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AC/323(HFM-199)TP/762

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STO TECHNICAL REPORT **TR-HFM-199**

Integration of CBRN Physical Protective Measures to Lessen the Burden on Personnel

(Intégration de mesures de protection physique NRBC pour alléger la charge sur le personnel)

This Report documents the findings of Task Group HFM-199.

Published June 2018

Distribution and Availability on Back Cover

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The NATO Science and Technology Organization

Science & Technology (S&T) in the NATO context is defined as the selective and rigorous generation and application of state-of-the-art, validated knowledge for defence and security purposes. S&T activities embrace scientific research, technology development, transition, application and field-testing, experimentation and a range of related scientific activities that include systems engineering, operational research and analysis, synthesis, integration and validation of knowledge derived through the scientific method.

In NATO, S&T is addressed using different business models, namely a collaborative business model where NATO provides a forum where NATO Nations and partner Nations elect to use their national resources to define, conduct and promote cooperative research and information exchange, and secondly an in-house delivery business model where S&T activities are conducted in a NATO dedicated executive body, having its own personnel, capabilities and infrastructure.

The mission of the NATO Science & Technology Organization (STO) is to help position the Nations' and NATO's S&T investments as a strategic enabler of the knowledge and technology advantage for the defence and security posture of NATO Nations and partner Nations, by conducting and promoting S&T activities that augment and leverage the capabilities and programmes of the Alliance, of the NATO Nations and the partner Nations, in support of NATO's objectives, and contributing to NATO's ability to enable and influence security and defence related capability development and threat mitigation in NATO Nations and partner Nations, in accordance with NATO policies.

The total spectrum of this collaborative effort is addressed by six Technical Panels who manage a wide range of scientific research activities, a Group specialising in modelling and simulation, plus a Committee dedicated to supporting the information management needs of the organization.

- AVT Applied Vehicle Technology Panel
- HFM Human Factors and Medicine Panel
- IST Information Systems Technology Panel
- NMSG NATO Modelling and Simulation Group
- SAS System Analysis and Studies Panel
- SCI Systems Concepts and Integration Panel
- SET Sensors and Electronics Technology Panel

These Panels and Group are the power-house of the collaborative model and are made up of national representatives as well as recognised world-class scientists, engineers and information specialists. In addition to providing critical technical oversight, they also provide a communication link to military users and other NATO bodies.

The scientific and technological work is carried out by Technical Teams, created under one or more of these eight bodies, for specific research activities which have a defined duration. These research activities can take a variety of forms, including Task Groups, Workshops, Symposia, Specialists' Meetings, Lecture Series and Technical Courses.

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Published June 2018

ISBN 978-92-837-2125-3

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List of Acronyms

2-CEES	2- Chloroethyl Ethylsulfide
AChE	Acetylcholinesterase
Al_2O_3	Aluminum Oxide
ALD	Atomic Layer Deposition
AMPs	Antimicrobial peptides
APCI-MS	Atmospheric Pressure Chemical Ionization – Mass Spectrometry
APR	Air Purifying Respirator
ARTS	Advanced Respirator Test System
ARTS+	New Exercises in Advanced Respirator Test System
ATD	Atmospheric Transport and Dispersion
ATR-FTIR	Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy
BOHSS	Bend Over Head Side to Side
BWA	Biological Warfare Agent
CAD	Chemical Agent Detection
CAP	Cold Atmospheric Plasma
CARC	Chemical Agent Resistant Coating
CB	Chemical and Biological
CB PRISM	Chemical and Biological Protected Integrated System Mask concept
CB/GSS	Chemical Biological Ground Soldier System
CBRN	Chemical, Biological, Radiological, Nuclear
CC SCBA	Closed Circuit Self Contained Breathing Apparatus
CDC	Carbide Derived Carbon
CFD	Computational Fluid Dynamics
CNC	Computer Numerically Controlled
CNT	Carbon nanotube
CPU	Computer Processing Unit
CSC	Carbon Silica Composite
CTD	Combined Technology Demonstration
CVD	Chemical Vapor Deposition
CWA	Chemical Warfare Agent
DB	Deep Breathing
DEEP	Diethyl ethyl phosphonate
DFP	Diisopropylfluorophosphate
DIMP	Diisopropyl Methyl Phosphonate
DMMP	Dimenthyl Methyl Phosphonate
FIMS	Fully Integrated Mask System
FS	Perfluoro-decyl-trimethoxysilane
GA	Tabun
GB	Sarin
GD	Soman
GUI	Graphical User Interface
HD	Sulfur Mustard
H-LEPM	Hybrid – Lagrangian-Eulerian Plume Model

HPC	High Performance Computing
HSS	Head Side to Side
HUD	Head Up and Down
HVLP	High Volume Low Pressure
IP	Individual Protection
LP	Lipopolysaccharides
MeS	Methylsilicate
MIST	Man In Simulant Test (protocol)
MLD	Molecular Layer Deposition
MOF	Metal Organic Framework
NB	Normal Breathing
NBC	Nuclear, Biological, and Chemical
NGRPS	Next Generation Respiratory Protection System
OP	Organophosphate
OPAA	Organophosphorous Acid Anhydrolase
PAA	Polyacrylic Acid
PADS	Passive Adsorbent Dosimeters
PAPR	Powered Air Purifying Respirator
PCFF	Polymer Constant Force Field
PF	Protection Factor
PIM	Polymers of Intrinsic Microporosity
PIMS	Partially Integrated Mask System
PP	Polypropylene
RBES	Respiratory Battlefield Evaluation System
SCIPUFF	Second order Closure Integrated PUFF (model)
SEM	Scanning Electron Microscopy
SH	Superhydrophobicity
SLA	Stereo Lithography Apparatus
SMP	Standard Military Protocol
SO	Superoleophobicity
STE	Source Term Estimation (model)
TBP	Tributyl Phosphate
TCFS	Trichloroperfluorooctylsilane
TiO_2	Titanium Dioxide
TMA	Trimethyl Ammonium
TSAD	Temporal-Spectral Anomaly Detector
UK	United Kingdom
US	United States
VOC	Volatile Organic Compound

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Integration of CBRN Physical Protective Measures to Lessen the Burden on Personnel

(STO-TR-HFM-199)

Executive Summary

This Task Group addressed integrated CBRN protection strategies. This report focused on outlining technologies that lower the burden on the individual by using a layered approach consisting of contamination avoidance, physical protection, hazard mitigation response, containment and recovery. The specific goal of the Task Group was to facilitate the communication and coordination of research on CBRN protection among the participating nations. This report outlines the active, passive and reactive protection technologies.

The trends of sensor miniaturization and network integration discussed in Chapter 2 will provide the warfighter greater flexibility on the battlefield to avoid contamination or quickly move out of contaminated areas. The combination of small, inexpensive and ubiquitous sensors that are seamlessly integrated can provide tools to determine contamination sources, reduce false alarms, and agent cloud tracking that will allow warfighters to confidently minimize their protection posture while avoiding contamination. This serves to lessen the burden by minimizing time in the highest protective postures. An ability to rapidly assess areas of high contamination can help warfighters to avoid or move out of them to reduce to total challenge on protective ensembles. Thus it may be possible to reduce protection performance and accept additional risk in favor of lower-burden ensembles.

The technologies discussed in Chapter 3 clearly show a trend toward improved performance at lower burdens. The development of new materials and application of nanotechnology lead this trend. New classes of materials such as Metal Organic Frameworks (MOFs) provide platforms that can be tuned for optimal pore size and chemical functionality that adsorb and detoxify agents. Garments can have enhanced capabilities with new classes of durable repellent coatings that incorporate nanomaterials, and nano-fiber aerosol barrier layers that increase protection with minimal additional weight or thermal load. Whole ensembles can be with computer-aided optimal design tools for respirators and garments. Overall, with the proper investments, developments in cutting-edge materials technologies can be exploited to improve protection while decreasing thermal burden.

Exposure to secondary contact with contamination can be mitigated by technologies that facilitate rapid decontamination. Traditionally, responsive actions have been logistically burdensome events that require the assistance of specialty units to achieve decontamination levels sufficient to allow the warfighter sustained reduction of high protective levels. New technologies have the potential to allow the same level of performance from actions performed by individuals or crews, and thus reduce overall the burden of protection. Chapter 4 provided a synopsis of technologies such as agent disclosure sprays that can rapidly identify areas of contamination to focus efforts and assess the results. When combined with a strippable, an agent disclosure system can identify the specific areas of coating to be removed, thus allowing a rapid resumption of the mission at a lower, and less burdensome, protective posture. Technologies to process sensitive equipment for decontamination can allow unencumbered use of these items as they are returned to service. This reduces burden by allowing the reduction from high levels of protection and reducing the logistical demand for replacing items simply because they are contaminated.

In all, there are many new emerging technologies that all will be able to contribute to enhanced warfighter safety related to CBRN risks and events, while reducing the physiological burden. The challenge will be to

build appropriate systems to use and balance all available options against the missions that are to be expected and planned. This report shows a series of technologies that will support these goals. The technologies should all be available in the short or medium term and therefore, benefits may be expected soon. Also, some of these technologies may be integrated into currently available systems and approaches and still enhance capabilities and/or protection. The need for enhanced protection and lowering the burden to the warfighter is expected to remain for the foreseeable future.

Intégration de mesures de protection physique NRBC pour alléger la charge sur le personnel

(STO-TR-HFM-199)

Synthèse

Ce groupe de travail portait sur les stratégies intégrées de protection NRBC. Le présent rapport s'est concentré sur la description des technologies qui allègent la charge pesant sur les personnes, à l'aide d'une approche multidimensionnelle comprenant un évitement de la contamination, une protection physique, une réaction d'atténuation du danger, un confinement et une récupération. Le but spécifique du groupe de travail était de faciliter la communication et la coordination des recherches sur les protections NRBC dans les pays participants. Ce rapport décrit les technologies de protection active, passive et réactive.

Les tendances à la miniaturisation des capteurs et à l'intégration des réseaux, discutées au chapitre 2, donneront plus de souplesse au combattant sur le champ de bataille pour éviter la contamination ou sortir rapidement des zones contaminées. L'association de petits capteurs bon marché, omniprésents et intégrés de manière fluide peut fournir des outils pour déterminer les sources de contamination, réduire les fausses alertes et suivre le nuage de l'agent, ce qui permettra aux combattants de minimiser leur posture de protection tout en évitant la contamination avec certitude. Cela réduit la charge en minimisant le temps passé dans les postures les plus protectrices. La capacité d'évaluer rapidement les zones de forte contamination peut aider les combattants à les éviter ou en sortir pour réduire la mise à l'épreuve des combinaisons de protection. Il pourrait ainsi être possible de réduire les performances de la protection et d'accepter le risque supplémentaire lié à des combinaisons moins lourdes.

Les technologies discutées au chapitre 3 montrent clairement une tendance à l'amélioration des performances pour un poids plus léger. Le développement de nouveaux matériaux et l'application de la nanotechnologie sont à l'origine de cette tendance. Les nouvelles catégories de matériaux telles que les structures organométalliques (MOF) fournissent des plateformes qui peuvent être adaptées pour offrir la taille de pores optimale et une fonctionnalité chimique qui adsorbe et détoxifie les agents. Les vêtements peuvent avoir des capacités améliorées, grâce à des revêtements répulsifs durables qui incorporent des nanomatériaux et des couches de protection à nanofibres contre les aérosols qui augmentent la protection en ajoutant un poids minimal ou une faible charge thermique. Les combinaisons complètes peuvent être conçues avec des outils de conception optimale des respirateurs et des vêtements, assisté par ordinateur. Dans l'ensemble, avec les investissements adéquats, l'évolution des technologies utilisant les matériaux de pointe peut être exploitée pour améliorer la protection tout en réduisant la charge thermique.

L'exposition à un contact secondaire avec la contamination peut être atténuée par les technologies qui facilitent une décontamination rapide. Traditionnellement, les interventions en réaction sont des événements lourds à gérer qui requièrent l'aide d'unités spéciales pour que les niveaux de décontamination atteints permettent une réduction prolongée des hauts niveaux de protection du combattant. Les nouvelles technologies ont le potentiel de permettre le même niveau de performance, que les actions soient réalisées par des individus ou par des équipes, ce qui réduit dans l'ensemble la charge de protection. Le chapitre 4 donne un sommaire des technologies telles que les aérosols de révélation des agents, qui peuvent rapidement identifier les zones contaminées pour focaliser les efforts et évaluer les résultats. Associé à un produit pelliculable, un système de révélation des agents peut identifier les zones de revêtement à éliminer, ce qui permet une reprise rapide de la mission avec une posture de protection plus basse et moins contraignante.

Les technologies servant à traiter le matériel sensible pour le décontaminer peuvent permettre un nouvel usage de ces articles lorsqu'ils sont remis en service. Cela réduit la charge en réduisant les niveaux de protection et les besoins logistiques de remplacement des articles parce qu'ils sont contaminés.

Au total, il existe beaucoup de technologies émergentes qui pourront contribuer à améliorer la sécurité des combattants face aux risques et événements NRBC, tout en réduisant la charge physiologique. Le défi sera de construire des systèmes adéquats pour utiliser et équilibrer toutes les options disponibles au regard des missions prévisibles et planifiées. Ce rapport indique une série de technologies qui faciliteront la réalisation de ces objectifs. Puisque les technologies devraient être disponibles à court ou moyen terme, on pourrait en récolter les bénéfices bientôt. D'autre part, certaines de ces technologies peuvent être intégrées dans les systèmes et approches actuellement disponibles et améliorer tout de même les capacités et/ou la protection. Dans un avenir proche, la nécessité d'une protection améliorée et d'une charge plus légère pour le combattant devrait persister.

Chapter 1 − INTRODUCTION

1.1 BACKGROUND

Participation in military operations is accompanied by the threat of exposure to Chemical, Biological, Radiological, and Nuclear (CBRN) agents. Historically, focus has been on the acute health effects of exposure to chemical weapons, and the specter of the use of biological, radiological and nuclear weapons. From World War I (WWI) until today impressive research and development efforts have been devoted to passive defence against CBRN agents comprising relevant elements such as threat analysis, various means of detection and identification, diagnosis, protection (both physical and medical), decontamination, and medical countermeasures. In recent years the awareness of the importance of health hazards resulting from exposure to other toxic materials encountered during military operations has grown steadily. Whereas the end of the Cold War may have lowered the threat of large-scale attacks of classical CBRN weapons, the new era brings new types of operations, mostly out of-area in a wide range of environments, where attacks can be isolated with predominantly local effects. Attacks could be unexpected, uncertain or initially unrecognized as a result of intended and unintended releases of classical, new and improvised agents, Toxic Industrial Materials (TIMs), including the likelihood of CBRN terrorism. Focus will therefore be more along the lines of consequence management versus general battlefield readiness. Doctrine is changing from “fighting dirty” to relocate, isolate the area and restore operations. The changing threat requires dual-use and integrated solutions rather than unique dedicated CBRN defence capabilities. Finally, casualty acceptance under these circumstances will be far less than when all-out CBRN warfare was anticipated during the Cold War. Nowadays, civilian occupational health regulations and standards will play a more predominant role. Past HFM Panel and its predecessors have focused on the toxicology as well as the medical counter measures against first chemical warfare agents (HFM-041), the operational toxicology of military relevant toxic hazards in general (HFM-057), later the broader spectrum of chemical toxic agents (ET-078) and also medical counter measures against biological agents (ET-091). Other elements of the so-called CBRN passive defence chain such as threat analysis, detection, reconnaissance, physical protection (either individual or collective) as well as decontamination of people and materiel have not been given the research and technology attention in the same manner. If doctrine and operational practice need to change as a result of the changing general picture shown above, the capabilities of current and emerging technologies should be made known to the proper communities in NATO (ACT, ACO, and CBRNWG). In the materiel community (NAAG/JCG-CBRN and its sub-groups as well as DAT) much attention is given to equipment requirements, but scientific support to all this is lacking throughout NATO (except for some) with limited attention given by the STO SET and STO AVT Panels. It is therefore recommended that the issues listed above be addressed in a single activity, enabling a more integrated approach to CBRN protection.

1.2 OBJECTIVES

The Task Group addressed integrated CBRN protection strategies. This focused on lowering the burden on the individual by using a layered approach consisting of contamination avoidance, physical protection, hazard mitigation response, containment and recovery. The specific goal of Task Group was to facilitate the communication and coordination of research on CBRN protection among the participating nations. The Task Group addressed the following topics:

- Defining current and emerging systems for integrated protection;
- Exploring, describing and assessing existing operational concepts and determine key contributing technologies;

- Assessing value and maturity of emerging enabling technologies;
- Facilitating dialogue with operational and technical communities; and
- Facilitating technical cooperation and data sharing.

1.3 APPROACH

This Report addresses the different aspects that should jointly contribute to the protection of the individual warfighters. The main idea is that the current CBRN protective systems provide too large a burden to the warfighters and/or too large a reduction of the operational capabilities of the warfighters. In the attempt to lower the burden it was hypothesized that a combination of methodologies would be needed to achieve this goal. The main reason for this being that the changing operational environments also changes the needs and requirements for the warfighter. Figure 1-1 shows a conceptual schematic overview of this systems approach.

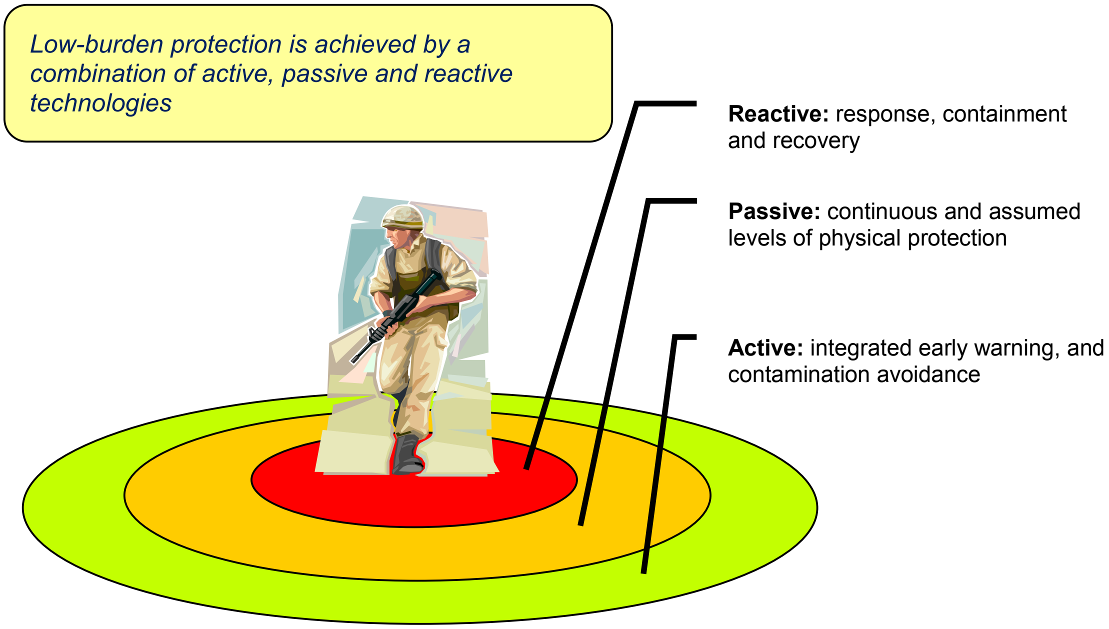


Figure 1-1: Graphic of the Systems Approach of Individual Protection in which Active, Passive and Reactive Technologies Combined Provide the Ultimate Goal of Warfighter Safety and Health.

1.3.1 Active Measures

Active Technologies are defined as technologies that would support the warfighter under operational conditions in enhancing their situational awareness, here on CBRN agents, which enables them to avoid or reduce exposure to CBRN hazardous agents. In view of current physiological strain levels and limitations that individual and/or collective protection systems induce, a systematic approach to reduce this burden should include active technologies that prevent or reduce direct exposure of warfighters to the CBRN hazards. As these active methods are mostly aimed at enhancing situational awareness these active technologies focus on sensor technologies and networking solutions to allow improved decision making for avoidance and exposure reduction. As these technologies have to fit in the larger systems approach of individual protection these technologies should not only focus on sensor technologies, but additionally focus issues such as:

- Data management;
- Network sharing of information;
- Prediction of future exposures;
- Determination of point of origin (source term estimation); and
- Reduction of false alarms.

Any system that is aimed at providing situational awareness to the warfighter should address these and related topics to enable decision making under operational conditions that allows avoidance and reduction of exposures.

When successful such technologies could significantly contribute to reduction of the physiological and logistical burden of individual (and possibly collective) protection, most notably by allowing a reduction in realistic operationally required protection levels – as exposures would be significantly reduced or even avoided. When reliable systems are introduced individual protective systems that would only provide limited levels of protection (‘emergency’ or ‘escape’) could realistically be implemented.

1.3.2 Passive Measures

Passive technologies would constitute the general approach that has been used to date. It is widely known, however, that the current systems, while able to provide high levels of protection, induce a high burden to the warfighter physiologically, psychologically and ergonomically. To achieve reduction of the burden, a systems approach is required that allows the use of Active and Responsive technologies to decrease and mitigate the risks of exposure to CBRN hazards. Still, it cannot be ruled out that limited exposures will occur, and therefore, some level of individual protection is expected to be needed. Many studies have focused on the physiological impact and reduction on task performance (ergonomics) of CBRN protective clothing, some studies have addressed psychological aspects, but only recently some studies have addressed the basic possibilities to make individual protection scalable, to allow more choice and decision making and trade-off analysis of required levels of protection and performance.

Generally, protective clothing imposes a burden to the wearer because of the barrier properties of the materials, reducing transfer of body heat and evaporated sweat, thus preventing optimal body cooling. Furthermore, with increase in thickness, stiffness and numbers of clothing layers, ergonomics and usability aspects decrease, leading to significant decrease in performance while wearing CBRN protective clothing. Although in military CBRN protective clothing, following AEP38, air permeable absorptive materials are widely used, these materials still provide higher levels of strain as compared to a typical Battle Dress Uniform (BDU) – especially with some existing requirements still suggesting that CBRN protective clothing be worn on top of the BDU, significant limitations in soldier operational performance are present. With an increasing amount of operations in challenging climatic conditions and general trends towards smaller scale scenarios of CBRN exposures development of new, thinner, more flexible materials that provide reliable protection, but possibly at a lower level, would lead to lower burden to the soldier – especially when concepts are developed that do not require wearing double layers for protection for prolonged times. For respiratory protection the challenges are somewhat different in that new filtration materials would be required that allow protection of the airways against wider ranges of hazards than has been considered in the past. To make sure the resistance of these new filtration materials does not become too high new materials are needed to obtain sufficient protection against a wide range of chemicals.

1.3.3 Reactive Measures

Reactive Technologies are those technologies that induce a change in a protective barrier and/or to the CBRN agents to minimize or eliminate the effects of the agents to the warfighter. Classically, reactive technologies have been used as decontamination agents and these two properties (reaction and decontamination) are closely linked. An additional area for reactive technologies, however, is the area of technology that helps disclose agents on contaminated surfaces.

In the context of this report, i.e. optimizing warfighter protection while minimizing the burden, reactive technologies may support these goals by allowing a reduction in protective performance of fabrics, allowing them to be more open and comfortable. The reactive technologies could be used and approached in different ways, possibly providing different layers/levels of protection. For example reactive technologies added to uniforms could provide additional protection directly, reactive technologies that disclose areas that have been contaminated will help reduce exposure of warfighters and reduce the amount of protection they will need, reactive technologies for rapid decontamination when warfighters have been exposed may improve outcomes and reactive technologies that allow better protection and easier decontamination of crucial, sensitive technologies will indirectly enhance and help to maintain capabilities for the warfighter after exposure to CBRN agents.

To optimize the application of these technologies for protection of the warfighter, operational procedures and processes may need to be adapted to strengthen their focus on the warfighter. Some of the technologies described here cover a very wide range and fall under the categories that coincide with the protection of sensitive equipment as the operational goals of preserving crucial technologies and protecting warfighters will mutually strengthen each other and could greatly enhance operational capabilities after an exposure to CBRN agents.

1.4 MAJOR FINDINGS

The technologies presented in this report all have the potential to contribute to lowering the burden and maintain sufficient protection to the warfighter, when the overall approach of contamination avoidance, mitigation and cleaning are jointly taken into account.

One general trend is the miniaturization of sensors, which not only makes them small and lightweight, but often reduces power consumption too. This important trend potentially allows groups of dismounted soldiers to take larger arrays of sensors, enhancing the overall sensor capability when all these sensors are connected to a common network. Low-cost, miniaturized sensors, including non-specific and embedded sensors, facilitate the availability of sensors to the dismounted warfighter, providing them with enhanced situational awareness. That will allow them to reduce exposure and identify fast routes to non-contaminated areas. Thus, overall hazardous exposure and contamination would be reduced and requirements for the protection levels of the protective clothing systems could be reduced, directly impacting the physiological burden to the warfighter.

False alarm reductions and source term estimation technologies is the approach to enhance overall specificity and sensitivity. Especially the specificity of the combined sensor technologies must be maximized to ensure a minimum of false alarms. False alarms not only cause a significant burden on the CBRN logistic chain, but also tends to reduce the trust in the system and lead to a reduction of use in operational environments.

Novel material technologies to improve absorption, filtration or blocking of hazardous agents are a critical component in reducing individual burden associated with passive protection. Examples of great technology developments are:

- Improved filtration and absorptive materials, to enhance the range or capacity of chemicals absorbed (or adsorbed);
- Development of new material (nano) technologies that enhance liquid repellence and protection;
- Improved integration of the clothing and mask systems to allow for better system protection;
- Improved insight in the behavior of the protective system to allow reduction of protective materials, also reducing the burden; and
- Enhanced operational capabilities due to the overall burden reduction by applying modular approaches for protective clothing as a system.

Combinations of these technologies and application of modular concepts would obviously lead to enhanced capabilities as well, but, these developments have been studied separately and not in combination with each other, integration issues will need to be studied to explore synergy effects of the technologies, or potential negative interactions.

The research in reactive technologies focuses around the development of coatings that provide reactive functionality, either disclosing agents or decontaminating them. Most of these technologies have been developed on solid or flexible, but continuous surfaces to disclose agents or decontaminate such surfaces, as is relevant for sensitive equipment. As explained before, that in itself is relevant for burden reduction to the warfighter, but more work may need to be done to expand these capabilities to fabric structures so (some of) these technologies may be integrated into the clothing itself, further allowing protection optimization.

At that point these decontamination (reactive) technologies may be considered as part of the passive protective technologies and in conjunction with that work to reduce consequences of contamination. When implementing decontamination technologies as part of the passive protective systems consideration should be given to the speed of decontamination that can be achieved when using the reactive technology on a fabrics or material structure. The combination of new technologies and new approaches to individual protection seems to provide opportunities for improving protection and lowering the burden. This approach will require optimization of the decontamination technologies on the passive protective systems (clothing, boots, gloves, respirator), rapid additional decontamination in the field and possibly secondary decontamination when needed further down the operational and logistics chain. With such a systems approach disclosure technologies will become very important as the knowledge on the size and magnitude of any contamination will be imperative to ensure optimization of the passive and reactive technologies to any type of contamination.

Chapter 2 − ACTIVE TECHNOLOGIES

2.1 INTRODUCTION

Active Technologies are defined as technologies that would support the warfighter under operational conditions in enhancing their situational awareness, here on CBRN agents, which enables them to avoid or reduce exposure to CBRN hazards. In view of current physiological strain levels and limitations that individual and/or collective protection systems induce, a systematic approach to reduce this burden should include active technologies that prevent or reduce direct exposure of warfighters to CBRN hazards. As these active methods are mostly aimed at enhancing situational awareness, these technologies focus on sensor technologies and networking solutions to allow improved decision making for avoidance and exposure reduction. As these technologies have to fit in the larger systems approach of individual protection these technologies should not only focus on sensor technologies, but additionally focus issues including:

- Data management;
- Network sharing of information;
- Prediction of future exposures;
- Determination of point of origin (source term estimation); and
- Reduction of false alarms.

Any system that is aimed at providing situational awareness to the warfighter should address these and related topics to enable decision making under operational conditions that allows avoidance and reduced exposure.

When successful, such technologies could significantly contribute to reduction of the physiological and logistical burden of individual (and possibly collective) protection, most notably by allowing a reduction in realistic operationally required protection levels – as exposure would be significantly reduced or even avoided. When reliable systems are introduced individual protective systems that would only provide limited levels of protection (‘emergency’ or ‘escape’) could realistically be implemented.

These developments, however, may require changes in current NATO operational procedures on sensor data management, analysis and reporting, as described in ATP45. As the data available would be needed within the local network of operations on the ground, as well as through the military hierarchy, additional procedures may need to be developed, either within ATP45 or as a new ATP, to allow both pathways for usage of the sensor data to be effective. In general this would strengthen a trend from hierarchical data reporting to network sharing and reporting of useful data.

This chapter describes some of the technologies that will enable these developments and provide some examples of how these technologies are progressing. In the first section (2.2) the use of small, embedded and low-cost sensors is described as these technologies may allow a relatively cheap and efficient way to build a distributed sensor data network. A disadvantage of distributed sensors may be that these sensors will have to be in contaminated areas to provide information of CBRN hazards. These sensors could also be point sensors that have some inherent risk of missing hazardous releases. Another approach to sensing technologies that may allow more widespread screening of an area would be using Stand-Off detector Systems (Section 2.3). An additional benefit of such system may also be that they do not necessarily have to be exposed to contamination, so they would be more easily recovered and adjusted as operational conditions change.

An important aspect of an enhanced CBRN situational awareness would be to predict hazard 'clouds' as well as estimate the source, i.e. the point of origin and amount that was released. In Section 2.4, technologies will be described that support these capabilities which would be relevant for exposure avoidance as well as intelligence on potential adversaries. Furthermore, it is important for such sensor networks to provide reliable data. When sensors would have high sensitivity but low specificity high rates of false alarms would reduce the usefulness of these systems to local operations. However, algorithms that exploit information from networked sensors (discussed in Section 2.5) can be used recognized and reduce impact of false alarms.

2.2 SMALL/EMBEDDED SENSORS

2.2.1 Bio-Sensors (Belgium)

2.2.1.1 Abstract

New technological advancements in molecular biology open access to bio-dosimeters and bio-sensors concepts. The biosensors use a multilayer concept with a passive sampling technology. The molecular targets from the surface of the inside of a B-agent are detected through the transformation of the binding of the target with a bio-chemical layer in a measurable signal through a transducer. More efforts are being made to continue the development of this transducer.

2.2.1.2 Introduction and Background

Conventional microbiological methods based on morphological features or biochemical identification are well developed but not well suited for the rapid identification technologies of some Bio Warfare Agents (BWAs). The safety, portability, and sensitivity are some important parameters that must be considered to propose an answer at the direct question: what types of bio-agents are present in my sample on the battlefield?

For 20 years, the technological developments in biology and molecular biology have given new ways to answer bio agent detection. Molecular genetic technology is actually the best way to identify a biological agent. But this technology is not fast enough to use in a first alerts system. To achieve this goal, the molecular genomic technology based detection must be accomplished by some (optico-) physical means.

The main core of the molecular genomic identification is the use of genetic markers (or targets) that can be amplified by Polymerase Chain Reaction (PCR). The follow-up of the genetic markers for certain BWA is progressively better documented through the reference systems like the real time PCR. However these lab based systems do not make it possible to determine presence/absence of biological agents for field operations in a timely manner.

With this intention, a follow-up of the genetic markers technology will have to be developed with small size physical devices for bio detection.

To prevent and treat an exposure to a bio agent before the development of symptoms, any bio detection technology for individual protection must follow two tendencies:

A) A detection of the agent in real-time.

B) A capability to trace the recent history (24 h) of the exposure.

This is called a detect-to-warn concept. Development of an individual biosensor or detector for bio-agents is not as easy. The challenge is to combine the autonomy of a system (load associated with heavy power supply) and the sensitivity of the same system that can be saturated by background particles with a long collection time.

Several groups of research are working to develop such a device. The only demonstrators of this kind of technology are bio-dosimeters and biosensors discussed below.

2.2.1.3 Technology

A bio-dosimeter is a portable bio collector and is fully active, whereas a biosensor is a portable passive electronic system. A bio-dosimeter typically contains an active sampler with a cartridge that must be read through an analyzer to make a decision of the presence/absence of a bio-agent. Due to its simplicity, a bio-dosimeter is easier to build than a sensor.

Active sampling is a main characteristic of a bio-dosimeter. The technological advancements in active collection of samples often use a pump to do filtration on a membrane or an inertial impaction in a direct way or with a cyclone both on solid or liquid media (Figure 2-1).

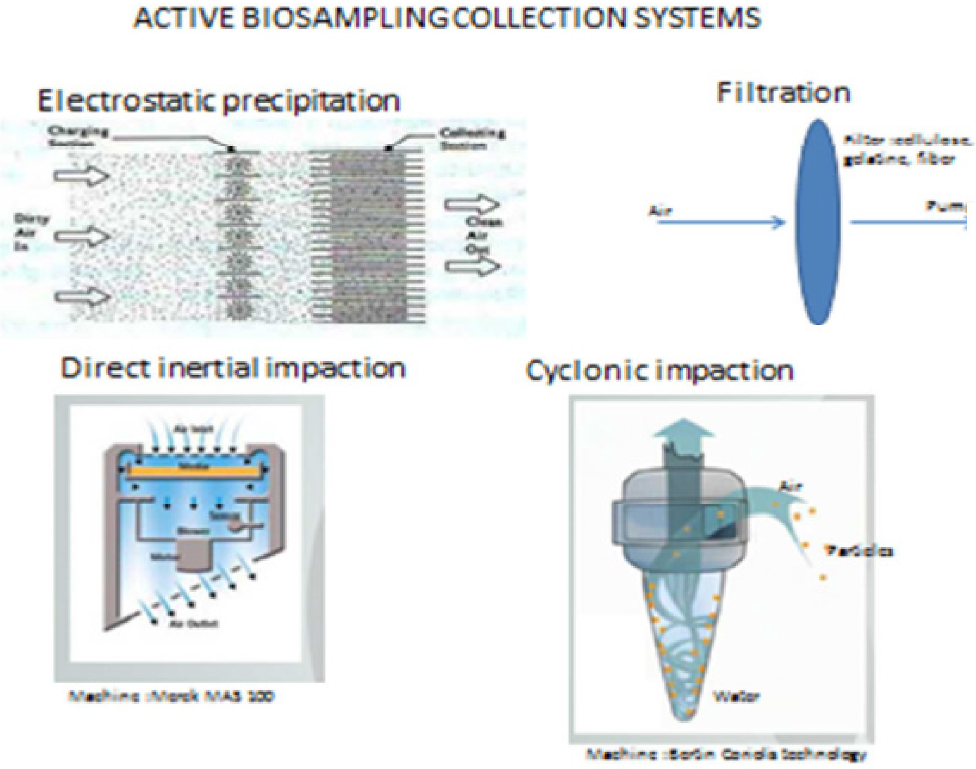
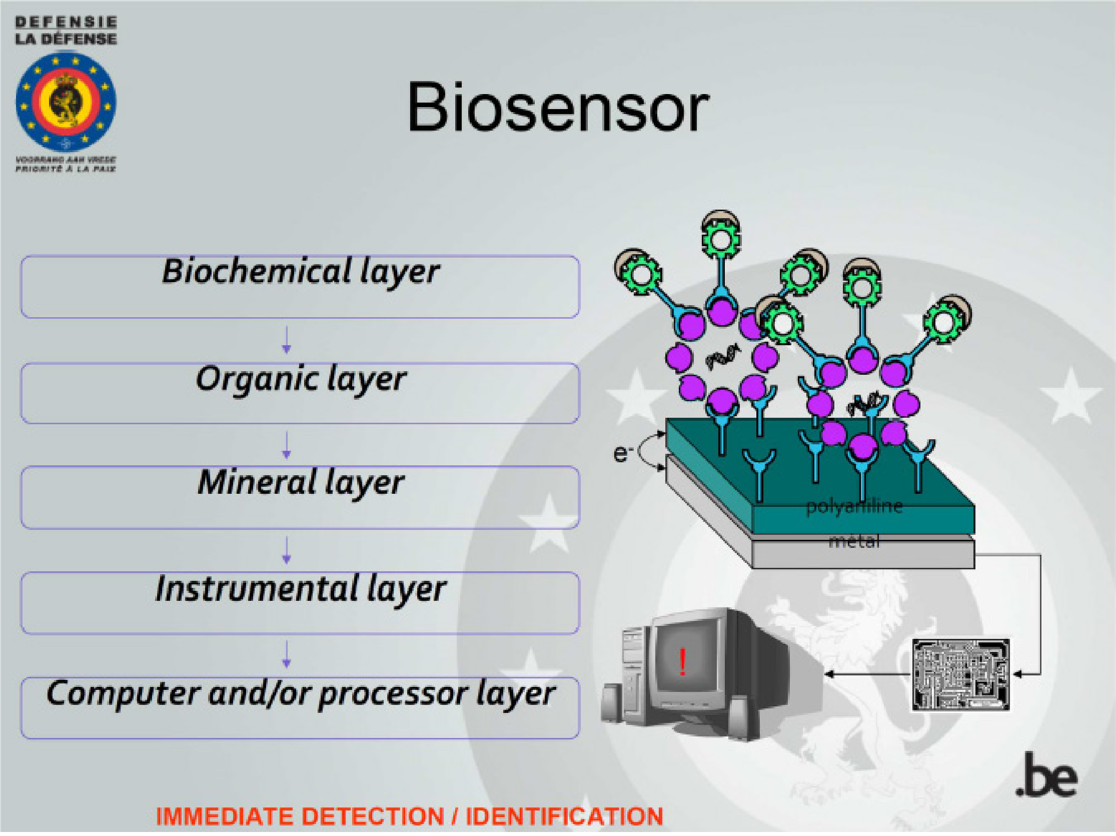


Figure 2-1: Collection Systems for Bio-Dosimeters.

After the collection of the samples in the cartridge, the use of referenced analytical technology like real-time PCR, ELISA (Enzyme Linked Immunosorbent Assay) or sequencing can be used to identify the biological agent. Rapid field technology like lateral flow assay can also be used but with less sensitivity and for a sub-set of agents.

There are difficulties to adapt this system to wearable size for a warfighter which negates the advantage of the simplicity of the technology. The actual models of bio-dosimeters are also too noisy and not discrete for use on a military battlefield. The discontinuity between the dosimeter and the necessary analysis step to identify the agent also negates the use on the battlefield. More efforts must be conducted to continue the development of biosensors.

In a biosensor, the sampling is always passive by diffusion, sedimentation, ad- or ab-sorption. The biosensors can answer the challenge of the size and increase the probability to wear on the uniform during operations. This can be possible because the conception of a sensor to use in biology is a succession of layers that can be miniaturized (Figure 2-2). The design of each individual layer is rather well controlled. The challenge is to assemble all the layers between them and especially to understand their interfaces.



DEFENSIE
LA DÉFENSE

VOORRANG AAN VREDE
PRIORITÉ À LA PAIX

Biosensor

Biochemical layer

Organic layer

Mineral layer

Instrumental layer

Computer and/or processor layer

IMMEDIATE DETECTION / IDENTIFICATION

Figure 2-2: Succession of Layers in a Biosensor.

The concept of biosensors consists of (Figure 2-3):

1) Passive collection system.
2) Use of a platform with molecular recognition events where the bio-targets can be used to detect and recognize biomolecules and genetic material.
3) Emission of a signal through a transducer and amplification of this signal.
4) Detection of the signal using microelectronics devices.

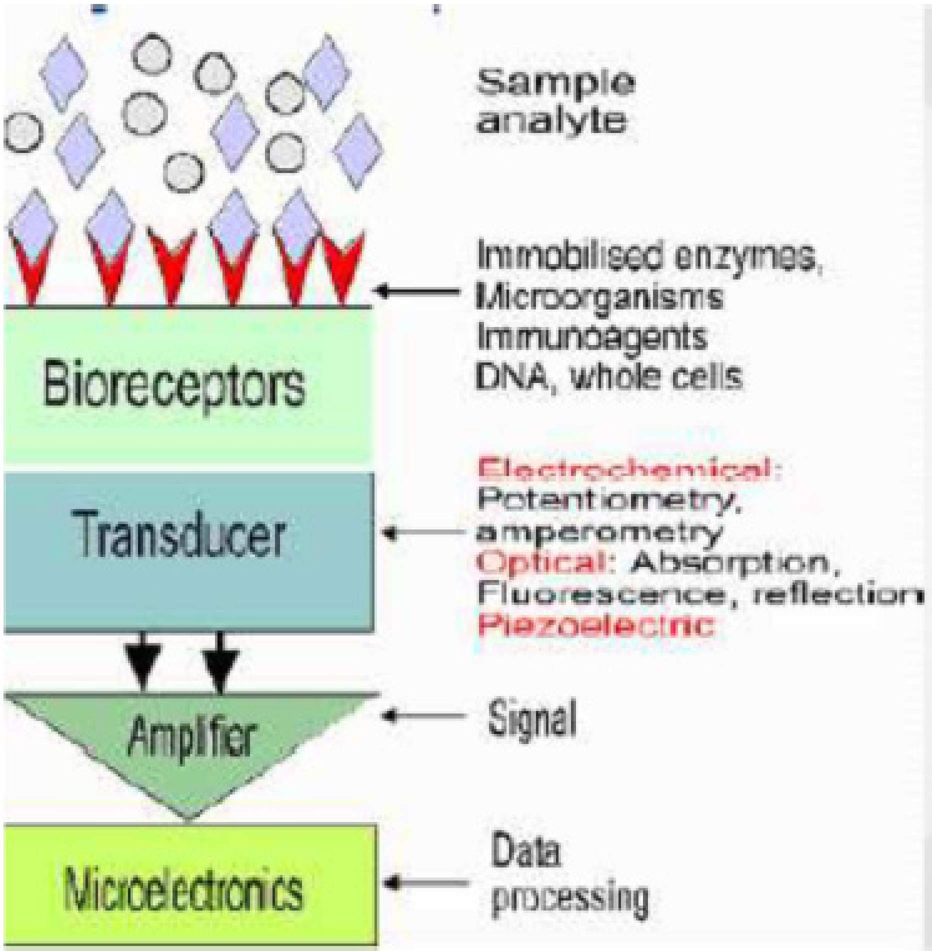
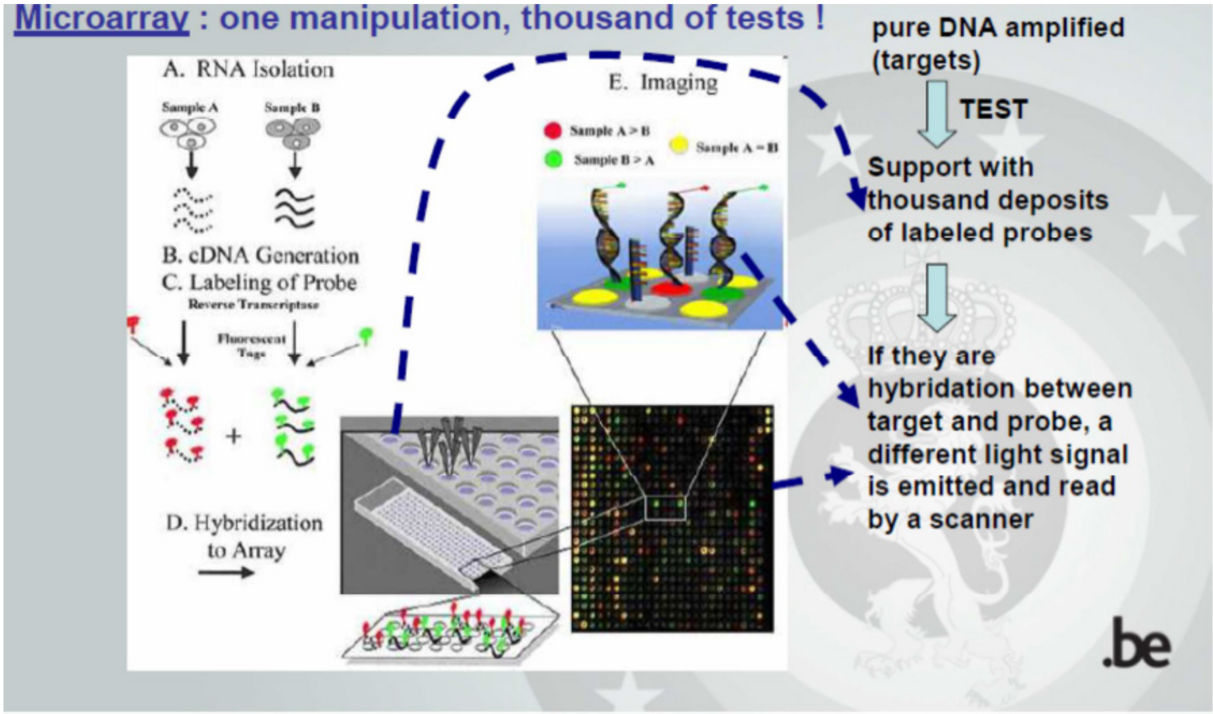


Figure 2-3: The Biosensor Concept.

