ABSTRACT

GLADISH, JUSTIN LEE. Analysis of Factors Influencing Methyl Salicylate Adsorption on Textile Skin Simulants. (Under the direction of Dr. Roger L. Barker and Dr. Keith Beck.)

This research studied adsorption of methyl salicylate (MeS) onto knit textile structures. It examines the feasibility of using knit materials as a skin simulant in Man In Simulant (MIST) protocols. MeS is used as a simulant for toxic chemical agents. Knit fabrics were studied because of their conformability to mannequin limbs, and the potential for using these materials to enhance the correlation between mannequin and human garment tests of chemical resistance of vapor protective ensembles. Experiments were conducted at different MeS concentration levels, airflows, and with moisture preconditioned fabric. Fabrics made of protein, cellulosic, and synthetic fibers were studied to provide a range of comparison among hydrophilic/phobic fiber types.

This research showed that the fiber composition and construction of knit fabric are the primary determinants of MeS adsorption. Knit materials made with protein-based fabrics, such as wool and silk, adsorbed more MeS than do knit materials made with nylon or cotton. Moisture preconditioning, designed to simulate adsorption of sweat on a mannequin, dramatically increases the adsorption of MeS.

The target MeS skin adsorption was calculated based on the theoretical mass adsorbed on an uncovered Natick PAD during MIST exposure. The target mass calculated was 0.6 mg/fabric swatch ($100cm^2$) of MeS. Preconditioned, moist, silk and nylon double knit adsorbed close to the MeS target mass with an approximate adsorption of 0.74 and 0.64 mg MeS respectively.

Analysis of Factors Influencing Methyl Salicylate Adsorption on Textile Skin Simulants

by
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Chapter 1: Introduction

1.1Purpose

This research studied adsorption of methyl salicylate (MeS) onto knit textile structures. It examined the feasibility of using knit materials as a skin simulant in Man In Simulant (MIST) protocols. MeS is used as a simulant for toxic chemical agents. Knit fabrics were studied because of their conformability to mannequin limbs, and the potential for using these materials to enhance the correlation between mannequin and human garment tests of chemical resistance of vapor protective ensembles. Experiments were conducted at different MeS concentration levels, airflows, and with moisture preconditioned fabric. Fabrics made of protein, cellulose, and synthetic fibers were studied to provide a range of comparison among hydrophilic/phobic fiber types.

The use of mannequins in MIST procedures is of considerable current interest and research has shown that MIST evaluations on current mannequins show higher MeS penetration than indicated on tests that employ human subjects[1]. A higher penetration causes mannequin studies to indicate a lower protection factor than in human tests. One major cause for the increased penetration is that human skin uptake of methyl salicylate depletes the amount of methyl salicylate inside the suit, thus reducing the amount of methyl salicylate recorded [1]. Additionally, when using human subjects during the standard MIST procedure, methyl salicylate passes over the skin surface and is collected on passive adsorbent dosimeters (PADs). These PADs are representative of a small surface area of the human, while the remaining skin surface is free to adsorb methyl salicylate.

Mannequins lack a skin/flesh surface. Typically, a mannequin surface is hard and

non-porous. This non-porous surface does not allow methyl salicylate to adsorb on the mannequin. Mannequin adsorption only takes place on the PADS, resulting in a lower protection factor than on a human.

An increase in protection factor was found when a protective undergarment was used on the mannequin under the protective suit[1]. Research has advanced in the development of a pseudo-skin that can be used on mannequins to mimic the methyl salicylate adsorption on human skin.

The MIST procedure testing chamber volume, which is large enough to provide free movement of 4 human subjects donning CPE's (chemical protective equipement), scaled down to provide a convenient evaluation method of the adsorption of methyl salicylate (MeS) on skin-simulant materials. Testing inside a MIST chamber requires four human subjects. Using a smaller testing volume can reduce use of human subjects and provide an accessible apparatus for the evaluation of smaller objects quickly.

1.2 Research Objectives

The objective of this research was to develop a better understanding of the adsorption process of MeS onto human skin. Knit fabrics were also evaluated for their potential of approximating the adsorption of MeS at the same rate as human skin. This comparison will be used to develop knit garments that can be used as mannequin skin-simulants to clothe the mannequin surface.

Specific tasks are to:

1. modify a current humidity/temperature controlled chamber for use in this MeS adsorption study.
2. evaluate the efficiency of methanol extraction to determine the amount of methyl salicylate on (preconditioned and ambiently conditioned) swatch fabrics
3. evaluate adsorption of methyl salicylate on selected knit fabrics.

Accomplishing these objectives will provide a foundation for future research involving several key aspects of the MIST program. These include the basis for materials for use as human skin simulants for use on mannequins. Furthermore, a small scale MIST apparatus will provide a platform to test individual closures on mannequin limbs and closers using artificial textured skin[2] as well as artificial skin with varying moisture content[3, 4]. Other technologies such as smart fabric[5] can also be evaluated.

Chapter 2: Literature Review

2.1 Chemical Protection Background

2.1.1 Establishment of Chemical Protection

Chemicals in liquid, vapor, and aerosol states can challenge suits and ensembles. Chemical challenges on suit ensembles may include combinations of liquid, vapor, and aerosol challenge agents. When workers are exposed to harmful chemicals, an exposure limit as well as an exposure time has been established for harmful chemicals. In the case of more harmful or fatal chemicals a minimum exposure limit is provided. In response to differing durations of exposure, chemical agents, and the physical state of the agent, many agencies have established performance requirements for protective garments. These

requirements assure the correct CPE is purchased; the agencies also set standards for the design of new protective garments.

Chemically protective clothing ensembles are characterized according to their resistance to specific chemical agents. Protection by these ensembles is tested in the presence of such chemicals. Because of the toxicity of some chemical agents, a chemical simulant is used in place of the toxic chemical. Toxicity of chemical agents requires the ensembles to be of high quality with reliable protection. Reliable protection includes the efficient use of encapsulating garments, two-piece suits, hoods, booties, gloves, respirators, and rain gear. These garments are tested for penetration and permeation of chemicals of various forms. Penetration of chemicals is defined as the movement through porous materials, seams, closures and other imperfections in clothing on a non-molecular level[6]. Permeation is defined as the passage, or diffusion of a gas, vapor, liquid, or solid through a barrier without physically or chemically affecting it.

2.1.2 Factors Affecting Dermal Adsorption

The skin is the largest organ in the human body, and at times can consume a large amount of energy. Regulating body temperature is a main function of the skin. The skin acts as a protective barrier to absorption as well as an absorptive organ. Adult human skin averages a surface area of approximately $2m^2$ and is our best protection from environmental dangers. The skin has many layers and each layer affects the rate challenge agents can penetrate the body. The layers of skin are presented below in Figure 1.

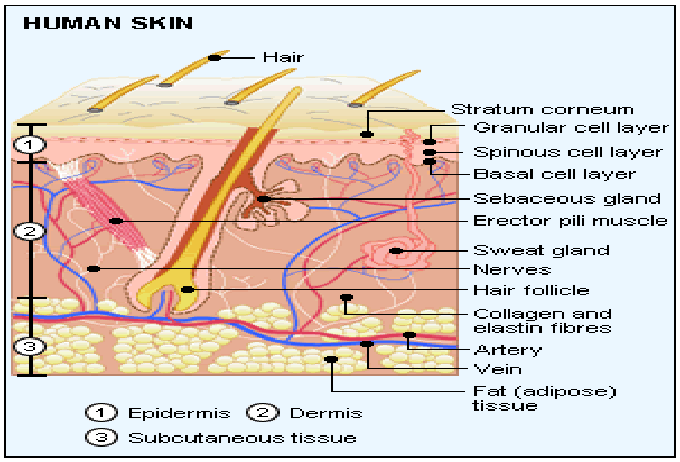


Figure 1: Cross-section of human skin[7]

The stratum corneum is composed of keratinized stratified squamous epithelial cells. This layer is a multi-cell layer of flattened cells with a cytoskeletal protein; keratin. Keratins are fibrous structural proteins. Compared to any type of transfer, skin diffusion is limited to the slowest, or in this case, the least permeable barrier[8]. It has been shown that the thickness of the stratum corneum is the rate-limiting barrier to the penetration of challenge agents.

Physiological factors of the skin contribute the ability of each layer to adequately protect the body from challenge agents by influencing the introduction and speed of penetration of a toxic agent into the bloodstream. Challenge agents move through skin membranes by passive diffusion or active transport. This absorption involves the following: partitioning of the molecule into the stratum corneum followed by diffusion through the stratum corneum, partitioning from the stratum corneum into the epidermis, diffusion through the epidermis and upper dermis, resulting in the final capillary uptake. The solute molecular weight is also a significant factor in penetration. Transdermal delivery into

circulation likely depends on the molecular weight of the solute regardless of whether the limiting step is diffusion through the stratum corneum[9].

Absorption of substances from outside the skin to beneath the skin is known as percutaneous absorption. These chemicals then enter the bloodstream and travel to various organs throughout the body. Transport across the skin occurs primarily by passive diffusion and is directly proportional to the concentration gradient[8].

Other factors that affect percutaneous, or skin, absorption include [10] skin age, health condition, species, anatomical location, metabolism, blood flow, physicochemical factors, and hydration. Exercise and heat cause increased skin temperature, sweating, and increase blood flow. Each factor alone, or together, contributes to an increased percutaneous absorption[11, 12]. Sweating has also been linked to an increased absorption of salicylate esters[13]. Swelling causes an occlusion of the stratum corneum and promotes percutaneous absorption and permeability[14]. Immersion of skin in water causes corneocytes (dead flat cells of the stratum corneum) as well as the intercellular spaces to take up water, while also breaking weak bonds between corneocytes resulting in cell separation[15]. Occluded sites, where evaporation is restricted, also increase absorption.

Diffusion is thermodynamically temperature dependent [16]. Temperatures of the stratum corneum typically fall in the range of 30-37^{o}C. Skin temperatures above 65^{o}C (149^{o}F) for protracted times (>1min) result in severe structural alterations[17]. A 10-degree stratum corneum temperature increase approximately doubles the in vitro permeability[18], while causing a 3-fold increase in bioavailability of methyl salicylate [19]. As drugs reach the dermis, an increased blood flow, from exercise, can increase the removal of cutaneous

drugs[20]. These effects, when combined with skin lacerations, abrasions, or skin deformations can increase the risks of toxic contamination when chemicals have breached a protective suit.

Differences of protection factors resulting from human-mannequin ensemble tests may be caused by two factors[1, 21]. The mannequin surface is non-porous and does not exhibit the mechanisms of absorption as outlined above for skin. At the location of closures, a mannequin also lacks a compressible "skin like material" around the wrist, neck, and ankles. It is more difficult to form a tight seal closure on a mannequin wearing rigid semi-permeable and non-permeable suits. This may increase methyl salicylate penetration into the protective suit. This issue may be alleviated by the addition of a conformable textile skin-simulant material covering the mannequin surface, therefore, understanding the adsorption of MeS on fabric swatches can be used to manufacture garments used to cover the mannequin surface.

2.2 Man In Simulant Test (MIST)

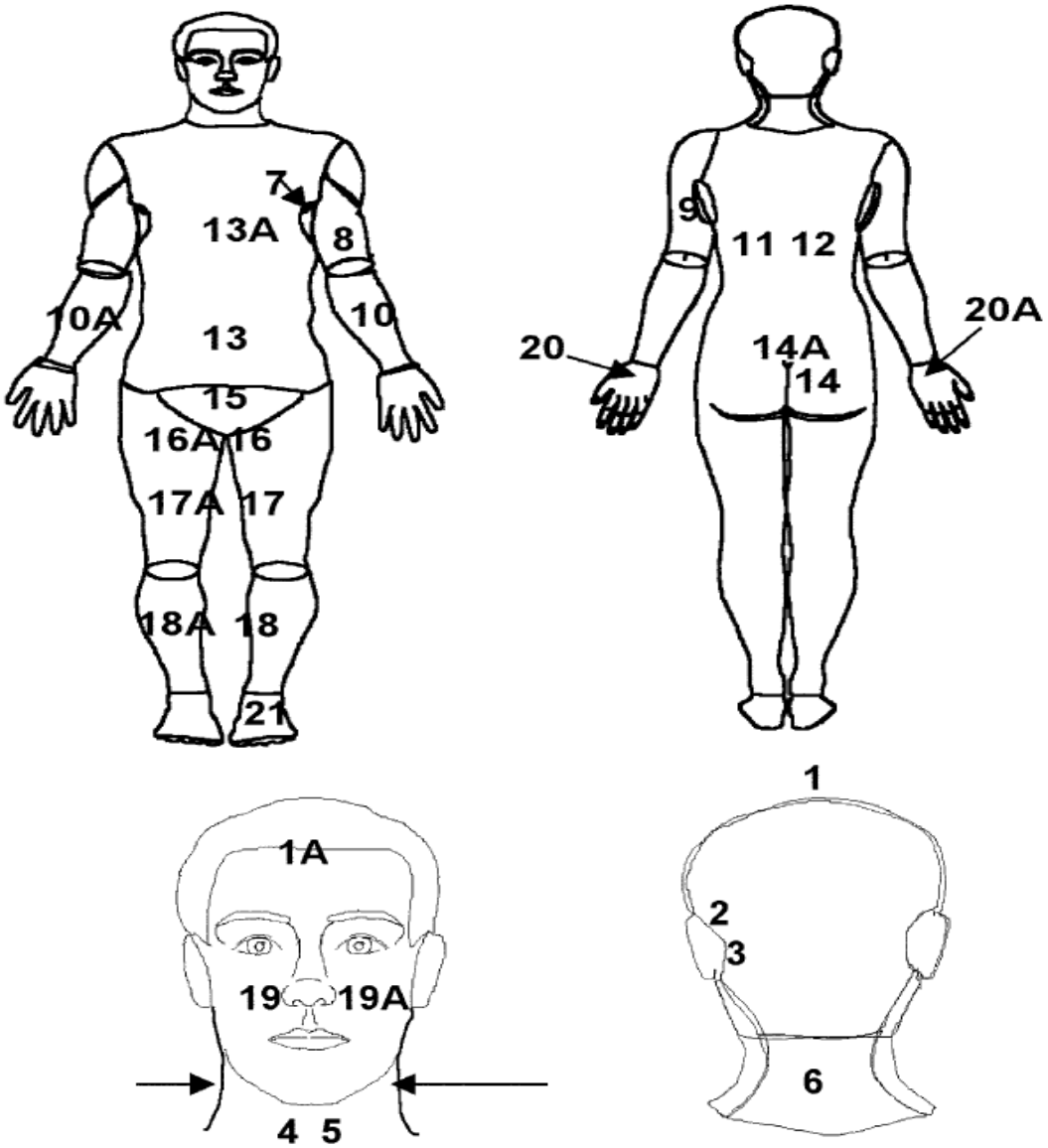
The Standard Test Method for Man-In-Simulant Test (MIST) for Protective Ensembles, provides a standard for testing garments and analyzing the results of chemical vapor penetration through a chemical protective ensemble [22]. This test evaluates the integrity of the ensemble by measuring the quantity of the challenge agent penetrating through closures by calculating the would-be skin adsorption. Man In Simulant Test refers to a systematic approach to test the protection from penetration by chemical agent simulant vapors through protective ensembles. Tests are conducted using human subjects. Human subjects have a skin sink that allows MeS to adsorb before reaching the PADs. During the

evaluations the humans begin to sweat. Sweating can increase the adsorption of MeS on the skin. The goal is to use a mannequin that can simulate sweating and also provide a similar skin adsorption spanning the entire mannequin surface.

