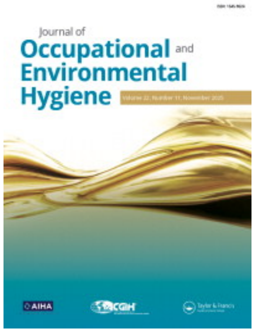

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Effects of polar and non-polar gun-cleaning solvent components on permeation characteristics of two major organic gunshot residues through disposable nitrile gloves

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ABSTRACT

While the hazards posed by lead in gunshot residues (GSRs) are recognized, little is known about the glove permeation of the organic components. The permeation behavior of the major organic GSRs methyl centralite and ethyl centralite through disposable nitrile glove material was investigated. The compounds were contained in three solvents: Hoppe's no. 9 gun cleaning solvent (GCS), n-decane, and a GCS surrogate, n-decane/ethanol 7:3 (w/w) mixture. The aim was to identify whether ethanol was the key driver of a previously reported carrier effect. A modified ASTM F739-20 method was used for permeation testing at $35.0 \pm 0.5\,^{\circ}C$ with closed-loop n-decane collection solvent without recirculation. Gas chromatography-mass spectrometry analysis facilitated GSR quantification. Significant differences occurred in intrarun but not interrun glove physical characteristics and in analyte permeation for the GCS and its surrogate. The GCS caused a substantial increase in permeation rate before a lower steady state permeation rate (SSPR). In contrast, n-decane/ethanol produced its SSPRs as the maximum permeation rate, but with decreased permeation rates and total permeated analyte mass. n-Decane solvent caused none of the GSR to enter the steady state and exhibited much longer breakthrough times. This study underscores the importance of considering the complete chemical composition of mixtures in assessing their interactions with glove personal protective equipment (PPE) and highlights the need for comprehensive testing protocols in PPE selection. Limitations included the lack of previous research on organic GSR glove permeation and challenges in comparing study results with manufacturer-reported glove resistance data. Adjusted concentrations for analytes and stepwise reconstitution of GCS components are recommended for future investigations. The present research provided insight into the glove permeation behavior of complex chemical mixtures for better glove PPE selection and testing practices.

KEYWORDS
Cleaning guns; cleaning gunshot; glove permeation; gun cleaners

Introduction

Guns may need to be cleaned by forensic science and criminology technicians, scientists and investigators, as well as by gun owners, hunters, sports markspersons, security personnel, police, and the military. It is generally acknowledged that workers exposed to hazards (including chemical residues) should have the benefit of protection via the hierarchy of controls (Morris and Cannady 2019). For those who sample gunshot residues (GSRs) and clean them from guns, the workplaces are often temporary, which precludes the use of the top tiers of controls, like elimination and substitution. Engineering controls are those present at crime scenes, areas where guns are fired, or in forensic laboratories (usually equipped with ventilation, glove boxes, and fume hoods). Administrative controls have involved worker training and the generation/implementation of standard operating procedures. Personal protective equipment (PPE) is generally covered, if at all, by "wear the appropriate glove" or a nonspecific equivalent. Since small sample sizes involve manipulative dexterity, this precludes the use of bulky and awkward chemically protective clothing (CPC) gloves, and thus, the use of disposable/examination gloves becomes necessary.

The present research characterized the permeation of representative organic non-polar GSR components through disposable nitrile glove material. This involved generating GSRs from a common firearm and cartridge; characterizing the GSRs by identifying and quantifying

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the GSR organics by gas chromatography-mass spectrometry (GC-MS); selecting the most abundant nonpolar GSR organics for permeation testing; defining a challenge gun cleaning solvent (GCS) – Hoppe's gun bore cleaner No 9 (Cribbs and Que Hee 2024) and a two-component mixture GCS surrogate to assess the carrier effect; performing the permeation tests with a modified ASTM F739 method; and assessing if the dominant polar component ethanol explained the permeation kinetics.

Methods

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) and published data regarding resistance to chemical permeation from key mixture components (Kimberly-Clark 2009, 2022). These also were the thickest nitrile disposable gloves made by Kimberly-Clark (Banaee et al. 2024). 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 before initial thicknesses were measured in triplicate with an Electronic Digital Micrometer Model CO-030025 (0–25 mm, 0.001 mm resolution) and weighed with a Mettler AE260 Analytical Balance (Hightstown, NJ, USA).