New technologies include:

- Hybridization on microarray (Figure 2-4): DNA/RNA from the targets bound specific oligonucleotides fixed on a solid support (e.g., glass, metal, …).
- Immunoassay on microarrays (Figure 2-5): Surface proteins of the targets bound monoclonal antibodies fixed on solid support.
- Aptamers (Figure 2-6): Surface proteins of the targets bound specific oligonucleotides (3D interactions) fixed on a solid support.



Microarray : one manipulation, thousand of tests !

pure DNA amplified (targets)

TEST

Support with thousand deposits of labeled probes

If they are hybridation between target and probe, a different light signal is emitted and read by a scanner

Figure 2-4: Hybridization on a Microarray.

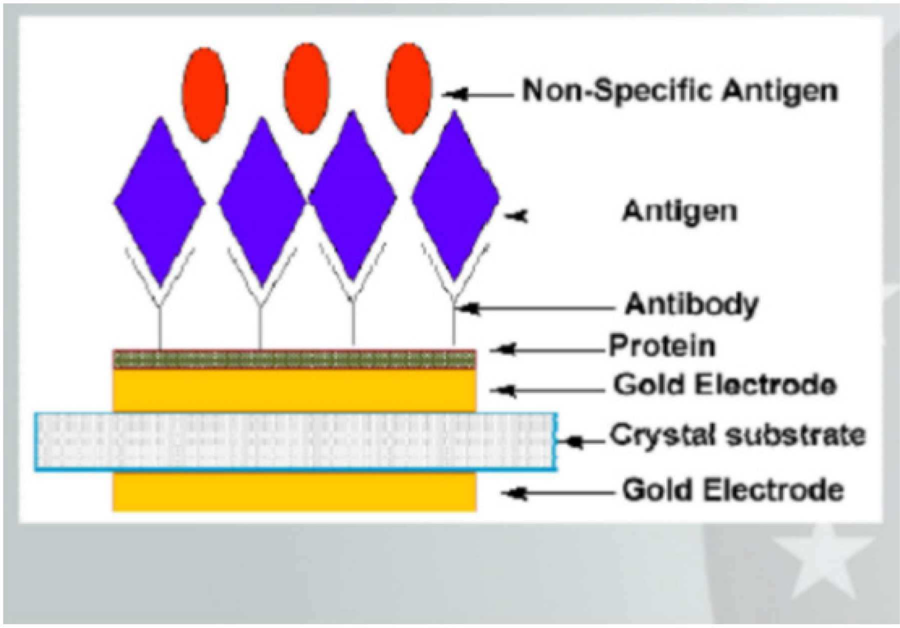


Figure 2-5: Immunoassay on a Microarray.

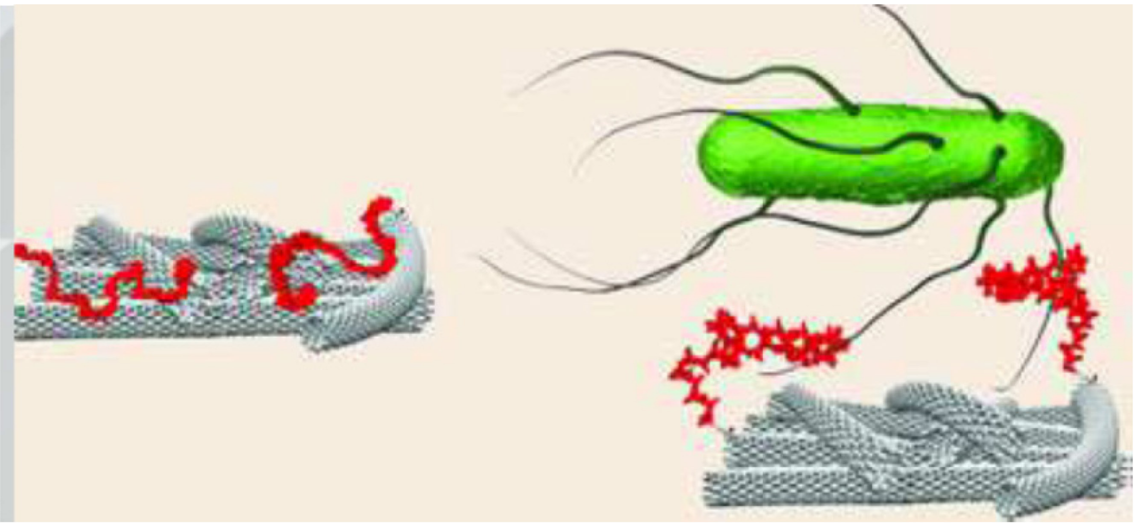


Figure 2-6: Aptamers (Red) on Fibers Bound the Surface on a Bacteria (Green) © Willey-VCH.

One of the difficulties of using these technologies with biomolecules is to attach them on the mineral layer of the sensor. A robotic spotter (Figure 2-7) must be used to "print" the mineral layer treated with an organic layer to fix the biochemical spotted products with chemical bounds (for example biotin).

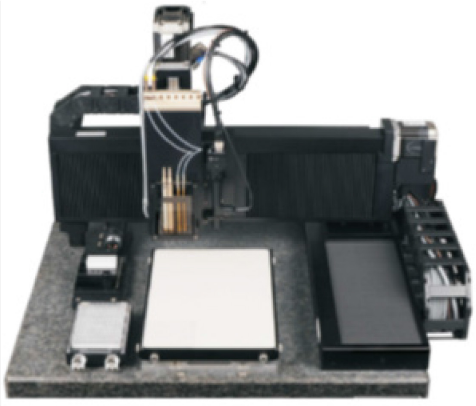


Figure 2-7: Some Technology for the Emission of Signal on a Biosensor.

After that, the engineering can offer a wide variety of devices to produce a signal associated with an electronic treatment (Figure 2-8):

- The modification of the locale resistivity on a semi-conductor chip.
- The production of an evanescence wave (light or fluorescence) on an optical fiber (Figure 2-9).
- The use of the cantilever effect on microscopic captors (Figure 2-10).
- Sophisticated systems like Microwave Accelerated Metal-Enhanced Fluorescence (MAMEF) (Figure 2-11).

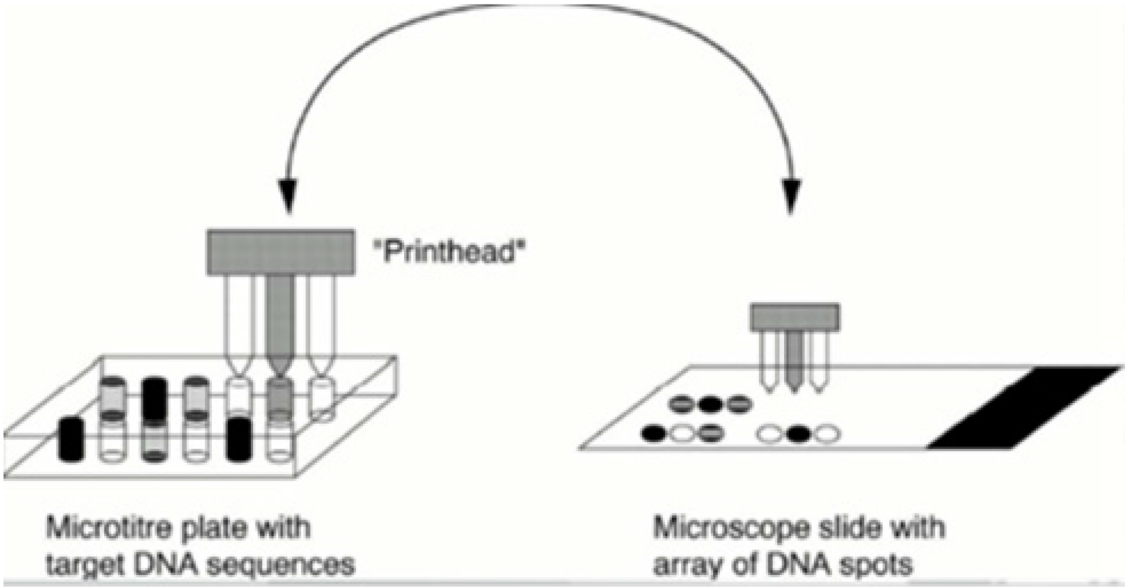


Figure 2-8: Robotic Spotting of Biomolecules on a Support to Compose a Sensor.

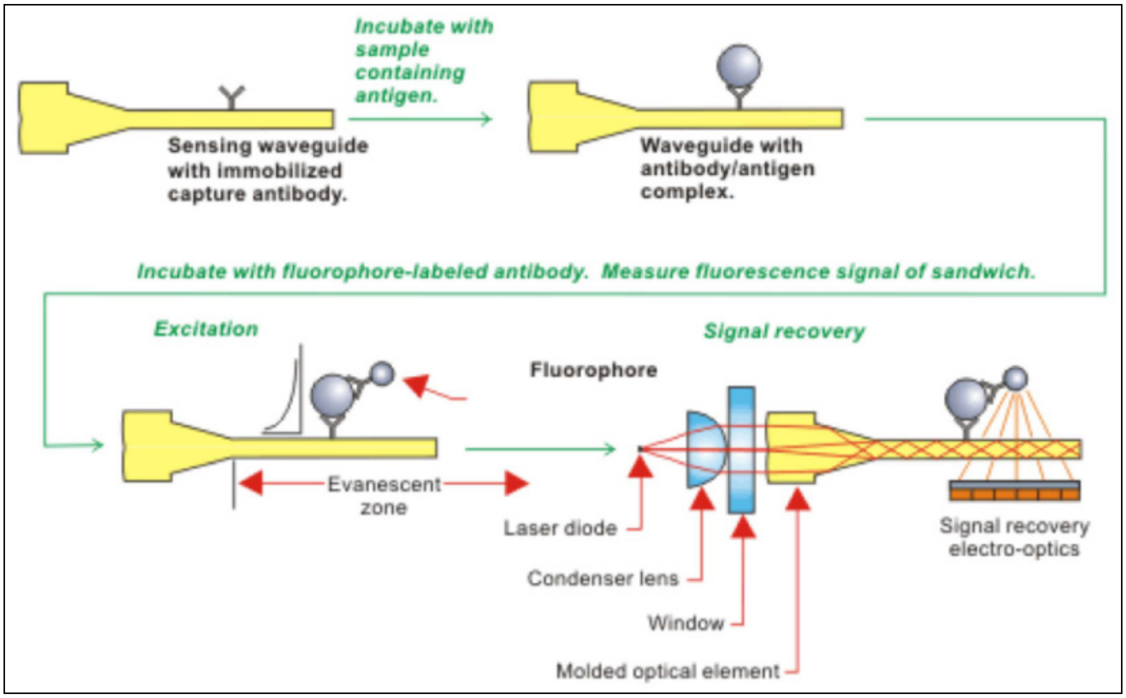
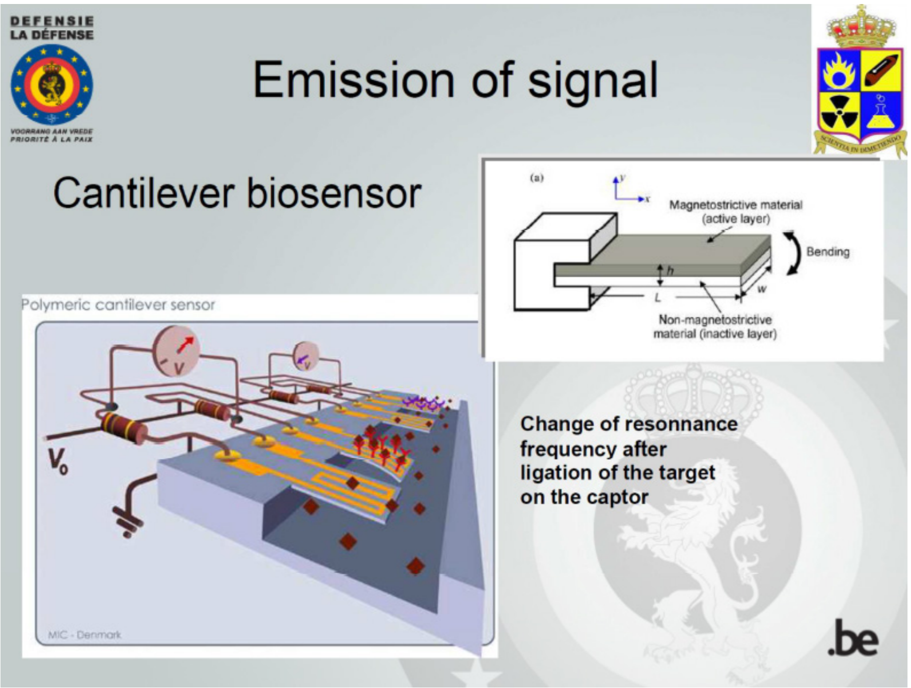


Figure 2-9: The Evanescence Wave Concept.



DEFENSIE
LA DÉFENSE

Emission of signal

Cantilever biosensor

Change of resonnance frequency after ligation of the target on the captor

.be

Figure 2-10: The Cantilever Biosensor Uses the Change of Resonance Frequency (which is measured) on a Cantilever Solid Microscopic Support where Detectable Biochemical Events Occurs on Fixed Biomolecules.

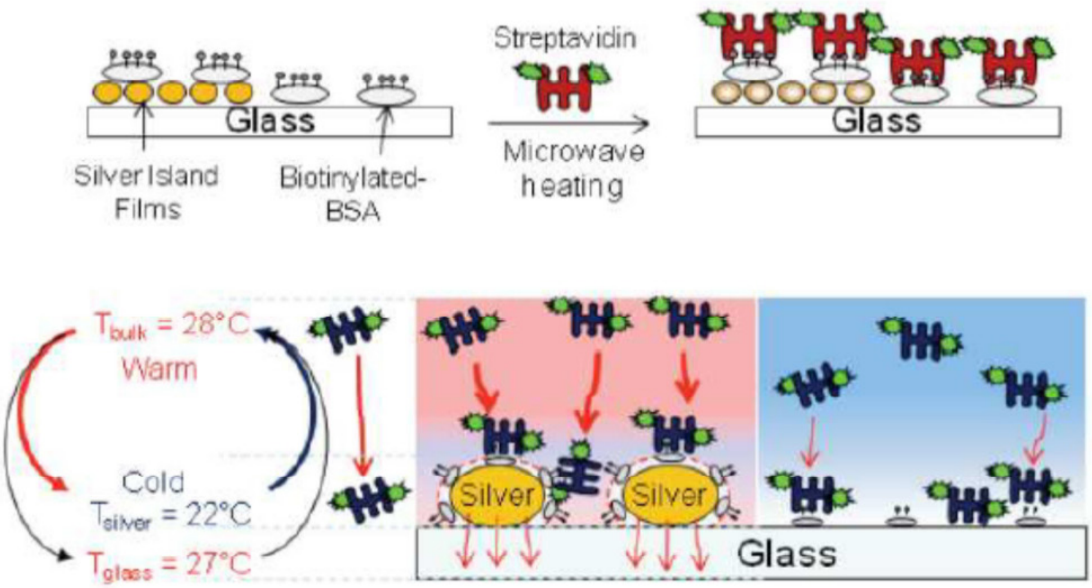


Figure 2-11: MAMEF or Microwave Accelerated Metal-Enhanced Fluorescence: (http://theinstituteoffluorescence.com/Publications%20pdf/57.pdf).

Future miniaturization of big powerful technology used in bio detection like LC-MS, FLAPS or nanopore sequencing (http://www.nanoporetech.com/) could be possible and maybe offer new means to use bio detection on clothes. Biosensors still are the most promising way to an individual bio detection service.

2.2.1.4 Conclusions

For field use, it is clear that the biosensors have the advantage of discretion compared to the bio dosimeters. The current drawback to biosensors includes the difficulty of assembly. The near future will be undoubtedly dedicated to the multi-layer bio-sensors. This is due to new industrial techniques to assemble that will make it possible to assemble with state of the art technologies. The reliability and robustness on theater of operations remains to be evaluated.

2.2.2 The Utility of Wearable Sensing for Warfighter Health and Protection

2.2.2.1 Abstract

Current battlefield technology for front line human protective measures is currently lacking the ability to detect and assess risk of a biological and chemical threat to provide timely medical countermeasures. The current reliance on diagnosing the warfighter post onset of overt symptoms leads to impact of mission due to disruptive symptomology.

In recent years, there has been a significant growth in the development of miniature environmental sensors and commercial wearable sensors which would lead to future operational forces' ability to identify these threats pre-symptomatically and without mission disruption. For the purpose of this paper, we will discuss both person-worn sensors (Physiological monitoring) and miniaturized environmental sensors which can be person-worn all as "Wearable Sensors." These technologies will also lead to increased early warning of both chemical and biological exposure for improved mission capabilities and incident management. Where current armed forces rely on larger and continuous battlefield surveillance methods, the move to individual soldiers with wearable sensors for CB exposure would provide a significant real time monitor over wide areas of the battlefield with higher resolution and fidelity.

The S&T challenge is to obtain warning of threat exposure prior to onset of mission disruptive symptoms and the ability of the force to not rely on symptomology. Ultimately this ability can lead to the quicker deployment of medical countermeasures and protective equipment leading to a change in tactics, operations and the ability to save lives of warfighters. This paper will review the ability of wearable sensors to impact the warfighter and to review benefits and limitations of the science and technology drive for future investments.

2.2.2.2 Introduction and Background

Wearable sensors are not new concepts for soldiers in the field. Figure 2-12(a) shows a soldier wearing a GPS device circa 1980. However, with advances in the electronics industry with the miniaturization and reduction of power requirements needed in the semiconductors and the integration of highly complex circuits, wearable sensors are now functional with minimal invasiveness to the person, Figure 2-12(b) and Figure 2-12(c). This advancement in the commercial wearable market can be applied to the defence communities of interest to greatly enhance warfighter health, performance and protection. Generally, wearable sensors for military use can be broken into a few categories:

- Miniaturized environmental sensors (dosimeters, gas monitors).

- Physiological health monitors (PSM).
- Biomarker monitors.

(a) (b) (b)

Figure 2-12: Advancing Progress of Technology Reducing Sensor Size and Utility (a) GPS circa 1980; (b) Smart Watch; (c) Wearable Medical Sensor.

A large portion of S&T research is focusing on development of sensor technology, associated biomarkers for physiological measurement, and area networks for data communication within and across systems to create a single communication dashboard for status monitoring. There are major challenges as noted by a US DoD workshop on Development of Wearable technologies to optimize warfighter health and performance. These challenges include:

- S&T – wearable systems must accommodate operational noise (e.g. motion, dirt, moisture, temperature) using algorithmic processing or other methods to achieve near-perfect physiological readings.
- Clinical Validation – Physiological status assessed by wearable technologies must be associated with medical diagnoses, treatment responses, and functional performance, and verified by DoD medical personnel and policy makers.
- Regulatory – Devices intended to diagnose disease or other medical conditions may require approval by regulatory bodies prior to use.

Leveraging advances in wearable technology to increase warfighter survivability after exposure to chemical and biological threats by maximizing early warning and thereby enabling informed time-sensitive decisions, maybe achieved specifically through host-based sensors. The goal of the program is a suite of wear-and-forget sensors to provide warning of threat exposure prior to acute symptoms. This suite would not include specific diagnostics capabilities, but rather it would provide a cue for further testing of a potential exposure. Such a capability would fill gaps in existing and planned near and mid-term environmental chemical and biological detection systems to broaden the range of threats addressed and prevent surprise.

To accomplish this, program efforts will be directed at:

- Developing an optimized suite of non-invasive sensors to collect human physiological metrics (e.g., heart rate, temperature, eye tracking, gait) and algorithms that rapidly analyze the collected metrics to provide actionable information regarding future health or performance at the individual and unit level;

- Developing robust animal models of health and performance prediction pre- and post-exposure to chemical and biological agents, environmental toxins, and battlefield stresses to better define the data required to expand the predictive power of an all-threat wearable sensor system for the warfighter; and
- Publishing findings to inform S&T investments, program of requirement impact, and possible rapid prototyping and fielding of a version 1 capability.

Current capabilities rely on a warfighter experiencing overt mission disruptive symptoms to trigger a visit to the doctor. In this model, by the time an evaluation of the warfighter is complete, screening assay results are collected, and therapeutics are administered – the warfighter is not combat ready for a period of time. The mission has been disrupted. The future concept – a suite of wearable host-based health readiness and chemical/biological exposure monitors – would allow persistent monitoring of a wide range of relevant general health and chemical/biological targets that relies on pre-symptomatic responses to an injury or exposure. When an alert occurs, the warfighter would be able to get to the doctor sooner and the data from the suite of monitors would provide a general health alert and/or an assessment of the type of threat for the doctor to investigate. Subsequently, screening assays can be targeted to threat type and therapeutics can be administered earlier. The warfighter is combat ready sooner and mission disruption is minimal compared to the existing kit. Other benefits of a suite of monitors could include earlier use of personal protective equipment in the field, greater risk awareness, more effective quarantine, greater force readiness, and improved data for long-term health and performance monitoring.

2.3 POINT DETECTION

2.3.1 PTR Spectroscopy (Germany)

2.3.1.1 Measurement System

PTR-MS (Proton Transfer Reaction – Mass Spectrometry) technology enables real-time measurement of volatile organic compounds. PTR-MS allows the simultaneous real-time monitoring of Volatile (Organic) Compounds (VOCs) present in ambient air (Figure 2-13).

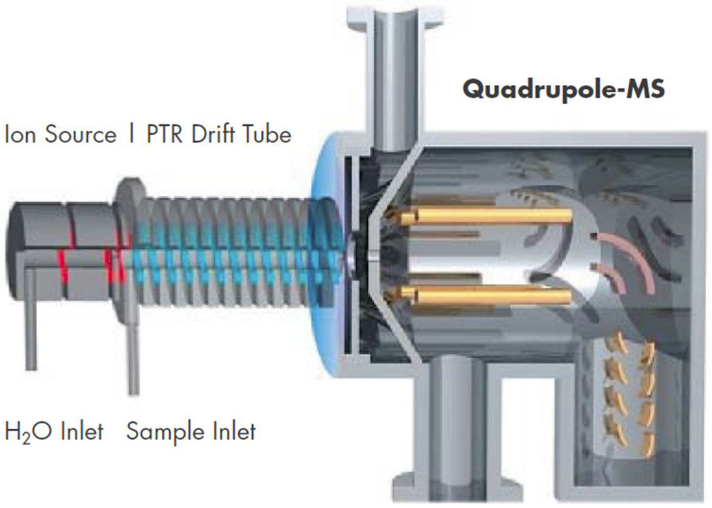


Figure 2-13: PTR-MS Schematic Drawing.

PTR-MS provides absolute quantitative analysis in real-time (response time < 100 ms). The generation of the precursor reagent ions and the chemical ionization of the VOCs are individually controlled and spatially separated processes. This leads to constant and well defined conditions in the drift tube (unlike Ion Mobility Spectrometry (IMS), Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS) and similar technologies) making the determination of absolute concentrations possible without the use of gas standards.

The fundamental process in a PTR-MS instrument is the interaction of protonated water (H_3O^+) with the target gas (R). During this interaction a proton transfers from the hydronium to the trace gas molecule, which leads to a protonated and therefore ionized molecule (RH^+) and a neutral water molecule (H_2O). The proton transfer is energetically possible for all VOCs with a proton affinity higher than that of water (166.5 kcal/mol).

Ion Source

Production of H_3O^+ (optionally also NO^+ and O_2^+) ions at high purity levels (> 99%) from water vapor in a hollow cathode discharge. For an efficient ionization an abundant supply of H_3O^+ ions is necessary. In the most PTR-MS instruments these primary ions are generated in a dedicated ion source that has been developed and was continuously improved to perfection over many years by our renowned experts.

In the ion source H_2O is broken down in a hollow cathode discharge. In a second step the fragments recombine to protonated water ions (H_3O^+) with very high purity (up to 99.5%) and can therefore be injected directly into the PTR drift tube without the need of an interconnected mass filter, which would lead to an inevitable loss of primary ions and eventually result in a higher concentration required to detect the ions.

PTR Drift Tube

The VOC trace gases in the sampled air undergo (mostly) non-dissociative proton transfer from H_3O^+ ions, which are injected into the drift tube via a specially designed inlet (pressure in the drift tube ~ 2.2 mbar); alternatively charge and hydride ion transfer or association reactions of NO^+ and O_2^+ can be utilized.

In the PTR drift tube the actual ionization process of the trace gas molecules takes place. As all common constituents of ambient air (N_2, O_2, Ar, CO_2, etc.) have a lower PA than water, the air itself acts as a buffer gas and only Volatile Organic Compounds (VOCs), which are usually present in very small densities, get ionized. Compared to electron impact ionization, the energy transfer in the PTR process is very low. This effectively suppresses fragmentation and leads to mass spectra that are easy to interpret.

Analyzing System

The analyzing system consists either of a quadrupole mass filter in conjunction with a secondary electron multiplier which allows mass separation and detection of the ions or a Time of Flight (ToF) mass spectrometer which separates the ions according to their mass to charge (m/z) ratio. The resolution is sufficient to distinguish between isobaric molecules and makes an unambiguous identification possible.

Unlike other technologies (e.g. SIFT-MS) PTR-MS does not dilute low concentrated samples by a carrier gas and does not lose precursor ions on their way through a mass filter between the ion source and the drift tube. This makes PTR-MS very sensitive to trace gases in the sample air. Very high intensities of precursor ions and thus real single-digit ppt-range detection limits are the resulting benefits of PTR-MS technology.

Proton transfer from H_3O^+ is a soft ionization method, keeping fragmentation rates rather low as compared to e.g. electron impact ionization often used in GC-MS instruments, thus minimizing coincidences in the mass spectra and improving the identification capability. H_3O^+ ions do not react with any of the major components present in clean air due to their low proton affinity.

A major advantage of PTR-MS is that the samples do not need to be prepared before the measurement (e.g. pre-concentration or chemical separation procedures), thus whole-air samples can be introduced directly into the drift tube allowing for dynamic headspace sampling or VOC flux measurements.

No gas supply is necessary to operate PTR-MS (i.e. for H_3O^+ and NO^+ reagent ions).

2.3.1.2 Experiments

The Chemical Warfare Agents (CWA) Sarin, Soman, Cyclosarin and Tabun were characterized by Proton Transfer Mass Spectrometry (PTRMS). It was found that the organophosphonate and organophosphate type nerve agents tend to fragment depending on the systems adjustments whereas extremely stable ion species are formed at Atmospheric Pressure Ionization (API) conditions like in Ion Mobility Spectrometry (IMS).

The extent of fragmentation can be suppressed by choosing low drift voltages and, much more effective, by using ammonia as reagent gas.

In any case and regardless whether water or ammonia acts as the reagent compound in gas phase ion chemistry at drift voltages around 400 V ionization efficiency meets a maximum. Under those conditions, nerve agents fragment almost completely at pure water chemistry which impairs identification with a high level of confidence significantly. Suppression of fragmentation is required in respect of unambiguous identification and to dispense with the need of a time-consuming pre-separation of multi compound sample mixtures. Switching to ammonia chemistry resolves the problem. The drift voltage can be kept at 400 V. In case of ammonia chemistry fragmentation does not take place distinctly and only peaks corresponding to clusters of un-fragmented nerve agents appear which creates the prerequisites for identification capabilities in near real-time.

On the other hand detection and identification is then based on the molecular ion species and not on a distinct signal pattern. Although agent fragmentation is unfavorable this phenomenon can still deliver additional structural information and, therefore, confirm presence of an agent based on an organophosphorous basic structure. Fragments like fluoro-phosphonic acid do not allow the unambiguous identification of nerve agent but they indicate that the un-fragmented target compound can be traced back to a phosphorous organic basic structure and, therefore, it contributes to increase the level of identification confidence. From this perceptive aimed fragmentation at water chemistry is useful with respect to structural substantiation of data obtained at ammonia chemistry. Of course, it is also possible to operate a PTR system permanently on water chemistry and switch to ammonia as soon as distinct fragments like fluoro-phosphonic appear. In contrast to IMS it is easily possible to switch between water and ammonia chemistry within a few seconds under PTRMS ionization conditions at about 2 mbar. Drift voltage may be changed as well in this context which takes even less time.

Adding ammonia to the sample gas instead of substituting the water reservoir of the system by an ammonia source is easy to put into practice and brings along another advantage: the initial process of ionization in the hollow cathode is not affected under any circumstances. This means that solely H_3O^+ are produced initially and, therefore, calculation models to determine the compound fragmentation should be applicable even if ammonia is added to the drift tube.

Furthermore, in context of this work it was found that PTR-Quad-MS (Proton Transfer Quad Mass Spectrometry) and PTR-ToF-MS (Proton Transfer Time of Flight Mass Spectrometry) spectra recorded under the same experimental conditions differ from each other in detail although the PTR hardware should be identical according the manufacturers statement.

Generally and at both, water and ammonia chemistry, differences concerning the proportional distribution of protonated species and their particular reagent gas adduct clusters (single, double and mixed clustered) have been observed. In PTR-ToF-MS spectra significantly more reagent gas clusters appear. Considering the PTR hardware of both systems being identical this phenomenon is an indication that some reagent gas clusters might not reach the detector plate in the PTR-Quad-MS and get lost depending on cluster stability, the PTR-MS interface and/or the type of mass spectrometer. If this hypothesis was applicable the ToF detector is better suited for nerve agent detection due to less ion losses.

Furthermore, especially at water chemistry the proportional distribution between fragmented and un-fragmented agents is different. Less fragmentation has been observed in PTR-ToF-MS compared to the quadrupole system. Fragmentation and forming of product ions, takes place in the drift tube. Therefore, this phenomenon might be an indication for differences in respect of the PTR hardware. Because fragmentation is unfavorable in any case this phenomenon suggests PTR-ToF-MS to be particularly suited for nerve agent detection.

In overall conclusion it was found that both, PTR-Quad-MS and PTR-ToF-MS, are suitable to detect nerve agents, highly sensitive and with a very high level of confidence in near real-time. In the end the PTR-ToF-MS seems to be an even more suitable technology for nerve agent detection because its sensitivity and detection rate. Considering that also reagent ion clusters contribute to total agent concentration it as also important that this type of ion species do not drop away PTR-ToF-MS.

PTR-ToF-MS is a remarkable and promising technology for future CWA detector technologies in terms of bridging the analytical gap between IMS and classical (Gas Chromatograph – Mass Spectrometry) GC-MS in field applications.

2.3.1.3 Conclusions

The Chemical Warfare Agents (CWA) Sarin, Soman, Cyclosarin and Tabun were characterized by Proton Transfer Mass Spectrometry (PTRMS). It was found that PTRMS is a suitable technique to detect nerve agents highly sensitive, highly selective and in near real-time. Methods were found to suppress molecule fragmentation which was significant under PTRMS hollow cathode ionization conditions. In this context the drift voltage (as one of the most important system parameters) was varied and ammonia was introduced as an additional chemical reagent gas. Auxiliary chemicals like ammonia affect ionization processes and are quite common in context with detectors for chemical warfare agents based on Ion Mobility Spectrometry (IMS). With both, variation of drift voltage and ammonia as reagent gas, fragmentation can be effectively suppressed. Suppression of fragmentation is crucial particularly concerning the implementation of an algorithm for automated agent identification in field applications. On the other hand appearance of particular fragments might deliver additional information. Degradation and rearrangement products of nerve agents are not distinctive for the particular agent but for the chemical class. It was found that switching between ammonia doped and ordinary water ionization chemistry can easily be performed within a few seconds. Making use of this effect it is possible to switch between fragment and molecular ion peak spectra. Thus, targeted fragmentation can be used to confirm identification based just on single peak detection. PTRMS turned out to be a promising technology for future CWA detectors. In terms of sensitivity, response time and selectivity (or confidence of identification respectively) PTRMS performs as a bridging technology between IMS and Gas Chromatography Mass Spectrometry (GC-MS).

2.4 STANDOFF DETECTION

2.4.1 Standoff Detection of CWA and BWA (Norway)

2.4.1.1 Abstract

Standoff detection systems provide the possibility of an early warning of a threat, and can be used for large area surveillance and situational awareness. Their sensitivity is lower than point detectors, and standoff detectors should be used as a useful complement to the existing suite of detectors.

2.4.1.2 Introduction and Background

The capability of detecting airborne chemical and biological warfare agents at a distance is often referred to as standoff detection. Several different techniques are used which all have in common that detection is non-contact, i.e. without sample acquisition. The detection distance can range up to several kilometers under good measurement conditions, and the technology can provide substantially increased situation awareness and gives the possibility for timely activation of protective measures or, for mobile forces, the possibility to avoid contamination.

The sensitivity of standoff detection will necessarily be lower than for techniques that analyze acquired samples. Therefore, it seems unlikely that standoff detectors can replace personal detectors or local area detectors. However, they can be a very useful supplement to the suite of CBRN detectors.

2.4.1.3 Technology

Several techniques that utilize unique spectroscopic features of the threat to be discovered are being used, but the technology depends on the threat to be detected.

CWA Detection

CWAs (Chemical Warfare Agents) in the gas phase have distinct spectral lines that can be used for detection, and most commercial systems for standoff detection use a passive detection scheme in which one examines how the thermal radiation from the background is affected after transmission through the atmosphere. The presence of a CWA (or TIC (Toxic Industrial Chemicals)) in the atmosphere will leave a spectral fingerprint on the background radiation that is detected. This fingerprint is integrated along the optical path of the radiation. Therefore, such systems only give direction information about the threat and no distance information. Current military systems in use are either FTIR (Fourier-Transform Infrared) detectors that acquire the full optical spectrum, or infrared detectors in combination with scanning filter wheels that study the irradiance at a fixed set of wavelengths (typically 10 – 20). The latter technique is used in combination with a detector array and hence provides an image. Most FTIR-based techniques use a single-pixel detector that is scanned vertically and horizontally to build a 2D-image. Detector arrays for FTIR are currently available in low quantities for the civilian market, but can be expected to be available even for a larger military market in the future.

Fourier Transform Infrared Spectroscopy (FTIR)-based detection is flexible in terms of which CWAs or TICs to look for as the full infrared spectrum is recorded and detection is software-based using a library of material absorption spectra, and one may select or deselect substances of interest. Scanning filter technology, on the other hand, is technologically simpler, but is less flexible, because it uses a fixed set of wavelengths. A limitation for both technologies is that it can only detect substances that have absorption lines in the infrared. This applies to all known CWAs, but for some of the TICs (e.g. Cl_2) detection is not possible.

A challenge for passive spectroscopic techniques for standoff CWA detection is to obtain sufficient sensitivity, in particular under conditions with little thermal contrast. If the temperature of the CWA gas is close to that of the background, the sensitivity of the detector will be low, and the detection threshold will be high. Work is in progress to improve this, but the requirement for a temperature difference is still a fundamental limit that renders the CWA-detectors insensitive under certain environmental conditions.

Active techniques use a laser that is reflected off a target and detected at the sensor. The simplest version of this uses two different wavelengths of which one is absorbed and one is not absorbed by the threat. By comparing the detected signals on the two wavelengths, a difference in amplitude will indicate the presence of the threat. If more wavelengths are used, more gas lines can be studied and more threat agents can be detected. Such instruments are more sensitive that those based on passive detection, but are technologically more complex, and can only detect threats that have lines at wavelengths that are available with infrared lasers.

BWA Detection

Biological aerosols contain a vast number of different molecules and do therefore not have the same kind of fingerprint spectra as the CWAs. There is no military standoff detection system available yet, but there exist several standoff detection demonstrators. These all use active techniques that utilize the fluorescence properties, infrared backscatter and absorption properties, or depolarization properties of the agents. The main challenge is to obtain sufficient sensitivity and a low false alarm rate. In particular, discrimination between agents and naturally occurring biological aerosols (like pollen) is a major challenge. For techniques that use fluorescence, operation during high ambient light conditions also reduce performance.

2.4.1.4 Conclusions

The major advantages with a standoff detection system for CWAs or BWAs include the possibilities of detection without contamination, early warning, situational awareness and large area surveillance. Several standoff systems for CWA detection are commercially available, while there are only demonstration systems for BWA detection. The most common CWA standoff detection systems use passive detection and give information of direction, but not distance to threat. Their performance is also weather dependent.

Detection without sample acquisition and analysis is challenging and the threshold for detection is significantly higher than for point detection techniques where samples are acquired. Therefore, a standoff detector does not render all traditional point detectors obsolete, but is rather a useful supplement to them.

2.5 SOURCE TERM ESTIMATION

2.5.1 Chemical/Biological Source Term Estimation (United States)

2.5.1.1 Abstract

Accurate simulations of atmospheric transport and dispersion rely heavily on the source term parameters necessary to characterize the initial release. These source parameters are in many cases not known and consequently based on rudimentary assumptions. A computationally efficient modelling and simulation algorithm that combines backward trajectory and variational data assimilation techniques can improve characterization of release source parameters resulting in a more precise downwind hazard assessment.

2.5.1.2 Introduction and Background

Many types of Atmospheric Transport and Dispersion (ATD) models (e.g., Gaussian plume, Gaussian Puff, Lagrangian Particle, Kinematic Trajectory) are commonly used to predict downwind hazards from atmospheric releases such as Chemical or Biological (CB) warfare agents. However, the utility of these models is limited by the accuracy of the often unknown source term parameters such as location of release, agent type, mass of release and meteorological conditions which are not always well characterized. To mitigate the uncertainty in the source term, a model to predict these variables prior to performing a forward, or downwind hazard prediction has been developed.

The underlying algorithm consists of a combination of modelling systems, including the Second order Closure Integrated PUFF model (SCIPUFF), its corresponding Source Term Estimation (STE) model, a Hybrid – Lagrangian-Eulerian Plume Model (H-LEPM), its numerical adjoint, and the software infrastructure necessary to link them. Figure 2-14 illustrates schematically how SCIPUFF and its STE model are used to calculate a "first guess" source estimate based on the available chemical or biological plume and meteorological observations. The H-LEPM and corresponding adjoint are then used to iteratively refine the SCIPUFF based STE estimate using variational data assimilation techniques. The entire process from beginning to end is completely automated and requires no human intervention assuming automatic data feeds from fielded CB detection systems.

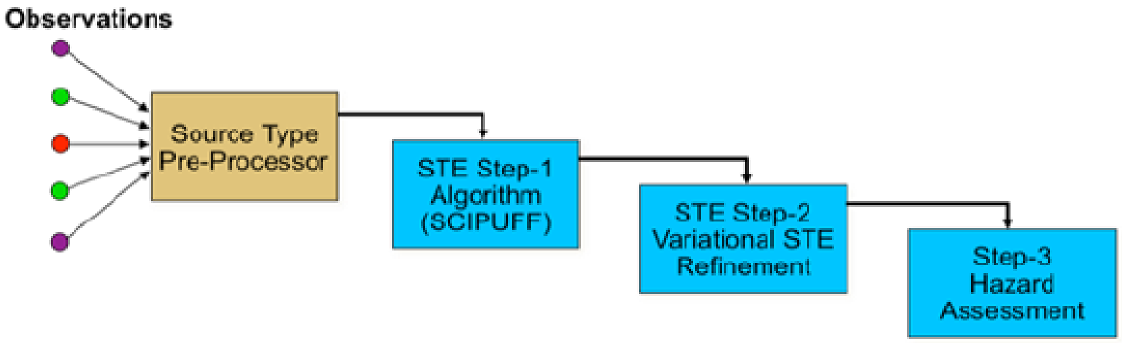


Figure 2-14: Schematic of the STE Algorithm.

The first component utilizes time-series observations (if available) in a source-type pre-processor algorithm to estimate the release type (Instantaneous vs. Continuous). The algorithm uses the length of time that a polynomial fit curve of the concentration time-series is above the sensor noise floor, normalized by the wind speed, to attempt to characterize if the release type can be classified as a short/instantaneous release vs. a longer continuous release.

The second component of this algorithm uses a backward trajectory-based methodology to produce a first guess estimate of the release parameters. This component utilizes the SCIPUFF ATD model. SCIPUFF is a Lagrangian puff model, which uses a collection of three-dimensional Gaussian puffs to represent an arbitrary time varying concentration field. Each individual puff is transported and diffused by the ambient mean wind and turbulent fields, in a Lagrangian framework, similar to standard Lagrangian particle models. The first guess source parameters are computed through an inverse, or adjoint, plume modeling process, where the winds are reversed and a series of chemical releases are made from the chemical sensor observation locations. Inverse (adjoint) plume solutions from the sensor locations with valid detections are handled as separate tracers and then combined in a post-processing step that triangulates the release location, time, and corresponding release mass. Each adjoint field defines an estimate of the release mass at all upwind locations, in both space and time.

The post-processing searches this space for locations where the multiple estimates from different sensor locations are consistent.

The third component of the STE algorithm uses variational data assimilation techniques to iteratively refine the first guess solution provided by the inverse SCIPUFF STE component. In this component of the algorithm, a relatively simple Gaussian plume model has been developed. Because this model uses dispersion information computed on a Lagrangian reference frame, but provides a solution in the Eulerian reference frame, this model is referred to as the Hybrid – Lagrangian Eulerian Plume Model (H-LEPM). The H-LEPM model relies on a forward SCIPUFF simulation to provide a time-history of the dispersion characteristics for the given meteorological conditions. This information is derived from the SCIPUFF STE component described above and provides a computationally efficient means to closely replicate the dispersion patterns produced by SCIPUFF in an Eulerian reference frame. The H-LEPM is intentionally kept very simple in an effort to simplify the development of a numerical adjoint for the H-LEPM. The forward H-LEPM and its numerical adjoint provide the necessary numerical components required to solve the variational minimization problem where we seek to identify the source parameters that minimize the difference between the forward H-LEPM model and the sensor observations. The H-LEPM and corresponding adjoint are then used to iteratively refine the SCIPUFF based STE estimate parameters. In the final step of the algorithm the refined source parameters (Release Mass, Release Location, Release Time) are used in a final forward dispersion simulation using the SCIPUFF model (Figure 2-15).

