

ABSTRACT

BRADHAM, ASHLEY ELIZABETH. Development of a System for Analysis and Selection of CBRN Boot Materials. (Under the direction of Dr. Roger Barker and Dr. Keith Beck.)

Current boots used for chemical, biological, radiological, and nuclear (CBRN) incidents provide good protection but are often heavy, uncomfortable and inflexible. There is a need for finding a new CBRN material, but the current standards for material resistance against threats like toxic industrial chemicals (TICs) do not use an approach that is similar to how CBRN boots are used in the field.

A new system was developed to expose and decontaminate materials multiple times to determine if a more lightweight flexible material could provide protection throughout the service life of a CBRN boot. Several materials were screened for their absorbance to a battery of TICs, and the results were compared to a rubber sample taken from a certified CBRN boot. Decontamination procedures were compared and the most efficient method was selected. The material that performed the best was subjected to one-day and four-day field simulation procedures. One-day in the field was defined as three exposures with decontaminations following each exposure.

Finished leather was determined to be a viable option for CBRN boot application using the new methods developed. Neither the rubber nor leather performed best with all TICs. However, the leather had higher residual levels of semi-volatile TICs than the rubber control. A wipe test confirmed that there was very little or no detectable TIC on the material surface. This research contributed an important element enabling development of a new leather CBRN boot.

Development of a System for Analysis and Selection of CBRN Boot Materials
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BIOGRAPHY

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Following high school, she moved to Raleigh, North Carolina to attend North Carolina State University (NCSU). During her undergraduate career, she was awarded the Charles H. Stone Scholarship from the American Association of Textile Chemists and Colorists (AATCC). While pursuing her degree, she worked as a lab assistant for Tumbling Colors and a lab technician for HueMetrix. During the summer of 2008, she wrote a laboratory exercise on high internal phase emulsion, which was incorporated into an undergraduate polymer chemistry laboratory manual. She completed the University Scholars Program and was a textile student mentor. Ashley was a member and held leadership roles in the AATCC student chapter, Sigma Tau Sigma Textile Honors Fraternity, and Phi Psi Professional Textile Fraternity. She was also inducted into Phi Kappa Phi Honors Society in 2008. Along with school activities, she worked as a volunteer for Relay for Life, Rex Hospital, and the Katrina relief in Gulfport, Mississippi. In 2009, Ashley graduated Valedictorian and Summa Cum Laude with a Bachelor of Science degree in Polymer and Color Chemistry. At graduation, she was awarded the AATCC Outstanding College Graduate of the Year and the Chester H. Roth Honor Award.

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selecting a new material for Chemical, Biological, Radiological, and Nuclear (CBRN) protective boots. This research, under contract with CTTSO/TSWG, has allowed her to attend and present at the Personal Protective Equipment Conference and the AATCC International Conference. Ashley will graduate with a Master of Science degree in May, 2011.

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Chapter 1. Introduction

1.1 Purpose

Chemical, Biological, Radiological, and Nuclear (CBRN) first responders and other hazmat teams rely on their clothing ensembles for protection. The gear used by these responders includes boots that must resist not only a wide range of chemical challenges, but also have puncture, abrasion, and flash fire resistance. To meet the high level of protection required by CBRN boots, responders have adopted a boot made from dense rubber materials. These rubber boots are typically heavy and inflexible, and can cause physiological stress and blisters from skin abrasion. Discomfort resulting from CBRN boots reduces the length of time a responder can spend in the field. First responders that choose a lighter, thinner CBRN boot often find that the stability and traction of this design is limited. A new material for these boots would increase the comfort and work performance of CBRN responders.

An important feature for CBRN gear is decontamination and reuse. CBRN boots are expensive, and boots that can survive multiple training exercises and events are beneficial to the budgets of the military and firefighters. A challenge for new materials developed for CBRN boots is determining if they are rugged enough for multiple exposures to a range of chemical challenges, decontamination solutions and scrubbing while maintaining the appropriate level of protection. Currently, the National Fire Protection Association (NFPA) performance requirements for protective ensembles used in chemical and biological terrorism incidents involve testing a specimen for permeation resistance against toxic industrial chemicals (TICs) and warfare agents for at least 60 minutes.[1] This method does not replicate the real use of these materials in the field. To determine if new materials are

candidates for CBRN use, there is a need for new test methods that involve multiple chemical exposures and decontamination procedures that mimic the use of the materials in the field.

Part of the need for new test procedures includes determining the best performing and most efficient decontamination procedure. There is little information available on the efficiency of the current military decontamination procedure. Investigating new decontamination solutions and approaches could lead to better removal of a chemical challenge with minimal material damage.

1.2 Research Objectives

The objective of this research was to create a laboratory based system for analysis and selection of new materials for use in construction of reusable tactical CBRN boots. The system would mimic the use of CBRN boots over a typical service life, and determine if a candidate material is rugged enough to maintain an appropriate level of protection before being implemented into a prototype for certification.

Project tasks included:

1. Development of methods to expose and decontaminate a material sample in a way that simulates the use of a CBRN boot. Specific questions addressed by this task are as follows:
 - a. How many chemical exposures and decontamination cycles are typical during the CBRN boot service life?
 - b. What types of exposure are expected in the field?

- c. What is the current decontamination procedure used by CBRN responders? Is this current decontamination procedure adequate, or is there a new procedure that could be more effective?
2. Development of extraction and analytical methods that could determine the amount of a challenge chemical remaining in a material sample after exposure and decontamination.

Completing these tasks would provide a system for analyzing the performance of materials for CBRN use that is unlike any current standard test method. New methods will aid in determining if a more flexible, comfortable boot material could survive multiple uses in the field. Boot manufacturers could benefit from these methods because they assist in the selection of a new material before the development of a boot prototype for official certification. The overall objective of this research is to provide a more comprehensive test system that may lead to the next generation tactical CBRN boots that provides more comfort and stability for the user.

Chapter 2. Literature Review and Background

2.1 Toxic Industrial Chemicals

2.1.1. Standard Lists of Toxic Industrial Chemicals

CBRN response teams can encounter a number of chemical threats including liquid and gaseous Toxic Industrial Chemicals (TICs) and warfare agents. The testing of warfare agents requires special facilities and approvals. Therefore, it was decided that this project would test materials using TICs. A TIC is a gaseous, liquid, or solid chemical used in

industrial processes around the world and may be available in large quantities.[1,2] TICs could be hazardous to human health due to their chemical classification, such as a carcinogen, teratogen, corrosive agent, nerve agent, etc. They may also be hazardous due to their reactivity. For example, a TIC could be a chemical that is highly explosive, flammable or combustible.[2] Toxic industrial chemicals that are used against the military pose a very different threat from typical weapons such as firearms. The properties of TICs make them capable of mass casualties if large quantities were accidentally spilled or if they were used in a terrorist attack.[1,2] They can be spread over a wide range, reside on many different surfaces and remain there for an extended period of time.[3] TICs may be harmful in many different forms, such as liquid pool, gas or fine aerosols.

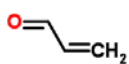
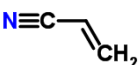
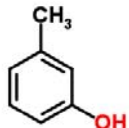
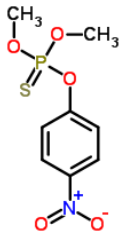

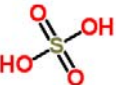
The National Fire Protection Association (NFPA) 1994 standard requirements for chemical and biological protective boots, requires testing with the liquid industrial chemicals including acrolein, acrylonitrile and dimethyl sulfate.[1]. However, using a battery of TICs with a wide range of chemical and physical properties would give a better indication of a sample's performance. The Occupational Safety and Health Administration (OSHA) list of TICs and NFPA 1994 standard document was consulted for determining what chemical challenges should be used in this project.[1,2] The final list of TICs was agreed upon by project advisors, which included experienced members of the protective clothing community. The volatile chemical challenges including acrolein and acrylonitrile. Low-volatility challenges included methyl parathion, morpholine and *m*-cresol. Also, 37% sulfuric acid was chosen to represent an inorganic TIC.

2.1.2. Background on Selected Toxic Industrial Chemicals

2.1.2.1. Summary of TIC Properties

Some properties and characteristics of the selected TIC are listed in Table 2.1. The boiling points of some TICs were references for the development of gas chromatography (GC) methods. The density of a TIC was helpful in calibrating the pump used for delivering the TIC to a material sample (section 3.3.1).

Table 2.1 Summary of Selected TIC Properties

TIC	Structure	Boiling Point	Density (g/mL)
Acrolein ^a		53 °C (127 °F)	0.839
Acrylonitrile ^b		77.3 °C (171.14 °F)	0.806
<i>m</i> -Cresol ^c		203 °C (397.40 °F)	1.030
Methyl Parathion ^d (commercial insecticide)		>109 °C (>228 °F)	1.06
Morpholine ^e		126 - 130 °C (258.8-266 °F)	0.990
Sulfuric Acid ^f		290 - 338 °C (554-640.4 °F)	1.84

See references ^a[4-6] ^b[6,7] ^c[6,8] ^d[6,9] ^e[6,10] ^f[6,11]

2.1.2.2. Acrolein

Acrolein is rated as a medium hazard on the OSHA TICs list and is a chemical challenge in the NFPA 1994 standard.[1,2] This TIC is a concern because it is used in the manufacturing of many different products. It is a common intermediate in the manufacturing process of some pharmaceuticals, resins and other chemical compounds.[5,12] Acrolein is used as a biocide for killing weeds in agriculture and used to remove algae in water. It has been added to methyl chloride refrigerant to act as a warning agent due to acrolein's strong odor.[5,12] Acrolein is produced when wood, tobacco and many other items are burned. It can also be found in leather tanning processes and may be incorporated into chemical weapons.[5,12,13]

Acrolein can be fatal at 10 ppm if inhaled or absorbed through the skin.[4,5] In lower concentrations, it can burn the skin, burn the eye, and when inhaled can destroy tissues in the mucous membrane and respiratory tract.[4] The dermal median lethal dose (LD50) for a rabbit is 200mg/kg.[4] There are few documented mass spills of pure acrolein. However, a man in Idaho using acrolein herbicide on moss in canals was killed when he broke a pipe containing the chemical with his vehicle.[14] He was splashed with acrolein and inhaled the vapors. There was also a large spill of acrolein into a creek in Oregon in 1996, which resulted in the killing of thousands of fish.[15] While acrolein will decompose in the environment over time, mass casualties can result if humans and wildlife are exposed to large quantities.

2.1.2.3. Acrylonitrile

Acrylonitrile is listed as a medium hazard on the OSHA TICs list and is also a chemical challenge in the NFPA 1994 standard.[1,2] Acrylonitrile has been used as a monomer and co-monomer in the production of polymers. It has also been used in the manufacturing of other chemical compounds such as pharmaceuticals, dyes and fumigants.[5]

OSHA regulations state that over an average workday, a person cannot be exposed to more than 2 ppm of acrylonitrile in the air or 10 ppm in a 15-minute period.[7,16] OSHA also states that there should be no human contact with liquid acrylonitrile. Adsorption of acrylonitrile through the skin can cause skin irritation and toxic symptoms that seem to be a result of changes in the central nervous system. The dermal LD50 for a rabbit is 63mg/kg.[7] It is a known mutagen and suspected human carcinogen. Nervous system cancer develops in animals exposed to acrylonitrile.[5,7] In July 2010, the Covington Fire Department and other responders assisted with a spill of acrylonitrile from a barge collision on the Mississippi river.[17] The acrylonitrile was being transported for use in polymerization processes.

2.1.2.4. *m*-Cresol

m-Cresol is used as a solvent for polymers in making products such as resins. It is also used in the production of explosives and fumigants.[5] *m*-Cresol can cause chemical burns, and is poisonous through skin adsorption, inhalation, and ingestion.[5,8] The lower dermal LD50 for a rabbit is 620mg/kg.[8] It is known to have human mutagenic effects and may be a carcinogen. The OSHA exposure limit during a typical eight- hour work day is 5 ppm.[8] In 2005, two trains collided in Graniteville, South Carolina. Chlorine gas was released from one of the train cars,

and the train was also carrying liquid cresol and sodium hydroxide.[18,19] Although chlorine gas was a threat to more people because it was released in the air, there was concern for the corrosive hazards of the liquid chemicals for responders at the scene of the accident. Another incident involving a rail car occurred in North Charleston, South Carolina in 2008. Firefighters and hazmat teams responded to a leak of cresol from a rail car that released a total of 5 gallons.[20] The transportation of m-cresol in large quantities makes it a concern for first responders.

2.1.2.5. Methyl Parathion

Methyl parathion is an organophosphate commonly used as an insecticide in agriculture. It can be used to control pests on many crops such as corn, wheat, cotton, soybeans, and potatoes.[21] Methyl parathion is highly toxic and insecticides containing this chemical are restricted in many areas. The use of methyl parathion insecticide requires certification in the United States.[22] If methyl parathion is used in a terrorist act or is involved in a large spill, it would most likely be in the form of a commercial insecticide that would be easy to obtain. Therefore, a commercial insecticide known as Cheminova Methyl 4 EC was chosen for this research, and it contains 4 pounds of methyl parathion per gallon of liquid.[21] This liquid has a mixture (by weight) of 30-60% methyl parathion, 30-60% naphtha, 7-13% xylene, and 0.5-1.5% valeric acid.[9] The threshold limit value (TLV) is $0.2\text{mg}/\text{m}^3$ for methyl parathion and the dermal LD50 for a rat is $662\text{mg}/\text{kg}$.[9] The insecticide can be poisonous and fatal if inhaled or ingested. It is easily absorbed into the skin and can result in symptoms such as vomiting, headache, frothing of the mouth, coma

and death.[9] In 2007, 50 gallons of methyl parathion was spilled at a plant making insecticide for cotton crops. People living within 5,000 feet of the plant were evacuated and government agencies responded to the spill.[23]

2.1.2.6. Morpholine

Morpholine has been used as an intermediate in the production of rubber, optical brighteners, pharmaceuticals, agricultural products, dyes, resins, etc.[24] It has also been used in some leather treatment and tanning processes.[25-27] The International Programme on Chemical Safety recommends that leathers contaminated with pure morpholine should be discarded to avoid skin contact.[22] Enhanced leathers were one of the materials considered for use in the new CBRN boots. Morpholine was chosen as a TIC to make sure new leather materials could withstand the harshness of morpholine and similar chemicals.