Current mannequins can simulate some physiological functions. Sweating mannequins [23-26] and thermal mannequins [27][[28]][[29][[30] have been used extensively in garment evaluations.

Not all ensembles are seamless. Contamination can occur around zippers, boot fittings, gloves, seams, facemasks, and other closures and interfaces. This MIST procedure allows the detection of challenge vapors penetrating through closures. These vapors then adsorb onto strategically located patches placed around the body underneath the protective garment.

There are 30 strategic locations for evaluation. These locations are chosen to represent a range of body areas and are located close to the interface of gloves, boots, two-piece ensembles, facemasks, and respirators. A passive adsorbent dosimeter is placed at each location. These locations can be seen in Figure 2.



PAD LOCATIONS

1- scalp (SCA)
1A – forehead (F)
2- behind l. ear (LE)
3- behind l. ear up. (LED)
4- neck left (NE)
5- neck right.(NED)
6- nape (NA)
7- l. armpit (LA)
8- l. inner up. Arm (LIU)
9- l. out.up.arm. (LOU)
10- l. forearm (LFA)
10A- r. forearm (RFA)
11- mid. Back (MB)
12- mid. back. dup. (MBD)
13- abdomen (AB)
13A- chest (C)
14- r.butt (RB)
14A- low.back (LB)
15- groin (GR)
16- crotch (LCR)
16A – crotch (RCR)
17- l. inner thigh (LIT)
17A – r. inner thigh (RIT)
18- l. inner shin (LIS)
18A- r. inner shin (RIS)
19- cheek (RM)
19A – cheek (LM)
20- left hand (G)
20A- right hand (GD)
21- foot (B)

Figure 2: Passive adsorption dosimeter locations on test subjects[22].

Passive adsorbent dosimeters are adhesive backed pads 25 by 35 mm by 0.02 mm containing 40 mg of adsorbent Tenax TA. Tenax TA adsorbs the chemical vapor. Following the MIST test, the vapor is recovered from the Tenax TA using thermal desorption and analyzed by gas chromatography or methanol extraction and high performance liquid chromatography [22].

Because human subjects are used during the test and because of the threat of possible contamination, toxic nerve agents are tested using appropriate chemical simulants, e.g. MeS. During testing, methyl salicylate (MeS), oil of wintergreen, is used as the chemical simulant. MeS is used because its vapor pressure, density, and water solubility are similar to that of distilled mustard (HD) gas.

Human test subjects are subjected to numerous physical activities during the 30-minute test. These are routine stationary and physical movements that test the ensemble's integrity during wear and use. A 30-min exposure time is used to mimic the response time of a first responder to a chemically contaminated area.

Chamber temperature is maintained at approximately 27^{o}C with 65% relative humidity. Airflow through the chamber remains constant at 2-5 mph. Real-time concentration of MeS is closely monitored and maintained at 100 mg/m^3(16ppm) using infrared spectroscopy[22].

The test chamber is stainless steel and can accommodate four human test subjects. To prevent leaks the chamber is maintained at a negative pressure. Methyl salicylate is re-circulated by fans above a false ceiling. Adjacent to the chamber is a control room and an airlock entry/exit room. In the entry/exit room the test subjects can undress and the PADs

can be safely removed without PAD contamination and without methyl salicylate leaking into the immediate environment.

At the conclusion of the MIST procedure, the PADs are opened and the Tenax TA adsorbent is removed and placed in adsorbent tubes. From here, the MeS is thermally desorbed from the Tenax TA and analyzed by gas chromatography.

2.3 Simulants/Methyl Salicylate

Analogs and simulants are most commonly used as replacement chemicals for chemical warfare agents (CWA's). Analogs include chloroethyl ethyl sulfide (CEES) and diisopropyl fluorophosphonate. Analogs are structurally similar to CWA's but are not chemical warfare agents. However, these analogs are very toxic. Historically, methyl salicylate, (MeS: $C_8H_8O_3$) CAS #119-36-8 (MP Biomedicals, LLC), with a minimum purity of 95%, has been used as a simulant to evaluate HD exposure. methyl salicylate is found in many topically applied ointments. An organic ester, MeS is a clear pale yellow oily liquid. Methyl salicylate is slightly soluble in water (1g/1500 ml water [31], highly soluble in chloroform, ether, alcohols, and glacial acetic acid. Molecular weight, vapor pressure, and solubility of methyl salicylate are similar to that of HD. Although structurally MeS bears no similarity to HD, or VX, as can be seen in Figure 3, it is assumed that chemicals with similar chemical and physical properties will behave in similar fashion. Vapor pressure of MeS and some nerve agents differ, therefore, MeS is not recommended as a nerve agent simulant.

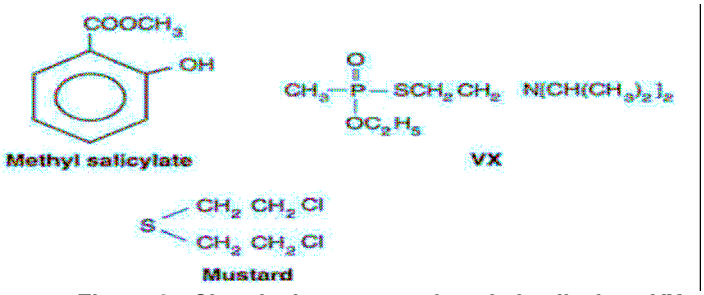


Figure 3: Chemical structure of methyl salicylate, VX, and Mustard (HD)

Studies have proven the physical relationship between HD and MeS, and the adsorption and skin deposition of MeS and HD in the isolated perfused porcine skin flap (IPPSF). The porcine skin flap is very similar to the human skin[32, 33]. The porcine model allows the use of vascularized tissue, hair follicles, and sweat ducts that may alter the permeation. This model is also beneficial and feasible when human trials are not feasible. Many tests have shown that both the pig and rhesus monkey skin permeability are similar to humans. However, using the swine skin as an adsorption model provides morphological and histiochemical similarities to the human skin. Swine skin composition is also similar to that of human skin. Site-specific adsorption in human skin is related to skin permeability at different locations. The swine model reflects this, and provides a useful tool for the assessment of toxic agents at various locations, as well as site-specific absorption rates. Results are then extrapolated to humans. Permeation of MeS through swine skin is site specific, like human skin, and has comparable permeation as that of human subjects[33]. This is important for the protection and evaluation of CPE's at different body locations. Skin percutaneous absorption and skin deposition of MeS and HD comparisons show similar results in the IPPSF model system[34]. Comparison of percutaneous flux of HD and MeS shows that MeS is appropriate to use as a simulant for HD, as compared with other

compounds. Other studies[33, 35-37] provide agreement that MeS is an appropriate simulant.

Breakthrough data on fabric were compared for HD and MeS. These results were the basis for choosing MeS as a simulant for the MIST program. Results showed that MeS penetrates fabrics approximately 30% slower than HD, with breakthrough occurring after three or four days of challenge[38]. Because of this, the MIST procedure can be used to assess the integrity of seam, closures, and interfaces of the CPE. The MeS should not penetrate the garment within the 30-minute testing time. However, this limitation would skew the data as penetration can occur at stressed, torn, and lacerated locations of the garment during testing procedures.

Use of MeS is suggested by other characteristics. These characteristics include medical/safety aspects, environmental impact, chemical/physical properties, sampling/detection/analytical methods, agent/simulant correlations, reproducibility, and transportation/storage/disposal requirements[35].

Acute toxicity from oral salicylates begins at 150mg/kg (10.5 gm in a 70 kg individual). The human exposure during the MIST procedure is 8 orders of magnitude below the toxic dose. This is assuming a nude human subject, with a MeS absorption rate of 2%, inside the mist chamber for 30 minutes [22]. During the MIST procedure human subjects will don CPE.

2.4 Passive Adsorbent Dosimetry

2.4.1 Passive Samplers

Passive samplers are easy to use and help determine the amount of personal exposure to volatile chemicals. Passive samplers do not have moving parts, pumps, or flow controllers

and have been used to measure gas concentration over long periods of time[39]. Passive adsorbent dosimeters are non-evasive adhesive-backed foil packets that can be placed on the skin of the human test subjects.

Passive samplers are different from active samplers. During active sampling, the sampling rate is determined by a pumping flow rate through a tube. Passive samplers, however, use the diffusive uptake rate, which is dependent on variables external to the sampling device, which in turn, determines the molecular diffusivity of the target analyte[40]. These variables include humidity, temperature, simulant concentration, flow, and properties of the simulant.

It has been shown that Ficks First Law of Diffusion can describe the uptake rate of each component for a given sorbent[40]. The diffusive uptake rate of MeS was shown to follow Ficks First Law of Diffusion[22, 38, 41]. Ficks first law is steady state diffusion where $J_{in} = J_{out}$,

$$J = -D\frac{\partial \phi}{\partial \chi}$$

where

$$J = \frac{mol}{m^2 \cdot s}$$

$$D = \frac{m^2}{s}$$

$$\phi = \frac{mol}{s}$$

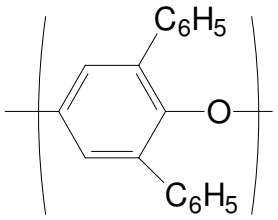
where J is the diffusion flux ,D the diffusion coefficient ϕ (for ideal mixtures) is the concentration in dimension, χ is position. Using Ficks Law, D is proportional to the velocity of the diffusing particle.

Ficks First Law for use on the PAD can be stated as: amount = dosage*flowrate. Although uptake rates can be calculated and are directly proportional to the molecular diffusivity of the simulant, it is important to understand that the uptake rate can be affected by the interaction of the passive sampler membrane (thickness and material) and adsorbent.

In the MIST Chamber, passive samplers are used because of the simplicity and ease of use. Passive dosimetry samplers used during MIST tests are Natick samplers. Natick PADs are covered by a high-density polyethylene (HDPE) barrier, which provides the diffusive sampling surface. This film is produced to have a penetration rate similar to human skin when exposed to MeS[22]. Below the HDPE film is a Nylon/Foil Barrier film. This film meets Mil-B—131H, "Barrier Materials Water Vapor Proof, Greaseproof, Flexible, Heat-sealable" for Type 1 Class 1 as written in the ASTM Standard f2588-06[22]. This film consists of 4 layers, and provides moisture and oil protection. Inside the packet is 40 mg of the sorbent 60 to 80 mesh Tenax TA. The sole source of these PADS, known as "Natick samplers" is Syon ITW Devcon in Danvers, MA.

2.4.2 Tenax TA

Tenax TA has been designed to trap volatiles and semi-volatiles from air. Tenax TA has a low affinity for water and low levels of impurities. Tenax TA a 2.6-diphenylene oxide polymer resin. The chemical formula is shown if Figure 4.



Tenax

Figure 4: Tenax TA chemical structure.

Desorption of the methyl salicylate is crucial for the evaluation of the chemical protective ensemble. PADs are limited because they do not provide a real-time sensing technique. Therefore, it is paramount that the PADs are not contaminated and are efficient at desorption of methyl salicylate.

2.5 Protection Factors, Local Analysis and Systemic Analysis

Using the percutaneous adsorption rates of HD on skin, and the amount of adsorbed MeS on the PADs, local and systemic protection factors are determined for each garment. The analysis estimates the protection of an ensemble by measuring the amount of MeS adsorbed for each body region. The amount of simulant that penetrates the skin and enters the regional tissue or blood is referred to as the absorbed dose, whereas the amount of simulant that reaches and injures cells is known as the effective dose[38]. The outer layer of skin has dead cells and therefore skin exposure does not confirm toxic reactions. Nor does vapor passing over the skin cause harm. Measuring the absorbed dose would require biological monitoring. Instead, indirect methods require simulating the skin penetration resistance and knowledge of skin penetration. Many physiological factors affect dermal penetration as previously discussed. Following decontamination and retrieval of the pads, the exposure is calculated using the following arrangement of Ficks First Law:

$$\mu = \frac{m}{Ct},$$

Where:

μ = uptake rate (cm^3/min)

Ct= Chamber Vapor Dosage $\frac{mg \cdot \min}{cm^3}$

m = mass in mg

$$\mu = 10 \frac{cm^3}{\min}$$

Using the average vapor chamber concentration as the dosage, the MeS uptake rate is calculated. The uptake rate is used to calculate the dosage on each PAD (Ct). Protection factors and exposure limits are then calculated.

Protection is determined by the concentration of MeS outside the suit compared to the concentration obtained on the PAD inside the suit. Because human skin absorbs differently at different body locations, the protection factor is determined for each of the 30 specific anatomical locations where PADs are placed. Exposure is defined by protection factors.

These factors include the following: Local Physiological Protective Dosage Factor ($PPDF_i$), the physiological protective factor at a specific location on the body, Physiological Protective Dosage Factor (PPDF), the factor by which the protection is improved against vapor exposure when protected compared to an unprotected body exposure, and the Systemic Physiological Protective Dosage Factor (PPDF), a physiological protective dosage factor determined for the entire ensemble[22].

Protection factor is the ratio of the MeS concentration outside the suit to that inside the suit:

$$PF_i = \frac{Ct_{outside}}{Ct_{inside}}$$

Figure 5: Calculation of Protection Factor (PF) [22].

Calculating site-specific protection factors (PPDF) uses the following equation:

$$LocalPPDF_i = \frac{OSED_i}{25} PF_i$$

Figure 6: Calculation of site specific protection factor (PPDF) [22].

where the specific onset of symptoms exposure dosage, $OSED_i$ is used. This limited dosage is derived from the calculated threshold concentration of mustard agent that causes blistering and ulceration in 10% of the population at the specific PAD region location[22].

Calculation of the protection factor of the entire ensemble system (PPDF) is calculated in a similar fashion using a weighted body region analysis provided below:

$$PPDF_{sys} = \frac{\sum_i ED_{50i} dz_i}{\sum_i \frac{ED_{50i} dz_i}{PF_i}}$$

Figure 7: Calculation of ensemble protection factor (PPDF) [22].

where the ED_{50i} is for an exposure that causes severe effects for the body region, and dz_i is the area of body region for the PAD tested.

2.6 Analytical Techniques

MeS concentration in methanol solutions (extract) were analyzed by UV-vis spectroscopy (Varian Cary 3E). MeS concentration in the chamber was monitored using a

FTIR (Fourier Transform Infrared) Spectroscopy (FTPA2000 CIC Photonics).

2.7 Transfer Theory of MeS into Textile Fabrics

2.7.1 Sorption Mechanics

Transfer mechanisms of methyl salicylate into fabric can be considered similar to the transfer mechanisms of water vapor into a fabric. Water passes through a fabric via diffusion, wicking, and sorption. Sorption includes absorption and adsorption. Wicking, which largely begins at fabric saturation, is the transfer of liquid and will not be considered in this study. Diffusion and sorption will be of primary concern for the transfer of methyl salicylate vapor toward a fabric.

Diffusion of vapor molecules is considered a process of mass transfer that is driven by a concentration gradient through the fabric[42]. Thus, diffusion is the movement of molecules through the pores and interstices of the fabric material[43].

Absorption is commonly referred to the movement of moisture from one side of the fabric to the other as the fabric absorbs the moisture and swells. On the other hand adsorption is the attachment of the molecules on the surface of the fabric. Adsorption results when two phases come into contact. An increase in concentration of a particular phase then occurs at the interface. As this occurs the molecule can migrate through the fabric. Sorption and diffusion are related. It has been debated whether absorption swelling in fibers can cause thermal motion to disrupt chain segments within a fiber and thus increase diffusion, or swelling decreases paths for diffusion[44-46].

Many chemical vapor filter systems use different materials for filtering. Many activated carbon fabrics contain carbon particles that have a physically adsorbing surface.

Carbon particles can be in the form of carbon fibers and carbon powders. Other routes included chemically treating the fabric surface to selectively adsorb chemicals.