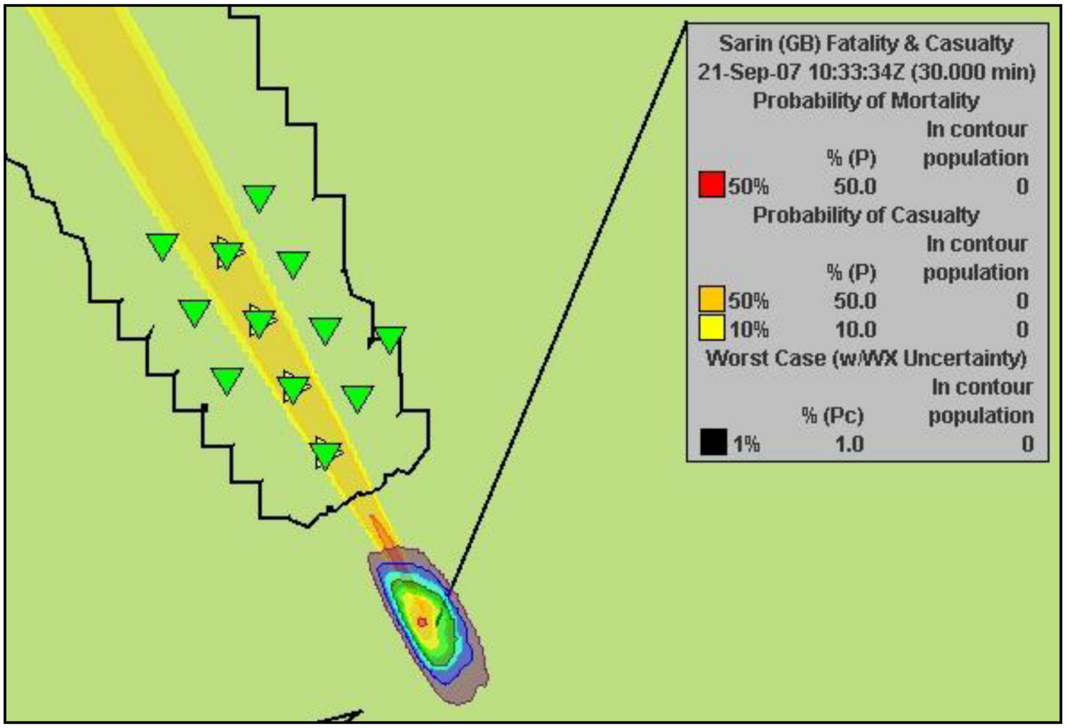


Figure 2-15: Example Probabilistic Source Term Estimate and Associated Refined Forward Hazard Prediction (sensor locations are indicated by green triangles).

The algorithm described above has been implemented into a proto-type which has been integrated into US modeling and simulation tools. This proto-type implementation achieves the entire STE process from loading the meteorological and CB observations, to estimating the source term, to the final depiction of the plume hazard based on the observational data provided. The demonstration works within the framework of the Graphical User Interface (GUI) that can utilize observational data formatted in the Allied Nuclear, Biological, and Chemical (NBC) messaging formats (ATP-45), and illustrates its functionality in supporting the warfighter.

2.5.1.3 Analysis of Results and Conclusions

The STE algorithm is a step towards providing a fully automated capability to quickly characterize the source parameters of an outdoor CB dispersion event and produce a hazard prediction solution, which closely matches the observations. While numerous approaches to this problem exist, each with their own strengths and weaknesses, this approach attempts to address this problem in an operational environment where computational resources are limited and a timely solution is critical.

Future work will progress in a number of areas. First, the software will be continue to be hardened and tested in a broader set of scenarios to ensure the existing algorithm works robustly. Second, addressing the situation where the solution breaks down and is under-determined is planned. The approach is to develop methods to better characterize the background error covariance from available information. If successful this work will allow the algorithm to address multi-dimensional problems with multiple viable solutions without needing an operator to manually specify the background errors to narrow the search. Finally, it is anticipated that this work will be extended as part of a system to characterize source parameters in urban environments.

2.5.2 Practical Example Small Networked Sensors to Locate Noxious Sources (Netherlands)

2.5.2.1 Introduction

This subsection describes small networked sensors that can be used to locate noxious sources. Chemical monitoring with electronic noses (e-noses) in the Port of Rotterdam serves as a practical example. The e-nose is a non-selective on-line detection system that responds to changes in the air composition/quality. By using (semi-conductors and/or chemical) sensors for detection and recording in combination with artificial intelligence software for memory data analysis, e-noses are able to monitor and guard applications with the potential of gas emissions that could pose a risk of odor nuisance, environmental damage or hazardous situations. As such, e-noses have potential for civil, industrial and military use (Figure 2-16).

Figure 2-16: Example of Existing Sensor for Detection of Noxious Gases In or Near the Port of Rotterdam.

2.5.2.2 Working Principle and Potential

The Port of Rotterdam is one of the world's major centers for oil and chemicals. Therefore, odor exposure is inevitable in the port area and the neighboring residential areas. On a yearly basis, inhabitants of the neighboring areas file approximately 4000 – 5000 odor complaints or incidents. In order to record and identify these odorous gases, an array of semi-conductor gas sensors are used in an e-nose. These sensors have not been programmed to detect specific gases, rather, the combination of four sensors will provide a recording that, if it provides a similar graph under similar circumstances, could provide a fingerprint for identification of gases in the air. For example, in Figure 2-17 and Figure 2-18 an array of four different semi-conductors is exposed to fumes containing fuel oil and H_2S. It is clear that each semi-conductor reacts differently with the chemicals, henceforth resulting in a distinct signal.

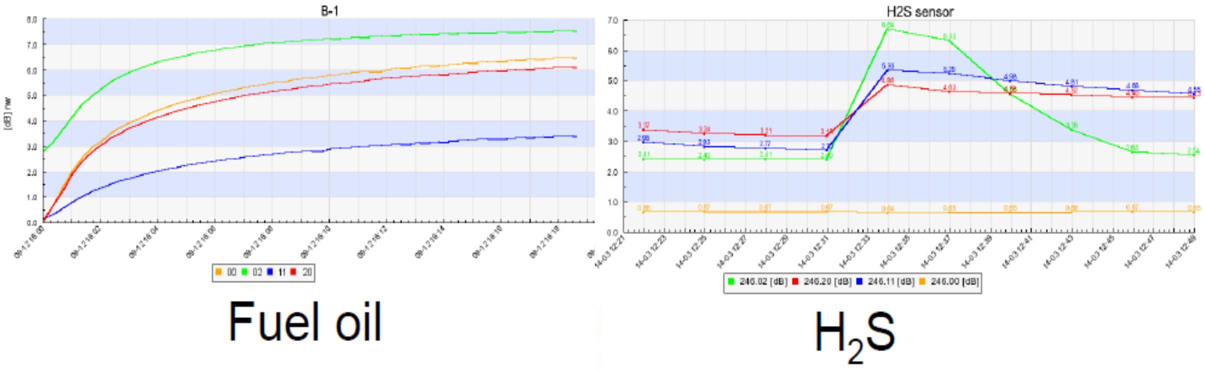


Figure 2-17: Examples of A-Specific Responses to Different 'Agents', the Combined A-Specific Sensor Responses Lead to Specific Signatures for Each Agent, thus Providing a Relatively Simple Low-Cost Response System.

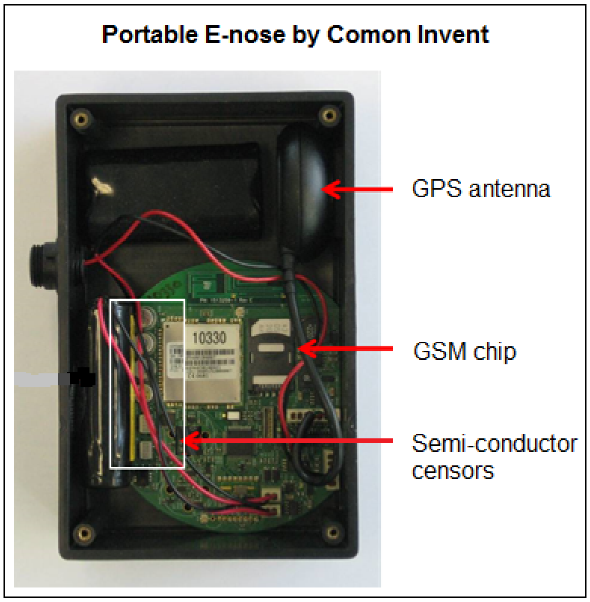


Figure 2-18: Low Cost Components for the E-Nose System.

In two pilot studies, known as “Chemical monitoring with electronic noses in the Port of Rotterdam”, electronic noses (e-noses) helped investigate the complaints filed by people in the neighboring residential areas and trace the sources. The array of four semi-conductor gas sensors were used in a network of 10 e-noses (in an area of 50 square kilometers) and two mobile e-noses (in pilot project one) and extensively in a network of 30 e-noses (in an area of ten square kilometers) and five mobile e-noses (in pilot project two). The studies showed that there is a clear relation between odor plume and odor complaints. Approximately 77 percent of the odor complaints matched with e-nose recordings. In fact, in some cases, the e-nose was able to record a change in air composition 45 minutes before the first complaints were registered. Odor observation can help with validation of sensors. Taking into account the direction of the wind, the sensor network can help identify the source, thereby enabling the “ejector” to reduce odor exposure and impact of the emission. One should note also that not every chemical incident has an odor emission, but that does not inhibit detection by the e-nose as they are also able to register odorless chemicals (that can still be toxic).

Human smell sensing can be experienced once vapors have impact on the “sensor part” of the nose, which is followed by four functions: detection, recording, memory search and identification. This process can be replicated by machines. An e-nose, for instance, is an instrument comprising a variety of gas sensitive sensors. The e-noses that are used in the Port of Rotterdam performed measurement of air composition on the basis of conductivity of semi-conductors consisting of metal alloys. The semi-conductor, for example, is a very small layer of tin oxide that is put under tension. When it comes into contact with molecules in the air, oxygen radicals leave the sensor’s surface. Dependent on the type of binding, the substance at the surface is oxidized or reduced. As a consequence, the conductivity of the semi-conductor will change. With pure air, this is a continuing process which produces a standard background. However, when a (chemical) component, different than the usual components, reaches the sensor surface, the conductivity will notably change. Thus, there is a marked change pertaining to the standard/normal background.

As mentioned previously, the e-nose can consist of different semi-conductors, each with its own features. Using the e-nose’s recordings, it is possible to recognize patterns, also known as “fingerprints.” Ultimately, these fingerprints can be used to identify gases. However, first, an electronic nose needs to be “trained” with qualified samples so as to build a database of reference. For instance, an array of sensors could be taught what a standard environment is and what the acceptable limits are as well as to start recording as soon as the sensors detect a chemical compound that goes outside this acceptable range. Furthermore, it is possible to transmit sensor signals of e-noses in the field to an online data communication linked to a database on a remote computer system using a GSM chip (one of the unique features of the e-noses used in the Port of Rotterdam area). Each incoming e-nose reading can be compared with known fingerprints stored in a database. This method enables real-time environmental monitoring and identification and quantification of gases.

2.5.2.3 Applications and State-of-the-Art

The e-nose can be used for signaling and, to a certain extent, identification of gas patterns with the help of a database. Using fairly standard electronic components, small and robust devices can be produced at low costs, which add to the possibility to use e-noses effectively (and profitably) in numerous civil and industrial areas (Figure 2-19). For instance, the e-nose could serve as an odor management tool. The pilot project in the Port of Rotterdam showed that an e-nose network can be used to monitor the odor and safety situations in a specific area. As the system was able to record changes in air composition before neighboring residential areas were confronted with the fumes, e-noses could (potentially) be used to trace the source early in order to limit the impact of the gas fumes and decrease the number of odor complaints. In a similar way, it could be used as a process management tool for industry and perhaps even contribute to optimization of industrial processes.

Figure 2-19: Flexible Systems for the E-Nose Allowing Distributed Sensing Capabilities.

The pilot projects in the Port of Rotterdam also showed that e-noses can monitor 24/7 and provide real-time information online (refreshing the data every so often, three minutes *in casu*). Provision of real-time information could make e-noses suitable to be used as a safety management and incident control tool. It has a fast recognition of (unexpected and/or industrial) emissions resulting in incidents and could, therefore, contribute to faster and better information gathering and decision making. It could be a useful tool for first responders among others. As such, it has military potential as well. E-noses could be applied to areas such as personnel and population safety and security as well as compound protection. For instance, one could install e-noses in the area surrounding a military compound. The e-nose could emit warning beeps as soon as it the sensors detect air that goes outside the range of acceptable limits compared to the standard environment.

E-noses could potentially also be installed on military convoys. Obviously, the sensor will have to take into account exhaust gases of the other vehicles. If one can recognize the recordings e-noses show when they detect exhaust gases, it is possible to correct it in order to better observe other (potential dangerous) gases in the air. When failing to do so, there is a chance that the exhaust gases frustrate reliable detection and recording of other gases in the air.

Another possibility would be to attach portable e-noses to soldiers' uniforms. When using a real-time monitoring system, one could see a change in atmosphere as soon as, for instance, the soldiers were to walk into an area where chemical agents have been used. Although the e-noses' records currently do not immediately reveal which gas is in the air (further sampling efforts are valuable for identification of the perceived gas), detection of a change in the atmosphere could provide a warning mechanism. It would thus be a suitable tool for gas reconnaissance (e.g. chemical warfare agents).

E-noses have great potential and provide a plethora of benefits in a variety of sectors. However, the suitability of an e-nose for a specific application is highly dependent on the required operating conditions of the sensors in the array and the composition of the gases being detected. For instance, when an e-nose is exposed to a one-folded gas under laboratory circumstances, its records will provide a certain fingerprint that can be used to identify that same gas if the e-nose would make a similar record under similar (laboratory) circumstances. For laboratory tests, where outdoor air conditions are currently under investigation with different operating conditions (e.g. temperature and humidity will be different in open-air applications), the recordings may show a different graph even though the gases in the atmosphere are exactly the same. It gets even more complicated when a variety of gases are present in the atmosphere. Not only is the e-nose not yet able to identify individual chemical species within sample gases, but, even under laboratory conditions, certain gases may “interfere” each other (for instance, this happens when an e-nose is exposed to ammonia and nitric oxide at the same time). Thus, even though e-noses offer quick real-time detections that can be used to locate (noxious) sources among others, in regard to identification of gases, it often stays uncertain what value can be assigned to the recordings.

2.5.2.4 Future

E-noses have enormous potential for numerous applications. Suitability of e-noses for a specific application will remain dependent on the required operating conditions of the sensors in the array and the composition of the gases being detected. It seems unlikely that a universal e-nose capable of identifying any gas type with high efficiency for all possible applications will be build. Nevertheless, the results of research so far are promising and learning processes of e-noses are developing. This encourages further development of the sensors. For instance, the potential of the mobile sensor networks could be further explored. This could include, for instance, exploring possibilities of adding sensors to human beings. The functionality that the e-nose offers is pre-eminently suitable to register deviations pertaining to “normal” air composition. As such, it could serve as a low-cost reconnaissance or alarming detector that can be worn as part of a uniform. Since one does not immediately know which substance is detected, it would also be interesting to explore possibilities to interlink e-noses with sampling equipment. This could help identify gases and provide input for creating and expanding a fingerprint database. It is important to keep taking into account selectivity and sensitivity limitations of e-nose sensor arrays (and the fact that an array may consist of many different sensors) while building a database. One could explore possibilities for creating software to correct differences between sensors so as to develop a more harmonized database that can be used for a variety of sensors.

2.6 FALSE ALARM REDUCTION

2.6.1 False Alarm Reduction Research (United States)

2.6.1.1 Abstract

Stand-alone point-detection systems are designed to sound an alarm based on a single detection of a target-like signal. However, many point sensors work on spectral principles in which alarms are issued if the spectrum measured at the current time matches the known spectrum of a threat agent. Although these instruments continuously collect data, no temporal information is used to determine whether or not to alarm. In addition, because alarm decisions are made by each sensor individually, a significant number of false alarms can result, which reduces the effectiveness of the detection system. It is possible to reduce false alarms from a network perspective by employing a temporal-spectral approach applied to multiple chemical and/or biological point detectors.

2.6.1.2 Introduction and Background

When using a network of multiple chemical (e.g. Lightweight Chemical Detector (LCD-3)) or biological (e.g., Tactical Biological – TACBIO) point-detection systems, the problem becomes how to best fuse data from the network to reduce/eliminate false alarms and improve system performance. A novel temporal-spectral approach, developed for passive standoff systems, can be used to fuse the information provided by a network of point detectors.

By monitoring the data (spectrally) provided by the sensors over time (temporally), it is possible to identify the detectors that have seen a significant temporal-spectral change. In addition, combining and comparing this temporal-spectral information from the identified detectors can greatly increase the Signal-to-Noise Ratio (SNR) over that of a single spectral-based detector. This significant increase in SNR allows the detection thresholds to be raised and the false alarm rate to be significantly reduced.

The temporal-spectral detection algorithms function to detect targets by using statistics from time t_1 to detect targets at time t_2. The algorithms are developed as follows. Let l represent the number of spectral samples and let $\mathbf{x}_{t1}$ be an $l \times 1$ column pixel vector at sample time t_1. In multivariate statistical analysis the Mahalanobis distance squared of a test pixel spectrum from the mean of the background class is given by:

$$D_{AD} = \left(\mathbf{x}_{t_1} - \hat{\boldsymbol{\mu}}_{t_1}\right)^T \hat{\mathbf{C}}_{t_1}^{-1} \left(\mathbf{x}_{t_1} - \hat{\boldsymbol{\mu}}_{t_1}\right) \tag{1}$$

And in the literature is known as an Anomaly Detector (AD). In Equation 1, $\hat{\boldsymbol{\mu}}_{t1}$ and $\hat{\mathbf{C}}_{t1}$ are the estimated mean and covariance respectively.

By turning Equation 1 into a ratio and making use of past statistics we can form the Temporal-Spectral Anomaly Detector (*TSAD*), which is given as follows:

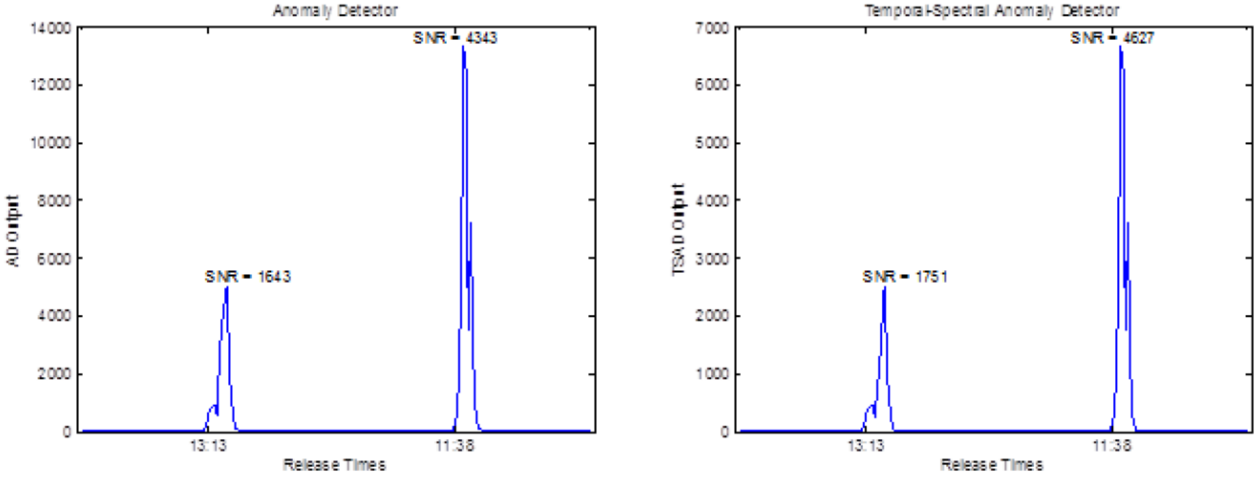
$$D_{TSAD} = \frac{\left(\mathbf{x}_{t_2} - \hat{\boldsymbol{\mu}}_{t_1}\right)^T \hat{\mathbf{C}}_{t_1}^{-1} \left(\mathbf{x}_{t_2} - \hat{\boldsymbol{\mu}}_{t_1}\right)}{\left(\mathbf{x}_{t_1} - \hat{\boldsymbol{\mu}}_{t_1}\right)^T \hat{\mathbf{C}}_{t_1}^{-1} \left(\mathbf{x}_{t_1} - \hat{\boldsymbol{\mu}}_{t_1}\right)} \tag{2}$$

Equation 2 is a ratio of anomaly detectors. In order for the *TSAD* to improve detection performance the anomaly (e.g. gaseous plume) is assumed not to be present at time t_1 or at least that the concentration of target gas has increased from time t_1 to time t_2. Under this assumption the ratios in Equation 2 will be larger than one for any spectrum t_2 $\mathbf{x}$ that contains an anomalous temporal signal.

In order to further enhance SNR performance temporal averaging can be applied. Each window can use a different amount of spectra averaging, but in general windows t_1 will use more averaging than window t_2 (Figure 2-20).

2.6.1.3 Analysis of Results

Baseline algorithms for both the TAC-BIO and LCD-3 detectors have been developed. For the LCD-3, preliminary analysis against a two year long environmental data set show that most, if not all, of over 15,000 false alarms recorded during the data collection period could be eliminated. For the TAC-BIO detectors, false alarms were reduced by 80%.



(a) **(b)**

Figure 2-20: (a) AD SNR Results Using Fluorescence and Coincidence Histories; (b) TSAD SNR Results Using Fluorescence and Coincidence Histories.

2.6.1.4 Conclusions

Although current stand-alone point-detection systems are designed to sound alarms based on a single detection of a target-like signal, spectral and temporal principles can be employed in a networked system to allow for a greater anomaly detection capability. These algorithms can be utilized to increase the signal-to-noise ratio that allow detection thresholds to be raised and the false alarm rate to be significantly reduced. Preliminary testing has shown a false alarm reduction of nearly 100% in LCD-3 point chemical detectors and 80% in TAC-BIO point biological detectors.

2.7 CHAPTER CONCLUSIONS

The sections on sensor technologies show that progress has been made on new technologies that can support protection of the warfighter against CBRN agents. One general trend is the miniaturization of sensors, which also reduces power consumption. This important trend potentially allows groups of dismounted soldiers to take larger arrays of sensors, enhancing the overall sensor capability when all these sensors are connected to a common network. In addition to the miniaturization of specific sensors the use of unspecific and/or low cost sensors (possibly with reduced sensitivity and reliability) may further enhance the overall network sensing capability, provided there is a sufficiently large number of them distributed within the relevant operational environment. The entire scope of low cost, miniaturized sensors facilitates the availability of sensors to dismounted warfighters and may provide them with enhanced situational awareness. This will allow them to reduce exposure and identify fast routes to non-contaminated areas. The overall effect will be a reduction in hazardous exposure, which may result in lower requirements for protective capacity and allow protective ensemble designs that are more focused on lowering the physiological burden to the warfighter.

An important challenge is determining and meeting the required specificity or targets for the sensors. Meeting requirements for a limited set of hazards/agents targets is more feasible than a wider range of hazards/agents likely to be needed (CWA, BWA, TICs, and TIMs). Furthermore, the numbers of sensors and the complexity of a networked system must be considered as part of the logistical burden. Any wearable sensor system for warfighters must, therefore, analyze the balance and trade-offs between benefits to exposure reduction, clothing physiological burden reduction, and potential increases in cost and complexity of networked sensor system.

In addition to small sensors that provide strengths in networks and large numbers, additional sensing capabilities, such as stand-off detection systems provide value. The use of distributed sensors in the area where warfighters operate will not be able prevent all exposure, but can reduce the number of personnel exposed and the total dose to those exposed. That may happen when the warfighters are directed away from contamination or given the opportunity to seek shelter before the arrival of agents. The technologies mentioned in this chapter may facilitate such capabilities and therefore, reduction of the burden to the warfighter.

For both technological general approaches, i.e. low-cost distributed sensor networks and stand-off detection the basic idea to use these technologies to establish the source of contamination release should also build further situational awareness of the contamination. This estimation of the source and its volume and time characteristics will further support understanding of the area where warfighters may safely go and thus further reduce or avoid contamination. It may also provide information to help suppress further attacks.

False alarm reductions are an important topic across all sensor and source term estimation technologies. The approach is to enhance overall specificity and sensitivity. Especially the specificity of networked sensor technologies must be maximized to ensure a minimum of false alarms. False alarms not only cause a significant burden on the CBRN logistic chain, but also tends to reduce the trust in the system and lead to a reduction of use in operational environments. Trust in the warning system leads to more confidence in assuming only the minimum protective posture required for the situation and furthers the lessening of burden.

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Chapter 3 − PASSIVE TECHNOLOGIES

3.1 INTRODUCTION

Passive Technologies would constitute the general approach that has been used to date. It is widely known, however, that the current systems, while providing high levels of protection, induce high physiological, psychological and ergonomic burdens to the warfighter. To achieve reduction of the burden, a systems approach is required that allows the use of Active (Chapter 2) and Responsive (Chapter 4) technologies to decrease and mitigate the risks of exposure to CBRN hazards. Even though contamination can be avoided, limited exposures will occur, and therefore, some level of individual protection will be needed. Many studies have focused on the physiological impact and reduction on task performance (Ergonomics) of CBRN protective clothing; other studies have addressed psychological aspects. Recently, studies have addressed the basic possibilities to make individual protection scalable, to allow more choices and decision making and conduct trade-off analysis of required levels of protection and performance.

Protective clothing imposes a burden to the wearer because the barrier materials reduce heat and water-vapor transport, thus preventing optimal body cooling. Furthermore, with increase in thickness, stiffness and numbers of clothing layers, ergonomics and usability decrease, leading to significant degradation in performance while wearing CBRN protective clothing. Although air permeable absorptive materials are widely used (as per AEP38), these materials still provide higher levels of strain when compared a typical Battle Dress Uniform (BDU). This can be more pronounced given some existing requirements that still require wearing the CBRN protective clothing on top of the BDU. With an increasing amount of operations in warmer climatic conditions and general trends towards smaller scale scenarios of CBRN exposures, development of new, thinner, more flexible materials that provide reliable protection is needed.

The challenge for respiratory protection is responding to a wider range of hazards than has been previously considered. This will require new filtration materials to remove high-volatility chemicals that comprise many of the Toxic Industrial Chemicals (TICs). In this chapter an overview of some novel materials is provided (Section 3.3) that should facilitate developments towards new absorptive materials for respiratory protection, and then a few recent developments on new concepts for assessment and modeling are described (Section 3.2). In Section 3.4 new concepts for scalable protection are presented for clothing systems to demonstrate the possibilities. These concepts should allow lower resistance to air flow, heat exchange and sweat evaporation.

These new concepts may require new directives and guidelines. The scalability of protection will introduce more choices of protection levels during operations. This may also affect NATO guidelines on protection levels, such as the dress states as called out in AEP38. As the scalable protection systems introduce more choice in selection of protection and burden, these choices may also introduce more risk and appropriate risk management procedures, preferably based on optimal situational awareness will have to be present to mitigate these risks.

3.2 ASSESSMENT AND MODELING

3.2.1 Introduction and Thermal Assessment and Modeling (Belgium/Netherlands)

3.2.1.1 Introduction

An important aspect of working in CBRN protective clothing, next to the provided protection itself, is the physiological burden it poses to the wearer. Military CBRN protective clothing is designed to be air permeable and depends on the absorption of the agent by activated carbon. In contrast to full barrier materials, that block all air, agents, and human heat loss, military CBRN protective clothing enhances the ability for heat loss. That is because the most important part of human heat loss under warmer conditions is through the evaporation of sweat. Thus, evaporation of sweat is much enhanced by an increased air flow through and under the clothing. But, a too high air flow will limit the capabilities of the absorptive material in the clothing to absorb/repel the agent, thus, reduce protection. To optimize clothing systems in terms of their protection and their thermal burden, models have been developed to support design and development of protective clothing.

3.2.1.2 Principles of Physical Protection

Physical protection against CBRN agents involves blocking the physiological absorption of the agents. In CBRN protective clothing, which is mainly geared towards protection against Chemical Warfare Agents the protection is achieved by using air permeable materials with activated carbon to absorb the agents and allow ventilation of the protective clothing to achieve some level of comfort.

Physical protection is usually considered for three physical states vapors, liquids and aerosols. Activated carbon is the principal technology used in the protection against agent vapors. This is most effective for vapors with higher molecular weights (larger organic compounds). Activated carbon and barrier materials are used to protect against liquids and often enhanced by finishing the garments with liquid repellent functionality. There is a large area of research on improving this super liquid repellent function. Semi-permeable membranes are used to block the liquids and vapors. The filtration mechanism for aerosols is fundamentally different from vapors and liquids, and requires a separate filtration layer for air-permeable protective clothing. As with protection against vapor, clothing closures and interfaces are a crucial aspect in the effective protection that a clothing system provides.

To ensure protection against all agents, a barrier material, blocking all air flow and agent, would be a good option. However, full barrier suits, with maximized protection, not only pose a very heavy thermal burden to the wearer, they also limit the human performance to a very low level, which is incompatible with most military operations. Also, the duration of operations would be limited if Self-Contained Breathing Apparatuses (SCBA) are used. For barrier systems that rely on external air and filtration, interfaces between mask and suit, and often also between suit and gloves and boots, are introduced. These interfaces are always a weak spot in the physical protection and any leakage at those areas will dramatically decrease the effective protection. There is evidence that air permeable systems will actually perform better than barrier systems (either impermeable materials or semi-permeable membranes), as the ventilation through the clothing enhances absorption of the agent. In the barrier systems a distinction needs to be made between complete impermeable materials and semi-permeable membranes. The latter are designed to have a certain level of water vapor transport and therefore, allow some sweat evaporation. Compared to impermeable materials this reduces heat strain. Compared to air permeable materials this water vapor transport is not yet large enough to reach similar levels of heat strain.

In the air flow, relevant to respiratory protection, similar processes play their part. Obviously, an air permeable medium is required to ensure that the soldier is able to breathe. The filter that is placed in the air flow before the mouth needs to be designed to absorb all agents before entering the mouth. As the breathing rate of a soldier, especially during hard work, may be high, a considerable absorption capacity is required. Also, the allowable doses for agents in the respiratory system are generally lower than those on the skin.

3.2.1.3 Modeling and Predicting Physical Protection

Several modeling approaches have been worked on to be able to predict ventilation effects that allow CWA absorption but maximize clothing ventilation for comfort. The most fundamental way is to predict the flow through the clothing and around the body by numerical Computational Fluid Dynamics (CFD) methods [1]-[3] – see also Figure 3-1. These methods potentially lead to a good description of a steady state in flow and absorption and ventilation processes. At the level of a cylinder, representing a 3D model for parts of the human body, these models have been developed and evaluated and are able to predict experimental data fairly well. The dynamics of the system with a moving human being under changing conditions, however, very much complicates this process to the extent that the CFD modelling calculations take a very long time. In practice these are still only feasible under stable and stationary conditions. Also, the drawback is that a large amount of parameters on the clothing, the environment and the human is needed to obtain these accurate results. Finally, comparison to actual experimental data, with human subjects in protective clothing exposed to (simulated) agents, has not yet been done. The CFD models, still potentially have a great future for development of CBRN protective clothing and evaluating its performance in practice. But it will take years before these models have been properly evaluated, validated and verified.

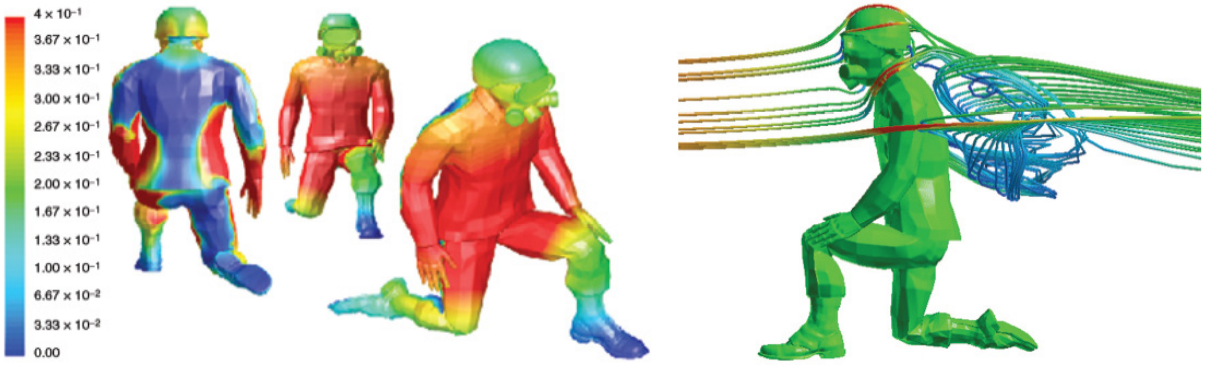


Figure 3-1: Indicative Examples of CFD Simulation Results for a Whole Body. Pictures from US RDECOM Natick Soldier System [41].

Another more analytical approach [4]-[5] allows a basic evaluation of the transport processes through and around the clothing. Brasser *et al.* (Figure 3-2) have studied this in a set-up at cylinder level and this incorporates all aspects of the heat and mass transfer processes that are relevant to the human in protective clothing. At cylinder level these models have been verified and validated on a cylinder with one (absorptive) clothing layer. When real world 3D processes are added (ventilation, local leakage) and multiple clothing layers, this modelling method quickly reaches the limits of its possibilities. On the other hand the modelling method allows very fast simulation of different conditions and requires only a limited amount of known parameters of the clothing. This method, therefore, is useful in quickly analyzing different clothing configurations and their relative differences. The method seems less useful in predicting protection and exposure levels in realistic conditions.

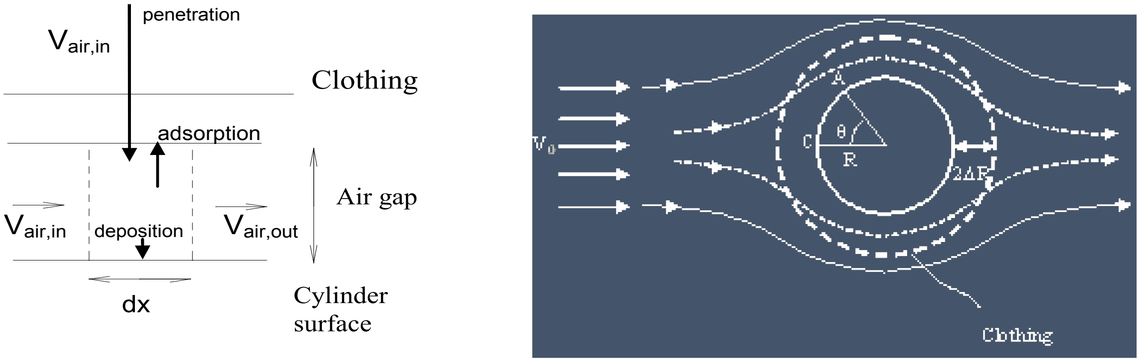


Figure 3-2: Schematic View of the Analytical Approach in Which Several Processes from the Full CFD Simulations Have Been Neglected or are Estimated. Results and picture from Brasser, TNO, Netherlands [4]-[5].

Combination of the two approaches, in which basic processes are studied in full CFD studies and analytical and empirical relationships between parameters are obtained and then put into an analytical approach, may benefit from the best of both worlds and lead to faster simulations and quicker results than CFD models at a more reliable level than the current analytical models provide [6]-[7] (Figure 3-3).

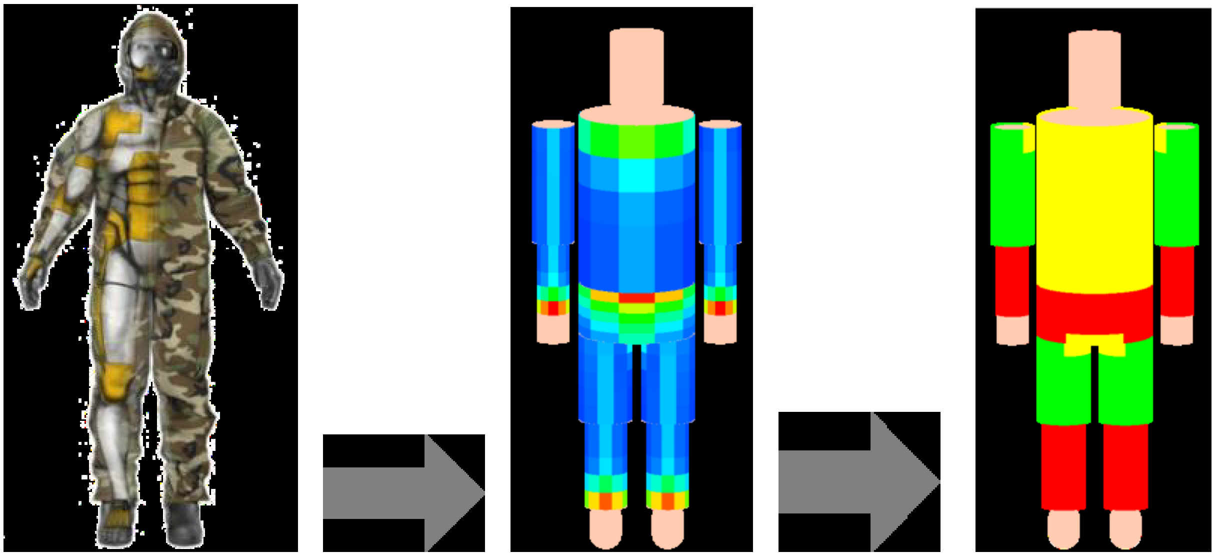


Figure 3-3: Schematic View of a Mixed Model and the Ideas to Translate from a Whole Human, via Cylinders to an Assessment of Exposure of the Human Body with CBRN Clothing. Pictures from Natick Soldier Center, USA [41].

3.2.1.4 Principles of Thermal Strain and Physiological Burden

When working, humans produce heat, due to the inefficient working of the muscles. This heat helps to maintain body temperature, but it may also lead to heat strain problems when the heat loss is lower that the heat production over a long time. Most severe cases of heat strain and corresponding heat illnesses can develop in 15 to 20 minutes, during periods of intense exercise with very low heat loss due to clothing or an excessive environmental climate. There are four main factors that contribute to the development of heat strain in humans: climate, exercise, individual factors and clothing. A good overview of the thermal physiology and the relevant factors is provided by Parsons [8].

Skin temperature increases in humans, and if that does not sufficiently help to relieve the produced heat, we start to sweat. The evaporation of sweat is a very powerful way of removing heat from the body. Therefore, clothing systems that impede the evaporation of sweat may cause severe heat strain even under moderate conditions. The international standard ISO7933 provides guidelines and a model to predict heat strain under different working conditions. However, for higher levels of protective clothing, these models have not been sufficiently evaluated and validated. CBRN protective clothing and especially gas impermeable clothing limit evaporative power to almost zero [9] and imposes high thermal-physiological load to the wearer. The ergonomic aspects of clothing induce a physiological burden as the worker cannot properly perform tasks and also, the task performance requires more energy, cf. Figure 3-4 [9]-[10]. Literature on these latter aspects is available, but very few product standards actually require tests in these directions. Some very basic ergonomics testing is part of ASTM F1154-10 “Standard practices for qualitatively evaluating the comfort, fit, function, and durability of protective ensembles and ensemble components.” These tests provide quite limited information and impose minimal requirements on freedom of movement and task performance. No clear requirements currently exist on the relative performance degradation that is allowable in the working environment. Testing is available, but not yet incorporated into standards due to lack of experience with objective and quantified testing.

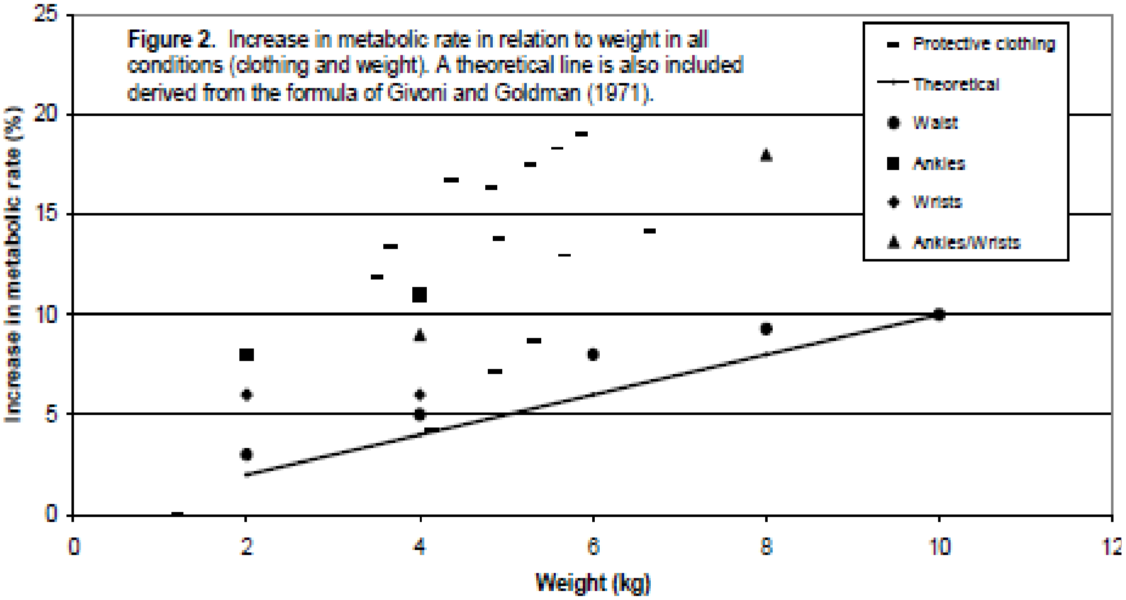


Figure 3-4: Effects of Clothing Bulk and Weight [9]-[10], from EU Project “ThermProtect” [13].

In most cases, the ergonomics evaluation of protective products is performed after they have been produced. More research has been focused over the last few years on (thermal) comfort properties of textiles [11] as comfort is a very complex property, influenced by many different factors, thermal, as well as sensory and psychological [12]. In the area of CBRN individual protection, limited attention has been given to the usability and ergonomics of the systems, and even less to the tactile and wear comfort aspects of these systems. There would be room for improvements in these areas as well as the relationship between tactile skin stimulation and irritation and its relationship with dermal uptake rates of potential hazardous CBRN agents.

3.2.1.5 Modelling and Predicting Thermal Strain

Just as with protection there have been several efforts to model and predict the heat loss from humans. The human thermal physiology has been described well in various models of which the Fiala model [14] is currently most widely distributed and used. The human physiology is well validated with this model, the effect of protective clothing, however, is not well described. Therefore, to predict human responses while wearing CBRN protective clothing, this model is not yet sufficiently useful. Within the US Army another approach has been chosen and their model is based on the very extensive database of human subject experiments, also with (CBRN) protective clothing [15]. Their model is validated for wearing clothing, but is only valid within the metrics and constraints that have been studied. The model results also have limited use for improvement of design of protective clothing. The UK and Canada have similar models that include combinations of the models above but these are not generally available. Canada [16] has produced tables with guidelines for working times under various conditions, including wearing CBRN protective clothing. These tables have been incorporated into NATO ATP-65.

In the Netherlands TNO has developed a computer simulation model (SCOPE-Light) that predicts the heat strain in humans with a specific focus on the impact of protective clothing. SCOPE-Light may also be used to show how different clothing systems will perform under different actual working conditions and may be used to optimize clothing systems [17]-[21]. The model has been developed for the Netherlands Armed Forces and its focus has been on predicting safe working times and work-rest schedules for military personnel wearing (protective) clothing and providing some degree of prediction of discomfort. An example of study results is given in Figure 3-5 – the model allows one to clothe different areas of the body with different numbers and types of layers. This not only allows study of changes in a layer, but also the effect of differences in body area coverage.