Morpholine is hazardous because it can cause burns through all routes of exposure. Skin burns can occur if morpholine is absorbed.[10] If ingested, there can be burns to the gastrointestinal tract, and burns can occur in the respiratory tract if it is inhaled. The permissible exposure limit to morpholine during an eight-hour work day is 20 ppm according to OSHA.[10] The dermal LD50 for a rabbit is 500 μ L/kg. There have been several reports of morpholine spills. In 1981, Bremerton, Washington firefighters were called to a depot where a 55-gallon drum containing morpholine was punctured.[28] Firefighters cleaned the area using protective clothing and washed the diluted chemical into the sewer system.

2.1.2.7. Sulfuric Acid

The inorganic selection for this project was sulfuric acid. It is listed as high in the hazard index of the OSHA TICs list.[2] Sulfuric acid is produced in such mass quantities for industry that it has been used as an indicator for economic strength.[29] The majority of sulfuric acid goes into the making of fertilizers. It is used in industries such as mining, petroleum alkylation, pulp and paper. Sulfuric acid has been used in the production of dyes, pigments and inorganic chemicals.[29] It is also utilized in the leather tanning industry.[26] Sulfuric acid is used in pickling of leather in the tanning process. Pickling alters the collagen in the skin to create conditions suitable for other reactions during tanning.[13]

Sulfuric acid can cause severe burn to the skin and to the digestive tract if ingested. Inhalation of sulfuric acid can cause burns in the respiratory tract and may be fatal. Continuous exposure to concentrated sulfuric acid mist is a carcinogenic to humans.[11] In 2002, hazmat teams responded an overturned rail car that spilled thousands of gallons of sulfuric acid in Knoxville, Tennessee.[30] It is important that a new CBRN boot material be resistant to this TIC because of its availability in large quantities and high hazard that could be fatal if spilled or used in a terrorist act. The project panel determined that a 37% solution of sulfuric acid should be used for testing because that would be more realistic in the field than 99%.

2.2 CBRN Boot Materials

2.2.1. Properties of Commercially Available CBRN Boots

There are different brands of CBRN boots available on the market that are certified for hazmat use. One of the popular boots used by some hazmat teams is made from an

undisclosed chemical resistant polymer.[31] This boot meets NFPA 1991-2005 requirements for vapor protective ensembles including permeation resistance, flame resistance, electrical hazard, puncture resistance and abrasion resistance. The requirement also includes toe impact resistance, compression resistance, slip resistance, cut resistance and ladder shank bending resistance. The polymer used to create these boots is made by liquid injection molding, which eliminates seams to make them liquid proof.[31] Encapsulating chemical suits worn for CBRN protection are made with a bootie to protect the foot. The design of this boot includes a large foot to account for the added bulk of a bootie. The producers of this boot claim that decontamination is easy because of the smooth outer surface.[31] They also claim that donning and doffing is easy with the stretch fasteners used in the boot design.

Another popular CBRN boot is constructed using multiple layers of butyl and natural rubber.[32] Along with providing flame, heat and chemical warfare protection, this boot advertises a 20% reduction in weight compared to other fire resistant rubber boots. In contrast to the boot discussed previously, this design has a taller shaft for tibia protection.[32] The boot meets requirements included in NFPA 1971-2007, NFPA 1002-1995, NFPA 1994-2007 (Class 2 and 3), and CSA Z195-2002 standard documents. The boot manufacturers claim 24-hour protection against chemical warfare agents. The boot instructions state that they can be decontaminated, but if the boots are used according to NFPA 1994-2007, they are single use only and should not be decontaminated.[32]

2.2.2. Considerations for New CBRN Boot Materials

The ideal CBRN boot would provide protection along with comfort, flexibility, ankle support, slip resistance and minimal heat entrapment. Unfortunately, current boots lack a balance of these properties, and this can significantly affect the performance of the military or hazmat teams. Complaints about the performance of chemical protective boots were expressed in an article by the Marine Corps Times and Los Angeles Times.[33] This article reported that a Marine fell 4 feet and broke his leg in two places after slipping as a result of poor traction from his rubber boots. The Marine was wearing rubber boots that were pulled over normal combat boots to provide chemical and biological protection. When wearing these boots, Marines have to spend extra time airing their feet to prevent trench foot, which can result in severe infection in areas where skin has peeled on the foot. Although the Marines are protected from chemical threats, they are frustrated with the restrictions in movements and hazards that come with wearing these boots.[33] Heat and sweating of the foot can cause peeling, and blisters also develop as a result of thick inflexible materials or improper boot fit.[34] These blisters, along with being painful, can decrease quality of work and reduce the amount of time a responder is in the field.

Often in an attempt to reduce cost, boot features such as comfort and reuse are forfeited.[34] Leather materials are popular for work boots but in the past have not been viewed as a material for chemical protection because of their porous structure. The presumption in industry is that the structure of leather will cause it to retain more chemical than rubber.[35] Even though leather boots can provide a more comfort and stability, it has always been assumed that rubber boots are more protective and easier to decontaminate.[35]

There are new finished leathers that may provide protection while adding comfort. Finishing materials can change the surface characteristics of the material to reduce the amount of chemical absorbed.[36] New composite materials that are thinner and light weight may also provide a better option for CBRN boots. Along with a surface finish, composites may have an engineered structure that can control the movement of liquids. Altering the outer and inner structure of a material could affect the amount of sorption, permeation, and penetration of a chemical.[36] When testing new materials, it is important to keep in mind that the end result should produce a boot that is stable, comfortable and durable. These properties will help reduce job fatigue and injury.[34]

2.3 Exposure and Decontamination of CBRN Materials

There have been many studies on the exposure and decontamination of TICs on textile fibers and fabrics. However, there is little research on leather materials and composites that could be used for CBRN boots. A study by W.L. Gore & Associates compared the residual level of chemicals commonly found during firefighting in leather and rubber samples.[35] They saturated a material sample in a chemical challenge for 30 minutes. The battery of chemicals included carbon disulfide, tetrachloroethylene, isooctane, acrylonitrile, dimethyl formamide, and diethyl amine.[35] After exposure, the samples were decontaminated first by rinsing for 30 sec. in cold water, then scrubbing 30 sec. with a soft brush using 1.2% of liquid detergent. The samples were rinsed a second time with cold water for 30 sec. and finally air dried at room temperature for 16 hours. Any surface contamination was noted by visual inspection, and contamination within the sample was measured by

collecting off-gas from 30 minutes of thermal desorption at 160°C then analyzing with gas chromatography.[35] After decontamination, Gore found no visual surface contamination on any samples, and the leather had lower residual levels of all chemicals compared to the rubber. For example, the rubber samples retained 288 µg of isooctane after decontamination and the leather sample only retained 0.2 µg.[35] These results challenge the common assumption that leather boots are not sufficient for chemical protection. However, the methods used by Gore do not replicate repeated exposure and decontamination in the field. It would be beneficial to test with a new battery of TICs that included more semi-volatile challenges that are harsher toward leather and more likely to be encountered by hazmat teams. Also, there is was an interest in learning if new decontamination methods could yield lower residual levels for both leather and rubber. The following sections review other laboratory procedures and results for exposing and decontaminating fabrics to TICs to help determine methods that might be useful for testing boot materials.

2.3.1. Exposure

Human exposure to chemicals from protective clothing can be from chemical or physical degradation that results in material failure, penetration, and permeation.[37] Penetration occurs when a chemical moves through a material by voids, pores, imperfections, seams, etc.[37-39] Permeation of a material occurs by the molecular flow of a chemical.[37,39] In permeation, molecules adsorb to a material surface, diffuse through the material and desorb out of the opposing side.[38,39] Chemical protective garments are usually made from a plastic or rubber, and the performance of these materials can depend on

the chemical challenge or mixture.[40] Materials can have surface or “matrix” contamination.[40,41] Surface contamination is most affected by the properties of a contaminant and its affinity for a surface. “Matrix” contamination is when a material becomes a reservoir for a chemical due to penetration or permeation of a chemical.[40-43] Some factors that influence matrix contamination include concentration, physical state, temperature, contact time, and barrier pore size.[43] Pore contamination can be very challenging to decontaminate. Therefore, it is important to prevent a chemical challenge from entering pores by applying a surface finish or reengineering the material construction. “Matrix release” occurs when the material slowly release the chemical over time.[42] If a material exhibits “matrix release” the gradual continuous exposure could lead to harmful human effects. “Matrix release” may expose workers by touching the garment or inhaling off-gassing from garment storage.[40] An article by S.Z. Mansdorf suggests doing a study with multiple exposures and decontaminations to examine the potential of a material to act as a reservoir and exhibit matrix release.[42]

One of the objectives of this project was to find a new CBRN boot material using laboratory techniques that would mimic the field exposure to chemical challenges. A group of project advisors with field experience provided guidance for choosing the appropriate testing conditions. They agreed that the exposure procedures should represent two years of field use, which would include four total events (days) of exposure. During a day, a hazmat team member would typically be exposed three separate times with decontaminations following each exposure. It was determined that some of those exposures should simulate a splash. A splash exposure would account for incidents when CBRN boots step into TIC

puddles or if TIC is spilled on the boot during handling. Another exposure would incorporate a situation where a boot is hit against a surface, which could provide enough pressure to force a TIC deep into the material. This type of exposure would account for incidents where the responder stubs their toe or has their foot braced against a wall. The different exposures would occur over four separate days for a total of 12 exposures to a TIC.

2.3.2. Decontamination

Human exposures to TICs could occur during handling of protective clothing if it has not been decontaminated properly. A solution to this would be having single use items that are carefully thrown away after use. However, single use items are usually cheap because of the large number that must be purchased. The low cost often means they are not protective enough for highly toxic incidents.[42] Therefore, fully encapsulating suits are necessary but they are much more expensive so they must be reused. This makes selecting an appropriate decontamination procedure extremely important for CBRN ensembles and there are no standard tests to validate the effectiveness of a decontamination procedure.[42] The following content explores various studies of decontamination procedures to understand what approaches have been taken in the past. The goal in understanding these results is to analyze and validate the best decontamination procedure for CBRN boot materials.

Surface contamination is usually easy to remove, with the efficiency determined by visual observation.[40] However, matrix contamination is much more challenging to remove and detect in the field. Physical decontamination includes scrubbing, which works best for dislodging surface contaminants.[41,43] Chemical decontamination can include the use of

surfactants, weak acids or bases for neutralization, and solvents such as the ones used in dry cleaning. However, a solvent may degrade some personal protective equipment (PPE) and could be harmful if it permeates through the material while the suit is being decontaminated on the wearer.[41,43] Another method of decontamination can include placing PPE in a chamber with hot air for thermal desorption, but this method works best for volatile chemicals.

One study determined the absorption of pesticides in fluorocarbon finished and unfinished protective fabrics after multiple washings.[44] A 0.2-mL aliquot of pesticide was pipetted onto the fabric sample and allowed to sit for 10 s. Then the fabric samples were lifted vertically to allow the remaining surface chemical to roll off. The laundering procedure included the American Association of Textile Chemists and Colorists (AATCC) 61-1980 standard. This involved a 12-min wash cycle with 0.2% detergent, and 25 steel balls for agitation. There were two rinse cycles at 5 and 3 minutes. The water temperature was 49°C (120°F) for all cycles.[44] In addition to laundering, some trials involved a pretreatment spray or a commercial degreaser. The extraction procedure involved placing the samples in 100mL of distilled acetone and shaking in closed Teflon containers for 1.5 hours. This procedure was repeated for a total of two extractions per sample.[44] Then gas chromatography was used for analysis. Keaschall et al. found that the fluorocarbon finish significantly reduced the amount of pesticide absorbed by the fabric through four launderings. The authors suggest using a “heavy duty liquid detergent” for decontamination and recommend restoring the fluorocarbon finish after four launderings to ensure protection for continued use.[44]

Another test analyzed a field decontamination procedure on fluoropolymer protective equipment exposed to a battery of chemicals ranging in physical properties, two of which were acrolein and acrylonitrile.[41] This test determined how well the fluoropolymer materials were decontaminated by first exposing them to 20 mL of liquid chemical for 1 hour in a penetration cell positioned horizontally. The chemical was removed, and then 20mL of 5% liquid Tide[®] solution was allowed to sit for 4 minutes on the material.[41] Then a soft brush was used to scrub the material for 1 min. After the solution was drained the material was blotted dry for 10 min. A permeation test cell was used determine off-gassing by passing nitrogen over the sample for approximately 12 hours onto a collection medium.[41] Then the material was solvent extracted and analyzed by gas chromatography. Sinofsky et al. also chose five chemicals to test material performance with a permeation cell after decontamination. This test was to determine if any degradation of the material had occurred during decontamination. The assumption was that degradation in the materials would result in a change in the permeation results.[41] The time and amount of chemical used during the exposure of the materials was extreme and not likely to be seen in the field. Overall, even though some chemical was extracted from the fluorocarbon materials, it was determined that the material was still “safe”. They also found no significant difference in the permeation results for materials that had been decontaminated. Therefore, there was no degradation from the decontamination procedure.[41] This study incorporated a decontamination procedure but it was not repeated multiple times like field use.