Hoppe's No. 9 gun bore GCS was purchased from Amazon (Seattle, WA). It is the best overall GCS of 2025 according to *Outdoor Life* and is used throughout the world (Moore and Freel 2025). The appropriate Safety Data Sheet (Bushnell Holdings 2016) indicated the following composition: ethyl alcohol, 15–40%; kerosene, 15–40%; oleic acid, % not available; amyl acetate, 5–10%; and ammonium hydroxide, 1–5%. Gas chromatograph-mass spectrometer (GC-MS) analysis revealed the presence of 29.7 ± 5.9 weight % of ethanol, the dominant polar organic solvent component (Cribbs and Que Hee 2024). The nonpolar organic fraction of kerosene was also shown to include 1,2,3,4-tetrahydro-6-methyl-naphthalene, methyl salicylate (0.6%), β-isosafrole, oleic acid, ethyl oleate, and amyl acetates. PPE guidance was to use protective clothing impervious to the ingredients.

The n-decane (99%) used for the collection of permeates as described in Cribbs and Que Hee (2024) and the sodium dichromate (99%) to produce 55% relative humidity for conditioning gloves at room temperature were secured from Fisher Scientific (Chino, CA, USA).

Methyl centralite (99%), ethyl centralite (99%), diphenylamine (99%) as internal standard (IS), and 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 a Millipore Simplicity Water Purification final polishing system (Temecula, CA).

No established internal vendor was allowed by the University of California Los Angeles to sell the researchers firearms or ammunition. Thus, these materials were purchased from local public businesses. The Ruger Mini-14 (a lightweight single-action semi-automatic rifle equipped with a short-stroke gas piston) used for the generation of GSR was procured from Big 5 Sporting Goods (Santa Paula, CA). The Federal 5.56×45 mm North Atlantic Treaty Organization (NATO) 55 gr Full Metal Jacket ammunition was purchased from Turner's Outdoorsman (Oxnard, CA).

ASTM F739-20 compliant 1-inch internal diameter glass permeation cells model I-PTC-600, including aluminum flanges, Teflon gaskets, bolts, and nuts, were purchased from Pesce Lab (Kennett Square, PA, USA) to constitute closed-loop collection systems without recirculation. Temperature control at $35.0 \pm 0.1\,^{\circ}$C and mixing of the permeation cell contents were achieved by dipping the cell up to its stems in a Fisher Shaking Bath Model 2870 (Chino, CA, USA).

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

A Fisher Scientific Centrific 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 microsyringes, 0–10 μL (Reno, NV, USA) facilitated GC-MS sample injections.

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

Calculations

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 in 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 min.

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

$$D = l^2/6L_t \quad (1)$$

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).

Generation of gunshot residue, its sampling and analysis, and selection of analytes and solvents

GSRs were initially generated with a Ruger Mini-14 rifle chambered in 5.56 × 45 mm NATO by firing 1,000 rounds of Federal 5.56 × 45 mm NATO 55 gr Full Metal Jacket ammunition at a firing rate of approximately 10 rounds per minute. The GSR generation occurred between 10 am and 12 pm 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. The GSR dry solid generated was removed from the firearm receiver, bolt, and barrel with a new nylon cleaning brush (cleaned with Hoppe's No. 9 gun bore cleaner, then ethanol and dried in a vacuum desiccator to constant weight) and collected into a pre-weighed Teflon container that was then capped. The vial was inserted into a cooler with ice packs and stored there for transport to the laboratory, where it was placed in a −15 ± 2 °C freezer until analysis.

The collected GSR was prepared for analysis by dissolving a thawed dry mass of 10.0 mg in 1 mL of n-decane in a volumetric tube. The solution was ultrasonicated for 10 min to ensure complete dissolution of the GSR. 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 °C, held for 4 min, ramped to 280 °C at 1 °C/min, and then held for 20 min at a 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 GSR peaks of the largest areas of the over 200 peaks were found to be the non-polar methyl centralite and ethyl centralite and were thus chosen for sensitivity and polarity reasons. The remaining dissolved GSR was retained for future GSR testing.

For the optimized temperature program to resolve the two centralites from the GCS components and the diphenylamine IS, 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, 1,000, 10,000, 25,000, 50,000, and 100,000 μg/mL of the combined equal concentration standards in n-decane in triplicate.

