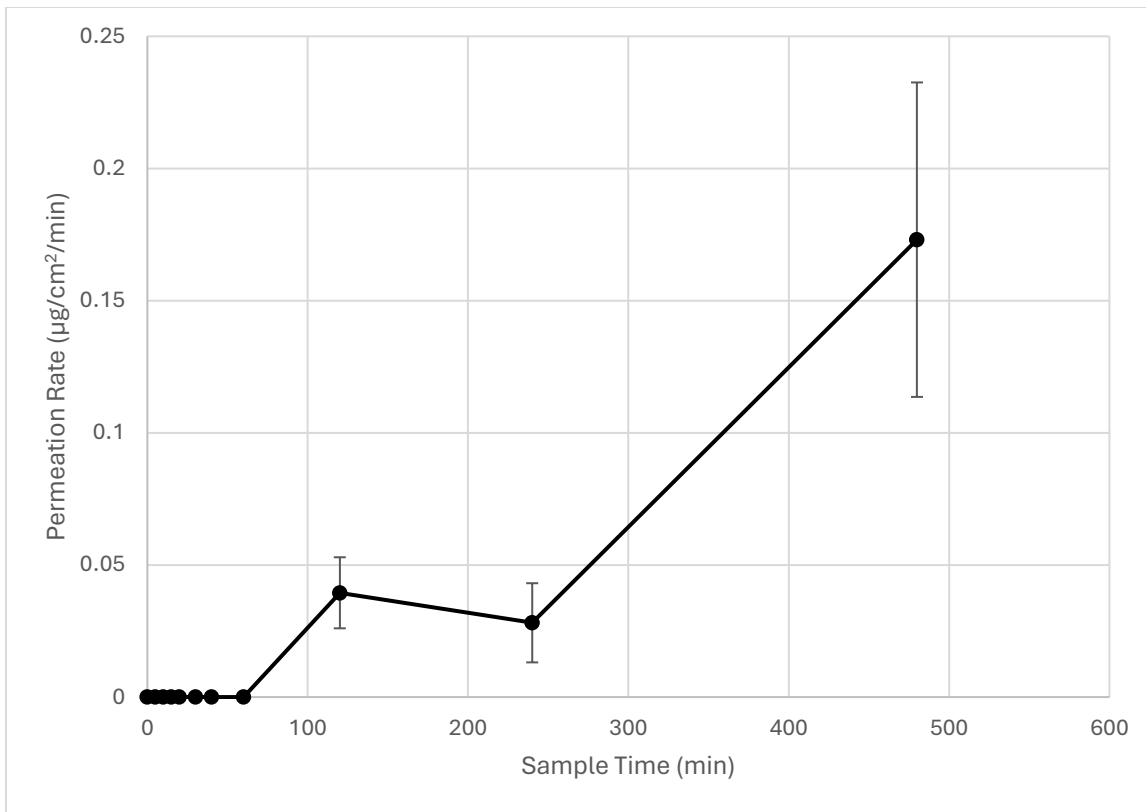


Figure 3.4. Ethyl centralite average permeation rate in n-decane solvent

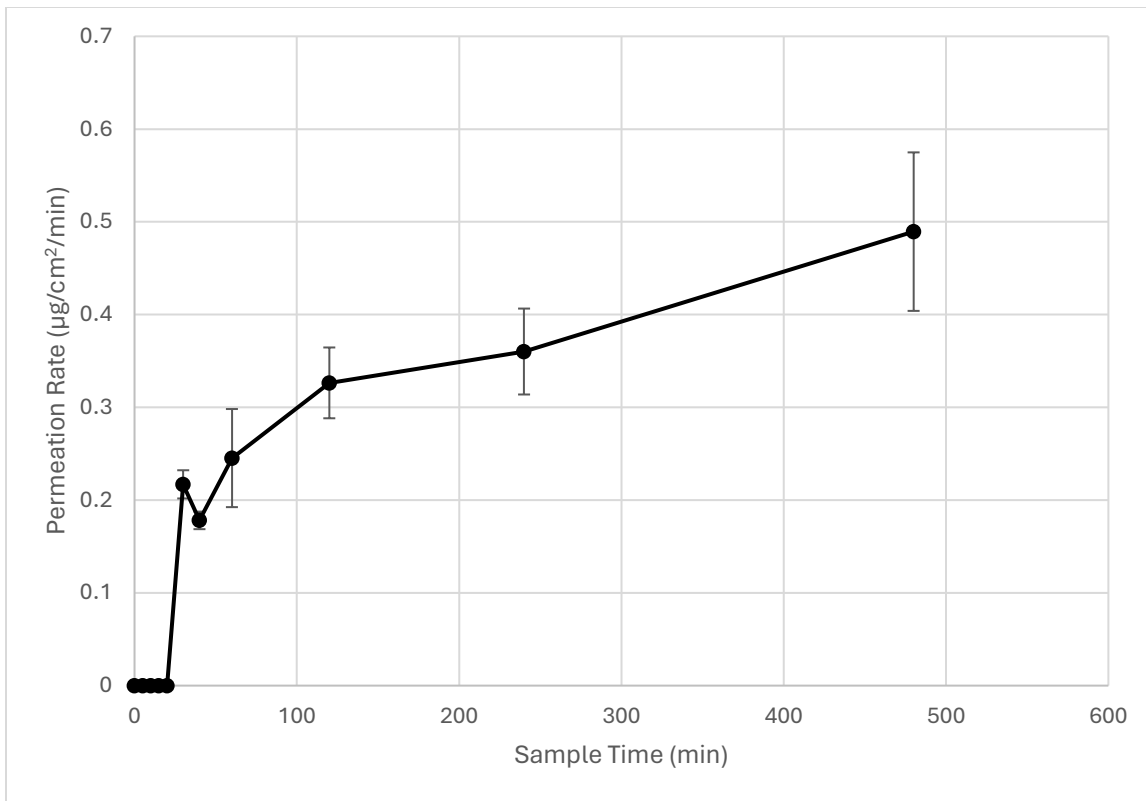


Figure 3.5. Methyl centralite average permeation rate in n-decane/EtOH solvent

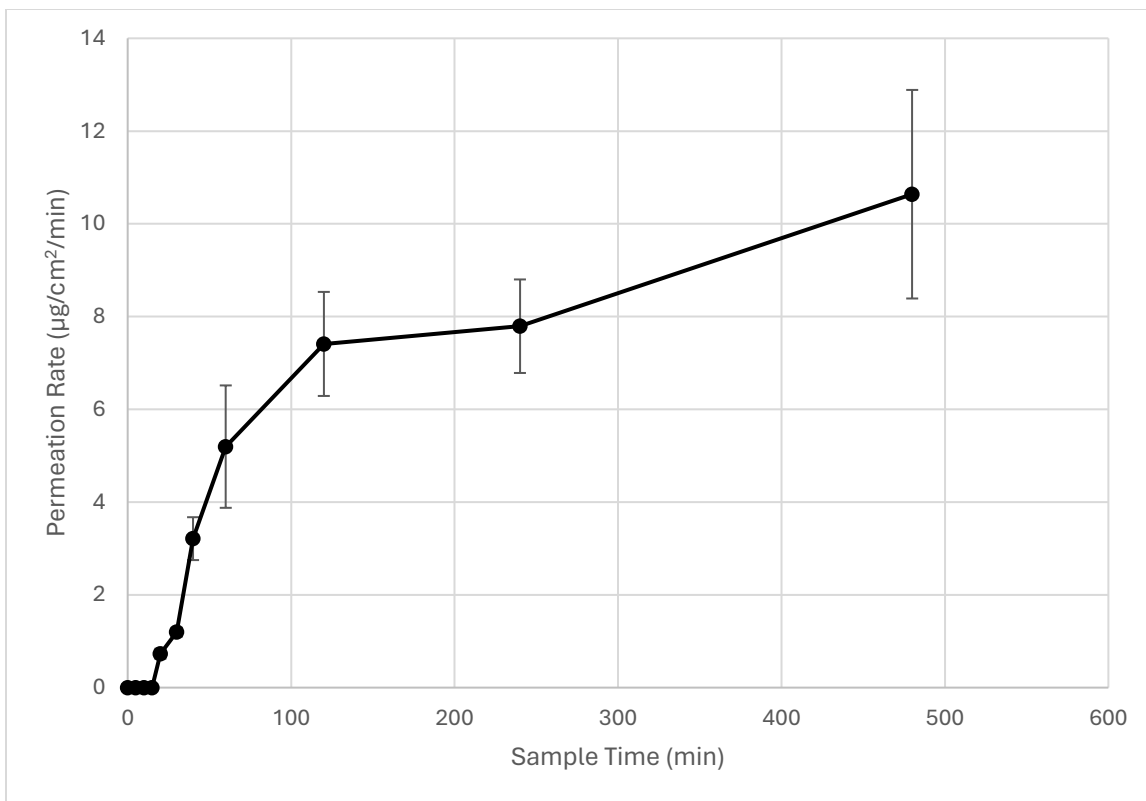


Figure 3.6. Ethyl centralite average permeation rate in n-decane/EtOH solvent

3.9. TABLES

Table 3.1. Glove physical data before and after permeation for three different gloves corrected for blank glove data in Hoppe's solvent.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
1	147 ± 1	153 ± 1	248.0 ± 0.2	258.9 ± 0.2
2	148 ± 1	147 ± 1	251.2 ± 0.1	262.9 ± 0.1
3	143 ± 1	147 ± 1	225.9 ± 0.1	236.2 ± 0.1