A study by T.R. Carroll et al. focused on developing a method for determining how well hazmat clothing was decontaminated in the field.[40] First the study tested the field

decontamination procedure on swatches of polymer protective gear in the laboratory. The sides and back of the swatches were sealed. Then they were submerged into a challenge chemical for 15 minutes, blotted dry and decontaminated. The decontamination procedure mimicked what hazmat teams used, but the time was shorter to account for the amount of decontamination that one section of material would receive.[40] The decontamination procedure included a 30-second rinse with room temperature water from a shower head, a wash for 30 seconds using a soft brush and 12 g/L of liquid Tide[®] in water, patting off surface wetness with a paper towel, removing the tap from the swatch, and hanging it in a fume hood for 21-24 hours.[40] The samples were thermally desorbed and gas chromatography was used for analysis. These methods were tested in the field by sealing the edges and the back of sample swatches from protective clothing. Then the swatches were taped onto the outside of a protective suit. In the field study, a manikin wearing the altered suit was exposed to ethyl acetate using a garden sprayer.[40] The taped swatches and samples from the turnout gear were analyzed by placing them in a thermal desorption chamber with detection tubes. Detection tubes in the chamber changed color if a specific chemical was volatilized in the air. Leather samples from the knee pad of turnout gear were cut out after exposure in the field study and fresh leather samples were cut for testing with the laboratory method. The study found no residual ethyl acetate in either the field or laboratory leather samples after decontamination. Therefore, the laboratory and field method of decontamination agreed well.

Input from this projects advisors noted that the current decontamination procedure used in the field first involves scrubbing a pair of boots for at least five minutes with brushes

dipped in a solution of detergent and water. The concentration of the detergent in water was not known. Then boots are scrubbed for an additional 5 minutes with a separate brush dipped in 5% solution of calcium hypochlorite (HTH). Finally the boots are rinsed in water and allowed to air dry. The boots are then put into sealed bags for 24 hours. Samples are taken from the bag headspace in the afternoon sun to determine the efficacy of the decontamination. An article by S.Z. Mansdorf recommends this bagging technique to test the effectiveness of matrix decontamination and using a solvent soaked wipe to test the effectiveness of surface decontamination.[43] There was an interest in testing the efficiency of this decontamination procedure after multiple exposures of the boots to high concentrations of a variety of TICs. There was also an interest in testing the efficacy of different procedures and solutions to determine if there could be better methods of decontamination.

2.4 Standard Test Procedures for Chemical Protective Clothing

2.4.1. NFPA 1994 Standard

The requirements for a new CBRN boot include certification with the NFPA 1994 *Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents*. [1] The new boots must be certified as a Class 2 element for “terrorism incidents involving vapor or liquid chemical hazards where the concentrations are at or above the Immediately Dangerous to Life and Health (IDLH) level requiring the use of self-contained breathing apparatus (SCBA)”. [1] This standard requires testing protective clothing for chemical resistance using the ASTM F 739 cell for permeation of liquid and gases. In one hour, the

material used in a CBRN boot must not exceed an “average cumulative permeation” of $4.0 \mu\text{g}/\text{cm}^2$ for the liquid chemical warfare agent, Distilled Mustard (HD).[1] The liquid chemical warfare agent, Soman should not exceed $1.25 \mu\text{g}/\text{cm}^2$. Toxic chemicals including liquid acrolein, acrylonitrile and dimethyl sulfate, along with gaseous ammonia and chlorine should not exceed an “average normalized breakthrough time” of more than 60 minutes.[1] Each of the chemicals used has a specified concentration that is required, and can be found in the NFPA 1994 – 2007 edition standard document, section 8.7.4.2. Liquid toxic industrial chemicals are used in a concentration density of $10 \text{ g}/\text{m}^2 + 1 \text{ g}/\text{m}^2$ and $- 0\text{g}/\text{m}^2$.[1] The standard also involves using the permeation procedures after flexing and abrading the samples. A sample from the upper portion of a boot will be subjected to 10,000 flexes as specified in NFPA 1994 -2007 section 8.1.6. Then the portion of the sample that received the most flexing will be subjected to an abrasion procedure listed in section 8.1.4. This abrasion procedure is an ASTM D 4157 standard, which involves 10 cycles of abrading with 600 grit ultrafine silicon carbide sandpaper and 1.6 kg (3.5 lb) of pressure on the sample. After the flexing and abrading conditioning, the samples are tested with the permeation cell. This technique analyzes for fatigue in materials.

2.4.2. Standards for Material Resistance to Chemical Penetration

The ASTM F 903 Standard Test Method is for *Resistance of Materials Used in Protective Clothing to Penetration by Liquids*. [38] This standard tests the resistance to penetration of a liquid chemical in constant contact with the outer surface of a material. A test apparatus is built containing a vertically mounted cell that is connected to by an air line

to a pressure gage. The cell has a chamber for holding a chemical challenge. A material sample is loaded into the cell with the outer surface of the material facing the chamber of the cell.[38] The opposing side of the material faces a transparent cover for observation. A liquid chemical challenge is delivered to the chamber of the cell and is held in place against the material. The pressure applied in the cell and the duration of the exposure time can be determined by choosing the appropriate circumstances listed in Table 2 of the ASTM F 903 document.[38] The results of this test are reported as pass or fail. Signs of penetration can be detected by viewing the back side of the sample through the transparent cover. If there is penetration observed visually in form of noticeable wetness or change in coloring of the sample, then the material fails the test.

ASTM also provides other penetration standards for protective clothing that are not as harsh as the ASTM F 903 method. ASTM F2130 *Standard Test Method for Measuring Repellency, Retention, and Penetration of Liquid Pesticide Formulation Through Protective Clothing Materials* is used predominantly for testing personal protective garments used for agriculture workers who spray pesticide.[45] A material specimen placed on top of an absorbent collector paper is loaded onto a sample holder. A pipette is used to dispense a small aliquot of the chemical challenge onto a material surface for 10 minutes. Then a separate piece of absorbent paper is placed on the material surface for two additional minutes. The material specimen, absorbent paper, and collector paper are extracted separately twice with 50 mL increments of solvent and shaken for 30 min.[45] Then gas chromatography or another analytical method can be used to analyze the extract. The amount of chemical detected from the collector paper indicates the penetration of liquid

through the material specimen. The analyte extracted in the material specimen is used to calculate retention, and the analyte extracted from the absorbent paper is used to calculate repellency.[45]

The International Organization for Standardization has a standard known as ISO 6530 *Protective Clothing - Protection Against Liquid Chemicals – Test Method for Resistance of Materials to Penetration by Liquids*. [46] The scope of this method tests if a material is resistant to deposition of a chemical that has been sprayed or splashed onto its surface. In this procedure, absorbent paper is loaded onto a concave side of a semi-cylindrical transparent gutter sitting at a 45° incline. Then the material sample is secured on top of the absorbent paper.[46] The sample end furthest from the liquid chemical delivery is folded under so that chemical running down the sample does not come in contact with the exposed edge of the sample. A pump with a needle and syringe is placed 10 cm from the top surface of the incline. The syringe is filled with 60 mL of chemical and it is delivered to the sample at a rate of 1 mL per second for a total of 60 s. The liquid run off from the sample is collected in a beaker at the bottom of the incline. The weight of the absorbent paper, beaker and material sample are all recorded to determine the index of penetration, repellency, and absorption.[46]

2.4.3. Wipe Methods

A concern for hazmat responders is the threat they face after the job is over and they take off their chemical protective clothing. A responder may be exposed to hazardous chemicals while removing their gear if the protective ensemble is not decontaminated

properly. Also, if a material is decontaminated on the surface, there may still be chemical left in the internal matrix that can make its way to the surface over time while the protective equipment is in storage. As mentioned in the decontamination section (2.3.2), some hazmat teams place protective equipment in a bag and sample the air in the bag after a 24 hour period to determine the efficiency of a decontamination procedure. However, surface sampling of the equipment could also be useful to test for low volatility chemicals that may not be detected by sampling the air.

Surface sampling using a wipe has become a growing technique and has resulted in standards and guidelines from organizations such as ASTM International and OSHA. ASTM International has several standards on wiping methods for surfaces contaminated with dust particles, lead, beryllium, organic compounds and other metals. The standard most relevant to the sampling of TICs would be ASTM D6661 *Standard Practice for Field Collection of Organic Compounds from Surfaces Using Wipe Sampling*.^[47] In this standard, a 7.6 cm cotton gauze wipe is wetted with 2 mL of a solvent and wiped vertically and then horizontally across a sample. The wipes are then solvent extracted and the extract is analyzed with the appropriate analytical technique, such as gas chromatography. This method is recommended for organic compounds such as pesticides. Both ASTM International and OSHA state that the ideal surface sampling medium is smooth and nonporous.^[47,48] In the OSHA guidelines, the contaminant is extracted from the wipe using agitation in solvent and then analyzed with the appropriate chromatographic method. The higher the extraction efficiency the better, but OSHA recommends at least a 75% average extraction efficiency or higher for wipes.^[48]

Protection from exposure to pesticides is important not only for agriculture workers but also because of the threat they pose if used in mass quantities for a terrorist act. In a study presented at the ASTM Symposium on Surface and Dermal Sampling, researchers compared wipe materials and solvents for pesticide residue.[49] One of the wipes tested was a Ghost Wipe™ made by Environmental Express. A Ghost Wipe™ is a nonwoven polyvinyl alcohol copolymer material that is approved by the American Industrial Hygiene Association and meets ASTM requirements for ASTM E1792 for sampling lead in surface dust.[50] After wiping a surface, this wipe can be completely digested in an acid solution. Then the acid solution can be analyzed for the contaminant. However, Deziel et al. moistened the Ghost Wipe™ with deionized water (4 mL, DI) and did not use an acid solution for digestion.[49] Another type of wipe method used in the study was a Twillwipe/Cleanroom Cotton Wipe comprised of 100% cotton twill weave and supplied by MG Chemicals. One Twillwipe (TW) was moistened with 2 mL of DI water and another Twillwipe (TI) was moistened with 2 mL of isopropanol.[49] The three different wipes were used to collect samples by wiping in an “s” pattern on a 1 square foot area of stainless steel spiked with a mixture of pesticides. Multiple trials were run using high and low concentrations of pesticide. All the wipes were extracted using Soxhlet extraction with a mixture of isopropanol, hexane and DI water. The extract was analyzed using gas chromatography-mass spectrometry with selected ion monitoring. The results revealed that the amount of analyte collected by the three different wipe systems was significantly different. The Twillwipe moistened with isopropanol had the lowest detection limit and the highest collection efficacy.[49] For example, the % mean collection efficiency for malathion

organophosphates was 60.2% for TI, 46.4% for Ghost Wipes™, and 23.8% for TW. Another organophosphate, chlorpyrifos had a % mean collection efficiency of 71.0, 24.9, and 7.7 for TI, Ghost Wipes™, and TW respectively.

2.4.4. Gaps in Standard Test Procedures

Elements in CBRN protective ensembles are usually expensive; therefore it is desirable for these garments to be decontaminated after exposure for reuse. For example, the service life of a pair of CBRN boots could be at least two years, which would include a minimum of 12 chemical exposures and decontaminations. The multiple uses of the boots may cause material fatigue and removal of repellent surface finishes that can reduce the level of protection over time. The durability of the materials and any surface finishes will also depend on the chemical challenge.[39] Therefore, when testing the resistance of CBRN materials, it is important to simulate multiple uses the field while using a wide range of TICs with varying chemical and physical properties. Unfortunately, current standards for CBRN ensembles do not include methods that mimic how the materials are used in the field.[39] The NFPA 1994 standard tests for the permeation resistance of materials involves abrasion and flexing.[1] This technique does account for physical fatigue of a material but does not incorporate the use of a decontamination procedure. Concentrated decontamination solutions can be harsh toward some materials and should be included in the analysis of material and repellent finish performance.

In the field, a CBRN boot may encounter large quantities of TICs in puddles. That TIC may be pressed against the boot material if an object is dropped on the foot, if a

contaminated boot is braced against a wall, or if a responder trips over an object. Extra pressure on a contaminated boot can force a TIC into the internal structure of a material. The ASTM F 903 standard can be used to simulate the impact pressure from an object or chemical splash.[51] The results of an ASTM F 903 test are reported as pass or fail which provides very little information to the manufacturers and consumers of these protective materials.[39] The ASTM F 903 method is a good exposure method for material samples but incorporating a way to quantify the amount of chemical retained within the sample could provide additional useful information. The ISO 6530 standard quantifies the amount of TIC retained by a material with gravimetric results. Although these methods are useful for exposure, they alone are not a good representation of how a boot is exposed during the total service life of a CBRN boot.

To analyze the performance of new CBRN materials and reassess current materials, there is a need to develop a procedure that incorporates multiple rigorous exposures and a decontamination technique that mimics field use.[39] There should also be the development of efficient extraction and analytical techniques that can determine the amount of chemical left in the total volume of a material after a decontamination procedure.[39] The gravimetric techniques used by some current standards are not accurate for detection of TICs after decontamination because it cannot be determined exactly what substance still remains. There must be detection of a TIC from the analysis of the extract of decontaminated materials. Even small amount of a TIC that is trapped within material structures may be hazardous through “matrix release” over time. Therefore a wipe test could be added to determine if any of residual TIC would be available on the surface of a material after an extended drying

period. The wipe would then be subjected to the same extraction and analysis techniques as the material sample. A test method that combines procedures that mimic the use of CBRN materials with multiple exposures, decontaminations, wipe tests, extractions, and sensitive analytical techniques could provide better understanding of material performance and aid in the selection of a new CBRN material.