The amount of vapor adsorbed before reaching equilibrium is controlled by temperature, pressure, and the nature of the adsorbent and adsorbate[47]. In the case of adsorbing chemical agents, some materials that adsorb one particular agent might not be effective against other chemical agents. The surface of the adsorbent can also become contaminated by humidity and particulates. This surface can also degrade over time and when exposed to the challenge chemical.

Chemically treating a fabric for adsorption verses active carbon adsorption differ in their adsorbing mechanics. In the case of the former, a chemisorption process occurs, while in the latter, physiosorption takes places. The difference between the two is largely found in the strength of the interaction. Van der Waals forces, similar to condensation phenomena, contribute to physical adsorption while forces of chemical reactions are associated with chemisorption[47]. This often involves a specific site on the adsorbent for adsorption, thus limiting the amount of adsorption and often resulting in the formation of a monolayer. This also keeps the adsorbate from migrating[48]. During chemisorption, the adsorbed material is often difficult to remove. Physisorption occurs when the adsorbate comes in contact with the surface of the adsorbent. Because there is not a chemical bond, these types of adsorptions are reversible. There is a low heat of adsorption, which causes little physical disruption to the adsorbing surface. During physical adsorption the adsorbate is not required to nor limited to only adsorbing on selective active sites. The un-bonded side of the adsorbent surface attracts vapors via van der Waals forces to satisfy the force imbalance. Therefore, the adsorbate can

migrate into pores.

Both physical adsorption and chemical adsorption reach equilibrium quickly because activation energy is not required[48].

Adsorption of the adsorbate begins with adsorption at isolated sites, continues toward entire surface coverage, then to multi-layer coverage, and if the pressure continues to increase, the adsorbate will fill the pores and complete coverage of the material will occur. For the adsorbate mathematical approximations are available for predicting the pore size, surface area, micro pore volume, and isotherms from experimental data[49].

For the case of carbon particles, the surface area can be greatly increased by the size and shape of the particle. Not only does the shape affect adsorption, but also the porosity within each carbon particle increases the surface area to maximize adsorption capacity. Channels within the particle can provide areas for the adsorbate to migrate and fill. This type of benefit increases the surface area and maximum adsorption and occurs in the Tenax TA powder used in the passive samplers of the MIST procedure.

2.7.2 Sorption Theory

Ideal sorption surfaces are clean and uniform. Sorption includes the migration of two phases together. Following this initial interaction, migration then continues across the material. Finally, the adsorbate can be desorbed, by increasing the temperature. Desorption is possible because adsorption is exothermic in accord with Le Chatelier's Principle. Summarized, Le Chatelier's Principle simply states that a change in concentration, volume, pressure, or temperature can shift the equilibrium. In the case of desorption, addition of heat causes the breaking of bonds and hence the removal of MeS. Adsorption isotherms describe

the relation between the adsorbed amounts of vapor, at any constant temperature, with the vapor pressure.

For example, moisture isotherms relate the amount moisture regain in a fiber to the concentration of water in the environment.

Langmuir isotherms describe monolayer adsorption. The Langmuir adsorption does not take multilayer adsorption of a substance into account. Multilayer adsorption has been described using the Brunauer, Emmet and Teller Equation (B.E.T.). The BET equation applies similar adsorption thermodynamics. Kinetic differences of these equations has been well presented elsewhere[47].

At equilibrium the Langmuir isotherm is related to the number of sites on the surface by the equation:

$$k'S'=k''P(S-S')$$

where S is the number of adsorption sites, S' the number of sites that are occupied, and S-S' is the number of free sites. The BET equation is derived for multi-layer adsorption as:

$$\frac{\chi}{v(1-\chi)} = \frac{1}{v_{mon}c} + \frac{\chi(c-1)}{v_{mon}c}$$

χ = Pressure/Vapor Pressure of adsorbate at tested temperature $\frac{P}{P^o}$

v = STP volume of adsorbed adsorbate

v_{mon} = STP volume of the amount of adsorbate required to form a monolayer

c = Equilibrium constant used the in Langmuir isotherm multiplied by the adsorbate

vapor pressure. Figure 8 shows the Langmuir and BET adsorption isotherms.

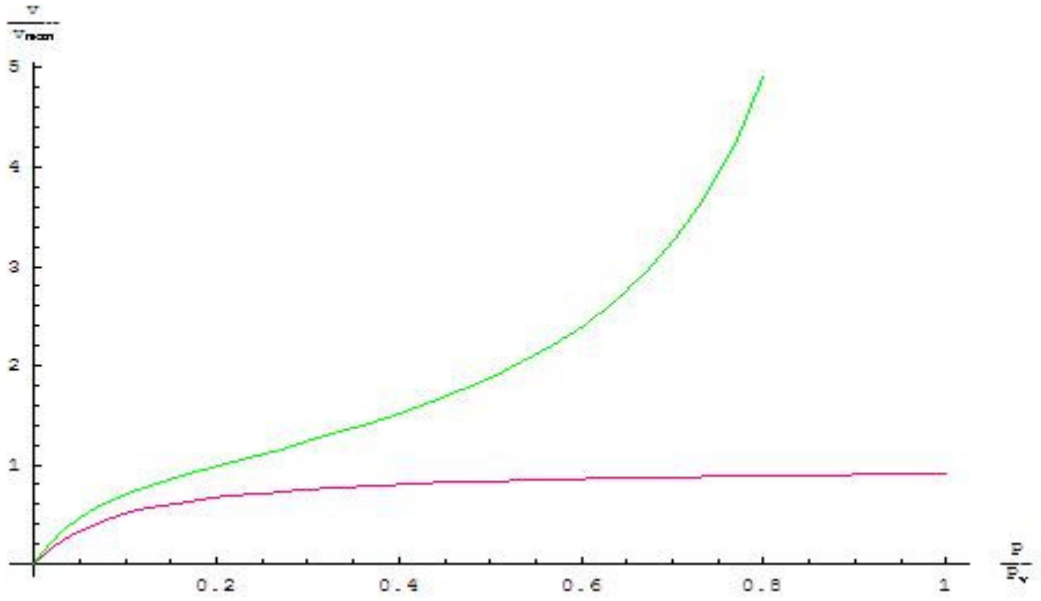


Figure 8: Langmuir adsorption isotherm (bottom) and BET adsorption isotherm (top) [50]).

Difficulties of surface adsorbing systems arise when the surface is contaminated. Contamination occurs when other particles compete for locations. This is considered poisoning of the active sites, or area, which can be caused by particulates and water molecules. This limits the maximum adsorbing capacity.

2.8 Fabric Materials Selection

Previous research has evaluated two types of pseudo-skin materials: carbon cloth with a layer of polyethylene film on top and a carbon layer with a thin semi-permeable membrane[51]. Neither has established a material that adsorbs methyl salicylate at the same rate a human skin. This research will evaluate selected knit fabrics as skin adsorption simulants.

It has been shown that adsorption of organophosphorous vapors was significantly higher on polyester membranes than polyvinyl chloride or polytetrafluoroethylene[49]. While vapors adsorb differently on different membranes, the same trend could occur with MeS on different knit fabrics composed of different fibers.

Chapter 3: Experimental

3.1.1 Experimental Approach

The experimental approach was to assess the effects of the following variables on the adsorption of MeS on selected knit fabric: apparatus type, MeS exposure concentration, MeS exposure time, fabric knit design, water gained on fabric, and fabric fiber type.

The experimental plan included the modification of a temperature and humidity-controlled chamber to accommodate MeS in addition to constructing a method to introduce fabric samples into the chamber for the evaluation of MeS adsorption.

MeS adsorption was compared at different flow-rates as well as different MeS concentrations to study the effects each variable has on the adsorption of MeS on the selected fabrics. These designs are referred as the chamber design and the tube design.

To quantify a comparable skin adsorption of MeS on fabric, the target skin adsorption was based on the MeS adsorption of a Natick PAD. Natick PADs were also used to verify the chamber MeS concentration. The materials used are outlined below.

3.1.2 Materials

Fabrics selected for evaluation incorporated a range of differences including the following: hyrophobicity/hydrophilicity, crystallization, and core sheath fiber structure. Knits were chosen because they could potential form a tight fit on a mannequin. TestFabrics

Inc. provided scoured samples shown in Table 1. Using the same knits will help compare the relationships between different knits and fibers.

Table 1: Fabric test samples.

Fabric (Style Number)	Fiber	Knit Structure
Bleached Cotton (437w)	Cellulose	Cotton Jersey
Bleached Cotton (460)	Cellulose	Cotton Interlock
Wool (532)	Protein	Jersey
Silk (601)	Protein	Crepe deChine
Texturized Nylon 6,6 (314)	Polyamide	Double Knit
Nylon 6 (304)	Polyamide	Tricot-Bright

Fiber structure differs for each. Keratin (wool) exists in an alpha helical structure, where fibroin in silk exists in beta-pleated sheets. Cotton, a cellulosic fiber, is hydrophilic much like silk and wool. Nylon has significantly fewer active groups to adsorb moisture compared to protein and cellulosic fibers. These differences should not only be evident in the amount of moisture regained during preconditioned conditioning, but also in the amount of MeS adsorbed during chamber trials. Changes in adsorption with preconditioned fabric should provide insight towards a fabric that can be used with a sweating mannequin.

Molecular composition and fabric structure are major influences in moisture adsorption with fibers. MeS was expected to follow adsorption trends similar to that of water. In cellulosic fibers, hydroxyl groups (-OH) strongly attract water. Carbonyl groups (-C=O) in the main chain of proteins as well as N-H groups also have affinity toward water. In the case of synthetic polymers, there are fewer hydrophilic groups in the chain structure. Nylon, has some C=O and N-H groups.

Non-crystalline regions provide a loose network where active groups can adsorb

water molecules and the fiber can swell. Fiber swelling can increase the diffusion of challenge materials in the vapor state. Spherical molecules diffuse slower than linear molecules. Swelling of fibers can also increase the surface area of the fiber.

Figure 9 shows the molecular structure of the fibers used.

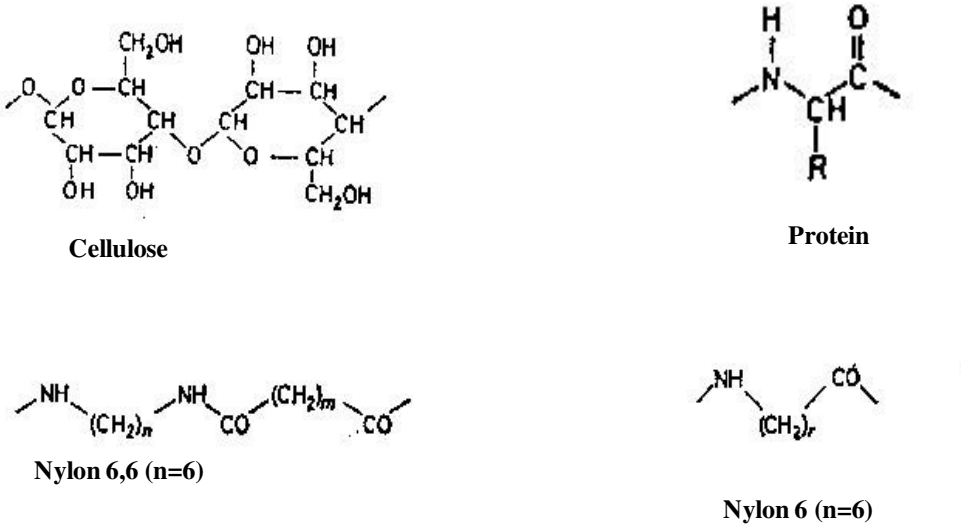


Figure 9: Chemical structure of cellulose, nylon double knit, nylon 6, and protein fibers.

3.1.3 Chamber Modification and Operation

Swatch testing was effected inside an Esquec Platinous 2G Serious temperature and humidity controlled environmental chamber. The total operating volume is 225 Liters. Water vapor was added from a heated coil submerged in a water tray at the bottom of the chamber. Air temperature was maintained using nichrome-heating wires. The chamber was dehumidified using a coolant system. This cooling system ran external to the chamber and caused moisture to condense inside the chamber. Circulation was attained by a line flow fan sending air through a blow port resistor[52].

To access the chamber during use, and to prevent leakage of methyl salicylate, a new

door was constructed. The original chamber door was removed and replaced by with a Lexan 9034 polycarbonate sheet (GE). Lexan 9034 (¼" thick) was cut to size to replace the original chamber door. Lexan 9034 was chosen because of its chemical resistance, durability, and insulative properties.

Samples were introduced to the chamber via an airtight acrylic sample box purchased from Terra Universal. Samples were manipulated manually via access into the chamber from neoprene glove and glove ports (Renco Corporation). The modified chamber door can be seen in Figure 10 below, methyl salicylate was introduced to chamber using a type D diffusion vial with a Dynacalibrator 340 (VICI Metronics) gas generating system. This system contains calibrated gas systems for a dilution flow and carrier flow. A permeation chamber houses a type D diffusion vial. Each can be seen in Figures 11 and 12 below.

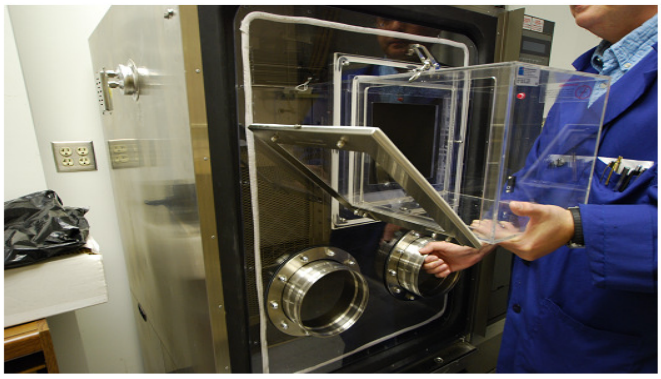


Figure 10: New chamber door showing sample access box and glove ports.

Figure 11: Type D diffusion vial for methyl salicylate.

Figure 12: Control face of Dynacalibrator gas generator.

Construction details of the chamber modifications are outlined in the appendix. The sample inlet door from inside the chamber is shown in Figure 13.

Figure 13: View, from inside chamber, of access door opening into the sample air lock.

During operation, the gas generator oven was conditioned to 110^{o}C. After equilibrium was reached the gas generator was switched from "mode" setting to the "span" setting, causing the dilution stream and the chamber output stream to mix and be sent out of the gas generator via the stream outlet. The stream outlet is plumbed to the methyl salicylate chamber inlet of the Mini-Mist Chamber.

3.2 Apparatus Effects

The testing apparatus provided different airflows, MeS concentrations, and exposure times as outlined in Table 2. The chamber experiments also incorporated preconditioned and ambiently conditioned fabric analysis to mimic sweating skin.

Table 2: Comparison of experimental parameters for the chamber and tube setup.

	[MeS] (ppm)	Air Flow	Exposure Time (min)
Tube Apparatus	16	0.5 LPM	30
Chamber Apparatus	~4-5	Dynamic and Static	90

3.2.1 Tube Design

To evaluate the adsorptive properties of the selected fabrics without the Mini-Mist Chamber, the gas generator was directly connected to the tube design with the fabric inside. The tube apparatus consisted of Tygon tubing (5/8" ID) configured with a hose barb fitting to allow direct connection to the gas generator outlet stream. The fabric covered the inner wall of the tube allowing methyl salicylate to flow through the hollow cylinder created by the fabric, and hence over the fabric. Based on the diameter of the selected tubing, dimensions of the fabric were 4.78 cm by 20.9 cm to prevent the fabric from overlapping on itself when rolled and placed inside the tubing, while also using a sample area of 100 cm^2 to stay consistent with chamber experiments. Figure 14 shows the design of the tube apparatus.