Three solvents were selected for testing: 1) n-decane only, 2) a 7:3 (w/w) mixture of n-decane and ethanol, and 3) the GCS. These were chosen to explore the effects of organic polar solvent components when mixed with non-polar solvents. The 7:3 mixture of n-decane and ethanol simulates the GCS relative to its nonpolar components to ethanol ratio, and allows comparisons between the two.

The ethanol content in the GCS had been shown previously to be 30% (w/w) (Cribbs and Que Hee 2024). The 2022 Safety Data Sheet (Bushnell Holdings 2022) implied that methanol (1–5%), isopropanol (5–10%), and ammonium hydroxide at <1% were also part of the polar fraction. The non-polar fraction consisted mostly of kerosene (30–60%), amyl acetate (1–5%), 2-methylbutyl acetate (1–5%), and 4 other single non-polar organics each <1%. The dominant non-polar component, kerosene, is a petroleum fraction typically of a mixture of straight-chain, branched-chain, and alicyclic hydrocarbons, typically of 9 to 16 carbon atoms, depending on the crude oil source and the refining process (King 1988). The collection solvent n-decane was known not to degrade Kimtech Blue nitrile (Cribbs and Que Hee 2024), and the shorter chain octane was known not to permeate the thinner Sterling nitrile disposable glove within 480 min compared with heptane 134 min, jet fuel (kerosene) 82 min, and hexane 16 min (Kimberly-Clark Worldwide 2015). Decane has been used as a surrogate for the aliphatic and alicyclic components of kerosene in flame testing (Zeng et al. 2013). It was desired to assess whether ethanol alone, as the dominant polar solvent, was responsible for the carrier effect and the permeation kinetics of the simulated GSR in GCS.

The initial concentrations of the simulated GSR analytes in the GCS solvent were 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 1.1 mg/mL methyl centralite and 52.2 mg/mL ethyl centralite.

Permeation cell experiments

The ASTM F739-20 standard test method for permeation of liquids and gases through protective clothing materials under conditions of continuous contact was used for permeation testing (ASTM 2020) involving four permeation cells with conditioned and non-leaking glove palm swatches 45 mm in diameter challenged by analytes in 10 mL of solvent in three cells and permeates collected with 10 mL of n-decane in all four cells (Cribbs and Que Hee 2024).

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. Additional sampling occurred at 5, 10, 15, 20, 30, 40, 60, 120, 240, and 480 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. An aliquot of 10.0 μL of 10.0 mg/mL diphenylamine IS was added to each vial after sample collection to create a diphenylamine concentration of 0.909 mg/L. All samples to be analyzed were stored in a freezer at −15 ± 2 °C.

Analysis of the thawed samples involved GC-MS using the appropriate SIM parameters and the optimized temperature program. Samples were processed from the earliest to the latest sampling time in the sequence cell blank, 1, 2, and then 3. The manual integration mode was used for all sampling times.

Concentrations for methyl centralite and ethyl centralite were calculated for each cell using the internal standards' linear regression equations. Average concentrations and their standard deviations were calculated by averaging the individual component concentrations from cells 1, 2, and 3, corrected by values for the blank cell 4 to account for the effects of the collection fluid.

The standardized breakthrough time (SBT) was defined (ASTM 2020) as the time interval that included the permeation rate of 0.10 µg/cm^2/min. The steady state permeation rate (SSPR) was the maximum extended horizontal portion of the permeation rate versus time curve.

Results

Identification of methyl centralite and ethyl centralite in gunshot residue

GC-MS injection of the GSR dissolved in n-decane yielded a total ion (scan) chromatogram using the optimized column temperature program. The choice of which compounds in the gunpowder fouling should be selected for permeation depended on concentration, sensitivity, and resolution from the over 200 components of the GSRs and the more than 250 compounds of Hoppe's GCS. The GC-MS Mass Spectral Library assigned the largest two peaks to be most likely the two gunpowder stabilizers, methyl centralite (1,3-dimethyl-1,3-diphenylurea; CAS RN 611-92-7; PubChem 2024a with NIST mass spectrum) and ethyl centralite (1,3-diethyl-1,3-diphenylurea; CAS RN 85-98-3; PubChem 2024b). Both had weak molecular ions M + of m/z 240 for methyl centralite and m/z 268 for ethyl centralite, with respective base ions at m/z 134 and m/z 148. This led to the selection of the centralite ion set of m/z 77.0, 106.0, 120.0, 134.0, and 148.0 for GC-MS analyses. Pure standards, both solids, were purchased, and the retention times and mass spectra agreed, confirming the identifications. The concentration of diphenylamine, the IS, and a possible gunshot stabilizer (Maitre et al. 2018) was below detection in the GSR.