2.5 Accelerated Solvent Extraction

2.5.1. Introduction

One of the oldest methods of solvent extraction is Soxhlet extraction, which is essentially a room temperature extraction that requires large amounts of solvent and several hours for completion. Since the development of Soxhlet extraction, other methods such as microwave extraction, automated Soxhlet extraction, sonication extraction and supercritical fluid extraction have been used to reduce the amount of time and solvent used.[52] Accelerated Solvent Extraction (ASE[®]) is one of the newest techniques that utilizes high pressures and temperatures to increase extraction efficacy. Figure 2.1 shows a schematic and procedure of the ASE[®] 200 system produced by Dionex.[53] In this system, a sample cell enters an oven and is filled with the programmed amount of solvent. The oven can reach a maximum temperature of 200° C and a sample cell pressure of 3000 psi.[54] The pressurized sample cell allows for the temperature of the extraction to occur above the boiling point of the solvent. The typical static extraction time using this technique is between 5-10 min.[52] The liquid extract is purged into a collection vial by compressed nitrogen gas. ASE[®] can

refill the sample cell with fresh solvent if several extractions are desired for the same sample. It also has four different solvent reservoirs, which allow for mixing or switching of the

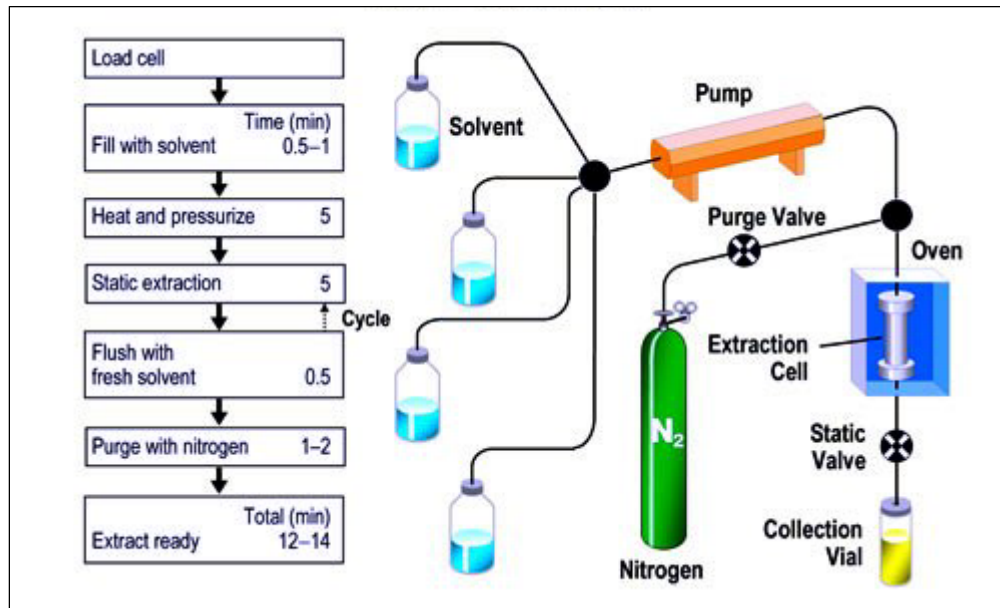


Figure 2.1 Accelerated Solvent Extractor (ASE[®]) 200 Schematic

solvents between extractions.[54] At one time, the ASE[®] 200 can be loaded and programmed to automatically extract up to 26 samples and each could have a completely different extraction set up, including time, temperature, pressure, and solvents.

2.5.2. Advantages

The automation of the ASE[®] makes the handling of many samples more efficient because less time is spent measuring solvent and preparing for extraction. The capacity for the ASE[®] system to reach high temperatures and pressures increases solubility effects, mass transfer, and disruption of surface equilibria, which makes the solvent extraction more efficient.[52] Richter et al. discusses the increased ability of a solvent to solubilize an analyte and faster diffusion rates with increasing temperature.[52] Compared to other extraction systems, the ASE[®] can have faster extraction times because its design allows for multiple cycles of fresh solvent to come in contact with the same material sample. The amount of solvent initially dispensed into the sample cell can be flushed into the collection tube and new solvent can be introduced. A larger concentration gradient is created between fresh solvent and the sample matrix.[52] This creates faster mass transfer of analyte in the material into the fresh solvent, and ultimately leads to faster extraction time.

The objective of the creating a system to test CBRN materials was to use it for finding a new flexible material for boots. However, many flexible lightweight materials for boots, such as leathers, are porous and analyte could be trapped in the pores even after decontamination. After exposing and decontaminating the materials, it is important to use an extraction technique can remove analyte from the total volume of the sample to give an accurate amount of remaining contaminate. Adjusting both temperature and pressure in the ASE[®] can increase the disruption of surface equilibria in a material sample, creating better extraction. Pressurized liquid helps to overcome the adsorption of contaminants to the surface of a material sample, and thermal energy from high temperatures can break the

interaction of a contaminant within the material matrix. The hydrogen bonding, dipole interactions, and van der Waals forces are disrupted and the activation energy needed for desorption of an analyte from the material matrix is reduced.[52] The high pressures reached in the ASE[®] allow for solvents to remain liquid even at temperatures above their boiling point. Higher temperatures cause solvents to have lower viscosity and reduces the surface tension of a solvent, contaminate and material sample.[52] This enables the solvent to have more penetration of a material matrix and faster dissolving of an analyte. Solvent extraction techniques that are done at atmospheric pressure do not have the benefit of forcing solvent in to the pores of a material. Richter et al. compares the effects of using high pressure in the ASE[®] system to high-pressure liquid chromatography.[52] The pressure in the sample cell forces the liquid to have more intimate contact throughout the material matrix for better extractions.

Tables 2.2 and 2.3 contain data comparing the time and amount of solvent used in several solvent extraction techniques.[55] There are some extraction techniques, such as microwave and supercritical fluid extraction, which have utilized the benefits of adjusting temperature and pressure for better extractions. However, the ASE[®] system offers more flexibility in method development. The system can easily accommodate different solvents and a wide range of sample sizes within one run, while saving time and solvent.

Table 2.2 Extraction Times of Various Extraction Techniques

Technique	Average Extraction Times*
Soxhlet	4–48 h
Automated Soxhlet	1–4 h
Sonication	0.5–1 h
SFE	0.5–2 h
Microwave	0.5–1 h
ASE 150/350 with in cell clean-up	0.2–0.3 h

* “Extraction times are based on a per sample basis. This estimate does not include sample weighing, loading, or concentration, although it does include sample filtering, if necessary. In-cell clean-up is a technique used with ASE flow-through design, to add absorbent directly to the extraction cell that retains interferences. This technique further increases time savings.”[55]

Table 2.3 Solvent Usage of Various Extraction Techniques

Technique	Solvent Usage*
Soxhlet	150–500 mL
Automated Soxhlet	50–100 mL
Sonication	150–200 mL
SFE	5–50 mL
Microwave	25–50 mL
ASE 150/350**	5–200 mL

* “Solvent usage are based on a per sample basis. Additionally, ASE has many cells sizes to adapt to sample size requirements”

** “Solvent saver mode provides further reduction in solvent consumption.”[55]

2.5.3. Considerations

Concerns for any extraction technique are carryover and cross-contamination. With systems that use high temperatures, there may be concern of thermal degradation. All of these issues were addressed with the ASE[®]. [56,57] The ASE[®] system eliminates cross-contamination by having low dead volume and automatic solvent rinses of the instrument can be programmed between samples. [56] The possibility of thermal decomposition was investigated using dichlorodiphenyltrichloroethane (DDT) because it will break down into dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD). [52,57] Endrin was also used because it breaks down into endrin aldehyde and endrin ketone. Both DDT and endrin are known for their use as insecticides. Sand was spiked with the DDT and endrin, then the sand was extracted using ASE[®] at 150° C. Gas chromatography with an electron capture detector was used to analyze the extract. There was no DDE, DDD, endrin aldehyde, or endrin ketone in the extracts, which indicated that no thermal degradation could be detected. [52,57] However, it is always important to be aware of the properties of the target analyte and optimize the system conditions.

2.6 Chromatography

2.6.1. Gas Chromatography

The toxic industrial chemicals (TICs) acrolein, acrylonitrile, m-cresol, morpholine, and methyl parathion are best analyzed using gas chromatography. The Occupational Safety and Health Administration (OSHA) and the Centers for Disease Control and Prevention

(CDC) are involved in protecting the public from exposure hazardous substances, and therefore have published gas chromatography methods for detecting these TICs.

A morpholine method has been developed for gas chromatography with a flame ionization detector (GC/FID). A MDN-1, nonpolar methylsilicone column, was used with a length of 30 m, inner diameter (i.d) of 0.32 mm and a stationary phase thickness (df) of 1.0 μm .^[58] The injector and detector temperatures were set at 200° C and 250° C respectively. The oven temperature program consisted of ramping from 50° C to 110° C at 10° C per minute.^[58] The column gas flow was set at 2.0 mL/min and the 1.0 μL injections were made with a 10:1 split ratio. Morpholine had a retention time of 4.45 min. and the total run time was 6 min.^[58] The limit of quantitation of morpholine for this method was 45 ppb.

There is a GC/FID method developed by OSHA for cresol isomers.^[59] Although there is no resolution of the cresol isomers with this method, it is could still be used to detect a sample exposed to *m*-cresol. The method requires a 1.83 m, 3.18 mm outer diameter (o.d) stainless steel column packed with 0.1% SP-1000 80/100 Carbopack™ C.^[59] Carbopack™ C is made of silver trifluoromethanesulfonate particles and is suggested for analytes containing phenol functional groups.^[60] The number 80/100 is the manufacturer description for the size of the Carbopack™ C particles, which will range from 149 microns and 177 microns. The injector and detector temperatures were set to 225° C and the oven was set to 210° The flow of the nitrogen carrier gas was set to 20 mL/min. The limit of quantitation for cresol for this method is 0.01 ppm.^[59] Another method for all cresol isomers was also developed for a GC/FID.^[61] This method requires an injection temperature of 250° C and a detector temperature of 300° C. The column was ramped from 160° C to 225° C at a rate of 3° C

per minute. The column was a 30 m, 0.32 mm ID with 0.25 mm df Stabilwax DA fused silica capillary.[61] Sabilwax DA is a Crossbonded[®] acid-deactivated Carbowax[®] polyethylene glycol polar stationary phase manufactured by Restek. The carrier gas for this method was helium with a 1 mL/min flow rate.[61]

Acrylonitrile has been analyzed with a nitrogen phosphorus flame ionization detector (GC/NPD) with a limit of quantitation of 0.3 ppm.[62] A 6.1 m; 3.18 mm o.d stainless steel column was packed with 10% SP-100 on 80/100 Supelcoport, which is a mixture diatomaceous earth, silicon dioxide, quartz and free fatty acid. The injector and detector temperature were both set at 200° C, and the column was set at 100° C.[62] An additional method for acrylonitrile had the same injector and detector temperature settings but the column was set at 85° C.[63] This method was developed for GC/FID and used a 3 m, 3mm stainless steel column with 20% SP-1000 on 80/100 Chromosorb WHP. Chromosorb WHP is an acid washed, high performance combination of diatomaceous earth, silicon dioxide and quartz.

Methyl parathion is a popular TIC used to test the resistance of textiles and chemical protective clothing. Therefore, there are many gas chromatography methods used for detecting methyl parathion using gas chromatography.[44,64,65] Methyl parathion methods have been developed for GC using a flame photometric detector (FPD).[66] The NIOSH Manual of Analytical Methods provides methods for several fused silica capillary columns.[66] For a 30 m, 0.32 mm i.d, 1.0 df, DB-5 weakly polar column containing 5% phenyl and 95% methyl silicone, the column temperature program consisted of ramping from

125° C to 275° C at a rate of 4.0° C per minute. The retention time using this column was 23.75 minutes.[66]

Acrolein has been analyzed using gas chromatography with a GC/NPD.[67] The column for this method is a 1.83 m, 6.35 mm o.d glass column packed with 10% UCON 50-HB-5100 and 2% KOH on 80/100 Chromasorb W-AW. UCON 50-HB-5100 is a polyalkylene glycol monobutyl ether polymer and Chromosorb W-AW has been acid washed. The injector and detector temperatures were set at 180° C and 275° C respectively. The carrier gas used was helium at a flow rate of 30 mL/min. The temperature program for the column consisted of a ramp from 100° C to 140° C at 4° C per minute and then a second ramp from 140° C to 180° C at 20° C per minute.[67] The column was held at 180° C for the remainder of the 25-min. run period. This method used 0.8- μ L injections and had a limit of quantitation of 2.7 ppb.[67] Another method developed using GC/NPD had a 2-m; 2-mm glass column with 5% SP-2401-DB on Supelcoport (100-120 mesh).[68] SP-2401-DB indicates that part of the stationary phase has been deactivated for basic compounds and is meant for separating alkaloids. Helium was the carrier gas used at a flow rate of 30 mL/min. The injector temperature was set at 230° C, while the detector was set at 250° C. The column temperature profile included holding at 90° C for 8 min, then ramping at 20° C per minute to 200° C and holding for 11 min.[68]

2.6.2. Thermal Desorption

For this project, it is important that the extraction and analysis of TICs result in an accurate representation of what is within a material at the end of exposure and

decontamination. However, traditional solvent extraction techniques can involve handling of the extract solution during preparatory procedures before chromatography, such as rotary evaporation or dilution. This handling could cause inaccurate measurements of volatile TICs.[69] Therefore, the volatile TICs, acrolein and acrylonitrile, were analyzed using thermal desorption-gas chromatography-flame ionization detection (TD-GC-FID). In this technique, material samples are placed in stainless steel tubes and heated to volatilize the analyte.[70] Then inert gas moves through the tube and carries the thermally desorbed chemical to a cold trap where it is collected before being volatilized again and sent to gas chromatography column. The collection of the analyte on the cold trap before injection into the GC keeps the injection band small, this process is known as refocusing.[70]

One disadvantage of this preparation technique is the sample size limitations from the thermal desorption (TD) tubes.[70] A material sample is cut into smaller samples for TD. Then the amount of analyte detected by the GC/FID will have to be extrapolated to determine the amount in the total exposed area. Although there is no human handling of an extraction solution, there is still a complicated two-step heating process. The heating, cooling, heat transfer lines, and high flow rate can all lead to analyte loss.[70]

Chapter 3. Experimental

3.1 Experimental Approach

The following procedures present a system to analyze new materials for CBRN application. The methods are presented in the order they should be performed. Three replicates were used for each material in all procedures.