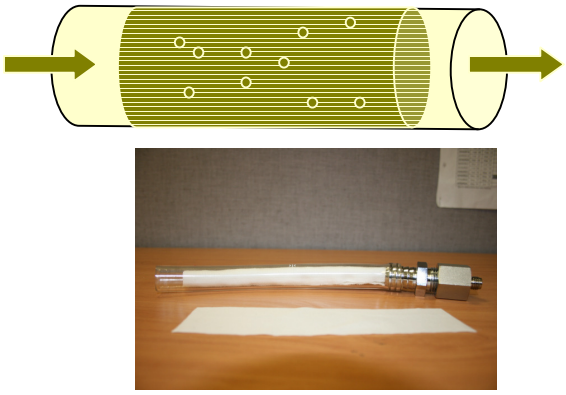


Figure 14: Tube apparatus with arrows indicating flow of MeS vapor (above) and the tube apparatus (below).

Following an exposure of 30 minutes to a stream flowing at 0.5 Lpm with 16 ppm of methyl salicylate, the samples were cut in half, to ease the extraction process, loosely rolled into 4 dram vials, and washed with methanol (10 mL). Next the vials were shaken and samples were analyzed by UV-Vis spectrophotometry

3.2.2 Chamber *Design*

Sample fabrics were placed inside the chamber on a tray, raised approximately 4 inches off the chamber floor, allowing the vapor to pass over the fabric. The same fabric was used in the chamber evaluations and in the tube design experiments. The chamber apparatus controlled MeS at approximately 5 ppm for 90 minutes. At a MeS concentration of 5 ppm, the fabrics had to be exposed for 90 minutes to have the same amount of MeS exposure as in the tube design. Figure 15 shows the chamber design apparatus.

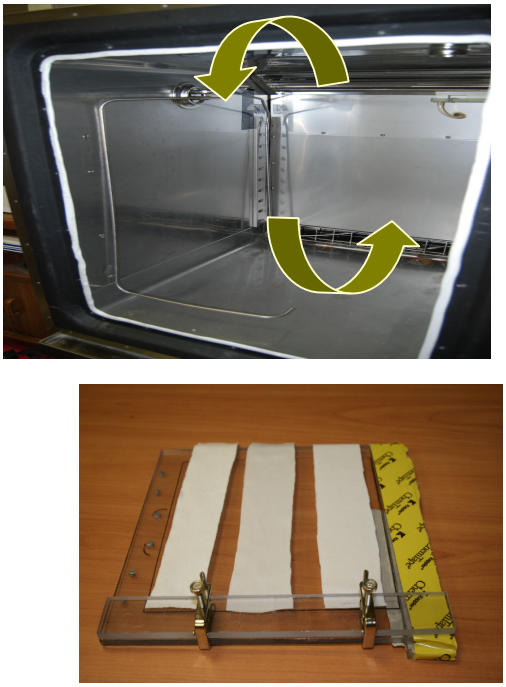


Figure 15: Sample tray for fabric placed inside chamber (bottom), and the chamber airlflow regime (above)

3.3 Analysis for MeS Adsorption on Test Fabrics

3.3.1 Extraction Efficiency and Calculation Technique

To evaluate the fabric samples for methyl salicylate adsorption, methyl salicylate extraction efficiency with methanol was determined. Methanol extraction of methyl salicylate from the fabric samples was used because MeS is soluble in methanol, and methanol is a good solvent for UV-Vis analysis. Therefore, a target mass was determined and samples were prepared of differing concentrations around the target to create a UV-Vis calibration curve. This approach is outlined below.

Because the Natick PADs adsorb at a rate similar to the skin, and the selected fabrics will be compared to the adsorption of methyl salicylate on the Natick Pads, the target skin absorption rate was determined from the Natick Pads using Ficks Law: Amount = dosage*flow rate. Flow rate through the polyethylene layer equals 10 mL/min, and during MIST the dosage equals 100 mg/m^3 (16ppm) during 30-minute exposures. The calculated target mass is 0.03 mg. The Natick Pad has a polyethylene layer sample area of 2.6 cm by 1.77 cm with a total sample area of 4.6 cm^2. To ensure adequate detection, the fabric sample size, and hence the mass detectable, was scaled up by a factor of 20, resulting in a target mass of 0.6 mg on a sample fabric size of approximately 100 cm^2.

Calibration solutions (10 mL) of methanol/methyl salicylate were prepared to develop a calibration curve. Solutions were mixed in 4-dram vials. The density of pure liquid methyl salicylate is 1174 mg/mL. Using the density of methyl salicylate, sample concentrations surrounding the target adsorption mass were calculated. These dilutions represent 5%, 10%, 25%, 75%, and 150% of the target. A sample of 300% of the target was prepared and used to

measure the extraction efficiency of methanol. A sample volume of 10 mL was used during extraction of MeS from the fabric samples. To prepare the solutions, methyl salicylate (1 µl) was mixed with the appropriate volume of methanol (by pipet) as shown in Table 3 and described below.

Table 3: Calibration solutions prepared using 1 ul of methyl salicylate with methanol. Solutions surround the target mass of 0.6 mg of methyl salicylate on an area of 100 cm^2.

MeS in Methanol (mg/ml) on 100 cm^2 area Natick PAD	% of Target	PPM	Methanol for Dilution (ml) with MeS (1ul)	Vial Number
0.005625	5%	5.625	Diluted 1:1 of B	A
0.01125	10%	11.25	Diluted 1:1 of C	B
0.0225	25%	22.5	Diluted 1:1 of D	C
0.045	75%	45.	Diluted 1:1 of E	D
0.090	150%	90.	13	E

The standard solution of Vial E was prepared with methyl salicylate (1 µl) and methanol (13 mL). Five mL was removed from vial E, placed in vial D and diluted with methanol (5 mL). Vials A, B, and C were prepared in the same fashion, by removing 5 mL from Vials B, C, and D respectively. Note the target mass, 0.6 mg, has changed in Table 2 to reflect the concentration of the target mass diluted in 10 mL of solution. The target concentration is therefore $\frac{0.06mg}{mL}$.

Target Methyl Salicylate Concentrations used in the calibration curve are as follows:

Target absorption at 30 minutes = 0.6 mg

Target methyl salicylate concentration in vial with 10 mL of methanol:

$$\frac{0.6mg}{10mL} = \frac{0.06mg}{mL}$$

Density of Methyl Salicylate= $\frac{1175mg}{mL}$

Dilution calculations:

300% of target mass solution = $\frac{0.18\text{mg}}{\text{mL}}\ \frac{methylsalicylate}{methanol}$

$$\frac{1175mgmethylsalicylate}{mL} \bullet \frac{1mL}{1000\mu L} = \frac{1.175mgmethylsalicylate}{\mu L},$$

And $\frac{\frac{1.175mgmethylsalicylate}{\mu L} \bullet 1\mu L}{6.5mLmethanol} = \frac{0.18mg}{mL}$

150% of target mass solution = $\frac{0.09\text{mg}}{\text{mL}}\ \frac{methylsalicylate}{methanol}$

$$\frac{1175mgmethylsalicylate}{mL} \bullet \frac{1mL}{1000\mu L} = \frac{1.175mgmethylsalicylate}{\mu L},$$

And $\frac{\frac{1.175mgmethylsalicylate}{\mu L} \bullet 1\mu L}{13mLmethanol} = \frac{0.09mg}{mL}$.

The calibration curve from the standards and its results can be seen below in Table 4 and Figure 16. A Linear Direct fit was used to include zero as the origin. As a result, the R-squared value, or correlation coefficient, was equal to 0.99999.

Table 4: Calibration Standards used for the MeS/Methanol UV analysis calibration curve.

	Concentration mg/L	Abs.
Std. 1	**5.265**	**0.14**
Std. 2	**11.25**	**0.2814**
Std. 3	**22.5**	**0.5634**
Std. 4	**45.**	**1.1188**
Std. 5	**90.**	**2.2325**

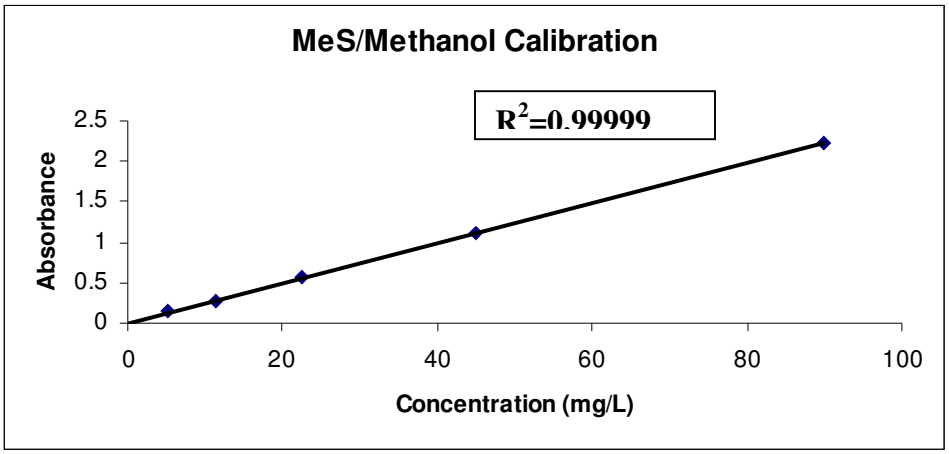


Figure 16: Calibration Curve of MeS/Methanol with a Linear Direct Fit.

Fabric extraction efficiency was determined by placing 1 mL from of 0.18 mg MeS/mL solution, from Vial E, on a 50 cm^2 sample of each fabric. The fabric was given 5 minutes to soak in the solution and allow the methanol to evaporate. The fabric was then rolled up and placed into a 4 dram vial, washed with methanol (10 mL), shaken, and analyzed. The data given in Table 5 indicate the extraction efficiency of the method is good.

Table 5: Extraction efficiency of MeS on ambiently conditioned fabric and preconditioned conditioned fabric using methanol.

Fabric (50 cm^2)	Methyl Salicylate Ambiently conditioned Fabric (mg)	Methyl Salicylate Preconditioned Fabric (mg)
Cotton Interlock	**0.207**	**0.207**
Cotton Jersey	**0.201**	**0.228**
Wool	**0.234**	**0.204**
Silk	**0.210**	**0.191**
Nylon double knit	**0.220**	**0.183**
Nylon Tricot	**0.196**	**0.187**
Standard	**0.179**	**0.179**

The mass from UV analysis is slightly higher than the standard solutions. The slight difference is thought to be caused by the fabric thickness. Thicker fabrics can make it more difficult to extract the MeS. Table 6 shows small increases of MeS absorbance. The fabrics were placed in vials with methanol only, and the solution was extracted and placed in the UV-VIS.

Table 6: MeS response (mg) of test fabrics in methanol solution without MeS exposure

Fabric	MeS (mg)
Cotton Jersey	0.066
Cotton Interlock	0.101
Wool	0.110
Silk	0.022
Nylon double knit	0.047
Nylon Tricot	0.063

3.3.2 Analytic Procedures

One μL and volumes, in mL, of MeS and methanol (Fisher, ACS certified), respectively, were measured using an Eppendorf Repeater^{TM} Plus pipette.

Calibration at 305 nm generated an equation for conversion of MeS absorbance to concentration. During UV-vis analysis of MeS, the calibration absorbance was measured at 305 nm. Prior to each run a blank of pure methanol was tested. Between sample runs the cuvette was thoroughly rinsed twice with pure methanol and allowed to dry completely.

In the case of some fabrics, the uptake of methanol varied with fabric structure. Therefore, small errors could arise in the exchange of methanol throughout these fabrics to saturate the fabric and remove all MeS.

3.3.3 Verification of Methyl Salicylate Chamber Concentration

To verify the accuracy of the MeS concentration, the chamber outlet was connected to an FTIR spectrometer. Vapor samples were drawn out of the chamber, from the same location as the sample tray during fabric analysis, via a vacuum pump at 0.5 Lpm. To prevent contamination of the vacuum pump, an activated carbon filter was placed in line following the FTIR instrument and before the vacuum pump and flow meter. MeS concentration, measured by FTIR, consistently remained between 4-5 ppm. Using this target of 4-5 ppm, fabric exposure time was increased to 90 min as compared to that of the normal MIST exposure of 30 minutes. Natick PADs were then placed inside the chamber during sampling to verify the consistency of the MeS concentration in the chamber.

Natick PADs, possessing a known uptake rate, were placed in the chamber to verify the MeS concentration in the chamber. The PADs were placed on the chamber walls as well as on the sample tray where the fabrics were evaluated. The target for 90-minute exposure with a concentration of 4-5 ppm is 0.3 mg. Natick PADs should not be affected by concentration, airflow, or humidity; and are therefore, a good indicator of MeS concentration at various positions in the chamber.

Table 7: Methyl Salicylate recovery (mg) from Natick PADs after exposure for 90 minutes inside the chamber at 4-5 ppm of Methyl Salicylate.

Natick PADs Location in Chamber	mg	Standard Deviation
Sample Tray (Chamber On)	0.060	0.008
Sample Tray (Chamber Off)	0.038	0.000
Chamber Wall (Chamber On)	0.042	0.008

Data in Table 7 imply that airflow differences, seen with the chamber on and off, influence the adsorption of MeS into the PAD. It was also noticed that a decrease in adsorption was found when the PADs were placed on the chamber walls.

When the chamber is on, airflow on the tray can be a mix of normal and horizontal flow onto the PAD. This normal flow can possibly force air into the PAD resulting in the high adsorption of 0.06 mg per PAD. Whereas, on the chamber wall the air flow is strictly horizontal to the PAD.

With the chamber off, the airflow is strictly that of diffusion. Natick PAD results from the chamber wall and sample tray with the chamber off, 0.04 each, were close to the theoretical calculated adsorption of 0.03 mg per PAD.

It should be noted that adsorption and distribution of the Tenax adsorbent within the PAD, has not been commented on in literature. PADs placed on the wall result in shifting the Tenax towards the bottom half of the PAD. When PADs were placed on the tray, the Tenax was shifted for equal distribution underneath the polyethylene layer. However, this shift is small, and in the case of PADs on human subjects the Tenax will be constantly shifting, equilibrating any dead volume spaces within the PAD.

3.3.4 Fabric Moisture Preconditioning Procedure

Preconditioned fabrics were prepared by placing the ambiently conditioned fabric between 2 pieces of blotter paper. Blotter paper was immersed in de-ionized water and passed through an Atlas Wringer under 30 pounds of force to squeeze out excess water. Fabric-blotter paper combination was placed inside zip locked plastic bags and allowed to condition for 24 hours. Four fabric samples were placed between each pair of blotter paper. This allowed the direct removal of all fabric samples in the zip lock bag to be placed into the testing chamber at the same time.