Table 3.2. Glove physical data before and after permeation for three different gloves corrected for blank glove data in n-decane solvent.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
1	141 ± 1	141 ± 1	239.3 ± 0.1	240.7 ± 0.1
2	139 ± 1	140 ± 1	262.3 ± 0.1	263.4 ± 0.1
3	142 ± 1	144 ± 3	262.5 ± 0.1	264.2 ± 0.1

Table 3.3. Glove physical data before and after permeation for three different gloves corrected for blank glove data in n-decane/EtOH solvent.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
1	148 ± 1	153 ± 1	248.0 ± 0.2	258.9 ± 0.3
2	143 ± 1	147 ± 1	251.2 ± 0.1	262.9 ± 0.1
3	144 ± 1	147 ± 1	255.9 ± 0.1	236.2 ± 0.1

4. EFFECTS OF DIFFERING GLOVE MATERIALS ON SIMULATED ORGANIC GUNSHOT RESIDUE PERMEATION CHARACTERISTICS

4.1. ABSTRACT

The objective was to study the effects of differing glove materials on the permeation of gunshot residues compared to those materials in isolation. Simulated gunshot residues of methyl centralite and ethyl centralite dissolved in simulated gun cleaning solvent mixture of 7:3 n-decane and ethanol was utilized to challenge two varieties of disposable gloves materials, nitrile rubber and polyvinylchloride, using the closed-loop ASTM F739 cell without recirculation and n-decane collection followed by capillary gas chromatography-mass spectrometric quantitation of the permeated compounds. The nitrile only glove combination provided the greatest reduction in permeation. The second greatest reduction was a mixture of nitrile and vinyl gloves, with vinyl specifically facing the challenge solution. However, for Hoppe's the kerosene components appeared at the standardized breakthrough time. A combination of vinyl only glove material caused the increased permeation of ethyl centralite compared to methyl centralite, where all other combinations of materials saw the reduced permeation of ethyl centralite compared to methyl centralite. Persons utilizing personal protective equipment, such as gloves, may not be afforded the expected resistance to chemical permeation when a specific combination, or orientation of those combinations, are utilized. More research is needed to produce better glove testing measures to assure the safety and health of workers, especially when multiple types of materials are utilized in the glove structure, such as with laminate gloves.

4.2. INTRODUCTION

In 2020, the United States full-time equivalent worker incidence rate for non-fatal skin diseases or disorders was 1.8 per 10,000 for 19,800 cases, the second largest non-fatal injury (Bureau of Labor and Statistics 2020), with a major cause for these injuries being exposure to organic chemicals. Personal protective equipment (PPE) is often the only defense considered to combat these occupational injuries, with gloves being one of the most ubiquitous articles of PPE utilized in the workplace. The most common glove type used to reduce exposure to aqueous solutions is a disposable nitrile glove (Anna 2003; Grand View Research 2022). These gloves are also preferred because of their comfort, ergonomics, affordability, and convenience of use (Anna 2003). However, disposable nitrile gloves do not resist permeation of all types of chemicals (Anna 2003). They are predicted to have the largest global compound annual growth rate (5.8%) of any non-powdered disposable glove type from 2022 to 2030 (Grand View Research 2022).

Glove manufacturers commonly use the ASTM F739-99 standard (ASTM 1999) and the ASTM F739-12 standard (ASTM 2012) to conduct permeation testing of gloves. Temperature requirements for these tests are user-defined ± 1 °C for the 1999 standard, or at 27 ± 1 °C for the 2012 standard. Only the ASTM D6978-05 standard, a similar permeation testing standard specifically for chemotherapy drugs, specifies a testing temperature of 35 ± 2 °C, a temperature expected of human skin (Nadel et al. 1971). The most recent ASTM F739 standard at the time of this publication is the ASTM F739-20 standard (ASTM 2020).

Previous research has been conducted on the effects of utilizing multiple layers of glove materials compared to only single layers. In general, the permeation was lowered when multiple layers of gloves were used compared to single layers (Banaee & Que Hee, 2020), although the exact level of reduction varies between studies (Song 2017, Liu 2019). Other recent studies have characterized the permeation of chemicals through laminated materials, but do not compare the

results to each individual layer that makes up the laminate (Aoki & Miyauchi 2024). However, no research was found that studied the effects of differing glove materials on the permeation of gunshot residues compared to those materials in isolation.

This research sought to characterize the effects of multiple dissimilar glove materials on the permeation of simulated gunshot residues in a n-decane/ethanol mixture.

4.3. METHODS

4.3.1. Materials

Commercially available disposable nitrile gloves (Kimberly-Clark XL powder-free disposable Lavender nitrile exam gloves, unlined and unsupported, No. 53104) were selected due to their wide use and popularity (Grand View Research 2022), along with published data regarding resistance to chemical permeation from key mixture components (Kimberly-Clark 2015). Glove pieces of 1.50 in. (3.76 cm) in diameter were cut from the palm and conditioned overnight at room temperature and 54% relative humidity as described elsewhere (ASTM 2012) before their initial thicknesses were measured in triplicate with an Electronic Digital Micrometer Model CO-030025 (0-25mm, 0.001 resolution), and weights with a Mettler AE260 Analytical Balance (Hightstown, NJ, USA).

The n-decane (99%) used for collection of permeates and the sodium dichromate (99%) used to produce 55% relative humidity to condition gloves at room temperature were secured from Fisher Scientific (Chino, CA, USA). Methyl centralite (99%), ethyl centralite (99%), diphenylamine (99%), and analytical grade ethanol (99.5%) originated from Sigma Aldrich (St. Louis, MO, USA). Helium (99.9999%) was purchased from Air Liquide (El Segundo, CA).

Water was from a Millipore Milli-Q Water System and Millipore Simplicity Water Purification final polishing system (Temecula, CA).

ASTM F739-12 compliant 1-inch internal diameter permeation cells model I-PTC-600, including aluminum flanges, Teflon gaskets, bolts, and nuts were purchased from Pesce Lab (Kennett Square, PA, USA). It is a non-recirculating closed-loop system. Temperature control was achieved by dipping the cell up to its stems in a Fisher Shaking Bath Model 2870 held at 35.0 ± 0.1 °C (Chino, CA, USA).

An Agilent 6890N Network GC System and 5973 Network Mass Selective (MS) Detector equipped with an Agilent fused silica capillary column 60 m x 0.320 mm x 1.0- μ m DB-1701 film, part number 123-0763 (Santa Clara, CA, USA) were used for analysis.

A Fisher Scientific Centrifuge Model 228 was used to centrifuge samples. A Branson Ultrasonicator Model B2200R-1 mixed samples. An American Optical MicroStar hand-held microscope (Buffalo, NY, USA) allowed examination of materials. Hamilton Micro-syringes, 0-10 μ L (Reno, NV, USA) facilitated GC-MS sample injections.

Standards were produced using Eppendorf pipets/tips and Pyrex volumetric flasks, and permeation collection samples were stored in 2-ml borosilicate glass vials, all from Fisher Scientific, Chino, CA, USA.

4.3.2. Calculations

All calculations were performed on Microsoft Excel 365 version 2402 and IBM SPSS version 20.0.0.0 (190). These included linear regressions for the method of internal standards where slopes, intercepts, standard deviations, correlation coefficients, and p-values were calculated.

The cumulative mass for each challenge cell was calculated by multiplying the observed concentration by the volume in the test cell corrected for mass already sampled at the time of sampling.

Analyte permeation rates were calculated by dividing the differences of the collection side analyte mass between adjacent sampling times in mg or μg by the glove exposed area in cm^2 , and by the sampling time interval in minutes (min).

The diffusion coefficient D in cm^2/min of a challenge chemical was calculated using the following equation:

$$D = \frac{l^2}{6 \cdot L_t} \quad (\text{Equation 1})$$

where l is the glove thickness in cm, and L_t is lag time in min from the time intercept at zero permeation of a component mass/area versus sampling time plot.

Statistical differences between representative values and their standard deviations involved Student t testing at the $p \leq 0.05$ level and ANOVA testing at the $p \leq 0.05$ level (Rosner 2016).

4.3.3. Selection of Glove Materials

Previous experiments utilized nitrile gloves due to their ubiquity, availability, and cost effectiveness. A second type of glove material is needed to verify the effects of multiple material types on permeation characteristics. After review of several options, polyvinylchloride (PVC), was chosen as a second glove type due to the same reasons as for the nitrile gloves: PVC gloves are also commonly used in the workplace, in many industries, and are relatively cost effective to procure. PVC also offers differing chemical resistances when compared to nitrile gloves, primarily for increased resistance to acids and oils. Studies have shown that latex gloves have

decreased permeation resistance to ethanol compared with nitrile gloves (Phalen 2014, Chin 2010).