3.2 Chemicals and Instrumentation

3.2.1. Chemicals

The chemicals used in this study included morpholine, acrylonitrile, *m*-cresol (all 99%), and 0.1N NaOH that were purchased from Acros Chemicals. Acetone, isopropanol (99%), sulfuric acid (37N), calcium hypochlorite (granular certified), dried potassium hydrogen phthalate (ACS grade) were purchased from Fisher Scientific. Acrolein (90%) was purchased from Aldrich Chemicals. Tide[®] original scent high efficiency powder detergent was purchased at a local retailer. Methyl 4EC Insecticide with 4 pounds of methyl parathion per gallon was purchased from Cheminova.

3.2.2. Extraction and Analytical Instruments

Semi-volatile chemicals, *m*-cresol, morpholine, and methyl parathion, were extracted with a Dionex Accelerated Solvent Extractor (ASE)[®] 200. A nitrogen tank (UHP Grade 5.0) was attached to the ASE[®]. The instrument used Dionex 22-mL stainless steel cells to hold the material samples and 60-mL glass collection vials (precleaned) with septa from Environmental Sampling Supply. The semi-volatile chemicals were analyzed on a Hewlett Packard Gas Chromatograph/Flame Ionization Detector (GC/FID) 5890 Series II with a Hewlett Packard 7673 GC/SFC Injector containing an Agilent 10- μ L 5181-1267 syringe. Gases used for the GC/FID included compressed helium (UHP Grade 5.0), air (zero grade 0.1), and hydrogen (ultra high purity). Separation was achieved with an Rtx[®]-5 Amine (30 m, 0.25 mm ID, 0.5 μ m) column from Restek. Software used for processing was HP GC ChemStation 98'.

Volatile chemicals, acrolein and acrylonitrile, were extracted using a Markes International Thermal Desorption (TD) Autosampler Series 2 Ultra. The sample tubes in TD were stainless steel Safelok™ tubes pack with glass beads (0.5-mm) and glass wool. Software for the TD was Unity version 4.1.15. The TD was connected to a Markes International Series 2 Unity² Coldtrap packed with Tenax TA. The coldtrap was connected to an Agilent 7890A GC/FID. Separation was achieved with an Rtx[®]-1 (30 m, 0.25 mm ID, 1 µm) column from Restek. The software used for processing was GC ChemStation 09'. The inorganic sulfuric acid was extracted using materials in AATCC Test Method 81.[71] A Mettler Toledo DL58 Titrator with DG111-SC electrode was used for analysis. The titration required 10-mL pipettes and 100-mL titration cups.

3.3 Procedures

3.3.1. Modified ISO 6530 Splash Test Screening

The first test in the system for selecting a new CBRN boot material was a modified ISO 6530 splash test to screen which materials posed the most potential. The assembly of the apparatus is discussed in ISO-6530 section 4.1 and Figure 1 of the ISO-6530 standard document.[46] However, the transparent film and absorbent paper were not used. A non-sterile blunt pipetting needle that is 10.16 mm (4 inches) long with an inner diameter of 0.09 mm was used. A pump from New Era Pump Systems Model No. NE-1010, 12 VDC volts, 1.0 amperage was used. Three polypropylene containers with lids, capable of holding approximate 300mL were used for collection. Additional materials included a balance with accuracy of 0.01g, and 101.6 mm (4 inch) x 101.6 mm (4 inch) lint free absorbent wipes.

The pump and syringe should be capable of delivering $60 \text{ cm}^3 (\pm 1 \text{ cm}^3)$ in $60 \text{ sec} (\pm 1 \text{ sec})$. The viscosity of the challenge chemical can affect the flow rate delivered by the pump. To make sure that the pump delivered the correct amount of liquid in the specified time, the pump was calibrated. Calibrating the pump first required multiplying 60 mL by the density of the challenge chemical to determine how much the chemical volume should weigh. An empty polypropylene container was weighed and tared on the balance. A syringe with needle was filled with the challenge chemical and placed on the pump. The container was placed under the syringe needle. The needle was bent to deliver the chemical in a downward stream. The needle and syringe are pictured in Figures 3.1 and 3.2. The pump



Figure 3.1 Bent Non-Sterile Syringe Needle



Figure 3.2 Needle Attached to Syringe

was set to deliver 60 mL and timed for 1 minute. Then once the liquid delivery was finished, the container was weighed. If the weight delivered did not equal the calculated weight, the

volume delivery on the pump was adjusted. Once the correct weight was delivered, it was repeated five times.

A test specimen (6.35 cm by 30.48 cm) was cut and placed in a labeled polypropylene container. A larger sample size that covers the whole gutter could be used, but the sample size used in this procedure was reduced because of the limited amount of material. Another empty container was labeled for receiving the challenge chemical. A third container was labeled and held an absorbent wipe. All three containers were weighed with lids to the nearest 0.01 g. To begin the test, 2.54 cm of one end of the material specimen was folded under. Then the fold was held in position as the specimen was placed onto the gutter, with the folded end farthest from the pump. Folding the bottom of the sample kept any TIC from being absorbed by the edge of the material. The material was attached to the gutter with two clips on both sides, as pictured in Figure 3.3. The top edge of the sample was mounted 25.4 mm from the top of the gutter. Along with clips, a piece of 49 mm x 63.5 mm double sided tape was placed on the back of material samples that did not conform to the shape of the gutter. If tape was used, this was accounted for in the weight of the sample.

The labeled empty container was placed under the edge of the gutter to collect the test liquid running off the specimen. The syringe was loaded onto the pump so that the tip of the needle was 100 mm (± 2 mm) from the inclined surface of the gutter. The needle was aligned so that the liquid started to contact the top, center of the sample surface. Figure 3.4 shows the setup of the test apparatus. The cover of the gutter was placed on top of the test specimen, and then the pump was started. Once the liquid finished dripping into the collection container, the lid was placed on the container. Then starting on the specimen edge



Figure 3.3 Attachment of Material to Gutter with Clips

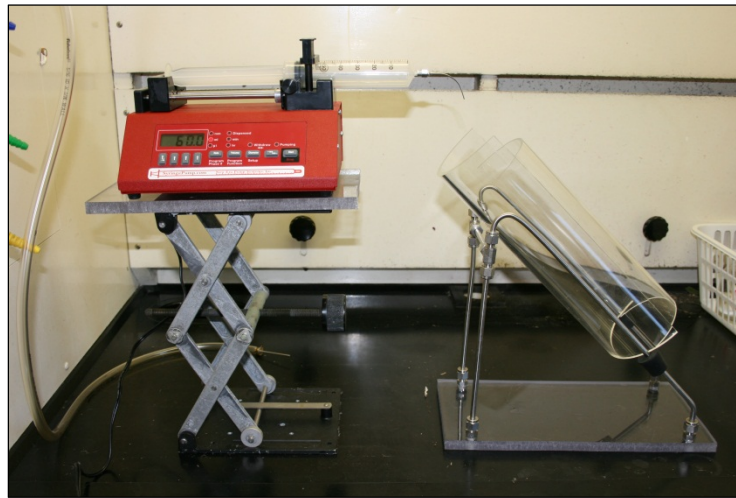


Figure 3.4 Experimental Setup for Modified ISO 6530 Splash Test

nearest to the syringe, the absorbent wipe was used to wipe the entire length of the sample. The wipe was placed back in the appropriate labeled container with a lid. Next, the specimen was removed and placed in the appropriate container with a lid. The three containers with the liquid, wipe and material were weighed to the nearest 0.01g. After the test, the gutter was wiped and rinsed with the proper cleaning solvent to remove any residual chemical.

3.3.2. One-Day Field Simulation

Note that it was recommended that one day of training should have three exposures and three decontaminations of protective gear. The first two exposures simulate the material being splashed with the challenge chemical. The final exposure simulates an incident including pressure of the TIC against the material surface in ASTM F 903-03 cell.

3.3.2.1. First Exposure

It was important to only expose the outer surface of the test material to the challenge chemical. The chemical could not touch the edges or the back side of the material. The device in Figure 3.5 was developed to test multiple samples with a small sample size while simulating splashed chemical sitting on the material surface. Figure 3.5 shows what the device looks like with the material samples in place. More screws could be added to the edges of the top and bottom plates of the device for a better seal.

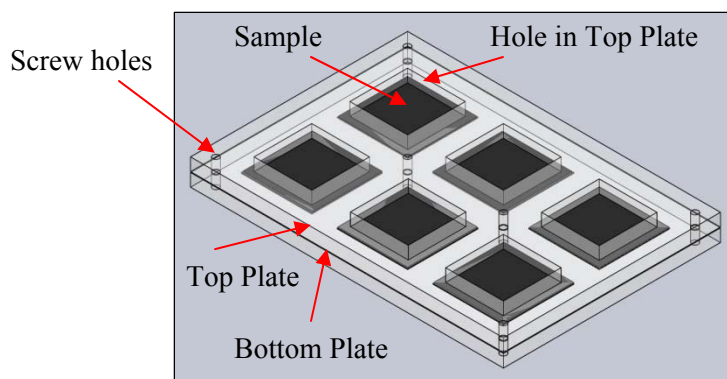


Figure 3.5 New Lab-scale Splash Simulation Device

Gore™ Joint Sealant tape (3/16 inch x 30 inch) was placed around the edges of each square hole on the sample side of the top plate. A 48.8-cm² sample was cut and weighed. A small piece of double-sided tape was put on the back center of the sample. The sample was placed on the bottom plate of the splash device. Then the top part of the splash device, Gore™ tape side down on the sample, was screwed to the bottom plate. A pipette was used to place 1 mL of the challenge chemical in the center of the material and it was allowed to sit on the sample for 3 min. Then the surface liquid was wiped off with a lint free absorbent wipe. The sample was removed and weighed. The tape was left behind on the plate. It was determined that the small amount of fibers left on the tape was negligible. After exposure, the sample was ready for the first decontamination procedure.

3.3.2.2. First Decontamination

A mechanical scrubbing decontamination device was developed for this project, and it is pictured in Figure 3.6. This device used a linear actuator to scrub a material sample back

and forth horizontally. Several scrubbing heads such as different brushes and sponges were used in the development of the decontamination procedure. The scrubbing head Figure 3.6 was the rough bristle brush. However, ultimately this head was replaced with a soft sponge pictured in Figure 3.7. The reasons for this choice are discussed in Appendix A.1 of this paper.

The decontamination procedure first involved sealing the edges of the previously exposed material sample with tape. In the field, the decontamination procedure scrubs only the outside of the boot, so decontamination solution should be kept from the edges and back of the material. The sample was then placed on the decontamination device with the exposed surface facing the scrubber. A Scotch-Brite[®] heavy duty scrub sponge (4.5 inches x 27 inches x 0.6 inches) was soaked in 12 g/L granulated Tide[®] and tap water solution. Then the sponge was secured to the scrubbing device with the yellow, soft side facing the material surface. A 453.5g weight was added to the top of the scrubbing arm to create total of 680.4g of weight on the material including the weight of the decontamination device arm. A timer was set for 5 min. and then decontamination device was turned on. After scrubbing for 30 sec., which was equivalent to 10 total strokes of the sponge, the device was turned off and the material soaked in the decontamination solution for the remaining 4.5 min. The sample was removed and rotated 90°. The sample scrubbing procedure was repeated with a new sponge soaked in a solution of 71 g/L calcium hypochlorite in tap water. After the final scrubbing, the sample was rinsed for 30 sec. in tap water and allowed to dry for 1 hr and then the sample weight was recorded.