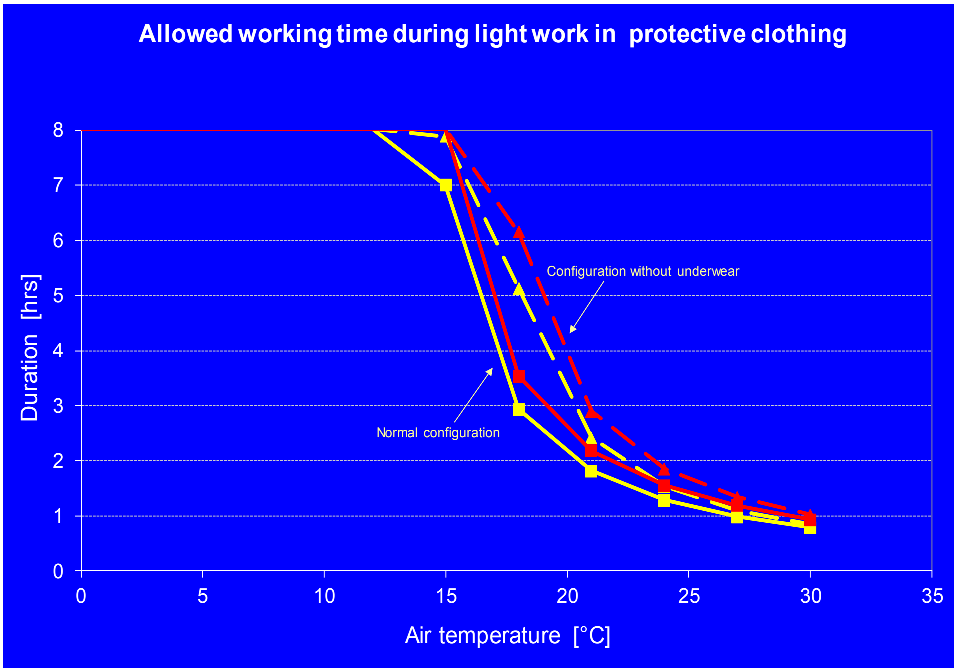


Figure 3-5: An Example of Simulation Results with Different Configurations of Clothing and the Predicted Safe Work Duration for Various Environment Temperatures (x-axis) [19].

3.3 NEW MATERIALS

3.3.1 Omniphobic Fabric Coatings − Superhydrophobic Ultraoleophobic Nylon: Cotton (United States)

3.3.1.1 Abstract

When protective gear is contaminated by CWA, cleaning the surface requires considerable time, money and large amounts of logistical support. Protective gear that exhibits Superhydrophobicity (SH) and Superoleophobicity (SO) would provide substantial reduction in the threat associated with CWA, and would support full-dimensional protection based on technologies that reduce the contact time and area between the CWA and protective gear since contamination avoidance can be achieved by shedding CWA prior to decontamination. Many current textile materials do not resist the full range of real CWA. In addition, most of these fabrics lose their effectiveness under dry and wet abrasion. New fabrics were developed that combine new yarn structures with new fabric constructions that have the required geometry and surface chemistry to provide SO and SH materials while resisting structural changes when abraded.

3.3.1.2 Introduction and Background

Surface modification of soft materials has recently gained a great deal of interest from both academia and industry. The objective was to extend a previously developed mathematical analysis of SH and SO fabric structures in order to develop durable SH and SO fabric that repels liquids over a wide range of surface tensions, volatilities, densities, viscosities, and chemical components such as major Chemical Warfare Agents (CWA). Specifically the materials:

- Enabled shedding of CWA (GB, GD, and VX) as well as impure agents via super-oleophobic technology.
- Developed CWA-repellency test methods along with simulants.
- Created robust CWA-repellent fabric.

By combining current state-of-the-art technologies in SO, robustness, and fabric construction, they aimed to extend the research to ensure shedding of CWA and to overcome the low abrasion resistance of current materials. This was achieved through three technical approaches, described in the following sub-sections.

3.3.1.2.1 Molecular Modeling of the Chemical Interactions Between CWA and the Polymer/Fabric Surface

Some SO fabrics resist G-agents, but not their simulants, others resist the simulants, but not the agents. When liquid is in contact with a solid, the molecules can reorient to minimize the liquid-solid surface energy. Likewise, the molecules making up the solid surface also reorient. This reorientation is difficult to measure experimentally, but is readily modeled theoretically using Molecular Dynamics (MD) simulations. In this effort, the interaction between CWA droplets and fluorochemically modified polyamide and cellulosic fiber surfaces were modeled. This approach was used to simulate the interactions of real CWA and CWA simulants with fluoro-modified textile surfaces.

3.3.1.2.2 Modeling and Preparation of Biomimetic Artificial Duck Feathers

Duck feathers use the Lotus effect to create their robust SH nature. However, they maintain their SH even as the duck rubs against embankments and submerged debris. They are able to shed water even after dry and wet abrasion because the structure of the feathers keeps the filaments spread to an optimum spacing to ensure superhydrophobicity of the feathers, i.e. they exhibit durable SH. The fibers were modeled and they also modeled yarn and fabric structures to determine fabric constructions that will enhance the durability of SO and robustness of fabrics, especially against CWA, that is constructed with artificial duck feather yarns.

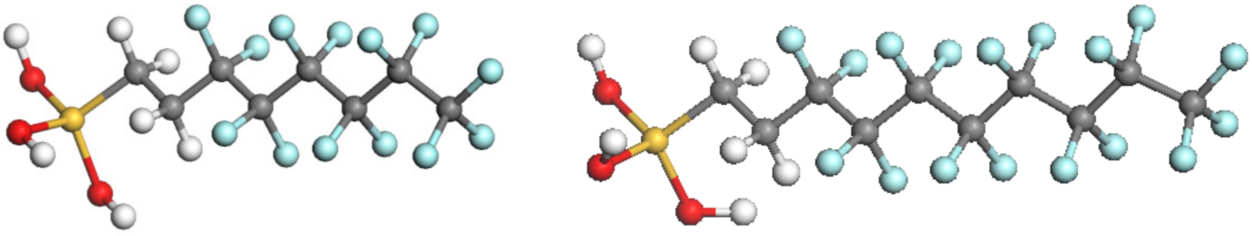
3.3.1.2.3 Fabric Construction and Evaluation

Fabric constructions were explored to combine the simulated duck feather yarns into the fabric structures designed in the previous effort. In order to maintain the required yarn spacing in the fabric, new fabric constructions, such as a leno weave double cloth, were required. Once prepared, the fabrics were evaluated for their wetting behavior and robustness to ensure the fabrics retain their properties, even after abrasion and laundering. At the culmination of the proposed project the investigators provided a robust CWA repellent fabric sample.

3.3.1.3 Results and Discussion

3.3.1.3.1 Molecular Modeling of the Chemical Interactions Between CWA and the Polymer/Fabric Surface

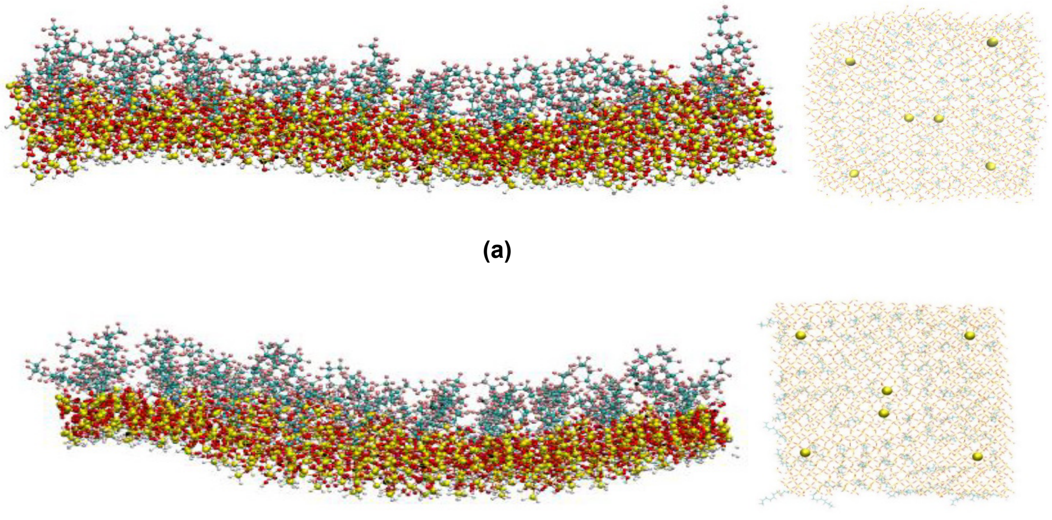
The amorphous cellulose and Polypropylene (PP) surfaces were built as reference surfaces and to validate the method. The molecular model of both surfaces were created in the Accelrys Materials Studio® software program [22] and run with the LAMMPS [23] software program and utilizing the High Performance Computing (HPC) [24] Center at NC State. The Polymer Consistent Force Field (PCFF) was used because it is proven to be accurate and efficient in polymer simulations. In the experiments with the nylon-6 and TCFS, the nylon-6 fabrics were first treated with PAA then TCFS and finally either the C8 or the C6 fluorosilane, whose molecular structures are given in Figure 3-6. TCFS is assumed to fully cover the substrate surface and to be fully crosslinked after treatments. However, it is too computationally (and time) demanding to calculate the entire system during the MD simulations with such little gain in accuracy. Thus, a new idea of using the silica crystal structure as the "substrate" to mimic the TCFS treatment layer was conceived. This model is appropriate when the end group of the fluorosilane ($-Si(OH)_3$) is also assumed to be fully crosslinked with each other during treatment. Additionally, one fluorosilane chain is grafted on one crystal unit cell of the silica, which equates to about 40% percent coverage of fluorosilane on the TCFS surface. We chose to model both C6 and C8 since there are some regulatory concerns about the use of the C8 substance and thus there is interest in C6 as an alternative.



(a) (b)

Figure 3-6: Chemical Structure of the (a) C6 and (b) C8 Fluorosilanes used in the Experiments and Simulations. Colors indicate hydrogen (white), carbon (gray), oxygen (red), silicon (yellow) and fluorine (blue). The same color scheme is used in all subsequent figures.

During the simulation process, the fluorosilane chains physically interact with each other, and the surface reorients and equilibrates at an energetically favorable position at that temperature. A screenshot of the molecular model of the final equilibrated structures from the MD simulations are given in Figure 3-7.



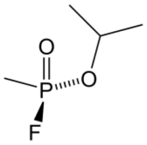
(a)

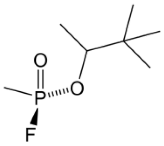
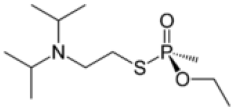
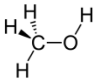
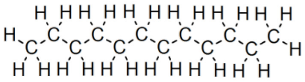
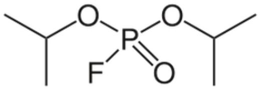
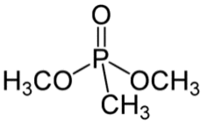
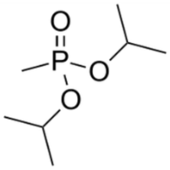
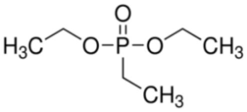
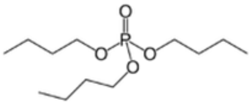
(b)

Figure 3-7: Snapshots from the MD Simulations of Equilibrated Structures of the Silica Crystal Surfaces that are Treated with (a) C6 and (b) C8 Fluorosilanes. Both the side view (right) and bottom view (left) are given. Yellow balls indicate the silicon atoms at the bottom that were fixed in place. Surface size is 86 X 87 Å^2.

The interaction energies that were calculated from the MD simulations for each G-agent and simulant with both the C6 and C8 fluorosilane surface is listed in Table 3-1. Note that DFP, DMMP, DIMP and DEEP are considered to be simulants for GB and GD, whereas TBP is used as a simulant for VX [28]. A negative value for the interaction energy indicates that the liquid is attractive toward the fluorsilane surface, and the larger the absolute value is, the stronger the attraction is. For the three CWAs, both GB and VX are observed to have a stronger preference for the C8 than the C8, whereas the opposite is true for GD. For both fluorosilane surfaces, the strongest interaction energies were observed with GD, DFP, and DMMP. In contrast, DEEP has low interaction energy according to our simulations, suggesting that it may not be the ideal simulant for GB or GD. The interaction energy with both fluorosilane surfaces for TBP and DIMP is in the same range as VX and GB, thus suggesting that they have the potential to be good simulants for these CWAs. However, note that while the interaction energy is one indication of the suitability of a simulant, there are other factors that need to be considered, including molecular alignments and the presence of impure agents.

Table 3-1: Summary of the Interaction Energy between CWA or Simulants and Each Fluorsilane Surface Calculated from the MD Simulations.

CWA and Simulants	Structure	Initial Density (g/ml)	Interaction Energy (× 10^3 kcal/mol)	
			C6 Treated Surface	C8 Treated Surface
GB		1.09	-1.8 ± 0.6	-2.6 ± 0.5

CWA and Simulants	Structure	Initial Density (g/ml)	Interaction Energy (× 10^3 kcal/mol)	
			C6 Treated Surface	C8 Treated Surface
GD		1.02	-9.7 ± 0.6	-8.7 ± 0.4
VX		1.01	-1.7 ± 0.3	-2.6 ± 0.4
methanol		0.79	-3.8 ± 0.3	-1.2 ± 0.4
dodecane		0.75	-1.0 ± 0.3	-1.8 ± 0.4
DFP		1.06	-8.0 ± 0.6	-6.0 ± 0.4
DMMP		1.15	-6.8 ± 0.6	-5.6 ± 5.6
DIMP		0.98	-2.6 ± 0.6	-1.8 ± 0.6
DEEP		1.02	-0.2 ± 0.3	-0.0 ± 0.3
TBP		0.97	-1.4 ± 0.5	-0.8 ± 0.4

3.3.1.3.2 Modeling and Preparation of Biomimetic Artificial Duck Feathers

The air space in a solid structure has been strongly emphasized as a key factor to enhance the oleophobicity of fabrics because the air between fibers supports a liquid droplet to survive on top of the rough surface. For woven fabrics, the effect of air space in a multifilament yarn is considered to improve the performance of oleophobicity. It plays an important role while developing the idea for creating a protuberance on a fiber surface by predicting the impact of the different amount of air spaces on changing of liquid behavior; the protuberance of fiber surface helps neighboring fibers to keep the enough air spaces in a multifilament yarn.

The modification of the fiber surface shown in Figure 3-8 can be performed by bio-mimicking Lotus leaves (Figure 3-9) while chemically modifying their surfaces with fluorochemicals to enhance their performance. The previous modeling was extended and surface modification of several superhydrophobic and superoleophobic structures was modeled to make them perform better as a self-cleaning superoleophobic surface against the challenging CWA such as GB (24 dyne/cm) and GD (25 dyne/cm) that includes a fluorine group; and the simulants of the agents that have similar volatility and similar or lower surface tension. Based on the fiber shown in Figure 3-9(a), the segment of monofilament fiber produced via photopolymerization, we designed a fiber shape as shown in Figure 3-9(b), and model a surface the fiber that has the morphology of *Nelumbo Nucifera* as presented in Figure 3-9(c).

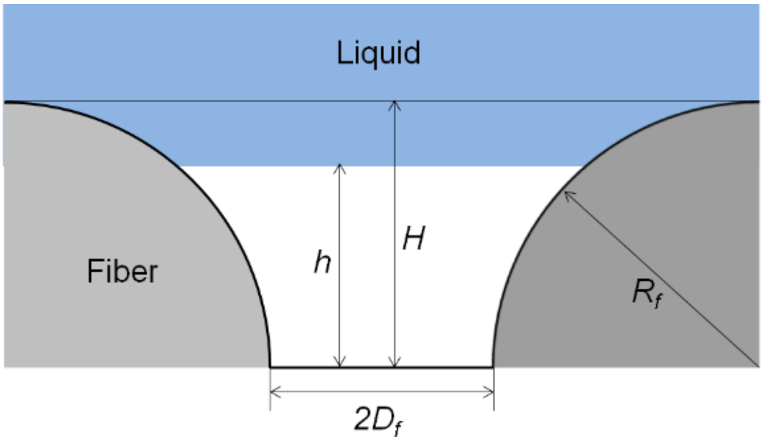
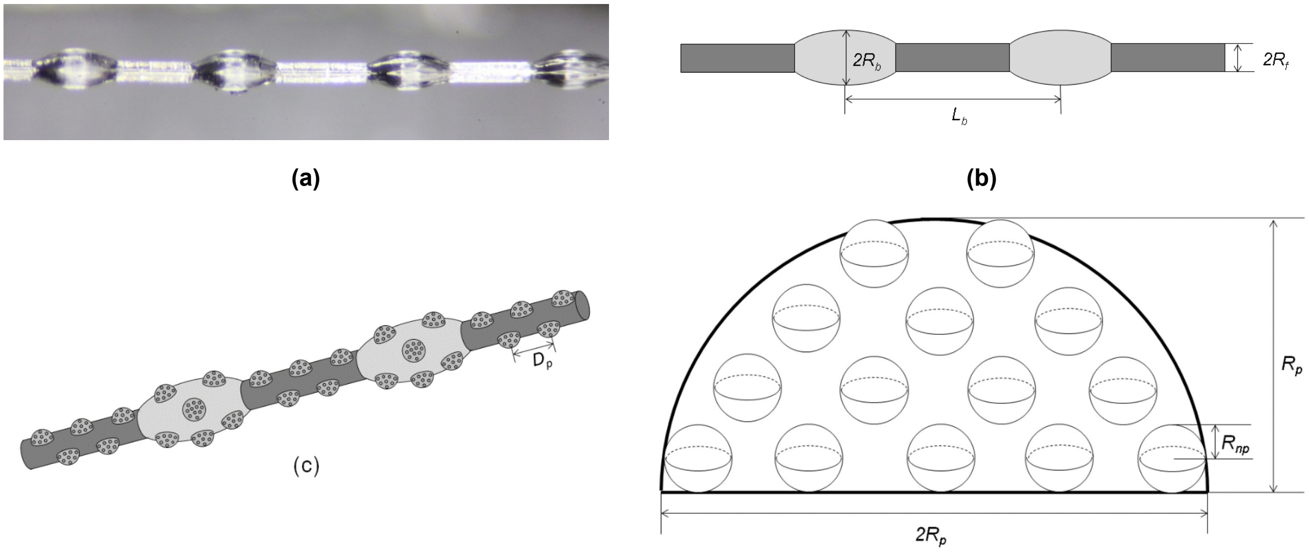


Figure 3-8: Wetting of a Cassie-Baxter Surface Made of Cylindrical Fibers.



(a)

(b)

(c)

(d)

Figure 3-9: Images of a Photopolymerized Nylon Fiber (a); A Modeled Surface of the Photopolymerized Nylon Fiber (b); Fiber with Protuberances of a Lotus Leaf (c); and a Protuberance that has Sub-Protuberances on the Surface (d).

The purpose is to create permanent, low surface energy beads on the surface of fibers to hold the yarn structure open in the same way that the barbs on a duck's feathers keep the feather structure open to provide water repellency (Figure 3-10). They completed a literature search and developed a continuous process for producing biomimetic duck feather monofilaments. In addition, they provided the relationship between the design parameters of the yarn to the process conditions needed to generate this yarn.

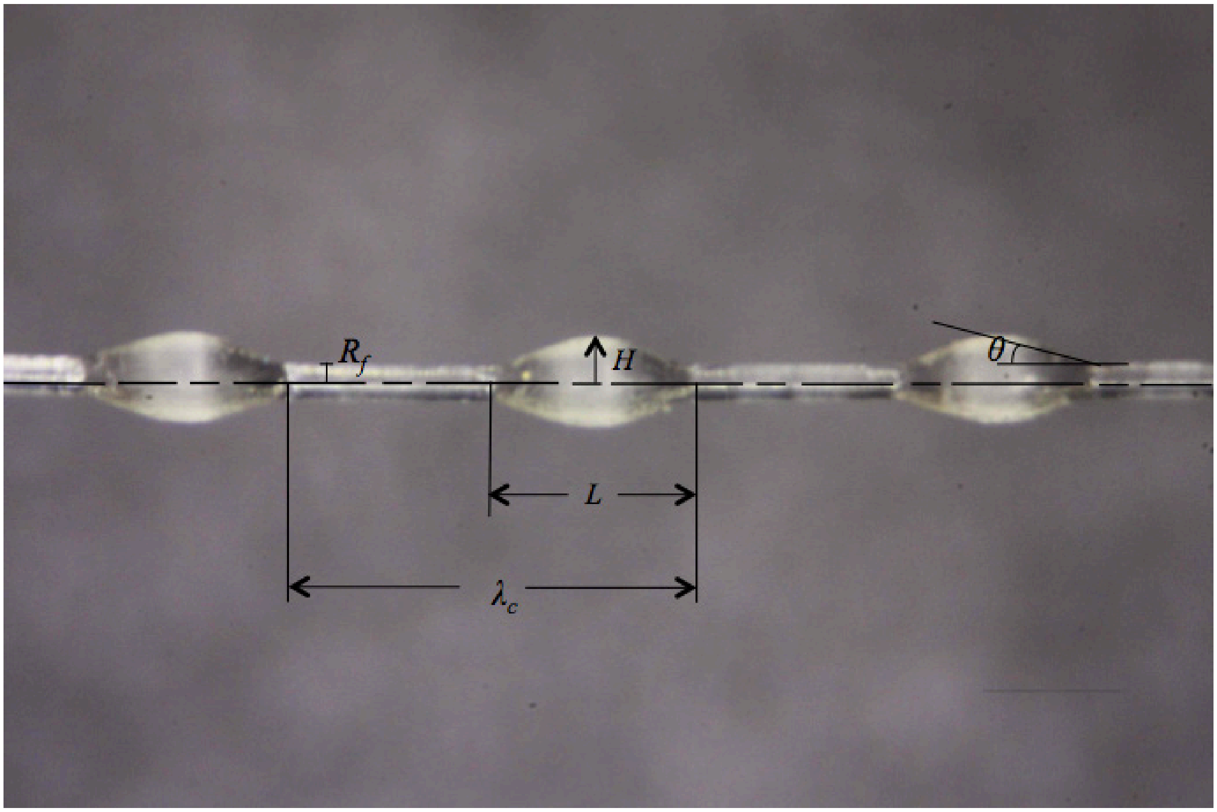


Figure 3-10: A Magnified Image of a Biomimetic Duck Feather Monofilament is Shown Along with the Filament Radius, R_f, Bead Height, H, Bead Length, L, Wavelength Between Beads, λ_c, and the Contact Angle Between the Bead and the Filament.

3.3.1.3.3 Fabric Construction and Evaluation

(a) Fluorination of Nylon Surfaces with C6 and C8

Nylon fabric was cleaned to remove any contaminants, and the TCFS was grafted from the nylon surface.

The SEM images in Figure 3-11 show a perfluoro-decyl-trimethoxy-silane (FS)-treated trichloro-perfluoro-octylsilane (TCFS)-treated polyacrylicacid (PAA)-treated nylon fiber that has needle-shape protuberances on top of the fiber surface. Note: the needle-shape protuberances are highly recommended in order to minimize the area of direct contact between a liquid and a solid.

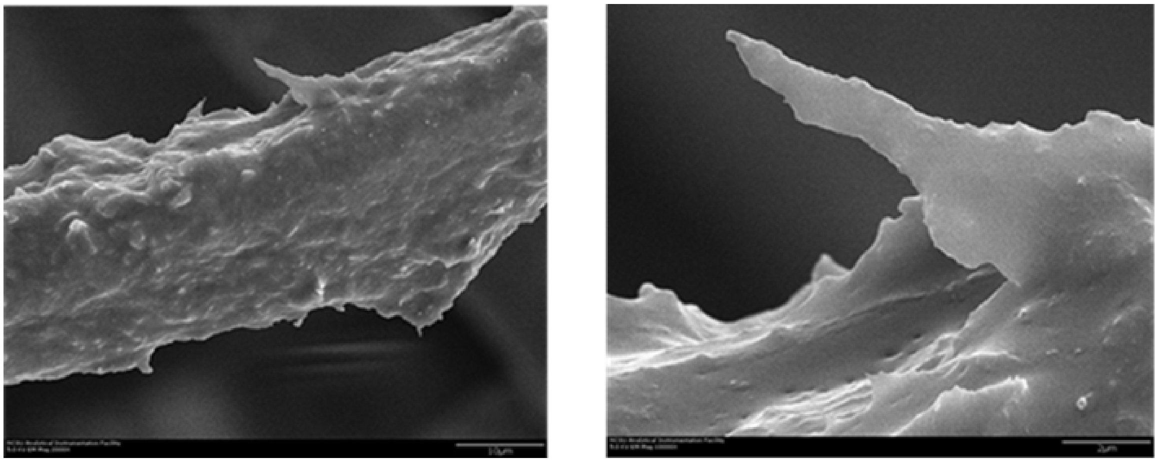


Figure 3-11: SEM Image of a Fluorinated Nylon Fiber with Newly Developed Coating Technology. The nylon surface has needle-shape multiscale protuberances that can provide reduced contact between a liquid and a solid as reported in FY 12.

Based on the newly developed coating technology, the coating was evaluated for the wetting behavior of the fabrics shown in Table 3-2 with live target CWAs: GB, GD, and VX.

Table 3-2: The Fabric Samples Tested with CWA and Results.

Sample# and Tested Agent	Fabric Structure	Treatment Processes				45° Roll Off Test	Residual Agent (mg)	% of CA Remaining
2-1 GB	Nonwoven fabric 1	PAA	TCMS twice	FS		Drop rolled off, half soaked	5.9	29.5%
2-2 GB	Nonwoven fabric 1	PAA	TCFS twice	FS		Drop rolled off, half soaked	1.9	9.5%
2-3 GB	Nonwoven fabric 1	PAA	TCMS	TCFS	FS	Drop soaked immediately		
2-4 GB	Nonwoven fabric 1	PAA	TCFS twice			Drop soaked immediately		
2-5 GB	Nonwoven fabric 2	PAA	TCMS twice	FS		Drop rolled off, some soaked	2.9	14.5%
2-6 GB	Nonwoven fabric 2	PAA	TCFS twice	FS		Drop rolled off, some soaked	1.8	9.0%
2-7 GB	Nonwoven fabric 2	PAA	TCMS	TCFS	FS	Drop rolled off, half soaked		

Sample# and Tested Agent	Fabric Structure	Treatment Processes				45° Roll Off Test	Residual Agent (mg)	% of CA Remaining
2-8 GB	Nonwoven fabric 2	PAA	TCFS twice			Drop soaked slowly		
2-9 GB	Knit fabric	PAA	TCFS twice	FS		Drop soaked immediately		
2-10 GD	Nonwoven fabric 1	PAA	TCMS twice	FS		Drop rolled off, some soaked	5.7	28.5%
2-11 GD	Nonwoven fabric 1	PAA	TCFS twice	FS		Drop rolled off, some soaked	6.1	30.5%
2-12 GD	Nonwoven fabric 1	PAA	TCMS	TCFS	FS	Drop rolled off, some soaked	4.8	24.0%
2-13 GD	Nonwoven fabric 1	PAA	TCFS twice			Drop rolled off, some soaked		
2-14 GD	Nonwoven fabric 2	PAA	TCMS twice	FS		Drop rolled off, some soaked	9.2	46.0%
2-15 GD	Nonwoven fabric 2	PAA	TCFS twice	FS		Drop rolled off, some soaked		
2-16 GD	Nonwoven fabric 2	PAA	TCMS	TCFS	FS	Drop rolled off slowly, soaked		
2-17 GD	Nonwoven fabric 2	PAA	TCFS twice			Drop beaded and soaked		
2-18 GD	Knit fabric	PAA	TCFS twice	FS		Drop rolled off, some soaked		
2-19 VX	Nonwoven fabric 1	PAA	TCMS twice	FS		Drop rolled off, some soaked		
2-20 VX	Nonwoven fabric 1	PAA	TCFS twice	FS		Drop rolled off, no visible residue	0.5	2.5%
2-21 VX	Nonwoven fabric 1	PAA	TCMS	TCFS	FS	Drop rolled off, some soaked		
2-22 VX	Nonwoven fabric 1	PAA	TCFS twice			Drop rolled off, spread and soaked		

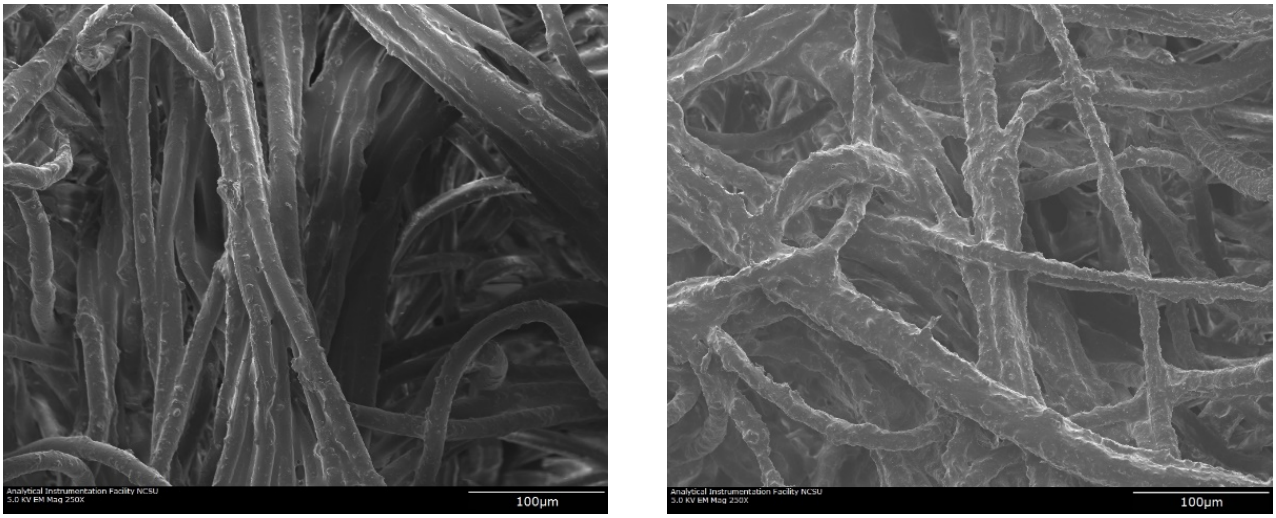
Sample# and Tested Agent	Fabric Structure	Treatment Processes				45° Roll Off Test	Residual Agent (mg)	% of CA Remaining
2-23 VX	Nonwoven fabric 2	PAA	TCMS twice	FS		Drop rolled off, some soaked		
2-24 VX	Nonwoven fabric 2	PAA	TCFS twice	FS		Drop rolled off, some soaked		
2-25 VX	Nonwoven fabric 2	PAA	TCMS	TCFS	FS	Drop rolled off, some soaked		
2-26 VX	Nonwoven fabric 2	PAA	TCFS twice			Not performed		
2-27 VX	Knit fabric	PAA	TCFS twice	FS		Drop rolled off, some soaked		

PAA:	Polyacrylic acid.
TCMS:	Trichloromethyl silane.
TCFS:	Trichloro (1H, 1H, 2H, 2H – perfluorooctyl) silane.
FS:	(Heptadecafluoro – 1, 1, 2, 2 – tetrahydrodecyl) trimethoxysilane.

According to the CWA test results, the fabrics grafted with PAA, TCMS (twice), and FS perform better than other treated fabrics. In addition, they found that air-permeability of treated fabric (ASTM D737) is largely dependent on the fabric structures and dimensional stability, e.g. with our coating technology, air-permeability increased after treating knit fabrics: from 243 to 302 $ft^3/min/ft^2$. The new coating technology will become a powerful tool for our newly developed materials: durable and breathable CWA-repellent textile fabrics.

The fiber coatings were re-worked and increased evenness of the FS Coating. When FS was treated in the presence of ultrason, the coating has the high degree of evenness, which can be seen from the comparison of SEM pictures in Figure 3-12.

As shown in Figure 3-12 the presence of ultrason can make the fabric treated more evenly. Small needle shape structures can be seen everywhere in Figure 3-12(b). However, the ultrasonic technology cannot be used to long. The fiber and coating can be decomposed if the ultrasonic treatment time is unnecessarily long.



(a) (b)

Figure 3-12: (a) The Image of Sample Without Ultrasonic in FS Treatment; (b) The Image of Sample Using Ultrasonic in FS Treatment.

Added Nano and Submicro Roughness to the Fiber Surfaces by adding $NaHCO_3$ during the final washing step of the TCFS treatment, including adding nano and submicro roughness to the fiber surfaces. This technology added even more roughness to the fibers while maintaining the breathability of the fabrics. The surface of treated fabrics is shown in Figure 3-13.

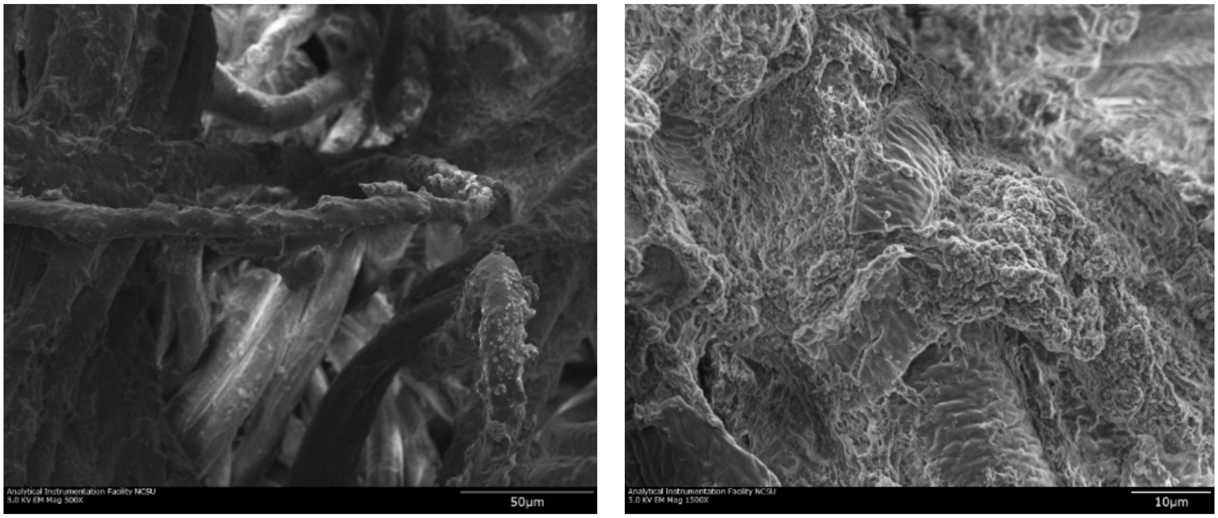


Figure 3-13: $NaHCO_3$ Can Increase the Roughness of the Surface Due to the Air Generated During Heating.

$NaHCO_3$ can decompose under heat. If we wash the fabric in TCFS treatment using $NaHCO_3$, there will be air generated due the decomposition of $NaHCO_3$. The air is trying to get out when the reaction is happening. Therefore, more rough structure can be formed, which makes the fabric achieve better CWA repellency.

(b) Duck Fibers Synthesis

To form continuous droplets with specific shape and size on fiber (Figure 3-14), three steps are needed:

1) Coat the fibers with a suitable monomer;
2) Allow the coating to separate into droplets; and
3) Immediately polymerize them into a permanent structure on the fibers.

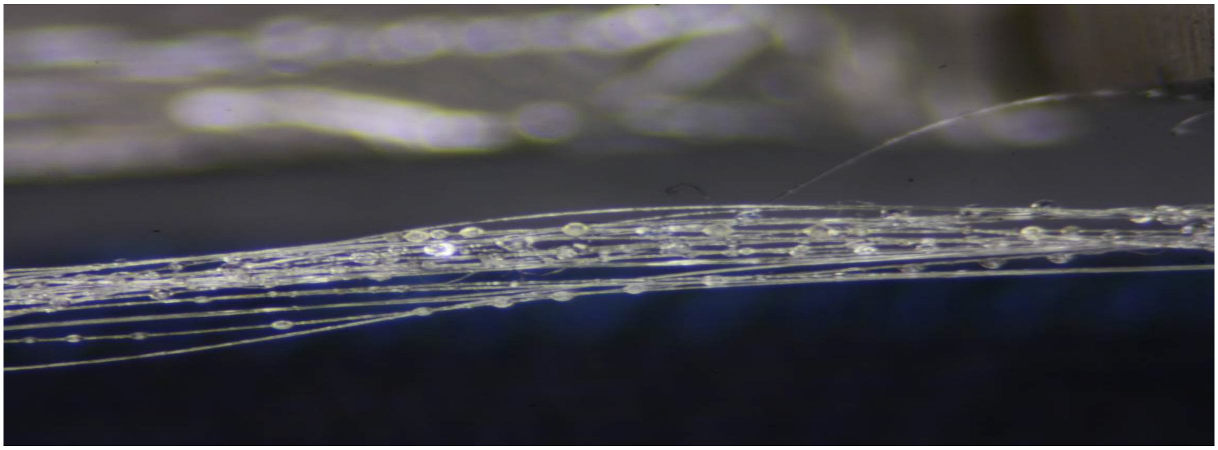


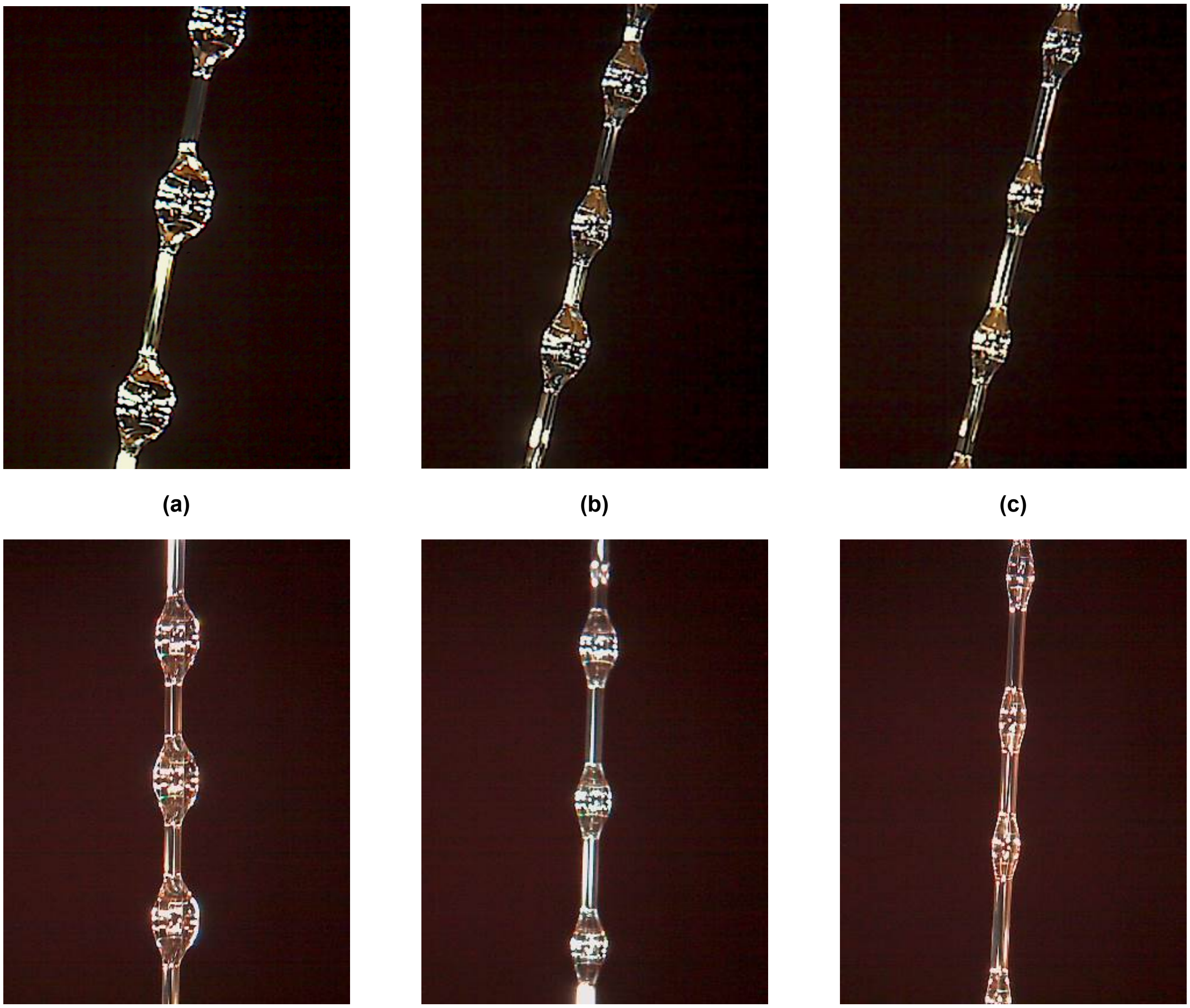
Figure 3-14: A Lightly Twisted, Multifilament Biomimetic Duck Feather Yarn is Shown. The yarn consists of 24 filaments, each containing multiple beads to maintain the yarn openness.

In the first step, the coating is formed by drawing a fiber out of a liquid bath to form an annular shape as discussed by Quere [42]. After the annular coating has formed, the coating is allowed to separate into bell shaped drops under the action of surface tension via the Plateau-Rayleigh instability and then they are polymerized under UV light.

The goal of the duck fibers synthesis was to create a continuous multifilament yarn that remains open, much as the barbs on a duck feather keep the feather open, making it super-repellent. There are three essential steps for creating the biomimetic duck feather yarn:

1) Open a continuous filament yarn;
2) Coat each filament with the similar structures as those developed above; and
3) Reconsolidate the biomimetic yarn into a compact, but open yarn.

The steps for preparing biomimetic duck feather monofilaments are as follows: A nylon monofilament is pulled through a curved tube that contains Plastibond 30A. A thin layer of Plastibond 30A coats the monofilament. The coating undergoes the Plateau-Raleigh instability to generate liquid beads on the monofilament. The coated monofilament then passes through a tube that is illuminated with UV light, which causes the coating to photopolymerize and harden into the final structure. A small amount of a residual liquid remains on the surface and is removed by passing it through a methanol bath and between two sponges. Finally the monofilament with beads on it is wound up. Originally a low speed windup was used, this has been replaced with a constant speed windup and the duck feather mono-filament can be produced continuously at 4 m/min. A typical filament is shown in Figure 3-15. The height, H, of the beads is more than twice the filament radius, the length of the bead, L, is more than 5x the fiber radius, and the bead spacing is more than 10x the filament radius.



(a) (b) (c)

(d) (e) (f)

Figure 3-15: Equilibrium Drop Shapes After Completion of the Plateau-Rayleigh Instability Driven Drop Separation for Plastibond 30A at (a) 6.41 cm/s, (b) 4.40 cm/s and (c) 1.85 cm/s Coating Speeds, and for Kaydol at (d) 13.8 cm/s, (e) 9.65 cm/s and (f) 4.41 cm/s Coating Speeds.

It is clear that the drop volumes are different for the two liquids and for the different speeds. Higher coating speeds result in larger drop sizes in accord with the LLD and visco-inertial regimes of the fluid coating theory [25] presented in our last report. In the purely inertial regime, the coating thickness gets thinner with higher coating speeds, which is counter to our findings. In addition, at similar coating speeds (Figure 3-15(b) and (f)), Plastibond 30A forms larger drops than Kaydol. This demonstrates that the fluid coating thickness is influenced not only by the coating velocity, but also by other factors such as the liquid viscosity, surface tension and density.

In summary, the yarn was improved, opening continuous process for multifilament yarn by:

1) Removing the yarn's finish oil.

2) Used triboelectric charging to cause the fibers to repel each other.
3) Used a comb-like structure to maintain the fiber separation. In a separate, non-continuous process, we have shown that the process conditions for monofilament can be applied to the multifilament yarn used.

Finally, a proof-of-concept biomimetic duck feather yarn has been produced.

3.3.1.4 Conclusions

- Modeled and created a breathable CWA shedding fabric that beads up GB, GD, and VX.
- The first drop of 20 µL GB, GD, and VX cleanly rolled off our newly developed fabrics at the inclination angle of 45°.
- If the second drop of G-agents is deposited exactly onto the same spot that the first drop rolled off, the second drop leaves moderate amount of trail. The result proves that our theory on the molecular dynamics is close to be accurate although more investigation is necessary. According to our modeling in Task 1 and 4, molecular interactions between a fluorinated surface and CWA occurs in pico – nano-seconds, and the invisible residue of the first drop of CWA that rolled off our fluorinated fabric can help the second drop soak into the same fabric.
- A VX drop deposited onto our fabric can sit on top of the surface until being removed, while G-agents can stay 5 – 7 minutes on the same fabric.
- Naturally rough cellulosic fibers such as linen provides better CWA shedding after being fluorinated.
- The fabrics can be evenly treated with fluorochemicals in the presence of ultrason.
- Nano to submicro meter scale protuberances can be created by adding $NaHCO_3$ during the fluorination of the fiber surfaces.