4.3.4. Permeation Cell Preparation

The ASTM F739-12 standard test method for permeation of liquids and gases through protective clothing materials under conditions of continuous contact was used for permeation testing (ASTM 2012) with four permeation cells. Glove swatches 45 mm in diameter were cut from the palm areas. The swatches were examined with the hand-held microscope to detect deficiencies, holes, abrasions, or other defects. The test materials were then conditioned in a desiccator (Fisher Scientific, Chino, CA, USA) at $55 \pm 1\%$ relative humidity, maintained by a saturated aqueous solution of sodium dichromate, and 27 ± 2 °C for 24 hours. After removal from the desiccator, glove thicknesses were measured (micrometer) and their weights (balance). The swatches were then placed in the test cells between their gaskets, and the locking bolts tightened to 5.0 ft·lb by torque wrench. Water was placed on the collection side of each cell and the cells placed on top of brown paper towels to check for leaks. After one hour of no leaks, the water was drained, the cells disassembled, cleaned with neutral liquid detergent and water, rinsed with deionized water, and then air-dried. The swatches were returned to the desiccator for an additional 24 hours of conditioning. Care was taken to assure that the correct materials were placed in their correct orientations for each specified permeation test

4.3.5. Sample Collection

The collection sides of the assembled cells were filled with 10 mL of n-decane. After visual inspection that no leaks immediately occurred, the cells were placed in the shaker water bath. The experimental solution was then introduced into three of the four cells. A 100- μ L sample was immediately taken from each collection side and deposited into separate 1-mL vials

precooled to $-15\text{ }^{\circ}\text{C}$. $10\text{ }\mu\text{L}$ of 10.0 mg/mL diphenylamine internal standard was added to the vials after sample collection, for a final diphenylamine concentration of 0.909 mg/mL . The bath was set to shake at $75 \pm 1\text{ rpm}$. A sample of the bath water was also taken for analysis. All samples were stored in a freezer at $-15 \pm 2\text{ }^{\circ}\text{C}$. Additional sampling occurred at 5, 10, 15, 20, 30, 40, 60, 120, and 240 min, the shaker being stopped temporarily. After 480 min, the fluids from the collection sides were retained in 10-mL graduated cylinders. Another sample of the bath water was taken for analysis to confirm no leaks. Samples were stored in a freezer at $-15 \pm 2\text{ }^{\circ}\text{C}$.

4.3.6. Sample Analysis

Analysis of the samples involved GC-MS using the appropriate IS method and SIM parameters as used in Chapter 3. Samples were processed from the earliest to the latest sampling time in the sequence cell blank, 1, 2, and then 3. Manual integration was used for all sampling times.

Concentrations for methyl centralite and ethyl centralite were calculated for each cell using the internal standard linear regression equations. Aggregate concentrations were calculated by averaging the individual component concentrations from cells 1, 2 and 3, corrected by values for the blank cell.

4.4. RESULTS

4.4.1. PVC:NITRILE

Changes in glove physical characteristics before and after permeation for three glove combinations are shown in Table 4.1. Significant changes in thickness were observed for all glove pieces. Swelling of the glove material was observed to be $59 \pm 3\text{ }\mu\text{m}$ for vinyl gloves, and 53 ± 4 for nitrile gloves, when corrected the blank glove material. The increase in glove mass

post permeation testing was observed to be 11.6 ± 0.2 mg for nitrile gloves, while PVC gloves decreased in mass by -1.3 ± 1.2 mg when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The limit of quantitation was $0.1 \mu\text{g/mL}$ and limit of detection was $0.01 \mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.0072x - 0.0012$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.0075x - 0.001$. The r value for both equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite through a nitrile(N)/PVC (nitrile facing challenge(C)) glove combination are shown in Figure 4.1 and Figure 4.2, respectively. The permeation rate behavior shows a largely Type A permeation behavior pattern. The standardized breakthrough time (SBT) occurred at 2.5 ± 2.5 min for methyl centralite and ethyl centralite. The steady state permeation rate (SSPR) was calculated to be $2.44 \pm 0.29 \mu\text{g/cm}^2/\text{min}$ for methyl centralite and $1.66 \pm 0.16 \mu\text{g/cm}^2/\text{min}$ for ethyl centralite. The L_t was calculated to be 10.6 ± 2.7 min for methyl centralite and 10.0 ± 2.0 min for ethyl centralite. The diffusion coefficient was calculated to be $1.62 \pm 0.44 \times 10^{-5} \text{ cm}^2/\text{min}$ for methyl centralite and $1.69 \pm 0.32 \times 10^{-5} \text{ cm}^2/\text{min}$ for ethyl centralite. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 0.60 ± 0.10 mg at 60 minutes and 5.95 ± 0.61 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0.38 ± 0.07 mg at 60 minutes and 4.03 ± 0.28 mg at 480 minutes.

4.4.2. NITRILE:PVC

Changes in glove physical characteristics before and after permeation for three glove combinations are shown in Table 4.2. Significant changes in thickness were observed for all glove pieces. Swelling of the glove material was observed to be $29 \pm 3 \mu\text{m}$ for PVC gloves, and 47 ± 3 for nitrile gloves, when corrected for the blank glove material. The increase in glove mass post permeation testing was observed to be $8.4 \pm 0.7 \text{ mg}$ for nitrile gloves, while PVC gloves decreased in mass by $-4.7 \pm 0.7 \text{ mg}$ when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The limit of quantitation was $0.1 \mu\text{g/mL}$ and limit of detection was $0.01 \mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.0072x - 0.0012$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.0075x - 0.001$. The r value for both equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite through a nitrile/vinyl (nitrile facing challenge) glove combination are shown in Figure 4.3 and Figure 4.4, respectively. The permeation rate behavior shows a largely Type D permeation behavior pattern. The SBT occurred at $12.5 \pm 2.5 \text{ min}$ for methyl centralite and ethyl centralite. The SSPR was calculated to be $1.35 \pm 0.12 \mu\text{g/cm}^2/\text{min}$ for methyl centralite and $1.03 \pm 0.12 \mu\text{g/cm}^2/\text{min}$ for ethyl centralite. The L_t was calculated to be $8.1 \pm 5.6 \text{ min}$ for methyl centralite and $13.2 \pm 6.4 \text{ min}$ for ethyl centralite. The diffusion coefficient was calculated to be $1.99 \pm 1.26 \times 10^{-5} \text{ cm}^2/\text{min}$

for methyl centralite and $1.04 \pm 0.47 \times 10^{-5} \text{ cm}^2/\text{min}$ for ethyl centralite. Estimates for diffusion coefficients utilizing the equation proposed in this experiment generally require that a type A permeation curve has occurred. However, these estimates are provided for reference, and may not necessarily be accurate. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be $0.48 \pm 0.10 \text{ mg}$ at 60 minutes and $4.04 \pm 0.12 \text{ mg}$ at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be $0.30 \pm 0.06 \text{ mg}$ at 60 minutes and $2.94 \pm 0.13 \text{ mg}$ at 480 minutes.

4.4.3. NITRILE:NITRILE

Changes in glove physical characteristics before and after permeation for three glove combinations are shown in Table 4.3. Significant changes in thickness were observed for all glove pieces. Swelling of the glove material was observed to be $35 \pm 1 \text{ }\mu\text{m}$ for collection cell facing nitrile gloves, and $52 \pm 2 \text{ }\mu\text{m}$ for challenge cell facing nitrile gloves, when corrected for the blank glove material. The decrease in glove mass post permeation testing was observed to be $-0.1 \pm 0.3 \text{ mg}$ for collection cell facing nitrile gloves, while challenge cell facing nitrile gloves decreased in mass by $-0.8 \pm 0.1 \text{ mg}$ when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The limit of quantitation was $0.1 \text{ }\mu\text{g/mL}$ and limit of detection was $0.01 \text{ }\mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.0072x - 0.0012$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.0075x - 0.001$. The r value for both equations

was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite through a nitrile/nitrile glove combination are shown in Figure 4.5 and Figure 4.6, respectively. The permeation rate behavior shows a largely Type A permeation behavior pattern. The SBT occurred at 35 ± 5 min for methyl centralite and 50 ± 10 min for ethyl centralite. The SSPR was calculated to be $0.28 \pm 0.03 \mu\text{g}/\text{cm}^2/\text{min}$ for methyl centralite and $0.17 \pm 0.02 \mu\text{g}/\text{cm}^2/\text{min}$ for ethyl centralite. The L_t was calculated to be 25.6 ± 7.4 for methyl centralite and 33.9 ± 5.8 for ethyl centralite. The diffusion coefficient was calculated to be $0.56 \pm 0.16 \times 10^{-5} \text{ cm}^2/\text{min}$ for methyl centralite and $0.41 \pm 0.07 \times 10^{-5} \text{ cm}^2/\text{min}$ for ethyl centralite. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 0.03 ± 0.01 mg at 60 minutes and 0.63 ± 0.05 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0.01 ± 0.01 mg at 60 minutes and 0.39 ± 0.02 mg at 480 minutes.