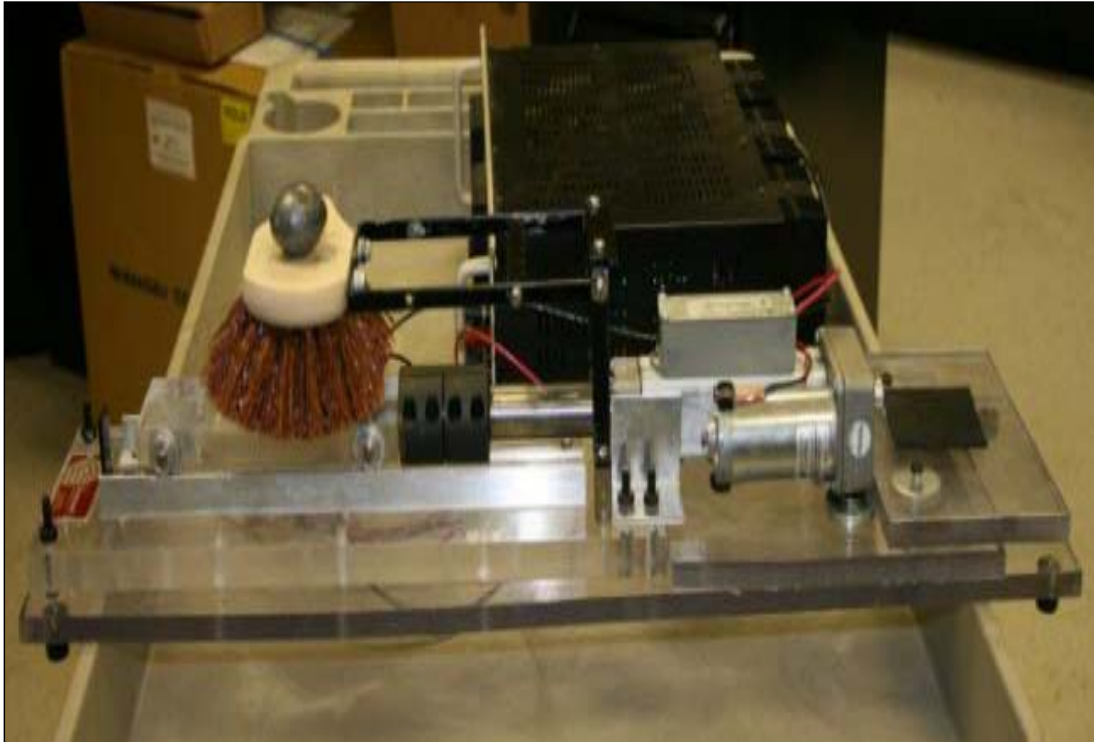


Figure 3.6 Decontamination Device



Figure 3.7 Sponge That Attaches to Decontamination Device

In the field, the total area of the boots is scrubbed with both the detergent and bleach solution for five minutes each. Laboratory technicians scrubbed the boots manually for five

minutes to determine the number of scrubs typical per boot. A scrub was one forward and back motion. The number of scrubs for the total area of the boot was used to calculate the number of scrubs that a 48.8 cm² sample would encounter. The actuator was set to scrub the whole length of the sample.

3.3.2.3. Second Exposure and Decontamination

After drying for one hour following the first exposure and decontamination, the same material was exposed to a second exposure and decontamination with the same procedures discussed in sections 3.3.2.1 and 3.3.2.2.

3.3.2.4. Third Exposure and Decontamination

After the second hour drying following exposure and decontamination, the final exposure of the material sample used a modified ASTM F 903- 03 procedure for a simulation of a high level exposure to TICs involving impact pressure.[38]

The parts and assembly of the exposure cell are located in Table 1 and in Figures 1-8 in the ASTM F-903 - 03 standard document.[38] The penetration cell for this experiment did not use a gasket or transparent cover. However, it did have a borosilicate disc (Diameter ~57.2 mm, Thickness ~12.7 mm) that was inserted into the hole of the restraining ring and is pictured in Figure 3.8. To begin the procedure, calipers were used to measure the thickness of each specimen to nearest 0.02 mm and the average of three measurements was recorded.



Figure 3.8 Disc Placement in the Restraining Ring of Penetration Cell

The weight of the samples was also recorded to the nearest 0.001g. The specimen was loaded “in the test cell with the normally outside surface toward the chemical chamber”, shown in Figure 3.9.[38] Then the sample was secured in place by placing the restraining ring on the back side of the sample and bolting the pieces of the cell together, as pictured in Figure 3.10. The cell was loaded into the testing apparatus shown in Figure 3.11, so that the material sample was vertical. This test was done at ambient temperature and a timer was



Figure 3.9 Material Sample Loaded into Penetration Cell



Figure 3.10 Assembled Penetration Cell



Figure 3.11 Penetration Test Apparatus

set for 3 min. Tygon™ tubing fitted to a syringe as pictured in Figure 3.12 was inserted into the test cell to fill it with approximately 60 mL of the challenge chemical. An air line was quickly connected to the test cell to provide 2 psi of pressure for 1 minute. Then the pressure

was released and the chemical remained in contact with the material surface at ambient pressure for the additional 2 minutes. After the elapsed time, a collection container was set under the cell and the liquid was drained. After draining, the material sample was removed

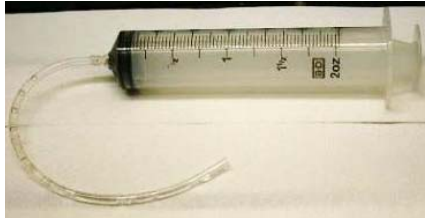


Figure 3.12 Syringe Used to Deliver Challenge Chemical To Penetration Cell

from the cell and the surface chemical was wiped away with a lint free absorbent wipe. The test specimen was observed for any discoloration or indications of liquid penetration. If liquid penetrated the material at any point during the three minute test period, then the material failed and no further testing was carried out on that sample. Material samples that passed were weighed and placed in an air tight container. The test cell was flushed with proper solvent to clean it for the next exposure.

After the ASTM F 903 exposure, the sample was decontaminated with the same procedure listed in section 3.3.2.2 of this document, except the material was allowed to dry for at least four hours after the decontamination. The dried sample was then extracted and analyzed with the appropriate methods in section 3.3.6.

3.3.3. Four-Day Field Simulation

The four-day exposure used similar procedures to the ones used in the one-day field exposure except the ASTM F 903 cell exposure was not done until the last exposure of the last day. It was determined by the project panel that this was an extreme exposure scenario that should only be done once during the simulation.

The first day of exposure began with the exposure procedure in section 3.3.2.1 followed by the decontamination procedure in section 3.3.2.2. This exposure and decontamination procedure was repeated two additional times for the first day. The same procedure for the first day was repeated for the second and third days. At the end of each day the sample was allowed to dry for at least four hours. Then, if the material had a surface finish, for example a fluorocarbon coating, the finish was restored and allowed to dry for at least twelve additional hours before starting the next simulated day.

The final (fourth) day of simulation first consisted of two exposures using the procedure in section 3.3.2.1 with decontaminations following each exposure and using the procedure in section 3.3.2.2. The final exposure followed the procedure using the ASTM F 903 cell in section 3.3.2.4 and then the sample was decontaminated again with the procedure in section 3.3.2.2. Once the sample had dried for at least four hours, it was extracted and analyzed with the appropriate method.

3.3.4. Wipe Test

A wipe test was used to test if any of the low volatile TICs were available to touch on the surface of the material after four-days. A clean cotton cloth was soaked in isopropanol

and wiped across a sample that had completed the four-day simulation procedure. After wiping in one direction then the sample was rotated 90° and wiped again. Then the wipe was extracted and analyzed with the same procedure as the material sample.

3.3.5. Extraction Methods

3.3.5.1. Semi-Volatile TICs

The ASE[®] was used to extract the semi-volatile TICs, including *m*-cresol, methyl parathion, and morpholine from the material sample. The rubber solid control samples used in this study were from a CBRN boot that was currently certified for chemical resistance and assumed to retain very little chemical. Therefore, a leather material was used to determine the extraction method. The goal of the extraction was to recover any TIC left inside the material. For the ASE[®] method development, a 25.9 cm² material sample was weighed. Six drops of one TIC were placed in the center of the sample and allowed to sit for three minutes. When the time was complete, the surface chemical was wiped with a lint free absorbent wipe and the material was weighed again. The samples were loaded into the extractor stainless steel cells containing a paper filter in the bottom. Glass beads were poured into the cells to fill empty space.

Methanol, acetone and isopropanol (IPA) were each used to make solutions with the semi-volatile challenge chemicals to determine the effect on the GC/FID results. IPA produced the best chromatograms for all chemicals. Therefore, IPA was tested as the extraction solvent and performed well. Each sample was extracted with the ASE three separate times with IPA to ensure that all of the TIC was removed. The amount of chemical

detected by GC/FID (the methods are discussed in section 3.3.6) after extraction was compared to the amount of chemical absorbed by the material gravimetrically to calculate the percent chemical extracted. Table 3.1 shows that methyl parathion and *m*-cresol were recovered well at 150°C with three cycles of fresh solvent and three minute static time at each cycle. The morpholine was harder to remove from the leather samples. The tanning process in leather can leave the material acidic and morpholine has been used to treat leather.[26,27] Morpholine is basic and the reactions in the leather could be the reason why not all of the morpholine was recovered.

Table 3.1 ASE[®] Method Development with Leather

Method	% Chemical Extracted		
	Methyl Parathion	<i>m</i> -Cresol	Morpholine
150°C/3 cycles/3 min.	>99%	>99%	
150°C/3 cycles/6 min.			38.8
175°C/3 cycles/3 min.			60.3
175°C/3 cycles/6 min.			78.1
195°C/3 cycles/6 min.			70.7
195°C/5 cycles/6 min.			73.8

Between extraction temperatures 175°C and 195°C, an average of approximately 74% of the morpholine absorbed was recovered. However, the maximum extraction temperature for the ASE[®] is 200°C and 195°C is potentially damaging to the instrument. Therefore, since the amount extracted for 175°C and 195°C is approximately the same, 175°C was chosen for the final extraction method. The same extraction method was applied to all three chemicals.

Increasing the extraction temperature for the methyl parathion and *m*-cresol only insured that >99% of the chemical was being extracted.

In the final method for the ASE[®], the total exposed area (25.9 cm²) was cut from the center of the material sample. Next, the cut piece was rolled and placed in to a 22-mL ASE[®] sample cell, with a paper filter and glass beads. The oven temperature was set to 175°C. There was no preheating of the samples in the ASE[®]. The program for one extraction of a sample first involved filling 25% of the cell volume with isopropanol (IPA) and holding at 1500 psi for 6 min. Then the IPA was released into the collection vial and the cell was filled again with fresh IPA for an additional 6 minutes. This process was repeated for a third cycle, then a final purge of the cell was set for 60 sec. Then two more extractions, each involving three total cycles of fresh solvent and holding at 6 min per cycle, were done with the same sample. Therefore, the sample was exposed to a total of 9 increments of fresh solvent.

3.3.5.2. Volatile TICs

The volatile TICs, acrolein and acrylonitrile were removed from the material by thermal desorption. The thermal desorption system was connected to the gas chromatograph. The method for the thermal desorption is included in the gas chromatography method for acrolein and acrylonitrile in section 3.3.6.2.

3.3.5.3. Inorganic TIC

The inorganic TIC, 37% sulfuric acid, was extracted using AATCC test method 81.[71] In summary, the 25.9 cm² exposed area was cut out of the material sample and

placed in 250mL of boiling water for 10 minutes. Then the material sample was removed from the extract.

3.3.6. Analytical Techniques

3.3.6.1. GC/FID for Semi-Volatile TICs

The gas chromatography methods for *m*-cresol, morpholine and methyl parathion were all carried out on the same column. This enabled faster and more efficient analysis because time was not wasted changing columns between each chemical. After the semi-volatile TICs were extracted with the ASE[®], the extract was analyzed by gas chromatography with a flame ionization detector (GC/FID). The chemicals were analyzed on the same Rtx[®]-5 amine column. For all samples, the carrier gas was helium and the combustion gases were compressed air and hydrogen. All methods were run in splitless mode. The gas flow for morpholine and *m*-cresol was 1.70 mL/min and 2.70 mL/min for methyl parathion. In the method for *m*-cresol, the injector and detector temperature were set at 285°C. The oven was programmed at 60°C, held for 1 min., ramped to 200°C at 25°C/min., then ramped to 285°C at 30°C/min. In the method for methyl parathion, the injector and detector temperature were set at 250°C and 295°C, respectively. The oven was programmed at 60°C, held for 1 min., ramped to 195°C at 25°C/min., then ramped to 250°C at 10°C/min. For the morpholine method, the injector and detector temperature were set at 280°C. The oven was programmed at 60°C, held for 1 min., ramped to 120°C at 10°C/min., then ramped to 280°C at 50°C/min. and held for 2 min.

Table 3.2 shows the calibration results for *m*-cresol, methyl parathion, and morpholine TICs. Table 3.2 also notes the average retention time for each chemical. *m*-Cresol and methyl parathion were calibrated using solutions ranging from 3 ppm to 3000 ppm in IPA. Morpholine was calibrated from 30 ppm to 3000 ppm in IPA. The limit of detection (LOD) “is the smallest quantity of analyte that is “significantly different” from the blank”[72] The standard deviation is calculated from the mean signal of replicates of a sample and measures random variation (noise). The limit of quantitation (LOQ) “is the smallest amount of analyte that can be measured with reasonable accuracy”.[72] An example calculation of the LOD and LOQ for *m*-cresol is below:

$$\text{LOD} = 3s/m \quad \text{where, } s = \text{standard deviation of a low concentration sample}$$

$$m = \text{slope of the calibration curve}$$

$$\text{LOD} = [3(464 \text{ area counts})]/2263 \text{ area counts/concentration (ng/}\mu\text{L)} = 0.6 \text{ ng/}\mu\text{L}$$

$$\text{LOQ} = 10s/m$$

$$\text{LOQ} = [10(464 \text{ area counts})]/2263 \text{ area counts/concentration (ng/}\mu\text{L)} = 2.1 \text{ ng/}\mu\text{L}$$

Table 3.2 GC/FID Calibration Results for Semi-Volatile TICs

TIC	<i>m</i> -Cresol	Methyl Parathion	Morpholine
Retention Time	5.429	10.358	4.232
R²	0.9999	0.9999	0.9999
Slope	2263	429	1415
Standard Deviation of Low Concentration Sample	464	81	533
Limit of Detection (ng/μL)	0.6	0.6	1.1
Limit of Quantitation (ng/μL)	2.1	1.9	3.8

3.3.6.2. TD/GC/FID for Volatile TICs

The same TD and GC oven method was used for both acrolein and acrylonitrile. All of the tubes were placed in the TD instrument and desorbed at 200°C for 12.5 min. using helium carrier gas with a flow of 20 mL/min. The desorbed chemicals were sent to the cold trap. The cold trap was heated to 300°C at 20°C/sec then held for 3 min. to volatilize the trapped materials and transport them to the GC column. Before entering the GC column the acrylonitrile volatilized sample was split 2:1. The acrolein sample was run in splitless mode. The oven was programmed at 35°C, held for 1 min., ramped to 55°C at 10°C/min., held for 2 min, ramped to 80°C at 2°C/min., held for 1 min., ramped to 130°C at 20°C/min.

