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Applicator Exposure to Glycol Derivatives and Total Volatile Organic Compounds during the Application of Spray Polyurethane Foam Insulation

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Applicator Exposure to Glycol Derivatives and Total Volatile Organic Compounds during the Application of Spray Polyurethane Foam Insulation

by

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DEDICATION

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ABSTRACT

There is currently high demand for new building materials, which are considered "environmentally friendly," or "green" for both new construction and renovations. Spray polyurethane foam (SPUF) insulation has gained significant acceptance by both consumers and the construction industry due to its high R-value, which results into significant energy savings among other things. Despite its acceptance by consumers and the construction industry, consideration must be given to potential chemical exposures to applicators installing these products.

This study sought to determine, through quantitative experimentation, if there was a release of glycol derivatives including, diethylene glycol (DEG), ethylene glycol (EG), and propylene glycol (PEG), during the application of SPUF. In addition, total volatile organic Compounds (tVOCs) and various environmental parameters were also collected during this research.

This study utilized a two-component small-scale SPUF kit manufactured by the Dow Chemical Company, known as the FROTH-PAK™ kit. This specific kit is typically used by the construction industry to fill cavities, cracks, floor and wall penetrations, and expansion joints of buildings.

In order to determine the presence of these glycol derivatives, personal breathing zone samples were collected during the application of the SPUF during three application trials. Glycols derivatives were measured using active sampling techniques. Supplementary parameters including tVOCs, ambient and wet-bulb temperature, relative humidity, carbon monoxide, and carbon dioxide, were measured using direct-reading techniques. During this study several modifications were made to the work area and the air sampling methodology to

assist in verifying the presence of the glycols and the conditions in which they may be present in the air during the application of SPUF insulation. All samples were sent to an accredited laboratory and were analyzed by the Nation Institute of Occupational Safety and Health Method 5523.

During this study, measurable amounts of diethylene glycol and propylene glycol were detected in two of the trials in which no ventilation in the work area was utilized. During one trial in which a work area ventilation system was utilized, none of the glycols were detected in the laboratory analysis above the limit of detection given the analytical method. Ethylene glycol was not detected in any of the samples submitted for analysis. The results for the tVOC measurements were inconclusive.

Based on the results of the air sampling, it is likely that exposure to diethylene glycol and propylene glycol may occur under certain conditions. However, due to the limited number of samples and the variation between the samples collected in this study, a generation rate or concentration buildup estimate for comparison of the OELs was not conducted. These conditions include the quantity of ventilation used during application, the application duration, and proper operation of the SPUF application equipment. Based on the results, there is evidence that additional research may be needed in this area.

CHAPTER 1: INTRODUCTION

Background and Significance

Energized by environmental awareness, government regulations, and rising energy costs, the global market for “environmental friendly” or “green” building materials has expanded exponentially in the past decade. One of the fastest growing areas of building materials used in this green phenomenon is spray polyurethane foam (SPUF) insulation.

Manufacturers and resellers of the SPUF insulation tout the benefits of using SPUF insulation due to its energy efficiency, versatility, thermal/mechanical performance and reported environmental benefits. The acceptance of this material into built environments has also been propelled by the support of federal government entities such as the United States Department of Energy (USDOE) and state and local building departments, which have included these products in their building codes.[1, 2]

While many of the physical characteristics of SPUF insulation have been studied extensively, there has been little published research regarding the potential chemical exposures to applicators who are involved in the installation of SPUF into the built environment (i.e. office building, homes, etc.). Recently, the Nation Institute of Occupational Safety and Health (NIOSH) and the United States Environmental Protection Agency (USEPA), and the United States Consumer Products Safety Commission (USCPSC), have decided to take a closer look at SPUF insulation during the different life stages of handling. These stages include manufacturing, application, and post installation of the product.

NIOSH has engaged in collecting information to determine if potential exposures exist for applicators installing SPUF products. In March 2012, authors of the NIOSH sponsored science blog presented a request titled “Help Wanted: Spray Polyurethane Foam Insulation

Research".[3] The authors expressed interest in gathering additional exposure data on chemical agents such as amines, phosphates, and glycols during the installation of SPUF products.[3]

In response to the need for additional data, this research was conducted to gather air monitoring data for glycol derivatives, which are chemical components of the SPUF formulation. Typically, most glycols are not a significant inhalation exposure concern at normal temperatures. However, when heated or sprayed their vapor pressure may rise, resulting in high airborne concentrations.[4] Given that the chemical curing process of SPUF is exothermic (i.e. generates heat) and that the product is sprayed, the possibility of exposure potentially exists. This research is intended to determine if measurable levels of glycol derivatives including diethylene glycol, ethylene glycol, and propylene glycol, are present in the air inhaled by applicators using a commercial grade two-component kit during the installation of SPUF insulation.

Limitations and Assumptions of This Research

There are a number of limitations associated with this research. This research utilized a commercial grade two-component SPUF kit obtained from one manufacture. Therefore, the results obtained from this research may be limited to this particular manufacture's formulation. This research study does not evaluate the potential adverse health effects associated with the inhalation of chemical agents such as glycol derivatives or tVOCs. Due to limitations of the amount of SPUF which could be applied from one kit and the cost of outside laboratory analysis, this research study was limited in the number of samples which could be collected. This research study does not address reported questions concerning the SPUF insulations outside of the application process, such as continued off-gassing, sensitization to certain chemical components or being a source of objectionable odors.

CHAPTER 2: BACKGROUND

Polyurethanes and Polyurethane Foam (PUF)

Polyurethanes are a complex class of polymers that are basically ester-amide derivatives of carbonic acids.[5] Polyurethane compounds are formed by reacting polyisocyanates with polyalcohols (or "polyols"), thus they are often referred to as two-component systems. First developed commercially circa 1937 – 1941, polyurethanes are used to make foams, coatings, adhesives, elastomers, and elastomeric fibers. Polyurethane foam (PUF) is a polyurethane based material that can be produced in a flexible form, as seen in car seats and bedding, and in rigid forms as seen in building panels and refrigerator housings. Spray applied polyurethane foam (SPUF), the focus of this research, is a rigid type of foam. Table 1 briefly summarizes the achievements associated with polyurethanes.

Table 1. Polyurethane Timeline

Year	Notable Achievement
1937	Dr. Otto Bayer discovers the basic polyurethane chemistry.
1940	Rigid foam first introduced into aircraft
1948	First insulation application – a beer barrel
1960	Steel sandwich building panels begin
1969	Automobile bumpers for increased safety
1979	Spray building insulation invented
1980	Polyurethane based sandwich panels started
1990	First passive house built in Germany, using polyurethane insulated window frames
1992	NASA's Endeavour space shuttle uses polyurethane to protect external fuel tanks
2011	Airbus, who use polyurethane technology in their airplanes, reach their 10,000th order
2011	Polyurethane foam used as a lightweight design and high-performance insulator for e-cars

Source: www.polyurethanes.org

Polyurethanes, PUF, and SPUF Production

As the use of polyurethanes continues to expand, so does its global production and economic impact. In 2010, polyurethane based materials represented $38.1 billion in shipments and receipts, employing 309,900 workers in the United States (U.S.)[6] Within the U.S. polyurethane market, the total production of two-component SPUF in 2011 was estimated to be 350 million lbs, compared to 323 million lbs in 2010.[7]

The building and construction industry accounts for 34.6% of annual total U.S. polyurethanes consumption.[6] A major use of polyurethanes in the building and construction industry is for PUF and SPUF insulation.[6, 8] The building and construction industry represents one of the largest applications of rigid PUF and SPUF as insulation for walls, ceilings, attics and roofs, insulated panels, and around doors and windows of new and retrofit buildings.[9] Rigid SPUF is one of the fastest growing segments in the insulation market 5%.[6] Overall employment of U.S insulation workers is projected to grow 38% from 2012 to 2022; with employment of floor, ceiling, and wall insulators projected to grow 26% and for mechanical insulation workers to grow 47%. This is considerably faster than the average for all occupations.[10] It is predicated that demand for insulation and insulators will continue to be added into existing buildings to save energy.[10] Residential applications of SPUF is predominant in the developed economies of North America and Europe primarily resulting from stringent regulations for energy efficient structures.[6] This is because SPUF can effectively protect against air infiltration, which accounts for up to 25-40% of a home's energy loss.[11] The SPUF products also help seal out moisture, dust, smoke, outside noise and insects.[12, 13]

Energy used by commercial and industrial buildings in the U.S. is estimated to be responsible for nearly 50% of emissions of greenhouse gases (GHGs) that contribute to global climate change resulting in increased demand for energy conservation.[14] This increasing demand for improved energy efficiency and building performance is reflected in the development of more stringent building energy codes. An example of this is the Massachusetts

Commercial Energy Code, which was the first jurisdiction to require building envelope air barrier systems in non-residential construction.[2, 15, 16] This energy code conforms to U.S. Department of Energy (USDOE) program goals to significantly reduce building energy consumption.[16] Recent changes in the 2012 residential codes now also require air tightness in residential buildings.[1]

There are two common SPUF types. Closed cell has 1.75 foam density, and open cell which has a 0.5 foam density. In most commercial applications, closed cell foams are utilized while in residential applications open cell foam is predominantly sprayed. The use of closed cell foam is gaining residential market share due to its higher R-value and moisture barrier properties.[17] Rigid SPUF's low-density closed cells retain most of the low thermal conductivity blowing agents in the cells until they are destroyed. This attribute makes SPUF an efficient thermal insulating material with insulating R-values ranging from 5.6 to 8 per inch.[18, 19]

PUF and SPUFs, when applied, form a strong, lightweight, low-density structure that is both dimensionally stable and moisture resistant with low vapor transmission characteristics.[6] SPUFs typically have excellent adhesion to surfaces with which they come into contact during the foaming process and provide some rigidity to structures to which they are applied.[9]

In construction it can be used as a continuous barrier to seal building envelopes and performs as external weather and moisture barrier, preventing air and moisture infiltration and exfiltration.[2] SPUFs when applied on-site, forms a seamless layer of insulation, seal gaps and seams during application, and cover irregular shapes that are hard to insulate with rigid PUF boards.

The properties of PUF and SPUF allow for development of thermal insulating products that are self-supporting. This makes it possible to increasing space utilization by building thinner walls and lower profile roofs, which can reduce operating costs.[8]

Applicators can purchase SPUF in containers as small as 12 oz. spray cans, 50-pound cylinders or in larger professional 55-gallon drums. There is a growing market for small-scale two-component kits which can have theoretical yields ranging from 12 to 620 board feet (0.03 to 1.46 cubic meters).[11] This study used a small-scale kit manufactured by the Dow Chemical Company (Dow) known as "FROTH-PAK." The Dow FROTH-PAK kit (Dow kit) is typically used for insulation and air sealing, and to fill cavities, cracks, floor and wall penetrations, and expansion joints.[10,12, 20]

The Dow kit had features common to many of the larger capacity spray polyurethane foam products, such as the chemical reaction of an A component and B component. The safety data sheets (SDSs) for the kit provided details of the various chemicals, which make up the SPUF product; see Table 2.

Product Reaction and Chemical Composition

PUF are characteristically known for their two-component reactions of isocyanates such as MDI (Methylene diphenyl diisocyanate) and polyols (polyester or polyether resins) in the presence of a blowing agent and various additives.[20, 21]

Most SPUF products utilize a two-component system in which components are held in separate cylinders or drums. Components are directed through a special SPUF gun, nozzle, or straw at which point the chemicals begin to react.[22] The polyol may contain additives such as tertiary amine catalysts to alter reactivity, flame retardants to reduce flammability, silicone surfactants to enhance cell size, and blowing agents to adjust foam density.[3, 5] Additional additives can include flame retardants, fillers, extenders, bacteriostats, and dyes.[5, 20]

Mechanical blowing agents have low boiling points and expand as gas bubbles once the reaction temperature reaches the boiling point of the blowing agent. The gas bubbles expand the polyurethane mass. Initially, many commercial SPUF application products relied on chlorofluorocarbons (CFCs), such a CFC-11, as the primary mechanical blowing agent due to ease of use in processing as well as its thermal conductivity characteristics.[19] However, most manufacturers have switched to hydrochlorofluorocarbons (HCFCs) to meet compliance standards related to ozone depleting substances.[5]

Mixing of the A component with the B component starts the chemical reaction or polymerization.[5, 22] The reaction is exothermic, meaning it produces heat. As the chemical reaction occurs, the viscosity of the SPUF material increases until the reaction forms the polyurethane solid. The chemical curing reaction can exceed 200^{O}F.[23] To limit the amount of thermal activity and prevent spontaneous ignition of the material, manufactures provide limits to the application thickness of the SPUF.

The time SPUF takes to chemically react to produce the final SPUF, is referred to as the curing rate. It is an important determinant for health effects and varies depending on the type of SPUF insulation, applicator technique, foam thickness, ambient temperature, and relative humidity.[24] Chemical curing allows the SPUF to be dispensed, expanded, and skinned over in 30 to 40 seconds.[13] It is completely cured and tack free in less than 1 minute.[25]

A Component – Isocyanate

The Dow kit, used in this study, consisted of two cylinders. One cylinder was labeled as "A Component – Isocyanate." Depending on the manufacturer, the A Component of a SPUF kit may be referred to as the ISO side, Side A, A Side, or Part A. The A Component is often referred to as the "ISO or Isocyanate side" due to it generally consists of 60-100% isocyanate depending on the manufacturer. In the case of the Dow kit, the isocyanate is diphenylmethane diisocyanate (pMDI).[26] PMDI is a member of the diisocyanate family Methylene diphenyl diisocyanate (MDI or 4,4' –Methylenediphenyl diisocyanate). Monomeric MDI is formed as a byproduct of pMDI synthesis and is not typically separated from the mixture.[27] Both MDI and pMDI are reactive with water, which can result in the production of amines, oligoureas, and carbon dioxide. For this reason, these chemicals are always stored under an inert gas such as nitrogen until use.[27]

The balance of the contents of the A Component typically include a foam blowing agent. In the case of the Dow kit 1,1,1,2-Tetrafluoroethane (5-10%), which assist in the cell structure formation. The specific chemicals included in the B component are listed in Table 2.

B Component – Polyol

The second cylinder included in the Dow kit was labeled “B Component – Polyol”. The B component is commonly referred to as the polyol component, B Side, Side B, Part B, Component B, or the isocyanates blend depending on the manufacturer. The B component contains a variety of proprietary chemicals that provide specific performance functions such as catalyst, flame retardant, and additional blowing agents. The foam blowing agents in the Dow kit are 1,1,1,2-Tetrafluoroethane (HFC-134a) and 1,1,1,3,3 – Pentafluoropropane (HFC-245fa).[28] Blowing agents are characteristically insoluble and have high volatility.[24]

Table 2. Dow Kit SPUF Chemical Ingredients

Part A	Component	CASRN	Amount
	Diphenylmethane Diisocyanate, isomers and homologues	9016-87-9	>= 60.0 - <= 100.0%
	4,4’ –Methylenediphenyl diisocyanate (MDI Isomer)	101-68-8	30.0 - 60.0%
	1,1,1,2-Tetrafluoroethane	811-97-2	>= 5.0 - <= 10.0%
	Note: CASN 101-68-8 is an MDI isomer that is part of CASN 9016-87-9.		
Part B	**Component**	**CASRN**	**Amount**
	Sucrose , propylene oxide	9049-71-2	<= 25.0%
	Water	732-18-5	<= 20.0%
	Dimethyl Siloxanes and Silicones, 3-Hydroxypropyl Methyl, Ethoxylated	68937-54-2	<= 20.0%
	1,2-Benzenedicarboxylic Acid, 3,4,5,6-Tetrabromo-, mixed Esters with Diethylene Glycol and Propylene Glycol	77098-07-8	<= 20.0%
	Dimethylbis((1-oxoneodecyl)oxy)stannane	68928-76-7	<= 20.0%
	Triethyl phosphate	78-40-0	<= 20.0%
	Polyester polyol	1221716-56-8	<= 10.0%
	Tris(1-chloro-2-propyl) phosphate	13674-84-5	<= 10.0%
	Diethylene glycol	111-46-6	<= 10.0%
	1,1,1,2-Tetrafluoroethane	811-97-2	<= 5.0%
	2-Ethylhexanoic acid potassium salt	3164-85-0	<= 5.0%
	Proprietary additives	-	<= 5.0%
	Polyethylene glycol	25322-68-3	<= 2.0%
	1,1,1,3,3 - Pentafluoropropane	460-73-1	<= 2.0%

*Source of Information
FROTH-PAK™ 650 AF HFC CLASS A ISO Spray Polyurethane Foam [26]
FROTH-PAK ™ 650BF HFC CLASS A POLYOL [28]

Selection of the Chemicals of Interest

Isocyanates (MDI, pMDI) are the largest component of the SPUF mixture and are reported to be the leading cause of occupational asthma in occupational settings; they have been studied extensively.[27] The health effects of glycols may not appear to be as significant as MDI or tris (1-chloro-2-propyl) phosphate (TCPP). However, a number of research groups and regulators including OSHA and the AIHA, indicate that the glycols group of chemicals require additional toxicological research.[29] Therefore, this research focuses on the glycol derivatives ethylene glycol, diethylene glycol, and propylene glycol. Ethylene glycol and diethylene glycol are candidates for further work.[30] SIDs has stated that depending upon use and exposure, member countries should assess possible risk associated with renal (EG and DEG) and/or developmental toxicity (EG) for the lower molecular weight glycols.[30]

Glycols were selected from the chemicals listed by NIOSH needing additional research due to their inclusion in the SPUF chemical makeup. Glycols are characterized as hydrocarbons that have two hydroxyl groups attached to separate carbons in an aliphatic (hydrocarbons) chain.[4] The glycol derivatives have varying acute health effects including irritation of the throat, mild headache, lower backache, loss of consciousness, central nervous system (CNS) depression, and nystagmus, fast uncontrollable movements of the eyes.[31]

In general, glycols have low vapor pressures at normal temperature and pressure (NTP). NTP is defined as air at 20^{o}C (68^{o}F) and 1 atm (29.92 in Hg). Inhalation of the vapors and aerosols are of low concern unless they are heated, agitated, or sprayed.[4] Inhalation exposures to glycols have historically been limited, reportedly due to these characteristics.

Ethylene Glycol (EG)

Ethylene glycol (EG), CASRN 107-21-1, is manufactured by oxidation of ethylene in the presence of acetic acid to form ethylene dictate, which subsequently hydrolyzed to EG.[32] EG characteristically is a colorless, practically odorless, syrupy liquid with a sweat taste at NTP.[4]

Alternative names for EG include 1,2-dihydroxyethane, 1,2-ethanediol, 2hydroxyethanol, ethylene alcohol, glycol, and ethylene dehydrate.[33, 34]

EG is used to make antifreeze in heating and cooling systems. It is also used as an industrial humectant and in de-icing solutions for cars, airplanes, and boats.[34] It is an ingredient in hydraulic brake fluids, inks used in stamp pads, ballpoint pens, and print shops, a solvent in the paint and plastics industries, and used in the production of polyester fibers.[35]

Workplace exposures to EG are typically uncommon due to its low vapor pressure at NTP.[4] EG vapor and mist can be inhaled, particularly when it is heated, agitated, or sprayed (NIOSH). The substance can be absorbed into the body by inhalation and through the skin.[36] Adverse health effects have been reported from exposure to mists.[34, 37]

In one study of a group of women working in a setting with heated EG, nystagmus (uncontrollable eye movement) was observed. A number of the women were subject to attacks of unconsciousness. The attacks ceased on discontinuing exposure to EG vapors.[4]

EG has water absorbing properties and repeated exposure can remove water from the tissues in your body and cause loss of body water thru urination.[35] EG is a skin, eye, and mucous membrane irritant.[37] Human systemic effects by ingestion and inhalation include, eye lacrimation, general anesthesia, headache, cough, respiratory stimulation, nausea or vomiting, and pulmonary, kidney and liver changes.[33, 34] Some studies have found that EG may have effects on the central nervous system (CNS). Indications as to whether EG causes cancer or developmental defects has not been determined.[34]

Diethylene Glycol (DEG)

Diethylene glycol (DEG), CASRN 111-46-6, is manufactured commercially as a by-product of EG production. It can be produced by reaction between EG and ethylene oxide.[38] DEG is characteristically described as a colorless, odorless, syrupy liquid with a sharply sweat taste, similar to that of EG. It is a relatively non-volatile liquid at NTP and is soluble in water.[38, 39]

Like EG, DEG is used in antifreeze solutions. It is also used as a lubricant and finishing agent for wool and other fabrics, a solvent for dyestuffs, in composition corks, glues and personal care products such pharmaceuticals and toiletries.[38] In addition, it is also used in manufacturing of polyethylene terephthalate and used in natural gas processing.