4.4.4. PVC:PVC

Changes in glove physical characteristics before and after permeation for three glove combinations are shown in Table 4.4. Significant changes in thickness were observed for all glove pieces. Swelling of the glove material was observed to be $33 \pm 2 \mu\text{m}$ for collection cell facing PVC gloves, and $33 \pm 3 \mu\text{m}$ for challenge cell facing PVC gloves, when corrected the blank glove material. The decrease in glove mass post permeation testing was observed to be -2.3 ± 1.6 mg for collection cell facing PVC gloves, while challenge cell facing PVC gloves decreased in mass by -10.7 ± 1.4 mg when corrected for the blank glove material. As all blank glove materials underwent the same method as the challenge glove materials, the final results

have been corrected for changes in the blank material to eliminate the effects of n-decane on the glove material.

The limit of quantitation was 0.1 $\mu\text{g/mL}$ and limit of detection was 0.01 $\mu\text{g/mL}$ for both analytes. The linear regression equation for methyl centralite was $y = 0.0072x - 0.0012$ where y is the analyte/internal standard response ratio and x is the analyte concentration. The linear regression equation for ethyl centralite was $y = 0.0075x - 0.001$. The r value for both equations was > 0.999 and the p value for both equations was < 0.05 . The relative retention times for methyl centralite/diphenylamine was 1.804 and for ethyl centralite/diphenylamine was 1.900.

The permeation rate curves for methyl centralite and ethyl centralite through a PVC/PVC glove combination are shown in Figure 4.7 and Figure 4.8, respectively. The permeation rate behavior shows a largely Type A permeation behavior pattern. The SBT occurred at 7.5 ± 2.5 min for methyl centralite and ethyl centralite. The SSPR was calculated to be 2.18 ± 0.22 $\mu\text{g/cm}^2/\text{min}$ for methyl centralite and 2.04 ± 0.29 $\mu\text{g/cm}^2/\text{min}$ for ethyl centralite. The L_t was calculated to be 18.0 ± 8.4 min for methyl centralite and 20.7 ± 8.4 min for ethyl centralite. The diffusion coefficient was calculated to be $0.82 \pm 0.51 \times 10^{-5}$ cm^2/min for methyl centralite and $1.66 \pm 0.28 \times 10^{-5}$ cm^2/min for ethyl centralite. The estimated cumulative mass of methyl centralite in the collection cell was calculated to be 0.45 ± 0.07 mg at 60 minutes and 5.29 ± 0.65 mg at 480 minutes. The estimated cumulative mass of ethyl centralite in the collection cell was calculated to be 0.47 ± 0.08 mg at 60 minutes and 5.20 ± 0.15 mg at 480 minutes.

4.4.5. ANOVA Analysis

ANOVA analysis was conducted on the permeation characteristics of total permeated mass, SSPR, and SBT, with glove material and orientation as the group factor. ANOVA analysis results are shown in Table 4.5. The results showed that there was a significant difference

between the permeation characteristics for glove material and orientation for all permeation characteristics at the $P \leq 0.05$ significance level.

More specific analysis was performed by conducting a Student *t*-test for each glove material combination and each permeation characteristic for each analyte, excluding SBT due to its calculation procedure given the method used to conduct the permeation tests. These results are shown on Tables 4.6. to Table 4.8. For steady state permeation rate, all combinations of glove materials for both analytes were significantly different at the $P \leq 0.05$ significance level except for the methyl centralite PVC:N & N:N pairing, which had a calculated P-value of 0.341. The ethyl centralite P-value for this pairing was 0.033. For total permeated analyte mass, all combinations of glove materials for both analytes were significantly different at the $P \leq 0.05$ significance level except for the methyl centralite PVC:N & N:N pairing, which had a calculated P-value of 0.058. The ethyl centralite P-value for this pairing was 0.002.

4.5. DISCUSSION

As discussed in previous chapters, ethanol has played a significant role in the increased permeation rates of other non-polar components in a challenge solution through nitrile gloves via a carrier effect. Interestingly, the results in this study show there are likely more mechanisms at play when different materials are used. The initial hypothesis for this experiment was that differing glove layers would provide increased resistance to the permeation of chemicals due to different permeation characteristics between materials, when compared to similar thickness single-material combinations. This hypothesis has largely been proven false, given the clearly superior protection shown by the dual-layer nitrile results. However, the results also show that there are significant caveats attached to that conclusion.

The results of this study have shown that the permeation rate behavior between the differing-material combinations is dependent on the orientation of the materials in the cell. When nitrile faced the challenge solution cell, the permeation rate behavior was largely of the Type A behavior pattern. This behavior changed significantly when PVC material faced the challenge solution cell, and the permeation rate behavior then resembled a Type D permeation rate behavior. This change in permeation rate behavior is likely the driver for the significantly reduced permeation characteristics, namely SSPR and total permeated analyte mass in the N:PVC glove material combination. Common sense would lead most to believe that the orientation of the material would lead to generally insignificant differences in the results, given that the analyte must permeate through essentially the same distance of the same materials. However, the results show that this assumption is unequivocally false.

Other oddities also persist in the results of this study. While the total mass increase for glove material combinations was not significantly different, the change in glove material thickness was. Despite equivalent total material thicknesses before the permeation test, the nitrile facing challenge solution material combination ended the permeation test with a total material thickness of $315 \pm 7 \mu\text{m}$, the vinyl facing challenge solution material combination ended the permeation test with a total thickness of $266 \pm 2 \mu\text{m}$, a difference significant at the $P \leq 0.05$ level. This is due to a significantly decreased swelling of the PVC material in the PVC facing challenge solution material combination permeation test. There was no significant difference in the swelling of nitrile material between these tests.

Further oddities in the results surface in the permeation characteristics of the nitrile only material combination permeation test. Previous studies have shown that when a dual layer of nitrile glove material is compared to a single layer of the same material, increasing the thickness

of the nitrile by a factor of 2, there is likewise a decrease in the SSPR and total permeated analyte mass through the material by a factor of 2 (Liu 2019 & Song 2017). This relationship was not shown in the present results. Compared to the dual nitrile layer test, the other glove material combinations the steady state permeation rate and total permeated analyte mass increased by approximately a factor of 10 and, in the case of the N:PVC test, a factor of five.

The results of the N:PVC test have multiple discrepancies compared to other material combinations. The most immediate difference when compared to all other tests in the presence of a type D permeation rate curve behavior, where all other material combination exhibited a type A permeation rate curve behavior. The presence of the type D permeation rate curve behavior resulted in a drastically reduced steady state permeation rate and total permeated analyte mass; a reduction of nearly a factor of 2. There were also reductions in the swelling of the PVC glove material compared to other material combinations. The mechanism by which the orientation of the nitrile and PVC material causes such a drastic change in permeation characteristics is currently unknown.

Finally, it is worth noting that the difference between the permeation characteristics between methyl centralite and ethyl centralite were significantly different at the $P \leq 0.05$ significance level in all material combinations except the dual PVC layer combination, where there was no significant difference in any permeation characteristic between the analytes. It may be that the difference in polarity between methyl centralite and ethyl centralite, where the octanol-water partition coefficient is roughly an order of magnitude larger in ethyl centralite, may cause the hindrance to the diffusion of ethyl centralite through nitrile material. This effect may be less prominent in PVC material, and thus the only material combination where the

difference in permeation characteristics between methyl centralite and ethyl centralite is insignificant is the combination that lacks any nitrile material.

4.6. LIMITATIONS

No previous study conducted on the permeation of methyl centralite and ethyl centralite through differing glove material layers was found. In fact, no study regarding the permeation of any chemical through differing disposable glove materials was located. Furthermore, while the ASTM provides standard methods for testing the permeation of chemicals through glove materials, no known chemical resistance chart for the gloves used in this study provide additional information that would allow this study to fully recreate the conditions which generated their reported results, especially the collection solvent, open- or closed-loop sampling design, testing temperatures, or the analytical instrument and method used. Because of this lack of information, it is not entirely possible to compare the stated effectiveness as published by the glove manufacturer to the results found in this study.

4.7. CONCLUSIONS

This study investigated the permeation characteristics of methyl centralite and ethyl centralite through a combination of glove materials, namely nitrile and PVC gloves. The results revealed significant differences in permeation behavior based on glove material orientation within the permeation cell. When nitrile faced the challenge solution cell, a Type A permeation behavior pattern predominated, whereas when PVC faced the challenge solution cell, a Type D pattern was observed.