3.3.5 Target Skin Adsorption Mass Calculations

The target fabric mass adsorption of 0.6 mg is based on the following calculations for a Natick PAD, where m, is the mass adsorbed, μ the flux into the PAD, and Ct the chamber dosage:

$$\mu = \frac{m}{Ct},$$

Where: $\mu = 10 \frac{cm^3}{\min}$

m= mass in mg

Ct= Chamber Vapor Dosage $\frac{mg \cdot \min}{cm^3}$

The chamber dosage is 16 ppm methyl salicylate hence:

$$16\text{ppm} = \frac{100mg}{m^3}$$

Therefore:

$$\frac{100mg}{m^3} \bullet \frac{m^3}{1000000cm^3} = 0.0001 \frac{mg}{cm^3}$$

Therefore chamber dosage concentration on the Natick Pad after 30 minutes of exposure to the chamber dosage of Methyl salicylate is:

$$\frac{0.0001mg}{cm^3} \bullet 30\min = \frac{0.003mg \cdot \min}{cm^3}$$

Rearranging equation 1 yields the mass in mg of Methyl Salicylate absorbed:

$$m = u \cdot Ct,$$

Therefore:

$$\text{m} = \frac{10cm^3}{\min} \bullet 0.003 \frac{mg \cdot \min}{cm^3} = 0.03mg$$

The target mass adsorbed on a Natick PAD is 0.03 mg or 30,000 ng. The adsorption area of the PAD is 4.6 cm^2. The area of the fabric samples is 100 cm^2. Therefore, the target mass is scaled up by a factor of 20, as 0.03 mg. Whereas the mass/area remains unchanged, $\frac{0.006mg}{cm^2}$, as follows:

$$\frac{0.03mg}{4.6cm} = \frac{0.006mg}{cm^2} \text{ or,}$$

$$0.03mg \bullet 20 = 0.6mg \text{ , and } \frac{0.6mg}{100cm^2} = \frac{0.006mg}{cm^2}$$

3.3.6 MeS Solubility

Methyl salicylate is slightly soluble in water at 0.66 mg/g water [31]. Therefore, the solubility of MeS into water inside the chamber was tested. A calibration curve was prepared in the same fashion as the MeS/methanol calibration curve. The curve is given below in Figure 17 and the R-squared value, 0.99985, is shown in Table 8. A petri dish, having a diameter of 3.5 in (248 cm2), was placed inside the chamber for 90 minutes. The water was removed and analyzed in UV-Vis. MeS concentration in the water was 20 mg/L. Therefore, MeS concentration in 1 gram of water is 0.02 mg MeS/g water. This indicates that increased MeS adsorption on preconditioned fabric is not the result of MeS solubility in the moisture that was gained on the fabric.

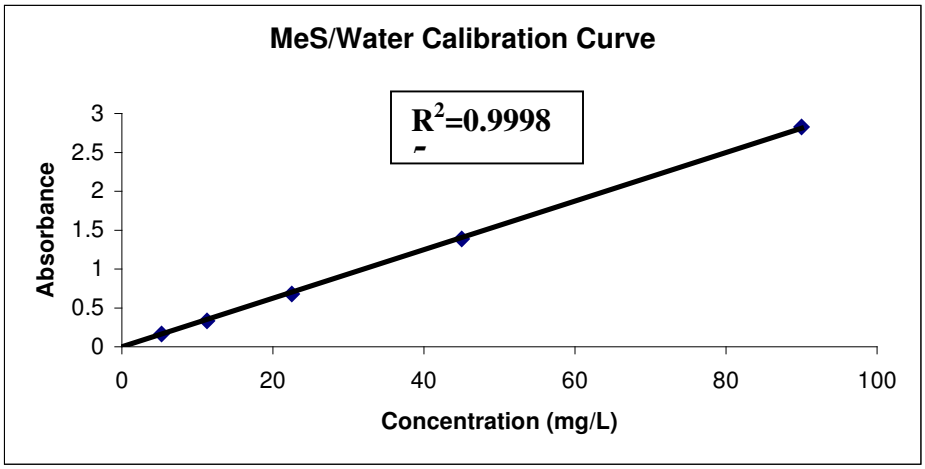


Figure 17: Calibration Curve with a Linear Direct Fit of MeS in water.

Table 8: Calibration Standards used for the UV analysis calibration curve

	Concentration mg/L	Abs.
Std. 1	5.265	0.1647
Std. 2	11.25	0.3335
Std. 3	22.5	0.6775
Std. 4	45.	1.3855
Std. 5	90.	2.8288

Chapter 4: Results and Discussion

The following analysis will discuss the effects of fiber type, construction, and fabric basis weight on MeS adsorption. Fabric samples were tested following conditioning in an ambient environment and preconditioned using the described moisture preconditioning procedure. Table 9 shows the dimensional properties of the knit fabrics that are of concern during the following analysis. The data used in the plots below represent averages of triplicate measurements on each test sample. Sample averages are provided in Appendix B. Standard deviations of each experimental run (in triplicate) are shown in Appendix B.

Table 9: Knit test fabrics.

Fiber	Regain % [53]	Knit Construction	Basis Weight (g/m2)	Thickness (mm)
(A) Nylon	4	Tricot	73	0.28
(B) Nylon	4	Double knit	260	0.94
(C) Silk	10	Crepe deChine	72	0.18
(D) Wool	14	Jersey	205	0.92
(E)Cotton	7-8	Interlock	187	1.11
(F) Cotton	7-8	Jersey	124	0.67

The following analysis focuses on fabrics tested in the chamber. Chamber and tube comparisons are described in Appendix C.

Figures 18-23 relate fabric basis weight (g/m^2), fabric fiber type, water gained (g), and MeS(mg) adsorption on fabric samples.

Figure 18 shows a large increase in MeS adsorption on preconditioned fabrics (triangle) when compared to ambient fabrics (box). Fabrics of silk and wool (C and D respectively) displayed the largest increase of MeS adsorption when preconditioned. Figure 18 shows ambient conditioned fabrics did not reach the target level for MeS adsorption of 0.6 $mg/100\ cm^2$. However, moisture preconditioned silk, wool, and nylon double knit all surpassed the target adsorption in the Tenax Pad for MeS. MeS adsorption increases as fabric basis weight increases for fabrics of similar fiber content. This trend is observed for both ambient and preconditioned test fabrics.

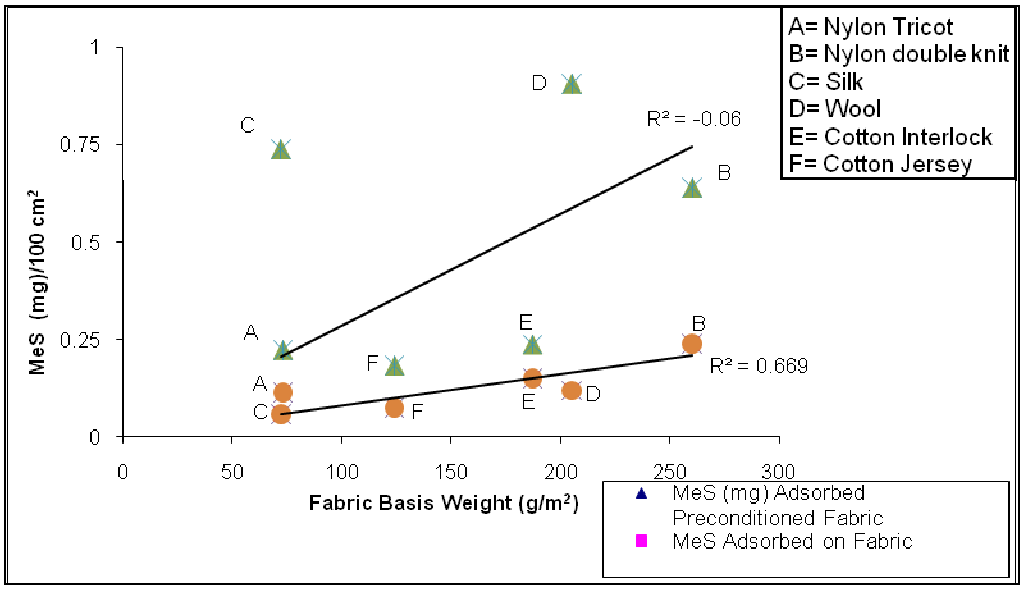


Figure 18: MeS adsorbed on ambient (box) and preconditioned fabric (triangle) swatches.

Figure 19 shows the adsorption of MeS normalized per fabric mass. It can be seen that, for a weight normalized mass, nylon fabrics (A, B) adsorb similar amounts of MeS. MeS adsorption on cotton materials are also similar (E, F). The silk test fabric (C) adsorbed more MeS per fabric mass than the wool material.

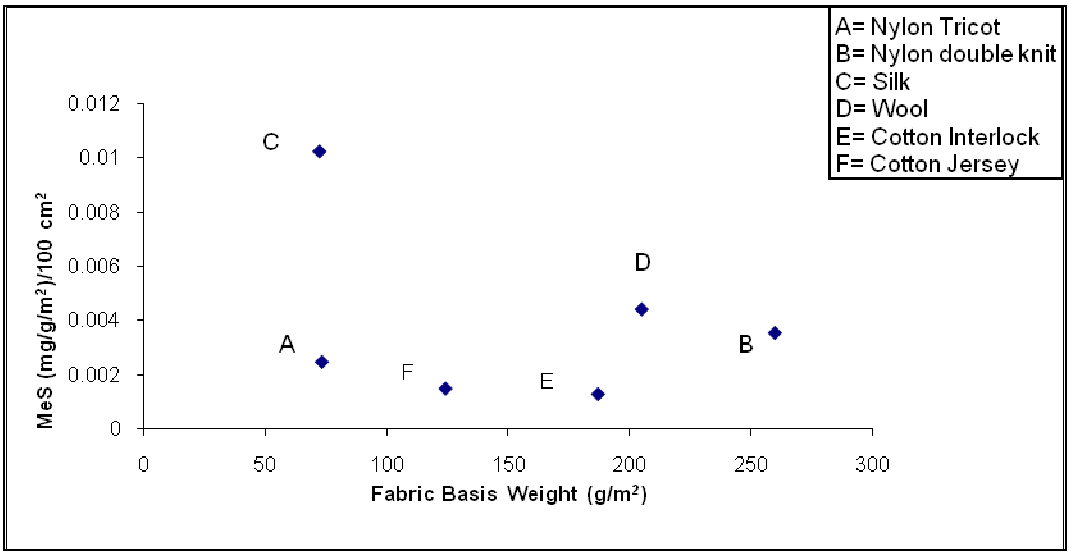


Figure 19: MeS adsorbed per fabric mass on moisture preconditioned test fabrics.

Figure 20 shows the relationship observed between fabric thickness and MeS adsorption. For cotton and nylon fabrics, an increase in fabric thickness results in an increase in MeS adosorbed. The same trend in noticed for silk and wool, although the increase is slight. Nylon displays the largest MeS adsorption difference with a change in fabric thickness. These results are similar to the results of MeS adsorbed compared with fabric basis weight in Figure 18.

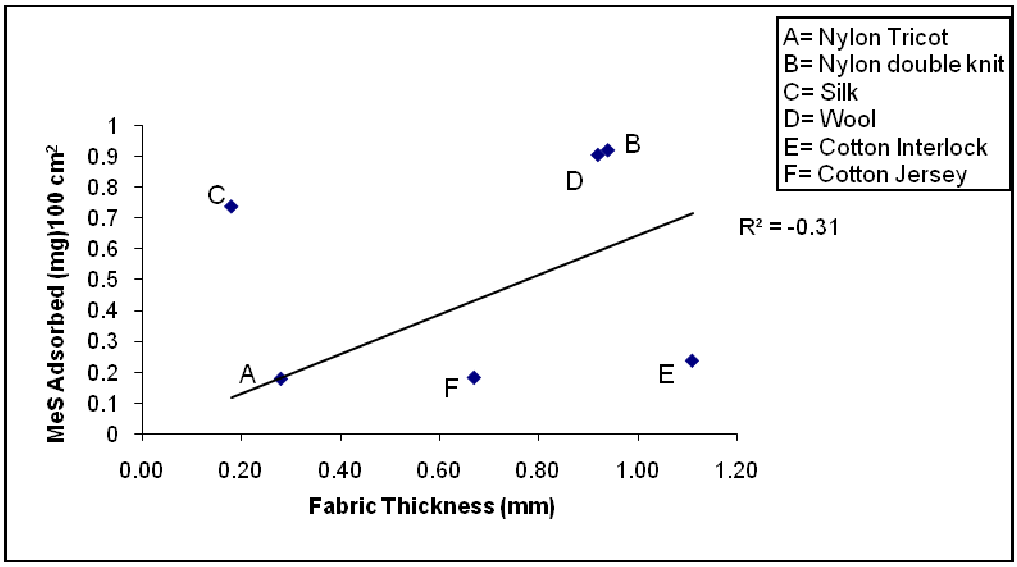


Figure 20: Fabric thickness and MeS adsorbed on preconditioned fabric.

Since moisture preconditioning was observed to have a dramatic effect on MeS adsorption, additional analysis was conducted to show the relationship between the amount of MeS adsorbed by preconditioned fabrics.

Figure 21 shows the relationship between fabric basis weight and moisture gained as a result of the preconditioning procedure. This data shows that moisture gained increases with fabric basis weight for knit materials of similar fiber content. These data indicate that moisture uptake is influenced by thickness and by fabric basis weight.

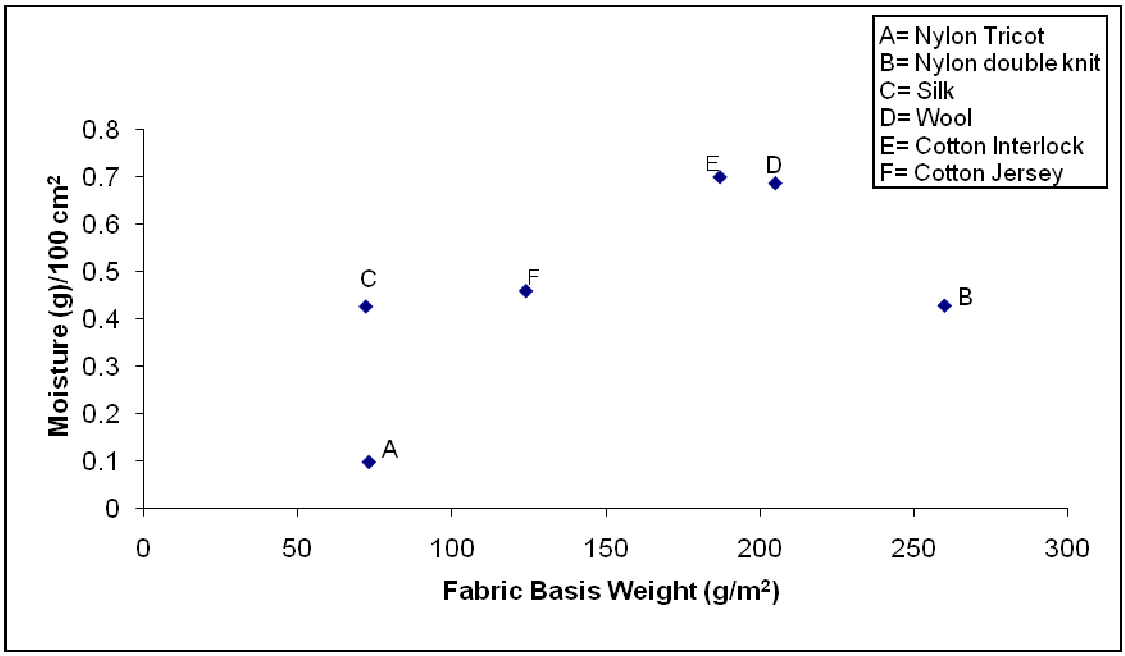


Figure 21: Fabric basis weight and moisture gained during preconditioning.

Figure 22 shows fabric basis weight and MeS adsorbed per water gained (mg/g) on each fabric swatch. These data show that as fabric basis weight decreases, the amount of MeS adsorbed increases. In comparison to wool (D), silk (C) and nylon (A) adsorbed a high amount of MeS per fabric weight.

