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Permeation of a firearm cleaning solvent through disposable nitrile gloves

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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 quantitation of the permeated compounds using capillary gas chromatography–mass spectrometry. 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 despite 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 of 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 manufacturer 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 semi-quantitative risk assessment confirmed the unacceptability of both gloves. Persons using 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 ensure the safety of workers.

Keywords

American Society for Testing and Materials (ASTM); chemical exposure; firearms; gun cleaning solvents; personal protective equipment

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Introduction

In 2020, the United States' full-time equivalent worker incidence rate for nonfatal skin diseases or disorders was 1.8 per 10,000 for 19,800 cases, the second highest rate for nonfatal injuries (BLS 2020). A common cause for these injuries is exposure to organic chemicals. Personal protective equipment (PPE), especially gloves, to protect hand skin from liquids, is often the first and last line of defense against chemical exposure. 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 nonpowdered disposable glove type from 2022 to 2030 (Grand View Research 2022).

Glove manufacturers commonly use the ASTM F739–99a 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 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 nonpolar 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 identifies 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 (Ansell 2019; Kimberly-Clark 2015), 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.

Methods

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 (0–25 mm, 0.001 resolution) and with a Mettler AE260 Analytical Balance.

Hoppe's No. 9 Gun Bore Cleaner was purchased from Amazon. 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 should 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 obtained from Fisher Scientific. Methyl salicylate (99%), analytical-grade ethanol (99.5%), lauric acid (99.9%), and isosafrole were from Sigma-Aldrich. Helium (99.9999%) was purchased from Air Liquide. Water was sourced from a Millipore Milli-Q Water System and Millipore Simplicity Water Purification final polishing system.

ASTM F739–12–compliant 1-in. internal diameter permeation cells, model I-PTC-600, including aluminum flanges, Teflon gaskets, bolts, and nuts, were purchased from Pesce Lab, which is a nonrecirculating 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.

An Agilent 6890 N Network GC System and 5973 Network Mass Selective Detector equipped with an Agilent fused silica capillary column 60 m × 0.320 μm 1.0 mm DB-1701 film, part number 123–0763, was used for analysis.

A Fisher Scientific Centrific Model 228 was used to centrifuge samples. A Bransonic Ultrasonicator Model B2200R-1 was used to mix samples. An American Optical MicroStar hand-held microscope allowed examination of materials. Hamilton Micro-syringes, 0–10 μL, facilitated gas chromatography–mass spectrometry (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.

Calculations

All calculations were performed using Microsoft Excel 365 v2212. 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 milligrams or micrograms by the glove exposed area in square centimeters and by the sampling time interval in minutes.

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

$$D = \frac{l^2}{6 * L_t}, \tag{1}$$

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

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

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 hr to assess phase separation visually.

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 mode (*m/z* 30–550 at 70 eV). The initial temperature program was 80 °C for 4 min, ramped at 10 °C/min up to 250 °C for 10 min, and finally increased at 10 °C/min to 280 °C and held for 10 min at a helium flow rate of 2.5 mL/min. The injector, column–mass spectrometer link, and quadrupole temperatures were respectively 280, 230, and 150 °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, with other temperatures the same as above.

For quantitation by the internal standard (IS) method for Lavender gloves with the selected ion monitoring mass spectrometry mode, 100-µL triplicate standards of Hoppe's (µg/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-µL volume of 1,000 µg/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 as follows: 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 vs. analyte concentration were 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. Group 5, the *β*-isosafrole 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, 1,000, 10,000, 25,000, 50,000, and 100,000 μg/mL of the combined equal concentration standards in n-decane in triplicate.

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 at 55 ± 1% relative humidity, maintained by a saturated aqueous solution of sodium dichromate, and 27 ± 2 °C for 24 hr. After removal from the desiccator, glove thicknesses were measured (μm) and their weights (balance) measured. 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 were placed on top of brown paper towels to check for leaks. After 1 hr of no leaks, the water was drained and the cells were 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 hr of conditioning.

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-μL 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, with the shaker 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.

Sample analysis

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

Concentrations for ethanol, methyl salicylate, and β-isosafrole 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 of whether the permeation was differential or concerted and thus to determine whether an aggregate permeation rate could be calculated for Hoppe’s rather than individual component rates.

Results

Initial testing

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, though 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.