Gunshot residue solution challenges

Common results for all solvent challenges included: a lower limit of quantitation of 0.1 μg/mL and a limit of detection of 0.01 μg/mL for both methyl and ethyl centralite analytes; the relative retention time with respect to the IS for methyl centralite was 1.804, and 1.900 for ethyl centralite; the linear regression equation for methyl centralite was $y = 0.00058x - 0.00742$ where y is the analyte/diphenylamine internal standard (IS) response ratio and x is the analyte concentration; for ethyl centralite, the linear regression equation was $y = 0.00074x - 0.00178$; the r values for both were >0.999 and their p values were ≤0.05; the intrarun and interrun swelling or mass increase never exceeded 10% relative standard deviation relative to the original value allowing Equation (1) to be used.

Tables 1–3 contain intrarun and interrun glove material thickness and weight data before and after permeation on conditioned/reconditioned glove materials. Figures 1–6 depict interrun permeation rate versus time data with arithmetic mean and one standard deviation imprecision data.

Hoppe's gun cleaning solvent

Changes in glove physical characteristics before and after permeation in the GCS are shown in Table 1. All individual glove pieces, excluding blanks and n-decane data, showed statistically significant increases in intrarun mass and thickness (except glove 2 for thickness) at the $p \le 0.05$ level. The interrun swelling of the glove material was 3 ± 3 µm or 2.1 ± 2.1%, not significant at $p \le 0.05$. Similarly, the interrun increase in glove mass was 11.0 ± 0.7 mg or 4.6 ± 0.3%, also not significant at $p \le 0.05$.

The interrun permeation rate scattergrams, along with arithmetic mean standard deviation imprecision for methyl centralite and ethyl centralite, are shown in Figures 1 and 2, respectively. The percent relative standard deviation (RSD) for both ranged from 5 to 15% after the SBT of 12.5 ± 2.5 min for both methyl centralite and ethyl centralite. A substantial increase in permeation rate was observed between the SBT and 120 min, with a maximum permeation rate of 35.9 ± 3.2 μg/cm^2/min (8.9% RSD) for methyl centralite and 27.4 ± 2.4 μg/cm^2/min (8.8% RSD) for ethyl centralite. The steady state permeation rate (SSPR) over the steady state period was 19.9 ± 3.6 μg/cm^2/min for methyl centralite (18% RSD) and 19.8 ± 6.0 μg/cm^2/min for ethyl centralite (30% RSD). The L_t was 9.7 ± 0.7 min for methyl centralite (7.2% RSD) and 13.3 ± 1.0 min for ethyl centralite (7.5% RSD). Using Equation (1), the diffusion coefficient D was calculated to be (38.4 ± 2.8)

Table 1. Glove physical data before (B) and after (A) permeation (P), including change (absolute and relative) from before permeation (C) and their intrarun standard deviations for challenges in n-decane solvent for three different gloves corrected for blank glove data.

	Thickness				Weight			
Glove	BP (µm)	AP (µm)	C (µm)	C (%)	BP (mg)	AP (mg)	C (mg)	C (%)
1	147 ± 1	153 ± 1	6 ± 2	4.2 ± 1.4	248.0 ± 0.2	258.9 ± 0.2	10.9 ± 0.4	4.4 ± 0.2
2	148 ± 1	147 ± 1	−1 ± 2	−0.7 ± 1.4	251.2 ± 0.1	262.9 ± 0.1	11.7 ± 0.2	4.7 ± 0.1
3	143 ± 1	147 ± 1	4 ± 2	2.8 ± 1.4	225.9 ± 0.1	236.2 ± 0.1	10.3 ± 0.2	4.6 ± 0.2
GM ± SD	146 ± 3	149 ± 4	3 ± 3	2.1 ± 2.1	241.7 ± 13.8	252.7 ± 14.4	11.0 ± 0.7	4.6 ± 0.3

The grand mean (GM) and its interrun standard deviation (SD), and C values are also provided.

Table 2. Glove physical data before (B) and after (A) permeation (P), including change (absolute and relative) from before permeation (C) and their intrarun standard deviations for challenges in n-decane solvent for three different gloves corrected for blank glove data.