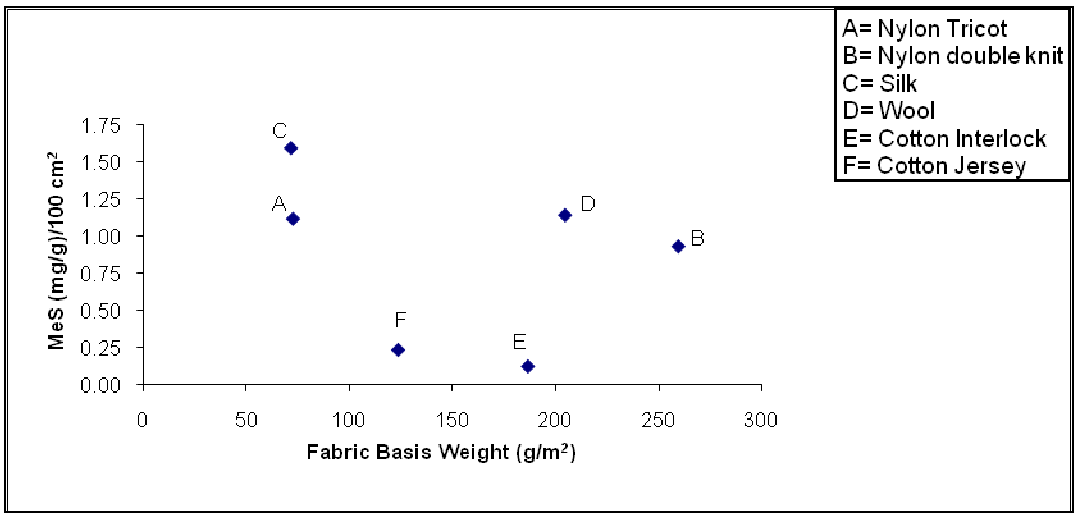


Figure 22: Fabric basis weight and MeS adsorbed per water gained (mg/g).

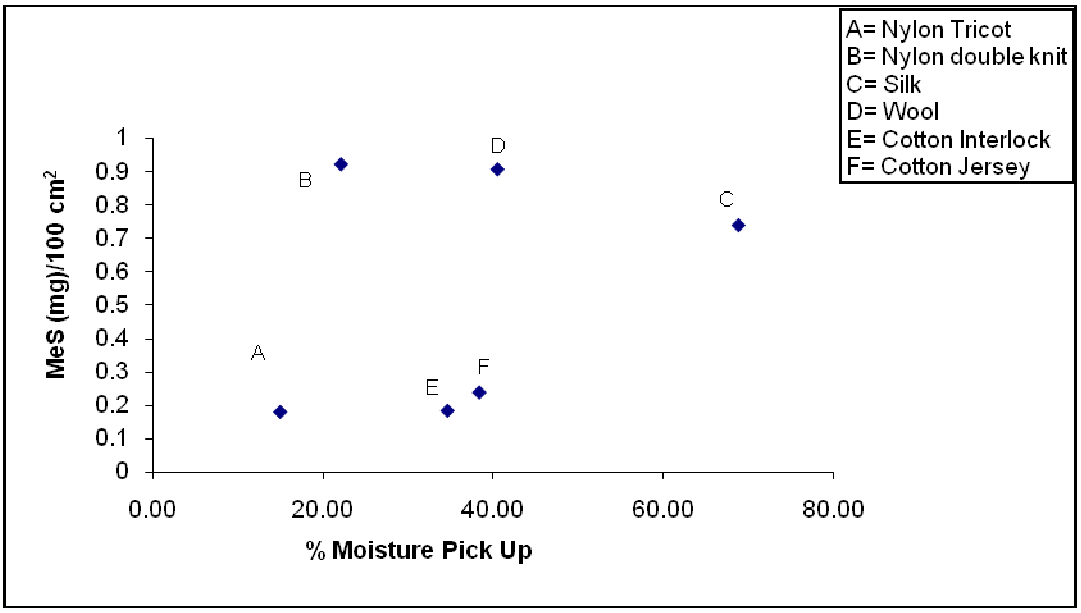


Figure 23: Percent moisture gained on fabric and MeS adsorbed.

Figure 23 shows the relationship between moisture gained and MeS adsorbed on each test fabric. The silk fabric (C) is the only fabric that adsorbed a moisture level close to saturation. Due to its greater thickness and weight, the double knit nylon sample (B), adsorbed significantly more MeS than the thinner knit construction nylon tricot (A).

Figure 22 shows that nylon tricot adsorbed a large amount of MeS per amount of water gained. These results indicate that MeS adsorbed is influenced by interacting factors. The amount of water gained is influenced by the fiber type and fabric basis weight (knit construction) and the amount of MeS adsorbed is then influenced by not only fiber type and fabric basis weight (knit construction), but also by the amount of moisture gained.

The quantity of water adsorbed on fabric is influenced by many factors. Fabric basis weight and fiber type have been shown to influence water uptake, and water uptake has been shown to influence MeS adsorbed.

Fiber structures in Figure 9 highlight the differences in the hydrophilic properties. Water adsorbed can cause fiber swelling. This swelling can increase surface of fibers providing a larger surface for MeS to adsorb.

Fabric thickness contributes to the amount of water adsorbed. The adsorption of MeS (mg/g) of water (g) of nylon tricot and silk supports these conclusions. Therefore, fabric thickness increases the amount of MeS adsorbed. Fiber type affects the amount of both bound and unbound water on the fabrics, and, as a consequence, the amount of MeS adsorbed.

These data further suggest that MeS adsorption is related to the type of knit construction and to the fineness of the yarns and fibers used in the knit fabric. This is consistant with the observation that the thin, finer, gauge nylon tricot (C) adsorbed more MeS than a heavier double knit nylon fabric. It may explain why silk fabrics adsorbed more MeS than the coarser wool knit. Yarn construction may effect the amount of MeS adsorbed. These effects are undoubtedly related to the available surface area for MeS adsorption.

Fibers with a high surface area to volume ratio can have an increased surface area when the fibers swell as a result of moisture gained. This effect can contribute to the increased MeS adsorption of preconditioned fabrics.

Fine fibers such as silk, when compared to a coarser fiber such as cotton, or wool may provide an adsorption surface that smoother and promote adsorption.

Unbound water appears to have a significant effect on MeS adsorption on some fabrics. Of the test fabrics evaluated, preconditioned and ambient conditioned, none adsorbed the target MeS mass pf the standardized PAD. However, wool, silk and nylon double knit each surpassed the skin target of 0.6 mg (0.86, 0.75, 0.66 mg respectively). Therefore, if used on a sweating mannequin, wool, silk, or nylon double knit may be a suitable candidate material as skin simulants.

Chapter 5: Conclusions

This research evaluated MeS adsorption on preconditioned and ambiently conditioned knit fabrics for ultimate use as a human-like skin simulant to cover the surface of a mannequin for use in a MIST procedure. This study produced significant insights that contribute to that goal. It showed that moisture preconditioning increased MeS adsorption in knit fabric structure.

It demonstrated that preconditioned nylon double knit adsorbed close to the level of the target of 0.6 mg of a standardized PAD used in the MIST protocol.

This research has shown that MeS adsorption on fabric is influenced by fabric weight and by the fiber used in the knit construction. These factors influence the amount of moisture absorbed during preconditioning. The mechanism by which moisture effects MeS adsorption

depends on the amount of bound and unbound water on the fabrics. Data show the influence between fabrics of similar fiber types is dependent on basis weight, or knit type.

This research has developed and demonstrated a small scale test apparatus for measuring MeS adsorption in swatch size materials. This study showed successful use of this apparatus to gain insights on the effects on MeS adsorption in knit fabrics.

Chapter 6: Recommendations

It is recommended to continue experimentation at different water saturation levels on nylon double knit, wool, and silk fabric. This will provide information for the effects of MeS adsorption on fabrics at different levels of moisture saturation.

A design of experiments is also recommended to systematically study the influence of the following factors on MeS adsorption in a group of knit fabrics with similar differences in factors including yarn size and knit fabric construction.

REFERENCES

1. Oudmaijer, H., Van Eenennaam, Richard, *Whole system testing of NBC protectiveclothing; Effect of leakage and comparison of different types of suits* TNO Defence, Security and Safety, Biological and Chemical Protection.

2. Shirado, H., *Realization of human skin-like texture by emulating surface shape pattern and elastic structure.* Symposium on haptic interfaces for virtual environment and teleoperator systems, march 25-26, IEEE, 2006.

3. Charkoudian, J.C., *Model human skin; United States Patent 4877454.* http://www.freepatentsonline.com/4877454.html 1989.

4. Corporation, M., *Epiderm technical specifications.* http://www.mattek.com/pages/products/epiderm/specification, Accessed 1/28/08.

5. Sensatex, http://www.sensatex.com/smartshirt.html, Accessed 1/28/08.

6. 1670-03, A.F., *Standard test method for resistance of materials used in protective clothing to penetration by synthetic blood*. 2003, American Society for Testing and Materials International

7. *Human skin model.* http://images.google.com/imgres?imgurl=http://www.mydr.com.au/content/images/categories/skinhair/skinstructure.gif&imgrefurl=http://sdlrc.mui.ac.ir/cms/en/index.php/module/HTML_Pages/action/ShowHTML_Pages/id/34&h=350&w=300&sz=26&tbnid=r1JScf8XEFsTbM:&tbnh=120&tbnw=103&prev=/images%3Fq%3Depidermis%26um%3D1&start=2&sa=X&oi=images&ct=image&cd=2. **Last Accessed 1/20/08**.

8. Muhammad, F., *Topical adsorption and toxicity studies of jet fuel hydrocarbons in skin* in *Graduate faculty of north carolina state university*. 2004, etd-08052004-124403, North Carolina State University.

9. Mangusson, B.M., et al., *Molecular size as the main determinant of solute maximum flux across the skin* The society for investigative dermatology, Inc, 2004. **122**: p. 993-999.

10. S, R., *Pharmacokinetic factors affecting epidermal penetration and percutaneous absorption.* Clin pharmacol ther, 1974. **16**: p. 873-883.

11. Wenger CB, R.M., *Forearm blood flow during body temperature transients produced by leg exercise.* J. Appl. Physiol, 1975. **38**: p. 58-63.

12. R., G., *Body heat balance in man subjected to endogenous and exogenous heat load.* Eur J. Appl Physiol, 1983. **51**: p. 419-433.
13. Wurster DE, K.S., *Investigation of some factors influencing percutaneous absorption.* J Pharm Sci, 1961. **50**: p. 288-293.

14. Scheuplein RJ, R.L., *Mechanism of percutaneous absorption.* J Invest Derm, 1974. **63**: p. 61-71.

15. *The Biology of the Skin*, ed. R.K. Freinkel MD, Woodley MD, David T. 2001, New York: Parthenon Publishing.

16. AM, K., *A biological brief on percutaneous absorption.* Drug dev Industr Pharm 9, 1983: p. 521-560.

17. Flynn, e.a., 1984.

18. Golden, e.a., 1987.

19. Danon A, B.-S.S., Ben-Zvi, Z, *Effect of exercise and heat exposure on percutaneous absorption of methyl salicylate.* Eur J. Clin pharmacol, 1986. **31**: p. 49-52.

20. Guy RH, M.H., *Drug delivery to local subcutaneous structures following topical sdministration.* . J. Pharm Sci, 1983. **72**: p. 1375-1380.

21. Houwelingen, T.V., Dickson, Eva Gudgiin, Tremblay-Lutter, Julie, *Human-mannequin comparisons in testing NBC protective clothing.* 2004.

22. F2588-06, A., *Standard test method for Man-in-simulant (MIST) for protective ensembles*. 2006, American Society for Testing and Materials International.

23. State, N.

24. Paul, H., L. Trevino, G. Gue, J. Rugh, R. Farrinigton, and C. King, *Phase II Testing of Liquid cooling Garments Usiing a Sweating Manikin, Controlled by Human Physiological Model.* Doc 2006-01-2239. SAE International, 2006.

25. Farrington, R., J. Rugh, D. Bharathan, H. Paul, G. Bue, and L. Trevino, *Using a Sweating Manikin, Controlled by Human Physiological Model, to Evaluate Liquid Cooling Garments.* Doc. 2005-01-2971. SAE International, 2005.

26. Richards, M.G.M.a.N.G.M., *Development of a sweating agile thermal manikin (SAM). Proceedings of the fourth international meeting of thermal manikins.* EMPA Switzerland, 27-28 Sept. 2001, 2001.

27. Holmer, I., *Thermal manikin history and applications.* European journal of applied physiology, 2004. **92**(6): p. 614-618.

28. Holmer, I.A.H., *Heated manikins as a tool for evaluating clothing.* Ann. Occup. Hyg, 1995. **39**(6): p. 809-818.

29. Endrusik, T.L., L. A. Stroschein, and R. R. Gonzalez, *Thermal manikin history: United States Military use of thermal manikins in protective clothing research. Measurement technology northwest.*

30. Service, R.F., *News focus technology: electronic textiles charge ahead.* Science, 2003. **301**(5635): p. 909-911.

31. J. O'Neil Maryadele, e.a., *Merck Index 13th Edition*, e.a. J. O'Neil Maryadele, Editor. 2001, Merck Co., Inc.

32. Riviere, J.E., et al., *The isolated perfused porcine skin flap as an in vitro model for percutaneous adsorption and cutaneous toxicology.* Critical Reviews in Toxicology, 1991. **21**(5): p. 329-344.

33. Duncan, E.J.S.e.a., *Site Specific percutaneous absorption of methyl salicylate and VX in domestic swine.* Journal of Applied Toxicology, 2002. **22**: p. 141-148.

34. Riviere, J.E., *Use of methly salicylate as a simulant to predict the percutaneous absorption of sulfur mustard.* Journal of Applied Toxicology, 2001. **21**: p. 91-99.

35. Seitzinger, A.T., et. al., *Use of methyl salicylate as a trialing chemical agent simulant*, C.r.d.a.e.c.a.p.g. MD, Editor. 1990.

36. Ground, D.P., *Agent/Simulant relationship study*. 1994, Dugway Proving Ground, Dugway, Utah.

37. Hughes, R.C., *Chemical sensing with an Integrated Preconcentrator/Chemiresistor Array.* Chemical and Biological Sensors and Analytical Methods II, 2001: p. 328-354.

38. Standing committee on program and technical review of the U.S. army chemical and biological defense command, n.r.c., *Technical assessment of the man in simulant test (MIST) program*. 1997. 86.

39. Brown, R.H., Environmental monitoring, 2000(2): p. 1-9.

40. Martin, A.N., et al., *Measurements of envirnmental 1,3-butadiene with pumped and diffusive samplers using the sorbent carbopack X.* Atmospheric environment, 2005(39): p. 1069-1077.

41. MacGregor, I.C., et al., *Determination of the Diffusive Uptake Rate of Methyl Salicylate (MeS) and Evaluation of the Performance of Three Types of Passive Adsorbent Devices*. 2005, Battelle Memorial Institute.

42. Shishoo, R.L., *Recent Developements in Breathable High Functional Fabrics.* Nonwovens World, 1987. **2**(1): p. 89-94.

43. Mecheels, J.H.e.a., *Moisture Transfer Through Chemically Treated Cotton Fabrics.* Textile h481 Research Journal, 1966. **34**(4): p. 375-384.

44. T., A.A., *Diffusion of Sorbed Water through Paper and Cellulose Film.* Tappi, 1970. **53**(7): p. 1320-1326.

45. Behmeann, F.W., et al., *Movement of Water in Wool: Experimental Determination of the Coefficients of Vapurous and Non-Vapourous Moisture-Conduction.* Journal of Textile Institute, 1964. **55**(3): p. t205-t213.

46. Caldwell, J.R., et al., *Vapor Permeable Water Resistant Fabrics.* American Dyestuff Reporter, 1967. **56**(3): p. 71-81.