GC-MS analysis—All standards met their purity specifications except for isosafrole, which contained 97.2 ± 0.1% isosafrole and 2.8 ± 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 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 of which were 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 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 total ion current 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 an estimated ethanol concentration in the Hoppe's mixture of 29.7 ± 5.9%. This is within the range of ethanol listed in the 2019 Hoppe's data sheet of between 10 and 30% (Bushnell Holdings 2019, 2022), and well within the expected concentration of the 2016 Hoppe's data sheet of between 15 and 45% (Bushnell Holdings 2016). The estimated concentration of methyl salicylate in Hoppe's was determined experimentally to be 0.59 ± 0.13%. The Hoppe's data sheets did not list methyl salicylate as a component (Bushnell Holdings 2016, 2019, 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.

Lavender nitrile glove permeation

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 1. Posttest thicknesses and masses of gloves 1, 2, and 3 are reported as their true values minus the blank difference, and their standard deviations are pooled with the standard deviation of the blank. All differences between pre- and posttest 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, the time in minutes at which the permeation rate reaches 0.1 μg/cm^2/min, occurred between 5 and 10 min; that is, 7.5 ± 2.5 min. 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

Hoppes increased in concentration. The aggregate permeation rates up to 60 min are shown in Figure 1. The estimated cumulative mass of Hoppe's in the collection cell was calculated to be 1.07 ± 0.17 g at 60 min.

Blue nitrile glove permeation

Changes in glove physical characteristics before and after permeation for three gloves are shown in Table 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 ± 0.4% for the challenge glove material compared to 4.9 ± 0.4% for the blank glove material. Because 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 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. The steady-state permeation rate was calculated as 1,642 ± 350 $\mu g/cm^2/min$. The lag breakthrough time was 17.3 ± 2.1 min and using Equation (1), the diffusion coefficient was $22.5 \pm 2.7 \times 10^{-7}$ cm^2/min. The equation is valid for no significant swelling or shrinking. The estimated cumulative mass of Hoppe's in the collection cell was calculated as 0.337 ± 0.034 mg at 60 min and 4.66 ± 0.55 mg at 480 min.

There was an increase in the signal area ratio of kerosene components compared to ethanol (Figures 3–5). 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 : ethanol signal ratio was approximately three to four 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.

Discussion

The analytes were selected because they were 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 as shown in Figures 1 and 2. This behavior is consistent with a "carrier effect"

(Banaee and Que Hee 2020; Perron et al. 2002) 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 although the standardized breakthrough times were 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/cm^2/min occurred for the Lavender glove at 30 min, compared with 2.16 ± 0.15 mg/cm^2/min at 120 min for the Blue glove. The major glove producers appear to emphasize breakthrough or detection times rather than steady-state permeation rates (Ansell 2016, 2019; Kimberly-Clark 2015). This lone criterion is not acceptable for the present data because the Blue glove is more resistant than the Lavender one.

Figure 2 shows that a Type D permeation (ASTM 2012) scenario 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, because the percentage difference in thickness between the pre- and posttest measurements were less than 10% for all glove pieces, it is unknown whether swelling was the primary driver. It is unlikely that actual penetration occurred because the gloves were examined under a hand-held microscope for physical defects, such as pinholes or breaks, both before and after permeation testing.

The breakthrough times of kerosene components were also significantly faster than expected. The Kimberly-Clark disposable nitrile glove chemical resistance guide lists a breakthrough time for kerosene of 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 break-through 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, facilitated 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 penetrationlike 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 Holdings 2022) indicates that in addition to 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 International Agency for Research on Cancer (IARC) Group 1 carcinogen, the latter because of the presence of polyaromatic hydrocarbons in the kerosene fraction. ATSDR 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 (ATSDR 1995). IARC lists fuel oils as possible human carcinogens but does not have a risk value associated with oral or inhalation routes of exposure (IARC 1989). Neither ASTM nor IARC has determined risks associated with dermal exposure to kerosene due to lack of data and studies. ATSDR has no minimum risk level associated with oral kerosene exposure due to "unsuitable" data. In contrast, ACGIH® recommends a kerosene threshold limit value (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 recommended exposure limit (REL) is 100 mg/m^3 (NIOSH 2023). There is no Occupational Safety and Health (OSHA) permissible exposure limit (PEL). The risk assessment situation for kerosene and therefore Hoppe's is muddled, with inhalation guidelines from as low as technologically possible for a human carcinogen to 200 mg kerosene equivalent/m^3. If the kerosene content is about the same as for ethanol (30%), 200 mg kerosene equivalent/m^3 is 667 mg Hoppe's/m^3 assuming no other contributions to toxicity. Thus, the 667 mg Hoppe's/m^3 is the equivalent air concentration time-weighted average over 8 hr. For a moderate workload, the 8-hr air volume inspired is about 10 m^3 (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).