Contrary to the initial hypothesis, which suggested increased resistance with differing glove layers, the study found that the orientation of materials significantly influenced permeation rates. Specifically, nitrile/PVC combinations exhibited higher resistance when nitrile faced the

challenge solution, while PVC/nitrile combinations displayed higher resistance when PVC faced the challenge solution. These findings underscore the importance of considering material orientation in assessing glove permeation characteristics.

Additionally, discrepancies were noted in swelling behavior and total mass changes among different glove material combinations. Notably, the nitrile only material combination did not follow expected trends observed in previous studies, indicating complex interactions between material properties and permeation behavior.

The lack of previous research on permeation through differing glove materials and the absence of comprehensive chemical resistance data for the gloves used constrain the ability to fully compare study results with existing literature or manufacturer specifications. Further research is warranted to elucidate the mechanisms underlying the observed permeation behaviors, and to refine testing methodologies for assessing permeation characteristics through multiple glove types.

4.8. FIGURES

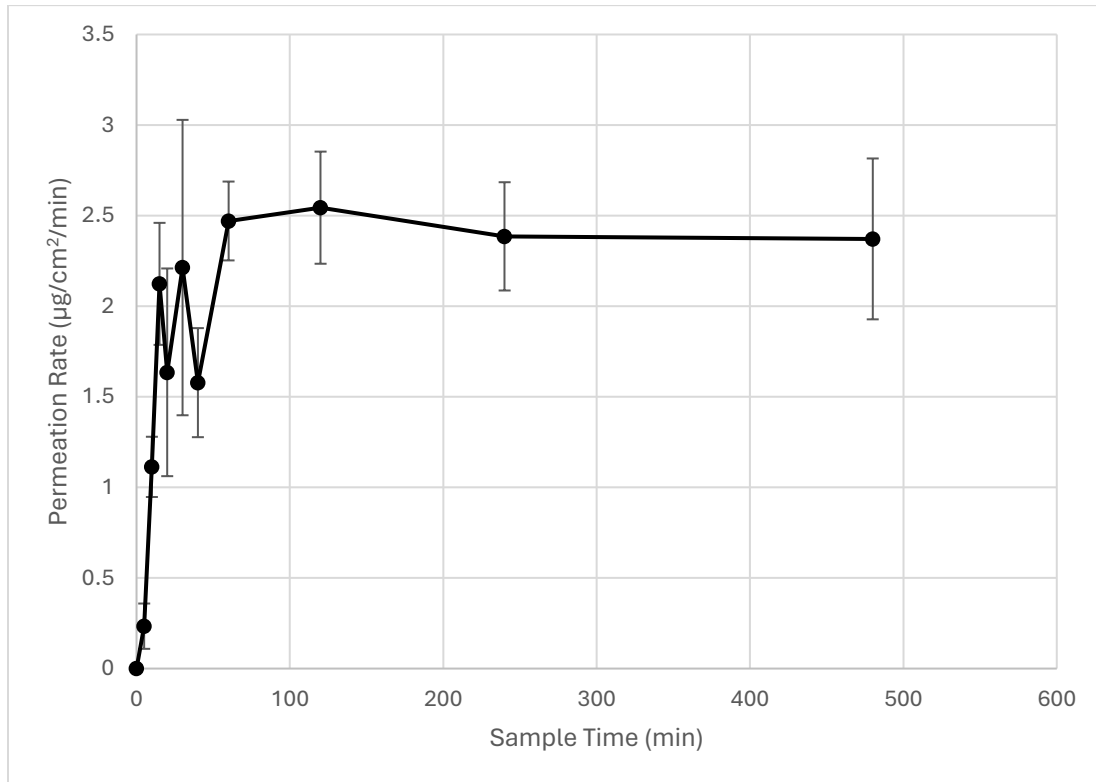


Figure 4.1. Methyl centralite average permeation rate through a nitrile/PVC (nitrile facing challenge) glove combination.

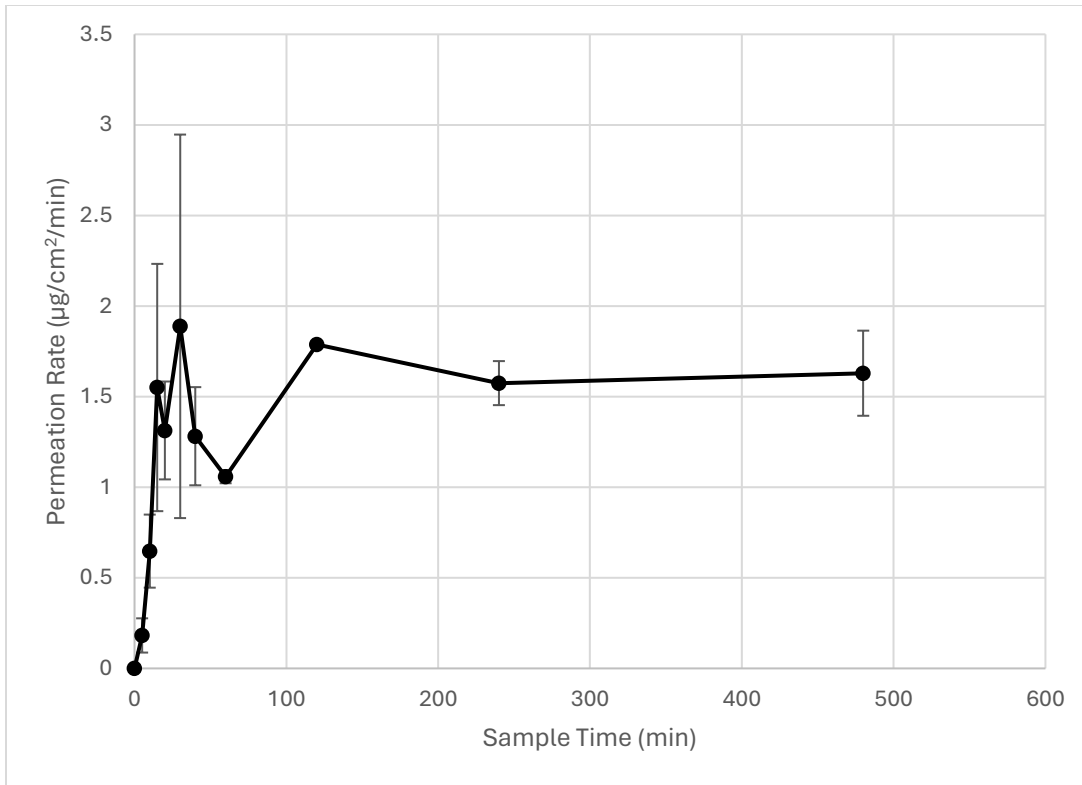


Figure 4.2. Ethyl centralite average permeation rate through a nitrile/PVC (nitrile facing challenge) glove combination

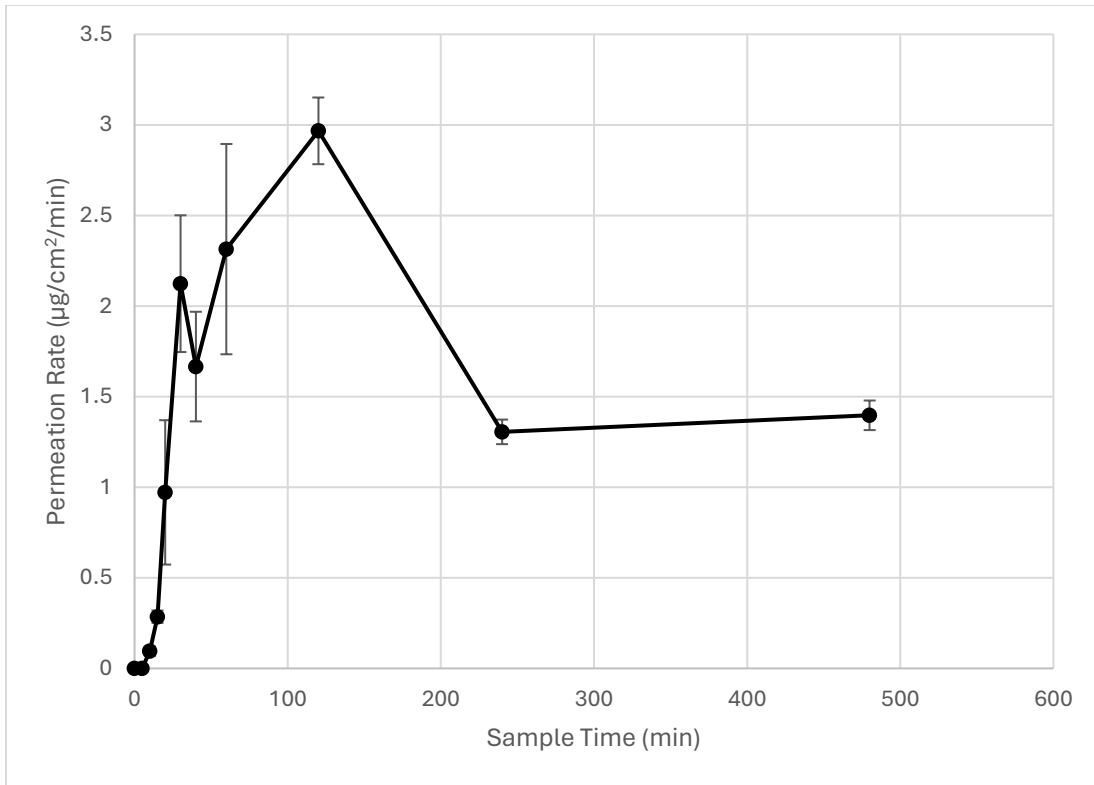


Figure 4.3. Methyl centralite average permeation rate through a nitrile/PVC (PVC facing challenge) glove combination