	Thickness				Weight			
Glove	BP (µm)	AP (µm)	C (µm)	C (%)	BP (mg)	AP (mg)	C (mg)	C (%)
1	141 ± 1	141 ± 1	0 ± 2	0 ± 0	239.3 ± 0.1	240.7 ± 0.1	1.4 ± 0.2	0.58 ± 0.08
2	139 ± 1	140 ± 1	1 ± 2	0.7 ± 1.4	262.3 ± 0.1	263.4 ± 0.1	1.1 ± 0.2	0.42 ± 0.08
3	142 ± 1	144 ± 1	2 ± 2	1.4 ± 1.4	262.5 ± 0.1	264.2 ± 0.1	1.7 ± 0.2	0.65 ± 0.08
GM ± SD	141 ± 2	142 ± 2	1 ± 4	0.7 ± 2.8	254.7 ± 13.4	256.1 ± 13.3	1.4 ± 26.7	1 ± 10

The grand mean (GM) and its interrun standard deviation (SD), and C values are also provided.

Table 3. Glove physical data before (B) and after (A) permeation (P), including change (absolute and relative) from before permeation (C) and their intrarun standard deviations for challenges in 7:3 n-decane/ethanol solvent for three different gloves corrected for blank glove data.

	Thickness				Weight			
Glove	BP (µm)	AP (µm)	C (µm)	C (%)	BP (mg)	AP (mg)	C (mg)	C (%)
1	148 ± 1	153 ± 1	5 ± 2	3.4 ± 1.4	248.0 ± 0.2	258.9 ± 0.2	10.9 ± 0.4	4.40 ± 0.16
2	143 ± 1	147 ± 1	4 ± 2	2.8 ± 1.4	251.2 ± 0.1	262.9 ± 0.1	11.7 ± 0.2	4.66 ± 0.08
3	144 ± 1	147 ± 1	3 ± 2	2.1 ± 1.4	255.9 ± 0.1	263.2 ± 0.1	7.3 ± 0.2	2.85 ± 0.08
GM ± SD	145 ± 3	149 ± 4	4 ± 7	2.8 ± 4.9	251.7 ± 4.0	261.7 ± 2.4	10.0 ± 6.4	3.97 ± 2.54

The grand mean (GM) and its interrun standard deviation (SD), and C values are also provided.

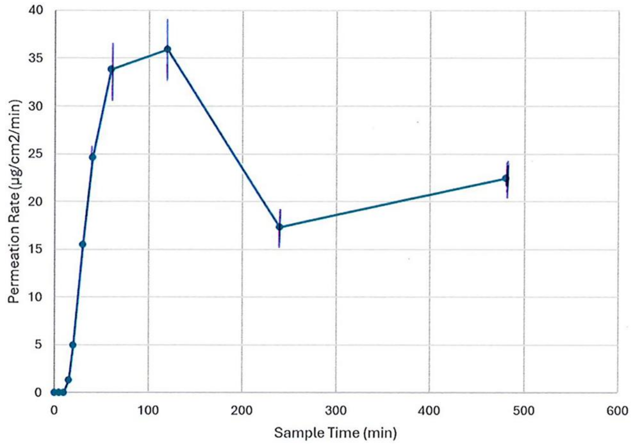

Figure 1. Methyl centralite average permeation rate in Hoppe's solvent for three Kimtech Blue gloves.

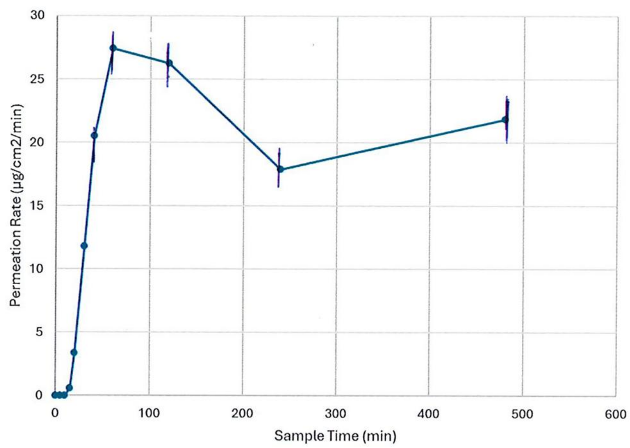

Figure 2. Ethyl centralite average permeation rate in Hoppe's solvent for three Kimtech Blue gloves.