Using three separate models for dermal permeation, the estimated maximum dermal permeation in Hoppe's per square centimeter per minute was 8.47 ± 5.1 µg and 15.4 ± 2.0 µg (Fiserova-Bergerova et al. 1990), 1.34 ± 0.80 µg and 0.671 ± 0.087 µg (Guy and Potts 1993), and 6,383 ± 3,800 µg and 231.4 ± 0.1 µg (Wilschut et al. 1995) for ethanol and methyl salicylate, respectively (Figures 6 and 7), at 8 hr of exposure for intact skin. Assuming an average human hand of 186 cm^2 area, the total dose absorbed after 8 hr would be 0.37 ± 0.22 g and 0.069 ± 0.009 g (Fiserova-Bergerova et al. 1990), 0.058 ± 0.35 g and 0.030 ± 0.004 g (Guy and Potts 1993), and 276.6 ± 166.5 g and 10.7 ± 1.4 g (Wilschut et al. 1995) for ethanol and methyl salicylate, respectively (Figures 8 and 9). All three models are unable to estimate the dermal permeation of kerosene because there is no set molecular weight for such mixtures. However, because 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. Because 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.

Limitations

No previous studies have been conducted on the permeation of firearm cleaning solvents through personal protective equipment, such as nitrile gloves. Furthermore, though 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 provides additional information that would allow this study to fully re-create the conditions that 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.

The primary goal of this study is not only to explore the permeation characteristics of a commercial-grade complex mixture through a ubiquitous glove material but also to establish a reproduceable method that reflects the conditions of materials as used by workers.

Conclusion

Hoppe’s gun cleaning solvent readily permeates through disposable nitrile gloves. 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 underneath would fare much better because it is possible that decreased co-permeation would occur. 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 permeated through both gloves, though the Blue glove was 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 shows a risk of exposure to gun cleaning solvents that permeate through disposable nitrile glove material.

A different analytical analysis technique, such as using an open-loop collection method with a nitrogen gas carrier connected to a flame ionization 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 to maintain the advantages of disposable gloves.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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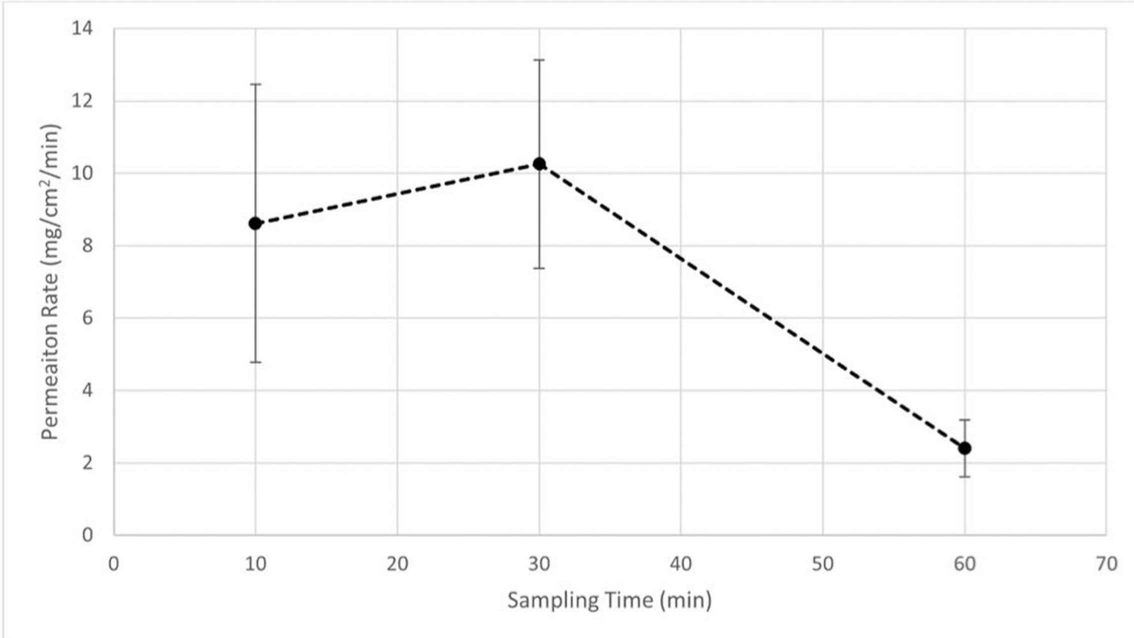

Figure 1.
Aggregate Hoppe's permeation rate through three Lavender nitrile gloves.