DEG can be absorbed into the body both by ingestion and inhalation.[30] Like other glycols, evaporation of DEG at NTP is minimal given its low vapor pressure, however a inhalation hazard may exist when it is heated or where mists or fogs are generated.[38]

Exposure to DEG may result in kidney impairment. Studies have indicated that ingestion could cause effects on the CNS and liver and even cause death. DEG exposure can result in insignificant to minor skin or eye irritation. Animal testing data suggest little hazard from short-term inhalation. Never the less exposures to vapor, fog, or mist should be minimized especially in chronic (i.e. long-term) exposure situations. Animal studies (mice) indicate that DEG is a reproductive toxicant affecting fertility and reproductive performance when given at high doses.[31]

Propylene Glycol (PG)

Propylene glycol (PG), CASN 57-55-6, is produced by the hydration of propylene oxide.[4] PG is a synthetic liquid substance that absorbs water. PG must be heated or violently agitated to produce a vapor.[4] PG is characteristically described as a colorless, practically odorless, tasteless, and slightly syrupy liquid at NTP.[39, 40] Other names for PG are 1,2-dihydroxypropane, 1,2-propanediol or monopropylene glycol (MPG), methyl glycol, and trimethyl glycol.

PG is used in organic synthesis including polypropylene glycol, polyester resins, cellophane and antifreeze.[4, 40] It is used as an emulsifier, food additive, anticaking agent, solvent, wetting agent, humectant, and in cleansing creams, plasticizers, hydraulic and brake fluids, bactericide, and textile conditioners.[4, 41] Like EG, PG is also used to make polyester compounds, and as a base for de-icing solutions. PG has been approved for use in certain pharmaceutical products by the U.S. Food and Drug Administration (USFDA) since 1942. They have classified PG as an additive that is "generally recognized as safe" for use in some foods and cosmetics.[4, 40] PG can be used to absorb extra water and maintain moisture in certain medicines, cosmetics, or food products. PG is also used to create artificial smoke or fog used in theatrical productions and firefighter exercise training.[31, 40]

PG occupational exposure would normally be limited to dermal and/or inhalation exposure.[4, 40] Again, due to its low vapor pressure, a significant amount of PG would not be expected to evaporate into the air under NTP conditions.[39]

Systemic toxicity is especially low and health hazards from PG are negligible. However, the substance is an eye irritant and repeated or prolonged contact may cause skin sensitization.[34, 41] Large amounts of PG increases the amount of acid in the body.[40]

Table 3 presents some basic chemical characteristics of the glycol derivatives sampled for during this research. Of particular significance is the vapor pressure of the glycols at NTP. The SPUF application process is expected to undergo a chemical exothermic reaction, which may result in internal temperatures up to 200^{0}F (93.3^{0}C).

Table 3. Summary of Select Glycols and their Chemical Properties

Substance	CASN	MW	VP (mmHg)	SG	BP
Diethylene glycol	111-46-6	106.12	0.01 at 20°C	1.118	245°C (473°F)
Propylene glycol	57-55-6	76.10	0.07 at 20°C	1.038	188°C (372 °F)
Ethylene Glycol	107-21-1	62.07	0.05 at 20°C	1.113	197.2°C (387.1°F)

Table Key

CASN:	Chemical Abstract Substance Number	SG:	Specific Gravity
MW:	Molecular Weight (Unit less)	BP:	Boiling Point
VP:	Vapor Pressure (mmHg)	°C:	Celsius
		°F:	Fahrenheit

Source of Information
NIOSH Method 5523[42]

In addition to glycols, a secondary group of chemicals generally referred to as total volatile organic compounds (tVOCs), which may be emitted during SPUF reaction process, were monitored. TVOCs were included in this study due to their potential negative health impacts as well as their relative ease to monitor. The health effects associated with tVOCs range broadly depending on the make-up of the tVOC concentration. In general, the health effects due to inhalation exposure can include irritation of the respiratory system and eyes, headaches, nausea, respiratory irritation, fatigue, and asthma symptoms. Sick building syndrome (SBS) and multiple chemical sensitivity (MCS) are suspected to be related to tVOCs.

Occupational Exposure Limits

A concern of polyurethanes is the potential negative health effects not only during manufacturing, but also during installation, and in the use and combustion of these materials.

Specific concerns related to SPUFs have arisen associated with isocyanates and fire retardants. Recent health complaints made by applicators applying the foam, and by residents in homes where the foam has been applied, are causing health officials such as NIOSH and USCPSC to take a closer look at these products during various segments of their lifecycle.

One concern is that applicators may be unaware of the hazards associated with the less discussed components such as glycols. This may result in lack of training or emphasis to prevent skin, eye and inhalation exposures, and the proper type of protections to use.[20]

As earlier mentioned, several chemicals in the SPUF mixture have been extensively studied and as such have had occupational exposure limits (OELs) established within the U.S. These include OSHA Permissible Exposure Limits (PELs), American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs), and American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Levels (WEELs). The available OELs typically used in the U.S. are listed in the Table 4.

Table 4. Established Occupational Exposure Limits

Part A Component Chemical	CASRN	List	Type	Value
4,4' –Methylenediphenyl diisocyanate (MDI Isomer)	101-68-8	ACGIH OSHA Table	TWA Ceiling	0.005 ppm 0.02ppm
1,1,1,2-Tetrafluoroethane	811-97-2	AIHA WEEL	TWA	1,000 ppm
Part B Component Chemical	**CASRN**	**List**	**Type**	**Value**
Sucrose, propylene oxide	9049-71-2	-	-	-
Water	732-18-5	-	-	-
Dimethyl Siloxanes and Silicones, 3-Hydroxypropyl Methyl, Ethoxylated	68937-54-2	-	-	-
1,2-Benzenedicarboxylic Acid, 3,4,5,6-Tetrabromo-, mixed Esters with Diethylene Glycol and Propylene Glycol	77098-07-8	-	-	-
Dimethylbis((1-oxoneodecyl)oxy)stannane	68928-76-7	ACGIH ACGIH OSHA Table Z-1	TWA(S) STEL(S) PEL	0.1 mg/m^3 0.2 mg/m^3 0.1 mg/m^3
Triethyl phosphate	78-40-0	AIHA WEEL	TWA	7.45 mg/m^3
Polyester polyol	1221716-56-8	-	-	-
Tris(1-chloro-2-propyl) phosphate	13674-84-5	-	-	-
Diethylene glycol	111-46-6	AIHA WEEL	TWA	Vapor and Aerosol 50 ppm Aerosol, only 10.0 mg/m^3
1,1,1,2-Tetrafluoroethane	811-97-2	AIHA WEEL	TWA	1,000 ppm
2-Ethylhexanoic acid potassium salt	3164-85-0	-	-	-
Proprietary additives	NA	-	-	-
Polyethylene glycol	25322-68-3	AIHA WEEL	TWA(P)	10.0 mg/m^3
1,1,1,3,3 - Pentafluoropropane	460-73-1	AIHA WEEL		300 ppm

Key to Table :

OSHA: Occupational Safety and Health Administration
PEL: Permissible Exposure Limit
ACGIH: American Conference of Governmental Industrial Hygienists

*Source of Information
FROTH-PAK™ 650 AF HFC CLASS A ISO [26]
FROTH-PAK ™ 650BF HFC CLASS A POLYOL [28]

ppm: Parts per million parts of air by volume
AIHA: American Industrial Hygiene Association
WEEL: Workplace Environmental Exposure Level
CSRN: Chemical Abstract Registry Number
mg/m^3: Milligrams per cubic meter of air
TLV: Threshold Limit Value
TWA: Time-Weighted Average (8-hour basis)
STEL: Short term exposure level

CHAPTER 3: STUDY METHODOLOGY

General Study Design

The following sections in this chapter outline the basic study design and the methodologies used to collect relative data. The methodology carried out during the SPUF application and data collection portion of the study is divided into ten sections including:

1. Study work area preparation
2. Mock wall construction
3. Data collection equipment
4. Equipment calibration
5. Air monitoring equipment setup
6. Background data collection
7. SPUF application equipment
8. Trial No. 1
9. Trial No. 2
10. Trial No. 3

A total of three trials were conducted during the application of SPUF insulation. During the course of this research a number of modifications were made to each trial, modifying the work area, ventilation, and the air sampling methodologies. The modifications were administered in order to address the findings and observations obtained during each prior trial. Each modification is discussed in detail within each respective trial. Prior to the initiation of any SPUF insulation application, a background study of the proposed work area was performed to determine if the work area would be acceptable.

Study Work Area Preparation

The primary work area for this study was within a residential garage. The initial step in the work area preparation included removal of all containers or items which were reasonably anticipated to be potential emission sources. The work area was further prepared by cleaning all surfaces with clean damp rags followed by vacuuming the surfaces with a brush attachment. The vacuum was fitted with a high-efficiency particulate air (HEPA) filter. The goal of the cleaning activities was to remove any loose dust particulates or any chemical emissions sources or residues which may have been present within the work area. Following the cleaning, 6-millimeter contractor's grade polyurethane sheathing was placed on the concrete floor. Additionally, sheathing was affixed on select wall surfaces and shelving with painters tape for protection from potential SPUF application overspray. An exhaust fan was installed in the exterior window. See Figure 1.

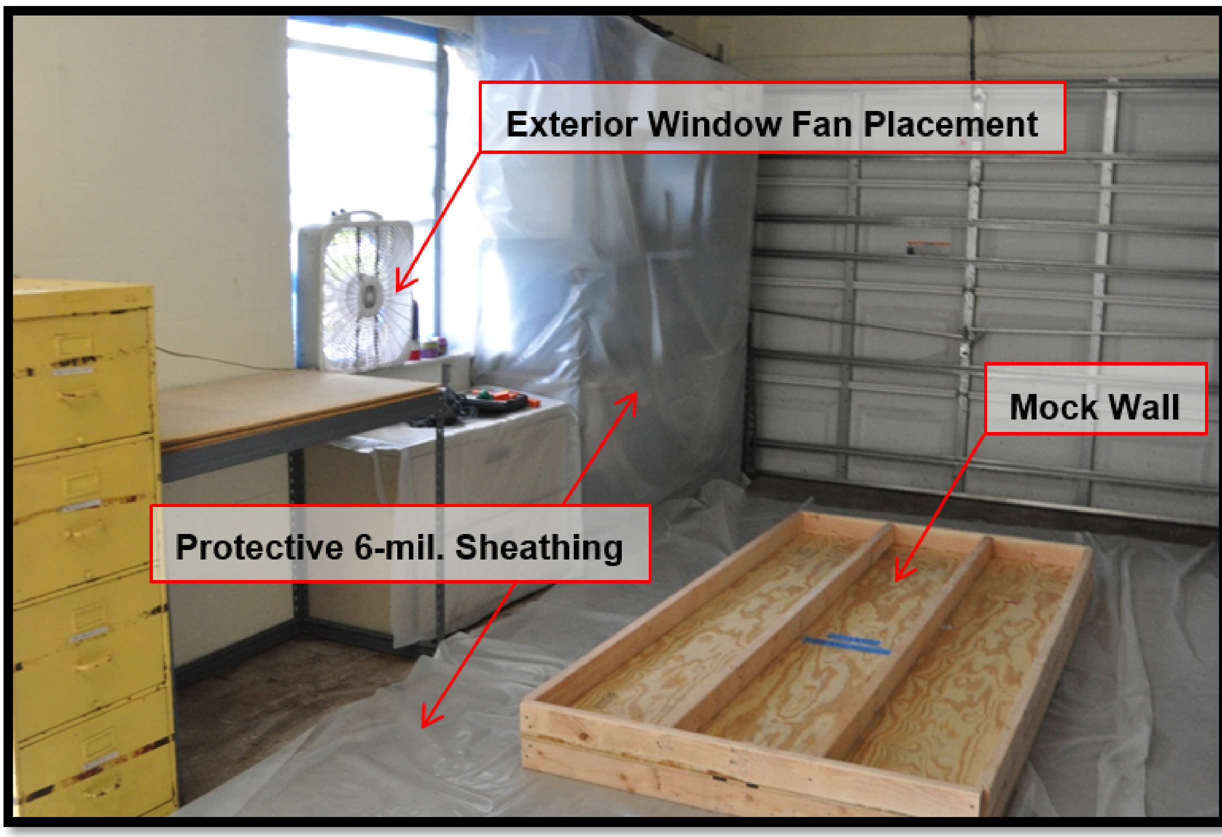

Figure 1. Photograph of Initial Layout of Work Area.

Work Area Ventilation Evaluation

The purpose of the fan at the exterior window was to provide a controlled and measurable amount of fresh airflow into the work area from both the outdoors and indoor non-work areas. The airflow from the fan exhaust was evaluated both qualitatively through air current tubes manufactured by the Drägerwerk AG & Co.© (Dräger), and quantitatively through the measurement of the face velocity at the intake of the interior face of the exhaust fan. The purpose of the evaluation was to verify that the work area was negatively pressurized to the adjoining non-work areas.

The quantitative airflow test was conducted by using a TSI Incorporated (TSI) VelociCalc Plus Model 8386 (VelociCalc) direct-reading velocity meter, a form of an anemometer. The initial step in the air flow evaluation was to determine the approximate velocity of the air exhausting from the fan. The total fan intake face area was calculated using Equation 1.

Equation 1. Area Calculation of Circular Fan Intake

$$A = \pi r^2$$

Where;

r = radius of circle (in)
A = area of fan intake (ft^2)
π = 3.14

The radius of the intake face of the fan measured to 9.75 in. Thus, $A = \pi \times r^2 = 3.14 \times 9.75^2 = 298.45\ in^2$ or 2.07 ft^2.

The fan intake face of the exhaust fan was then divided into nine like sized rectangles using painters tape for visual guidance. Each section measured approximately 6.5 in. by 6.5 in. square. The velocity was measured at the center of each rectangle with a minimum of three measurement recordings per rectangle. The three measurements were then averaged. The air velocity was measured in feet per minute (ft/min). The calibration certifications for the VelociCalc instrument used for this evaluation can be found in Appendix C. See Figure 2.

The individual face velocity measurements were used to determine the average face velocity using Equation 2.

Equation 2. Average Velocity

$$V = \frac{\sum n^{1-9}}{n}$$

Where;

V = velocity (ft/min)
n = number of measurements

The result using Equation 2. is V = $\Sigma n^{1\text{-}9}/n$ resulting in an estimated average velocity of 381 ft/min.

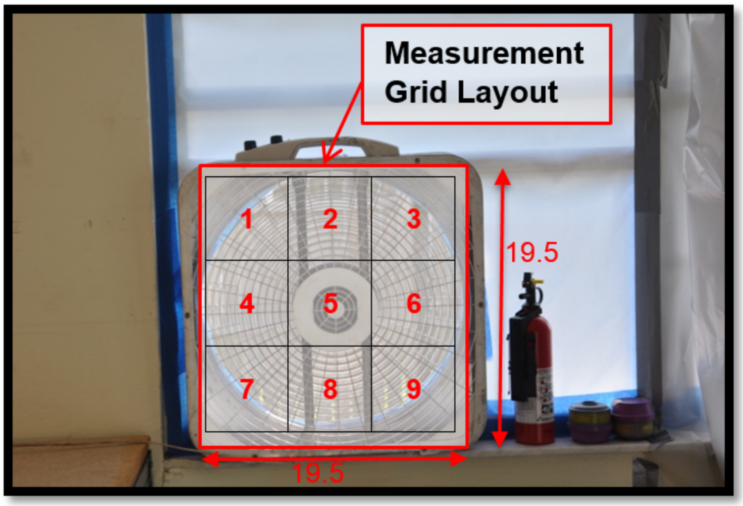

Figure 2. Photograph of Exhaust Fan with Velocity Measurement Grid Layout Overlay.

The estimated average velocity results using the instrument suggested that the airflow was significantly influenced at the intake face of the fan. This influence resulted in significant fluctuations in velocity readings from same locations as well as from different grid locations which can be seen in Table 5.

Table 5. Exhaust Fan Airflow Measurements (ft/min).

286	499	399
472	94	455
423	436	367

In an effort to minimize these fluctuations and increase the accuracy of the exhaust fan flowrate, a makeshift intake hood was constructed. The hood measured 19.5 in x 16.5 in, for an area of 321.8 in^2 or 2.2 ft^2. The hood was installed and the hood intake face was divided into nine rectangles and velocity was re-measured in the same fashion as previously measured. A photograph of the hood is shown in Figure 3, and measurements at the face of the makeshift intake hood are reported in Table 6.

Figure 3. Photograph of Makeshift Hood for Exhaust Fan.

Table 6. Post Hood Installation Airflow Measurements (ft/min).

135	140	128
127	132	123
112	117	91

With the hood in place, the velocity was recalculated. Using Equation 2. $V = \Sigma n^{1-9}/n$ (V = 1,105/9). Thus the average velocity was determined to be 123 ft/min with the hood attached.

The next procedure in the evaluation was to estimate the air flowrate that would be exhausted from the work area with the fan on. This was accomplished by using Equation 3.

Equation 3. Air Volume Calculation

$$Q = V x A$$

Where;

Q = airflow rate (ft^3/min)
V = velocity (ft/min)
A = area (ft^2)

Multiplying the velocity (V) of the air by the fan intake face area (A) results in the air flowrate (Q). In this equation, Q is the average flowrate and is expressed in units of volume per min. The measured air flowrate exhausting from the work area was measured to be 123 ft/min x 2.23 ft^2 = 274 ft^3/min.

The next step in the evaluation process was to determine the number of air exchanges per hour (ACH) for the work area using Equation 4.

Equation 4. Air Changes Per Hour Calculation

$$ACH = 60\ x\ \frac{CFM}{V}$$

Where;

ACH = air change rate per hour
CFM = airflow exhausted from the work area (ft^3/min)
V = volume of the room (ft^3.)

Room Size/Volume = 21.33 x 9.5 x 8.33 = 1,687 ft^3
CFM = 123 ft/min X 2.23 ft^2 = 274 ft^3/min

The volume of the work space was calculated by measuring the work area length, width, and height. The total volume of the work area was 1,687 ft^3. The result using Equation 4 is *ACH = 60 x CFM / V= 60 x* 274 / *1,687 = 9.75 ACH.*

If we were to assume uniform mixing, the complete volume of air filling the work area would be anticipated to change approximately 9.75 times over the course of one hour when the window fan was exhausting the air from the work area. This is an estimated value as many factors, such as work area physical characteristics and air infiltration in the work area, may influence the exchange rate.

The qualitative airflow test was conducted by using air current “smoke” tubes. The smoke tubes are glass tubes containing a chemical that produces a chemical fume (smoke).