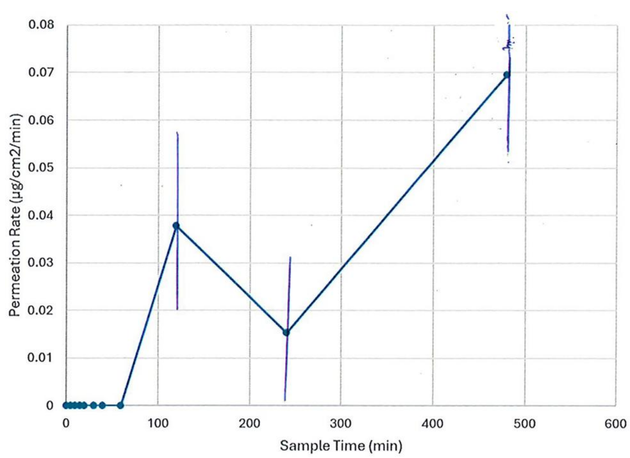

Figure 3. Methyl centralite average permeation rate in n-decane solvent for three Kimtech Blue gloves.

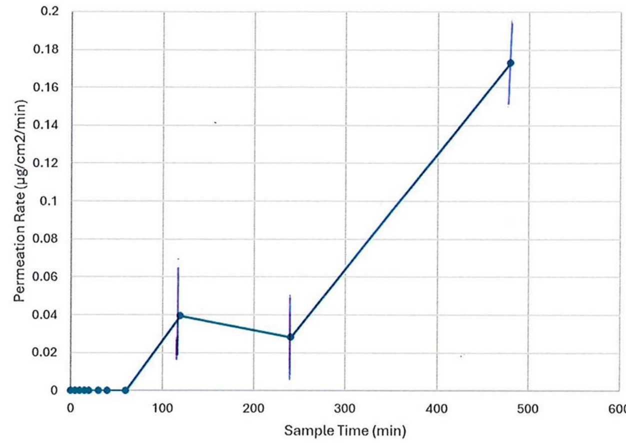

Figure 4. Ethyl centralite average permeation rate in n-decane solvent for three Kimtech Blue gloves.

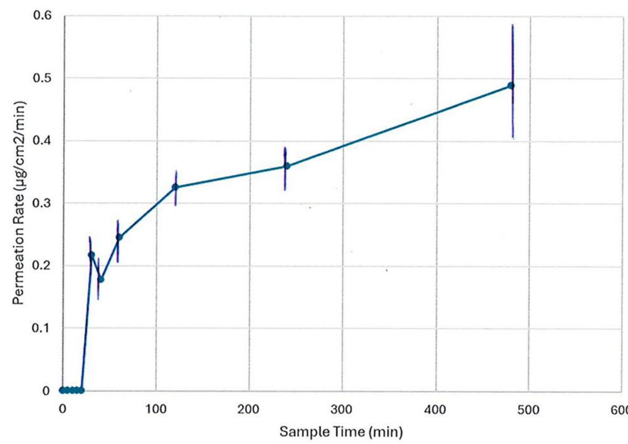

Figure 5. Methyl centralite average permeation rate in n-decane/EtOH solvent for three Kimtech Blue gloves.

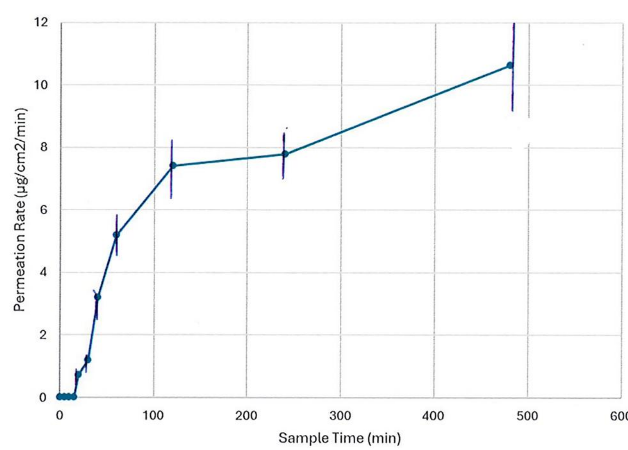

Figure 6. Ethyl centralite average permeation rate in n-decane/EtOH solvent for three Kimtech Blue gloves.