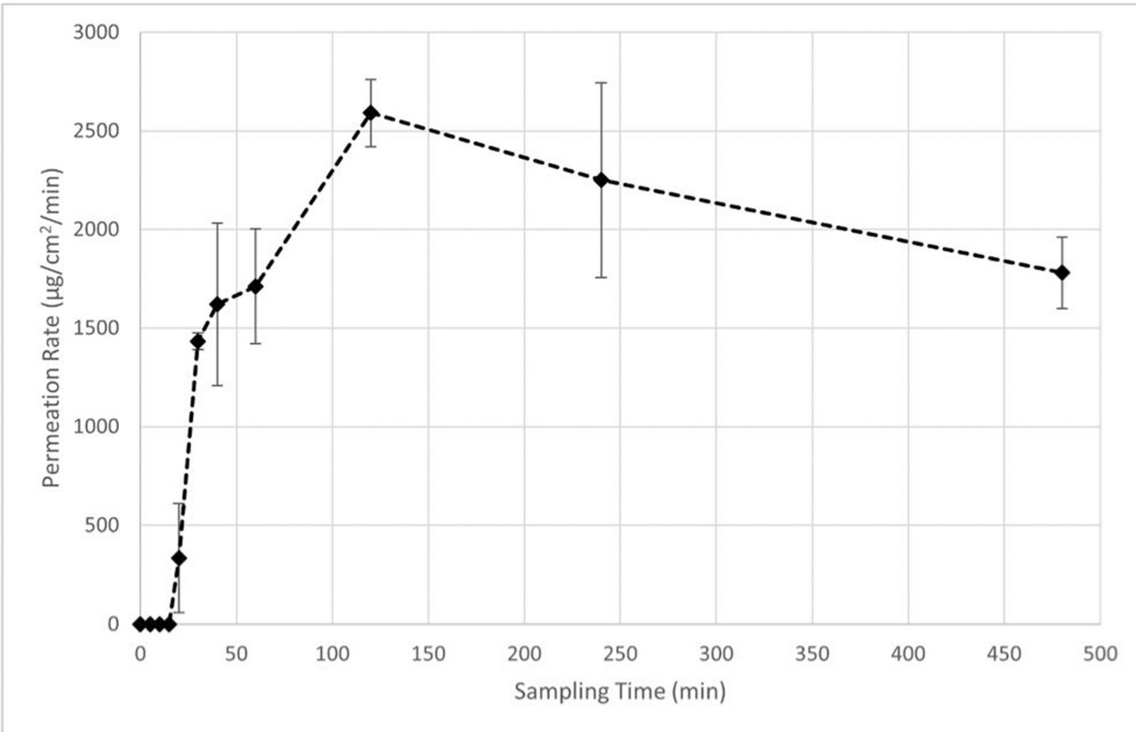

Figure 2.
Aggregate Hoppe's permeation rate through three Blue nitrile gloves.