3.3.2 Nano-Fibers for Filtration and Aerosol Barriers (United States)

3.3.2.1 Abstract

High-efficiency air filtration technologies have large cube and high pressure drops. There has been an effort within the US Department of Defense (DoD) to develop nanofiber filter media for individual protection to attain the particulate protection of High-Efficiency Particulate Air (HEPA) filtration at a lower pressure drop and smaller size. Furthermore, the goal of the nanofiber media developed should be robust enough for field testing. The ultimate goal of a recent effort was to develop nanofiber media that provide a reduced burden to warfighters without sacrificing protection. Novel shapes of this nanofiber media may be incorporated into advanced respiratory protection equipment such as an improved protective helmet being developed for the integrated chemical and biological protection suit.

A key objective of this effort was to develop an ultra-thin nanofiber filter media with significant improvement in aerosol collection efficiency to breathing resistance as measured by filter pressure drop). Also developed was a thin filter element as an exchangeable replacement to the pleated High Efficiency Synthetic Particulate Air (HESPA) media currently used in the general purpose protective mask. Although the nanofiber filter element does not yet meet all the performance criteria it seems to be a promising material. The nanofiber filter could enable larger sorbent beds for chemical vapors, reduced size, reduced breathing resistance, and/or novel highly conformal filtration systems.

3.3.2.2 Introduction and Background

The objective of the Nanofiber Aerosol Filtration effort was to develop nanofiber filter media for Individual Protection (IP) that exhibit the low particle penetration of commercial HEPA filtration media while providing a significant reduction in logistical burden. The ultimate goal being the development of a low-profile nanofiber filter media that is robust enough for field testing.

To understand some of the objectives, it is instructive to define a few terms. “Filtration performance” is the ratio of filter efficiency (particle collection efficiency) to the air flow resistance or filter pressure drop (ΔP) for a specified particle size and filter face velocity. “Filter Fractional Penetration” (FFP) is 1 minus fractional efficiency. The “filter face velocity” is the total volumetric flow rate through the filter divided by the surface area of the filter. The filter Figure of Merit (FoM) is one way of stating filtration performance as shown in the following example:

$$\text{FoM} = -\text{Log}(\text{FFP}) / \Delta P$$

Based on the example above, the FoM for fiberglass HEPA for 0.3 μm particles at the standard face velocity of 5.3 centimeters per second (cm/s) is approximately 12 1/kilopascals (kPa^{-1}).

At the start of this effort, flat-sheet fiberglass HEPA media 32 liters per minute (L/min) were the baseline aerosol filter media and filtration system for determining progress of our nanofiber filter media. There was an established goal of reducing size and pressure drop, but the surface area or shape of a nanofiber filter element in a filter system was not specified. As the program developed and a greater understanding of the goals and vision for future IP filtration systems were realized, the goal of developing shaped media that could conform to the face or head was incorporated. Initially targeted were large surface areas on the order of 250 (cm^2) with the concept of a large, but low, profile and conformal filter for use inside a protective helmet. Late in the effort, focus on the M61 filter canister as a test bed filtration system was pursued. HESPA filter media as a baseline material was added.

Developing electrospun nanofiber media for advanced respiratory protection presents several challenges because they need to achieve the following:

- Filtration performance of 99.99% efficiency at a (ΔP) less than 136 Pa.
- Chemical resistance against chemical weapons, Toxic Industrial Chemicals (TICs) and Toxic Industrial Materials (TIMs), and battlefield contaminants.
- Mechanical robustness to endure packaging and use.
- Curved shapes with large surface areas that will conform inside a protective helmet.

For fiberglass flat-sheet media, FoM=12 ±2 kPa^{-1} for 0.3-micrometer (μm) in diameter particles at 5.3 centimeters per second (cm/s) face velocity. The original goal of this project was to produce filter media with a FoM greater than 25 kPa^{-1}. Later, this goal was increased to be in excess of 70 kPa^{-1}.

3.3.2.3 Technical Discussion

The development of nanofiber filter media is motivated by the expectation of significant improvement in filtration Efficiency (Eff) per ΔP as the filter fiber diameter (d_f) is reduced to the length-scale of the mean-free path (λ) of the surrounding gas molecules (λ = 66 nanometers [nm]). To develop filter media with significant improvement in performance that are useful to the military, three basic elements that are required:

1) A fundamental understanding of aerosol filtration;
2) An understanding of nanofiber production and means to fabricate filter media from the nanofibers; and
3) An understanding of processes to impart chemical resistance to the nanofibers.

3.3.2.3.1 Theory of Developing Improved Filtration Performance

Filtration performance is determined by the structure of the fibrous media and is typically described by the filter media thickness (Z), the packing density of the fibers or solidity ($\alpha = 1 - $ void volume), the diameter of the fibers (and, in the case of real filters, their size distribution), and the velocity of the air or face velocity (V_0).

Pressure Drop

The pressure drop (ΔP) can be described in a fibrous-filter form of Darcy's law (Equation 1):

$$\Delta P = F\,[4\mu\alpha V_0 Z / \pi d_f^2] \qquad \text{(Eq. 1)}$$

where:

F = Drag coefficient
μ = Viscosity of the gas
α = Solidity
V_0 = Face velocity
Z = Filter media thickness
D_f = Fiber diameter

The drag coefficient, F, is well described in ideal fibrous media for fibers with large diameters ($d_f > 1$ µm), where the effect of slip of the gas molecules at the fiber surface (nonzero velocity at interface) is negligible. The significance of the gas-slip phenomenon is typically indicated by the Knudsen number ($K_n = 2\lambda/d_f$). For $K_n \ll 0.25$, the continuum mechanics (no slip) sufficiently describe drag on a fiber. K_n is 1.3 to 2.6 for fibers ranging from 100 nm to 50 nm; thus, slip flow or reduced drag occurs for media in this size range. An additional complication in calculating F for real filters is the variation in fiber, such as, size, orientation, and packing density within a piece of media. The empirical relationship developed by) is the most accurate expression for F for small K_n, as shown in Equation 2:

$$F = 16\pi\alpha^{1/2}(1+56\alpha^3) \text{ for } 0.006 < \alpha < 0.3 \qquad \text{(Eq. 2)}$$
$$F = 16\pi\alpha^{1/2} \text{ for } \alpha < 0.3$$

It is important to note that the work from Davies [43] was intended for media made with fibers ranging from 1.6 µm to 80 µm. The general approach used to account for gas-slip effects for $K_n \geq 0.25$ is to calculate a base drag (e.g., using Equation 2), and then to correct for slip effects. To correct for slip we used the empirical linkage (Equation 3) that appears to work well over a range of conditions:

$$1/F = 1/F_0 + 1.43\varepsilon^{1/2}(1-\alpha)(K_n/4\pi) \qquad \text{(Eq. 3)}$$

where:

F_0 = Reference drag
ε = the inhomogeneity factor; set to 1 because this is incorporated in Equation 2
K_n = Knudsen number

The pressure drop (ΔP) calculated for 100-nm fibers using Equations 1 through 3 is substantially lower than that expected from continuum mechanics or even by popular theoretical ΔP expressions that account for slip, such as the Josef Pich model.

Particle Collection

Particle collection in high-efficiency filtration is typically conducted by interception and diffusion mechanisms. Interception occurs when a particle comes into contact with the fiber while following the air-flow streamline. This mechanism depends upon the ratio of the particle diameter to the fiber diameter and is important for particles greater than 0.1 μm. The physical parameters of importance include particle diameter, fiber diameter, filter packing density, and depth.

Random Brownian motion drives particles less than 0.1 μm in diameter to the fiber, resulting in diffusional collection. The mechanism of collection depends on the ratio of the particle diffusion coefficient to the air velocity through the filter. The physical parameters of importance include particle diameter, air velocity, filter packing density, and depth.

Electrostatic attraction occurs when the particle or fiber or both have an electrostatic charge. The physical parameters of importance include particle charge, fiber charge, particle mass, air velocity, filter packing density, and depth. Electrospinning fibers to make filter media will charge the fibers while they are being formed, and therefore the electrospun fibers may exhibit electrostatic collection of particles. Although electrostatic collection is one way to improve particle collection efficiency per pressure drop, this collection is unreliable because solvent vapor, heat and humidity, and dust accumulation on the charge centers significantly reduce or eliminate the electret effect. Electrospun media that rely in part on electret filtration have shown decay in performance with time. It was demonstrated that 40% of filtration efficiency in fresh electrospun media comes from electrostatic effects and that it degrades with time.

The single-fiber efficiency (h) is the probability that a particular particle approaching a fiber on a specific path is collected. The overall fractional penetration ($Pt = 1 - Eff$) of particles through a filter is described by Davies [44], as shown in Equation 4:

$$Pt = exp[-4\alpha\eta Z/\pi(1-\alpha)d_f] \qquad \text{(Eq. 4)}$$

where:

Pt = Fractional penetration (ratio of outlet concentration divided by inlet concentration through filter as a function of challenge particle diameter).

η = Sum of the single fiber efficiencies for the various mechanisms (in this case, diffusion and interception).

Calculation for η in nanofiber filter media must account for the slip effects and the fibers that are often smaller than the particles they are collecting. The Brownian diffusion collection efficiency (η_D) as shown in Equations 5 and 6:

$$\eta_D = 1.6(1-\alpha)^{1/3}\ Pe^{-2/3}C_1C_2 \qquad \text{(Eq. 5)}$$

$$Ku = -(\ln \alpha/2) - 3/4 + \alpha - \alpha^2/4 \qquad \text{(Eq. 6)}$$

where:

Ku = Kuwabara number, a correction for the proximity of other fibers
Pe = Peclet number, based on the particle diffusion coefficient
C_1, C_2 = Parameters containing corrections for slip

Interception collection efficiency (η_I) can be calculated as shown in Equation 7:

$$\eta_I = 0.6(1- \alpha/ Ku))(1+K_{nf}/I)(I^2/1+I) \qquad \text{(Eq. 7)}$$

where:

K_{nf} = Fiber Knudsen number
I = Ratio of the particle diameter (d_p) to fiber diameter (d_f), d_p/d_f

Typically, the interception parameter is less than 1, but for a fiber diameter less than 100 nm, this is often not true. For a 300 nm particle (0.3 µm, a typical challenge size for testing HEPA media) being collected by a 100 nm fiber, the *I* is 3, compared with an *I* of 0.3 for a typical fiberglass HEPA filter. In other words, for nanofiber media, the interception mechanism is dominant and the collection efficiency should be higher.

Filter Figure of Merit

As previously mentioned, filter media performance is achieved by the combination of the efficiency (Eff = $1–P_t$) and the pressure drop. The FoM, also called the quality factor or filter quality, provides a means of comparing the Pt per ΔP for various media with different fiber sizes and media thicknesses. Different forms of FoM are expressed in the literature. Here, we use Equation 8 as follows:

$$\text{FoM} = -\log Pt/\Delta P \qquad \text{(Eq. 8)}$$

where:

ΔP = expressed in kPa.
FoM = measured for a particular particle size at a particular face velocity.

Typical commercial fiberglass flat-sheet HEPA media (e.g., flat sheet of filter material) have a FoM of 12 ±2 kPa^{-1} for 0.3-µm diameter particles at 5.33 cm/s.

3.3.2.3.2 Electrospinning of Nanofiber Filter Media

Electrospinning of Nanofibers

Electrospinning of polymers is a facile way to make non-woven mats with fibers less than 1 µm in diameter. Electrospinning is conducted by dissolving a polymer in a volatile solvent, flowing the solution through a needle, and applying a high voltage. The charged fluid is drawn into a fiber that undergoes chaotic whipping, which rapidly reduces the fiber's diameter. Although this seems to be a relatively simple process, consistent production of fibers below 200 nm is challenging. The fiber diameter and the quality of non-woven mats made from fibers depend upon the polymer solution and electrospinning conditions. These are multi-parameter processes where parameters often interact/interfere with one another.

Fabricating Filter Media from Electrospun Fibers

In addition to the challenge of obtaining high-quality nanofibers at or below 100 nm, another challenge is handling the delicate fibers and fabricating filter media made from them. Some of the approaches used by other researchers include spinning fibers greater than 200 nm and applying them as a thin coat on top of a coarse-fiber, non-woven filter media. The non-woven media used to support the nanofibers are typically low-efficiency media a with small pressure drop. This approach is aimed at improving the performance of the non-woven support media with the electrospun fibers. The advantage of having nanofibers, however, is compromised by the pressure drop of the coarse fiber media. To obtain the full advantage of nanofiber media, as predicted – the support for the nanofibers should make a negligible contribution to the pressure drop, the fibers need to be less than 100 nm in diameter, and the defects need to be minimized. As a case in point, calculations of FoM on various reported electrospun media yield a FoM that is no better than fiberglass flat-sheet HEPA. Oftentimes, the FoM is less.

An electrospinning process has been developed for fabricating nanofiber media. To do this the use of high performance polymers combined with additives to provide for sub-100 nm fibers with high strength was used. Coarse meshes with no inherent filtration efficiency and negligible pressure drop was used to collect the electrospun fibers. Other innovations include enclosed electrospinning environment for improved process control, real-time measurement of nanofiber mat formation (corresponds to filter media performance), and reduced handling of the nanofibers. Improvements included: increased fiber size and quality; reduction in media defects; and improvements in control of mat thickness and density provide for filter media with superior FoMs without electret enhancement. An important consideration in using polymer nanofibers to make filter media for chemical defence is that the polymers may be vulnerable to some chemical agents and TICs. A post-processing step after electrospinning to impart chemical resistance to the nanofibers was included in the research.

Nanofiber Media Morphology and Length Scales

Three levels (or length scales) of defects occur in the electrospun nanofiber media: the media level (e.g., uniformity of the fiber mat across the whole working area); the local fiber mat (e.g., a local depth direction and an area approximately 1 millimeter [mm] × 1 mm); and at the individual fiber level. A wide variety of factors impact the structures and defects that occur at these three different length scales. Interestingly, they are not necessarily coupled. For example, conditions were found that provide excellent fiber morphology with very poor uniformity of the nanofibrous material at the media level.

Chemically Resistant Nanofibers

Polymer nanofibers electrospun from solvents have the potential to be vulnerable to chemical agents and toxic industrial chemicals. Significant efforts to resolve this chemical vulnerability problem were investigated. Two basic tactics were investigated: coating nanofibers and using polymers that were more chemically resistant. For all of the techniques studied, there were trade-offs among the properties of chemical resistance, mechanical robustness (namely brittleness), and the fiber morphology needed to achieve high FoMs. Conformal coatings using gaseous precursors provided the best fiber morphology and the potential to achieve improved chemical resistance with acceptable compromise in mechanical properties. The most intriguing technique was the development of a polymer system that could be electrospun from a solvent, and then crosslinked to a chemically resistant form. However, due to time and resources applied to developing crosslinked fibers with acceptable morphology and mechanical properties, further development of the technology has not yet occurred. Nonetheless, there is still great potential for the idea of crosslinkable fibers if the appropriate resources could be applied. Two coatings were deemed as having the potential to provide chemically resistant nanofibers with the desired properties:

1) Coating with parylene; and
2) Coating with metal oxides or metal-organic films using the related techniques of ALD and MLD.

Coatings with Parylene

Parylenes (poly-para-xylylenes) are a unique group of thermoplastic polymers whose dimer precursors can, under the right processing conditions, vaporize in a uniform manner and be drawn down to deposit a very thin homogenous polymer film onto a substrate. This film, which can be as thin as tens of nanometers, forms a protective coating that is conformal and has desirable physical and chemical properties, such as resistance to degradation by aggressive chemicals. Parylene coating occurs via chain growth polymerization with no termination as the chain ends during growth. Monomers add to an active site at the end of each chain, growing from monomer to oligomer to polymer. The thickness of the resulting coating is primarily a function of the quantity of dimer used and can be controlled within 10% (of the coating's thickness). Temperature and pressure are also factors in the deposition rate.

Coatings via Atomic Layer Deposition and Molecular Layer Deposition

ALD is a vapor deposition technique used to deposit thin films of high-quality material. ALD is very similar to CVD, but ALD is unique due to its capability to coat extremely complex shapes, such as nanofibers with conformal inorganic layers of high-quality material. ALD is able to grow thin films with thicknesses down to a single monolayer. Another difference from CVD is that ALD precursors are strictly separated from each other in the gas phase. The reactions use gas phase precursors that react with a solid surface. Each half-reaction of the ALD process cycle is believed to be both sequential and self-limiting. The self-limiting nature provides for a constant and often submonolayer growth rate for each half cycle (typically 0.5 monolayer [45]). During ALD, one precursor is dosed until it has fully reacted with all possible surface sites, and the products and excess reactants are swept away using an inert carrier gas. This is referred to as the “A” reaction. A second precursor is dosed until the surface has fully reacted, and the excess reactant and products are removed from the reactor. This is referred to as the “B” reaction. One important distinction about ALD is that at the end of the “B” reaction, the same surface that was present at the beginning of the “A” reaction must be present. These reactions continue in an ABAB manner to grow a thin film of a desired thickness.

Unlike CVD, in which one or more precursors react and decompose on a surface to produce the desired thin film, ALD half-reactions occur only on the surface to avoid the possibility of gas phase nucleation of particles. This ensures that a particulate- and pinhole-free film is conformally deposited on the surface. Because the reactions occur only on the surface, they tend to need less thermal energy for activation. Many ALD reactions, including the TMA and H_2O process for depositing Al_2O_3, can be accomplished at room temperature. The temperature of ALD reactions is very important, and ALD growth of thin films can only occur within a certain temperature window.

3.3.2.4 Conclusions

Traditional fiberglass and new, synthetic flat-sheet media have been pushed to their limits. Development of the next generation of respiratory protection for improvements in current IP equipment and for new concepts in integrated chemical and biological protection suits will require novel materials and novel approaches to packaging. To make improvements to the current filter canister, new choices in particulate filter media are required. Likewise, for novel filters that will become even more conformal to the head or face, the filter media will need to address shape factors that are challenging for flat-sheet media and require improved performance of collection efficiency to pressure drop.

Figure 3-16 illustrates some potential applications for the nanofiber filter media: reduction of the height of the pleated HESPA filter; and development of thin, conformal, low-burden filters. The filter canister contains a precisely manufactured pleated particle filter element and a sorbent bed in a conformal package. If the nanofiber filter media can replace the existing pleated filter element in the canister, then it could increase the volume available for the sorbent bed by approximately 30%. The increased room for the sorbent bed, without increasing the size of the canister, will enable the incorporation of sorbents to address a broader range of threats, including emerging ones. Additionally, nanofiber media have been fabricated in conformal shapes with an even tighter fit to the head or face, which enables filter designers to access shapes not possible with flat-sheet media.

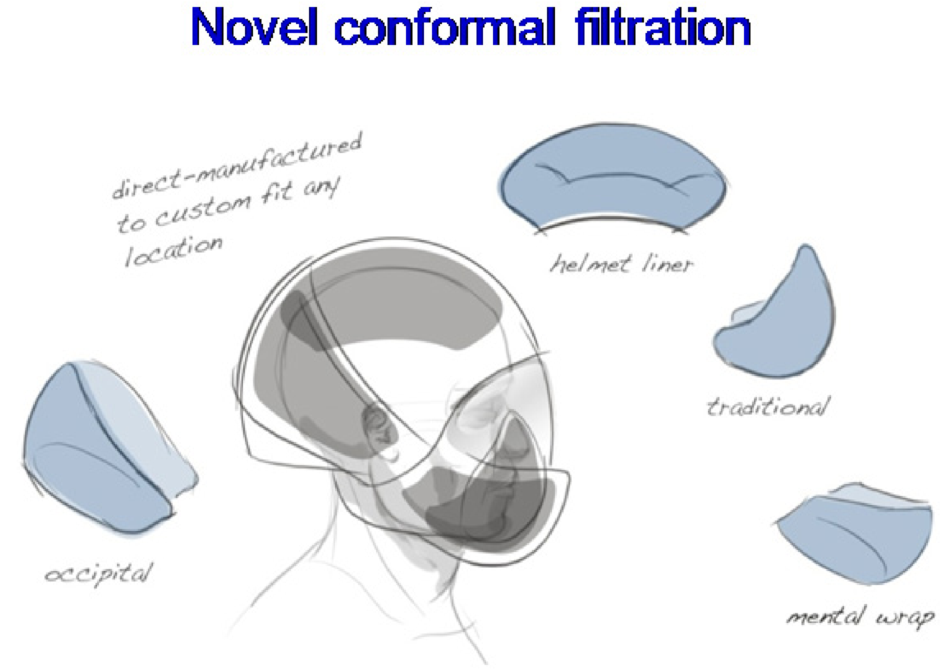


Figure 3-16: Novel Conformal Filter Media are Possible Using Nanofiber Filter Media.

3.3.2.4.1 *Summary of Project Advancements*

Significant improvements were made to the nanofiber filter technology. At the start of the program, the project was producing flat-sheet media based on PSu. At 5.3 cm/s, the efficiency for 0.3 µm in diameter particles was 99.97% to 99.99%, and the FoM was approximately 30 kPa^{-1}. This early media was vulnerable to plasticizing aerosols. As the project proceeded, the team developed a much deeper understanding of fiber and media morphology and the facts that limit filtration performance such as defects at several length scales. Several other polymer systems and changes in the electrospinning solution formulation were explored. Advances in control of the electrospinning process and in the polymer solutions enabled the production of media with improving performance.

Although excellence in filtration performance with the nanofiber media can be achieved, the key to success is developing a material that can withstand the rigors of the battlefield. Filters could be exposed to any number of chemical vapors or aerosols, which could damage polymer nanofibers. In addition to chemicals, the media must withstand mechanical challenges such as loading to high pressure drops and rough handling. Improving the chemical resistance of the nanofibers, while not compromising mechanical robustness, has been a significant focus for this project. More than 30 methods for improving chemical resistance were investigated. Initially there was consideration of two general categories: methods for improving the chemical resistance of PSu-based nanofibers; and methods for developing new polymer nanofibers.

Efforts to develop candidate materials for improving chemical resistance discovered that achieving a good balance of chemical resistance, mechanical robustness, and filtration performance (e.g., FoM) is both critical and challenging. It was discovered that achieving the desired fiber and mat morphology for providing high FoMs is significantly demanding and only possible with select polymers. For the polymers studied during this effort, only PSu-based and nylon-based polymers provided the needed structures to obtain high FoMs. For imparting improved chemical resistance, we discovered that coating and modification processes that use gas-phase reagents and detailed control of the reaction (e.g., coating or modification) process provided the most conformal coatings with the smallest degradation of FoM compared to the uncoated material. Currently, the most favored approach is to coat nanofibers with ALD, given the angstrom-level control and highly conformal coatings possible with the technique. Coating of nylon-based nanofibers is favored due to the superior filtration performance we have achieved with that polymer system.

Mechanical robustness of the filter media is critical. The conformal-shaped ALD coated nylon-based nanofiber filters developed by the end of Option Year 5 achieved significant improvements in burst resistance. Of the eight samples loaded with Arizona road dust to 2,500 Pa (10 in. of H_2O) pressure drop, none of them failed. The media was also demonstrated to withstand mild flexing with no change in filtration performance. However, the nanofiber media is admittedly delicate in that it has very poor abrasion resistance and does not tolerate one putting his or her fingers directly on the nanofibers. Once packaged, this abrasion resistance issue may not be a problem. In fact, we developed our process for fabricating nanofiber filters around the concept of minimizing the handling of nanofibers to reduce risk of damage. Additional methods of improving mechanical robustness were identified, such as the incorporation of nanomaterials that improve fiber strength and the addition of a protective scrim.

The project demonstrated the possibility of nanofiber filter media with improved filtration efficiency per pressure drop, which enabled the reduction of particulate filter size in a filter canister and/or reduction in breathing resistance. The chemical resistance of polymer nanofibers can be improved using ALD to coat the fibers. Nanofiber media is substantially tough to withstand huge pressure drops of 2,500 Pa. While further improvements are needed in terms of chemical resistance and pressure drop increase due to particle loading, the nanofiber filter is a promising material for enabling next-generation filtration systems IP.

3.3.2.4.2 Filtration Performance Benchmarks and Metrics

The original Nanofiber Aerosol Filtration effort used fiberglass flat-sheet HEPA media as the benchmark. The old standard for HEPA was 99.97% efficiency in filtration for 0.3 μm in diameter particles at the test velocity of 5.3 cm/s.

3.3.2.5 Recommendations / Path Forward

Additional characterization is needed for the coated conformal media and refinements in the filtration performance and ruggedization of the media before proceeding to larger scale production of media. An assessment of developing a scalable process needs to be conducted in order to develop a pilot process.

The nanofiber media technology and all its subcomponents developed in this effort are a technology platform with potential use for several applications. Some potential opportunities are as follows:

- Reactive nanofibers for self-decontamination of CWAs: ALD is a route to depositing a wide variety of metals and metal oxides. Some of these materials are known to have reactivity towards CWAs, converting them into less toxic chemicals. The sizes, orientation, and available reactive sites of these materials all influence their reactivity towards chemicals. Potentially nanofibers with various reactive chemistries to perform self-detoxification of CWAs could be developed.
- Nanofiber sensor and filter media incorporating sensing capability: ALD of nanofibers can functionalize the fibers to be reactive or responsive to various chemicals. The fibers can be constructed to be conductive or semi-conductive using these techniques. Sensors or filters with a sensing capability (filter with added functionality) could be developed to indicate to the user when a chemical is present. This concept may also have use as a residual life indicator in a filtration system.
- Nanofiber filter media for collective protection applications: The current nanofiber filter project is aimed at developing advanced media for Individual Protection (IP). A natural adjacent application of this technology is in collective protective applications in which size and weight are a premium, such as in vehicles and man-portable shelters.

3.3.3 Nanostructured Sorbent Materials (United States)

3.3.3.1 Abstract

Nano-structured sorbent materials have emerged as a promising Chemical Biological (CB) defence technology through research directed at nanoscale design, demonstrating properties can be flexibly tuned through modification of structural components. Computational methods used to predict appropriate sorbent structures, new synthetic strategies for building and scaling, and rapid screening methods are all necessary to develop novel sorbent materials targeted as enhanced CB protective materials. Researchers have demonstrated the ability to impart reactive sites with catalytic properties, as well as improve chemical and thermal stability and increase selective target molecule adsorption using crystalline nano-porous frameworks. Recent advances in development of metal-oxide/hydroxide based sorbents have demonstrated broad spectrum (TIC and CWA) removal capability in prototype filters. Here we summarize some of the aspects of ongoing developmental efforts of these materials.

3.3.3.2 Introduction and Background

Traditional CB adsorbent, activated, impregnated carbon is produced from raw carbonaceous materials that undergo a high temperature treatment process (activation), which develops the larger feeder pore structure that is ultimately the basis for activated carbon's adsorptive behavior and capacity. Performance of activated carbon is further enhanced with the addition of impregnants that either directly react or catalyze reactions involving traditional toxic chemicals. The advent of asymmetric threats, most notably Toxic Industrial Chemicals (TICs), requires that additional reaction chemistries be incorporated into the filter design. Due to the current breadth of toxic chemicals, engendering functionalities into carbon substrates becomes significantly more difficult. For example, oxidation techniques to improve TIC adsorption may have unwanted side effects of greatly increasing water adsorption. Furthermore, simply adsorbing toxic compounds is no longer sought, as these chemicals will concentrate and remain toxic in many cases.

Research and development of novel CB sorbents seek to take advantage of improvements in molecular design; hence the allure of nano-structured sorbent materials, like crystalline nanoporous frameworks. Using this approach, novel sorbent media development focuses on tailoring the substrate through rationale design and implementing a capture-and-destroy methodology against toxic chemicals.

Creating materials with greater reactive capacity while retaining physical adsorption tendencies will not only lead to more efficient media and offer protection against a wider range of chemicals; it will also provide on-demand capabilities to the user. Reducing the quantity of material necessary for removal of toxic chemicals may offer the reduction in physiological and logistical burden of currently fielded systems. Meeting these objectives requires the development of revolutionary materials.

3.3.3.3 Technology Needs and Challenges

The primary challenge of nano-structured sorbent material development is identifying/synthesizing efficient materials towards a wide array of toxic chemicals while minimizing burden to the user. Meeting this objective requires incorporating a high density of active sites into materials, with a focus on capture-and-destroy mechanisms for permanent removal. In air purification devices, it is important to provide thinner sorption beds over wider surface areas to reduce breathing resistance to the user while providing maximum protection. In commodities such as protective suits, for example, this paradigm holds in providing breathable materials with percutaneous protection capabilities, resulting in high protection levels while reducing thermal burden. Decontamination powders require the integration of catalytic functionalities to provide the necessary reactivity on a volume (and mass) basis, reducing the quantity of material needed to achieve detoxification.

Engendering functionality into substrates that target a variety of chemicals requires the coordination of chemistry, modeling, and synthesis disciplines. The ability to determine the necessary functional groups for toxic chemical removal and how to incorporate those functional groups onto the nanoporous system is paramount in guiding synthesis strategies. Models to predict interaction potentials currently exist; however, when targeting a capture-and-destroy methodology, new methods must be developed that incorporate bond-breaking into the model.

Novel efficient techniques for synthesizing crystalline nanoporous frameworks that increase yield while reducing cost are also sought. Clearly, current laboratory techniques produce materials on the gram-scale; when targeting transition for any application, materials must be produced on the ton-scale. New methods for scaling between these levels must be developed such that appropriate testing and evaluation can be completed to fully characterize novel media.

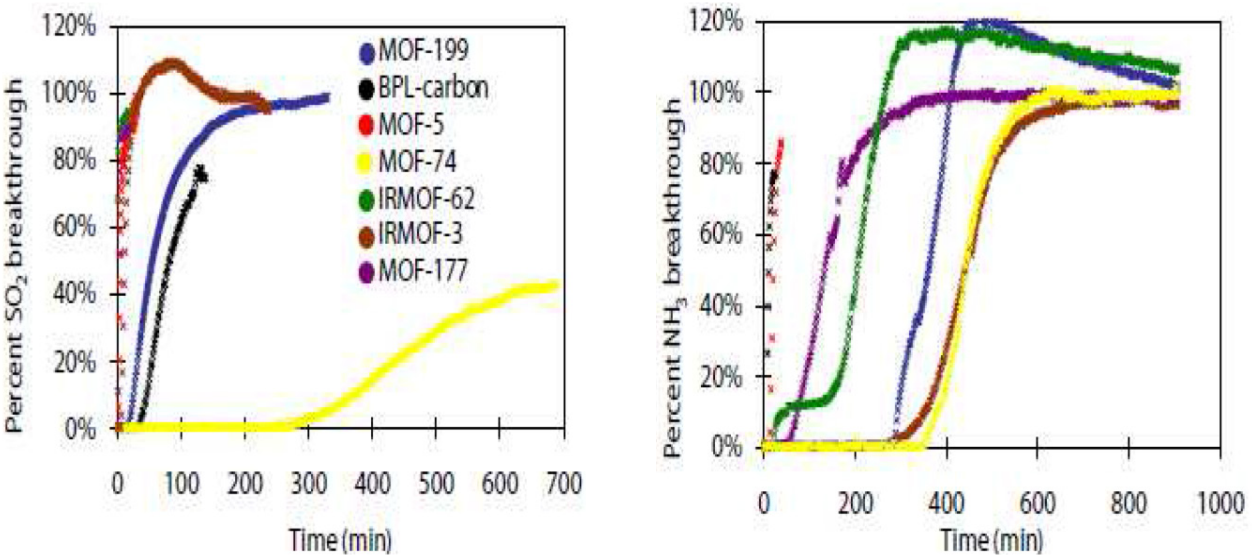
Simply developing materials that initially provide mechanisms for removal is insufficient. Materials must also be stable in ambient environments such that protection exists for long periods of time. This behavior is important when engineering systems for collective protection and/or suits and barriers that are vulnerable to constant moisture exposure as well as battlefield contaminants.

3.3.3.4 Technology Discussion

We are evaluating the potential of an array of porous materials such as Carbide Derived Carbons (CDCs), Carbon Nanotube-containing carbonaceous solids (CNTs), Polymers of Intrinsic Microporosity (PIMs), organosilicates, Carbon-Silica Composites (CSCs), Metal-Organic Frameworks (MOFs), and hydrous oxide-based media. These materials offer advantages such as high surface area, light weight, and engendered functionality as compared to activated, impregnated carbon. Targeted acid-base reactions and heterogeneous catalysis are traditional synthetic methodologies explored for removal of toxic chemicals from air. A diverse group of porous materials are being developed, however, similar functional groups/ metal catalysts for targeted reaction chemistries may be engendered. The intent then is to leverage knowledge across materials. Furthermore, nano-structured sorbents offer the advantage of creating an ordered array of functionalities into structures. Thus, the novelty lies in the incorporation of such chemistries to achieve multifunctional materials that exhibit properties such as bifunctional acid–based cooperativity.

Over the past several years' research has been conducted on MOFs for their ability to sorb toxic chemicals. Yaghi and coworkers evaluated several MOFs against eight toxic chemicals and surrogates [36].

This work showed that dynamic capacity in MOFs for targeted toxic chemicals was greatly improved by addition of reactive functionality. This point is clearly illustrated (Figure 3-17) by the ammonia breakthrough behavior for IRMOF-3 (brown), containing engendered amino functionality, and IRMOF-62 (green), which lacks any reactive functionality. MOF 5 (red) and MOF-177 (purple) performance, despite their high surface area as compared to carbon, are notably worse than carbon for sulfur dioxide and a number of chemicals tested. This further revealed that increased surface area alone does not necessarily improve performance capacity. Coordinatively unsaturated MOFs (MOF-199 (blue), MOF-74 (yellow)), generally, performed better than coordinatively saturated MOFs (IRMOF-62 (green), IRMOF-3 (brown)) in toxic chemical breakthrough experiments.



(a) (b)

Figure 3-17: Breakthrough Curves for Dry Conditions (0% RH) of Gaseous SO_2 (a) and NH_3 (b) in Benchmark MOFs Compared to Carbon.

Peterson *et al*. [37] expanded on this work (Figure 3-18) to identify the ammonia removal mechanism of MOF-199 (a.k.a. HKUST-1 or Cu3BTC2). This effort also highlighted the need to incorporate functionality, especially metals, in coordinatively unsaturated forms. These initial efforts exhibited the potential for using MOFs in toxic chemical removal, yet several shortcomings became evident. Some materials were found to be unstable in the presence of ambient moisture. A necessary requisite for air purification and decontamination commodities is the ability to resist degradation from humidity.

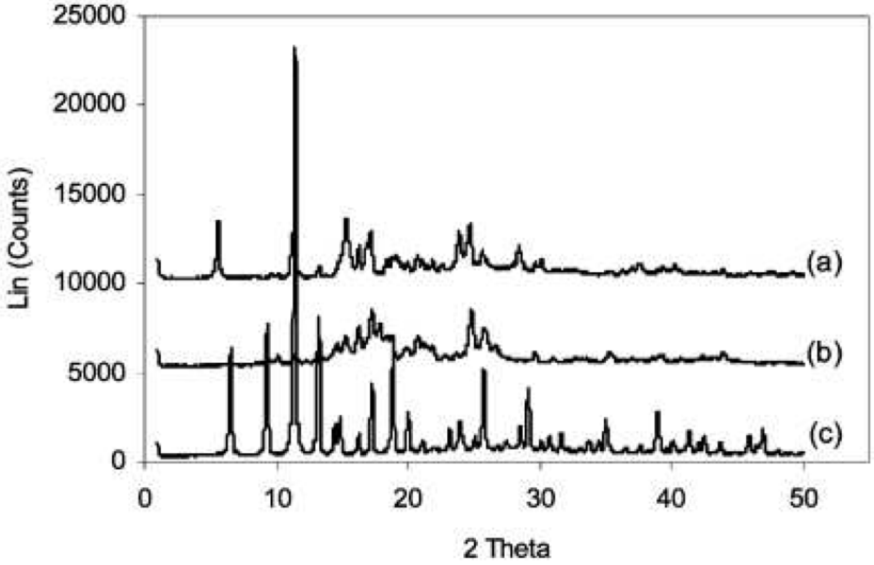


Figure 3-18: PXRD Data Indicates that MOF-199 Structure Changes Signification Upon Exposure to NH_3 at Humid Conditions (80% RH) (a) as Compared to Unexposed MOF-199 (c) – the MOF-199 Exposure to NH_3 at Dry Conditions (0% RH) (b) has a Diffraction Pattern Somewhere Between Exposed and Unexposed Sample.

The effort with MOF-199 indicated that the material was highly reactive towards ammonia, but was irreversibly damaged through reactions with carboxylic linking groups. This work revealed that coordinatively unsaturated metal center within the metal-oxide Secondary Building Units (SBUs) of the MOF are not desired as reactive sites for toxic chemicals (Table 3-3). The aim of the effort is to develop highly reactive materials, but stability is a major concern when considering long-term function in ambient environments. Also, water adsorption should not impede the adsorption of toxic chemicals. Competitive adsorption of water with toxic chemicals is a challenge that must be overcome.

Table 3-3: Calculated Porosity and Apparent Surface Area Values from Nitrogen Absorption Isotherm Data.

MOF-199 sample	BET Capacity (m^2/g)	Total pore volume at STP (cc/g)	DR[a] micropore volume at STP (cc/g)
Unexposed	1460	0.68	0.54
Dry, once-exposed to NH_3	150	0.68	0.06
Humid, once-exposed to NH_3	16.2	0.49	0.003

[a] Dublin-Radushevich adsorption isotherm equation.

Glover and coworkers used the MOF-74 substrate to evaluate several different metals in an isostructural setting [38].

This effort highlights the ability to use crystalline frameworks to determine relative effects of functionality on toxic chemical filtration. It reveals that water has a detrimental effect on toxic chemical adsorption capacity of MOF-74 due to preferential adsorption (Figure 3-19). Ultimately, this effort emphasizes the need to focus on engendering reactive functionality into materials that demonstrate specificity; adsorption sites will preferentially bind toxic chemicals. The study has helped lead to enhancements in MOF development, including the incorporation of multiple metals within a single substrate, a first step towards multifunctional materials.

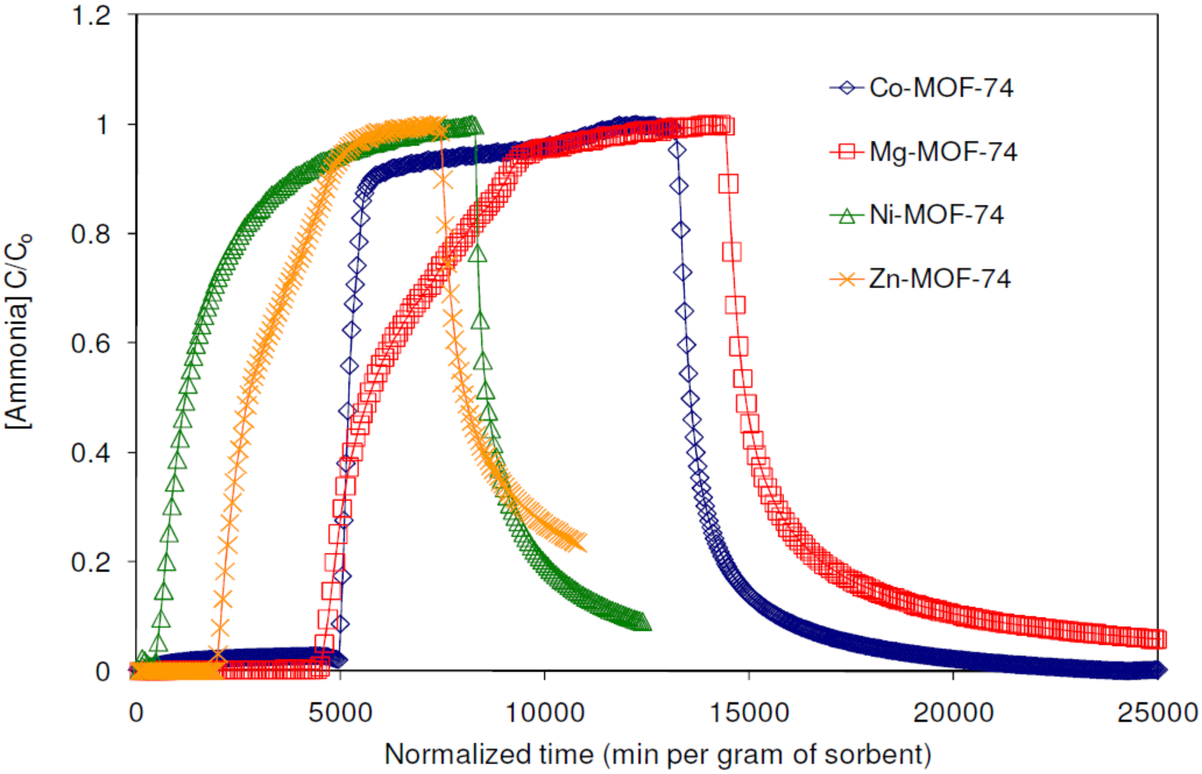


Figure 3-19: Breakthrough and Desorption Curves for Dry Conditions (0% RH) of Ammonia on MOF-74 Analogs. Desorption is achieved by passing clean air to the bed at the same temperature and pressure at which the toxic gas entered the bed.

More recently efforts have focused on selectivity, form, and scalability of nano-structured sorbent materials. Due to its excellent chemical and thermal stability, zirconium-containing MOF patented by the University in Oslo, UiO-66, is the subject of selectivity, form, and scalability studies. Selectivity considerations guide investigation of modification strategies that ensure the performance of materials is preserved under a range of environmental conditions (T, RH). Pre-synthetic strategies, such as ligand functionalization, and post-treatment processes, such as plasma deposition, are explored to improve water stability of MOF materials and competitive adsorption of ammonia over water. Walton *et al.* showed that water adsorption capacities in MOFs can be tuned by pre-synthesis ligand functionalization while maintaining the high stability of the parent material [39]. Studies were conducted on UiO-66 (parent material), amine-functionalized UiO-66 (UiO-66-NH_2), and dimethyl-functionalized UiO-66 (UiO-66-DM).

This work demonstrates that water uptake is reduced or increased through the addition of methyl or amine functionality (Figure 3-20) which imparts hydrophobic/hydrophilic characteristics to the material. This point is clearly illustrated by the water isotherms of UiO-66-NH_2 (blue triangles) which saturates at low relative humidity, while UiO-66-DM (red squares) show a drastic reduction in the uptake of water (> 50%) compared to UiO-66 (black dots).