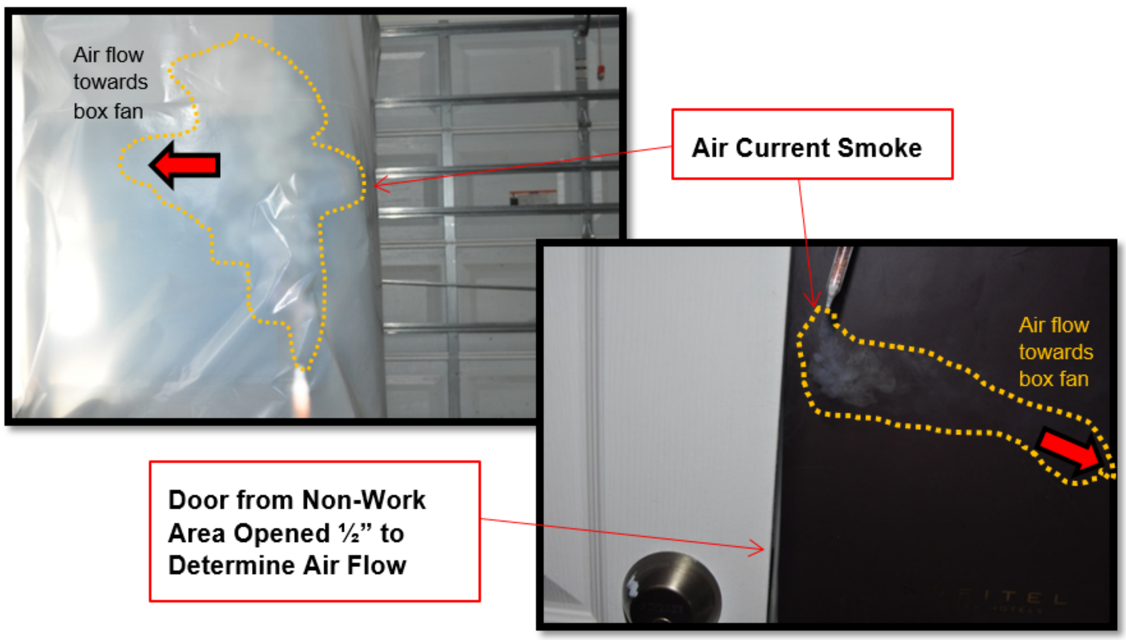

Figure 4. Photograph of Qualitative Ventilation Airflow Evaluation.

Mock Wall Construction

Wood wall sections, referred to as mock walls in this study, were constructed as a substrate for the SPUF application. The mock wall sections were constructed from typical and commonly found building materials. These were acquired from a local building supply store for each study. The mock wall sections were constructed in such a way as to mimic typical wall sections, which would be encountered by a SPUF applicator in a residential exterior wall, garage, or attic space. Each mock wall section was constructed of a 4 ft wide and 8 ft high sheet of plywood. Vertical dimensional lumber was screwed to both sides of the plywood. See Figure 5.

The materials were assembled to form a 4 ft x 8 ft mock wall section with an estimated area for SPUF application of 32 ft^2. Prior to assembly, both the plywood sheathing and the dimensional lumber were measured for moisture content using a calibrated Delmhorst BD-2100 moisture meter to ensure a dry surface for SPUF adhesion.

Figure 5. Photograph of Study Typical Mock Wall Section

For both ease of application of SPUF and safety purposes, the mock wall section was placed on its side with cavities running horizontally as seen in Figure 5. Specific layouts of the mock walls are discussed in their respective trial sections.

SPUF Application Equipment

The SPUF kit was ordered from an online retail supply warehouse company named AWarehouseFull. The company specializes in online sales of building tools and materials. The SPUF kit ordered was referred to as the Dow FROTH-PAK 650 kit. According to the manufacturer, this kit is designed to provide a theoretical yield of 650 board feet of cured SPUF at a nominal thickness of one inch. The theoretical yield is the industry standard for identifying sizes of two-component kits.[11] The theoretical yield calculations are performed in perfect laboratory conditions, which do not take into account losses of blowing agent or variations in application methods and types.[25]

The SPUF kit was ordered online and arrived in two boxes. Upon delivery, the outer shipping boxes were removed and the contents were removed from the manufacture's boxes. The cylinders were weighed and the kit's contents were photographically documented. The A Component cylinder weighed 59.2 lbs and the B Component weight 57.9 lbs. The Dow kit supplied came with the items listed in Table 7, and the SPUF Kit is shown in Figure 6.

Table 7. List of Contents Received in SPUF Kit.

1 Iso (A) cylinder	4 Fan spray nozzles - 259216
1 Polyol (B) cylinder	15 ft gun hose assembly (GHA)
8 Cone white spray nozzles - 259219	1 petroleum jelly packet

Figure 6. Photograph of Dow SPUF Kit Used in Study.

Given the limited quantity of SPUF material available for this study and the size of the surface area for application, the cone nozzle, Dow part number 259219, was used for each trial. See Figure 10. This nozzle design was expected to deliver a coverage width of approximately 3-4 in or medium output.[43] Prior to initiating the application of the SPUF, calculations were performed to estimate application area, which would be needed for each trial.

Table 8. SPUF Coverage Calculations Based on Dow 650 Kit.

Spay Depth (in)	Board Feet Covered	Mock Walls Area (ft^2)	# of Mock Walls Covered
1.0	650.0	56	12
1.5	433.3	56	8
2.0	325.0	56	6
Table Key in: inches ft^2: square feet			

A desired final cured SPUF thickness of 1.5 in. was selected to allow for at least three SPUF applications (i.e. three studies). See Table 8. The estimated time to cover 64 ft^2 was determined to take approximately eleven minutes (10.67 min), as seen in the Table 9.

Table 9. SPUF Nozzle Selection and Application Time Estimates.

	Rate of Spray	Est. Width (in)	Runs / Cavity	Time / Run (sec)	Time / Cavity (sec)	Cavities / Test	Total Time / Test (min)
White/ White back Cone	4/lb. min	3-4 in	4	20	80	8	10.67
White/Blue back Nozzle	4/lb. min	6-8 in	2	15	30	8	4.00
Table Key in: inch sec: seconds min: minute							

In addition to predetermining a desired thickness, for each trial a desired application time was also required. In order to sufficiently meet analytical requirements it was initially determined that each trial would last for eleven min. Although eleven minutes was the desired application time, this time was modified in each trial as each trial provided new information and the subsequent trial evolved.

The NS cone/spray nozzle was selected for this trial in order to provide the longest application time for the air sampling. The cone nozzle was expected to apply an approximately four inch wide path of foam. An example of the final configuration of the SPUF application gun with the cone nozzle affixed is presented in Figure 7.

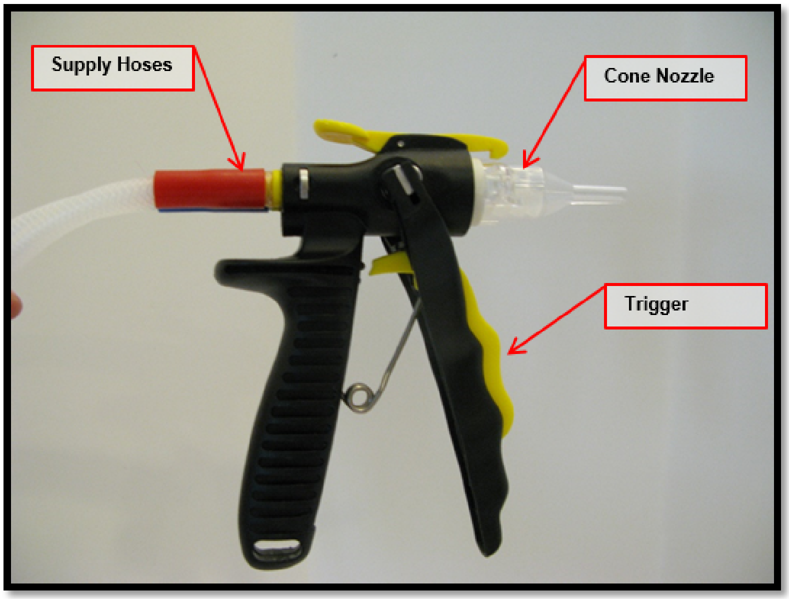

Figure 7. Photograph of SPUF Applicator Gun with Nozzles and Supply Hoses.

Safety and Personal Protective Equipment

The manufacturer of the SPUF kit outlined several safety and personal protective equipment (PPE) items, which should be used during the application of the SPUF product. These items were not supplied with the kit, however acquired through a locally accessible safety supply warehouse. For safety purposes, a class ABC fire extinguisher was kept on hand during all portions of the study. PPE used during this project included protective coveralls with boot and head covers, full-face respirator mask with organic vapor and HEPA particulate cartridges and heavy duty protective gloves. The model and manufacturer information for the PPE is listed in Table 10. Protective coveralls, gloves, and respirator cartridges were replaced prior to each trial.

Table 10. List of Personal Protective Equipment

Equipment	Use	Model	Manufacture
Coveralls	Body Protection	Tyvek	DuPont™
Gloves	Hand Protection	12" PVC; 660-L	Sperian
Respirator	Respiratory and Eye Protection	Full-face; 76008A	North
Respirator Cartridges	Respiratory Protection	7583P100	North

Data Collection Equipment

Data collection for this trial was conducted with both direct-reading data-logging instruments as well as active-integrated sampling with subsequent laboratory analysis. The direct-reading data-logging data collected included total organic compounds (tVOCs), carbon monoxide (CO), carbon dioxide (CO_2), ambient and wet-bulb air temperature, and relative humidity (RH). All direct-reading instruments were calibrated before and after the field investigation in accordance with their respective manufacturer's specifications. Applicable calibration techniques and documentation is further discussed in the calibration section of this study. A summary of the data collection techniques used in this trial are listed in Table 11.

Table 11. Summary of Data Collection Techniques

Parameter	Technique	Measurement Unit	Instrument/Model/Manufacturer
Glycols	active-integrated	µg	AirChek 52; and sorbent tube 226-57, SKC, Inc.
tVOCs	direct-reading	ppb	ppbRAE Plus & ppbRAE 3000, Ray Systems, Inc.
Temperature	direct-reading	^{o}F	Q-Trak™ IAQ Monitor, Model 7565, TSI, Inc.
Relative Humidity (RH)	direct-reading	%	Q-Trak™ IAQ Monitor, Model 7565, TSI, Inc.
Carbon monoxide (CO)	direct-reading	ppm	Q-Trak™ IAQ Monitor, Model 7565, TSI, Inc.
Carbon dioxide (CO_2)	direct-reading	ppm	Q-Trak™ IAQ Monitor, Model 7565, TSI, Inc.
Table Key ppb: Parts per billion ppm: Parts per million µg: Micrograms %: Percent ^{0}F: Fahrenheit			

TVOC Measurements

A ppbRAE Plus and a ppbRAE 3000 instrument, both manufactured by RAE Systems, Inc., were used to collected tVOCs measurements. Both instruments are direct-reading data-logging air analyzers have similar specifications, including detection range, resolution, and sensitivity. The ppbRAE 3000 instrument was used as a substitute for the ppbRAE plus instrument in the last two trials due to limitations in instrument availability. The calibration of this instrument is discussed in the calibration section and the factory calibration certificates can be found in Appendix C.

For the background study, the tVOC instrument was placed in survey mode, however during the three trials the instruments were placed in hygiene data-logging mode. The tVOC monitor uses a dual channel photo-ionization detector (PID) and an electrodeless discharge UV lamp as a high-energy photon source.[44, 45] As organic vapors pass by the lamp, they are photo-ionized and ejected electrons are detected as current, resulting in a reading on the digital display. The logged data was extracted from the instrument using manufacturer provided software referred to as ProRAE Suite.

Environmental Measurements

The ambient air temperature, wet-bulb temperature, RH, CO_2, CO concentrations, and atmospheric pressure were measured using a TSI Q-Trak™ IAQ Monitor, Model 7565 (Q-Trak) direct-reading data-logging instrument. This instrument was factory calibrated on May 7, 2014 to meet the Nation Institute of Science Technology (NIST) standards. The factory calibration certificates can be found in Appendix c. The time and date were entered into the instrument to synchronize with a master clock, which would be used for each trial. The Q-Trak was used to collect environmental measurements during trials 1 and 2.

The Q-Trak instrument has four sensors located in the detachable wand of the instrument. CO is collected by using an electro-chemical sensor and CO_2 collected using a nondispersive infrared (NDIR) sensor. Temperature and RH were determined using thermistor and thin film capacitive sensors, respectively. The data log information was retrieved using the TRAKPRO™ data analysis software provided with the instrument.

Active-integrated Sampling Measurements

The active-integrated sampling for glycols was conducted by constructing a standard industrial hygiene sampling train. The sampling train consists of a pump, a length of tubing, and a piece of sampling media.[46, 47, 48, 49] The sampling media for these studies were sorbent tubes.

Sorbent Tubes

For this study, SKC, Inc., product code 226-57, sorbent tubes were used to collect the glycols of interest, see Figure 9. The sorbent tubes used during this study were XAD brand which are resin tubes classified as porous polymeric sorbents.[50] The surface area of XAD tubes have less surface area than charcoal style sorbent tubes commonly used for sampling VOCs, resulting in a limited retention capacity.[50] The sorbent material is present in two sections, the first contains 100 mg and the back contains 200 mg of sorbent.[51] At the inlet of the tube, a section of filter is present before a piece of glass fiber filter (GFF) to trap the aerosolized glycols followed by two-sections of XAD sorbent material to adsorb glycol vapors. Foam plugs assist in holding the front and back sections in place. This design allows for separate evaluation of particulates and vapor phase exposures.[46] See Figure 8.

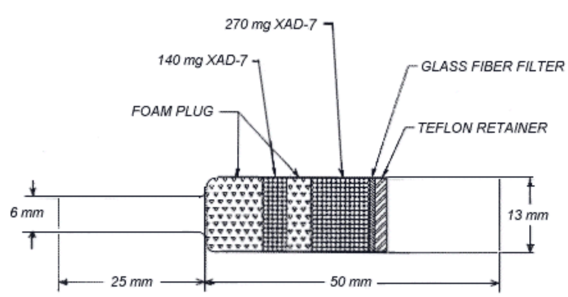

Figure 8. OSHA Schematic of Sorbent Media[37]

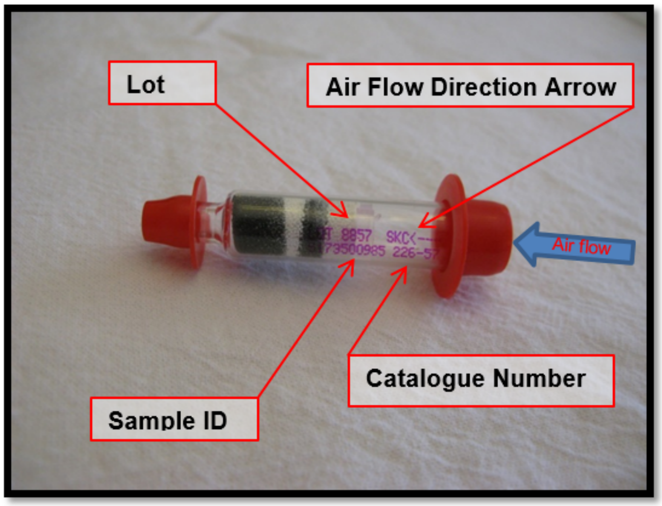

Figure 9. Photograph of Sorbent Tube.

PBZ Sampling Train Setup

In order to determine if applicators are exposed to glycols during the application of the SPUF, personal breathing zone (PBZ) samples were collected. For the PBZ sampling, a sampling train was assembled consisting of a personal air sampling pump, section flexible tubing, and sorbent tube media. The personal sampling pumps were calibrated using the methodology outlined in the calibration section of this study. The sorbent tube media was removed from its original package and all the pertinent data, such as sample identification and lot number were recorded.

Immediately before sampling, the small 6 mm diameter end protective cover of the sorbent tube was removed and the sample was attached to the end of the approximately 3 ft section of clear flexible tubing. The sampling tube was inserted into the open end of the Tygon tubing, making sure that the flow direction arrow was pointing toward the air sampling pump.

The air sampling pump was then attached to the applicator's belt. The sorbent tube media was attached to the applicators collar in a vertical position to avoid channeling and positioned so that it was vertical with the open end pointing downward, in the applicator's PBZ (within 12 in. of the applicator's face). The sampling train was also placed in such a manner as to limit the applicator's ability to perform the application or obstruct the sorbent tube inlet.

The pump was started and the flow reading was checked. The time, airflow reading on the pump, and other pertinent information was recorded on the sampling data sheet. The protective cap was removed just prior to the initiation of the SPUF application.

The PBZ air sampling pump was turned off at completion of the SPUF application and the time and the final pump data were recorded. The open air intake end of the sorbent tube was capped with the new caps provided by the laboratory. The sample was removed from the flexible tubing and the remaining open end was capped. The sorbent tube was properly labeled with the sample number that was indicated on the sampling data form. The sample was then placed in a container and the sample identifying information was written on the container. The container was placed in a laboratory supplied transport cooler.

Following the removal of the air sample, the primary calibration instrument was refitted and the flowrate was determined. The sampling time and volume sampled was recorded on the sample data form. After all the samples were collected, they were placed in the cooler. The samples were then sent to an AIHA accredited laboratory for analysis along with a field blank. The field blank was a sorbent tube from the same lot used for sampling. The blank was handled in the same manner as the collected samples, except that no air was drawn through it.

Area Sampling Train Setup

The background study and one of the trial studies utilized an area sampling methodology for the collection of glycols. For this type of sampling a sampling train consisting of a personal air sampling pump, flexible tubing, and sorbent material were used. For the area sampling, the sorbent tubes were placed at the end of a section of flexible tubing and mounted on a tripod, which extended to the approximate PBZ height.

Laboratory Methods & Analysis Techniques

Sorbent tubes used to collect the PBZ and area samples were sent to a laboratory for analysis. Air samples were analyzed using NIOSH Method 5523 for glycols, which was partially validation in May 1996.[42] The sorbent media was desorbed and analyzed for three specific glycol derivatives, ethylene glycol, propylene glycol, and diethylene glycol by the laboratory using NIOSH Method 5523.[42] Samples are desorbed with 2 mL methanol (ultrasonicated 30 min) and analyzed by gas chromatography (GC) using a flame ionization detector (FID).[42]

The laboratory reported the number of micrograms in both the front and back sections of the sorbent tubes and ppm based on the volume of air collected. Results of the sample analysis were provided by the laboratory approximately two weeks after submittal to the laboratory.

Equipment Calibration and Quality Control

The instruments were all calibrated either by the manufacturer or onsite prior to the use in the work area. The PBZ and area sampling trains were calibrated using a primary calibration device, a Defender 510 manufactured by Bios, Inc., which had previously been NIST calibration certified. The PBZ and area sampling trains were calibrated before and after sampling to accurately determine the volume of air sampled.

Pre-calibration to each sampling train was performed by connecting the air sampling train, consisting of the air sampling pump, flexible tubing and a representative piece of media, to the primary calibration device as seen in Figure 10. The air sampling pump was turned on and allowed to run for approximately five min. The “read” button was then depressed on the primary calibration device and the flowrate was measured. Five to ten measurements were recorded and averaged to determine the flowrate just prior to the air sampling during each trial. Following the collection of the air sample, a post calibration was conducted using the same methodology as the pre-calibration. The pre and post calibration rates were then averaged to get the final flowrate that would be used. Following the sample collection, a chain-of-custody was filled out for the collected samples. In addition, the expiration date and lot numbers were documented for each sorbent media tube collected.

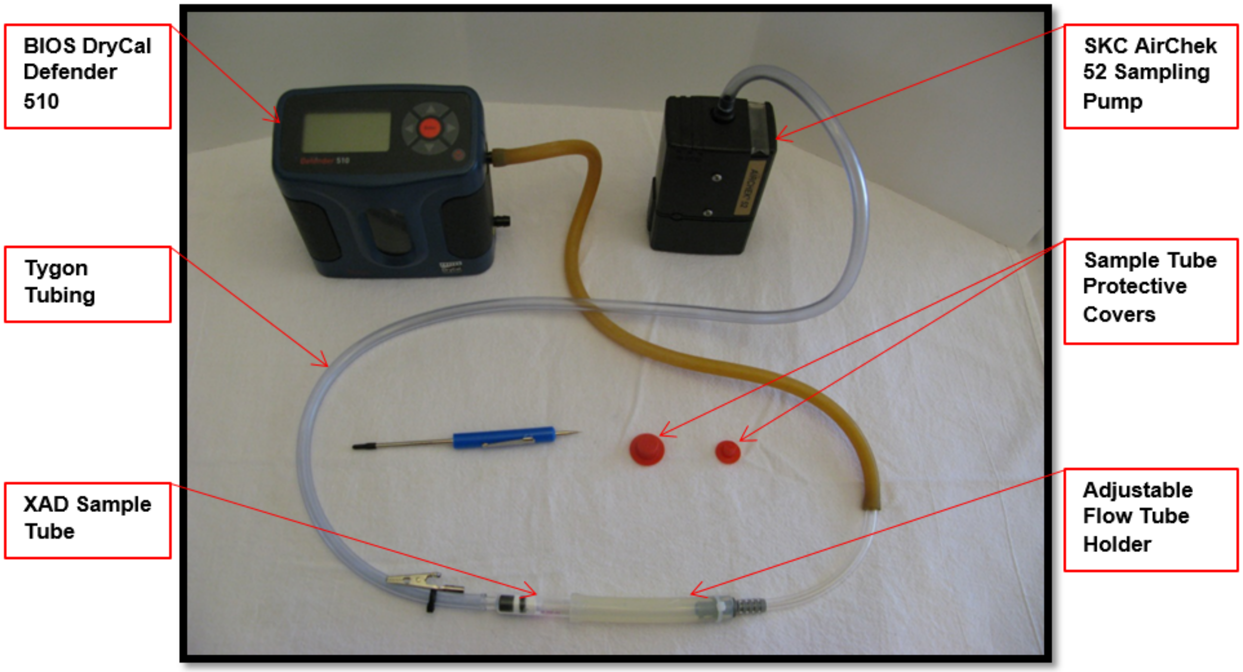

Figure 10. Photograph of Air Sampling Train Calibration Configuration.