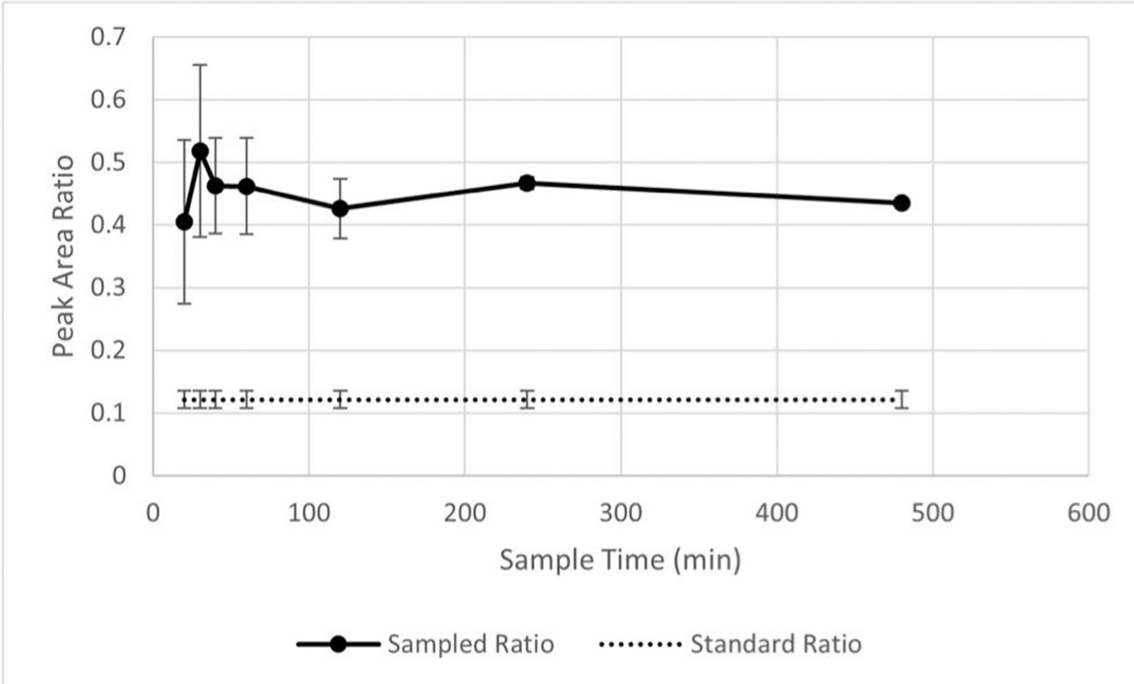

Figure 3.
Peak area ratios for methyl salicylate and ethanol.

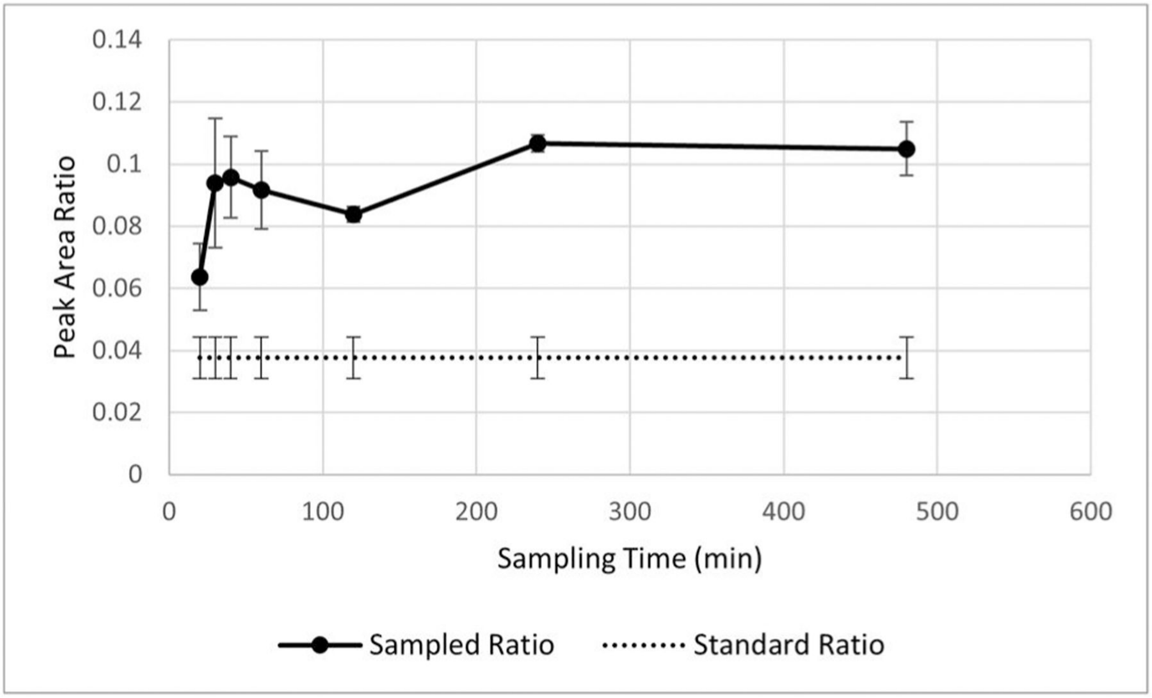

Figure 4.
Peak area ratios for 1,2,3,4-tetrahydro-6-methyl-naphthalene and ethanol.