$\times\ 10^{-7}$ cm^2/min for methyl centralite and $(27.9 \pm 2.1) \times 10^{-7}$ cm^2/min for ethyl centralite. The equation is valid for no significant swelling or shrinking, as confirmed by *Student* t *p* value > 0.05 for the interrun glove thickness data of Table 1 for a swelling of $2.1 \pm 2.1\%$.

The cumulative mass of methyl centralite in the collection cell was 5.9 ± 0.0 mg at 60 min and 57.0 ± 1.7 mg at 480 min. The cumulative mass of ethyl centralite in the collection cell was 0.5 ± 0.1 mg at 60 min and 52.3 ± 1.8 mg at 480 min.

n-Decane only solvent

Changes in glove physical characteristics before and after permeation are shown in Table 2. No significant changes in intrarun thickness were observed for any individual glove piece. The interrun swelling of the glove material was observed to be 1.0 ± 4.0 µm or 0.7 ± 2.8%. The interrun increase in glove mass post-permeation was 1.4 ± 26.7 mg or 1 ± 10%. The large imprecisions and small differences of the interrun data were largely responsible for the result of statistical non-significance.

The permeation rate curves for methyl centralite and ethyl centralite in a n-decane solvent are shown in Figures 3 and 4, respectively. The SBT occurred at 360 ± 120 min for ethyl centralite but was not achieved with methyl centralite. No SSPR was measurable by 480 min. The maximum permeation rate at that time was calculated to be 0.07 ± 0.02 μg/cm^2/min for methyl centralite (29% RSD) and 0.2 ± 0.1 μg/cm^2/min for ethyl centralite (50% RSD). Because no SSPR was achieved, no L_t was calculated. Consequently, the D could not be calculated either. The cumulative permeated mass of methyl centralite was calculated to be 0 ± 0 mg at 60 min and 0.1 ± 0.1 mg at 480 min. The cumulative mass of ethyl centralite was 0 ± 0 mg at 60 min and 0.2 ± 0.1 mg at 480 min.

n-Decane/ethanol 7:3 mixture solvent

Changes in glove physical characteristics before and after permeation are shown in Table 3. All individual glove pieces, excluding blanks, showed statistically significant increases in mass and thickness at the $p \leq 0.05$ level. Interrun swelling of the glove material was observed to be 4 ± 7 µm or 2.8 ± 4.9%. The interrun increase in glove mass post-permeation testing was 10.0 ± 6.4 mg or 4.0 ± 2.5% after blank glove correction.

The permeation rate curves for methyl centralite and ethyl centralite in an n-decane/ethanol 7:3 mixture solvent are shown in Figures 5 and 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 min for either analyte, with a maximum permeation rate of 0.5 ± 0.1 μg/cm^2/min for methyl centralite (20% RSD) and 10.6 ± 2.2 μg/cm^2/min for ethyl centralite (21% RSD), permeation rates having RSDs from 5% to 25% after the SBT. A SSPR period was observed beginning at approximately 120 min for both methyl and ethyl centralite. The SSPR was calculated to be 0.4 ± 0.1 μg/cm^2/min for methyl centralite (25% RSD) and 8.6 ± 2.0 μg/cm^2/min for ethyl centralite (23% RSD). The L_t was 39.2 ± 1.8 min for methyl centralite and 38.0 ± 1.2 min for ethyl centralite. Using Equation (1), D was (94.4 ± 4.4) × 10^{-7} cm^2/min for methyl centralite and (97.3 ± 3.1) × 10^{-7} cm^2/min for ethyl centralite. The cumulative permeated mass of methyl centralite was 0.005 ± 0.001 mg at 60 min and 0.5 ± 0.1 mg at 480 min, both having an RSD of 20%. Similarly, permeated ethyl centralite in the collection cell was calculated to be 0.8 ± 0.1 mg at 60 min (13% RSD) and 4.0 ± 0.2 mg at 480 min (RSD 5.0%).

Discussion

The swelling and increased mass behaviors of the glove material after challenge of the two GSR compounds in the GCS and 7:3 n-decane/ethanol were similar, as shown by generally statistically significant intrarun data at $p \leq 0.05$ but statistically not significant corresponding interrun data with % RSDs never exceeding 10%. The swelling data were more precise than the mass increase data for unknown reasons. The GSR SBTs were longer for the 7:3 n-decane/ethanol challenge (17.5 ± 2.5 min for ethyl centralite and 25 ± 5 min for methyl centralite) than for the GCS challenge (12.5 ± 2.5 min for both). In contrast, the n-decane challenge solvent caused both intrarun and interrun glove swelling and mass data to be not statistically significant, much longer SBTs (>240 min), and no measurable SSPRs over the 8-h run. These results do confirm that ethanol, the dominant polar organic solvent in Hoppe's GCS, does play a significant role in the increased permeation of the gunshot non-polar centralites through disposable nitrile gloves. The substantial relative abundance of ethanol in the GCS made it likely to be the prime driver of a carrier effect (Banaee and Que Hee 2020; Perron et al. 2002).