The ppbRAE units were supplied with a factory calibration certificate; however, a field calibration was performed as well to verify calibration. The field calibrations required first zeroing the instrument with the provided charcoal filter. The zeroing procedure was done outside in the ambient environment to limit interference from existing tVOCs in the work area. Following the zeroing, the span was performed. The spanning is performed by using a span gas with a known concentration, in this case Isopropylene, at a known concentration (10 ppm) which was supplied with the instrument. The Q-track was calibrated to NIST standards and a copy was retained.

Background Study

Study Design

Following the preparation of the work area as previously described, a mock wall was situated centrally within the work area atop polyethylene sheathing. The mock wall remained in place during the background screening process. This was done in order to identify any tVOC emissions that may be emitted from the mock wall building materials, which would be present in each future trials. The work area was screened for glycols and tVOCs to obtain baseline data that would be used to determine the air quality conditions within the work area prior to the study. The purpose of obtaining area air samples was to determine if background measurements of glycols and/or tVOCs within the work area would influence the data collection during future trial studies. In addition, environmental measurements were collected during the screening for future comparison purposes. The background work area encompassed the entire garage space, which had an approximate volume of 1,688 ft^3.

Glycol Air Sampling Procedure

The glycol screening consisted of collecting one area sample using active sampling methods and sorbent tubes described previously. The area air sampling pump was calibrated following the methodology discussed. The area glycol sampling was conducted for 30-min at a flowrate of approximately 1.0 L/min, which is in-between the NIOSH recommend minimum and maximum recommended air sampling flowrates, 0.5 L/min and 2.0 L/min respectively.[42]

As seen in Figure 11, the area glycol screening air sample was collected at the PBZ level approximately 24 in. from the mock wall.

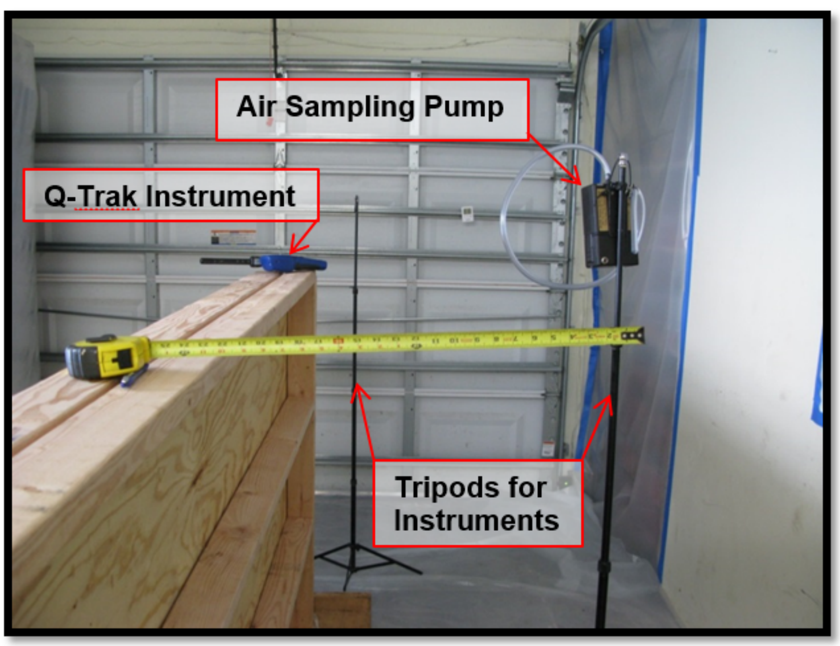

Figure 11. Photograph of the Area Sample Location

TVOC & Environmental Measurement Procedure

The work area was screened for tVOCs using the ppbRAE instrument placed on survey mode. The background screening for tVOCs included four steps: Initial screening, screening after removal of items, screen with fan running, and a screening just prior to the application of the SPUF.

During the initial screening, items that appeared to be associated with elevated VOCs (i.e. air compressor, tool storage area, paints and solvents,) were removed from the work area. The work area was then screened again to confirm the efficacy of the removed emissions sources.

Following the removal of the emissions sources, the work area was allowed to sit for 60 min, then the exhaust fan was turned on at the low setting. The area was then rescreened to ensure VOCs were not being drawn into the work area. The tVOC data was collected to determine if the potential existed for the make-up air, which air is entering the work area due to the volume of air being removed by the exhaust fan, contained significant measurements of tVOCs.

Environmental parameters collected including ambient temperature, wet-bulb temperature, RH, CO_2 and CO concentrations and atmospheric pressure were measured using the Q-Trak instrument, which was placed on a tripod at the PBZ level adjacent to the tVOC instrument.

Trial No. 1 Ventilated Work Area Preparation

Trial Design

Following the work area preparation as described in the Background Study, one mock wall was situated in the middle of the work area. The mock wall for this trial was framed on both sides of the plywood sheathing to provide six cavities or 64 ft^2 of surface area for potential SPUF application. During this trial, the previously discussed exhaust fan was turned on to allow for ventilation of the work area. The ventilation was measures to be 9.75 ACH using the previously evaluation methodology outlined. For Trial No. 1, the work area included the entire garage space, which measured 8.33 ft x 9.5 ft x 21.33 ft and had an approximate volume of 1,688 ft^3. The total area for SPUF application was 64 ft^2. The SPUF material was applied at a pace to achieve a nominal thickness of 1.5 in.

Glycol Air Sampling Procedure

In an effort to mimic exposure that may be encountered by a typical SPUF applicator, samples were collected from the applicators PBZ as earlier discussed. For Trial No. 1, two personal air sampling pumps were utilized to simultaneously collect PBZ air samples at different flowrates, 0.5 L/min and 2.0 L/min, which are representative of the minimum and maximum flowrates provided by the NIOSH Method 5523. The air sampling pumps were calibrated with the primary calibration device using the methodology earlier described.

The sorbent tube media was removed from its original package and all the pertinent data was recorded on the sample data form. Immediately before the sampling, the small diameter end protective cover of the sorbent tube media was removed and the sample was attached to the end of the approximately 3 ft section clear flexible tubing. The larger diameter end of the sorbent tube remained capped. The air sampling pump was then attached to the applicator's belt and the sorbent tube media was attached to the applicator's collar in the PBZ. The sorbent tube end cap was removed just prior to the initiation of the application of SPUF application.

The PBZ air sampling pump was turned off at completion of the SPUF application and the time and the final pump counter were recorded. The open air intake end of the sorbent tube was capped and removed from the flexible tubing at which time the remaining open end was capped. The sorbent tube was labeled with a sample number then placed in a container provided by the laboratory. The sample was placed in a laboratory-supplied transport cooler.

Following the removal of the air sample, the primary calibration instrument was refitted and the flowrate was determined. The sampling time and volume information was recorded on the sample data form.

After all the samples were collected they were placed in the cooler prior to sealing. The air samples were then sent to an AIHA accredited laboratory for analysis along with a field blank. The field blank was a sorbent tube from the same batch used for sampling. The blank was handled in the same manner as the sample sorbent tubes, except that no air was drawn through it.

TVOC & Environmental Measurement Procedure

Both the tVOC and environmental measurement instruments were placed at the end of the mock wall with their respective detection sensors placed at the PBZ height during the SPUF application. The instruments were programed to continuously data-log starting 30-min prior to the initiation of the SPUF application and run for 30-min following the ending of the SPUF application.

SPUF Application Procedure

Prior to initiating the SPUF application, equipment including hoses, spray gun, and nozzles were assembled and connected to the A and B components cylinders.

A petroleum lubricant was placed on each of the connecting fittings to assist in disassembly following the SPUF application. To initiate the SPUF application PPE was donned and the cylinder valves for both A and B components were opened. The SPUF was first applied along the edges of the cavity walls, the remaining portion of the cavity was filled in a horizontal pattern. The SPUF material was applied at a pace to achieve a nominal thickness of 1.5 inches, which resulted in an 8-min applications time. See Figure 12.

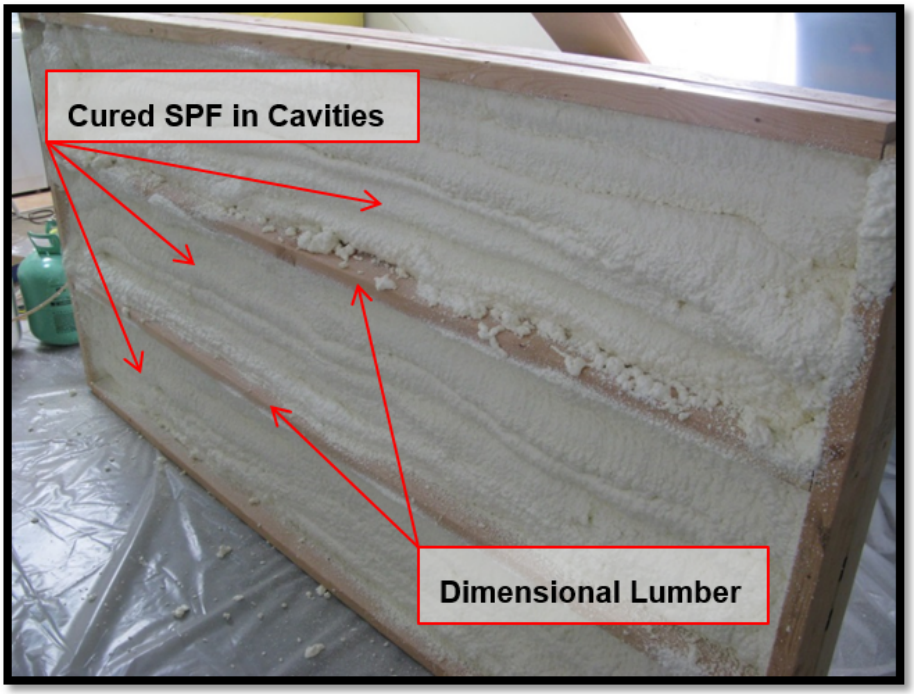

Figure 12. Photograph of Cured SPUF on Mock Wall.

Trial No. 2 Non-Ventilated Work Area Preparation

Trial Design

Based on the results of Trial No. 1, a second trial (Trial No. 2) was conducted implementing two notable modifications to the work area and one modification to the SPUF application quantity. The first modification to the work area was the elimination of the exhaust fan providing ventilation. The second modification was the reduction of the size of the work area.

The new work area was constructed using one mock wall section, wood framing, and polyethylene sheathing to form a small work area enclosure as seen in Figure 13. The enclosure was fitted with flaps of polyethylene sheathing on one end for access and egress purposes. The size of the work area measure 4 ft x 4 ft x 8 ft in and had an approximate volume of 128 ft^3. The total area for SPUF application was reduced to 32 ft^2.

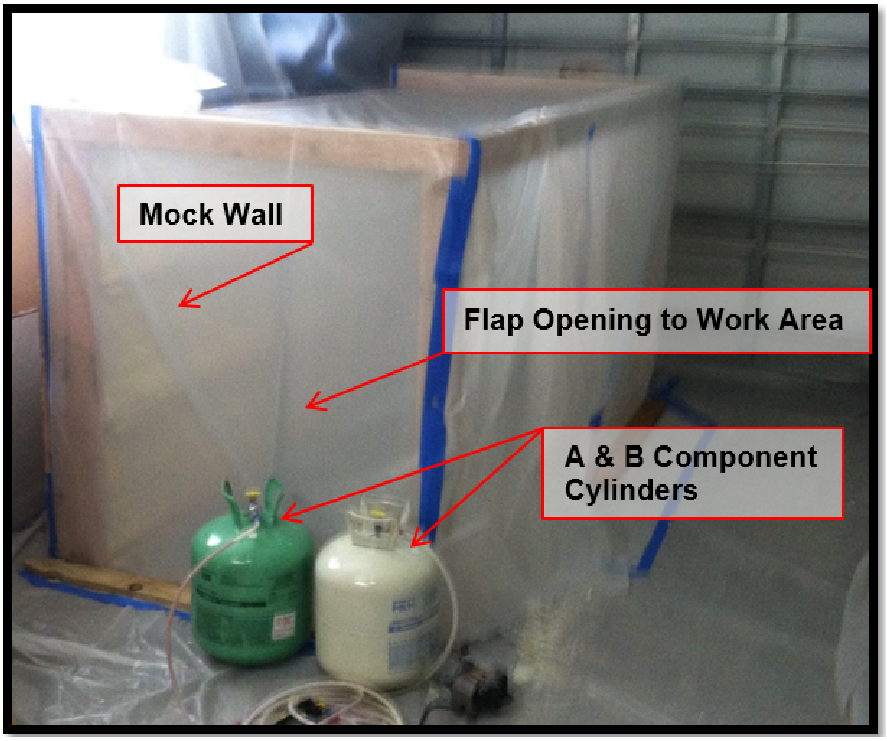

Figure 13. Photograph of Work Area of Trial No. 2.

Glycol Sampling Procedure

For Trial No. 2, the air sampling collection was modified in order to establish whether any glycols were released during the SPUF application. Two air samples were collected, one PBZ sample and one area sample. For the PBZ sample, a flowrate of 2.0 L/min was used and for the area sample a flowrate of 10.0 L/min was used. The samples were collected simultaneously during the SPUF application. Similar to the previous studies, the air sampling pumps were calibrated with the primary calibration device using the methodology described previously. Both PBZ and area sampling trains were set up as earlier discussed. The handling of the sorbent tube media and post calibration methodologies were the same as the previous two studies.

SPUF Application Procedure

The SPUF equipment was prepared in the same fashion as Trial No. 1, with the exception that the mock wall application area was reduced to only one side of the mock wall, or three cavities for a total SPUF application area of 32 ft^2. Similar to the previous trial, the desired cure SPUF thickness was 1.5 inches. See figure 13.

Trial No. 3 Work Area Preparation

Trial Design

Based on the results of Trial No. 2, a final trial was conducted. For Trial No. 3, one modification of the work area and one air monitoring modification were implemented during the SPUF application. For this trial, the work area was modified by using a mock wall for each side of the work area enclosure. The purpose for this modification was to increase the available surface area onto which the SPUF could be applied. The size of the work area for this trial measured 4 ft x 4 ft x 8 ft in length and had an approximate volume of 128 ft^3. The total area for SPUF application was approximately 64 ft^2. The air monitoring was modified from the previous trial by eliminating the area sample and collecting two PBZ air samples.

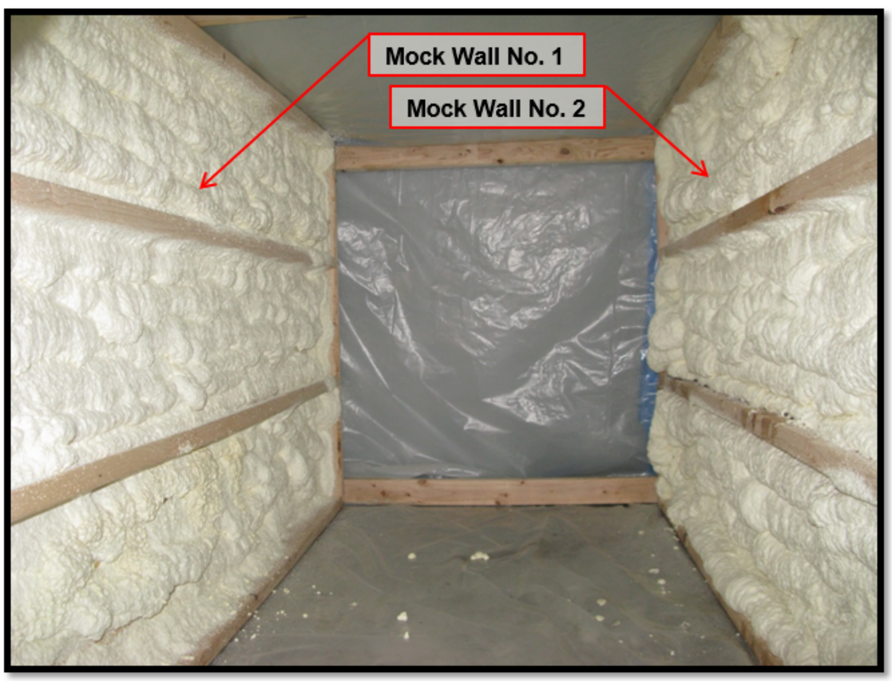

Figure 14. Photograph of Trial No. 3 Work Area with Applied SPUF on Two Mock Walls.

Glycol Sampling Procedure

Based on the results of Trial No. 2, the PBZ air sampling was collection conducted again, however in this instance; it was conducted in duplicate, utilizing two personal air sampling pumps. Both air sampling pumps were set to a flowrate of approximate 2.0 L/min. The samples were collected simultaneously, with each sample placed on the collar of the SPUF applicator. Both PBZ sampling trains were set up and the handling of the sorbent tube media and pre and post calibration methodologies were the same as the previous two studies.

TVOC & Environmental Measurement Procedure

Both the tVOC and environmental measurement instruments were placed at the end of the work area enclosure with their respective sensors placed at the PBZ height during the SPUF application. The instruments were programed to continuously data-logging starting approximately 30-min prior to the initiation and approximately 30-min following the ending of the SPUF application.

SPUF Application Procedure

The SPUF equipment was prepared in the same fashion as in Trial No. 2, with the exception that the mock wall application area was increased to include two mock walls, or six cavities for a total SPUF application area of 64 ft^2. Similar to the previous trial the cured SPUF thickness of 1.5 inches was desired. See figure 14

Summary of all Trials Modifications

During the course of the SPUF application, several modifications were made from the original trial design to subsequent studies. These modifications were made based on the results of each trial.

Table 12. Summary of Trial Modifications

Parameter	Trial No. 1	Trial No. 2	Trial No. 3
Work Area Volume	1,688 ft^3	128 ft^3	128 ft^3
SPUF Application Area	64 ft^2	32 ft^2	64 ft^2
Ventilation	On	Off	Off
Air Sampling	1 PBZ at 0.5 L/min 1 PBZ at 2.0 L/min	1 PBZ at 2.0 L/min 1 Area at 10.0 L/min	2 PBZ at 2.0 L/min
Table Key L/min: Liters per minute PBZ: Personal breathing zone Ft^3: Cubic Feet Ft^2: Square feet			

CHAPTER 4: RESULTS

This study included three SPUF application events, which are referred to as Trial No.1, Trial No. 2, and Trial No. 3. The purpose of each study was to determine if there was a release of glycol derivatives including, diethylene glycol (DEG), ethylene glycol (EG), and propylene glycol (PEG), resulting in an applicator exposer. In addition, tVOCs and environmental parameters were also collected during this research. During this study several modifications were made to the work area and the air sampling methodology to assist in verifying the presence of the glycols and the conditions in which they may be present in the air during the application of SPUF insulation. All samples were sent to an American Industrial Hygiene Association (AIHA) accredited laboratory and were analyzed by NIOSH Method 5523.

Background Study

A background study of the work area, which included the entire space of a residential garage, was conducted to gather baseline information and to determine the acceptability of the selected location to conduct future studies. For purposes of this study, it was necessary to collected background levels of glycols derivatives, tVOCs, CO_2, and CO.

The air sample results indicated there were no measureable background concentrations of glycol derivatives, which would interfere with the study. Direct-reading instrument measurements indicated that there were measureable amount of tVOCs, CO_2, and CO. In addition, ambient temperature, wet-bulb, and RH were measured. All of the direct-reading measurements were taken into consideration when comparing data collected pre- and post SPUF application in each of the three studies. During the background study, a ventilation system was developed to provide exhaust air from the work area. Through qualitative and quantitative measurement, the ventilation system was determined to be providing 9.75 ACH.