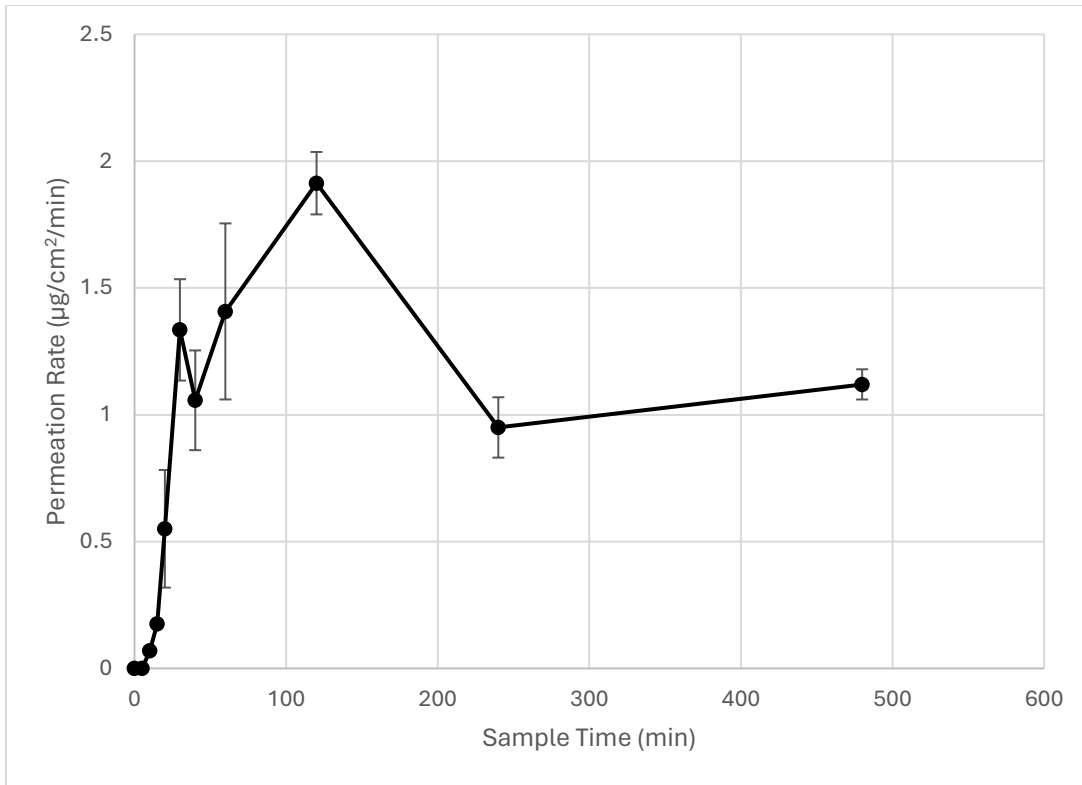


Figure 4.4. Ethyl centralite average permeation rate through a nitrile/PVC (PVC facing challenge) glove combination

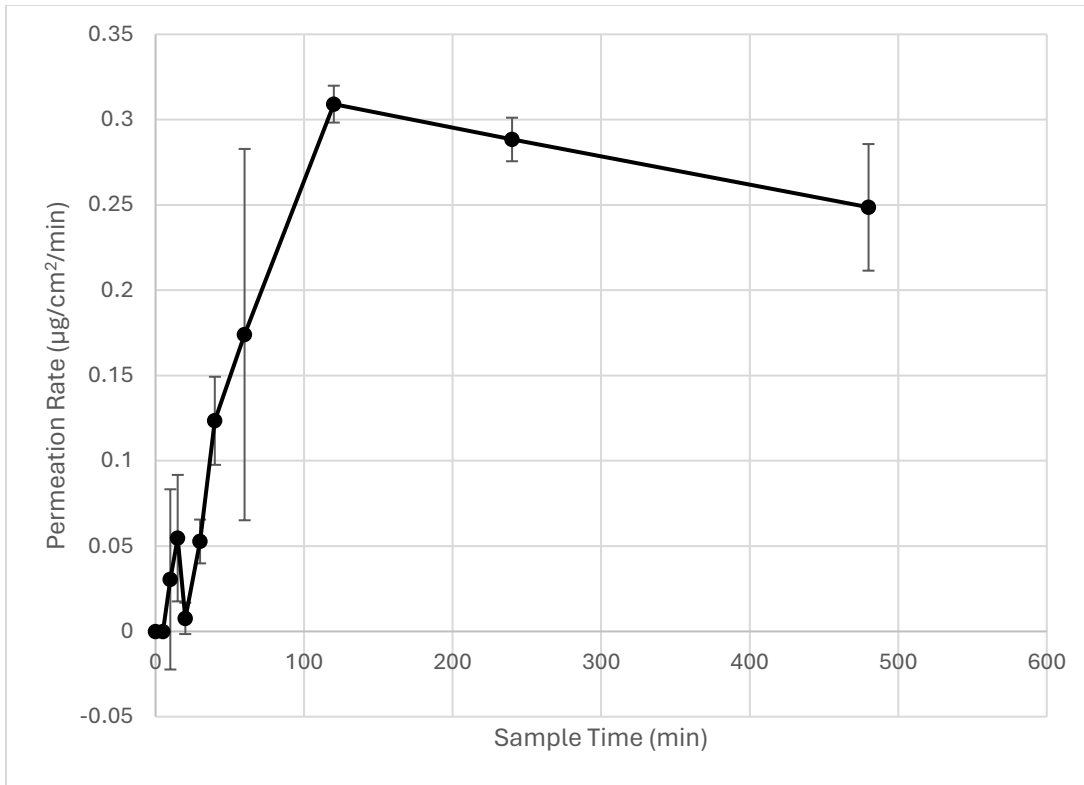


Figure 4.5. Methyl centralite average permeation rate through a nitrile/nitrile glove combination

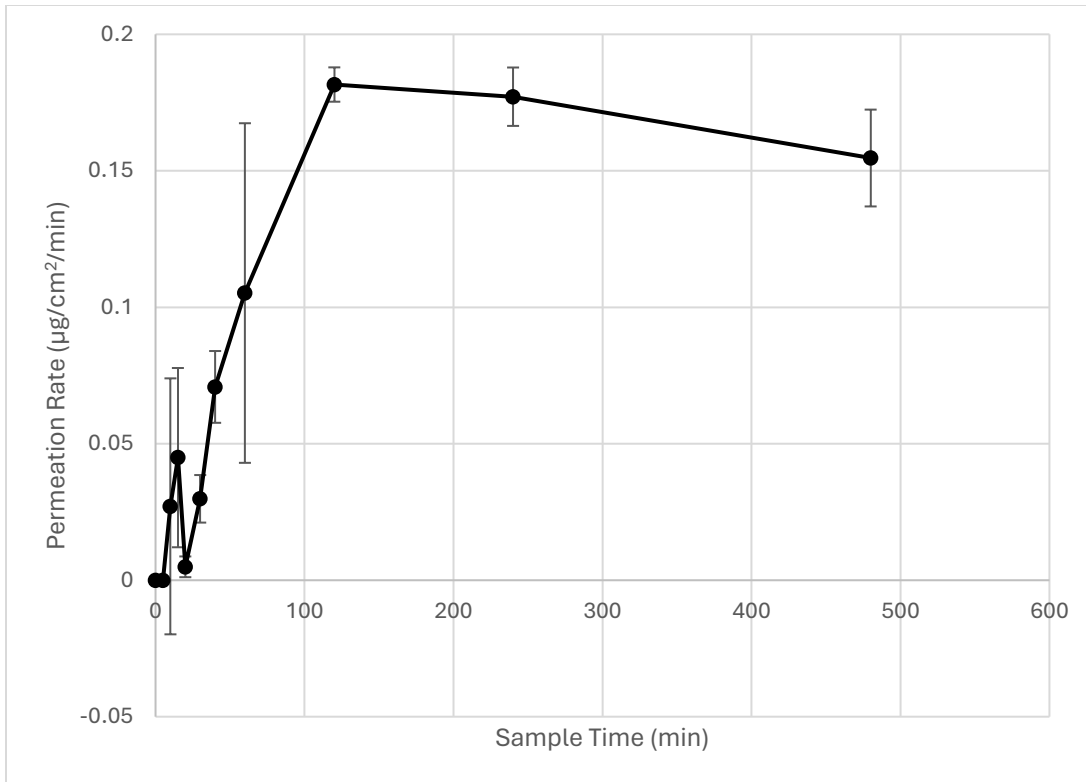


Figure 4.6. Ethyl centralite average permeation rate through a nitrile/nitrile glove combination