Each TD tube was loaded with glass wool, glass beads, and a sample strip. The strips for the rubber control were each 2.3 cm² and the strips for the leather were each 1.8 cm². Then the tubes were capped and placed in the instrument. The ng desorbed from three strips was averaged and proportioned to find the mg of TIC in the total exposed area.

To create the calibration curves for the volatile TICs, acrolein and acrylonitrile, the stainless steel thermal desorption (TD) tubes were loaded with Tenax (40mg) and spiked with separate calibration solutions. The calibration solution concentrations ranged from 200 ppm to 10,000 ppm of acrolein in IPA. The calibration solution concentrations for acrylonitrile ranged from 1000 ppm to 30,000 ppm in acetone. The results for the calibrations of acrylonitrile and acrolein are in Table 3.3. Calibrating by spiking Tenax can create a larger error than most calibration methods. This resulted in lower R² values for the volatile TICs. The LOD and LOQ were calculated in the same way presented in section 3.3.6.1

Table 3.3 GC/FID Calibration Results for Volatile TICs

TIC	Acrolein	Acrylonitrile
Retention Time	4.34	3.87
R²	0.9997	0.9959
Slope	0.3	6.4
Standard Deviation of Low Concentration Sample	0.27	1239
Limit of Detection (ng/μL)	3	581
Limit of Quantitation (ng/μL)	9	1936

3.3.6.3. Titration for Sulfuric Acid

The residual acid in these samples was extracted using AATCC test method 81-2006.[71] The liquid extracted from the samples was titrated with 0.01N NaOH using the Mettler Toledo DL58 automated titrator. The 0.01N NaOH solution was standardized using KHP to get a more accurate solution normality. Sample extract (10mL) was transferred into a titration cup and DI water was used to bring the solution to 50mL. Each extraction was titrated three times and the results were averaged. The uncertainty of the titrations was calculated by repeating the titration of a solution 13 times and calculating the standard deviation, which was 0.02 mL of consumed NaOH.

Table 3.4 shows titration results to determine the natural acidity of the samples after various amounts of decontamination. Control samples of the rubber and the leather were decontaminated but not exposed to the sulfuric acid. Then the samples were extracted and titrated to determine the natural acidity in the samples. Then the mg of acid found in the

control samples was subtracted from the mg of acid found in actual exposed samples. This gave a better indication of how much acidity is added to the material by the TIC.

Table 3.4 Titration Results for Acid in Unexposed Samples

Scenario	Rubber (mg acid)	Leather C (mg acid)
No Decontamination	0.14	0.67
One Decontamination	0.12	0.47
Three Decontaminations - One-Day Simulation	1.25	3.89
Twelve Decontaminations – Four-Day Simulation	0.00	4.35

Chapter 4. Results and Discussion

4.1 Splash Test

It has been assumed that the porous absorbent nature of plain leather is not sufficient for protection against toxic industrial chemical (TICs).[35] However, a new finished leather or leather composite could possibly provide a protective, comfortable material for boots. There were several high performance flexible leather materials or multilayer composites on the market. It was not cost effective to expose all of those materials to large quantities of a battery of chemicals. Therefore, the ISO 6530 splash test helped narrow down the best performing materials to use in the harsher field simulation tests. Table 4.1 shows a list of materials screened with the splash test. The rubber control sample was cut from a CBRN boot currently used in the field. Leather A, Leather B and Leather C were each treated with a

different repellent surface finish. The exact formulations for the surface finishes are unknown because the materials were treated with proprietary finishes by the manufacturers. The composite material was unique because of its textured surface, and the composition was also proprietary. Table 4.1 shows the splash test results for these materials compared to the rubber control. Gravimetric measurements were used to determine how much TIC was absorbed by the material in grams. Then the TIC density was used to convert grams to milliliters for a better comparison of the volume of TIC absorbed by the material to the 60 mL delivered. The less TIC absorbed by a material the more repellent it is. The leather composite had a surface texture that caused groves in the material to act as a reservoir. A smooth surface is better for CBRN boot materials. The leather C had the best performance and closest values to the control sample. Figures 4.1 and 4.2 show examples a leather and rubber sample after an acrolein splash test. From the Figure 4.1, there is obvious discoloration of the rubber suggesting a reaction of the acrolein with the material. Since Leather C had the least TIC absorbed, it was chosen for further testing

Table 4.1 Splash Test Materials Screening

Material Tested	Rubber Control	Leather A	Leather B	Leather C	Leather Composite
TIC Challenge	Absorbed (mL)	Absorbed (mL)	Absorbed (mL)	Absorbed (mL)	Absorbed (mL)
Sulfuric Acid	0.01	<0.00	0.02	<0.00	0.08
Acrylonitrile	<0.00	11.60	2.79	0.14	1.82
m-Cresol	0.12	0.64	0.05	0.10	0.31
Morpholine	0.06	0.23	0.08	0.06	1.56
Acrolein	0.09	9.72	0.16	0.19	1.31
Methyl parathion	0.06	--	0.07	0.06	--



Figure 4.1 Rubber Exposed to Modified ISO 6530 Acrolein Splash Test



Figure 4.2 Leather Exposed to Modified ISO 6530 Acrolein Splash Test

4.2 Decontamination

Once the best material was selected using the splash test screening, it was important to see if the material could be decontaminated. There would have been no reason to continue testing a material that could not be cleaned. There first was an interest in determining if there would be a better method for decontamination than the current method used in the field. The results of this investigation are in Appendix A.1. The best choice for decontamination was the procedure presented in section 3.3.2.2. The decontamination of Leather C was determined to be acceptable if the residual TIC left was similar to a decontaminated rubber control. To determine the ability of Leather C to be decontaminated, a harsh exposure was desired. The exposure method described in section 3.3.2.4 involving the ASTM F 903 cell

was used. The decontamination process used is presented in detail in section 3.3.2.2. After exposure and decontamination, the materials were extracted and analyzed with the appropriate techniques listed in sections 3.3.5 and 3.3.6. Table 4.2 shows the decontamination comparison of both the rubber and leather samples. The amount detected from the TIC extraction was divided by the total exposed area of the sample. The experiment revealed that the Leather C could be decontaminated to a level similar to the rubber control. The residual levels of sulfuric acid, acrylonitrile, acrolein, and morpholine were all comparable. Although the leather had a larger amount of residual *m*-cresol than the rubber, the leather was decontaminated better than the rubber exposed to methyl parathion. The combination of similar results between the rubber and the Leather C in both the splash test and decontamination experiment confirmed that further testing should be done with Leather C.

Table 4.2 Residual TICs After One Exposure and Decontamination

Material Tested	Rubber Control		Leather C	
	Residual ² (mg/cm ²)	%CV	Residual ² (mg/cm ²)	%CV
Sulfuric Acid	ND*		0.08 ± 0.01	11
Acrylonitrile	ND*		ND*	
Acrolein	ND*		ND*	
<i>m</i>-Cresol	0.54 ± 0.07	13	2.21 ± 0.07	3
Morpholine	0.73 ± 0.18	25	1.39 ± 0.21	15
Methyl Parathion	4.12 ± 1.03	25	1.06 ± 0.54	51

*ND = None Detected

4.3 One-Day Simulation

The one-day simulation was the first test of Leather C to multiple exposures and decontaminations. To determine if the material performed well it had to perform as well or better than the current CBRN certified rubber control material. The results for the one-day simulation are located in Table 4.3. The results revealed that neither material performed best with all chemicals. Each material had TICs that were repelled well and others that were a challenge. For example, even though the rubber control was cut from a CBRN boot it had higher residuals of methyl parathion than the Leather C. The Leather C was less resistant to *m*-cresol and morpholine. Variability in the samples could be a result of the handling of the samples through multiple exposures and decontamination procedures. Although, the leather performed well with the one-day simulation it was important to continue testing the materials to see how it would perform throughout the entire service life of a CBRN boot. As noted in Appendix A.1, the surface finish of the leather begins to show signs of wear after approximately 10 decontamination cycles. The one-day simulation only included three decontamination cycles. To truly understand if the leather material would remain protective, it had to be tested with more exposures and decontaminations after restoring the finish. The one-day simulation was another good way to make sure the Leather C was a suitable material before beginning the time consuming task of a four-day simulation.

Table 4.3 One-Day Simulation Results for Rubber and Leather C

Material Tested	Rubber Control		Leather C	
	Residual (mg/cm ²)	%CV	Residual (mg/cm ²)	%CV
Sulfuric Acid	ND*		0.04 ± 0.02	42
Acrylonitrile	NAD**		ND*	
Acrolein	0.54 ± 0.54	100	0.01 ± 0.01	100
<i>m</i>-Cresol	0.78 ± 0.22	28	2.55 ± 0.18	7
Morpholine	1.07 ± 0.97	91	3.12 ± 0.31	10
Methyl Parathion	5.26 ± 0.36	7	2.13 ± 0.29	14

*ND = None Detected

**None Accurately Detected, a small peak was observed but too small to measure accurately

4.4 Four-Day Simulation

The four-day simulation was a harsh procedure for the material samples. Both the rubber and the leather were exposed and decontaminated 11 times and on the 12th cycle, the TIC was pressed against the surface to test the performance of the material at its' weakest. The results in Table 4.4 show that the residuals of the semi-volatile TICs, *m*-cresol, morpholine, and methyl parathion increased from the amount detected in the one-day simulation. However, the residual levels of acrylonitrile and acrolein were still low or not detectable. It was expected that the residuals for all the chemicals in the four-day simulation to be the same or higher than the results from the one-day simulation. The acrolein and

acrylonitrile are difficult to detect because of their volatility and this could be a reason for variability. Although the thermal desorption extraction method involved less handling of the materials, the limited sample size and complex heating system can lead to lower detection limits and inaccuracies.[70] Both the one-day and four-day simulations were consistent in that the acrylonitrile and acrolein residuals were lower than any of the other TICs. Acrylonitrile and acrolein are not as much of a concern to CBRN boots as the other TICs. If they are splashed onto a boot they should quickly runoff because of their low viscosity or they will evaporate because of their low boiling point. They were still necessary in the development of these procedures because they were crucial in providing the battery of TICs with a complete range of physical and chemical properties.

In the final exposure of the materials, they are exposed to TIC with pressure using the ASTM F 903 cell. This cell has a clear insert that allows for observation of the back side of the materials throughout the entire test. It is important to note that while in the ASTM F 903 cell none of the TICs reached the opposite side of the material. Therefore, even at the end of the service life of the material, if the material is exposed to a TIC with pressure, it will keep the TIC from penetrating inside the boot. It is believed that in most situations, the repellency of the leather in combination with the boot shape will cause the TIC to roll off, and therefore result in lower residual TICs levels than what is presented by the four-day simulation. The different exposure methods used in the four-day simulation involve TIC sitting on the surface for an extended period of time which would be indicative of an extreme set of circumstances. Although the methods are extreme, they could provide a higher sense of security for customers purchasing boots because they know the materials used to construct the boots can

provide protection under harsh conditions. Figures 4.3 and 4.4 show 1 mL of *m*-cresol placed on the surface of the rubber and Leather C samples. The contact angle of the *m*-cresol with the rubber is much lower than that of the Leather C. The high contact angle with the Leather C indicates that the leather has a high degree of repellency and the liquid can roll off easier.

Table 4.4 Four-Day Simulation Results for Rubber and Leather C

Material Tested	Rubber Control		Leather C	
	Residual ² (mg/cm ²)	%CV	Residual ² (mg/cm ²)	%CV
Sulfuric Acid	0.03 ± 0.01	43	0.16 ± 0.05	31
Acrylonitrile	0.03 ± 0.03	100	ND*	
Acrolein	ND*		ND*	
<i>m</i>-Cresol	0.98 ± 0.14	15	6.50 ± 0.48	7
Morpholine	0.59 ± 0.27	45	4.99 ± 0.67	13
Methyl Parathion	5.50 ± 1.0	17	6.44 ± 0.91	14

*ND – None Detected



Figure 4.3 *m*-Cresol on Rubber Sample



Figure 4.4 *m*-Cresol on Leather C

4.5 Wipe Test

The four-day simulation showed an increase in the residual amount of semi-volatile TIC in the Leather C. The residual reported was the amount of TIC left in the whole volume of the material. There was an interest in determining how much of the TIC was available on the surface of the material to touch. Although, the end of the four-day simulation is the end

of the boot service life, it should still be safe to handle. After the final decontamination and drying, the samples were wiped with an isopropanol wipe. Then the wipe was extracted to determine how much TIC was available on the surface. The results are presented in Table 4.5. The wipe test indicated that the boots made of the rubber and Leather C would be safe to handle after 12 exposure and decontamination cycles. It should be noted that one sample out of three Leather C samples contained 0.1 mg/cm² of residual on the surface.