The background data collection included collecting active area air sampling for glycols for 30-min with a personal sampling pump adjusted to approximately 1.0 L/min. This resulted in a total air volume collected of 22.99 liters of air. The sample was collected at the PBZ height at a distance of 24 in. from the mock wall. The laboratory analysis indicated no glycol derivatives above the LOD. Environmental measurements including ambient temperature, wet-bulb, RH, CO_2 and CO were measured. The tVOC concentrations measured were used as a baseline for comparison during SPUF application. Data-logging information collected in the background study is shown in Figure 19 for comparison purposes.

Trial No. 1

Trial No. 1 was configured using the entire garage space as the work area and included the exhaust ventilation system to control air exchanges. During this trial sampling included active PBZ air sampling for Glycols. Two PBZ glycol samples were collected with personal sampling pumps during the application of SPUF. The air sampling pumps were adjusted to approximately 0.5 L/min and 2.0 L/min and resulted in total air volumes of 4.088 and 15.88 liters of air respectively. The total sample time for these samples was approximately 8-min, which coincided with the time to fill both 4 ft x 8 ft sections of mock wall containing six cavity bays, or 64 ft^2. The laboratory analysis indicated that no glycol derivatives above the LOD were present.

Trial No. 1 also included direct-reading instrument monitoring for tVOCs, which were measured approximatly 30-min prior to and after the SPUF application. Figure 15 shows the monitoring data for the entire period including during the application of the SPUF. For Trial No. 1, tVOC measurements from the time of the start of the application (18:02:21) began to increase until the application was stopped (18:10:21) as seen in Figure 16. During the study, a clear increase in tVOCs, reaching a maximum measurement over 600 ppm during the SPUF application was followed by a slow reduction after completing the application.

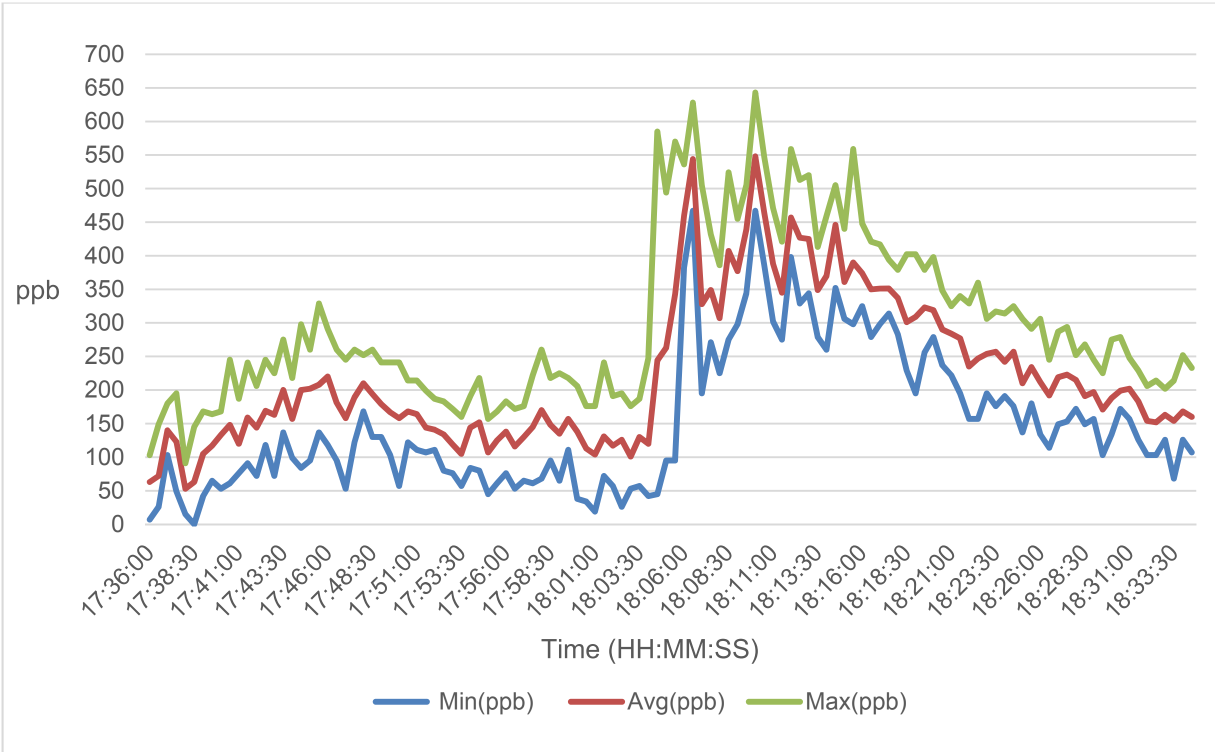

Figure 15. Comparison of Measured TVOCs During Background and Trial No. 1.

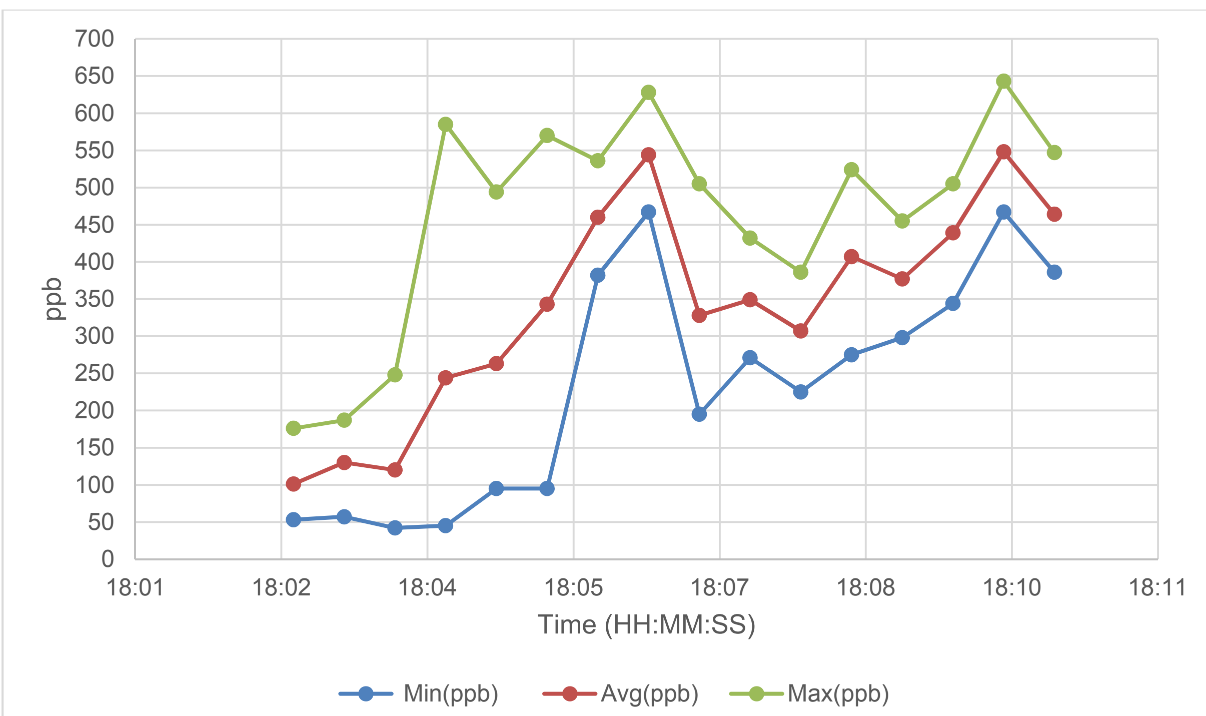

Figure 16. Trial No. 1 tVOCs Results Measured During SPUF 8 Minute Application.

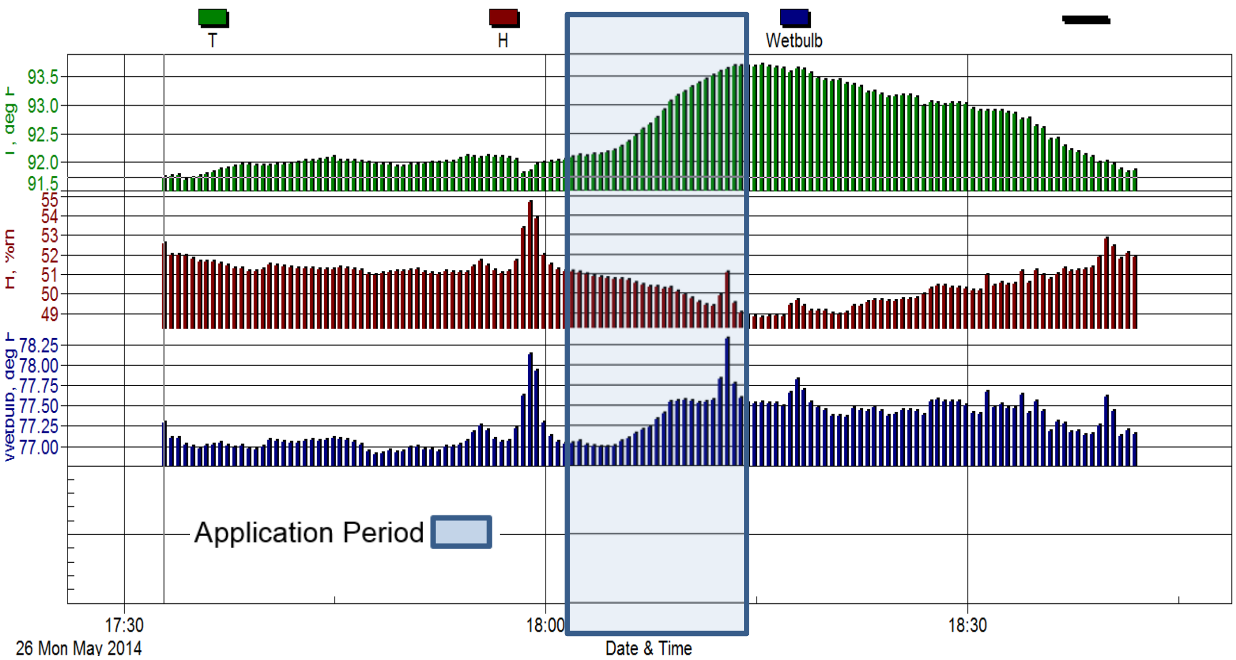

Figure 17. Trial No. 1 Temperature, RH, & Wet-bulb Measurements During SPUF Application and Entire Trial

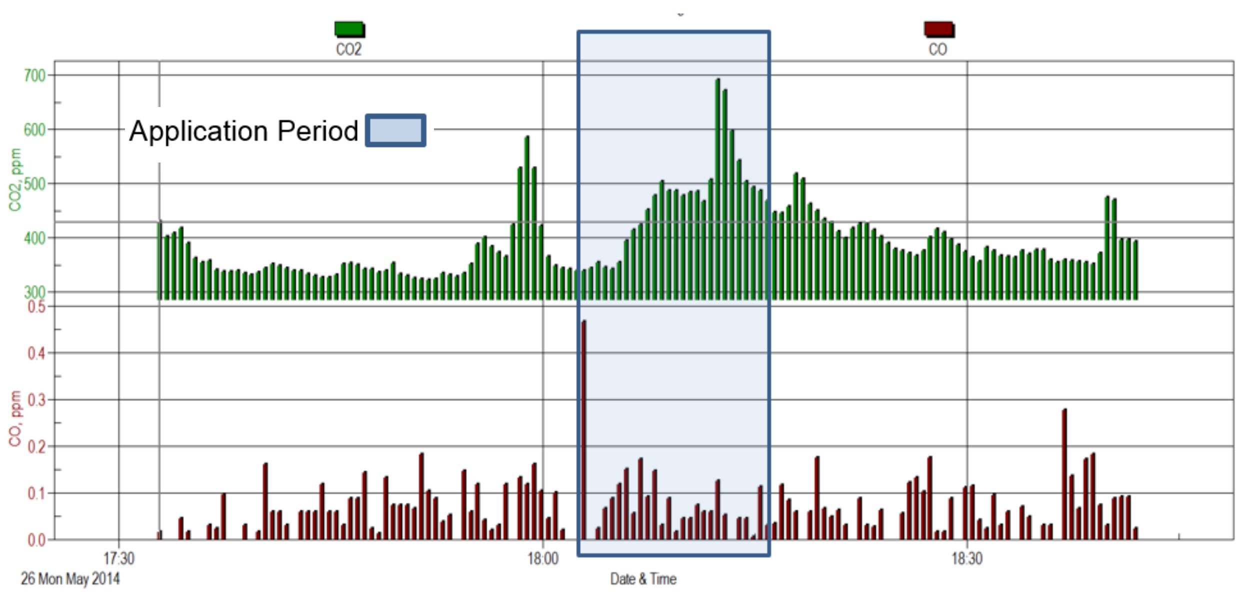

Figure 18. Trial No. 1 CO and CO_2 Measurements During Application and Entire Trial

Environmental measurements including ambient temperature, wet-bulb temperature, RH, CO_2 and CO were measured and are presented in Figures 17 and 18. The work area ambient temperature ranged from 92.1 to 93.3°F , and the wet-bulb temperature ranged from 77.0 to 77.6°F .

The work area RH measurements ranged from 49.7 to 51.0%. The direct-reading data-logging information for the ambient and wet bulb temperature and RH presented an inverse relationship, where when the ambient and wet bulb temperature was increasing, RH was decreasing during the application of the SPUF. The work area CO_2 readings ranged between 339 ppm and 504 ppm. The work area CO readings ranged between 0.0 ppm to 0.5 ppm. The direct-reading results are shown Figures 17 and 18.

Table 13. Trial No. 1 Summary of Direct-Reading Measurements

SPUF Application Data	Start (18:02:21)	Finish (18:10:21)	Min During Application	Max. During Application
Temperature (^{0}F)	92.1	93.1	92.1	93.3
RH (%rh)	51.0	49.7	49.7	51.0
Wet-bulb (^{0}F)	77.1	77.6	77.0	77.6
CO (ppm)	0.0	0.0	0.0	0.5
CO_2 (ppm)	340	484	339	504
tVOC max (ppb)	195	547	101	643

Table Key
ppb: Parts per billion
ppm: Parts per million
%: Percent
^{0}F: Fahrenheit

The SPUF component cylinder weights were measured prior to initiation of the SPUF application. Following the application, the cylinders were re-measured and it was determined that 11.4 lbs of A component and 9.6 lbs of B component were used during the 8-min study.

Trial No. 2

Given that glycols were not detected in Trial No. 1, a second study (Trial No. 2) was conducted with modifications to both the work area and the air sampling strategy. The modifications were done to represent more stringent conditions (i.e. less volume, no ventilation), such as what might be found in an attic space. The work area modifications included eliminating the exhaust fan as well as constructing a small enclosure to represent a small work area. The enclosure was constructed using one mock wall, wood framing, and polyethylene sheathing. The sampling strategy was modified to include area air sampling in concert with PBZ air sampling for glycols. The PBZ air sampling pump was adjusted to approximately 2.0 L/min and area air sampling pump was set at a flowrate of approximately 10.0 L/min.

Application time of SPUF during this study was 5 min 30 sec, which was the time needed to fill the 4 ft x 8 ft section of mock wall. The total air volumes collected were 11.05 liters and 55.0 liters, the PBZ and area sample respectively. The laboratory analysis identified glycol derivatives, diethylene glycol and propylene glycol. However, ethylene glycol was not detected above the LOD.

The component cylinder weights were measured prior to initiation of the SPUF application. Following the application, cylinders were re-measured and it was determined that 5.4 lbs of A component and 4.2 lbs of B component were used during the 5 min 30 sec study.

Trial No. 3

The detailed parameters of Trial No. 3 were developed based upon the results of the first two trials. Ventilation and the work area volume remained unchanged from Trial No. 2 with the exception of the installation of one additional panel of mock wall for SPUF application. The sampling strategy was also modified to include duplicate PBZ air sampling pumps for glycols.

The work area ambient temperature ranged from 88.5°F to 99.9°F, and the wet-bulb temperature ranged from 76.7°F to 81.2°F. The work area RH measurements ranged from 43.6 to 59.3%. The work area CO_2 readings ranged between 2,542 ppm and 4,076 ppm. The work area CO readings ranged between 0.0 ppm to 1.0 ppm.

Both PBZ air sampling pumps were set to a flowrate of approximately 2.0 L/min. The application time of SPUF during this study was 11 min 54 sec, which coincided with the time to fill the two 4 ft x 8 ft sections of mock wall containing six cavity bays. The total air volumes collected in this study were 23.55 and 23.38 liters for PBZ samples. The laboratory analysis during this sampling event identified glycol derivatives, diethylene glycol and propylene glycol above the LOD.

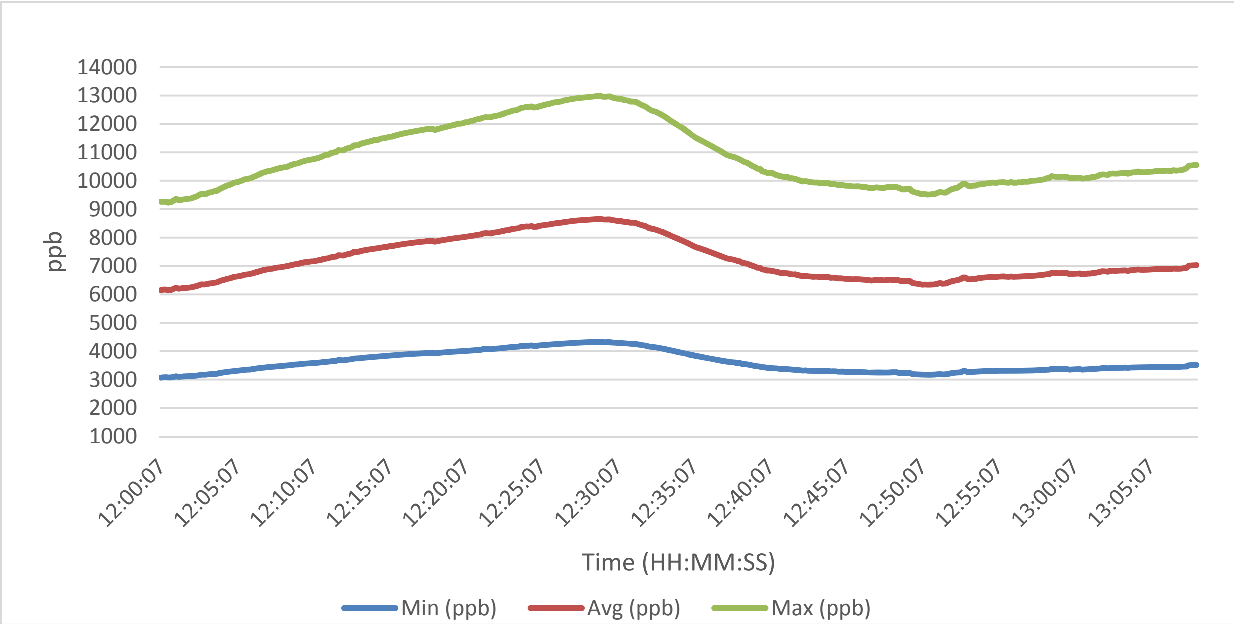

Figure 19. Trial No. 3 TVOC Measurements Collected During Entire Study

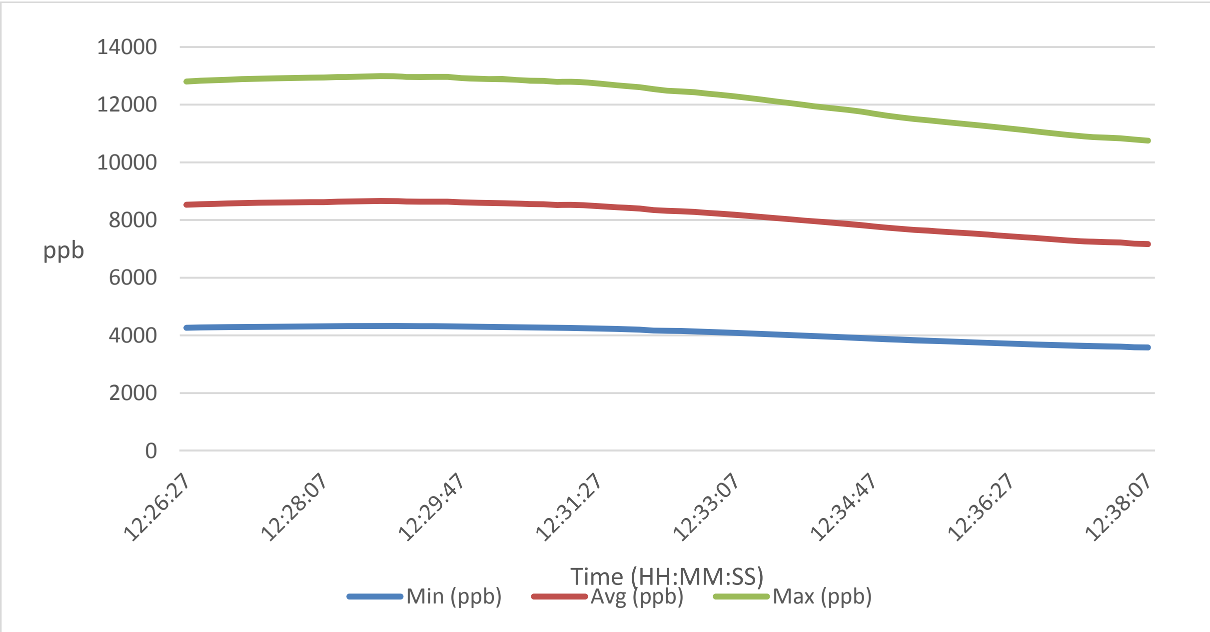

Figure 20. Trial No. 3 TVOC Measurements SPUF Application Only

Figure 19 shows the tVOCs prior to the initiation, during, and after the application of the SPUF. During Trial No. 3, a decrease in tVOCs can be seen during the application.