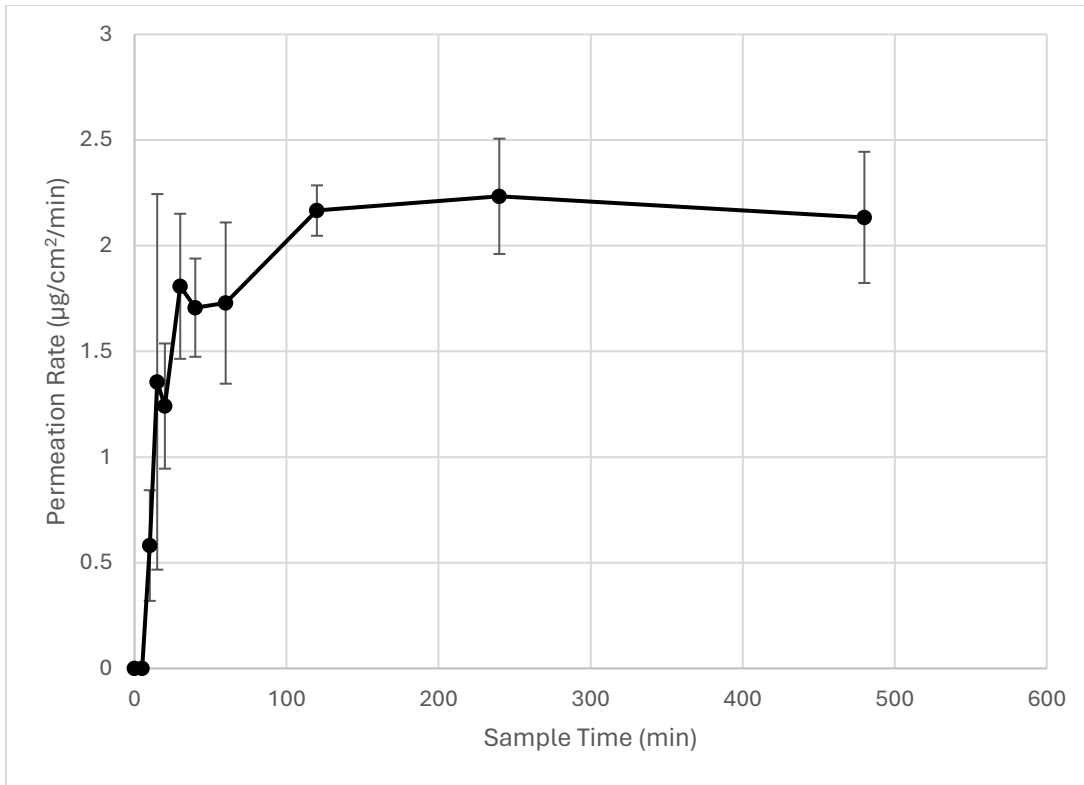


Figure 4.7. Methyl centralite average permeation rate through a PVC/PVC glove combination

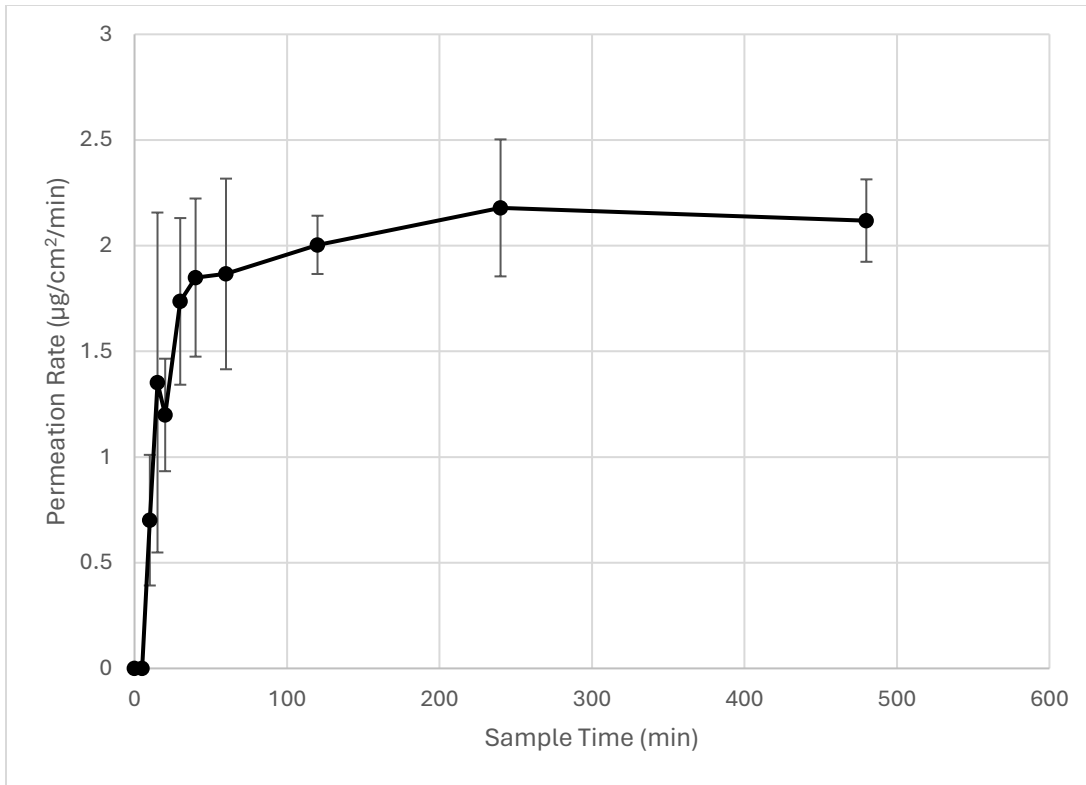


Figure 4.8. Ethyl centralite average permeation rate through a PVC/PVC combination

4.9. TABLES

Table 4.1. Glove physical data before and after permeation for three different gloves corrected for blank glove data through a nitrile/PVC (nitrile facing challenge) glove combination where V is polyvinylchloride and N is nitrile.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
V1	89 ± 2	146 ± 1	174.5 ± 0.5	173.5 ± 0.9
V2	91 ± 2	153 ± 1	166.9 ± 0.3	166.9 ± 0.6
V3	95 ± 1	151 ± 2	186.2 ± 0.2	183.4 ± 0.5
N1	96 ± 1	147 ± 1	137.6 ± 0.2	149.3 ± 0.3
N2	90 ± 2	139 ± 1	150.4 ± 0.3	162.0 ± 0.1
N3	96 ± 2	154 ± 1	157.3 ± 0.2	168.9 ± 0.2

Table 4.2. Glove physical data before and after permeation for three different gloves corrected for blank glove data through a nitrile/PVC (PVC facing challenge) glove combination where V is polyvinylchloride and N is nitrile.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
V1	92 ± 1	118 ± 2	149.2 ± 0.2	145.4 ± 0.1
V2	91 ± 1	121 ± 2	156.1 ± 0.1	150.8 ± 0.3
V3	94 ± 1	124 ± 1	162.2 ± 0.1	157.1 ± 0.1
N1	92 ± 1	142 ± 3	138.2 ± 0.2	146.8 ± 0.1
N2	91 ± 1	138 ± 2	140.3 ± 0.2	148.7 ± 0.1
N3	94 ± 1	138 ± 1	144.6 ± 0.1	152.6 ± 0.1

Table 4.3. Glove physical data before and after permeation for three different gloves corrected for blank glove data through a nitrile/nitrile glove combination where C is collection cell facing glove material and X is challenge cell facing glove material.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
C1	93 ± 2	130 ± 1	161.0 ± 0.1	161.2 ± 0.3
C2	95 ± 1	129 ± 1	157.8 ± 0.1	157.8 ± 0.1
C3	91 ± 1	125 ± 1	143.0 ± 0.2	142.6 ± 0.1
X1	89 ± 1	142 ± 2	140.6 ± 0.2	138.7 ± 0.1
X2	92 ± 1	144 ± 1	135.4 ± 0.1	134.7 ± 0.2
X3	95 ± 1	146 ± 2	152.9 ± 0.1	153.1 ± 0.1

Table 4.4. Glove physical data before and after permeation for three different gloves corrected for blank glove data through a polyvinylchloride/polyvinylchloride glove combination where C is collection cell facing glove material and X is challenge cell facing glove material.