47. Brunauer, S., *The adsorption of gases and vapors*. 1943.

48. Lowell., S., Sheilds, Joan E., et al., *Characterization of Purous Solids and Powders: Surface Area, Pore Size, and Density*. 2004: KLewer Academic Publishers.

49. Kimmitt, D., *Vapor transport in polymeric membranes.* Dissertatin presented to the graduate school of Clemson University, 1982.

50. wikipedia. [cited; Available from: http://en.wikipedia.org/wiki/Adsorption#BET.

51. Brasser, P., Houwelingen, TIny Van, *A theoretical and experiemental study of vapor deposition onto the Surface of a Dressed Boby Part.* AICHE J., . **submitted for publication**.

52. Corp, T.E., *Temperature and humidity chamber platinous g serious instruction manual tenth edition*. 1989.

53. Morton, W.E., Hearle, J. W. S, *Physical Properties of Textile Fibres*. 1975: Textile Institute and Butterworth & Co. LTd.

Appendices

Appendix A: Methodology and Detail of Chamber Modifications

Swatch testing took take place inside an Esquec Platinous 2G serious temperature and humidity controlled environmental chamber which was modified as follows.

Construction

Eighteen holes (1/4") were drilled approximately 3/16" from the outer edge of the Lexan sheet (GE). Each location coincides with the holes of the packing plate used for the inner packing on the chamber door.

Prior to affixing the new door to the chamber, a ¼" silicone gasket was glued in place to provide a strong seal between the Lexan sheet and the chamber.

Air-Lock Sample Box

Two necessary requirements of the door were addressed. Access from the sample box to the chamber without allowing methyl salicylate to escape (1); and a method to manipulate the samples while inside the chamber (2). These were resolved by the addition of a sample box and glove ports.

An acrylic standard air lock 11.5"W x 10"D x 10"L (Terra Universal) was used to reduce the amount of MeS released to the surrounding environment when samples were introduced into the chamber. Access to the air lock is via an easy swing down side door with a flip latch. For safety, and to reduce contamination, the sample box was modified to allow access to a purge stream. The air lock was made with a single 5/16" hole with a male 1/8" NPT threading. Another hole was drilled manually. On the opposite side of the manufactured hole, a pressure release valve was present. Using a 5/16" drill bit and a no: 27 tap, a 1/8" NPT, threading and hole were drilled in the place of the pressure release valve.

This provided an outlet for purge air.

To access this sample air lock from the inside of the chamber, a hole had to be cut into the Lexan sheet. A square with dimensions of 7" by 7" was removed from the Lexan sheet, in the desired placement of the air lock, and 6 holes were drilled through the Lexan sheet mirroring bolt locations on the air lock. Next, an airtight door was designed to prevent methyl salicylate inside the chamber from contaminating the contents inside the air lock.
On the chamber side of the Lexan sheet, Lexan strips of 1 ¼" wide and 11 ½" long and 8 ½" long, with a thickness of ¼", were solvent bonded with methylene chloride in a square arrangement around the cut square. This frame structure provides a snug fit for the door. The door was constructed using 3/8" Lexan measuring 9x8 ½".

Using a 3/16" drill bit, a uniform square groove on the door measuring 7 ½ x 7 ½" was removed. A cylindrical silicone gasket was inserted into the groove. The door was attached using a piano hinge 7 3/8" long using 4 5/32" machine screws. Holes for the screws were drilled using a 5/32" drill bit and threads were placed using a 10-32 no. 21 tap.

Glove Ports

Moving the samples from the air lock into the chamber, for methyl salicylate exposure, and back out of the chamber, for analysis, is accomplished manually through two 6" 16 gauge 316 stainless steel glove ports (Renco Corporation). Stainless steel was purchased because of the durability and the secure fit that could be made with the gaskets. For each port, a 6" hole was spaced equally from the side and cut into the Lexan sheet. Each glove port was attached using 10 screws with cap nuts with rubber gaskets on each side of the Lexan sheet to seal the port. Neoprene gloves (Renco Corporation), chosen for their chemical resistance, were

attached to the ports.

Methyl Salicylate

Methyl salicylate is introduced into the chamber via the uppermost tube fitting shown in Figure 30. Tube fittings shown in the picture were fitted in the chamber caps. Holes were drilled for ¼" diameter tubing. Swagelok fittings were used to tighten the 316 stainless steel tubing into the hole. Two rubber gaskets were used on both sides of the fitting to prevent leakage. Silicone sealant was applied around the fitting on both the inside and outside of the cap. The cap itself is sealed on the chamber by a ½ turn groove and GoreTex^{tm} PTFE sealant. Figure 24 shows the location within the chamber of the methyl salicylate inlet and outlet streams.

During operation, the gas generator oven is conditioned to 110^{o}C. After equilibrium is reached the gas generator is switched from "mode" setting to the "span" setting, causing the dilution stream and the chamber output stream to mix and be sent out of the gas generator via the stream outlet. Stream outlet is plumbed to the methyl salicylate chamber inlet.

Figure 24: Chamber inlet for methyl salicylate (top fitting) and chamber outlet for methyl salicylate (bottom fitting).

Appendix B: Data Tables
*Data discussed in chapter 4.

***Table 10: Methyl salicylate (mg) recovered from ambient fabric swatches during the tube and chamber experiments and chamber experiments with preconditioned fabrics.**

Fabric (100cm^2)	Tube Analysis with Fabric (Ambient)	Fabric (Ambient) Chamber On	Fabric Preconditioned Chamber Off	Fabric* Preconditioned Chamber On
Nylon Tricot	unavailable	0.12	0.21	0.22
Nylon double knit	0.10	0.24	0.54	0.64
Polyester Interlock	0.06	0.08	0.07	0.07
Polyester 56T	0.06	0.12	0.11	0.12
Silk	0.08	0.06	0.62	0.74
Wool	0.14	0.12	0.86	0.90
Cotton Jersey	0.12	0.08	0.16	0.18
Cotton Interlock	0.10	0.15	0.25	0.24

Table 11: Standard deviation of triplicate measurements for mass recovered on fabric swatches during the tube and chamber experiments and chamber experiments with preconditioned fabrics.

Experiment	Ambient Fabric Tube*	Ambient Fabric Chamber On	Preconditioned Fabric: Chamber Off	Preconditioned Fabric: Chamber On
Cotton Interlock	0.49	1.60	1.52	0.47
Cotton Jersey	*3.10	0.80	0.29	0.22
Wool	1.20	1.05	1.36	5.12
Silk	0.16	1.38	3.89	2.18
Dacron Interlock	0.18	0.27	0.05	0.46
Dacron 56T	1.36	2.35	0.25	0.87
Nylon double knit	1.46	0.69	0.64	0.87
Nylon Tricot	x	0.21	0.23	0.08

***Table 12: Fabric basis weight, water gained, and MeS adsorbed on preconditioned fabric during the chamber analysis.**

Fabric ($100cm^2$)	Water Gained (g)	MeS gained per water gained (mg/g)	Fabric Basis Weight (g/m^2)	(g-water/g fabric) %
Nylon Tricot	0.10	1.12	73	14.86
Nylon double knit	0.43	0.93	260	22.01
Polyester Interlock	0.18	0.00	106	17.53
Polyester 56T	0.28	0.01	206	14.53
Silk	0.43	1.59	72	68.71
Wool	0.69	1.14	205	40.39
Cotton Jersey	0.46	0.24	124	34.51
Cotton Interlock	0.70	0.13	187	38.25

*Table 13: Fabric thickness for cotton, polyester, nylon, silk and wool fabrics.

Sample ID	millimeter* 1	2	3	Avg.
Cotton Interlock	1.11	1.14	1.07	1.11
Polyester Interlock	0.63	0.63	0.64	0.63
Polyester 56 T	0.89	0.86	0.86	0.87
Nylon double knit	0.97	0.92	0.93	0.94
Wool	0.93	0.94	0.9	0.92
Silk	0.18	0.18	0.19	0.18
Cotton Jersey	0.69	0.68	0.65	0.67
Nylon Tricot	0.27	0.29	0.28	0.28

A second trial was performed with preconditioned fabric to determine the reproducibility of the initial results. Table 10 shows the MeS adsorption of a second run using wool, silk, and nylon double knit. MeS adsorbed on each fabric for both runs is consistent.

Table 14: Displays MeS adsorption of each experimental run on preconditioned fabrics of nylon double knit, wool, and silk in the chamber.

	Run 1	Run 2
Fabric	MeS (mg) Adsorbed on Preconditioned Fabric	MeS (mg) Adsorbed on Preconditioned Fabric
Wool	0.905	0.861
Silk	0.738	0.753
Nylon double knit	0.639	0.660

Appendix C: Statistics and Raw Data:

Figure 26 shows MeS adsorbed on preconditioned fabric and fabric conditioned at ambient temperature tested in the chamber and fabric conditioned at ambient temperature tested in the tube design. Figure 25 shows that for most fabrics, MeS adsorption increased on preconditioned fabric. Wool, silk, and nylon double knit showed a large increase of MeS adsorption on preconditioned fabric. Figure 25 also shows that fabrics of wool, silk, and nylon double knit were the only fabrics to adsorb close to the MeS target mass of 0.6 mg of MeS.

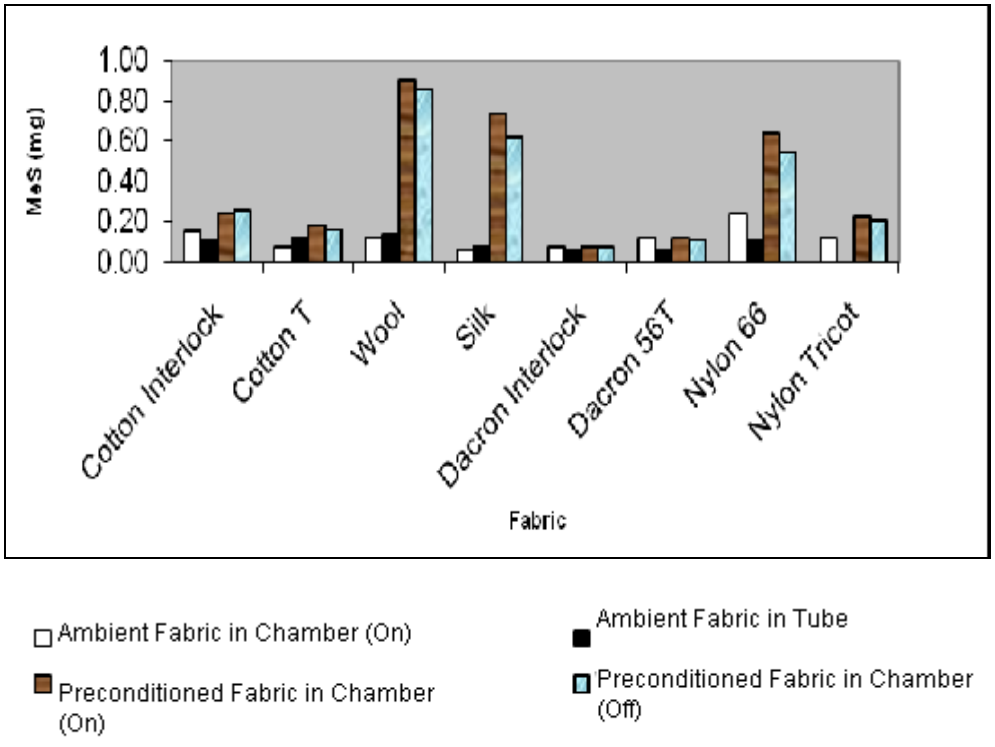


Figure 25: MeS adsorption on preconditioned and ambiently conditioned fabric for each apparatus

Data were analyzed statistically using a two-factor crossed, completely randomized design given below:

$$Yijk = \mu + \alpha i + \beta j + (\alpha\beta)ij$$

Where, μ = mean
αi = fabric i
βj = apparatus type j
$(\alpha\beta)ij$ = fabric and apparatus interaction ij

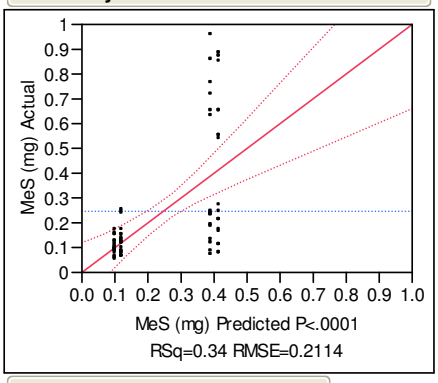
This analysis incorporates each sample and is more reliable than a simple comparison of the means of MeS adsorbed. JMP (SAS version 7) analysis shows that there is not a significant difference of MeS adsorption on preconditioned fabric regardless of the chamber option of "On" or "Off". This is shown in Figure 26. It can be seen in the Tukey Analysis there is not a significant difference of MeS adsorption on ambient fabric tested in the tube design and chamber design. However the analysis displays a significant difference of MeS adsorption on preconditioned fabric tested in the chamber when compared to ambient fabrics tested in both the tube and chamber designs. Therefore, the flow regimes used and the concentration and exposure times of the chamber and tube apparatus produced similar results. This shows that for each design, the airflow in the chamber and in the tube do not significantly influence the adsorption of MeS on the fabrics tested. The presence of water on the fabric is seen to significantly influence MeS adsorption. Statistical analysis of fabrics was not included due to the small sample size.

JMP Analysis

Response MeS (mg)

Whole Model

Actual by Predicted Plot



Summary of Fit

RSquare	0.339888
RSquare Adj	0.31482
Root Mean Square Error	0.211423
Mean of Response	0.244952
Observations (or Sum Wgts)	83

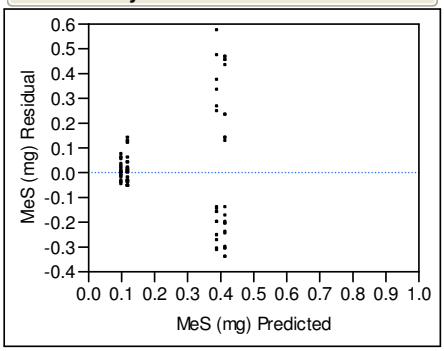
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	1.8182251	0.606075	13.5589
Error	79	3.5312627	0.044700	Prob > F
C. Total	82	5.3494878		<.0001*

Effect Tests

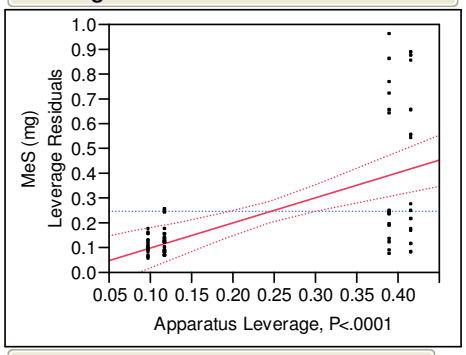
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Apparatus	3	3	1.8182251	13.5589	<.0001*

Residual by Predicted Plot



Apparatus

Leverage Plot



Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
Dry On	0.11875000	0.04315646	0.118750
Dry Tube	0.09861905	0.04613620	0.098619
Wet Off	0.41668182	0.04507546	0.416682
Wet On	0.39018750	0.05285566	0.390188

LSMeans Differences Tukey HSD

α= 0.050 Q= 2.62457

LSMean[j]

LSMean[i] Mean[i]-Mean[j] / Std Err Dif / Lower CL Dif / Upper CL Dif	Dry On	Dry Tube	Wet Off	Wet On
Dry On	0	0.02013	-0.2979	-0.2714
	0	0.06317	0.0624	0.06824
	0	-0.1457	-0.4617	-0.4505
	0	0.18594	-0.1341	-0.0923
Dry Tube	-0.0201	0	-0.3181	-0.2916
	0.06317	0	0.0645	0.07016
	-0.1859	0	-0.4873	-0.4757
	0.14568	0	-0.1488	-0.1074
Wet Off	0.29793	0.31806	0	0.02649
	0.0624	0.0645	0	0.06947
	0.13415	0.14878	0	-0.1558
	0.46172	0.48735	0	0.20881
Wet On	0.27144	0.29157	-0.0265	0
	0.06824	0.07016	0.06947	0
	0.09235	0.10743	-0.2088	0
	0.45053	0.47571	0.15582	0

Level		Least Sq Mean
Wet Off	A	0.41668182
Wet On	A	0.39018750
Dry On	B	0.11875000
Dry Tube	B	0.09861905

Levels not connected by same letter are significantly different.