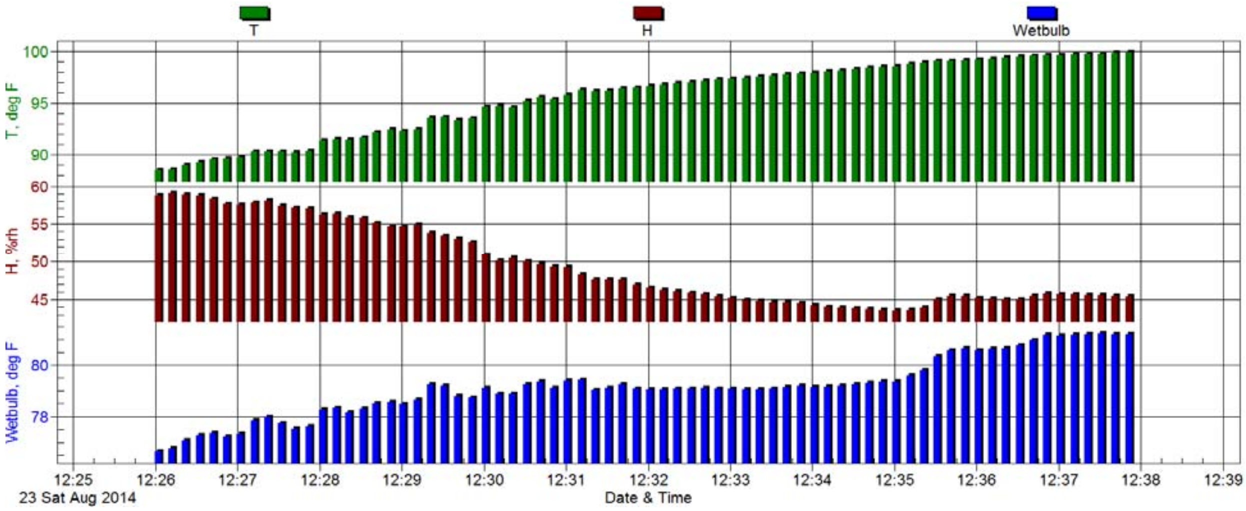

Figure 21. Trial No. 3 Temperature, RH, and Wet-bulb Measurements During SPUF Application.

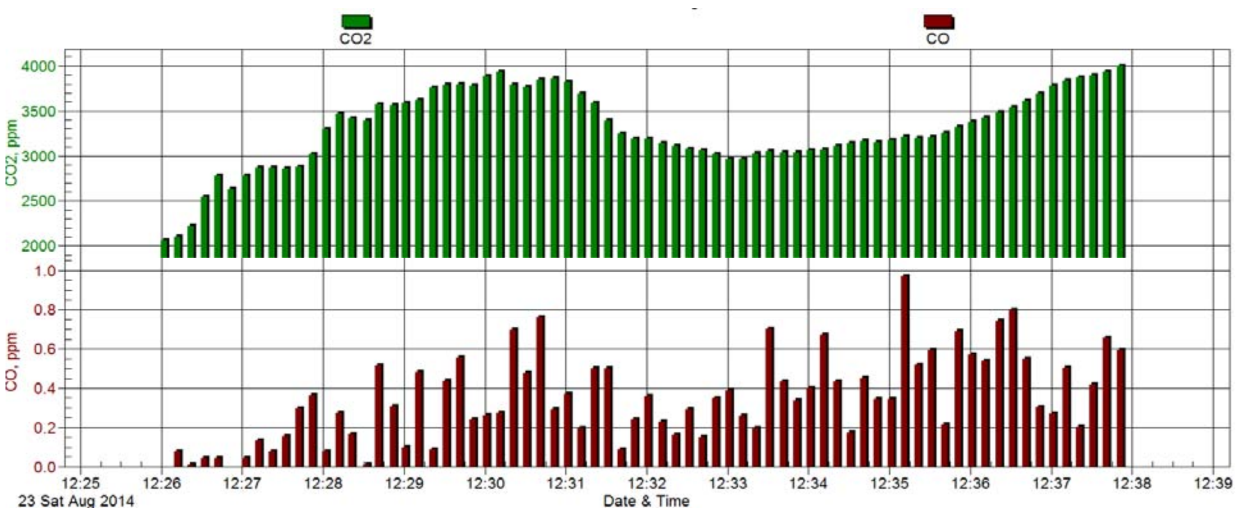

Figure 22. Trial No. 3 CO & CO_2 Measurements during SPUF Application

For Trial No. 3, the tVOC measurements at the time of the start of the application (12:26:30) began to increase until the application was stopped (12:38:00) as seen in Figure 21. The direct-reading data-logging information for the temperature, wet-bulb, and RH presented an inverse relationship, in which the temperature was increasing and the RH was decreasing during the application on of the SPUF.

The component cylinder weights were measured prior to initiation and following the application. When the cylinders were re-measured, it was determined that 12.6 lbs of A component and 9.8 lbs of B component were used during the 8-min study.

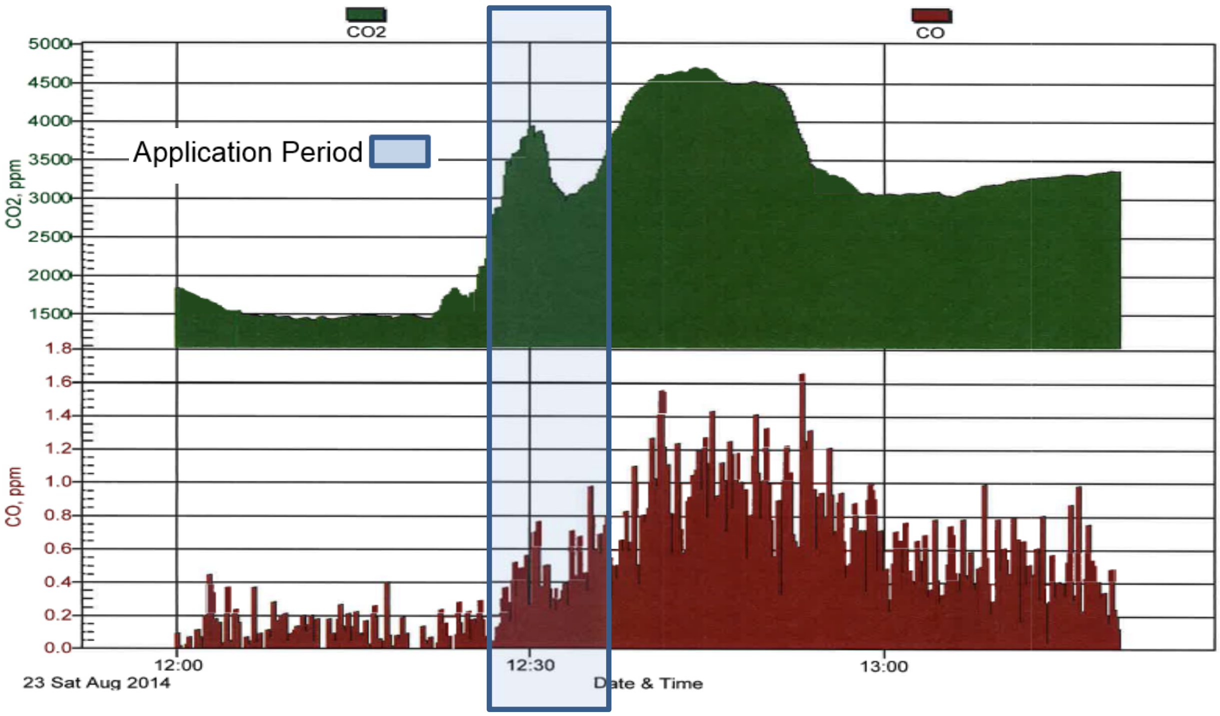

Figure 23. Trial No. 3 CO_2 and CO Measurement Collected During SPUF application.

Table 14. Trial No. 3 Summary of Direct-Reading Measurements

SPUF Application Data	Start (12:26:30)	Finish (12:38:00)	Min During Application	Max. During Application
Temperature (^{0}F)	89.3	99.9	89.3	99.9
RH (%rh)	58.7	45.3	43.6	58.7
Wet-bulb (^{0}F)	77.3	81.2	77.2	81.2
CO (ppm)	0.0	0.6	0.0	1.0
CO_2 (ppm)	2542	4076	2542	4076
tVOC max (ppb)	4271	3588	3588	4335
Table Key ppb: Parts per billion ppm: Parts per million		%: Percent ^{0}F: Fahrenheit		

The laboratory provided the analytical results in both mg/m^3 and ppm. The laboratory used Equation 5 to provide these results in mg/m^3 and Equation 5 and 6 to provide the results in ppm.

Table 15. Summary of Glycol Air Sampling Data Collection

Study ID	Background	Trial No. 1	Trial No. 1	Trial No. 2	Trial No. 2	Trial No. 3	Trial No. 3
Sample ID	BKG-052614	PILOT 05052614	PILOT 2052614	5173500925	5173500840	PBZ-901230	PBZ-901180
Date	5/26/14	5/26/14	5/26/14	7/13/14	7/13/14	8/23/14	8/23/14
Lab Report	L319636	L319636	L319636	L323368	L323368	L326587	L326587
Diethylene Glycol (ppm)	<0.099	<0.56	<0.14	0.4	0.32	0.28 (0.22)**	0.11 (0.
Diethylene Glycol (µg)	<9.9	<9.9	<9.9	19	77	29 (23)**	11 (5)
Ethylene Glycol (ppm)	<0.17	<0.94	<0.24	<0.35	<0.070	NA	NA
Ethylene Glycol (µg)	<9.8	<9.8	<9.8	<9.8	<9.8	NA	NA
Propylene Glycol (ppm)	<0.14	<0.78	<0.20	0.42	*0.37	0.25 (0.16)**	<0.14
Propylene Glycol (µg)	<9.9	<9.9	<9.9	14	*63	18 (12)**	<9.9
Sample Type	Area	PBZ	PBZ	PBZ	Area	PBZ	PBZ
Location	PBZ”24" from Mock wall	PBZ	PBZ	PBZ	AREA	PBZ	PBZ
Flow rate (L/min)	1.0	0.5	2.0	2.0	10.0	2.0	2.0
Duration	30 min	8 min	8 min	5.5 min	5.5 min	11.54 min	11.54 min
Volume of Air (L)	22.99	4.088	15.88	11.05	55	23.55	23.38

Table Key

PBZ: Personal breathing zone
ppm: Parts per million
L: Liters
L/min: Liters per minute

<: Less than the LOD
µg: micrograms
min: Minute

**Note 1: For Trial No. 2, propylene glycol, was detected in the back section of the sorbent tube, this suggest a breakthrough may have occurred.*

***Note 2: For Trial No. 3 According to the laboratory there may have been contamination of diethylene glycol; the instrument blank, the eluent blank and the media blanks recovered ~6.5 ug. It is believed that the contamination may be instrument related. According to the laboratory, samples from Trial No. 3 may be biased high due to this contamination.*

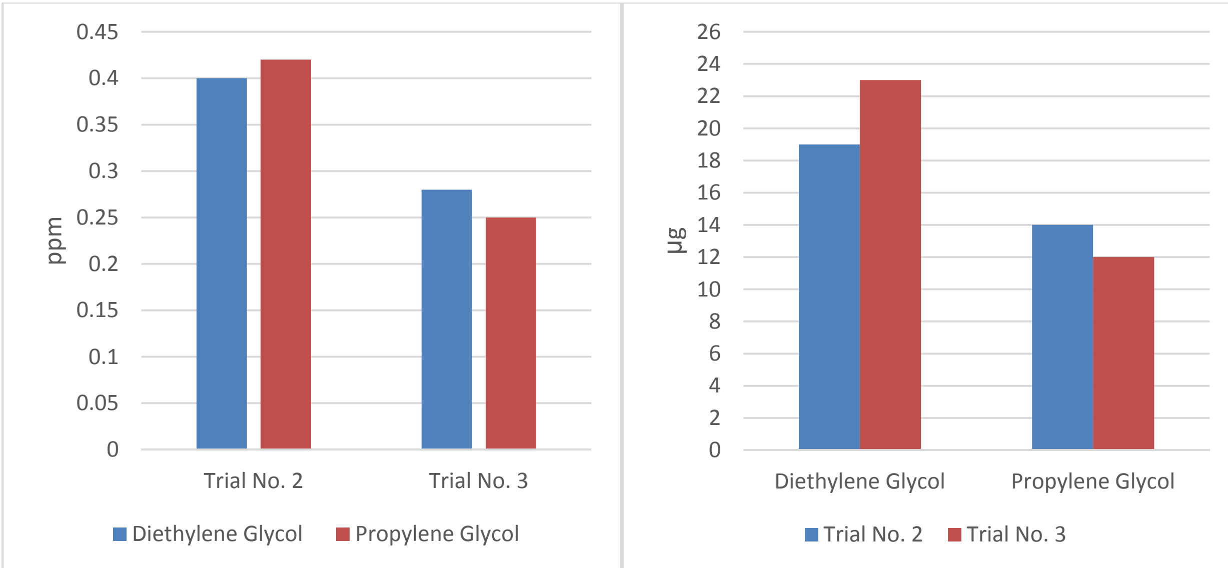

Figure 24. Comparison of Laboratory Results for Trial 2 and 3 in µg and PPM.

Equation 5. Laboratory Calculation to Determined PPM.

$$\frac{\text{Detected in µg}}{\text{Air volume in m}^3} = \text{mg/m}^3$$

Where,

µg = is the mass concentration detected by the GC analysis

m^3 = is the volume of air reported by the sampler

The results were reported by the laboratory in ppm and the available OELs for the glycols were listed in mg/m^3. The OELs were converted to ppm using Equation 6 provided by the ACGIH for comparison purposes.[52] The molecular weights for each glycol evaluated in this study are listed in Table 3.

Equation 6. Mg/m^3 to PPM Conversion at NTP

$$\text{ppm} = \frac{\left(\frac{\text{mg}}{\text{m}^3}\right)(24.45)}{\text{MW}}$$

Where,

24.25 = molar volume
MW = gram molar weight of substance
ppm = parts per million
mg/m^3 = milligrams per cubic meter

The result of Equation 6 for diethylene glycol is 1.7 mg/m^3 x 24.45/106.12 = 0.391 ppm.

To adjust for the detection of diethylene glycol reported by the laboratory blank, the laboratory concentrations were corrected by reducing the reported value by 6 µg. The ppm concentrations were then recalculated using Equations 5 and 6. The corrected values are presented in Table 15.

According to the SDS provided from the manufacturer, diethylene glycol can comprise up to 10% by weight of the polyol B Component. It is anticipated that a significant portion of diethylene glycol will be reacted during the chemical curing as it is necessary to form the SPUF cell structure. We can calculate what the saturation air level would be if enough liquid would simply be left in a room to evaporate using Equation 7. The percent of propylene glycol was not indicated in the SDS for this calculation.

Equation 7. Predicted Glycol Concentration Based on Vapor Pressure

$$ppm = \frac{P_V}{P_{atm}} \times 10^6$$

Where,

P_v = vapor pressure of diethylene glycol (0.01 mmHg)[42]
ppm = parts per million
P_{atm} = vapor pressure at NTP (760)

The result using Equation 7 is 0.01/760 x 10^6 = 13.16 ppm, which would be more than double the OEL of 5.43 ppm.

CHAPTER 5: DISCUSSION

In total, this research study included three SPUF applications, referred to as trials, to measure the release of glycol directives including DEG, EG, and PG, into the air. Once the release of glycols was confirmed, the goal of the research was to determine the potential exposure concentration to which an applicator may be subjected. Glycols were measured using active sampling techniques and supplementary parameters including tVOCs, ambient and wet-bulb temperature, RH, CO, and CO_2, were measured using direct-reading techniques.

During this study air sampling was conducted for glycols derivatives during all three trial applications. For Trial No. 1, the laboratory analytical results indicated that there were no detectible measurements of glycols in either of the PBZ samples collected at the minimum and maximum recommended NIOSH air sampling flow rates. This resulted in several modifications prior to initiating Trial No. 2. This was done in an attempt to increase the potential for detecting glycols and determining if a measureable amount was obtainable. To accomplish this, the exhaust fan system was eliminated, the work area was reduced, and the air sampling was modified to collect one PBZ sample and one area sample. The modifications done in Trial No. 2, which are summarized in Table 12, resulted in the detection of glycol derivatives, including DEG and PG as seen in Table 15 and Figure 24. Based on these results, Trial No. 3 was conducted with the same work area volume as Trial No. 2, however the SPUF application area was doubled. The PBZ air sampling again resulted in the detection of diethylene glycol and propylene glycol, shown in Table 15 and Figure 24. The results of the trials indicated that diethylene glycol and propylene glycol were indeed emitted during the application process. Ethylene glycol was not detected given the laboratory methods and subsequent LOD used in this analysis.

The side-by-side duplicate samples collected in Trial No 3 at similar air flow rates resulted in two significantly different detection results for both diethylene glycol and propylene glycol. In Trial No.3, the corrected results for diethylene glycol were 23 µg and 5 µg. Propylene glycol sample results were similar in variation. The samples had nearly identical flow rates and were situated parallel to each other, presumably capturing an air sample in the same location.

It is suspected that the hose from one of the pumps may have been kinked or the sampling tube may have been partially blocked by the Tyvek suite material however, neither of these situation can be confirmed.

Because of the limited number of samples and the variation between the side-by-side samples, it is difficult to assume a generation rate. Similarly, a buildup rate for the detected glycols could not be determined without making numerous assumptions.

During the initial Trial No. 1 and again during the final Trial No. 3, tVOCs were measured. The purpose of obtaining area tVOC measurement during this study was to determine if the application of SPUF results in the generation of tVOCs within the work area. The work area tVOC measurements were not intended to be used as a substitute for personal exposure sampling, but to determine if a significant level was produced. For Trial No. 1, there was a clear increase in tVOC concentrations during the application of the SPUF, which can be seen in Figure 16 and 17. However, the results from Trial No. 3 contradicted Trial No. 1 results. A decrease in tVOCs during Trial No. 3 application was measured and is shown in Figure 19. The difference in the results is not completely known, and is an area for potential future research. Different instruments were used for each of the studies, ppbRAE Plus and ppbRAE 3000. Both were from the same manufacturer, have similar specifications, and were calibrated in the same fashion. The range and accuracy of the instruments are similar, although the ppbRAE 3000 has a larger reference library.