Glove	Thickness before permeation (μm)	Thickness after permeation (μm)	Weight before permeation (mg)	Weight after permeation (mg)
C1	91 ± 1	124 ± 1	172.7 ± 0.1	169.9 ± 0.1
C2	90 ± 1	126 ± 2	158.0 ± 0.2	154.0 ± 0.1
C3	91 ± 2	122 ± 2	157.5 ± 0.2	157.1 ± 0.2
X1	91 ± 2	128 ± 1	149.3 ± 0.1	137.3 ± 0.1
X2	93 ± 1	122 ± 1	160.0 ± 0.1	151.1 ± 0.1
X3	93 ± 2	126 ± 1	158.0 ± 0.1	146.8 ± 0.1

Table 4.5. ANOVA table for permeation parameters amongst all glove combinations.

		Sum of Squares	df	Mean Square	F	Sig.
Total Mass	Between Groups	102784050	3	34261350.187	85.942	<0.001*
	Within Groups	7973170	20	398658.545		
	Total	110757221	23			
SSPR	Between Groups	13.524	3	4.508	58.467	<0.001*
	Within Groups	1.542	20	0.077		
	Total	15.067	23			
SBT	Between Groups	5336.115	3	1778.705	103.702	<0.001*
	Within Groups	343.042	20	17.152		
	Total	5679.156	23			

Table 4.6. T-test table showing p values for cell total permeated mass at 480 minutes methyl centralite. V is polyvinylchloride; N is nitrile; challenge solution is the far left of the combination

	V:N	N:V	N:N	V:V
V:N				
N:V	0.008			
N:N	0.004	0.005		
V:V	0.341*	0.008	0.007	

Table 4.7. T-test table showing p values for steady state permeation rates for methyl centralite. V is polyvinylchloride; N is nitrile; the challenge is the far left of the combination

	V:N	N:V	N:N	V:V
V:N				
N:V	<0.001			
N:N	<0.001	<0.001		
V:V	0.033	<0.001	<0.001	

Table 4.8. T-test table showing p values for total permeated mass at 480 minutes for ethyl centralite. V is polyvinylchloride; N is nitrile; the challenge is the far left of the combination

	V:N	N:V	N:N	V:V
V:N				
N:V	0.006			
N:N	0.002	0.003		
V:V	0.058*	0.003	0.003	

Table 4.9. T-test table showing p values of state permeation rates for ethyl centralite. V is polyvinylchloride; N is nitrile; the challenge is the far left of the combination

	V:N	N:V	N:N	V:V
V:N				
N:V	<0.001			
N:N	<0.001	<0.001		
V:V	0.002	<0.001	<0.001	

5. EXECUTIVE SUMMARY AND CONCLUSIONS

Some aspects of exposure harmful chemicals generated by the use and maintenance of firearms have been well studied and documented. However, a clear knowledge gap exists for the exposure to organic gunshot residues and, importantly, the effectiveness of personal protective equipment in the reduction of those exposures. The body of this research not only elucidated some aspects of the permeation of both gun cleaning solvents and gunshot residues, but serves as a foundation for future research in this untraversed path of occupational and environmental health sciences.

Experimentation in Chapter 2 found that Hoppe's gun cleaning solvent easily passes through disposable nitrile gloves. Thicker gloves, like those designed for chemical protection, are likely to offer better performance compared to disposable ones but at the cost of decreased manipulability of small objects. Another option could be to wear two disposable gloves. However, additional testing is necessary to confirm this. Using single disposable nitrile gloves, even the thickest ones, is not recommended for continuous handling of Hoppe's or equipment saturated with it. Both thicknesses of gloves allow Hoppe's to permeate, with the thicker Blue glove showing greater resistance in terms of mass permeated after breakthrough. Discrepancies in permeation parameters between this study and those reported by glove manufacturers may be due to differences in testing methods and materials. However, the method proposed here closely mimics real-world conditions for a gloved hand and demonstrates the risk of exposure to gun cleaning solvents permeating disposable nitrile gloves. Alternative analytical techniques, such as an open-loop collection method with a nitrogen gas carrier to an FID detector, could offer advantages for future testing, particularly for detecting the ethanol component of Hoppe's No. 9 Gun Bore Cleaner. However, this method may have limitations in determining the diffusion

coefficient. Future testing should prioritize exploring more resistant glove configurations and materials while retaining the convenience of disposable gloves.

Chapter 3 aimed to understand the underlying cause of a carrier effect observed in a prior investigation involving the use of Hoppe's as a challenge solution. The findings revealed significant variations in both the physical characteristics of gloves and their permeation properties when exposed to different solvents containing a common analyte. Permeation rate curves showed distinct behaviors: Hoppe's solvent exhibited a type D behavior, characterized by a notable increase in permeation rate following a standardized breakthrough time, whereas n-decane/ethanol mixtures displayed a type A behavior. The presence of ethanol in Hoppe's was identified as a primary factor driving the enhanced permeation of non-polar chemicals through nitrile gloves, although other polar components likely also contributed to this effect. Furthermore, variations in permeation behavior and total permeated mass were noted between Hoppe's and n-decane/ethanol mixtures, attributed to the presence of additional highly polar components in Hoppe's. These findings underscore the significant influence of specific polar chemical constituents present in complex mixtures like Hoppe's on permeation parameters and behavior through nitrile gloves. The study emphasized the importance of considering the complete chemical composition of mixtures when assessing their interactions with protective equipment. However, certain limitations were acknowledged, including the lack of prior research on the permeation of firearm cleaning solvents through personal protective equipment and challenges in comparing study results with manufacturer-reported glove effectiveness due to differences in testing conditions. Additionally, solubility considerations necessitate further investigation with adjusted concentrations between analytes and solvent groups. Overall, the study provides valuable insights into the permeation behavior of complex chemical mixtures

through disposable nitrile gloves, highlighting the need for comprehensive testing protocols and thoughtful considerations in protective equipment selection.

Chapter 4 delved into the permeation properties of methyl centralite and ethyl centralite through a blend of glove materials, specifically nitrile and polyvinylchloride gloves. The findings highlighted notable variations in permeation behavior depending on the orientation of the glove materials within the permeation cell. When the nitrile side faced the challenge solution, a Type A permeation behavior predominated, whereas a Type D pattern was observed when the PVC side faced the challenge solution. Contrary to the initial hypothesis, which proposed increased resistance with varying glove layers, the study revealed that material orientation played a significant role in permeation rates. Specifically, combinations of nitrile and PVC showed greater resistance when nitrile faced the challenge solution, while combinations with PVC facing exhibited higher resistance in the reverse configuration. These results emphasize the importance of considering material orientation when evaluating glove permeation characteristics.

Furthermore, differences were noted in swelling behavior and total mass changes among different combinations of glove materials. Notably, the combination with nitrile alone did not follow anticipated trends observed in prior studies, indicating complex interactions between material properties and permeation behavior. The limited existing research on permeation through various glove materials and the lack of comprehensive chemical resistance data for the gloves used pose challenges in fully comparing the study findings with existing literature or manufacturer specifications. Further research is necessary to elucidate the mechanisms underlying the observed permeation behaviors and to refine testing methodologies for evaluating permeation characteristics across multiple glove types.

In summary, this comprehensive research has addressed significant gaps in understanding the permeation properties of harmful chemicals associated with firearms use and maintenance, particularly focusing on gun cleaning solvents and organic gunshot residues. While some disposable nitrile gloves with sufficient thickness may aid in reducing the exposure to gun cleaning solvents and organic gunshot residues, they may not protect the wearer from some non-polar components of the exposed chemical as well as the wearer may expect. This is likely due to a large portion of gun cleaning solvents being composed of ethanol, a highly polar chemical, that drives a carrier effect which increases the permeation of other chemical components in the mixture. These results are generalizable to other mixtures that contain both a polar and non-polar component. While a culture of using multiple types of glove material exists in the personal protective equipment industry, such as with laminated gloves composed of multiple layers of differing materials, it may be the case that more research is needed to verify that the orientation of the materials maximizes the protective qualities of the glove, as opposed to artificially increasing the exposure to do poor orientation choice. This research will serve to inform future researchers and manufactures in best practices to optimize the protection of firearm users and maintainers worldwide.

6. SUGGESTIONS FOR FUTURE WORK

The research conducted here is highly preliminary. As previously stated, there have been no research articles located that address any of the specific hypothesis or methods utilized herein. Between the time that this research commenced and when it concluded, many optimizations were discovered that addressed previous shortcomings in the methods used. It would be highly beneficial for the research conducted here to be repeated with the later optimizations in mind. Because of the tremendous time commitment needed for the analysis collected in these experiments, even with late-stage optimizations utilized, it would also be beneficial to employ different analysis methods, such as utilizing direct reading instruments to continuously analyze the collection solution in the permeation experiments.

Furthermore, while lead has been the most commonly researched gunshot residue to date, it is still important to note that inorganic gunshot residues were not addressed in this research. The experiments conducted here should be repeated with a focus on inorganic gunshot residues as opposed to organic gunshot residues. Just as the modern body of research has failed to address organic gunshot residues in their potential detriments to human health, this research should not fail to address the well-known dangers of inorganic gunshot residues and seek to establish a framework of knowledge that allows best practices to be established to reduce exposure to both organic and inorganic gunshot residues.

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