However, the other polar components do affect the SBT results. Additionally, the permeation rate versus time behavior after breakthrough exhibited with the GCS is a pronounced type D permeation rate behavior (ASTM 2020) where the permeation rate versus time plot shape has a pronounced maximum followed by a lower SSPR (Figures 1 and 2) whereas that of the n-decane/ethanol challenge mixture in Figures 5 and 6 is type A (ASTM 2020) where the permeation rate versus time plot shape after breakthrough is of a concave rectangular hyperbola with the SSPR being the maximum permeation rate, this being the most frequent permeation curve shape (ASTM 2020). Physically, Type D behavior occurs for moderate to heavy glove material swelling, and Type A typically depicts little or no swelling. In the present results, the type D permeation rate behavior was accompanied by an exponential increase in total analyte permeated mass compared to other permeation metrics. While the SSPR was doubled by the GCS, the total permeated mass was more than five times that of the n-decane/ethanol solvent for ethyl centralite. The likely key factor in these differences is the presence of other polar components in the GCS, such as methanol, isopropanol, and ammonia water. It is also likely that 'trade secret' chemical components are also present that could influence permeation parameters and behavior when compared to the n-decane/ethanol mixture.

Another consideration is that n-decane was used as the non-polar surrogate instead 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 (King 1988). It was also desired to have as simple a system as possible with which to demonstrate the "carrier effect," and n-decane had been used as a surrogate for kerosene in other applications (Zeng et al. 2013). There could be some chemicals in the non-polar components (for example, the acetates) that may contribute to the observed changes in centralite permeation in the GCS. More research is therefore necessary.

Little has been published in the scientific literature on how to protect armed workers like the military, the police, security personnel, gun range maintainers, shooters, forensics technicians, and armed hunters when they clean their guns after shooting. Doubtless, any such military or police permeation data may lack security clearance. While a major current in Public Health is gun control (Black 2023; Office of the Surgeon General 2024; Schaeffer 2023; Stroebe and Leander 2024), users of arms to be cleaned should still be protected from GSRs that contain many inorganic, organic, and organometallic toxins (Goudsmits et al. 2015; Maitre et al. 2018; Manganelli et al. 2019; Meng and Caddy 1997; Moran and Bell 2013, 2014).

Limitations

No previous studies have been published in the scientific peer-reviewed journal literature on the permeation of GSR components in firearm cleaning solvents through PPE such as nitrile gloves. Furthermore, while the ASTM provides standard methods for testing the permeation of chemicals through glove materials, no known chemical resistance charts for the gloves used in this study provide the key information that would allow that study to fully recreate the conditions which generated their reported results, especially the collection fluid, 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 glove resistance to GCS components as published by the glove manufacturer with the results of the present study. Because of changes in the concentration of methyl and ethyl centralites between solvents due to solubility, the present study should be repeated at a lowered common concentration with gradual reconstitution of GCS components at their true concentrations.

Conclusions

This study investigated the cause of an apparent carrier effect in a previous study where Hoppes GCS no. 9 challenged disposable nitrile gloves. The present results revealed significant differences in glove physical characteristics and permeation among challenge solvents containing two gunshot residues, methyl and ethyl centralite. Permeation rate curves had a type D behavior for the GCS, with a substantial increase in permeation rate and permeated mass after breakthrough, followed by a lower SSPR. In contrast, type A behavior occurred for a n-decane/ethanol mixture that simulated the GCS but had less mass permeated. The presence of ethanol, the dominant polar organic solvent in the GCS, certainly increased the permeation of non-polar chemicals. However, other polar components in the GCS likely also contributed.

These findings suggest that the presence of certain polar chemical components in complex mixtures like Hoppe's GCS can significantly influence permeation parameters and behavior through disposable 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 glove personal PPE 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 insights into the permeation behavior of complex chemical mixtures through disposable nitrile gloves, emphasizing the need for comprehensive testing protocols and considerations in glove PPE selection.

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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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