Ambient and wet-bulb temperature as well as RH were collected in Trial No. 1 and 3 using a direct-reading instrument prior to, during, and after each study. This was to determine if there was a substantial increase in levels during the application of the SPUF. During both studies, an increase was measured for both ambient and wet-bulb temperatures during the application of the SPUF. At the same time, a decrease in RH was measured as seen in Figures 17 and 21. This inverse relationship is not surprising, however, the degree of temperature change (+10°F) in Trial No. 3 suggest that the chemical reaction produces a significant amount of heat.

CO_2 and CO were collected in Trial No. 1 and 3 using a direct-reading instrument prior to, during, and after each study, to determine if there was a substantial increase in concentrations during the application of the SPUF.

In both trials the CO_2 measurements indicated an increase during the application of the SPUF followed by a decrease as seen in Figures 18 and 22. CO_2 measurements can be influenced by a number of sources with the primary one being human respiration. While an increase was observed in each study, CO_2 was added to the work environment by the applicators breathing. This source could reasonably account for the increase although it should be mentioned that, according to the manufacturer, CO_2 is produced during the chemical reaction occurring with the curing of the SPUF.

During Trial No. 1 SPUF application CO measurements were recorded. The measurements were unremarkable from those collected from the work area prior to the initiation of the SPUF application and following the SPUF application. During Trial No. 3, CO measurements showed a clear increase during the SPUF application. The CO measurements increase from an average of 0.2 ppm prior to the application of the SPUF to an average of 0.8 ppm during the application as shown in Figure 22. CO is a by-product of incomplete combustion of organic matter. CO should not typically be present in an indoor environment, however, when present, indoor CO measurements should be less than or equal to outdoor measurements. During Trial No. 1 and Trial No. 3, outdoor CO concentrations were 0.0 ppm.

The exhaust ventilation was only used during the initial study, because based on the analytical results of Trial No.1, it was suspected that the ventilation system was potentially removing the chemical emissions created by the SPUF application process. As discussed in the previous sections, glycols were detected after the elimination of the exhaust ventilation system.

It should be noted that during this research there were two additional SPUF applications attempted; however due to equipment failure, they were not completed. Related information was thus excluded from this study. The equipment failure was associated with buildup of A Component, first in the mesh screen located at the supply hose and tank fitting, then later in the gun assembly where there appeared to be partially cured foam deposited. In both instances, the foam quality appeared to be compromised as a result of improper curing.

Conclusions

The purpose of this study was to determine if the glycol additives in the Dow SPUF kit released a measurable amount of glycol derivative vapors during its application. The release was predicted to occur due to the increase in volatilization associated with the spraying application of the product as well as due to an increase in the vapor pressure of the glycol additives caused by the heat produced from the exothermic reaction associated with the curing of the SPUF product. A release of glycol derivatives, diethylene glycol and propylene glycol, were confirmed. This was determined through laboratory analysis of air samples collected during three trial application of SPUF using both PBZ and area sampling following NIOSH methods. Ethylene glycol was not detected in any of the samples collected during this study.

The presence of air concentrations of diethylene glycol and propylene glycol were confirmed over short term applications of the SPUF material. Based on the results of the air sampling, it is likely that exposure to diethylene glycol and propylene glycol may occur under certain conditions. However, due to the limited number of samples and the variation between the samples, a generation rate or concentration buildup estimate for comparison of the OELs is not possible. These conditions include the quantity of ventilation used during application, the application duration, and proper operation of the SPUF application equipment. As seen in this study, ventilation may be the most effective method to control potential exposures. TVOC measurements in this study were inconclusive, and further evaluation is required. The rise in temperature as well as CO_2 concentrations, may be confounded by human activity within the work area. However, this finding does suggest, despite the source, that appropriate measures should be taken to control exposure to both. CO measurements showed an increase during the Trial No. 3 application which appeared to remain elevated for a period after ceasing application. CO production associated with the process is potentially an area for further research.

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APPENDIX A: ANALYTICAL RESULTS

GALSON LABORATORIES

Mr. Michael Kaniuga
University of South Florida
2415 Thrace Street
Tampa, FL 33605

June 05, 2014

DOH ELAP #11626
AIHA-LAP #100324

Account# 28107

Login# L319636

Dear Mr. Kaniuga:

Enclosed are the analytical results for the samples received by our laboratory on May 28, 2014. All test results meet the quality control requirements of AIHA-LAP and NELAC unless otherwise stated in this report. All samples on the chain of custody were received in good condition unless otherwise noted.

Results in this report are based on the sampling data provided by the client and refer only to the samples as they were received at the laboratory. Unless otherwise requested, all samples will be discarded 14 days from the date of this report, with the exception of IOMs, which will be cleaned and disposed of after seven calendar days.

Current Scopes of Accreditation can be viewed at www.galsonlabs.com in the accreditations section under the "about Galson" tab.

Please contact John Bailey at (888) 432-5227, if you would like any additional information regarding this report.

Thank you for using Galson Laboratories.

Sincerely,

Galson Laboratories

Mary G Unangst

Mary G. Unangst
Laboratory Director

Enclosure(s)

GALSON LABORATORIES

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 26-MAY-14
Date Received : 28-MAY-14
Date Analyzed : 02-JUN-14
Report ID : 834975

Account No.: 28107
Login No. : L319636

Diethylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
BKG-052614	L319636-1	22.99	<10	<10	<9.9	<0.43	<0.099
PILOT05052614	L319636-2	4.088	<10	<10	<9.9	<2.4	<0.56
PILOT2052614	L319636-3	15.88	<10	<10	<9.9	<0.62	<0.14

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: mln
Approved by : tlh
Date : 05-JUN-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 26-MAY-14
Date Received : 28-MAY-14
Date Analyzed : 02-JUN-14
Report ID : 834976

Account No.: 28107
Login No. : L319636

Ethylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
BKG-052614	L319636-1	22.99	<10	<10	<9.8	<0.43	<0.17
PILOT05052614	L319636-2	4.088	<10	<10	<9.8	<2.4	<0.94
PILOT2052614	L319636-3	15.88	<10	<10	<9.8	<0.62	<0.24

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: mln
Approved by : tlh
Date : 05-JUN-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than
> -Greater Than
NA -Not Applicable
mg -Milligrams
ug -Micrograms
ND -Not Detected
m3 -Cubic Meters
l -Liters
ppm -Parts per Million
kg -Kilograms
NS -Not Specified

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
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Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 26-MAY-14
Date Received : 28-MAY-14
Date Analyzed : 02-JUN-14
Report ID : 834977

Account No.: 28107
Login No. : L319636

Propylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
BKG-052614	L319636-1	22.99	<10	<10	<9.9	<0.43	<0.14
PILOT05052614	L319636-2	4.088	<10	<10	<9.9	<2.4	<0.78
PILOT2052614	L319636-3	15.88	<10	<10	<9.9	<0.62	<0.20

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: mln
Approved by : tlh
Date : 05-JUN-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES

LABORATORY FOOTNOTE REPORT

Client Name : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Date Sampled : 26-MAY-14
Date Received: 28-MAY-14
Date Analyzed: 02-JUN-14

Account No.: 28107
Login No. : L319636

Unless otherwise noted below, all quality control results associated with the samples were within established control limits or did not impact reported results.

Unrounded results are carried through the calculations that yield the final result and the final result is rounded to the number of significant figures appropriate to the accuracy of the analytical method. Please note that results appearing in the columns preceeding the final result column may have been rounded in order to fit the report format and therefore, if carried through the calculations, may not yield an identical final result to the one reported.

The stated LOQs for each analyte represent the demonstrated LOQ concentrations prior to correction for desorption efficiency (if applicable).

Unless otherwise noted below, reported results have not been blank corrected for any field blank or method blank.

L319636 (Report ID: 834975):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(6), GC-SOP-16(12), GC-SOP-8(11)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Diethylene Glycol	+/-16.7%	100%

L319636 (Report ID: 834976):
Total ug corrected for a desorption efficiency of 102%.
SOPs: GC-SOP-12(6), GC-SOP-16(12), GC-SOP-8(11)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Ethylene Glycol	+/-10.6%	95.9%

L319636 (Report ID: 834977):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(6), GC-SOP-16(12), GC-SOP-8(11)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Propylene Glycol	+/-16.7%	100%

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON

805929978135
Date:05/28/14
Shipper:FEDEX
Initials:dd
Prep:PSY305844

☐ New Client?

Report To*: MICHAEL KANIUGA
2415 THRACE ST.
TAMPA, FL 33605

Invoice To*: MICHAEL KANIUGA
SAME

Client Account No.*: 87

Phone No.*:

Phone No.:

Cell No.: 813 376 8052

Email:

Email Results To: MICHAEL KANIUGA

Purchase Order No.:

Email Address: mKANIUGA@Health.USF.EDU

Credit Card: ☒ Credit Card on File ☐ Call for Credit Card Info

☐ Samples submitted using the FreePumpLoan™ Program.

☑ Samples submitted using the FreeSamplingBadges™ Program.

Need Results By*:	(surcharge)
☒ Standard	0%
☐ 4 Business Days	35%
☐ 3 Business Days	50%
☐ 2 Business Days	75%
☐ Next Day by 6pm	100%
☐ Next Day by Noon	150%
☐ Same Day	200%

Site Name: TEST WORK AREA Project: USF THESIS Sampled By: MKANIUGA

Comments:

List description of industry or process/interferences present in sampling area:

State samples were collected in (ex. NY):

Please indicate which OEL this data will be used for: ☒ OSHA PEL ☐ ACGIH TLV ☐ Cal OSHA ☐ MSHA ☐ Other (specify):

Sample Identification* (Maximum of 20 characters; ID's longer than 20 characters will be abbreviated.)	Date Sampled* (mm/dd/yy)	Collection Medium	Sample Volume, Sample Time, or Sample Area*	Sample Units*: L, ml, min., in2, cm2, ft2	Analysis Requested*	Method Reference^	Hexavalent Chromium Process (ex. welding, plating, painting, etc.)*
Example	01/01/11	2pc UW PVC	960	L	Hexavalent Chromium (Cr6)	mod. OSHA ID-215	Welding
BKG-052614	05/26/14	GFF/XAD	22.88	L	Glycols (ethylene +	NIOSH 5523	No ACTIVITY
PLOT05052614	05/26/14	GFF/XAD	4.088	L	Glycols propylene +	↓	SPF APP
Pilot2052614	05/26/14	GFF/XAD	15.88	L	Glycols diethylene)		SPF APP
		226 57			per client		
					CK 5/29/14		

Report Referenced: 05-JUN-14 11:20

^Galson Laboratories will substitute our routine/preferred method if it does not match the method listed on the COC unless this box is checked: ☑ Use method(s) listed on COC

For metals analysis: if requesting an analyte with the option of a lower LOQ please indicate if the lower LOQ is required (only available for certain analytes see SAG):

For crystalline silica: form(s) of silica needed must be indicated (Quartz, Cristobalite, and/or Tridymite)*:

Chain of Custody	Print Name/Signature	Date/Time		Print Name/Signature	Date/Time
Relinquished by:	MICHAEL KANIUGA [signature]	5/27/14	Received by:		
Relinquished by:			Received by:	Dorothy Dermott [signature]	5/28/14 1358

Samples received after 3pm will be considered as next day's business.

*Required fields, failure to complete these fields may result in a delay in your samples being processed. Page 1 of 1

LAB ORIGINAL

Mr. Michael Kaniuga
University of South Florida
2415 Thrace Street
Tampa, FL 33605

July 23, 2014

DOH ELAP #11626
AIHA-LAP #100324

Account# 28107

Login# L323368

Dear Mr. Kaniuga:

Enclosed are the analytical results for the samples received by our laboratory on July 16, 2014. All test results meet the quality control requirements of AIHA-LAP and NELAC unless otherwise stated in this report. All samples on the chain of custody were received in good condition unless otherwise noted.

Results in this report are based on the sampling data provided by the client and refer only to the samples as they were received at the laboratory. Unless otherwise requested, all samples will be discarded 14 days from the date of this report, with the exception of IOMs, which will be cleaned and disposed of after seven calendar days.

Current Scopes of Accreditation can be viewed at www.galsonlabs.com in the accreditations section under the "about Galson" tab.

Please contact John Bailey at (888) 432-5227, if you would like any additional information regarding this report.

Thank you for using Galson Laboratories.

Sincerely,

Galson Laboratories

Mary G Unangst

Mary G. Unangst
Laboratory Director

Enclosure(s)

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 13-JUL-14
Date Received : 16-JUL-14
Date Analyzed : 17-JUL-14
Report ID : 841516

Account No.: 28107
Login No. : L323368

Diethylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
5173500925	L323368-1	11.05	19	<10	19	1.7	0.40
5173500840	L323368-2	55	78	<10	77	1.4	0.32

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: KAG
Approved by : tlh
Date : 23-JUL-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

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LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 13-JUL-14
Date Received : 16-JUL-14
Date Analyzed : 17-JUL-14
Report ID : 841517

Account No.: 28107
Login No. : L323368

Ethylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
5173500925	L323368-1	11.05	<10	<10	<9.8	<0.89	<0.35
5173500840	L323368-2	55	<10	<10	<9.8	<0.18	<0.070

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: KAG
Approved by : tlh
Date : 23-JUL-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 13-JUL-14
Date Received : 16-JUL-14
Date Analyzed : 17-JUL-14
Report ID : 841518

Account No.: 28107
Login No. : L323368

Propylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
5173500925	L323368-1	11.05	15	<10	14	1.3	0.42
5173500840	L323368-2	55	54	10	*63	*1.1	*0.37

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: KAG
Approved by : tlh
Date : 23-JUL-14 NYS DOH # : 11626
QC by: Karen Becker

< -Less Than
> -Greater Than
NA -Not Applicable
mg -Milligrams
ug -Micrograms
ND -Not Detected
m3 -Cubic Meters
l -Liters
ppm -Parts per Million
kg -Kilograms
NS -Not Specified

GALSON LABORATORIES

LABORATORY FOOTNOTE REPORT

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East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client Name : University of South Florida
Site : Test Work Area
Project No. : USF Thesis

Date Sampled : 13-JUL-14
Date Received: 16-JUL-14
Date Analyzed: 17-JUL-14

Account No.: 28107
Login No. : L323368

Unless otherwise noted below, all quality control results associated with the samples were within established control limits or did not impact reported results.

Unrounded results are carried through the calculations that yield the final result and the final result is rounded to the number of significant figures appropriate to the accuracy of the analytical method. Please note that results appearing in the columns preceeding the final result column may have been rounded in order to fit the report format and therefore, if carried through the calculations, may not yield an identical final result to the one reported.

The stated LOQs for each analyte represent the demonstrated LOQ concentrations prior to correction for desorption efficiency (if applicable).

Unless otherwise noted below, reported results have not been blank corrected for any field blank or method blank.

L323368 (Report ID: 841516):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(7), GC-SOP-16(12), GC-SOP-8(13)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Diethylene Glycol	+/-16.7%	100%

L323368 (Report ID: 841517):
Total ug corrected for a desorption efficiency of 102%.
SOPs: GC-SOP-12(7), GC-SOP-16(12), GC-SOP-8(13)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Ethylene Glycol	+/-10.6%	95.9%

L323368 (Report ID: 841518):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(7), GC-SOP-16(12), GC-SOP-8(13)
Results reported as (*) designate possible breakthrough or migration.
Reported result may be biased low.

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Propylene Glycol	+/-16.7%	100%

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES

6601 Kirkville Rd
East Syracuse, NY 13057-9672
Tel: 315-432-5227
888-432-5227
Fax: 315-437-0571
www.galsonlabs.com

☐ New Client?

Client Account No.*: 28107

Report To*: MICHAEL KANIUGA
2415 THRACE ST
TAMPA, FL 33605

Phone No.*:

Cell No.: 813 376-8057

Email Results To: MICHAEL KANIUGA

Email Address: MKANIUGA@mail.USF.edu

Invoice To*: MICHAEL KANIUGA
SAME

Phone No.:

Email:

Purchase Order No.:

Credit Card: ☒ Credit Card on File ☐ Call for Credit Card Info

109

☒ Samples submitted using the FreePumpLoan™ Program.

☐ Samples submitted using the FreeSamplingBadges™ Program.

Need Results By*:	(surcharge)
☒ Standard	0%
☐ 4 Business Days	35%
☐ 3 Business Days	50%
☐ 2 Business Days	75%
☐ Next Day by 6pm	100%
☐ Next Day by Noon	150%
☐ Same Day	200%

Site Name: TEST WORK AREA Project: USF THESIS Sampled By: MICHAEL KANIUGA

Comments:

List description of industry or process/interferences present in sampling area:

State samples were collected in (ex. NY):

Please indicate which OEL this data will be used for: ☒ OSHA PEL ☐ ACGIH TLV ☐ Cal OSHA ☐ MSHA ☐ Other (specify):

Sample Identification* (Maximum of 20 characters, ID's longer than 20 characters will be abbreviated.)	Date Sampled* (mm/dd/yy)	Collection Medium	Sample Volume, Sample Time, or Sample Area*	Sample Units*: L, ml, min., in2, cm2, ft2	Analysis Requested*	Method Reference^	Hexavalent Chromium Process (ex. welding, plating, painting, etc.)*
Example	01/01/11	2pc UW PVC	960	L	Hexavalent Chromium (Cr6)	mod. OSHA ID-215	Welding
6173500975	7/13/14	226-57	11.05	L	Glycols (ethylene	NIOSH 5523	APPLICATION
6173500840	7/13/14	226-57	55	L	propylene	↓	APPLICATION
					di ethylene		

Page 3 of 3 Report Reference 1 Generated:23-JUL-14 11:17

^Galson Laboratories will substitute our routine/preferred method if it does not match the method listed on the COC unless this box is checked: ☐ Use method(s) listed on COC

For metals analysis: if requesting an analyte with the option of a lower LOQ please indicate if the lower LOQ is required (only available for certain analytes see SAG):

For crystalline silica: form(s) of silica needed must be indicated (Quartz, Cristobalite, and/or Tridymite)*:

Chain of Custody	Print Name/Signature	Date/Time		Print Name/Signature	Date/Time
Relinquished by:	MICHAEL KANIUGA / [signature]	7/14/14	Received by:		
Relinquished by:			Received by:	M. Krause / M. Krause	7/16/14 0855

Samples received after 3pm will be considered as next day's business.

*Required fields, failure to complete these fields may result in a delay in your samples being processed.

Page 1 of 1

LAB ORIGINAL

GALSON LABORATORIES

Mr. Michael Kaniuga
University of South Florida
2415 Thrace Street
Tampa, FL 33605

September 02, 2014

DOH ELAP #11626
AIHA-LAP #100324

Account# 28107

Login# L326587

Dear Mr. Kaniuga:

Enclosed are the analytical results for the samples received by our laboratory on August 25, 2014. All test results meet the quality control requirements of AIHA-LAP and NELAC unless otherwise stated in this report. All samples on the chain of custody were received in good condition unless otherwise noted.

Results in this report are based on the sampling data provided by the client and refer only to the samples as they were received at the laboratory. Unless otherwise requested, all samples will be discarded 14 days from the date of this report, with the exception of IOMs, which will be cleaned and disposed of after seven calendar days.

Current Scopes of Accreditation can be viewed at www.galsonlabs.com in the accreditations section under the "about Galson" tab.

Please contact John Bailey at (888) 432-5227, if you would like any additional information regarding this report.

Thank you for using Galson Laboratories.