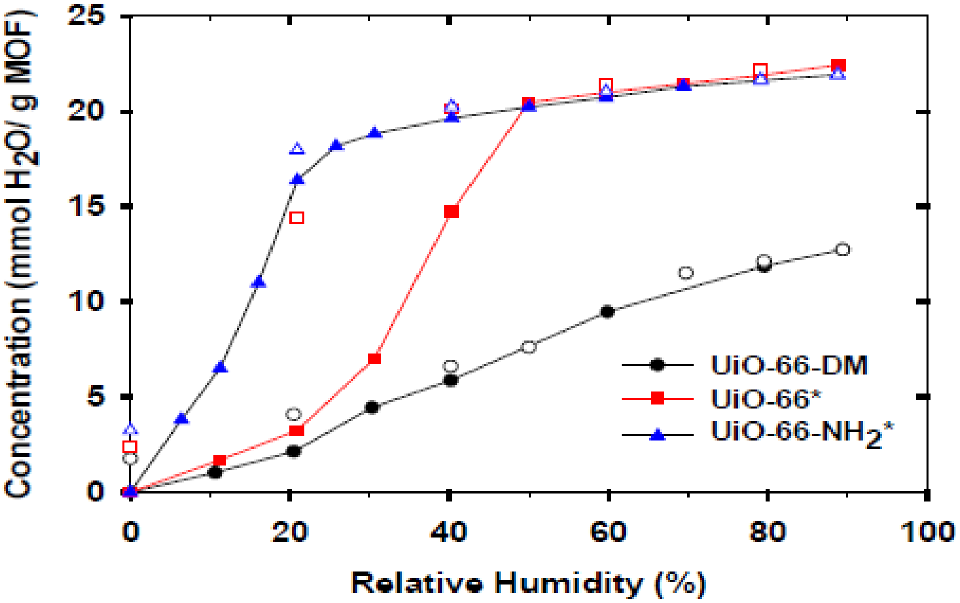


Figure 3-20: Water Vapor Sorption/Desorption Isotherm for Desovated Compounds of UiO-66-DM, UiO-66, and UiO-66-NH_2 (Closed symbols – adsorption; Open symbols – desorption) [40].

Scalability is an important consideration when assessing practical use of nano-structured sorbent materials for DoD applications. Technology maturation requires materials are verified in their engineered form (i.e. simulated filter bed). Performance evaluations of filter beds and prototypes require large quantities of materials; scale up synthesis from approximately 1-gram batches to 1-kilogram batches is necessary. Production of crystalline materials are particularly challenging since production rates to do not scale linearly. Research has focused on reducing the quantity of solvent used during synthesis and maximizing the yield of UiO-66 through investigation of the influence of various processing conditions. This effort has demonstrated more concentrated reactant solutions result in high fidelity, high yield (greater than one order of magnitude) UiO-66.

Current efforts focus on significant experimentation to evaluate the protection envelop afforded by the material. Maturation studies are underway to engineer powders into granules (Figure 3-21). Once granulated, material's breakthrough behavior is evaluated in a packed bed configuration within test tubes under canister simulated conditions. Transfer dynamics are studies as well as correlations between bed thicknesses, mesh size, pressure drop and filter life.

(a) (b)

Figure 3-21: 100 Grams of UiO-66 Powder (a) and UiO-66 Granules (b).

Once efficacy is demonstrated at the test tube level, nano-structured sorbent materials are fabricated into prototype filters which can meet desired performance specifications; optimization continues beyond transition of materials into ongoing Programs of Record. A key achievement of the nano-structured sorbent materials S&T effort is the transition of ZZAT/ASZM-T prototype filters (Figure 3-22).

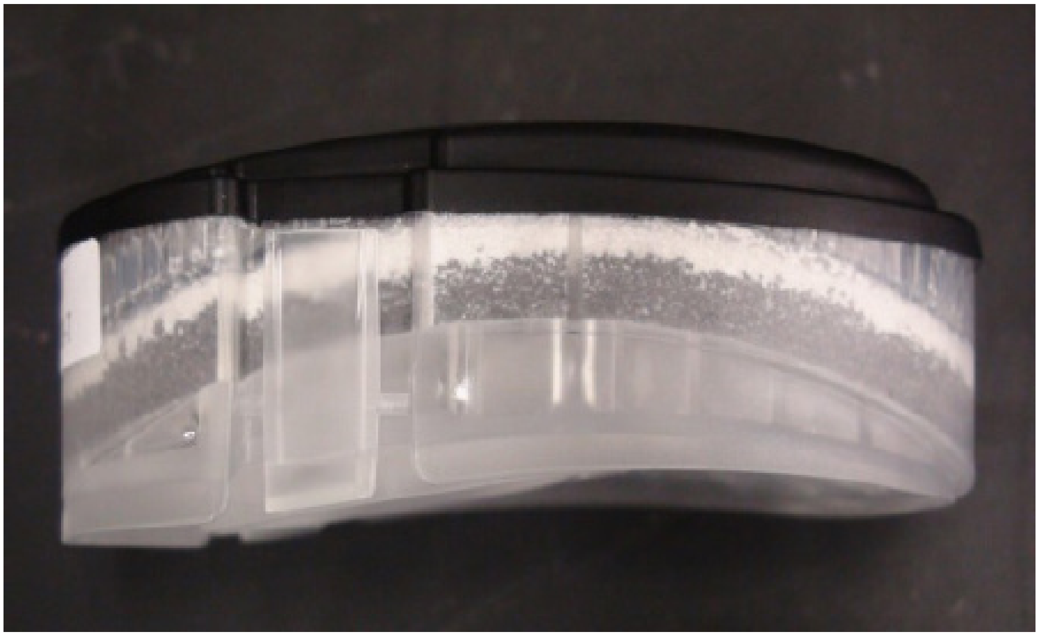


Figure 3-22: Picture of 50/50 ZZAT/ASZM-T Prototype Filter.

When determining if the technology can continue to mature for eventual transition to Programs of Record within the Acquisition community, two key factors that dictate the pace of transition are cost and toxicity. If the cost of raw materials significantly higher than currently fielded technologies, and significantly drive the final cost of the end item, transition may not occur, regardless of enhanced capabilities. Although somewhat obvious, materials must also pose limited toxicity to the manufacturer, and more importantly, the user. Clearly the synthesis and manufacture of MOFs and other crystalline materials will include toxic starting materials. The objective is to minimize that toxicity within the final material.

The final hurdle in technology transition is the ability to manufacture materials on a large enough scale such that advanced development can occur within Programs of Record. No longer are kilogram-scale quantities appropriate, as evaluation within end items requires significantly higher quantities. Here, pilot scale studies showing the ability to manufacture tons of material are necessary to achieve success.

3.3.3.5 Conclusions and Summary

The development of nano-structured sorbent materials will allow for targeted toxic chemical removal through capture-and-destroy mechanisms, resulting in more reactivity per unit volume, and offering reduced burden to the user. Moving away from legacy materials that have been used for the past century and moving towards molecularly designed crystalline nanoporous frameworks is only in its beginning stages. Many opportunities exist in modeling and synthesis to provide revolutionary materials capable of broad spectrum removal, molecular switching, and on-demand protection. Challenges in this program are not only in the conceptual and synthetic development of these materials, but also in their maturation. Revolutionary materials not only must provide enhanced capabilities, but do so while limiting costs. Moving forward demands the ability for multiple disciplines to coordinate efforts to bring these multifunctional, nano-structured sorbent materials to fruition.

3.4 SCALABLE PROTECTION

3.4.1 Mask-Helmet System Integration (United States)

3.4.1.1 Abstract

In the modern era of chemical and biological protective individual equipment a constant challenge continues to develop a respirator that can also easily interface with other equipment that the warfighter requires, particularly a soldier’s ballistic helmet. Issues such as logistics, physiological burden (i.e. restricted view, increased breathing resistance, increased thermal burden), and the amount of time required to don/doff the equipment as well as other requirements must considered. This précis will outline some of the research and progress accomplished thus far.

3.4.1.2 Introduction and Background

During 2010 a Chemical Biological and Ground Soldier System (CB/GSS) Combined Technology Demonstration (CTD) was conducted. The U.S. Government explored modular headgear system concepts as part of this demonstration. These systems formed the basis for headgear concepts for a Next Generation Respiratory Protection System (NGRPS). An effort was initiated to develop headgear concepts for potential NGRPS development.

3.4.1.3 Technology

An industrial partner developed two test bed system concepts based on the 3M™ 6000 series mask to assess the feasibility of helmet integration. These were designated as the Partially Integrated Mask System (PIMS) and the Fully Integrated Mask System (FIMS) and are shown in Figure 3-23 and Figure 3-24. The PIMS represented a "strap-on" concept and the FIMS represented a "snap-on" concept.

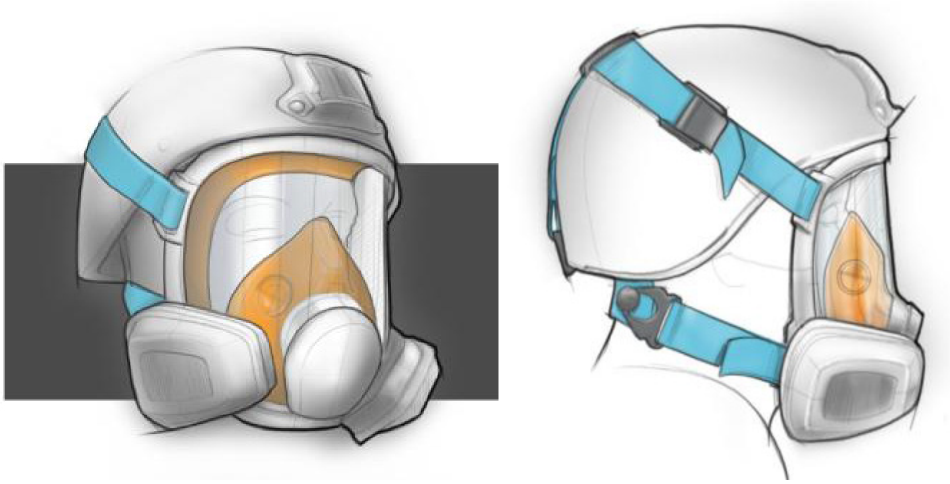


Figure 3-23: PIMS Test Bed System.

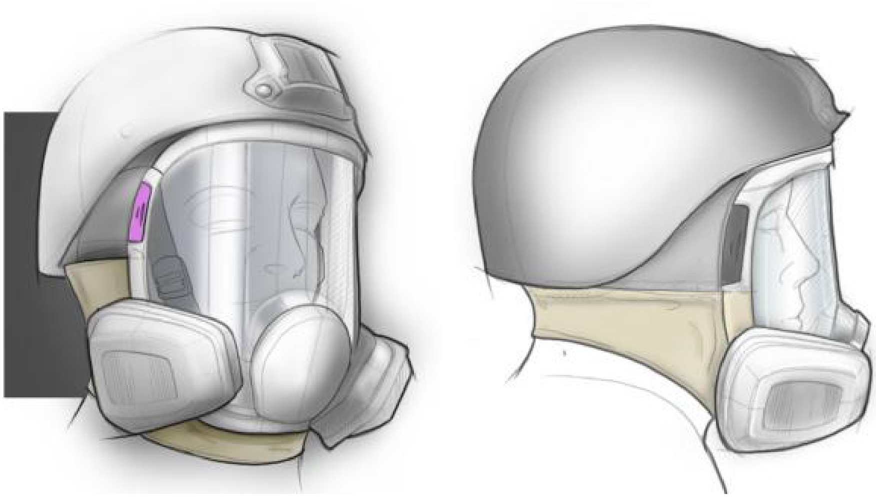


Figure 3-24: FIMS Test Bed System.

Preliminary integration studies demonstrated the feasibility of the PIMS and identified two fundamental integration approaches for the FIMS. One approach for the FIMS allowed the mask to float for seal adjustment. The mask would be snapped to a rigid helmet shell and all adjustments would be made on the mask. This approach is demonstrated in Figure 3-25 as the floating seal approach.

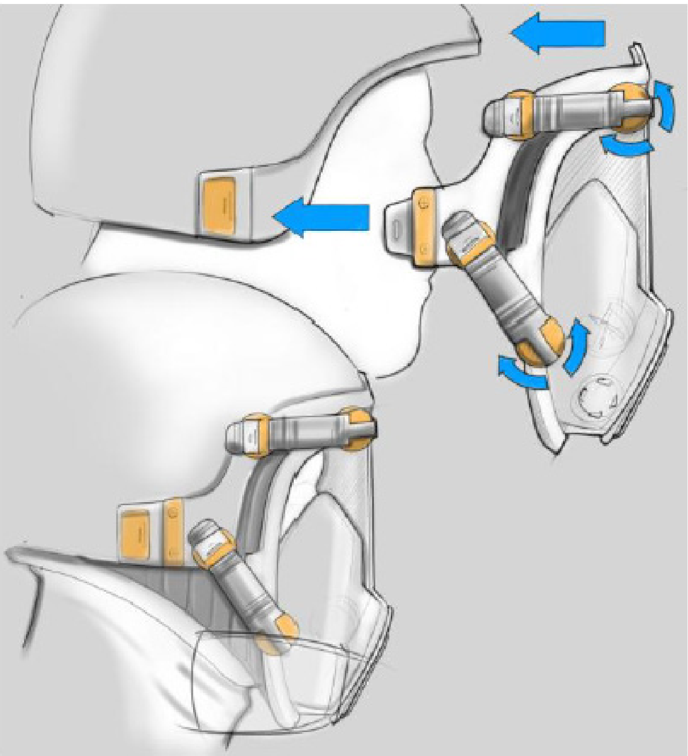


Figure 3-25: FIMS Floating Seal Approach.

A second approach for the FIMS required helmet liner adjustments to secure the seal. The mask would snap to a helmet liner and all adjustments would be made using the helmet liner. This approach is demonstrated in Figure 3-26 as the helmet liner approach. Both approaches were considered feasible but would require additional effort and were considered longer term options.

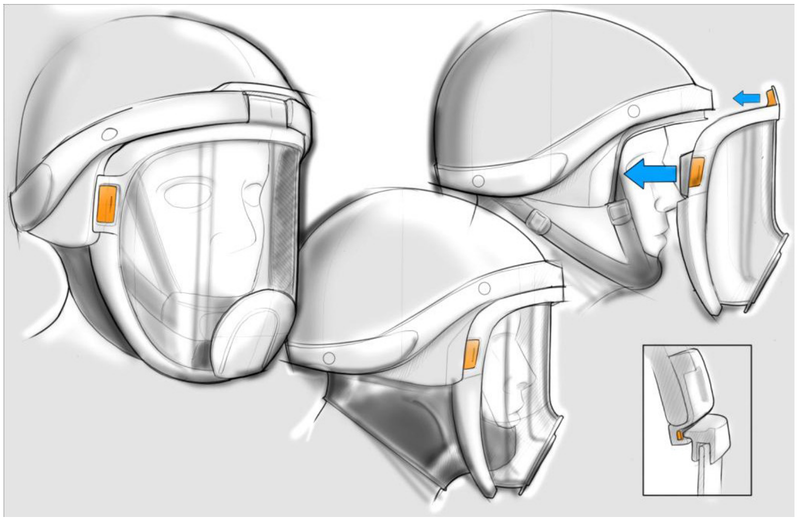


Figure 3-26: FIMS Helmet Liner Approach.

The team assessed various attachment and module design options using a test bed system concept model based a commercial mask. The headgear support system or helmet liner concept explored the direction of pull needed for mask sealing and allowed for mask seal refinement and attachment systems independent of the helmet shell geometry. This demonstrated that both the "strap-on and "snap-on" approach were feasible. The studies also verified that comparable protection could be achieved regardless of whether the mounting location was on the inside or outside of the helmet. A representation of the commercial test bed system concept model is shown in Figure 3-27.

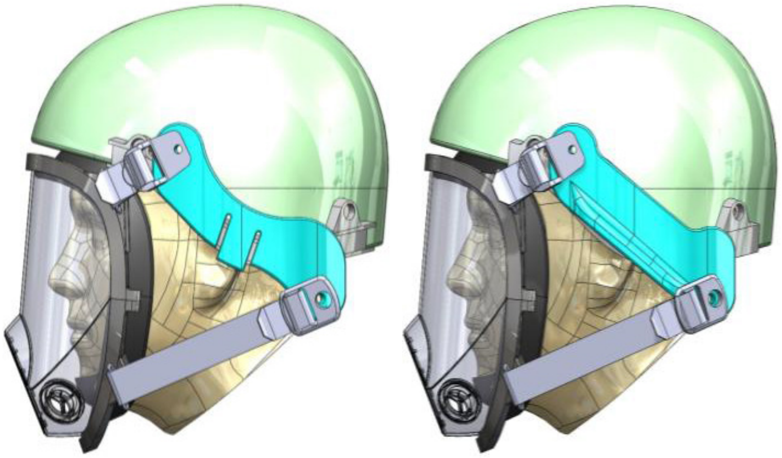


Figure 3-27: Commercial Test Bed System.

Approaches to develop a custom test bed system were evaluated at a preliminary design review. Emphasis during this review was on developing a scalable protection capability with the integration of fans into the system. A graphic representation of the custom test bed concept is shown in Figure 3-28.

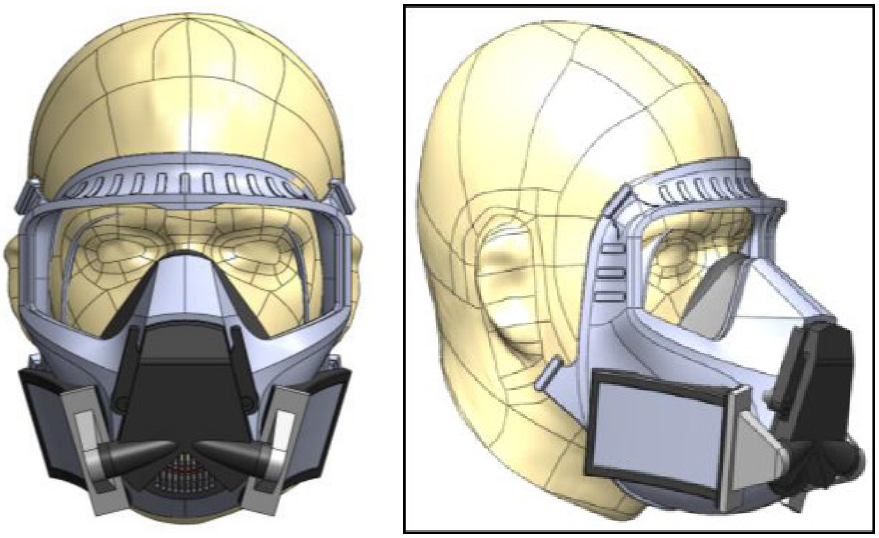


Figure 3-28: Custom Test Bed System Concept.

The Team completed development of the test bed system to include the development of a head support system concept. The test bed system used lever ratchets on the side of the head support system to attach and adjust the mask. These ratchets applied significant pressure to the mask seal and easily provided seal protection comparable to a mask with a traditional suspension. Testing of the fan system was less successful due to particles being generated by the fan and possible front module and component leakage. A graphic and picture of the custom test bed system is shown in Figure 3-29.

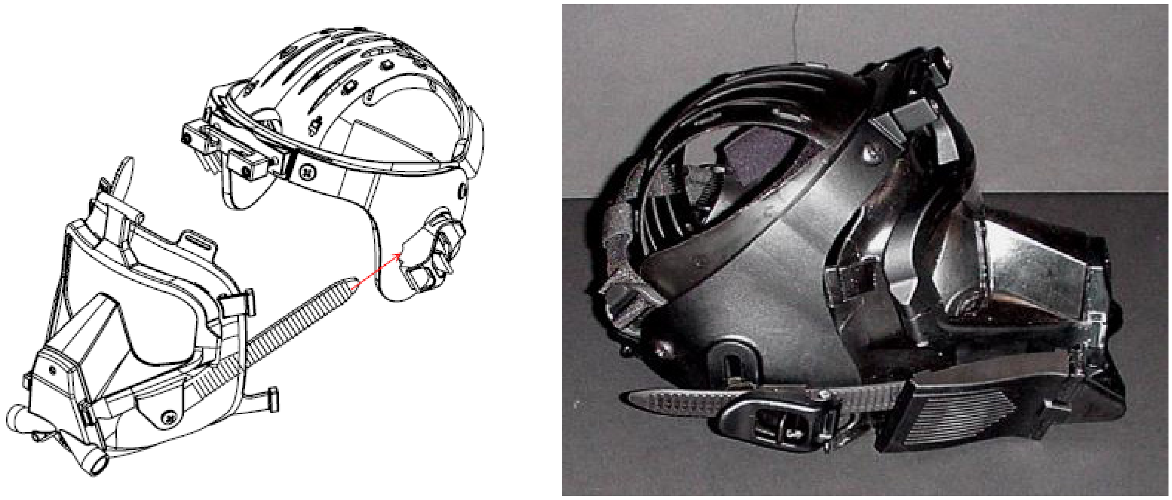


Figure 3-29: Custom Test Bed System.

To better determine the effectiveness of the test bed system concept, studies were transferred to an independent contractor. This contractor created a test bed system using the C50 mask. The C50 test bed system allowed for testing with reduced concern for front module and component leakage and fans were screened for generation of particles prior to assembly.

Based on the test bed system studies and the results of the CB/GSS demonstration, The Team developed concept graphics and poster layouts for a new Chemical Biological Protective Integrated System Mask (CB PRISM) concept. The CBPRISM concept used in the CB/GSS demonstration used a helmet liner filter system that could potentially conflict with impact protection requirements projected for the next generation helmet. In the new system concept, the filters would be added to the front of the mask and made as conformal as possible by integrating with the front module.

The new CB PRISM concept provides the best potential for a rapid don/doff mask that can donned without removing the helmet. Use of a head support system potentially avoids some of the helmet integration issues with the previous concept during the CB/GSS demonstration. Suit integration with the CB PRISM remains essentially the same in this concept with the main advantage of eliminating the hood from under the helmet. The concept feature for mask and suit attachment is shown in Figure 3-30.

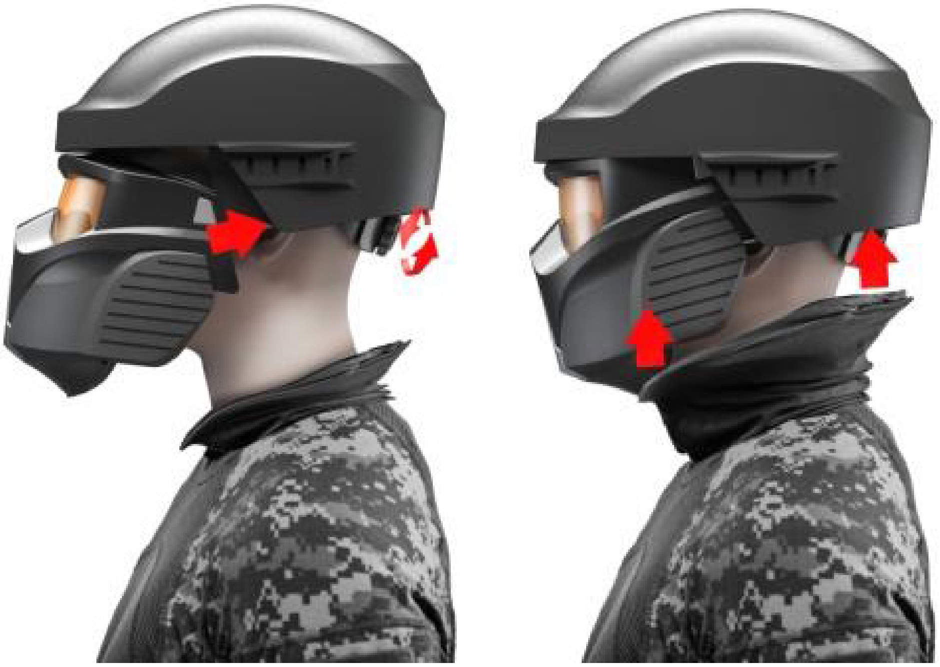


Figure 3-30: Mask/Suit Attachment Feature.

Another feature considered in this system concept is a retractable earflap. Such a mechanism would add some helmet weight for operations without the mask but would significantly facilitate connection of the mask and improve the interface for hood attachment. A sliding mechanism for the earflap could also be integrated with the attachment and adjustment mechanism to allow for seal adjustment of the mask. This would reduce the size of the mask because the earflap would not need to be attached to the mask. The feature for the retractable earflap is shown in Figure 3-31.

Figure 3-31: Retractable Earflap Feature.

For enhanced protection, a modular front module interface is envisioned. This module allows for the addition of an optional blower module which could be used for either traditional powered air purification or for dual cavity pressurization allowing for scalable protection, improved comfort, and improved lens defog. The option of dynamic response breathing could be incorporated and would be an additional option for this front module. The feature for a modular front module is shown in Figure 3-32.

Figure 3-32: Modular Front Module Interface Feature.

It is envisioned that additional refinement of the filter interface will be required to achieve suitable weapon interface performance. Next generation helmet programs are pursuing ballistic mandibles for facial protection and are exploring options for improving weapon interfaces. Current projected requirements do not require Chemical, Biological, Radiological, and Nuclear (CBRN) and facial ballistics protection at the same time. Should this change, weapon interface issues will be compounded further by the stand-off needed for ballistics protection and a filter interface.

3.4.1.4 Capability Assessment

Based on the results of the CB/GSS demonstration and the test bed evaluation, NGRPS capabilities were assessed and projected. Capability goals are defined as:

- Tailored Protection:
  - Enhancement; and
  - Scalability.
- System Integration:
  - Helmet Integration; and
  - Suit Integration.
- Weight Reduction.

The tailored protection and system integration goals address user requirements. The need for weight reduction is needed to satisfy headgear objective weights for the next generation helmet system. Additionally, there is a need to develop a Closed Circuit Self-Contained Breathing Apparatus (CC SCBA) as an option to further expand tailored protection. Goals for this development of the CC SCBA are to achieve significant weight reduction and to reduce logistical burden over current systems. Overall system goals are to extend operations in a CBRN environment.

To address these goals, a system concept was developed to include potential integration of powered options to support tailored protection capabilities. This concept also explores development of a CC SCBA as a means of further expanding scalability. A CC SCBA backpack combined with a powered air purifier or dual cavity pressurization unit would serve as a combination system with adjustable "on-the-fly" scalability. While all users would not require this capability, the ability to service this type of operation would further expand the utility of the headgear system. The concept for this CC SCBA combination system option is shown in Figure 3-33.

Figure 3-33: CC SCBA Combination System Concept.

A CC SCBA combination system would integrate the blower into the backpack. This allows the backpack to operate in filtered-air blowing mode when worn as a combination system until the added protection of the CC SCBA is needed. The combination system headgear concept uses a head support system similar to the revised CB PRISM to allow for mask integration and to secure the helmet shell. Efforts continue to explore options for a reliable low profile interface that will allow for adequate mask module sealing. A graphical representation of the head support system feature is provided in Figure 3-34.

Figure 3-34: Head Support System Feature.

Another feature included with this concept is the ability to scale down the system to a functional Air Purifying Respirator (APR) or Powered Air Purifying Respirator (PAPR). An internal fan would be used to support the PAPR configuration. The filter module could be applied to one side or both sides of the mask system depending on the internal configuration of the system and the requirements for weapon compatibility. Alternate size and thickness filters could be made available. The feature of an expandable filter module is shown in Figure 3-35.

Figure 3-35: Expandable Filter Module Feature.

Several options are available for the internal configuration of the CC SCBA system. The intent is to have a CC SCBA system that is scalable to meet operational needs and would range in duration from 1 hour to 4 hours. To minimize weight, technology advances are needed to support the CC SCBA concept. Efforts are underway to explore potential technology for the oxygen storage and carbon dioxide removal system. Options for developing a sensor based control system are also being explored to monitor and control oxygen and carbon dioxide content in an efficient manner. A potential representation of the CC SCBA internal configuration concept is shown in Figure 3-36.

Figure 3-36: CC SCBA Internal Configuration Concept.

3.4.1.5 Conclusions

Options for developing a NGRPS headgear system have been defined. Design concepts and poster layouts have been developed to provide a capability vision for the system. Concepts for headgear integration and tailored protection continue to evolve. More than one concept may be needed to satisfy all mission requirements.

3.4.1.6 Recommendations

Concepts for headgear integration and tailored protection need further refinement. User requirements are needed to aid in the selection of the best concept or concepts for military operations. Technology is needed to support CC SCBA development.

3.4.2 Dual-Cavity Respirator (United States)

3.4.2.1 Abstract

Concepts that enable the outer face seal of a chemical/biological respirator to be pressurized suitable for the military environment is being developed. Through de-coupling the airflow used for pressurization from that of respiration, the airflow required to pressurize the outer face seal is reduced by orders of magnitude. This is achieved through introducing a secondary cavity within which respiration is confined. The need for a reduced airflow is reflected in the size and power demands of the pump unit used to generate the positive pressure. Two distinct dual-cavity concepts are being considered.

3.4.2.2 Introduction and Background

The work described here was a research and development collaboration between the US and the UK on enhancement of respiratory protection. Respirators remain the primary means of protection for military personnel against the risk of inhalation of biological or chemical warfare agents. To function properly a seal must be formed between the respirator and the face of the wearer. Breaches in the face seal could allow ingress of toxic material. Recent advances in instrumentation that permits performance to be measured in field conditions have highlighted the susceptibility of present respirator technology.

The approach used in this research to overcoming breaches in face seal involves pressurizing the face piece using a man-mountable blower unit. However, historically these are bulky and require significant amounts of power and a multiple number of filter canisters. Consequently, this approach does not offer an acceptable military solution – hence, the reason to investigate a Dual-Cavity Respirator. A potential benefit of this technology is that owing to the isolation of the respired airflow, the dual-cavity arrangement lends itself to providing the warfighter with a real-time indication of respirator fit. This is achieved through monitoring the pressure within the outer cavity, which could be conveyed to the warfighter using a simple LED arrangement.

3.4.2.3 Technology

This program of work has focused on the development of a respirator which uses positive pressure to maintain a good protection level, but cannot be "out-breathed" and does not rely on face seal conformity. Dual cavity technology isolates the positive/negative pressure swing within a separate oro-nasal mask (nose cup), which has its own sealing locus around the nose and mouth. The eye space within the respirator is then purged with a small amount of filtered air using a blower unit, which also creates a positive pressure within the eye space. The dual cavity concept has been retro-fitted into a M53 mask during the course of this project.

3.4.2.3.1 Oro-Nasal Design

During the development of the oro-nasal mask, multiple options of half mask were evaluated for their shape and comfort and three were down selected for their individual features. Figure 3-37 shows the three down selected masks and how their individual features have been incorporated to form the final design.

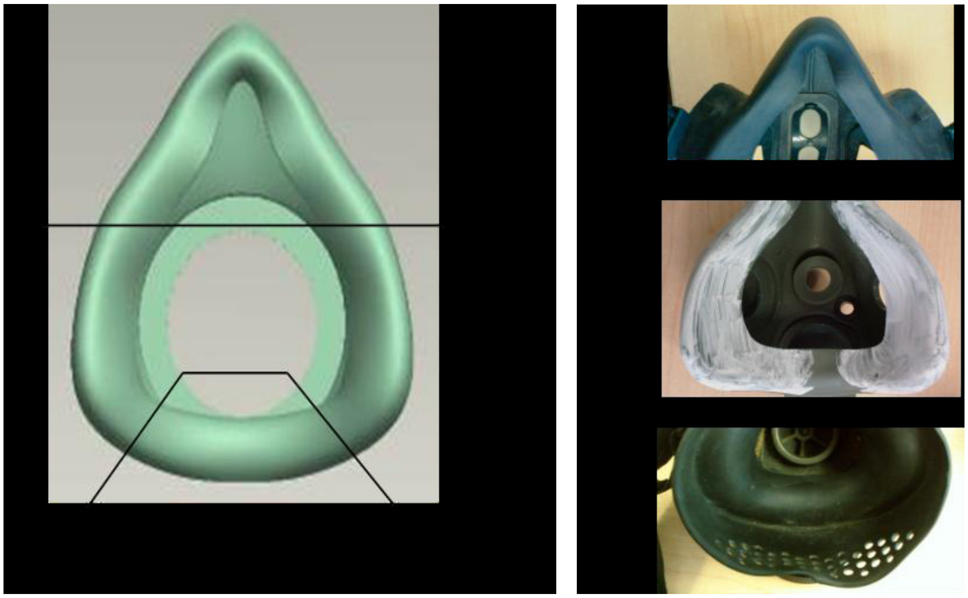


Figure 3-37: The Design Features for the Desired Oro-Nasal Mask, Taken from the Three Down-Selected Designs.

Mask 1 (top right) was chosen because of the shape around the bridge of the nose, mask two (middle right) was chosen because of the width around the checks and mask three (bottom right) was chosen because of the shape of the reflex seal.

To produce an accurate prototype of this oro-nasal design, a compression tool was designed to enable silicone to be cast to produce a testable mask. The CAD image is shown in Figure 3-38 and the actual design tool is shown in Figure 3-39.

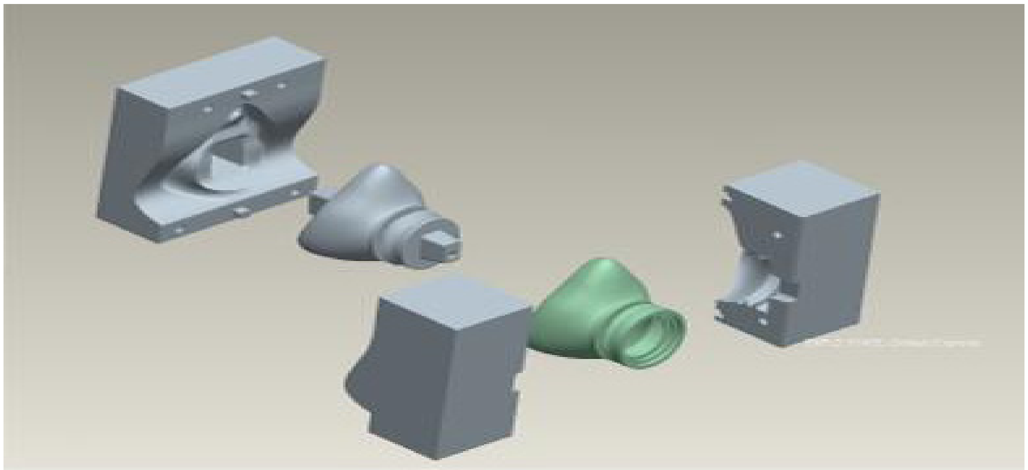


Figure 3-38: A CAD Image of the Compression Tool Used to Mold the Oro-Nasal Mask for the Dual Cavity Respirator.

Figure 3-39: The Mold Tool Used to Create the Silicone Oro-Nasal Mask Shown in Figure 3-40(a).

The design tool for molding the mask was created using a polyurethane board material which was cut to the desired shape using a Computer Numerically Controlled (CNC) machine. The center part of the tool was created using Stereo Lithography Apparatus (SLA) because of its complex shape. The theoretical mask and the actual silicone oro-nasal mask that was produced from this casting technique are shown in Figure 3-40.

(a) (b)

Figure 3-40: (a) The Black Oro-Nasal Mask Within the Figure has Been Molded Using the Design Tool; (b) The Grey Image Shows the CAD Image of the Oro-Nasal Mask.

3.4.2.3.2 Integrated Blower Unit

In order to generate a positive pressure a blower unit was needed to generate a positive pressure within the eye space. The requirements for the blower unit were:

- Demisting capability;
- Positive pressure;
- Capture / entrain penetrating material;
- Minimal flow rate (5 – 20 $L \cdot min^{-1}$); and
- Low power.

An extensive review into the available options was carried out in the early stages of the project and the favored miniature blower units, (small, Computer Processing Unit (CPU) fans), are shown in Figure 3-41. These blower units have the benefit of generating a high airflow, having low power demand, being small and being quiet.

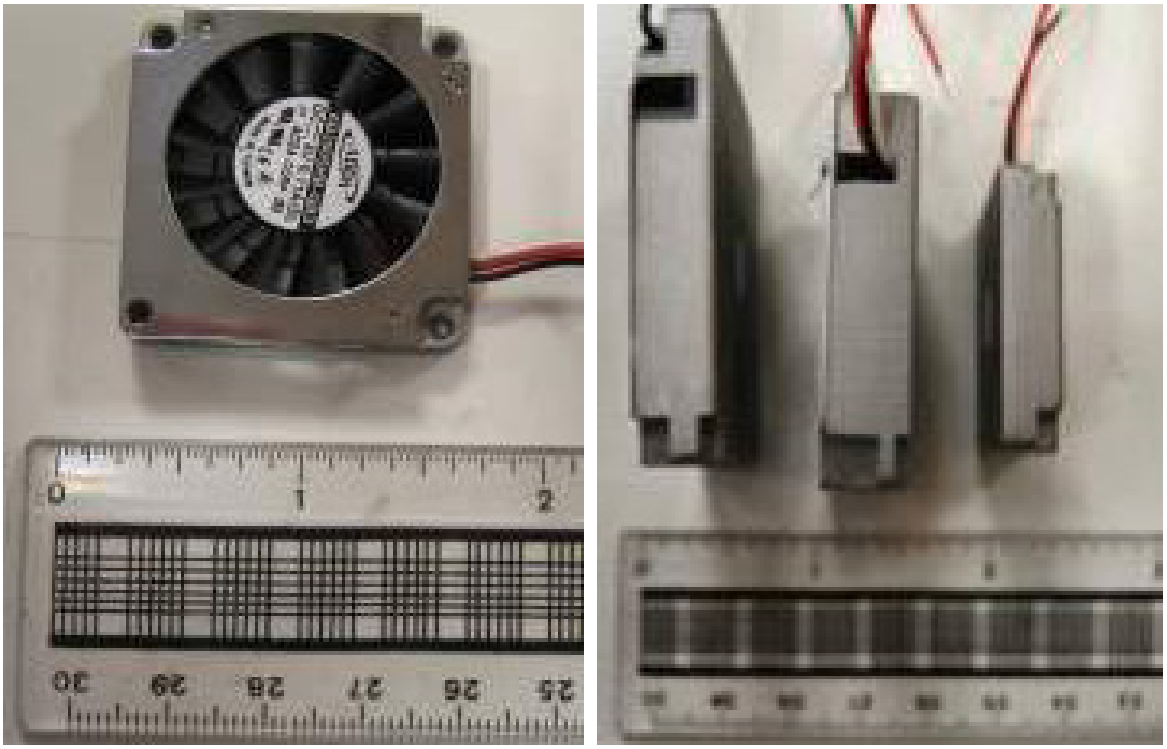


Figure 3-41: Down Selected Computer Fans that were Tested Within the Mask Platform.

Unfortunately, manufacturing of these blower units ceased during the course of the research, so versions, with a very similar specification were sourced when required. These blower units were embedded into the respirator platforms.

3.4.2.4 Final Design and Performance Testing

Based on the comparison of the different arrangements, it was established that independent filtration for the fan unit was the most desirable arrangement for the dual cavity respirator. Therefore, all final testing was carried out using a P3 EN143 filter for the fan unit and a standard conformal filter for the oro-nasal mask.

The fan unit was mounted to the inside of the eye space cavity and a small bespoke cable was created to allow power to be supplied via the communication port on the respirator, with a second cable connecting the external power supply to the respirator.

A series of laboratory-based measurements were carried out to assess the improved performance of the dual cavity respirator using the M53 respirator as a control. The tests involved 8 volunteers carrying out a series of head movements wearing both respirators in turn. The head movements were: Normal Breathing (NB), Head Side to Side (HSS), Head Up and Down (HUD), Bending Over moving Head Side to Side (BOHSS), Speaking the rainbow passage and Deep Breathing (DB). In the case of the modified mask, the volunteers were asked to breach the outer face seal using two fingers for one minute at the end of the series of exercises.

The in-mask particle count (oro-nasal mask) and in-mask pressure (eye space) were recorded simultaneously using the Respiratory Battlefield Evaluation System (RBES). The RBES operates two TSI Portacounts in parallel, which allows the challenge and in-mask particle count to be recorded simultaneously. The exercises were performed within a test chamber containing a high sodium chloride aerosol challenge.

The average Protection Factor (PF) achieved for each volunteer using the control mask is above the manufacturer's specification. However, Volunteer 2 showed severe leakage during the "bend over head side to side" exercise. This was because the respirator was slightly too large for this particular volunteer, and they commented that they felt a leak underneath the chin.

When one volunteer's protection data was compared from the unmodified mask to the dual cavity version, it was seen that the protection factor had increased from 104 to 105 with the minimum PF achieved in the dual cavity being higher than the maximum PF achieved in the unmodified version.

Compared with a negative pressure control respirator, a dual cavity respirator can enhance the level of protection by (approximately) at least one order of magnitude. There is also no observable inward leakage into the oro-nasal mask while the face seal was deliberately breached for a period of 1 minute.

The Advanced Respirator Test System (ARTS) uses a 106 challenge of shell ondina oil, which is diluted through an ARTS box before it reaches the porta count. The ARTS box dilutes the challenge by a known amount which is calibrated periodically throughout the testing. The ARTS process also uses a different set of exercises from that seen in the results shown previously, and includes a chewing exercise. The new exercises (known as ARTS+), utilize the more vigorous activities from an SMP, creating a respirator fit test which is more akin to military field trials.

ARTS+ was therefore used to test the dual cavity respirator. The respirator was used in its final arrangement (i.e. fan unit mounted inside the mask with an external power supply running the fan). Due to the different challenge involved compared with ARTS, and the more strenuous activities in ARTS+, it was necessary to use a different ethical protocol for this work (MoDREC PPE-066). The protocol used for this study required the volunteers to be from the military, which limited the volunteer pool available. There was also a limited budget at this stage in the project.

Therefore, only two people were tested using ARTS+. The mask was probed in both the oro-nasal mask and the eye space, so that protection measurements could be taken from both cavities while the fan was on and off.

From the limited data that was it was determined that some individual Subjects maintained their oro-nasal seal throughout all of the exercises, because the PF remained at a very high level regardless of a drop in eye space protection. However, some Subjects showed a range of protection data throughout the exercises, and the oro-nasal data mirrored the eye space, indicating that there was not a good oro-nasal mask fit. This is emphasized within the data from when the fan was switched off. The eye space on some Subjects filled with particles when the fan was switched off, which is believed to be due to the purge relief valve not sealing correctly. This problem could easily be rectified with a stronger valve.

One Subject's oro-nasal seal remained intact during the measurement with the fan off, and their protection factor remained at 106 for 5 out of 6 of the exercises, when there was very little protection offered by the out cavity. Another Subject's oro-nasal seal appeared to be compromised when the protection measurements were recorded, and when the mask was removed it was seen that the outer face seal had overlapped the inner seal. From the results it appears that it is imperative to keep a good oro-nasal seal, which fully supports the theory of dual cavity technology; the real time fit indicator should prevent such problems.

3.4.2.5 Conclusions and Summary

The dual cavity respirator concept has been taken to proof of principle level. It has been demonstrated that employing the dual cavity concept greatly reduces reliance on the respirator face seal to provide protection.

This has been achieved by utilizing a bespoke oro-nasal mask connected to the air inlet of the M53 via a bespoke air guide assembly. This created an inner cavity allowing the eye space to be purged with a small computer fan unit. The arrangement of the components within the mask was optimized during the development phases of the project, and it was established that the blower unit required independent filtration to allow the eye space to retain its pressure.

The air flow requirement was found to be optimized with a high flow, low pressure arrangement, which was achieved by having a constant purge valve allowing the respirator eye space to be constantly replenished with clean air. During the course of investigations, it was seen that only a minimal amount of pressure was required within the eye space to give excellent levels of protection within the oro-nasal mask (~ 5 mm H_2O/30 – 50 Pa).

A real time fit indicator has been created to allow the user to gain a real time feedback as to how well the mask is fitting, by monitoring the eye space pressure. The final concept of use of the real time fit indicator needs further consideration (i.e. use as a fitting tool or as a fit indicator during actual use).

The protection levels offered by the dual cavity mask were measured in comparison to the unmodified mask. It was seen that on average, the volunteers' protection was increased by an order of magnitude by using dual cavity technology. The performance of the dual cavity mask was also tested using ARTS+ which is a more rigorous set of exercises than standard fit tests, and more akin to SMP type activities. Based on the limited data collected, it was seen that the dual cavity mask gave excellent levels of protection in both the eye space and the oro-nasal space with the fan switched on. However, when the blower unit was switched off, the protection level of the eye space dropped, whereas the oro-nasal protection was maintained.