Table 4.5 Wipe Results for Rubber and Leather C Samples

	Residuals of TICs in Wipe for Rubber Control	Residuals of TICs in Wipe for Leather C
TIC challenge	mg/cm ²	mg/cm ²
<i>m</i>-Cresol	ND*	< 0.1**
Morpholine	ND*	ND*
Methyl Parathion	ND*	ND*

*ND = None detectable

**One of 3 specimens had 0.1 mg/cm² residual *m*-cresol

Chapter 5. Conclusions

Current CBRN boots that are typically made of rubber can be heavy and inflexible. There is a need to have a new flexible CBRN material that would provide comfortable, stable boots similar to those made of leather. Although, leather has previously been assumed to have poor chemical protection, a study by Gore found that leather could provide better protection than rubber against a small battery of TICs.[35] There are many finished leathers

and material composites on the market but laboratory methods were needed to determine which material would be best for making a new CBRN prototype. It was noted that current standards for testing materials such as the NFPA 1994, ASTM F 903, ASTM F 739, and ISO 6530 do not test materials the way they are used in the field. Therefore, a new system was developed to expose and decontaminate the materials. The study by Gore did incorporate a single decontamination procedure but multiple cycles of exposure and decontamination were needed to accurately represent field use. It was determined that one day of field use should include three exposures, each followed by a decontamination. The types of exposures include chemical splash and pressing of a chemical against the material to simulate an object falling on the boot or stubbing a toe. The expected life cycle of a hazmat boot is four days with a total of 12 exposures and decontaminations.

The new system developed first involved a splash test to screen materials. If a material performed similar to the rubber control then it was tested with a one-day simulation. If the material still performed well after the one-day simulation compared to the rubber control, then it was tested with a four-day simulation. An important part of the system was using the appropriate extraction and analytical methods. The ASE[®] system provided a fast and environmentally friendly extraction. This automated instrument automatically extracted samples with small amounts of solvents and utilized high temperatures and pressures to increase extraction efficacy of semi-volatile TICs. Developing the GC/FID methods for the semi-volatile TICs on the same column increased efficiency because columns did not have to be changed between chemicals. The TD/GC/FID technique for the volatile TICs proved to be more variable than the technique used for the semi-volatile TICs. The boiling extraction

and titration of the samples exposed to 37% H₂SO₄ was a simple technique. Natural acidity was found in unexposed material samples and was accounted for in the calculations of the exposed samples. These laboratory methods allowed for testing of materials before costly prototypes were made for certification. The methods could also be used in the future to test other CBRN materials for protection performance after multiple uses.

The modified ISO 6530 splash test helped to determine that out of the new materials, Leather C and the rubber control had the closest results. A raised textured surface, such as the one in the leather composite, does not perform well in CBRN boot applications. Groves on a material surface can become a reservoir for a TIC and could potentially cause difficulty during decontamination. Exposing the rubber control and Leather C to one ASTM F 903 exposure and decontamination helped to ensure that the Leather C could be decontaminated before further testing. An investigation into the best decontamination solution determined that the current decontamination procedure used in CBRN incidents was the best choice. However, a soft sponge was used instead of a rough brush and the detergent concentration was defined as 12 g/L.

The one-day stimulation revealed that neither the rubber control nor the Leather C performed the best for all TICs. The TICs *m*-cresol and morpholine were most challenging for Leather C, while methyl parathion was most challenging for the rubber control. The leather sample needs recoating after three decontaminations to ensure that the leather remains repellent. The four-day simulation test was necessary to make sure that the recoated leather material could be reused multiple times. The results after the four-day simulation showed an increase in the semi-volatile chemicals. It is important to keep in mind that the exposure

conditions were extreme compared to what is expected in the field. The system developed in this study used a larger variety of TICs than the Gore study.[35] This helped to further challenge the leather to get a better indication of its protection ability. Low residual levels of the volatile TIC, acrylonitrile, were observed both in the results of this research and the research by Gore. [35]

To make sure that the semi-volatile TIC residual was not available on the surface of the material to touch, a wipe test was used. A wipe test confirmed that there is no TIC that is detectable on the surface, except one Leather C sample out of three contained 0.1 mg/cm² of *m*-cresol. Although the methods used in the system provide a simulation of the use of CBRN materials in the field, the multiple exposures and decontaminations coupled with the extraction and analytical techniques involves a lot of handling of the materials and can explain variability between samples. Variability is more frequent with volatile chemicals that, if retained, are most likely in very small amounts.

This research has developed a laboratory method of exposing and decontaminating samples in a way that mimics field use, which is not available in current standard methods. From these methods a finished leather was identified as a material that could be a viable option for a new CBRN boots.

Chapter 6. Recommendations

Although a group of chemicals was selected for a variety of chemical and physical properties, testing with more TICs would provide more information about a materials performance. The results of this project showed that the repellency of a material depends on

the chemical challenge. Headspace gas chromatography could be an option for future analysis of volatile TICs. Volatile chemicals in the headspace gas of a vial can be directly injected into a gas chromatography system.

Testing for off-gassing of both the rubber control and the Leather C could check for matrix release of the residual TIC over time. Placing the material in a plastic and sampling the air in the bag over time could test for off-gassing. Also, surface sampling with a solvent wipe during this time could check for any semi-volatile TIC that is leached to the material surface. This will help to determine “how clean is clean”[43] The system developed by this work is a good way to determine if a material will be suitable for CBRN application before expensive prototypes and certification take place. However, after a prototype is developed, testing the boot with a manikin in chemical warfare simulant could provide a better indication of the boot performance with an entire CBRN ensemble. The use of manikins equipped with the ability to simulate human skin temperature, perspiration, and movement, etc. could greatly improve the selection of future CBRN ensembles.[39] Although manikins are very important, to use the manikin, a new material must be manufactured into a prototype before the material can be tested. Making prototypes could become costly. Therefore, bench-top techniques could be used to simulate the use of new CBRN materials in the field to screen materials for performance. Then a new material that performs well in laboratory tests can be made into a prototype for testing with the manikin. Combining new laboratory approaches with high tech manikins could provide manufacturers and the customers with even better protection and comfort when using CBRN ensembles.

Along with repellency, the materials should have the appropriate physical testing. The materials may have a repellent finish but if they cannot survive constant bending, resist tearing or bending then they are not suitable for CBRN application. The materials should also be tested for NFPA 1971 flame resistance.

Work could be done on converting the results of this new system into pass/fail results. A manufacturer or consumer will be more attracted to buying a product if the descriptions of the material performance are easy to understand. It would be ideal to provide quantitative and qualitative results to appeal to more people.

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APPENDICES

APPENDICES

A.1 Decontamination Procedures

While developing procedures to analyze materials for an enhanced performance CBRN boot, there was an interest in optimizing the decontamination procedure. The objective was to compare the decontamination efficiency used in the field to new decontamination solutions and procedures. The first task was to determine how well the current decontamination procedure performed. The procedure was provided by project advisors with experience in CBRN incidents. The total area of the boots was scrubbed for five minutes in an unknown concentration of detergent in water. Then they were scrubbed for an additional five minutes in a 48 oz. of calcium hypochlorite (HTH) in 5 gallons of water. The final step was to rinse the boots in water and let them air dry. By scrubbing a whole boot for 5 minutes it was determined that a 48.8 cm² sample of material would receive 30 seconds of continuous scrubbing. The brush recommended for the procedure was a long handled brush with long course metal bristles. The head of the brush was attached onto the decontamination device pictured in Figure 3.6. This brush was chosen because after the boots had been used, the stiff bristles made getting clay and other dirt off of the soles easier. However, scrubbing the rubber and leather with the rough bristles visibly damaged the surface of the materials. The surface scratches could lead to more uptake of a TIC and reduce the service life of the boots. A total of 12 decontamination cycles was expected to simulate two years of field use. For a 48.8 cm² sample, that would be a total of 1 minute of continuous scrubbing per cycle or a total of 12 minutes per service life. Figure A.1 shows a

rubber sample taken from a CBRN certified boot. The surface of the material is severely scratched after four minutes of decontamination. Figure A.2 shows scratches in the leather sample after only two minutes using the rough brush.

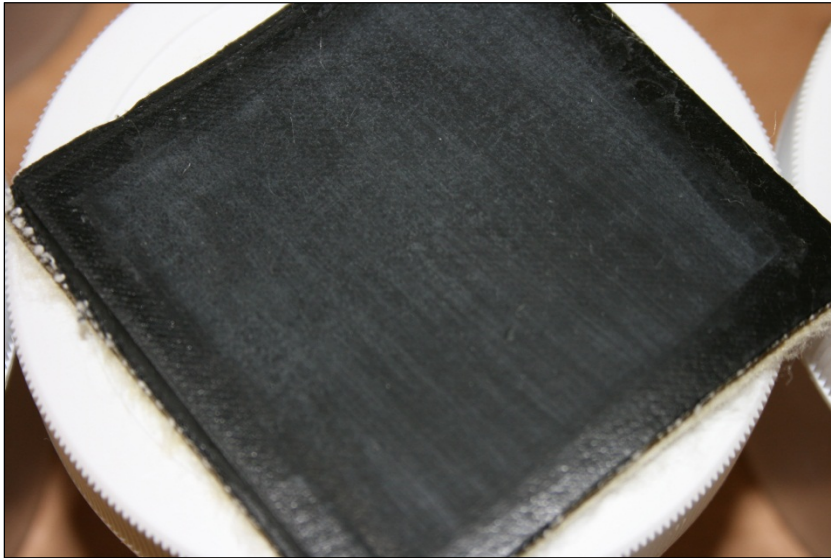


Figure A.1 Rubber Sample After Scrubbing Four Minutes with a Rough Brush



Figure A.2 Leather Sample After Two Minutes with a Rough Brush

A new method of scrubbing was needed to provide less damage to the material surface. The rough metal bristles may be useful for removing dirt and clay from the sole of the boot but it was not appropriate for the upper materials of the boot. Therefore, a soft sponge was used to scrub the materials instead. Figures A.3 and A.4 show a rubber and leather sample after 10 minutes of scrubbing with a soft sponge. The sponge eliminated any scratches on the surface of the material but there is noticeable wearing of finish on the leather. This loss of the repellent surface finish can reduce the protection of the material. Therefore, it was recommended that the surface finish be reapplied at the end of every day in the field or after three cycles of decontamination.



Figure A.3 Rubber Sample After Ten Minutes of Scrubbing with a Sponge



Figure A.4 Leather Sample after Ten Minutes of Scrubbing with a Sponge

Along with experimenting with different scrubbing materials other decontamination solutions and approaches were tested. Many different decontamination procedures were screened with one sample of leather exposed to morpholine. Morpholine was chosen because it was one of the harsher chemicals toward leather. The current decontamination procedure used in the field was tested with a sponge, horsehair brush, and rough brush on Leather B. There were no large changes in the efficiency of the decontamination, just that the sponge had the least damage on the material surface. The results are shown in Table A.1.

Table A.1 Residual Morpholine in Leather B After Decontaminating with Different Scrubbing Materials

Scrubbing Material	mg chemical /cm² material
Rough Brush	2.8
Horsehair Brush	2.7
Sponge	2.4

The Leather C that performed the best in the splash test procedure in section 3.3.1 was used in further testing of the decontamination procedure with a sponge. Only one sample was used during the tests because it was a screening for better decontamination procedures. Table A.2 shows the results of some decontamination procedures tried with Leather C. There was no large change in the residual TIC left between decontamination procedures. From the experiments it was determined that using detergent with calcium

hypochlorite (bleach) was better than using detergent alone. Some of the other experiments involving isopropanol (IPA) and hexane had low residual amounts. However, using large amounts of organic solvent in a mass decontamination is not practical, and large amounts of solvent themselves can be harmful. There was not enough of a difference in the decontamination results to suggest making changes from the decontamination procedure already used in the field. Therefore, it was decided that the current decontamination procedure would be kept in place, except with a sponge instead of a harsh brush and the concentration of the detergent was 12g/L in water.

Table A.2 Decontamination Approaches using Leather C

Experiment Description	mg chemical /cm² material
Sponge/1g/L Detergent in Water/71 g/L Calcium Hypochlorite (HTH)	1.6
Higher Concentration of Detergent (12 g/L)/71g/L Calcium Hypochlorite	1.3
Higher Concentration of Detergent (12 g/L)/71g/L Calcium Hypochlorite //longer scrubbing	1.5
Higher Concentration of Detergent (12 g/L)/Deck Cleaner	1.4
Detergent only - High concentration (12 g/L)	2.7
25 g/L detergent and 71 g/L HTH (combined solutions)	1.6
25 g/L detergent and 71 g/L HTH and IPA (combined solutions)	1.2
Higher Concentration of Detergent (12 g/L)/71g/L Calcium Hypochlorite/Acetic Acid (separate solutions)	1.6
HTH in DI H ₂ O and IPA	1.0
Higher Concentration of Detergent (12 g/L)/71g/L Calcium Hypochlorite with water flushing between solutions	1.1
Cationic Detergent	1.5
Anionic Detergent	1.8
Higher Concentration of Detergent (12 g/L)/Chlorox	1.6
RSDL/71g/L Calcium Hypochlorite	1.6
Oil	1.5
Hexane mixed with detergent	1.1
Easy Decon	1.3
Higher Concentration of Detergent (12 g/L)/Hexane Rinse/71g/L Calcium Hypochlorite	1.5
Versa Clean	1.6