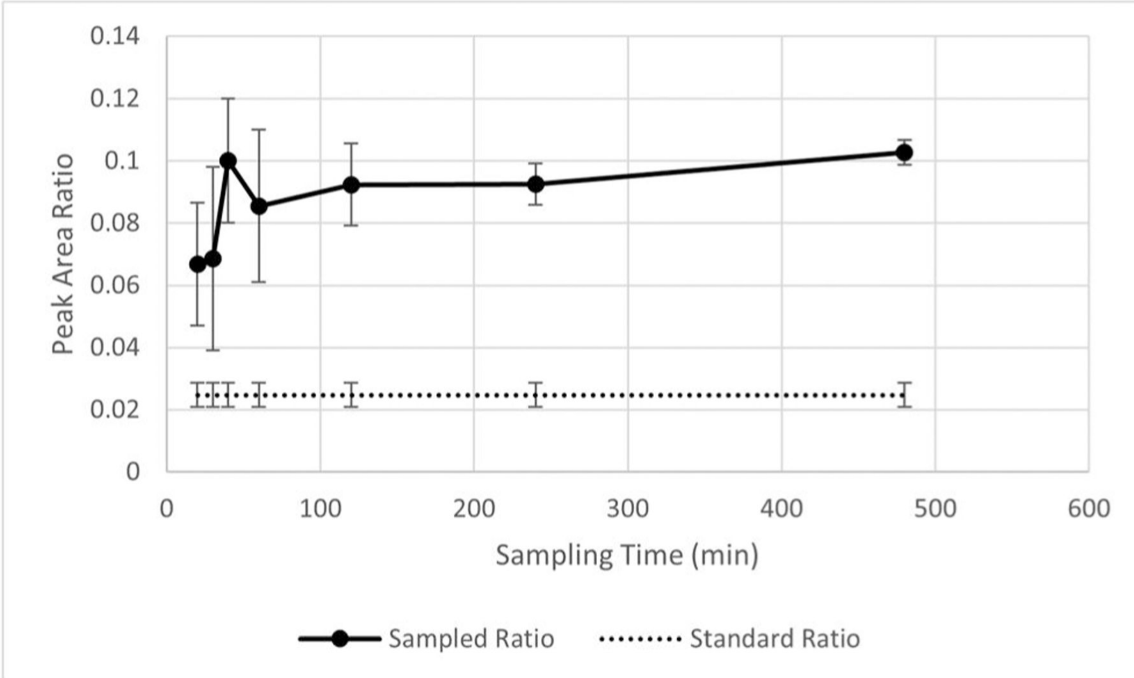

Figure 5.
Peak area ratios for β-isosafrole and ethanol.

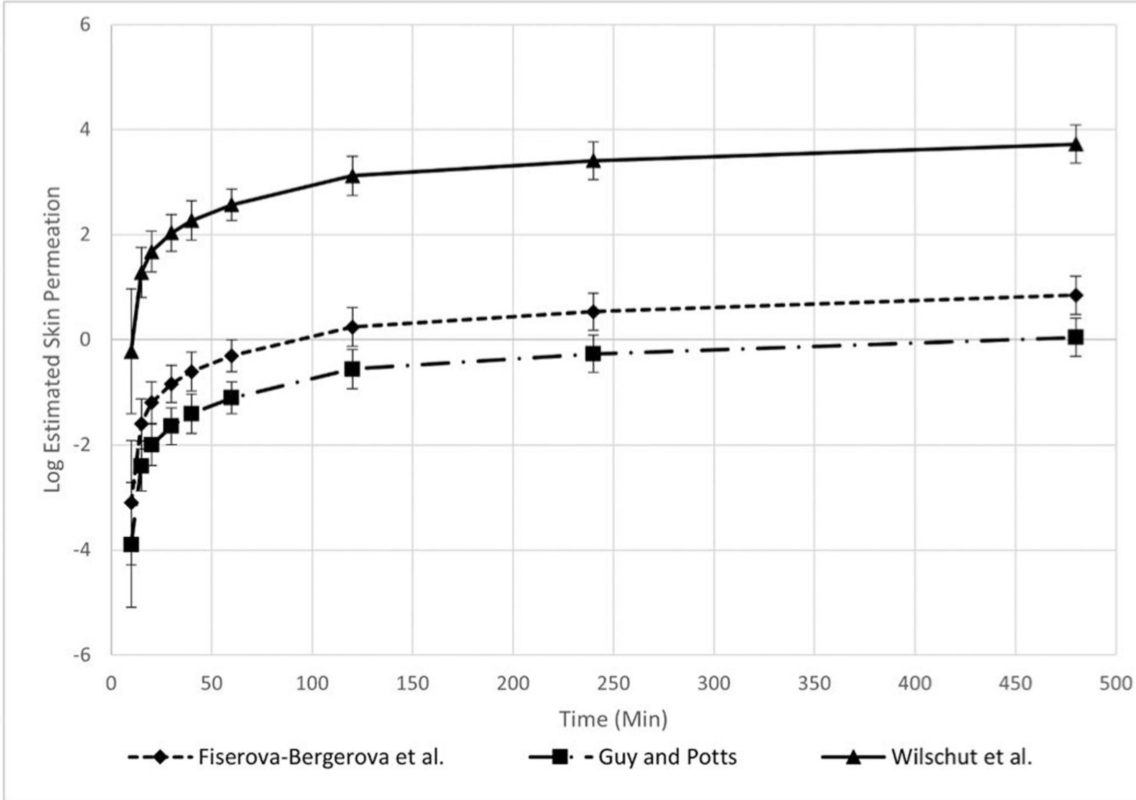

Figure 6.
Estimated log skin permeation rate for ethanol.