3.4.2.6 Recommendations (Potential Paths Forward)

The following recommendations are made for future testing and work required optimizing this mask:

- Run the mask from a battery rather than an external power supply.
- Retro-fit all sizes of the M53 to ensure that the increased levels of protection can be obtained across a wide range of subjects.
- Source/create a more rugged blower unit. The blower unit used in this iteration of the mask is suitable for demonstration of the principle. However, it would not be robust enough for military use.
- Compare the real time fit indicator read-out with real in mask pressure, to ensure that the sensor relays the correct information to the user.
- Test the performance of the mask in realistic battlefield.

3.4.3 Whole System Testing of Layer Approaches (Norway/Netherlands)

3.4.3.1 Introduction

In addition to materials innovations in clothing systems and similar to the innovations in respiratory protection (helmet/mask combinations) current innovations in protective clothing materials, designs and concepts may allow scalability of protection.

In the Dutch basic approach, based on theoretical considerations clothing based on multiple layers should constitute a system that allows CBRN protection to be scalable. With a layered concept the protection factors could be stepwise increased with a corresponding increase in physical burden. When desired or necessary it will be possible to improve on comfort and thermal strain without completely losing CBRN protection as is the case in current systems. To evaluate, under controlled conditions, what would be the effect of combinations of clothing layers on protection, a series of experiments was executed on clothed cylinders exposed to Methylsalicylate (MeS) vapor and with specially made clothing systems in Man-In-Simulant Test (MIST) protocol.

In the Norwegian approach the layered approach was further developed via a combination of design and materials, air permeable as well as air impermeable, membrane materials. To reduce the physiological burden the concept utilizes zipped air vents to reduce thermal stress when possible. The Normans system may utilize air permeable lightweight absorptive carbon materials either as initial layer and is combined with a membrane layer for high levels of protection.

3.4.3.2 Technology

To establish the protection levels of the light weight air permeable clothing systems material swatch tests need to be conducted. The highly air permeable absorptive carbon fabrics (e.g. carbon bead technology, carbon cloth technology) show below requirement protection levels when evaluated in convective flow tests following standards such as AEP-38. Therefore, additional methods needed to be developed that allow evaluation of these air permeable fabrics in conditions that are realistic, allowing air to penetrate but also escape the micro-climate between skin and clothing. A cylinder test was developed to conduct such evaluations. These Cylinder tests were executed at 1 and 10 m/s at a temperature of 21°C and moderate humidity (around 60%), the MIST protocol was conducted according to the standard NATO method. In both tests series Passive Adsorbent Dosimeters (PADs) were used as absorbents. The tested clothing materials on the cylinder were an air permeable activated carbon layer (Material A), a semipermeable membrane (Material B) and an air permeable “normal” textile layer (Material C), in the MIST chamber they were all dedicated activated carbon clothing layers, with high air permeability. The tests and experimental set-up have been described in Ormond et al. [46].

At 10 m/s wind speeds on the cylinder the permeable clothing layers hardly protect against vapor, not even with two layers combined. At 1 m/s wind speeds single clothing layers still provide low PF values, material A about 38, Material B, around 30 and material C around 1.5. Combining layers, material A as inner layer, even with material C as outer layer provides PF values of 700 and higher. Two layers of material A barely perform better than this combination of “C+A”. Material A as outer layer with material C as inner layer does not protect much better than a single layer of material A, see data in Figure 3-42.

The results of the MIST ‘whole system test’, in which volunteers dressed in prototypes of the various clothing layers, and combinations thereof, were in agreement with the findings mentioned above (Figure 3-43). By using either single layers or combinations of clothing prototypes the PF-value could be chosen in the range from low to high. The associated thermal burden, as predicted with a thermal physiology dynamics model, increased with the PF-value.

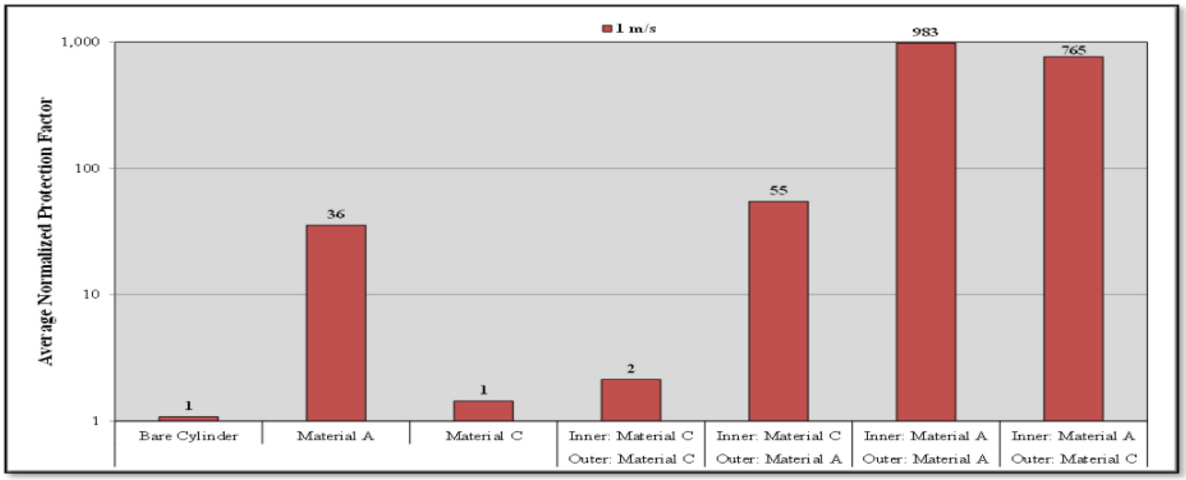


Figure 3-42: Enhanced Protection by Multi-Layer System, Dependent on Layering Order [47].

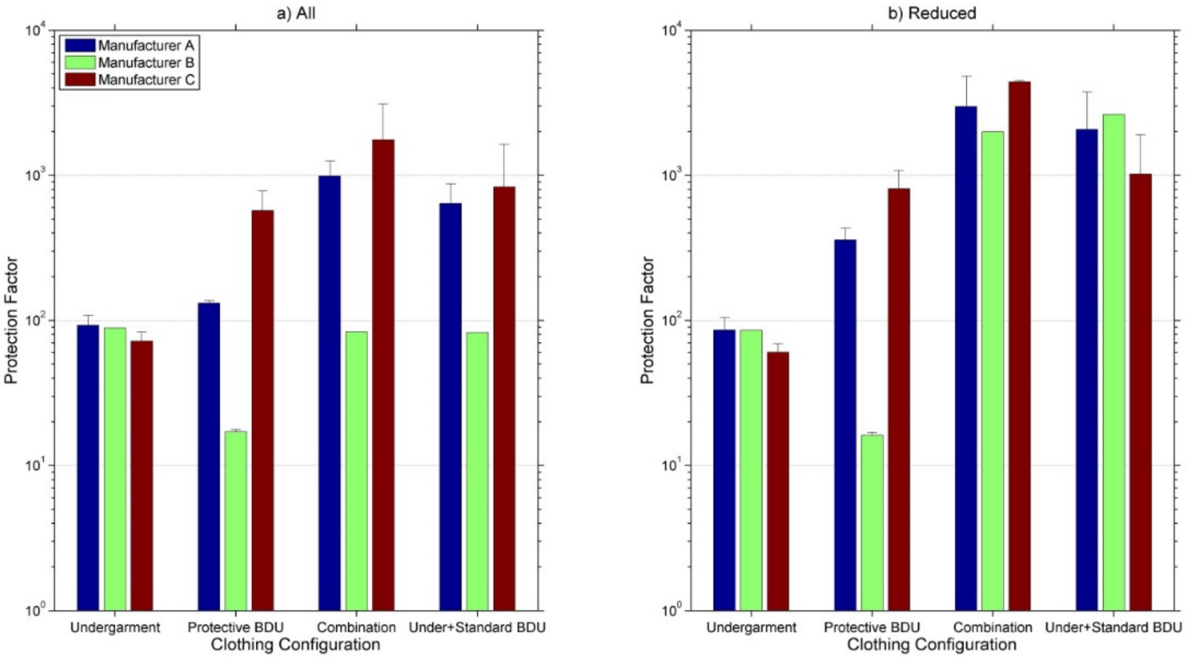


Figure 3-43: Evaluation of Experimental Layered Concepts. These concepts were made of available materials but not commercial off the shelf clothing products. The concept ‘undergarment’ refers to an absorptive undergarment only; ‘Protective BDU’ refers to an air permeable BDU type material that is made of an activated carbon absorptive material with normal underwear; ‘Combination’ is the combined wear of absorptive underwear and absorptive BDU; ‘Under+Standard’ BDU is the protective underwear with a regular (“normal”) BDU.

In addition to these conceptual evaluations, the Norwegian system (Normans’ concept) conducted tests and evaluations on their concept. Especially the lab and field tests with human subjects were of added value here and show the effectiveness of layered and modular approaches see Figure 3-44 and Figure 3-45.

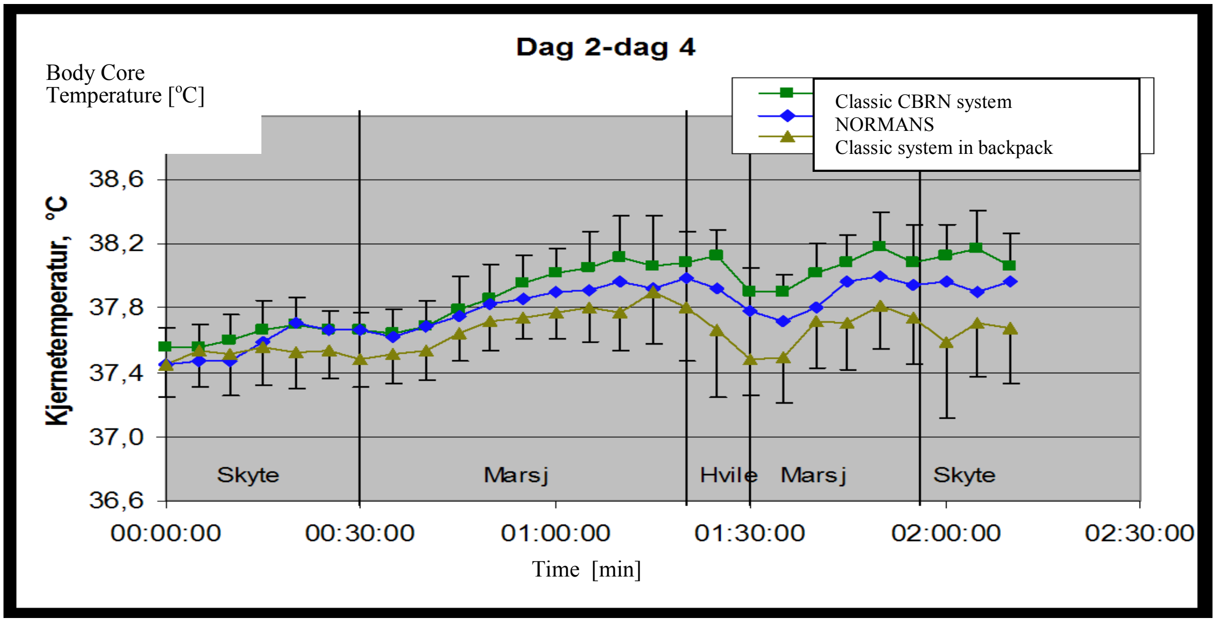


Figure 3-44: Physiological Thermal Strain Evaluation During a Field Trial with the New Modular Normans Concept versus a 'Classic' CBRN Concept.

Figure 3-45: Ergonomics – Donning Evaluations of the Normans Concept.

3.4.3.3 Capability Assessment

These results provide a clear indication that the effect of two layers mainly depends on the effective reduction of wind speed to the protective layer. Similarly the wind speed has a strong effect on the protection in these systems. The deposition of vapor on the PADs was equally distributed over the cylinder surface, suggesting there was no effect of the angle between wind and surface. This is different from the aerosol results in which significant effects of aerosol deposition on the angle of the surface to the wind were found. From these experiments we conclude that a scalable concept, with a well-balanced layer system, may be a very useful and successful concept for individual protective systems.

On the concept level the modular system provides advantages in terms of rapid donning and reduction of physiological burden in an operational environment. These modular systems would thus allow enhanced operational sustained capability when used in a lower threat level as compared to currently used systems. The renewed AEP-38 does provide guidelines to implement these systems and derive separate requirements for them in terms of materials tests. But, there is still a lack of adequate test and evaluations methods and that also complicates the setting of requirements for these systems and to identify the operational conditions of which these requirements should be derived.

3.4.3.4 Conclusions

The layered systems approach allows reduction of physiological burden, both from a fundamental perspective as well as conformed by whole system evaluations in the lab and realistic conditions. An important limitation currently to adequate assessment of these low burden modular concepts is the lack of appropriate methods to assess the actual protection of these systems and the materials. Although the Man-In-Simulant-Test will allow end evaluations of the full concepts in the protective states, there is a lack of test and evaluation methods to evaluate fabrics, closure systems, interfaces and vent/zipper systems before it needs to be integrated in a full system. But, using the systems evaluations both the Dutch and the Norwegian concepts demonstrated the ability for modular systems to reduce physiological burden when exposure was not present or allowed scalability of protection when combinations of protective layers were used.

Practical application, however, as well as integration with current operational doctrine may need additional thoughts as the minimal protective levels may be lower than currently in use, and, therefore, new decision criteria and procedures on how and when to use these systems may need to be developed.

3.5 CHAPTER CONCLUSIONS

When studying and discussing individual protection the first thing that is usually addressed is novel material technologies to improve absorption, filtration or blocking of hazardous agents in vapor, aerosol or liquid form. In this chapter some of the new material technologies were discussed and each of these technologies as well as combinations thereof could provide opportunities for improving protection and lowering warfighter burden.

Examples of significant technology developments in this Chapter, included:

- Improved filtration and absorptive materials, to enhance the range of chemicals absorbed (or adsorbed) and/or enhance absorption capacity.
- Enhanced liquid repellent capability and protection with new (nano)technologies.
- Improved integration of the clothing and mask systems to allow for better system protection.

- Improved insight in the behavior of the protective system to allow reduction of protective materials, also reducing the burden.
- Enhanced operational capabilities due to the overall burden reduction by applying modular approaches for protective clothing as a system.

Many of the technologies presented here are emerging from research labs and have not necessarily been transitioned to the protective clothing industry. Some of the technologies are further advanced than others, e.g. the liquid repellent textile technologies have been commercialized and will aid in helping to improve liquid protection in the field as part of the system. The technology is transitioned to industry and will be made available. Even if the technology seems to allow air permeability and therefore should allow heat and mass transfer, clothing requirements also have requirements of durability, laundering and usability (e.g. flexibility). These additional requirements, as explained in the first paragraph of this chapter may challenge the further development of these technologies. For respirator filtration materials this bar may be somewhat lower as a filtration canister is a less challenging construction to produce than a clothing product. Furthermore, many of these technologies have been evaluated for protective aspects only. On the other hand, even if these technologies will end up only partly as effective as discussed in this chapter, they will still strongly allow enhanced protection without increasing the burden when used as a system.

Combinations of the technologies presented here would obviously lead to enhanced capabilities as well, but these developments have been studied separately and not in combination with each other, integration issues will need to be studied to explore synergy effects of the technologies, or potential negative interactions.

Scalable protection and modular systems have also been described in this chapter. Although these systems did not have major technology advances, the approach of modular systems is innovative in itself. It may depend on highly air permeable lightweight absorptive materials, that are currently available, but in addition it will require enhanced situational awareness and decision making capabilities. This should then allow maneuver to a safe zone or allow sufficient warning time to don gear for enhanced protection and continue operations as planned.

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Chapter 4 − REACTIVE TECHNOLOGIES

4.1 INTRODUCTION

In addition to the Active and Passive Technologies, the Reactive Technologies may provide an additional layer of defence or support the overall goal of protecting the warfighter while minimizing the burden. In view of this systematic approach Reactive Technologies are those technologies that induce a change in a protective barrier and/or to the CBRN agents to minimize or eliminate the effects of the agents to the warfighter. Classically, reactive technologies have been used as decontamination agents and these two properties (reaction and decontamination) are closely linked. An additional area for reactive technologies, however, is the technology that helps disclose agents when they have contaminated surfaces.

In the context of this Report, reactive technologies may support these goals by reducing the agent challenge levels thus allowing a reduction in required protective performance of passive technologies. This would allow lighter weight, more breathable and more comfortable protective clothing. The reactive technologies could be used and approached in different ways, possibly providing different layers/levels of protection. For example reactive technologies added to uniforms could provide additional protection, reactive technologies that disclose areas that have been contaminated will help reduce exposure of warfighters and reduce the amount of protection required. Reactive technologies for rapid decontamination when warfighters have been exposed may reduce contact with agents and reduce risk to protected warfighters. Easier decontamination of crucial, sensitive technologies will indirectly enhance and help to maintain capabilities for the warfighter after exposure to CBRN agents.

To optimize the application of these technologies, operational procedures and processes may need to be adapted to strengthen their focus on the warfighter. Some technologies described here fall under the categories that coincide with the protection of sensitive equipment as the operational goals of preserving crucial technologies and protecting warfighters will mutually strengthen each other and could greatly enhance operational capabilities after an exposure to CBRN agents. In this chapter a fairly wide range of these technologies is addressed to explore the full spectrum of solutions that may support achieving the above mentioned goals.

4.2 DETECTION TECHNOLOGIES TO ASSESS DECONTAMINATION

4.2.1 Enzymatic Decontamination Assurance Sprays (United States)

4.2.1.1 Abstract

Agent disclosure enzymatic decontamination assurance sprays are one of the most sensitive CWA detection systems. These decontamination assurance sprays provides a unique ability to quickly locate even small amounts of agent contamination over a large area saving money and time during the decontamination process. Enzymatic Decontamination Assurance spray technologies will significantly improve the entire decontamination process.

4.2.1.2 Introduction and Background

The decontamination assurance sprays are non-toxic enzyme-containing water-based liquid sprays that function as colorimetric indicators of surface contamination. The sprays are sensitive enough indicate sub-microgram quantities of agent contamination on surfaces, providing the user assurance that a decontamination effort has been successful. In addition, this technology provides the ability to determine if and map where assets are contaminated with chemical warfare agents. When used as a first step in the decontamination process this provides the knowledge needed to triage assets and allow clean assets to skip the decontamination process. Mapping also allows for decontamination to be focused on the contaminated areas, saving decontamination resources and improving results. The sprays contain no toxic chemicals and are compatible with many materials. They are safe for use in all areas where water can be applied.

There are two different chemical agent class specific sprays, one for nerve agents and a second for blister agents. For both the color change is clearly visible a minute or two after spraying at even sub-microgram quantities of chemical warfare agent contaminations.

4.2.1.3 Nerve Agent Disclosure Spray

Chemical nerve agents function by blocking Acetylcholinesterase (AChE). In the nerve agent disclosure spray inhibition of AChE triggers an enzymatic system that changes the liquid spray from yellow to red within a few minutes for even small sub-microgram quantities of nerve agent (Figure 4-1). One limitation of this approach is that some components of this enzyme system need to remain separated until the disclosure reaction begins. To overcome this limitation the disclosure spray is applied using a two chamber sprayer mixing the components at the time of application. In the two chamber sprayer the disclosure spray is stable for over 12 hours at temperatures up to 40°C, while the lifetime of the mixed system after application to a surface lasts for tens of minutes to a couple of hours depending on temperature.

(a) (b)

Figure 4-1: Disclosure Spray Indicating Contamination on Terrain (a) and a Vehicle (b) by Turning Red.

In development it became apparent that when sprayed on vertical surfaces the indicator would run potentially spreading the contamination. A cellulose thickening agent was added to decrease running on vertical surfaces.

During limitation of the technology is that it is not possible to detect agents on surfaces with highly acidic/basic pH. The spray includes a buffering system to help address this, and it also has incorporated pH sensitive dyes that provide a purple invalid indication when the buffering system has been overwhelmed. This provides some mitigation of this limitation by alerting the user that the indication spray is not functioning on this surface. Aside from surfaces with extreme pH, like fresh concrete, the nerve agent disclosure spray functions well on a broad range of surfaces and even with a broad range of potential battlefield contaminants.

The cost of the nerve agent disclosure spray is a hurdle for fielding. The AChE enzyme was the largest driver of this high cost. At the start of the project AChE was only able to be obtained from electric eels, limiting production. AChE enzyme can now be produced recombinant in a *pica* based expression system. Efforts to examine insect and plant based expression systems along with optimizing the pica based system are ongoing to further reduce the costs for AChE production. In addition to the cost of producing the enzymes, the cost of fielding the disclosure sprays is also impacted by their limited shelf-life. The shelf-life and acceptable storage temperatures can be increased by lyophilizing the enzymes to remove water allowing the disclosure spray to be stored as a dry powder. The inclusion of excipients, like starches and sugars, before drying helps to stabilize the enzymes in the dried state resulting in an additional extension of shelf life and temperature stability.

Being a colorimetric indicator, white light is required to clearly read the response. In response to user requests to be able to use the indicator in the absence of white light development of a low-light system, using additional fluorescent or chemiluminescent indicators to complement the colorimetric change is underway.

4.2.1.4 Blister Agent Disclosure Spray

Similar to the nerve agent disclosure spray, the blister agent disclosure spray is a non-toxic enzyme based liquid spray that changes color in the presence of agent. The blister spray is applied red to surfaces but on clean surfaces changes to yellow within 1 – 2 minutes. In the presence of sulfur mustard, the solution remains red. The resulting detection color scheme is comparable to that employed by the Nerve Agent Disclosure Spray in which clean surfaces are yellow while those contaminated with agent are red.

The spray also contains a purple invalid indication under conditions where disclosure technology becomes inactive similar to the Nerve spray.

4.2.1.5 Analysis of Results and Conclusions

The agent disclosure spray is one of the most sensitive CWA detection systems, and provides a unique ability to quickly locate even small amounts of agent contamination over a large area. This allows the user significant cost savings in the decontamination process by enabling them to quickly map where contamination is allowing them to determine if an asset needs decontamination and allowing them to focus the decontamination primarily on the contaminated areas. It is estimated agent disclosure spray will cut the costs and time for a decontamination effort by three to five fold. In early field trials 96% of US soldiers felt the disclosure sprays enhanced their ability to decontaminate vehicles. Enzymatic Decontamination Assurance spray technologies will significantly improve the entire decontamination process.

4.3 COATINGS AND SURFACE TREATMENTS

4.3.1 Progress in Anti-Microbial Surfaces (United States)

4.3.1.1 Abstract

Biological warfare agents have become common vernacular since incidents such as the 2001 *B. Anthracis* (anthrax) attacks on federal mail facilities and office buildings. With global terrorism on the rise and the nature of today’s asymmetrical battlefield, there are even more pressing needs for effective, non-destructive decontamination techniques, particularly for the warfighter. Current biological decontamination methods are resource intensive, logistically burdensome, and when delayed by operational necessity, may be less effective than desired. Anti-microbial coatings have the potential to significantly reduce or eliminate these challenges through the development of self-decontaminating surfaces that have the capability to neutralize biological agents before they do harm.

The key objective of these efforts was to investigate/develop potentially reactive coatings to significantly reduce the risk to warfighters and reduce the burden of current decontamination approaches. This précis briefly examines fullerene (singlet oxygen producing) containing coatings, N-halamine copolymer coatings, nano-composite material coatings, silanol coatings, and embedding standard biocides in coatings. Additionally, this précis also examines a surface-segregating technique to promote the reactive elements to the solid-air interface of coatings so they are available to interact with agents.

4.3.1.2 Introduction and Background

In the battlefield, decontamination is a multi-step process consuming significant resources. The Operational and Thorough levels require extensive equipment washes, hundreds of gallons of water per vehicle and the use of corrosive and hazardous decontaminating agents. Anti-microbial coatings have the potential to significantly reduce or eliminate these challenges through the development of self-decontaminating surfaces. These surfaces have the capability to neutralize biological agents before they do harm – thereby transforming the current decontamination process.

The key objective of these efforts was to investigate/develop potentially reactive coatings to significantly reduce the risk to warfighters and reduce the burden of the current decontamination approach. This section briefly examines oxygen sensitized coatings, chemically resistant nanofibers, coatings with Parylene, coatings *via* atomic layer deposition and molecular layer deposition, N-Halamine Copolymers for biocidal coatings, silanol coatings, and N-Chloramide modified NOMEX® as a regenerable self-decontamination material for protection against chemical warfare agents.

4.3.1.2.1 Chemically Resistant Nano-Fibers

Polymer nano-fibers electro-spun from solvents have the potential to be vulnerable to chemical agents and toxic industrial chemicals. Significant efforts to resolve this chemical vulnerability problem were investigated. Two basic tactics were investigated: coating nanofibers and using polymers that were more chemically resistant. For all of the techniques studied, there were trade-offs among the properties of chemical resistance, mechanical robustness (namely brittleness), and the fiber morphology needed to achieve high FoMs. Conformal coatings using gaseous precursors provided the best fiber morphology and the potential to achieve improved chemical resistance with acceptable compromise in mechanical properties. The most intriguing technique was the development of a polymer system that could be electro-spun from a solvent, and then crosslinked to a chemically resistant form. However, due to time and resources applied to developing crosslinked fibers with acceptable morphology and mechanical properties, further development of the technology has not yet occurred. Nonetheless, there is still great potential for this idea of cross-linkable fibers if the appropriate resources could be applied to research. Two coatings were deemed as having the potential to provide chemically resistant nanofibers with the desired properties:

1) Coating with parylene; and
2) Coating with metal oxides or metal-organic films using the related techniques of ALD and MLD.

4.3.1.2.2 Coatings with Parylene

Parylenes (poly-para-xylenes) are a unique group of thermoplastic polymers (Figure 4-2) whose dimer precursors can, under the right processing conditions, vaporize in a uniform manner and be drawn down to deposit a very thin homogenous polymer film onto a substrate. This film, which can be as thin as tens of nanometers, forms a protective coating that is conformal and has desirable physical and chemical properties, such as resistance to degradation by aggressive chemicals. Parylene C (poly 2-chloro-p-xylylene) has a chlorinated benzene ring, which contributes to its low permeability to moisture and corrosive gases.

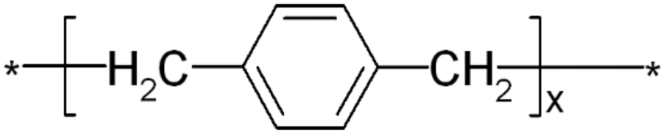


Figure 4-2: Parylene Polymer.

Parylene coating occurs *via* chain growth polymerization with no termination as the chain ends during growth. Monomers add to an active site at the end of each chain, growing from monomer to oligomer to polymer. The thickness of the resulting coating is primarily a function of the quantity of dimer used and can be controlled within 10% (of the coating's thickness). Temperature and pressure are also factors in the deposition rate.

4.3.1.2.3 Coatings via Atomic Layer Deposition and Molecular Layer Deposition

ALD is a vapor deposition technique used to deposit thin films of high-quality material. ALD is very similar to CVD, but ALD is unique due to its capability to coat extremely complex shapes, such as nanofibers with conformal inorganic layers of high-quality material. ALD is able to grow thin films with thicknesses down to a single monolayer. Another difference from CVD is that ALD precursors are strictly separated from each other in the gas phase. The reactions use gas phase precursors that react with a solid surface. Each half-reaction of the ALD process cycle is believed to be both sequential and self-limiting. The self-limiting nature provides for a constant and often sub-monolayer growth rate for each half cycle (typically 0.5 monolayer [52]). During ALD, one precursor is dosed until it has fully reacted with all possible surface sites, and the products and excess reactants are swept away using an inert carrier gas. This is referred to as the "A" reaction. A second precursor is dosed until the surface has fully reacted, and the excess reactant and products are removed from the reactor. This is referred to as the "B" reaction. One important distinction about ALD is that at the end of the "B" reaction, the same surface that was present at the beginning of the "A" reaction must be present. These reactions continue in an ABAB manner to grow a thin film of a desired thickness. As an example of the ABAB sequence, one of the most well studied ALD reactions is the Trimethylaluminum (TMA [$Al(CH_3)_3$]) and H_2O reaction to form aluminum oxide (Al_2O_3) (Figure 4-3).

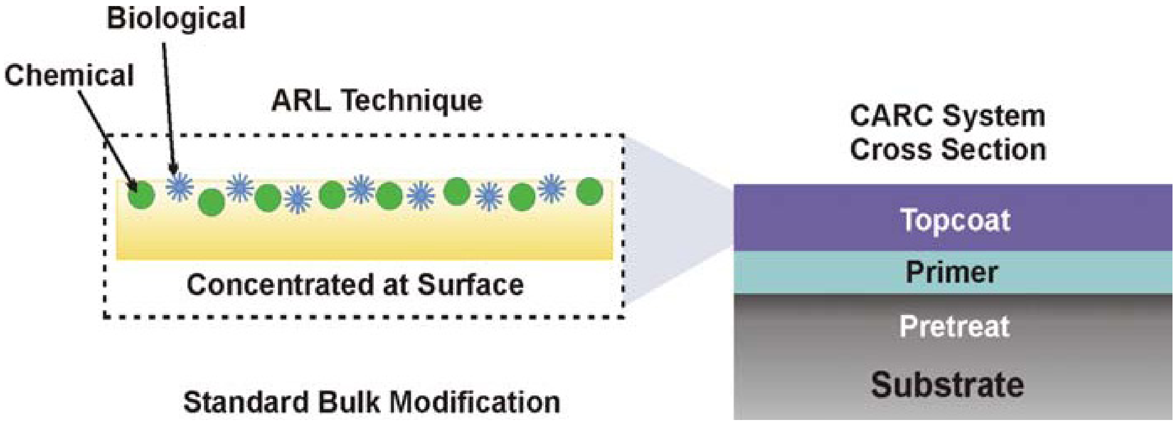


Figure 4-3: Representation of Coatings Showing Concentration of Active Components at Surface.

MLD is similar to ALD because it is also based on sequential and self-limiting reactions at the surface. MLD differs from ALD by the substitution of organic constituents in place of the metal organic precursors used in ALD. MLD expands upon the chemical concepts of ALD to integrate organic monomer and molecular building blocks into oligomeric and polymeric thin-film structures with precise control of film thickness. During MLD, a "molecular" fragment is deposited during one of the MLD cycles on surface reaction. Typically, the deposition of organic polymer films proceeds through many chemical strategies such as by a stepwise condensation polymerization reaction or ring-opening reaction at the surface. Additionally, when many ALD reactions proceed through two-step AB reaction cycles, MLD films can also be grown through three-step ABC reactions cycles. Additionally, existing ALD techniques can be combined with MLD techniques to grow hybrid organic–inorganic films to produce composite thin films.

4.3.1.2.4 N-halamine Copolymers for Biocidal Coatings

The resultant copolymers were coated onto cotton fabric through hydrolysis of alkoxy groups with formation of silyl ether bonding, opening of the epoxide ring and subsequent reaction with hydroxyl groups on cellulose, and by crosslinking between the hydroxyl groups on the copolymer and on cellulose, respectively. The coatings were rendered biocidal upon exposure to dilute household bleach solution. All of the coatings provided complete inactivation of about six logs of Staphylococcus aureus and Escherichia coli O157:H7 within minutes of contact time. The effects of the aforementioned tethering groups on wash fastness and ultraviolet light exposure were also studied (Figure 4-4).

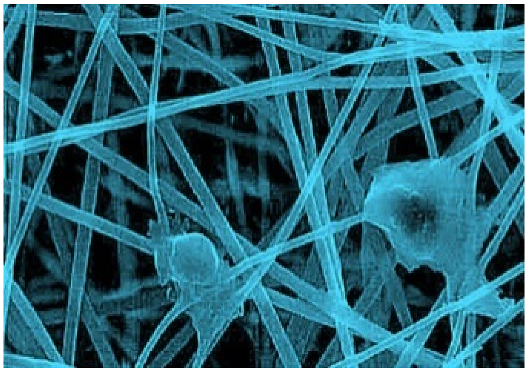


Figure 4-4: Representation of Biocidal Coating on N-Halimine Copolymers.

4.3.1.2.5 Silanols

This is a new class of silicon based antimicrobials called silanols ($R(CH_3)_2SiOH$) (Figure 4-5). The antimicrobial activity of the silanols was at least twice as strong as analogous alcohols. The silanols are prepared from the hydrolysis of chlorosilanes. The silanols can be prepared by low cost processes. Silanols degrade into the environmentally benign species of silica, CO_2 and H_2O instead of accumulating in the environment. Understanding the mechanisms of the antimicrobial action is critical for the development of antimicrobials with improved antimicrobial effects. A structural XIV dependency of the antimicrobial activity was investigated with four bacteria, Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, and one of the advantages of silanols over alcohols is that silanols can be used as chemically bound antimicrobials. Silanol can readily bind onto substrates containing hydroxyl groups such as textiles, plastics, metals or woods. A study of control release of silanol from the substrates is recommended to inactivate bacteria as well as maintain biocidal property for the lifetime of the substrates.

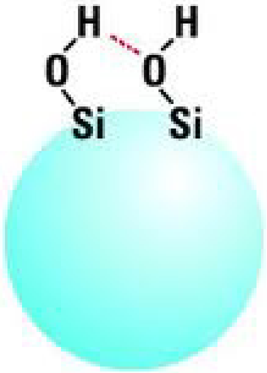


Figure 4-5: Representation of Silanol.

4.3.1.2.6 N-Chloramide Modified NOMEX® As a Regenerable Self-Decontamination Material for Protection against Chemical Warfare Agents

Recent interest in the treatment of textiles for chemical and biological agent defence has led to the creation of materials that contain N-chloramide moieties. These materials have demonstrated efficacy against weaponizable bacteria, mustard, and VX, as well as possessing antimicrobial properties against nuisance organisms that cause conditions such as athlete's foot or molds. Here, N-chloramides have been attached to NOMEX intended for use as self-decontaminating regenerable military textiles. The materials were assayed for content of active oxidizing agent, and tested for efficacy against 2-chloroethyl ethyl sulfide and Demeton-S, simulants for mustard and VX, respectively. The decomposition products for each reaction were identified as well as the reaction pathways to form each by-product as correlated to analogous products of mustard and VX. Furthermore, the rate constant for the neutralization of each simulant on the reactive material was calculated from data collected by GC-MS and ATR-FTIR real-time studies.

To evaluate N-chloramide-treated Nomex for performance against chemical weapons, the material was tested against 2-Chloroethyl-Ethylsulfide (2-CEES) and Demeton-S. A G-agent simulant was not selected because chloramides are known to be completely ineffective against these compounds, and since G-agents are non-persistent, the need for decontamination is not as critical. Reactions with 2-CEES were carried out in a temperature- and RH-controlled reaction cell. The cell was held at 25°C and 90% RH. Within 30 min, the materials neutralized 2-CEES via the formation of the sulfoxide. The toxic sulfone product was not detected. A stoichiometric challenge was conducted to determine the ratio at which the chloramide reacts with 2-CEES. The ratio was found to be 1:1; however, this information is of secondary importance to that of the challenge versus the chlorine load. For a 1.0-g/m^2 challenge, an average concentration of 10.2 mmol Cl/m^2 was sufficient to neutralize the HD simulant and still leave 3.3 mmol Cl/m^2. The stoichiometric data set was also used to determine the rate constant of the reaction at T = 25°C (kavg = 1.3 x 10^{-3} s^{-1}). Testing the treated NOMEX against Demeton-S showed equally impressive results. Originally 90% of a 1.0-g/m^2 challenge was degraded in the first minutes after exposure to the chloramide-treated fabric. The materials tested most recently revealed an average rate constant of 1.1 x 10^{-3} s^{-1} at T = 20°C. The primary oxidation product is not the extremely toxic EA 2192 analog, but a vinyl product formed from oxidation of the terminal thioether sulfur and subsequent rearrangement. The vinyl product formed still possesses certain structural requirements of nerve agents; however, its toxicity is unknown. The product is expected to be less persistent and also less stable in the body. While it is undoubtedly less toxic than Demeton-S itself, further studies need to be conducted to determine if this derivative presents any hazards to humans.

4.3.1.3 Conclusions

The potential for polymers and nano-fiber technology to enhance the protective properties of coatings is promising. These technologies are showing biocidal and chemical agent protective advantages deserving of further exploration.

4.3.1.4 Recommendations and Path Forward

The nanofiber media technology and all its subcomponents developed in this effort are a technology platform with potential use for several applications. Some potential opportunities are as follows:

- Reactive nanofibers for self-decontamination of CWAs: ALD is binding with a wide variety of metals and metal oxides. Some of these materials are known to have reactivity towards CWAs, turning them into less toxic chemicals. The sizes, orientation, and available reactive sites of these materials all influence their reactivity towards chemicals. These nano-fibers could potentially be combined with various reactive chemistries to perform CWA self-detoxification.
- Nanofiber sensor and filter media incorporating sensing capability: ALD and MLD of nanofibers can functionalize the fibers to be reactive or responsive to various chemicals. The fibers can be constructed to be conductive or semi-conductive using these techniques. Sensors or filters with a sensing capability (filter with added functionality) could be developed to indicate to the user when a chemical is present. This concept may also have use as a residual life indicator in a filtration system.
- Nanofiber filter media for collective protection applications: The current nanofiber filter project is aimed at developing advanced media for IP. A natural adjacent application of this technology is in collective protective applications in which size and weight are a premium, such as in vehicles and man-portable shelters.
- Using N-Halamine Copolymers in biocidal coatings demonstrated a six log inactivation of Staphylococcus Aureus and Escherichia Coli on cotton fabric and should be assessed for incorporation into combat uniforms and protective equipment.
- Silanol can be prepared with low cost procedures, demonstrated effective antimicrobial characteristics, and can readily bind to textiles, plastics, metal, and wood.

4.3.2 Assessment of Strippable Chemical Agent Disclosure Coatings (United States)

4.3.2.1 Abstract

Strippable polymer agent disclosure or “smart” coatings have the potential for achieving effective surface decontamination. Recent research demonstrated their usefulness for detecting and removing chemical warfare contamination from surfaces, which supplements their previously demonstrated efficacy to detect and remove radioactive isotopes and heavy metal elements from contaminated surfaces. In both instances, color change of the “smart” polymer coating reveals the areas of contamination. For chemical agents, the preferred concept of operation is to apply the coating prior to exposure and is described in detail by this section. In the case of radiological contamination, the warfighter applies the coating post-contamination and as the polymer coating cures to form a strong film it absorbs the radiological contaminants as they are absorbed in to the coating and contaminated surfaces are cleaned by removing the film. The key objective of this effort was to investigate/ develop potentially strippable chemical agent disclosure coatings to significantly reduced risk to warfighter and reduce the burden associated with current detection and decontamination approaches.

4.3.2.2 Introduction and Background

With the know burdens and limitations of current chemical agent detection and decontamination procedures, a peelable coating, capable of recognizing the presence of a chemical warfare agent, responding to mitigate and detoxify the hazard and disclosing the presence and location of chemical agents to an observer would be highly desirable for military use. Furthermore, development of passive systems that require no power to recognize the agents will provide a reduced logistical burden to the war fighter. Peelable coatings are an attractive option because they afford the war fighter the opportunity to assess the hazard in the field and provide the option to remove the coating. They are also useful because chemical agents have a tendency to penetrate porous surfaces such as paints, plastics and concrete, thus they present a persistent contact hazard. Use of chemical agent absorbing peelable coatings minimizes this problem by protecting the coated substrate. (Figure 4-6).

Figure 4-6: Strippable Coat Can Be Applied to a CARC-Coated Surface and Easily Scored, Peeled and Removed.

4.3.2.3 Technical Discussion

The strippable agent disclosure technology utilizes enzymes for the detection of Chemical Warfare Agents (CWAs) and other toxic chemicals. Enzymes drive colorimetric chemistries that provide the user with the ability to sensitively detect and map trace contamination. These technologies come in two distinct commercially available form factors: the Chemical Agent Detection Kit (CAD-Kit); and Agent Disclosure Sprays.

These sensors detect CWAs at trace levels instantaneously on the surface, enabling detection and mapping capabilities that other technologies cannot provide in a simple color-based format.

4.3.2.3.1 Peelable Coatings

A commercially developed peelable coating was originally developed for use as a temporary camouflage of military vehicles and subsequently found to have utility for CWA decontamination. The coating is a water-borne polyurethane dispersion. The tan coating could be applied to the olive green Chemical Agent Resistant Coating (CARC) protected surfaces to provide temporary camouflage in desert environments.

More recently, the coating has been engineered as a temporary protective coating that absorbs CWA contamination; it effectively reduces the surface contact threat and prevents CWA breakthrough. In a CWA contamination scenario, the coating can be scored and peeled to remove the contamination.

The peelable coating has also been validated to work well with the enzyme-based detection products. The Agent Disclosure Sprays can detect CWA hazards in the coating, enabling the user to map contamination and selectively remove the coating if and where the Spray reveals contamination (Figure 4-7).

(a) **(b)**

Figure 4-7: The Disclosure Coating Prototype Consumable (a) Contains Dried Powders (the user simply adds water to dissolve and stirs the additives into the coating) – Once Mixed, the Coating is Loaded into a Standard HVLP Sprayer (b) and Applied.

4.3.2.3.2 Disclosure Coating

The Agent Disclosure Coating was developed to address a perceived need: passive self-disclosing and self-decontaminating coatings that mitigate CWA contamination. At present, detector tape and paper are used in passive fashion on surfaces; however, it is not very sensitive and is prone to a high degree of false positives from interfering chemical. The enzyme additives enable a coating to determine the presence of CWAs on the coating more selectively. In fact, the peelable coating is an ideal platform for the enzymes; the enzymes remain highly active and are very stable once the coating is cured. The coating's wicking / absorptive capacity also brings the agent to the enzymes for detection.

The enzyme additives provide a unique capability to the coating. The embedded enzymes recognize the presence of CWAs and convert CWAs to acid products, which in turn react with a dye embedded in the coating to produce a localized red color change. At present, the coating contains enzymes capable of detecting G-series nerve agents, sulfur mustard (HD), and their respective simulants. Figure 4-8 demonstrates detection of a variety of agent simulants by the enzymatic additive. Volatile chemical agent simulants Diisopropylfluorophosphate (DFP, G-series) and 2-Chlroethyl, Ethyl Sulfide (2-CEES, HD half-mustard) are detected weakly at the surface because their evaporation rate exceeds the rate of sorption into the coating. When thickened with a polymer thickener, these simulants remain on the coating surface much longer and are absorbed, providing a robust red detection within 10 minutes. However, acidic aqueous interferents do not cause false positive because they are not absorbed by the coating. Many water-based interferents simply bead on the surface and are not absorbed.