Figure 26: JMP analysis of the response MeS adsorption to the factor of different apparatus designs.

RAW DATA

6/6 Cols / 64/62 Rows	Fabric	Apparatus	MeS (mg) / 100 cm2	Fabric Basis Weight (g/m2)	MeS Gained per Water Gained (mg/g)	Water Gained (g)
1	Cotton Interlock	Preconditioned On	0.243	187	0.13	0.7
2	Cotton Interlock	Preconditioned On	0.234	187	0.13	0.7
3	Cotton Interlock	Preconditioned Off	0.267	187	0.13	0.7
4	Cotton Interlock	Preconditioned Off	0.237	187	0.13	0.7
5	Cotton Interlock	Ambient On	0.17	187	▪	▪
6	Cotton Interlock	Ambient On	0.131	187	▪	▪
7	Cotton Interlock	Ambient On	0.15	187	▪	▪
8	Cotton Interlock	Ambient Tube	0.094	187	▪	▪
9	Cotton Interlock	Ambient Tube	0.101	187	▪	▪
10	Cotton Interlock	Ambient Tube	0.106	187	▪	▪
11	Nylon Double knit	Preconditioned On	0.63	260	0.93	0.428
12	Nylon Double knit	Preconditioned On	0.647	260	0.93	0.428
13	Nylon Double knit	Preconditioned Off	0.534	260	0.93	0.428
14	Nylon Double knit	Preconditioned Off	0.548	260	0.93	0.428
15	Nylon Double knit	Preconditioned Off	0.844	260	0.93	0.428
16	Nylon Double knit	Ambient On	0.237	260	▪	▪
17	Nylon Double knit	Ambient On	0.233	260	▪	▪
18	Nylon Double knit	Ambient On	0.249	260	▪	▪
19	Nylon Double knit	Ambient Tube	0.121	260	▪	▪
20	Nylon Double knit	Ambient Tube	0.087	260	▪	▪
21	Nylon Double knit	Ambient Tube	0.094	260	▪	▪
22	Wool	Preconditioned On	0.956	205	1.14	0.687
23	Wool	Preconditioned On	0.854	205	1.14	0.687
24	Wool	Preconditioned Off	0.877	205	1.14	0.687
25	Wool	Preconditioned Off	0.865	205	1.14	0.687
26	Wool	Preconditioned Off	0.646	205	1.14	0.687
27	Wool	Ambient On	0.124	205	▪	▪
28	Wool	Ambient On	0.124	205	▪	▪
29	Wool	Ambient On	0.113	205	▪	▪
30	Wool	Ambient Tube	0.144	205	▪	▪
31	Wool	Ambient Tube	0.122	205	▪	▪
32	Wool	Ambient Tube	0.149	205	▪	▪
33	Silk	Preconditioned On	0.759	72	1.59	0.426
34	Silk	Preconditioned On	0.716	72	1.59	0.426
35	Silk	Preconditioned Off	0.865	72	1.59	0.426
36	Silk	Preconditioned Off	0.877	72	1.59	0.426
37	Silk	Preconditioned Off	0.646	72	1.59	0.426
38	Silk	Ambient On	0.061	72	▪	▪
39	Silk	Ambient On	0.06	72	▪	▪
40	Silk	Ambient On	0.059	72	▪	▪

41	Silk	Ambient On	0.058	72	▪	▪
42	Silk	Ambient Tube	0.074	72	▪	▪
43	Silk	Ambient Tube	0.078	72	▪	▪
44	Cotton Jersey	Preconditioned On	0.186	124	0.24	0.459
45	Cotton Jersey	Preconditioned On	0.182	124	0.24	0.459
46	Cotton Jersey	Preconditioned Off	0.168	124	0.24	0.459
47	Cotton Jersey	Preconditioned Off	0.163	124	0.24	0.459
48	Cotton Jersey	Preconditioned Off	0.21	124	0.24	0.459
49	Cotton Jersey	Ambient On	0.078	124	▪	▪
50	Cotton Jersey	Ambient On	0.076	124	▪	▪
51	Cotton Jersey	Ambient On	0.071	124	▪	▪
52	Cotton Jersey	Ambient Tube	0.089	124	▪	▪
53	Cotton Jersey	Ambient Tube	0.151	124	▪	▪
54	Nylon Tricot	Preconditioned On	0.224	73	1.12	0.097
55	Nylon Tricot	Preconditioned On	0.225	73	1.12	0.097
56	Nylon Tricot	Preconditioned Off	0.206	73	1.12	0.097
57	Nylon Tricot	Preconditioned Off	0.205	73	1.12	0.097
58	Nylon Tricot	Ambient On	0.116	73	▪	▪
59	Nylon Tricot	Ambient On	0.114	73	▪	▪
60	Nylon Tricot	Ambient On	0.119	73	▪	▪
61	Nylon Tricot	Ambient Tube	0.111	73	▪	▪
62	Nylon Tricot	Ambient Tube	0.09	73	▪	▪

Figure 27: Raw date for MeS adsorbed on each fabric

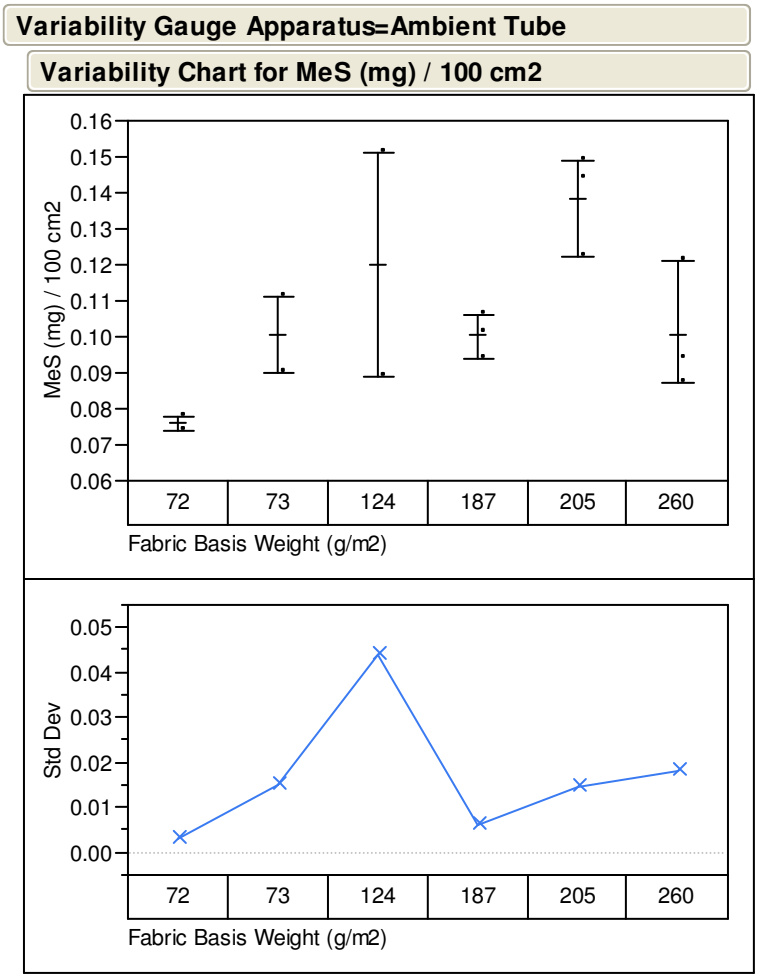


Figure 28: Variability and standard deviation of MeS adsorbed on ambient fabric in the tube apparatus.

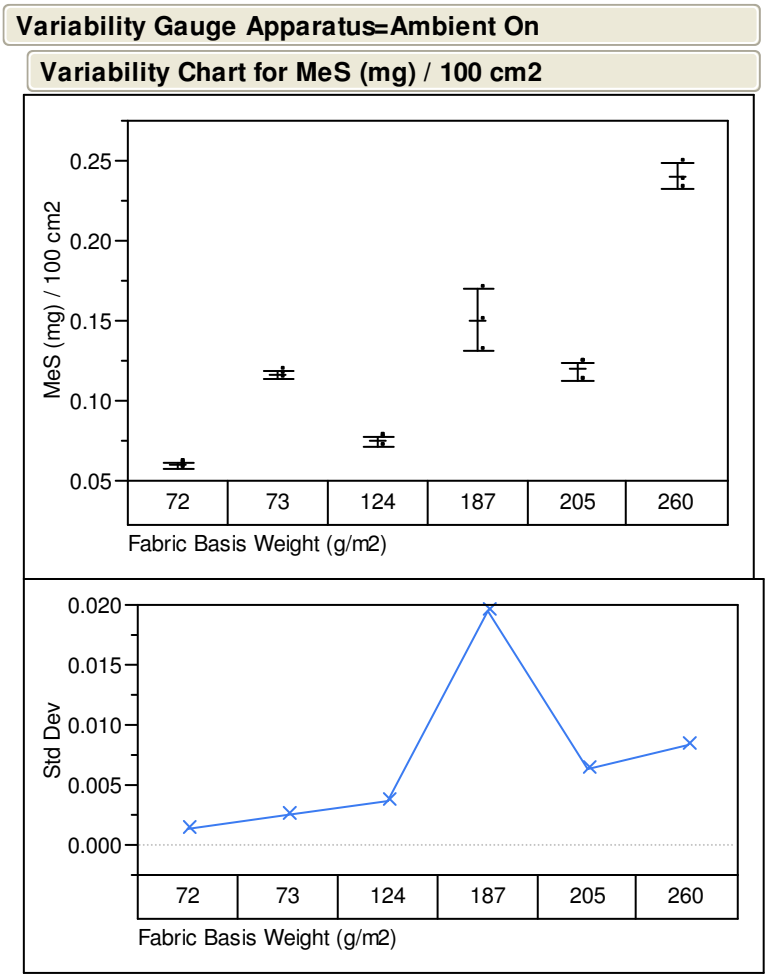


Figure 29: Variability and standard deviation of MeS adsorbed on ambient fabric in the chamber (On) apparatus.

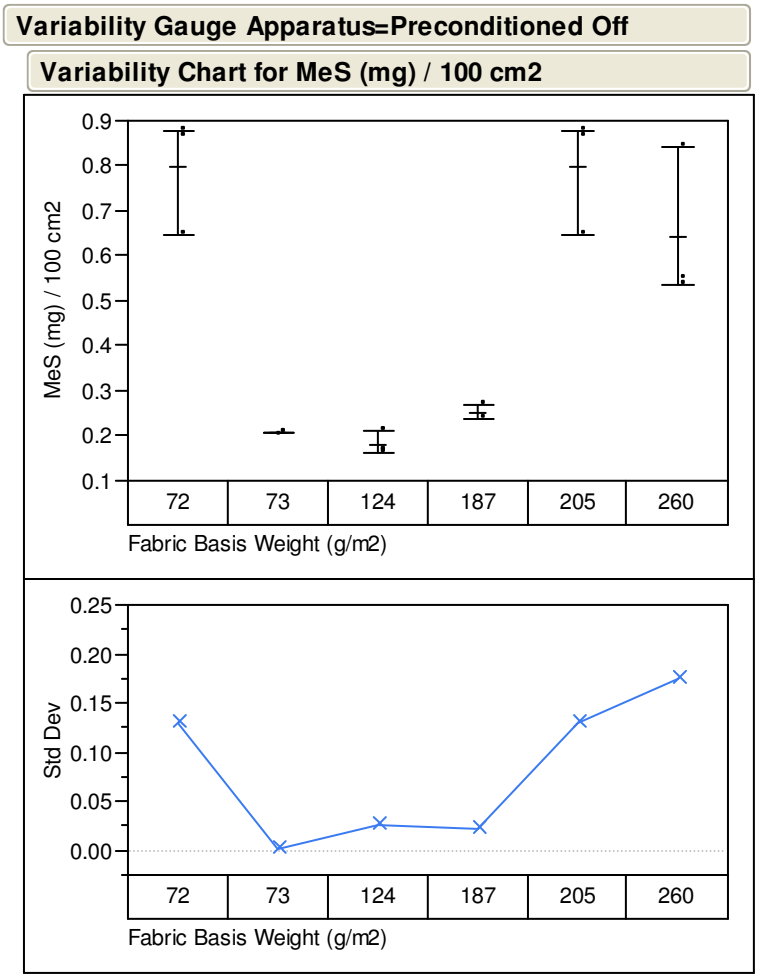


Figure 30: Variability and standard deviation of MeS adsorbed on preconditioned fabric in the chamber (Off) apparatus.

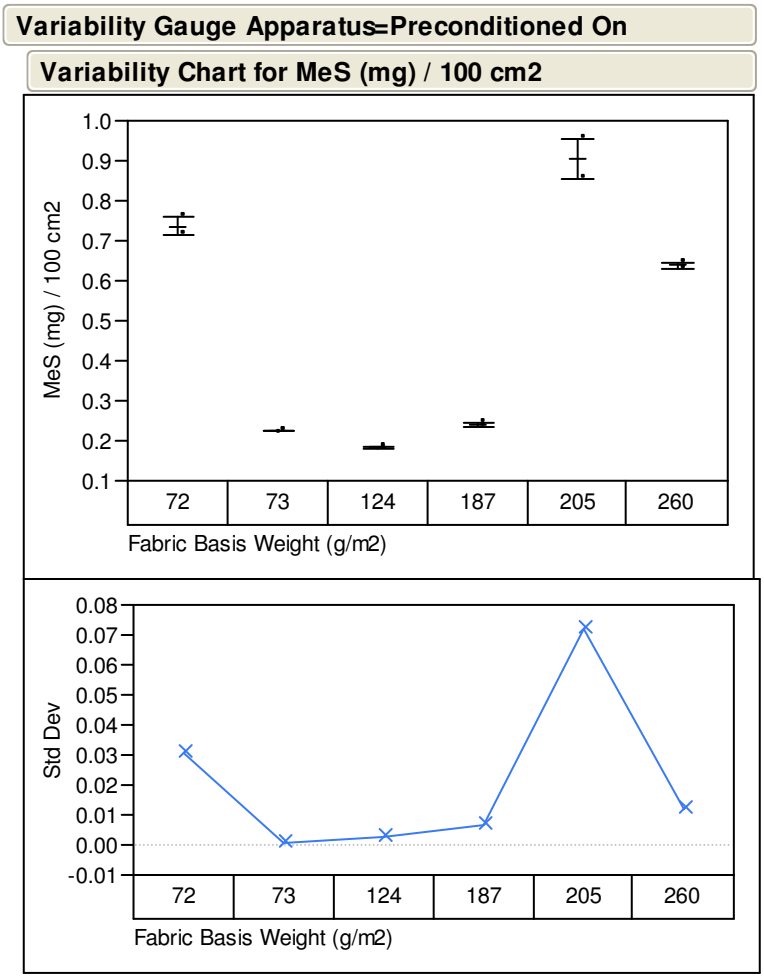


Figure 31: Variability and standard deviation of MeS adsorbed on preconditioned fabric in the chamber (On) apparatus.