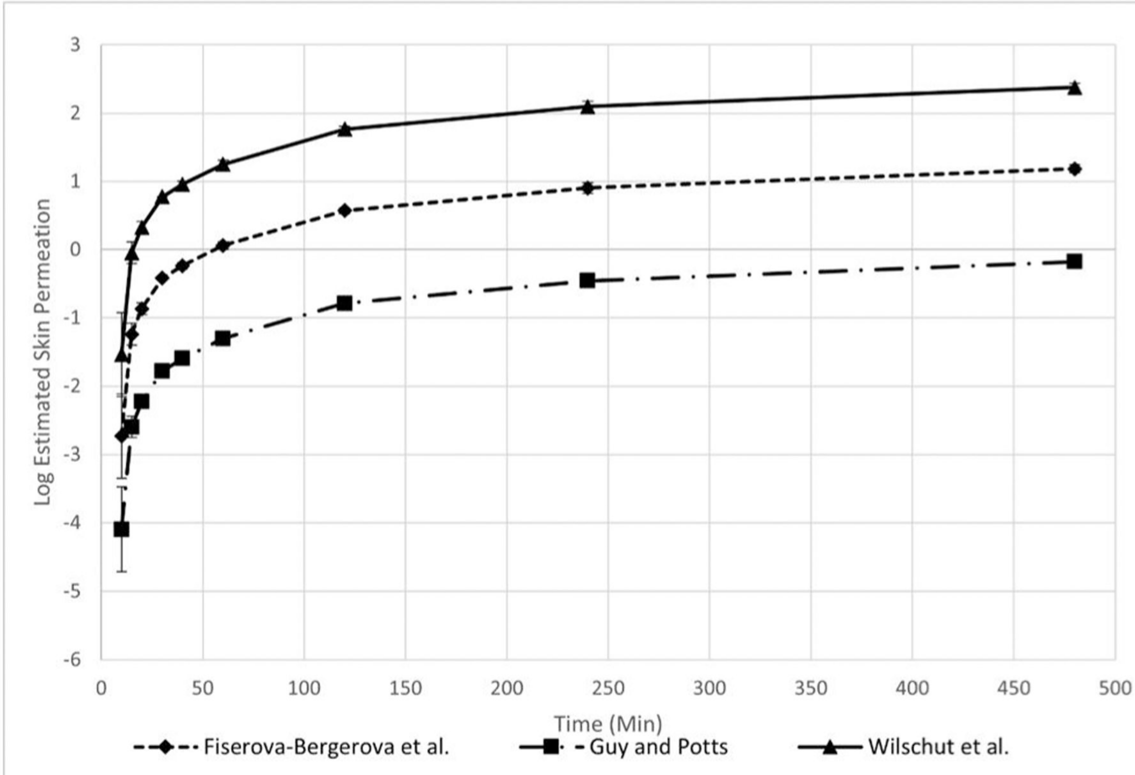

Figure 7.
Estimated log skin permeation rate for methyl salicylate.