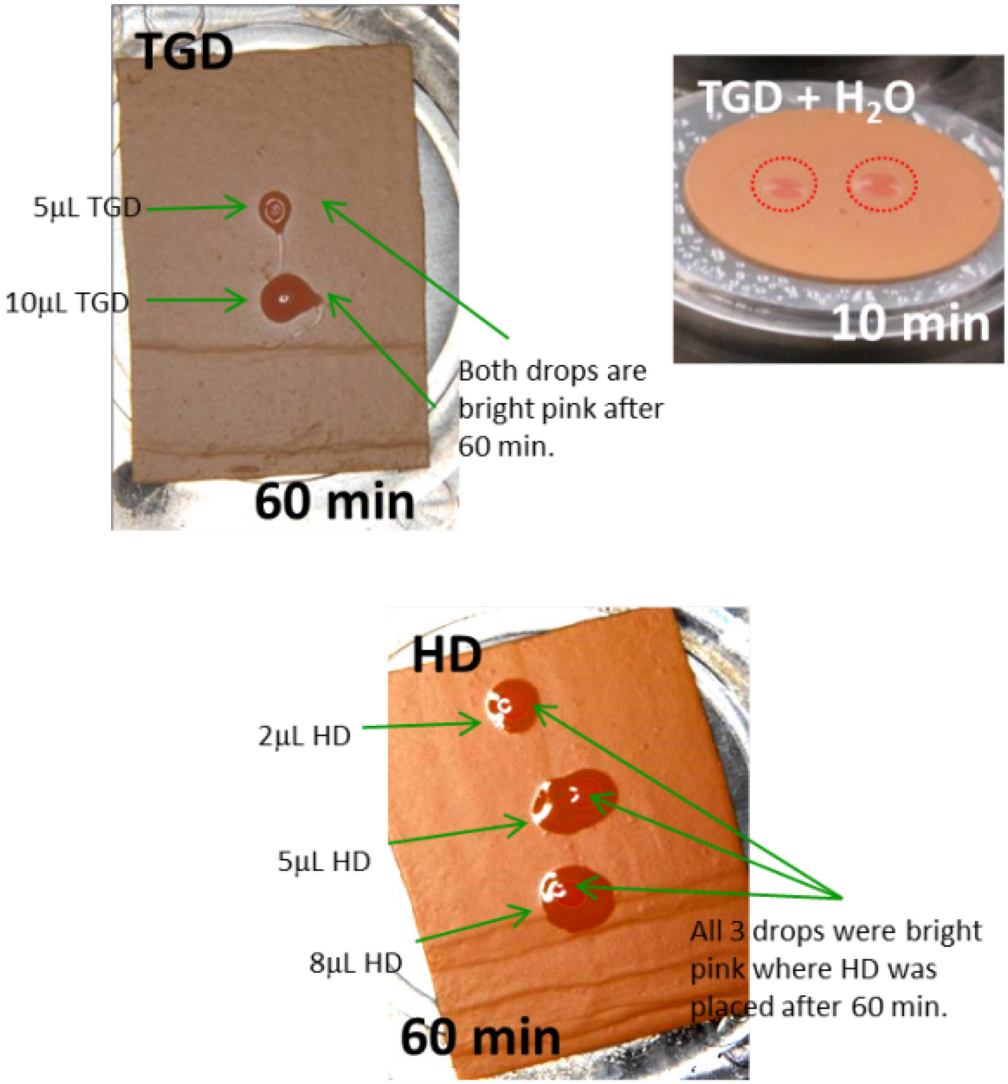


Figure 4-8: Coatings Detected Thickened GD (Top) and Neat HD (photos were taken at 60 minutes, except upper right taken at 10 minutes).

4.3.2.3.3 Preparation and Use

The Disclosure Coating consists of a three-part dry powder formulation (Figure 4-7). The enzymes are lyophilized individually with their own proprietary blend of buffers and stabilizer excipients and the dry powder from each enzyme preparation is stored in a plastic bottle. The dye is also stored separately as a lyophilized powder (although now switched to a pigment additive). To prepare for use, the user first adds the dye powder to the coating. Then, the user adds water to the enzyme powders and shakes them to dissolve them completely. They can then be added to the coating (maximum 30% dilution thereof), and then stirred using a drill with a paint stirring attachment for 1 – 2 minutes in order to homogenize the solution. Once mixed, the coating can be applied to a surface using a High Volume, Low Pressure (HVLP) sprayer. Each pass supplies approximately 20 mils (0.5 mm) of wet film thickness. A minimum of two passes are required. The coating is tack dry in under an hour and is fully cured within 2 – 3 days (depending upon environment).

4.3.2.3.4 CWA Detection

The coating was further developed during a demonstration that evaluated multiple next generation CWA decontamination technologies. During this effort, the Agent Disclosure Coating was evaluated for its ability to detect live CWAs. Coatings applied to CARC coupons had neat droplets of thickened GD or HD applied (Figure 4-8). The coatings turned red where local contamination was present. Only 60-minute pictures were taken for all but one test, wherein a 10-minute photo of GD detection was taken. These tests were done very early in the effort, and significant improvement in detection speed and enzyme activity have been realized since this time.

4.3.2.3.5 Enzyme Stability

To remain operationally viable, the enzyme additives must be robust as dry powders for pre-use applications and must be stable for operational mission lengths to ensure they will function over a period of several weeks to several months. The manufacturer has adapted the enzymes as dry powders to be stable for an excess of 6 months without any loss of activity. Data are shown in Figure 4-9 for the enzyme used to detect G-series agents, Organophosphorus Acid Anhydrolase (OPAA).

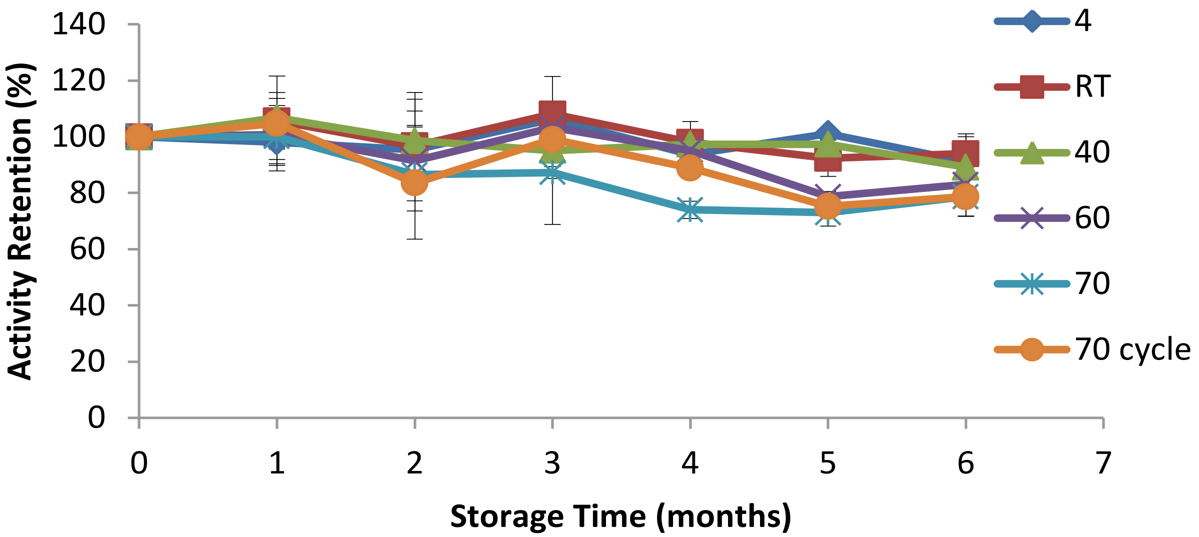


Figure 4-9: Dried Enzyme Powders Bulked with a Proprietary Excipient Demonstrate Remarkable Thermal Stability Even when Stored Continuously at Temperatures as High as 70°C.

4.3.2.3.6 Outdoor Detection

Coatings were exposed continuously for six weeks at various sites in the US in order to evaluate environmental effects on the coatings' ability to disclose CWA simulants. All samples were placed on south-facing buildings for up to 6 weeks (Figure 4-10), removed and evaluated for sensitivity. Local temperature and humidity were also tracked using data loggers.

Figure 4-10: Coating Samples Were Exposed in Four Locales for a Period Up to 6 Weeks.

The data results are shown in Figure 4-11. It is clear from the environmental data that exposure to several days of rainfall during weeks 2 – 4 caused both activity loss to the OPAA enzyme and leaching of the responsive dye. Dye loss, rather than enzyme activity reduction, likely contributed more to the compromised detection capability of coatings in this study.

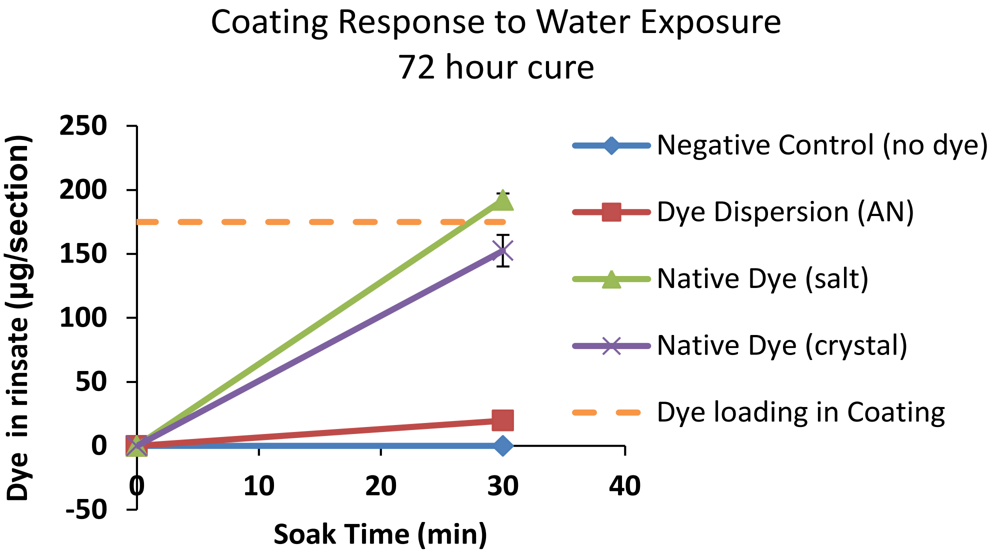
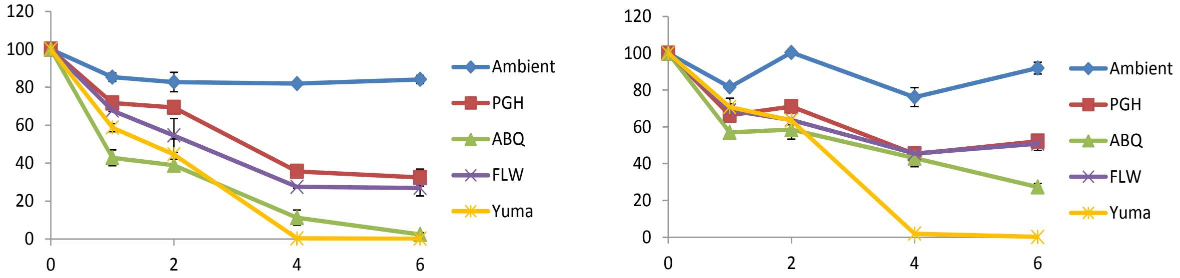


Figure 4-11: The Dye Dispersion (Red) Demonstrates Improved Retention Over the Previous Formulations (Green, Purple).

4.3.2.3.7 Improved Dye Retention

The research team worked with the coating manufacturer to develop a method for pigmenting the dye into a dispersion. This dispersion was then tested for improved retention of the dye. Dye was loaded into the coating and then allowed to cure. A total immersion rinse test was performed wherein coatings containing the pigmented dyes were rinsed alongside control coatings in which the dyes were added to the coating as powders. Data are shown in Figure 4-12. The retention was improved dramatically by the pigmentation.



Week 6 Performance

6 week exposure	Enzyme 1 (%)	Enzyme 2 (%)
Ambient	84	92
PGH	32	52
ABQ	2	27
FLW	27	50
Yuma	<1	<1

Simulant Detection (10 min contact)

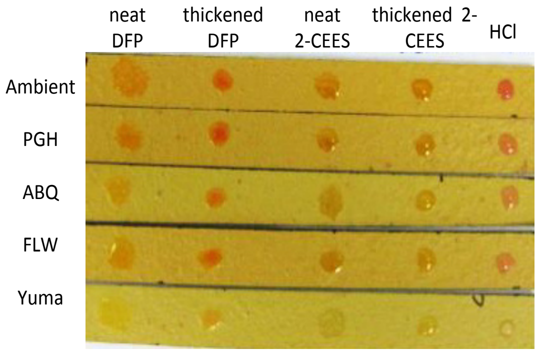


Figure 4-12: Top – Enzyme A (OPAA) and Enzyme B Retained Significant Activity After 6 Weeks Except in Yuma, where Several Days of Atypical Rainfall were Experienced (samples in other locations were not exposed to pooling rainwater); Bottom left – All Enzymes Demonstrated Sufficient Activity to Detect Simulants, Except the Yuma Samples and OPAA in Albuquerque; Bottom right – Simulant Detection Tests are Shown with All Samples Detecting Simulants Within 10 Minutes Except the Yuma Samples.

4.3.2.4 Conclusions

The potential for enzyme disclosure technology to enhance the protective properties and usefulness of coatings is promising. These technologies are showing operational advantages deserving further exploration.

4.3.2.5 Recommendation and Path Forward

Additional characterization is needed to advance strippable disclosure coatings to make them ready for use by the warfighter. This path forward includes: Disclosure Coating, Self-Decontaminating Coatings and Super-Absorbent Coatings discussed in the below sections.

4.3.2.5.1 Disclosure Coating

The research team recently accessed quantities of enzymes that are capable of hydrolytically decontaminating V-series nerve agents. The research team should continue to seek to develop a broad-spectrum coating that detects all nerve agents and HD. The research team should also formulate the full coating with the improved dye dispersion and perform extensive operational testing and chemical interference evaluation. The research team should then evaluate response time and detection limits for live CWAs at a third-party surety laboratory.

4.3.2.5.2 Self-Decontaminating Coatings

The research team is currently scaling expression of the decontamination enzymes and they should evaluate the potential to load significantly larger quantities of enzyme and buffers into the coating to enable a self-decontaminating coating.

4.3.2.5.3 Super-Absorbent Coatings

The manufacturer has developed a super-absorbent topcoat technology with improved CWA sorptive capacity. The research team is in the process of collaborating with the manufacturer to adapt the Disclosure Coating and self-decontaminating enzyme formulations to this platform.

4.3.3 Reactive Coatings (Germany)

4.3.3.1 Introduction

The need for new protective measures increases due to the growing concern over the use of toxic compounds as chemical warfare agents, pollutants and toxic industrial chemicals on the one hand and of biological agents on the other hand. Traditional protective gear for exposure or clean up-procedures relies on thick layers of dense rubbers and/or activated charcoal liners [1].

As one approach to overcome the limitations of the actual existing protective gear limitations reactive coatings are an interesting strategy for protection against low to moderate exposure levels. Highly reactive layer-by-layer coatings can be used as protective coatings intended for new applications for civilian and military personnel. The uses of scavengers to destroy toxic chemicals such as chemical warfare agents as well as biological agents was investigated [2]-[5].

4.3.3.2 Degradation of Chemical Compounds

Degradation of chemical compounds needs to overcome some limitations. Enzymes are highly selective, but there are a lot of discussions about the use of these catalysts under various environmental conditions. The search for new chemicals, that mimic enzymes turned out to be more difficult than scientists thought. Normal chemicals act in a stoichiometric way rather than in a catalytic way. Beside the enzymes, photo-catalytic degradation and the use of metal oxide nanoparticles in reactive coatings show promising results.

4.3.3.2.1 Enzymatic Degradation

Degradation of toxic compounds by enzymes is the most selective approach. Former concerns over the functionality being limited to very narrow environmental conditions as well as high production costs have become obsolete with new developments in non-aqueous environments and biotechnology. Organophosphorus Hydrolases (OPH, EC 3.1.81) and other organophosphate chemical warfare agents degrading enzymes sequestered in paints and coatings become available as tools to detoxify tabun (GA), soman (GD), sarin (GB), cyclosarin, VX and its isomeric analog Russian VX (R-VX) [6]. With the rapidly increasing database of natural enzyme diversity, recombinant DNA and bio-technologies will allow organophosphate coatings to be tuned to a specific application [6].

4.3.3.2.2 Photo-Catalytic Degradation

The most common technology used in reactive coatings takes advantage of the photocatalytic activity of titanium dioxide [7]. Titanium dioxide is a semiconductor metal oxide capable of photocatalytic degradation of both chemical and biological materials. TiO_2 is capable of absorbing energy equal to or greater than its band gap energy [8]-[9]. It is accepted that the incorporation of "untreated" titanium dioxide in polymers and coatings decreases the lifetime of the materials [7]. The most commonly used polymorphs of TiO_2 are the anatase and rutile crystal phases of the material. The mechanisms responsible for the self-cleaning process in TiO_2-containing surfaces have been studied extensively [7].

Different companies are using these effects to produce Commercial-Off-The-Shelf (COTS) products [7]. Some of these products claimed to be efficient against a variety of substrates. However, the big disadvantage of TiO_2 is its relatively large band gap energy (anatase, e.g. = 3.2 eV; rutile, 3.0 eV) and it can only be excited by about 5% of the total energy from the solar spectrum [10]. Therefore, efforts have been made to decrease the recombination rate of electron–hole pairs by contacting other semiconductors with the catalyst [10]-[11]. This shows potential for future investigations.

4.3.3.2.3 Chemical Degradation (Hydrolysis Using Nucleophiles)

A preferred chemical approach is the use of simple chemicals containing hydroxyl groups (e.g., solution of caustic soda). These chemicals can act as good nucleophiles and aid in breaking the P-X bond to give phosphoric acid and other less-toxic byproducts. For several decades, oximes were investigated as good nucleophilic agents with high selectivity for organosphosphorus agents [12].

Also, metal oxide nanoparticles with high activity for OP hydrolysis (e.g., MgO, CaO, TiO_2, ZnO and Fe_2O) have been reported [13]. Furthermore, Cyclodextrin (CD) and its derivatives are interesting candidates, because their hydrophobic cavity mimics the catalytic activity of enzymes [13].

4.3.3.3 Degradation of Biological Agents

The incorporation of novel reactive additives into coating formulations could lead to new functionalized coatings against biological agents.

New reactive additives for coatings purposes include:

- Quaternary ammonium biocides [14]-[15];
- Surface concentrating biocides [16];
- Functionalized coatings [17]-[18]; and
- Antimicrobial peptides [19].

Although innovative functional coatings have a germ reducing effect, none of them show activity against CWAs. One promising candidate antimicrobial peptides will be highlighted.

Antimicrobial Peptides (AMPs) constitute a diverse class of naturally occurring antimicrobial molecules with activity against a wide range of pathogenic microorganisms [20]. AMPs are short (range is typically from 12 – 100 amino acids residues in length) and show a rapid and efficient antimicrobial activity against a range of pathogens [21]-[22]. Over 1700 antimicrobial peptides have been isolated of both prokaryotic and eukaryotic organisms [23]. Antimicrobial activity of effective antimicrobial peptides is governed primarily by charge and hydrophobicity and the fact that the initial target is the negatively charged bacterial cell membrane [20].

The antimicrobial peptides can be divided into:

- Cationic antimicrobial peptides;
- Anionic antimicrobial peptides;
- Amphiphilic antimicrobial peptides;
- Ultrashort cationic antimicrobial peptides; and
- Lipopeptides which include an antimicrobial peptide [20].

The multiple modes of postulated actions of antimicrobial peptides reduce the ability of microorganism to develop resistance [24].

As biocides, antimicrobial peptides have the potential not only to eradicate most potential biological agents, but also show potential to eradicate the most resistant forms of clinically relevant biofilm forming pathogens. Furthermore, the potential for natural and synthetic peptides as therapeutic molecules go beyond the boundaries of microbial biofilm infection. Overall, antimicrobial peptides for use in self-decontaminating coatings fulfil a number of requirements expected from an ideal biocide, namely performance, environmental fate, safety and cost. [19]-[20].

4.4 LOW-IMPACT DECONTAMINATION TECHNOLOGIES

4.4.1 Sensitive Equipment Decontamination – "Cold" Plasma-Assisted Removal of Biological and Chemical Contaminants (Germany)

4.4.1.1 Introduction

Effective and near real-time decontamination systems for chemicals and biological materials on surfaces will address a range of needed capabilities within the military sector [25]. None of today existing decontamination techniques are able to destroy both chemical and biological agents without adverse effects on sensitive equipment, living tissue and surfaces being treated [25]-[28].

To address these needs, plasma-assisted processes have demonstrated their strong potential for cleaning surfaces for a long time [29]. Furthermore, "Cold" Atmospheric Plasma (CAP) sources, means less than 40°C at the point of application, have been developed in recent years, which opens up new horizons [30].

4.4.1.2 General Types of CAPs

Three general types of CAPs can be distinguished [30]:

a) Direct plasmas: use the surface as an electrode. The most widely used technology is the 'dielectric barrier' plasma source [31].

b) Indirect plasmas: produced between two electrodes. Different devices exist, from small 'plasma needles' to larger 'plasma torches' [30], [32].

c) 'Hybrid'-plasmas: a combination of the direct plasma production technique and the current-free property of indirect plasmas [33].

These three types can be described in a more detailed way. CAPs can be obtained in several ways, such as an electron beam, a dielectric barrier discharge, a radiofrequency discharge, a glow discharge, a corona discharge or a microwave discharge [34]. All these methods have their own operation modes and drawbacks and are described in Table 4-1 [34].

Table 4-1: Operation Modes and Drawbacks of CAPs [34].

	Operation Mode	Drawbacks
Glow Discharge	In a low-pressure chamber (less than 10 mbar), small electric fields (less than 1000 V/m) with comparatively low operating voltages. [35]	The low processing-rate limits its application to industrial processes.
Electron Beam	Electron beam induced plasma generates a small amount of x-rays.	Potential radiation hazard has to be addressed. High equipment cost and operating expense also limits its commercial application. [34]
Dielectric Barrier Discharge	As a plasma stabilizer, dielectric material is placed between two electrodes to produce micro discharges.	Generated particles will deposit as a thin film on the reactor's surface and causes other clean up problems. The generated plasma can handle only small molecular Volatile Organic Compounds (VOC).
Radiofrequency (RF) Discharge	Usually operate at a low-pressure state (< 133 mbar), with a frequency range between 2 and 60 MHz. Often fixed at 13.56 MHz.	These operation ranges limit its capacity and efficiency to decompose more stable contaminants such as carbon – halogen compounds. [34]
Corona Discharge	Relatively low power electrical discharge that takes place at near atmospheric pressure. To increase its operating pressure, the electric field should be increased comparatively.	Decrease of the energy-utilizing rate per unit volume and non-equilibrium energy discharge inside the reaction chamber.
Microwave Discharge	Operation mode at 2.456 GHz. Power absorption value is more effective in microwave than in RF plasma. [36]-[37]	Smaller processing capacity.

4.4.1.3 Plasma Interaction with Chemical Warfare Agents

In several studies the effect of atmospheric plasma towards the decontamination of chemical warfare agents or their surrogates was investigated [27], [51]. In a first approach the plasma jet was leaded directly onto the contaminated sample [27] using a feed gas mixture of helium and oxygen. A strong decontamination effect against surrogates of blister agents (2-chloro-ethyl phenyl sulfide as mustard gas simulant) and nerve agents (malathion as VX simulant) was found.

However a significant degradation was only seen at plasma temperature above 150°C. Despite the high temperature, the decontamination effect was a result of chemical degradation reactions and not consequence of evaporation effects, as in hot gas decon technologies [27]. In further experiments with a decon chamber and real chemical warfare agents these results could be confirmed [51]. A complete degradation of HD and GD could be obtained after two 2 minutes of plasma treatment. For VX, a process time of 16 minutes was needed. In these experiments, the process temperature was reduced to a "cold" 70°C in order to treat sensitive equipment. Nevertheless, a special gas mixture of helium and oxygen is still needed.

The degradation mechanism is controlled by oxidation reactions with active oxygen compounds like atomic oxygen O, singlet state metastable molecular oxygen O_2 and ozone O_3 [51] A closer analysis of these reactions is difficult, due to the short lifetime of these compounds. In particular the atomic oxygen is converted to molecular oxygen and ozone by interaction with Helium atoms. Hence, from a conceptual point of view, atmospheric plasma is able to destroy chemical warfare agents and to decontaminate sensitive equipment. However, the technique is very sensitive to the choice of the feed gas. A stabilization of reactive short-lived compounds in bigger chambers is also a future challenge.

4.4.1.4 Plasma Interaction with Biological Warfare Agents

Since the first data of the inactivation of microorganism using CAPs were published in 1996 [38], the increasing interest in CAP interaction with bacteria and viruses has led to new knowledge of low-temperature solutions for the sterilization of sensitive equipment, especially in the field of surgical instruments and medical devices. In addition to decontaminating equipment surfaces, CAPs may also be used for the decontamination of biological surfaces such as plants and animal or human tissue, respectively [30], [31], [39].

CAPs can affect biological agents such as viruses and bacteria. The mechanisms are based on the synergy of several biologically active plasma components [30]. Plasma-generated UV radiation and reactive molecules including free radicals and some ground state molecules as peroxides and ozone are the most important of them. Heat, charged particles and metastable-state molecules and atoms may also play an important role in the destruction of biological agents.

4.4.1.4.1 Bacterial and Biomolecule Inactivation

The generic capability of CAPs against microorganisms is well established under controlled laboratory conditions [32]. Both gram-positive and gram-negative bacteria can be inactivated by CAPs, with a more effective inactivation rate for gram-negative than for gram-positive. However, CAP treatment is also very effective for the treatment of spores [40]. SEM images of spores of *Bacillus subtilis* clearly show severe rupture to little alteration of He-O_2 CAP jet treated spores [40]. These results indicate clearly that singles spores can be treated effectively by CAPs. However, in a laboratory study the problem of physical shielding by the upper layer when cells or spores are stacked in thousands of layers has to be addressed properly [41]-[42]. Furthermore, one research area of current interest is the inactivation of bacteria, which are able to produce biofilms or a possibility to damage the biofilm itself. The biofilm (an extracellular polysaccharide matrix) acts as a physical shield for the embedded microorganisms and leads to a compromised inactivation of the embedded bacteria [43]. Relevant examples for food processing and dentistry include *Pantoa agglomerans* and *Streptococcus mutans*, and can be inactivated by CAPs [30]. Many microorganisms of health concern can be directly or indirectly inactivated by CAP treatment – for example Ehec, MRSA and *Clostridium difficile* among others [44]-[49].

4.4.1.4.2 Inactivation Mechanisms

Mechanisms of CAPs with prokaryotic cells involve two main aspects:

- The biological mechanisms: cellular components and processes through with bactericidal plasma species inactivate.
- The physical mechanisms: the bactericidal species delivered by CAP to cells [30], [32], [40].

As possible biological mechanisms membrane breaching, DNA damage, the affection of the metabolism, the degradation of Lipopolysaccharides (LPs) and cascading effects are investigated with different levels of evidence [30]. Many questions remain and need more biologist-led investigations. The possible physical mechanisms are better understood and in generally they depend on:

- The chemical working gas mixture.
- The temporal and spatial details of plasma generation [46].

The bactericidal effect of a particular plasma species depends on its reactivity and its concentration (plasma dosage). However, for further reading the interested reader is referred to available literature [50].

4.4.1.5 Summary and Outlook

Within the past decade, CAP technology has been used widely to inactivate biological agents and hazardous toxic chemicals. Today, plasma decontamination has the potential to be used in the decontamination of various surfaces including space craft, industrial exhausts, air and water streams, water disinfection, medical devices and living tissues of animals and humans. It is foreseeable – due to the rapidly expanding area of modern science and engineering – that scientists and engineers are able to develop new and broadly applicable plasma technologies, which are on the brink of being introduced into service in the very near future.

4.5 CHAPTER CONCLUSIONS

In this Chapter a wide range of technologies is described:

- Improved materials and coatings that resist contamination and/or accelerate weathering of agents.
- Agent disclosure, including detection technologies, to sort contaminated from clean, focus processes, and measure success.
- New processes and decontaminants for interiors and sensitive equipment.

As was described in the Introduction of this chapter these technologies may support the overall capabilities after CBRN agent exposure in operational conditions. In general the research in this area focuses around the development of coatings that provide reactive functionality, either disclosing or reacting with agents. Most of these technologies have been developed on solid or flexible but continuous surfaces to disclose agents or decontaminate surfaces, including sensitive equipment. As explained before, reactive technologies in itself is relevant for burden reduction to the warfighter, but more work may need to be done to expand these capabilities to fabric structures so (some of) these technologies may be integrated into the clothing itself, further allowing protection optimization. At that point these decontamination (reactive) technologies may be considered as part of the passive protective technologies and in conjunction with that work to reduce consequences of contamination. For implementation as part of the passive protective systems consideration should be given to the speed of decontamination that can be achieved when using the reactive technology on fabrics or material structure.

Amounts of reactive technologies that can be used will in practice be very limited to maintain comfort and wearability of the passive protective clothing systems. For the decontamination technologies, such an approach may be reasonable if these technologies are not expected to produce a hazard to the warfighter or their equipment. For the disclosure technologies the same would apply, having the capability to know if and where the warfighter was exposed will greatly help in potential casualty reduction but especially in increased efficiency of decontamination, thus reducing resources needed in the decontamination process.

The combination of new technologies and new approaches to individual protection seems to provide opportunities for improving protection and lowering the burden. This approach will require optimization of the decontamination technologies on the passive protective systems (clothing, boots, gloves, respirator), rapid additional decontamination in the field and possibly secondary decontamination when needed further down the operational and logistics chain. Current operational processes and procedures may not be well fitted to manage a new systems approach that attempts to have a staged decontamination, starting on the passive protective system and combining that with additional decontamination technologies. With such a systems approach disclosure technologies will become very important as the knowledge on the size and magnitude of any contamination will be important to ensure optimization of the passive and reactive technologies to contamination.

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Chapter 5 − CONCLUSIONS

5.1 INTRODUCTION

This Report addresses the different aspects that might jointly contribute to the protection of the individual warfighters. The central thesis is that the current CBRN protective systems impose too large of a burden to the warfighter and results in an avoidable loss of operational capabilities. The approach for lowering the burden requires a combination of methodologies in a systems approach. A conceptual schematic overview of this systems approach was given in Chapter 1 and discussed with respect to the changing operational environment and its consequences for CBRN protection. This systems approach, used throughout the Report, is presented in terms 'active', 'passive', and 'reactive' protection that are as follows:

- Active Technologies: any sensor and detection related technologies that will allow a prevention or reduction of exposure to hazardous CBRN agents. This would be the first and outer layer of defense against CBRN agents and, when successful, should avoid contamination.
- Passive Technologies: any protective technologies that will absorb, filter or otherwise block CBRN agents from reaching the human body. These technologies are traditionally envisioned as protective technologies and aim at preventing CBRN agents to contaminate the body when the warfighter is in a contaminated environment.
- Reactive Technologies: any technologies that are aimed at mitigating, reducing and/or eliminating the exposure after agents are disseminated. For example, removing contamination from objects that could continue to expose warfighters to agents through proximity or direct physical contact.

These three approaches are considered in combination to develop novel strategies to manage potential CBRN hazards and exposures. The overall aim of the analysis is to optimize the warfighter capabilities during operations with high risks of CBRN hazardous agent releases either accidental or intentional.

5.2 THE CHANGING OPERATIONAL ENVIRONMENT

During the Cold War, NATO prepared for military operations in a CBRN environment characterized by the potential for large agent releases from massed delivery systems that would contaminate thousands of hectares at a time, and necessitate sustained military operations in a contaminated environment. The current environment has less potential advisories with large stockpiles, but a greater array of actors, including non-state actors, with access to CBRN weapons technologies. This presents a new kind of threat. Likely scenarios many be smaller in scale, but could be more numerous. Three elements of the new environment include:

- The higher level of uncertainty for CBRN events.
- The likely smaller scale of the overall event in terms of size (area, volume and time).
- The potential wider range of CBRN agents, especially Chemical and Biological, than previously considered.

These three major differences may on the one hand directly interfere with a sometimes reduce protection and/or operational capabilities; on the other hand these differences may open new approaches to achieve the overarching goal of personnel protection, health and safety. In this chapter some generic conclusions will be drawn and pathways to solutions of these emerging issues will be provided. For each of the three issues some solutions in the areas of "Active", "Passive", and "Reactive" technologies will be discussed.

5.2.1 Higher Level of Uncertainty for CBRN Events

The range of potential threat actors has become larger and less certain. This includes non-state actors, who may also develop CBRN threat capabilities. As a consequence adequate preparedness for such events needs to be maintained. However, it is not practical to have armed forces continuously operating in CBRN protective gear. When traditional highly-protective CBRN protective clothing and equipment is used, this would lead to excessive physiological strain and deterioration of operational capabilities. Even state-of-the art lower burden protective clothing will not always be suitable for continuous use, because wear and tear and environmental contamination would lead to a reduction of protective performance, and generate a logistics demand for resupply.

Uncertainty may be countered by having counter-measures that are always on or available. Modularity is an important design aspect for achieving this availability and reduces risk. A system module can continuously provide some aspect of protection at a low-burden and be rapidly reinforced to provide a full-protection mode. Such modular systems, including effective helmet-mask combinations for quick respiratory protection, would allow regular equipment to be worn, while maintaining readiness for unexpected events. Such modular responsive technologies will have to be combined with “Active” and “Reactive” technologies to obtain an effective protection. Active technologies, mainly sensor system, should facilitate early warning of events and releases. As modular systems require some advance warning the incorporated sensor systems would ideally require stand-off detection systems and/or distributed sensor network systems that should provide CBRN related information outside the area where forces are active. Any other intelligence that would facilitate knowledge of enhanced risk of events would support the goal of reducing exposure to the warfighters.

5.2.2 Expected Smaller Scale of CBRN Events

Another consequence in a post-Cold War CBRN threat environment is reduction of actors with major quantities of agent stockpiles and delivery systems. Future scenarios may be more focused and strategic, rather than the large-scale terrain denial attacks previously considered.

Legacy protective technologies focused on heavy absorptive layers that provide high levels of protection for a prolonged duration. With the occurrence of smaller scale events the local concentration levels may stay still be high, but exposure duration and/or exposure area are expected to be much smaller. Warfighters will be more able to rapidly move out of the contamination zone, and smaller contamination clouds will disperse faster (than larger attacks) and have less of an impact. Therefore, requirements for passive protective systems should also be much lower in terms of overall dose exposure, however, not necessarily in initial concentration. Passive protective systems that allow very low initial breakthrough with limited absorptive capabilities, such as the newer activated carbon fibers used in some of the systems presented in Chapter 3, may be adequate for such scenarios. These technologies provide a more limited absorptive capacity but would allow reduced insulation, stiffness, breathing resistance or improvement on similar parameters that negatively impact warfighter performance. These developments have been described in Chapter 3 on passive protective technologies. Furthermore, the expected smaller scale of the events would potentially open up scenarios in which the exposed warfighters are able to quickly maneuver away from or around the CBRN agent release. Thus, active technologies would further allow overall reduction of exposures and this altogether could further reduce the passive protective requirements to the warfighter clothing and equipment. The Reactive technologies, presented in Chapter 4, could facilitate in disclosing and decontaminating any (limited) hazards that the warfighter or his/her equipment might have been exposed to. This might further reduce the needed protection in the warfighters’ clothing and equipment.

5.2.3 Potential Wider Range of Agents in CBRN Events

The potential wider range of hazardous exposures in the contemporary scenarios would stretch the capabilities of the Active, Passive and Reactive protective technologies with a wider range of agents to protect against. This wider range of agents may pose a challenge to current protective technologies to have effectiveness across the spectrum of threats. Although activated carbon is engineered to absorb a wider range of chemicals agents, is less successful with the more volatile TICs that could be used as improvised agents.

Developmental technologies presented in Chapters 2 through 4 are needed to respond to these threats. The combination of uncertainty in place, time and type of agent greatly enhances the need for diversity in sensor systems that are versatile, cover a wide range of agents with sufficient accuracy and reduced false alarm rates. Combining the technologies mentioned in Chapter 2 may facilitate these developments. For missions and conditions in which the specific threats would be known high accuracy and specific measurement equipment would allow early and rapid detection of the agents. In conditions where threats are unknown, however, combinations of specific and possible a-specific sensor systems (e.g., e-nose) could be used to achieve early detection and identification of hazardous chemical agents. Supporting technologies that were discussed in Chapter 2, e.g., False Alarm Reduction Rate technologies, would further enhance capabilities under such conditions reducing the need for immediate and continuous protection and thus enhancing warfighter capabilities.

In Chapter 3 (cf. Section 3.3) new absorptive technologies, such as MOFs and ZZATs were shown to have greater performance against a broader spectrum of threats. New durable repellent treatments provided fabrics with enhanced liquid repellency may further enhance overall protection in case of exposure to liquid challenges. The Reactive technologies (Chapter 4) presented may have very limited application for conditions where threats come from non-CWAs. On the other hand, risk management strategies may lead to the conclusion that decontamination and disclosure is much more important and relevant when CWAs and BWAs are involved than with other agents, especially TICs. On Biological agents, general antimicrobial activity may also have effectiveness against other health hazards and thus provide dual use capability.

5.3 INTEGRATION OF TECHNOLOGIES FOR LOWERING THE BURDEN

The changing environments that have been described in Section 5.2 would warrant reconsidering the requirements for individual protective clothing and equipment. Recent developments in NATO standardization have addressed this, and have opened up the previously strict requirements of NATO AEP-38 to allow for a risk management strategy. This approach proposes that, dependent on specific operational context and identified risks, the protection levels may be adapted to the specific mission requirements and support finding a balance between physiological burden of protective clothing and its protective requirements. The technologies presented in this report can contribute to lowering the burden, directly or indirectly, and maintain sufficient protection to the warfighter, when an overall integrated approach of contamination avoidance, mitigation and cleaning is taken into account.

The systems approach of Active, Passive and Reactive technologies can provide the capabilities that allow reduction of individual protection technologies while maintaining overall protection levels. Using compensating Active and Reactive technologies can be used to counteract negative consequences of the reduction in Passive protective technologies. Rather than relying on burdensome protection ensembles that are designed to protect against all possible exposures, Active and Reactive technologies can be used to limit exposures by either guiding the warfighter away from contamination or reducing secondary exposure, such as contact hazards, in areas of contamination. This will enhance outcomes in terms of overall warfighter operational capabilities with effective warfighter protection against CBRN agents.

The trends of sensor miniaturization and network integration discussed in Chapter 2 will provide the warfighter greater flexibility on the battlefield to avoid contamination or quickly move out of contaminated areas. The combination of small, inexpensive and ubiquitous sensors that are seamlessly integrated can provide tools to determine contamination sources, reduce false alarms, and agent cloud tracking that will allow warfighters to confidently minimize their protection posture while avoiding contamination. This serves to lessen the burden by minimizing time in the highest protective postures. An ability to rapidly assess areas of high contamination can help warfighters to avoid or move out of contaminated areas to reduce to total challenge on protective ensembles. Thus it may be possible to reduce protection performance and accept additional risk in favor of lower-burden ensembles.

The technologies discussed in Chapter 3 clearly show a trend toward improved performance at lower burdens. The development of new materials and application of nanotechnology lead this trend. New classes of materials such as Metal Organic Frameworks (MOFs) provide platforms that can be tuned for optimal pore size and chemical functionality that adsorb and detoxify agents. Garments can have enhanced capabilities with new classes of durable repellent coatings that incorporate nanomaterials, and nano-fiber aerosol barriers layers that increase protection with minimal additional weight or thermal load. Whole ensembles can be developed with computer-aided optimal design tools for respirators and garments. Overall, with the proper investments, developments in cutting-edge materials technologies can be exploited to improve protection while decreasing thermal burden.

Exposure to secondary contact with contamination can be mitigated by technologies that facilitate rapid decontamination. Traditionally, responsive actions have been logistically burdensome events that require the assistance of specialty units to achieve decontamination levels sufficient allow the warfighter sustained reduction of high protective levels. New technologies have the potential to allow the same level of performance from actions performed by individuals or crews, and thus reduce overall the burden of protection. Chapter 4 provided a synopsis of technologies such as agent disclosure sprays that can rapidly identify areas of contamination to focus efforts and assess the results. When combined with a strippable coating, an agent disclosure system can identify the specific areas of coating that need to be removed, thus allowing a rapid resumption of the mission at a lower, and less burdensome, protective posture. Technologies to processes sensitive equipment for decontamination can allow unencumbered use of these items as they are returned to service. This reduces burden by allowing the reduction from high levels of protection and reducing the logistical demand for replacing items simply because they are contaminated.

In practice, this systems approach will result in the need to redefine the requirements for individual protection before every mission, depending on specific mission profiles and risks. Although this approach may allow optimized protection, with minimized physiological burden, it would also require a redefinition of the systems approach in which the active, passive and reactive technologies in combination provide the safety and health and sustained operational capability for the warfighters. Consequently this will increase the challenges for mission preparation and potentially require procurement of specific individual protective equipment for each specific mission, with the additional infrastructure that needs to go with it in terms of communications and decision making structures.

The overall systems approach of Active, Passive and Reactive technologies will require optimization methodologies that allow objective trade-off analyses between a wide variety of technologies and quantification of the effectiveness and efficiency of each technology to the overall goal of warfighter protection. As this report intended to provide an overview of available technologies, this topic was not further addressed or studied. It will be imperative for operational preparation and success that such methodologies are available to conduct objective quantified analyses that demonstrate the benefits of selecting different systems. For example: prior to a mission risk assessment may show enhanced risk for chemical incidents. As explained before, having warfighters wear chemical protective clothing during all operations would lead to a too high burden and reduce operational warfighter effectiveness too much. When an overall systems approach is adopted, combining the Active, Passive and Reactive technologies to achieve the overall goals of optimal warfighters health and operational effectiveness the different available technologies will need to be weighed against these goals. It may need to be determined which systems should be used (or procured): sensor systems, versus improved 'low-burden' CBRN protective clothing versus medical countermeasures or a quick decontamination system. Such systems have widely varying properties, systems parameters and even outcomes. Comparing these and their effective contributions to warfighter performance, health, effectiveness and survival in terms of CBRN risk will be challenging. Currently very limited capabilities may exist to conduct such analysis in many countries. Some developments have been made in the area of Operations Research, but it may be difficult to combine very specific knowledge on sensor systems, protective clothing/respirator systems, decontamination systems and medical countermeasure systems into a single analysis, using appropriate missions specific scenarios to optimize warfighter outcome and effectiveness. This may the next challenge that needs to be addressed to maximize flexible use of all available technologies.

In all, there are many new emerging technologies that all may enable to contribute to enhanced warfighter performance and safety related to CBRN risks and events, while reducing the physiological burden. The challenge will be to build appropriate systems to use and balance all available options against the missions that are to be expected and planned. This report shows a series of technologies that will support these goals. The technologies should all be available in the short or medium term and therefore, benefits may be expected soon. Also, some of these technologies may be integrated into currently available systems and approaches and still enhance capabilities and/or protection. The need for enhanced protection and lowering the burden to the warfighter is expected to remain for the foreseeable future. Adoption of some of these technologies and their integration into the warfighters system should enhance capabilities and facilitate reduction of the warfighters burden where possible.

REPORT DOCUMENTATION PAGE

1. Recipient's Reference	**2. Originator's References** STO-TR-HFM-199 AC/323(HFM-199)TP/762	**3. Further Reference** ISBN 978-92-837-2125-3	**4. Security Classification of Document** PUBLIC RELEASE

5. Originator

Science and Technology Organization
North Atlantic Treaty Organization
BP 25, F-92201 Neuilly-sur-Seine Cedex, France

6. Title

Integration of CBRN Physical Protective Measures to Lessen the Burden on Personnel

7. Presented at/Sponsored by

This Report documents the findings of Task Group HFM-199.

8. Author(s)/Editor(s) Multiple	**9. Date** June 2018
10. Author's/Editor's Address Multiple	**11. Pages** 148

12. Distribution Statement

There are no restrictions on the distribution of this document. Information about the availability of this and other STO unclassified publications is given on the back cover.

13. Keywords/Descriptors

Chemical, Biological, Radiological, Nuclear (CBRN)
Enzymatic decontamination assurance spray
Individual protection
New materials
Reactive coatings
Respirator
Sensors
Standoff detection
Strippable coating

14. Abstract

Participation in military operations is accompanied by the threat of exposure to Chemical, Biological, Radiological, and Nuclear (CBRN) agents. Historically, focus has been on the acute health effects of exposure to chemical weapons, and the specter of the use of biological, radiological and nuclear weapons. This Task Group addressed integrated CBRN protection strategies. This report focused on outlining technologies that lower the burden on the individual by using a layered approach consisting of contamination avoidance, physical protection, hazard mitigation response, containment and recovery. In this report there are many new emerging technologies that are outlined that will be able to contribute to enhanced warfighter safety related to CBRN risks and events, while reducing the physiological burden. The challenge will be to build appropriate systems to use and balance all available options against the missions that are to be expected and planned.

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ISBN 978-92-837-2125-3