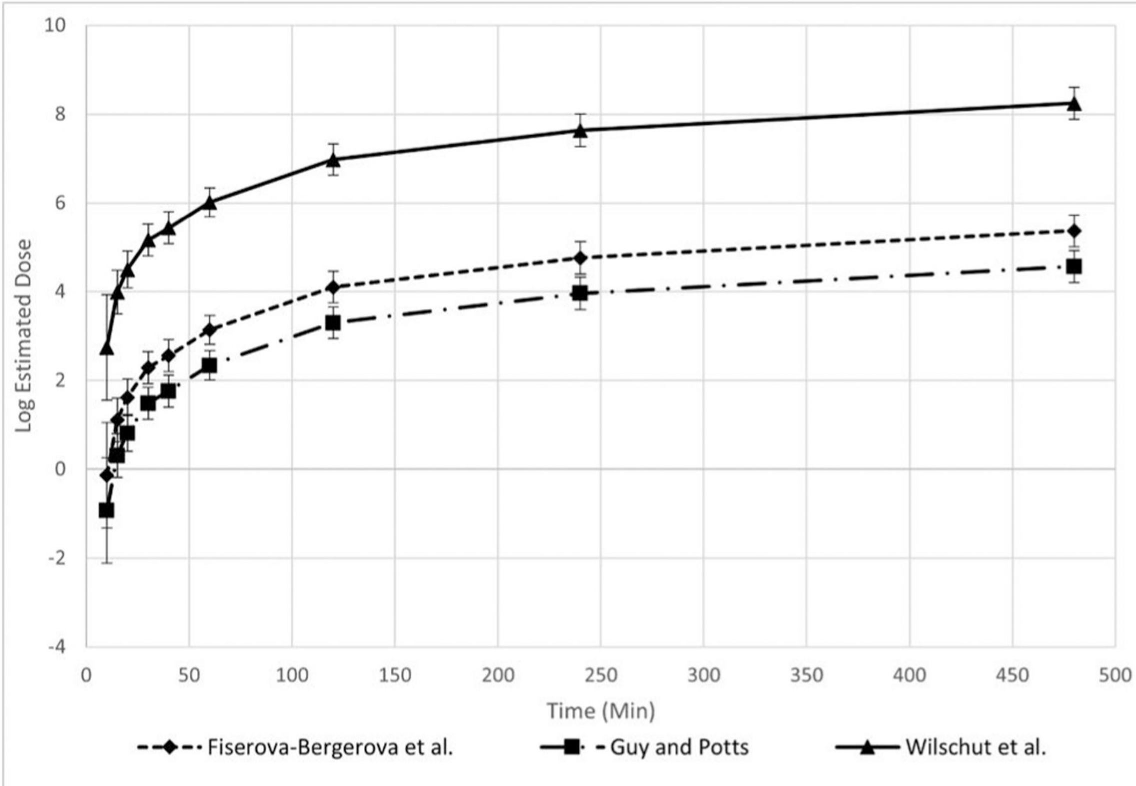

Figure 8.
Estimated log dose for ethanol.

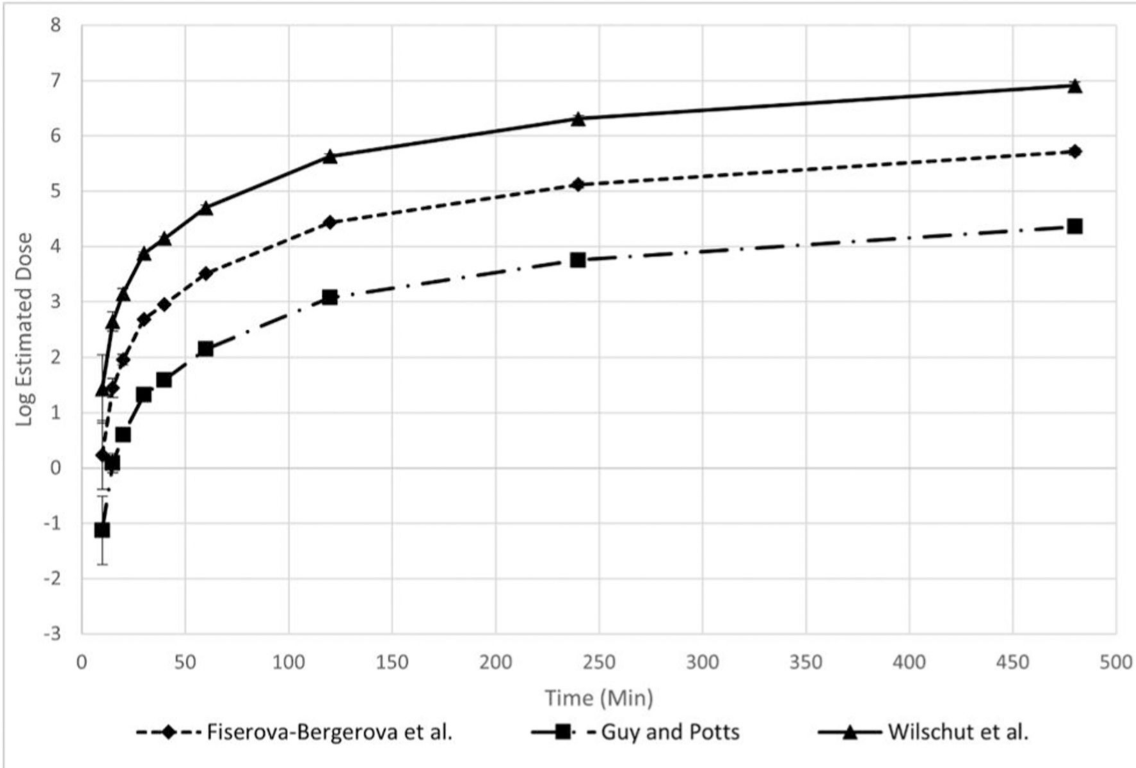

Figure 9.
Estimated log dose for methyl salicylate.

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Table 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.

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