Sincerely,

Galson Laboratories

Mary G Unangst

Mary G. Unangst
Laboratory Director

Enclosure(s)

GALSON LABORATORIES

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : SPF WORK AREA
Project No. : NSF THESIS

Date Sampled : 23-AUG-14
Date Received : 25-AUG-14
Date Analyzed : 27-AUG-14
Report ID : 847473

Account No.: 28107
Login No. : L326587

Diethylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
PBZ-901230	L326587-1	23.55	29	<10	29	1.2	0.28
PBZ-901180	L326587-2	23.38	11	<10	11	0.46	0.11

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: KAG
Approved by : tlh
Date : 02-SEP-14 NYS DOH # : 11626
QC by: JEM

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES

LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Client : University of South Florida
Site : SPF WORK AREA
Project No. : NSF THESIS

Date Sampled : 23-AUG-14
Date Received : 25-AUG-14
Date Analyzed : 27-AUG-14
Report ID : 847474

Account No.: 28107
Login No. : L326587

Propylene Glycol

Sample ID	Lab ID	Air Vol liter	Front ug	Back ug	Total ug	Conc mg/m3	ppm
PBZ-901230	L326587-1	23.55	18	<10	18	0.77	0.25
PBZ-901180	L326587-2	23.38	<10	<10	<9.9	<0.42	<0.14

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: 10. ug
Analytical Method : mod. NIOSH 5523; GC/FID
OSHA PEL : NA
Collection Media : 226-57

Submitted by: KAG
Approved by : tlh
Date : 02-SEP-14 NYS DOH # : 11626
QC by: JEM

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES

LABORATORY FOOTNOTE REPORT

Client Name : University of South Florida
Site : SPF WORK AREA
Project No. : NSF THESIS

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsonlabs.com

Date Sampled : 23-AUG-14
Date Received: 25-AUG-14
Date Analyzed: 27-AUG-14

Account No.: 28107
Login No. : L326587

Unless otherwise noted below, all quality control results associated with the samples were within established control limits or did not impact reported results.

Unrounded results are carried through the calculations that yield the final result and the final result is rounded to the number of significant figures appropriate to the accuracy of the analytical method. Please note that results appearing in the columns preceeding the final result column may have been rounded in order to fit the report format and therefore, if carried through the calculations, may not yield an identical final result to the one reported.

The stated LOQs for each analyte represent the demonstrated LOQ concentrations prior to correction for desorption efficiency (if applicable).

Unless otherwise noted below, reported results have not been blank corrected for any field blank or method blank.

L326587 (Report ID: 847473):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(7), GC-SOP-16(12), GC-SOP-8(13)
There appears to be a contamination of Diethylene Glycol; the instrument blank, the eluent blank and the media blanks recovered ~6.5ug. It is believed that the contamination may be instrument related. Samples may be biased high due to this contamination.

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Diethylene Glycol	+/-16.7%	100%

L326587 (Report ID: 847474):
Total ug corrected for a desorption efficiency of 101%.
SOPs: GC-SOP-12(7), GC-SOP-16(12), GC-SOP-8(13)

Accuracy and mean recovery data presented below is based on a 95% confidence interval (k=2). The estimated uncertainty applies to the media, technology, and SOP referenced in this report and does not account for the uncertainty associated with the sampling process.

Parameter	Accuracy	Mean Recovery
Propylene Glycol	+/-16.7%	100%

< -Less Than	mg -Milligrams	m3 -Cubic Meters	kg -Kilograms
> -Greater Than	ug -Micrograms	l -Liters	NS -Not Specified
NA -Not Applicable	ND -Not Detected	ppm -Parts per Million	

GALSON LABORATORIES
6601 Kirkville Rd
East Syracuse, NY 13057-9672
Tel: 315-432-5227
888-432-5227
Fax: 315-437-0571
www.galsonlabs.com

☐ New Client?

Report To*: Michael Kaniuga
2415 Thrace St.
Tampa, Flori

Invoice To*: SAME

Client Account No.*: 28107

Phone No.*:

Cell No.: (813) 376-8052

Phone No.:

Email:

Email Results To: Michael Kaniuga

Email Address: mkaniuga@mail.usf.edu

Purchase Order No.:

Credit Card: ☐ Credit Card on File ☐ Call for Credit Card Info

☐ Samples submitted using the FreePumpLoan™ Program.

☑ Samples submitted using the FreeSamplingBadges™ Program.

Need Results By*:	(surcharge)
☒ Standard	0%
☐ 4 Business Days	35%
☐ 3 Business Days	50%
☐ 2 Business Days	75%
☐ Next Day by 6pm	100%
☐ Next Day by Noon	150%
☐ Same Day	200%

Site Name: SPF Work Area Project: USF "Thesis" Sampled By: M. Kaniuga

Comments:

List description of industry or process/interferences present in sampling area:

State samples were collected in (ex. NY):

Please indicate which OEL this data will be used for: ☒ OSHA PEL ☐ ACGIH TLV ☐ Cal OSHA ☐ MSHA ☐ Other (specify):

Sample Identification* (Maximum of 20 characters, ID's longer than 20 characters will be abbreviated.)	Date Sampled* (mm/dd/yy)	Collection Medium	Sample Volume, Sample Time, or Sample Area*	Sample Units* (L, ml, min., in2, cm2, ft2)	Analysis Requested*	Method Reference^	Hexavalent Chromium Process (ex. welding, plating, painting, etc.)*
Example	01/01/11	2pc UW PVC	960	L	Hexavalent Chromium (Cr6)	mod. OSHA ID-215	Welding
BBZ-901230	8/23/14	SKC 226-57	23.55	L	Glycols & Propylene Glycol	NIOSH 5523	SPF applied
PBZ-901180	8/23/14	SKC 226-57	23.38	L	Glycols	NIOSH 5523	SPF applied

Page 5 of 5 Report Reference:1 Generated:02-SEP-14 17:12

^Galson Laboratories will substitute our routine/preferred method if it does not match the method listed on the COC unless this box is checked: ☐ Use method(s) listed on COC

For metals analysis: if requesting an analyte with the option of a lower LOQ please indicate if the lower LOQ is required (only available for certain analytes see SAG):

For crystalline silica: form(s) of silica needed must be indicated (Quartz, Cristobalite, and/or Tridymite)*:

Chain of Custody	Print Name/Signature	Date/Time		Print Name/Signature	Date/Time
Relinquished by:	Michael Kaniuga	8/27/14 12:15	Received by:	[signature]	8/25/14 1035
Relinquished by:			Received by:		

Samples received after 3pm will be considered as next day's business.
*Required fields, failure to complete these fields may result in a delay in your samples being processed.

Page 1 of 1

LAB ORIGINAL

APPENDIX B: SAMPLING PUMP CALIBRATIONS

Table B1 Sampling Pump Calibration Background and Trial 1

	Background		Trial No. 1			
Pump ID	876137		876164		876051	
	Pre (L/min)	Post (L/min)	Pre (L/min)	Post (L/min)	Pre (L/min)	Post (L/min)
1	1.0288	1.0454	0.5043	0.5123	1.9890	1.9781
2	1.0316	1.0464	0.5061	0.5148	1.9877	1.9809
3	1.0305	1.0472	0.5063	0.5142	1.9890	1.9808
4	1.0339	1.0469	0.5089	0.5174	1.9913	1.9800
5	1.0318	1.0441	0.5081	0.5176	1.9930	1.9050
Average	1.0313	1.0460	0.5068	0.5152	1.9900	1.9650
Standard Deviation	0.0019	0.0013	0.0018	0.0022	0.0021	0.0335
Coefficient of Variance	0.0018	0.0012	0.0036	0.0043	0.0011	0.0171
Average Flow	1.0387		0.5110		1.9775	

Air sampling pumps pre and post calibrated for each Trial with BIOS Defender 510-M.

Table B2 Sampling Pump Calibration Trial 2 and 3

	Trial 2				Trial No. 3			
	876137		High Flow Pump		876051		876137	
Pump ID	Pre (L/min)	Post (L/min)	Pre (L/min)	Post (L/min)	Pre (L/min)	Post (L/min)	Pre (L/min)	Post (L/min)
	2.0100	2.0010	9.9	9.9	2.0602	2.0149	2.0882	1.9899
1	2.0113	2.0110	10.0	9.8	2.0613	2.0103	2.0256	1.9932
2	2.0114	2.0114	9.9	10.4	2.0606	2.0169	2.0554	1.9923
3	2.0110	2.0110	10.1	10.5	2.0634	2.0129	2.0599	1.9939
4	2.0110	2.0111	9.9	9.9	2.0713	2.0134	2.0617	1.9936
5	2.0013	2.0110	10.1	9.9	2.0691	-	2.0599	1.9926
6	2.0070	2.0134	9.9	10.0	2.0683	-	2.0568	1.9903
7	2.0113	2.0103	10.1	9.9	2.0683	-	2.0596	1.9942
8	2.0130	2.0112	9.9	10.0	2.0699	-	2.0606	1.9952
9	2.0111	2.0110	10.0	9.9	2.0765	-	2.0592	1.9932
Average	2.0091	2.0102	10.0	10.0	2.0669	2.0137	2.0587	1.9928
Standard Deviation	0.0043	0.0033	0.1	0.2	0.0053	0.0024	0.0149	0.0017
Coefficient of Variance	0.0021	0.0017	0.0	0.0	0.0026	0.0012	0.0072	0.0008
Average Flow	2.0097		10.0		2.0403		2.0258	

APPENDIX C: CALIBRATION CERTIFICATIONS

INSTRUMENT CALIBRATION REPORT

Pine Environmental Services, LLC.
3902 Corporex Park Drive, Suite 450
Tampa, FL 33619
Toll-free: (877) 259-PINE (7463)

Pine Environmental Services, Inc.

Instrument ID 22844
Description ppbRAE 3000
Calibrated 8/29/2014 12:03:41PM

Manufacturer Rae Systems
Model Number PGM-7340
Serial Number/ Lot Number 594-903835
Location Florida
Department

State Certified
Status Pass
Temp °C 26.4
Humidity % 42

Calibration Specifications

Group # 1
Group Name Isobutylene
Stated Accy Pct of Reading

Range Acc % 0.0000
Reading Acc % 3.0000
Plus/Minus 0.00

Nom In Val / In Val	In Type	Out Val	Out Type	Fnd As	Lft As	Dev%	Pass/Fail
10.00 / 10.00	PPM	10.00	PPM	10.03	10.03	0.30%	Pass

Test Instruments Used During the Calibration **(As Of Cal Entry Date)**

Test Standard ID	Description	Manufacturer	Model Number	Serial Number / Lot Number	Last Cal Date/ Opened Date	Next Cal Date / Expiration Date
FL ISO 10PPM	FL Iso 10 ppm 17L	Airgas	GP11005	GAL-1-16		7/22/2015

Notes about this calibration

Calibration Result Calibration Successful
Who Calibrated Patrick Bingaman

All instruments are calibrated by Pine Environmental Services, LLC. according to the manufacturer's specifications, but it is the customer's responsibility to calibrate and maintain this unit in accordance with the manufacturer's specifications and/or the customer's own specific needs.

Notify Pine Environmental Services, LLC. of any defect within 24 hours of receipt of equipment
Please call 866-960-7463 for Technical Assistance

INSTRUMENT CALIBRATION REPORT

Advanced Labs, Inc.

Pine Environmental Services, Inc

Instrument ID R6641
Description TSI 8386 VelociCalc Plus
Calibrated 11/13/2013

Manufacturer TSI
Model Number 8386
Serial Number 03100116
Location New Jersey
Temp 72

Classification
Status pass
Frequency Yearly EOM
Department
Humidity 22

Calibration Specifications

Group # 1 | **Range Acc %** 0.0000
Group Name Velocity | **Reading Acc %** 3.0000
Stated Accy Pct of Reading | **Plus/Minus** 0.00

Nom In Val / In Val	In Type	Out Val	Out Type	Fnd As	Lft As	Dev%	Pass/Fail
0.00 / 0.00	ft/min	0.00	ft/min	0.00	0.00	0.00%	Pass
40.00 / 40.00	ft/min	40.00	ft/min	36.00	40.00	0.00%	Pass
70.00 / 70.00	ft/min	70.00	ft/min	67.00	69.00	-1.43%	Pass
100.00 / 100.00	ft/min	100.00	ft/min	95.00	99.00	-1.00%	Pass
150.00 / 150.00	ft/min	150.00	ft/min	139.00	147.00	-2.00%	Pass
325.00 / 325.00	ft/min	325.00	ft/min	318.00	323.00	-0.62%	Pass
700.00 / 700.00	ft/min	700.00	ft/min	681.00	695.00	-0.71%	Pass
1000.00 / 1000.00	ft/min	1000.00	ft/min	975.00	1,010.00	1.00%	Pass
1500.00 / 1500.00	ft/min	1500.00	ft/min	1,460.00	1,515.00	1.00%	Pass
2000.00 / 2000.00	ft/min	2000.00	ft/min	1,990.00	2,020.00	1.00%	Pass
5000.00 / 5000.00	ft/min	5000.00	ft/min	4,955.00	5,150.00	3.00%	Pass
8000.00 / 8000.00	ft/min	8000.00	ft/min	7,920.00	8,230.00	2.88%	Pass

Group # 2 | **Range Acc %** 0.0000
Group Name Temperature | **Reading Acc %** 0.0000
Stated Accy Plus / Minus | **Plus/Minus** 0.50

Nom In Val / In Val	In Type	Out Val	Out Type	Fnd As	Lft As	Dev%	Pass/Fail
70.00 / 71.24	°F	71.24	°F	71.60	71.30	0.08%	Pass

Group # 3 | **Range Acc %** 0.0000
Group Name Humidity | **Reading Acc %** 3.0000
Stated Accy Pct of Reading | **Plus/Minus** 0.00

Nom In Val / In Val	In Type	Out Val	Out Type	Fnd As	Lft As	Dev%	Pass/Fail
30.00 / 31.80	%	31.80	%	31.60	31.70	-0.31%	Pass

Group # 4 | **Range Acc %** 0.0000
Group Name Pressure | **Reading Acc %** 1.0000
Stated Accy Pct of Reading | **Plus/Minus** 0.000

Nom In Val / In Val	In Type	Out Val	Out Type	Fnd As	Lft As	Dev%	Pass/Fail
-4.000 / -4.120	inH2O	-4.120	inH2O	-4.130	-4.130	0.24%	Pass
4.000 / 4.100	inH2O	4.100	inH2O	4.115	4.115	0.37%	Pass
8.000 / 8.140	inH2O	8.140	inH2O	8.146	8.146	0.07%	Pass
12.000 / 12.220	inH2O	12.220	inH2O	12.190	12.190	-0.25%	Pass

Advanced Labs, Inc., Windsor Industrial Park, 92 North Main Street, Bldg 20, Windsor, NJ 08561, 800-301-9663

INSTRUMENT CALIBRATION REPORT

Pine Environmental Services, LLC.

3902 Corporex Park Drive, Suite 450
Tampa, FL 33619
Toll-free: (877) 259-PINE (7463)

Pine Environmental Services, Inc.

Instrument ID 5638
Description TSI Q-TRAK 8554
Calibrated 9/5/2013 5:55:17PM

All instruments are calibrated by Pine Environmental Services, LLC. according to the manufacturer's specifications, but it is the customer's responsibility to calibrate and maintain this unit in accordance with the manufacturer's specifications and/or the customer's own specific needs.

Notify Pine Environmental Services, LLC. of any defect within 24 hours of receipt of equipment
Please call 866-960-7463 for Technical Assistance

Page 1

Standard Order

Pine Environmental Services LLC
3902 Corporex Park Drive, Suite 450, Tampa, FL 33619
Toll Free (877) 259-7463 - Local (813) 620-1001
Fax (813) 620-4810
www.pine-environmental.com

PACKING

CONTRACT NUMBER: **F028701**
CONTRACT DATE: 9/9/2013
BEGIN DATE: 9/10/2013
TAKEN BY: LAA

SHIP DATE: **9/9/2013** **MON**

BILLED TO: 12-EN08540
ENVIRON INTERNATIONAL
ATTN: ACCOUNTS PAYABLE
10150 HIGHLAND MANOR DRIVE
SUITE 440
TAMPA, FL 33610

SHIP TO:
PINE ENVIRONMENTAL SERVICES
ATTN: MICHAEL KANIUGA
3902 CORPOREX PARK DR
STE 450
TAMPA, FL 33619

CONFIRM TO: MICHAEL KANIUGA LADKINS@PINE-ENVIRONMENTAL.COM (813) 376-8052

PROJECT #:

Comment: 1 DAY RENTAL

CUSTOMER P.O.:	SHIP VIA:	SHIPPER ID:	TERMS:
DOE FT WALTON	Customer Pick Up		Net 30 Days

ITEM NUMBER	TYPE	WAREHOUSE	UNIT	ORDERED	SHIPPED	BACK ORDER
RAIR16105 IAQ- TSI Q-Trak	R	FL1	EACH	1.00	1	
GP10100 Cal Kit - Std -Regulator/Gas/Tedlar Bag	R	FL1	EACH	1.00	⌀	

DUSIRAK

Asset # 1110194 309075

MesaLabs

NVLAP®
NVLAP Lab Code 200661

Calibration Certificate

Certificate No. 5032821

Product Defender 510 Low Flow

Serial No. 118762

Cal. Date 2/5/2014

All calibrations are performed in accordance with ISO 17025 Mesa Laboratories, Inc., 10 Park Place, Butler, NJ, 07405, 800-663-4977, an ISO 17025:2005 – accredited laboratory through NVLAP. This report shall not be reproduced except in full without the written approval of the laboratory. Results only relate to the items calibrated. This report must not be used to claim product certification, approval, or endorsement by NVLAP, NIST, or any agency of the Federal Government.

All units tested in accordance with our test number PR17-13 using high-purity nitrogen or filtered laboratory air.

As Received Calibration Data

Technician Zenaida Ortiz

Lab. Pressure 760 mmHg

Lab. Temperature 22.9 °C

Instrument Reading	Lab Standard Reading	Deviation	Allowable Deviation	As Received
29.844ccm	30.0335ccm	-0.63%	1.00%	In Tolerance
99.505ccm	100.265ccm	-0.76%	1.00%	In Tolerance
500.79ccm	500.65ccm	0.03%	1.00%	In Tolerance

Mesa Laboratories Standards Used

Description	Standard Serial Number	Calibration Date	Calibration Due Date
ML 500-10	113784	3/19/2013	3/19/2014

```
LogDat2 Data File

Model Number:   7565-X
Serial Number:  7565X0906004
Probe Model Number    982
Probe Serial Number   P09070029
Test ID:   1
Test Abbreviation:    Test 001
Start Date:     10/2/2013
Start Time:     17:01:57
Duration (dd:hh:mm:ss):    232:16:26:00
Log Interval (mm:ss): 0:05
Number of points:     3
Notes:     Test 001

Statistics Channel:   CO2   T     H     CO    BP
     Units:     ppm   deg F %rh   ppm   inHg
     Average:   1199  83.7  62    0.9   29.92
     Minimum:   299   81.5  56.4  0     29.73
     Time of Minimum: 14:16:49   14:16:49   9:27:57    14:16:49   17:02:02
     Date of Minimum: 10/14/2013 10/14/2013 5/23/2014  10/14/2013 10/2/2013
     Maximum:   2953  86    65.9  2.7   30.05
     Time of Maximum: 17:02:02   9:27:57    17:02:02   17:02:02   9:27:57
     Date of Maximum: 10/2/2013  5/23/2014  10/2/2013  10/2/2013  5/23/2014

Calibration     Meter:     11/20/2012
Calibration     Sensor:    CO2   T     H     CO
     Cal. Date  5/7/2014   5/7/2014   5/7/2014   5/7/2014

Date Time CO2   T     H     CO    BP
MM/dd/yyyy hh:mm:ss   ppm   deg F %rh   ppm   inHg
10/2/2013  17:02:02   2953  83.8  65.9  2.7   29.73
10/14/2013 14:16:49   299   81.5  63.9  0     29.98
5/23/2014  9:27:57    345   86    56.4  0.1   30.05
```

MesaLabs

NVLAP®
NVLAP Lab Code 200661

As Shipped Calibration Data

Certificate No. 5032821
Technician Sonia Otero

Lab. Pressure 743 mmHg
Lab. Temperature 22.5 °C

Instrument Reading	Lab Standard Reading	Deviation	Allowable Deviation	As Shipped
30.114ccm	30.199ccm	-0.28%	1.00%	In Tolerance
100.69ccm	100.815ccm	-0.12%	1.00%	In Tolerance
501.9ccm	501.805ccm	0.02%	1.00%	In Tolerance

Mesa Laboratories Standards Used

Description	Standard Serial Number	Calibration Date	Calibration Due Date
ML-500-10	113779	4/23/2013	4/23/2014

Calibration Notes

Mesa is an ISO 17025-accredited metrology laboratory. Each Bios DryCal primary gas flow standard is dynamically verified by comparing it to one of our laboratory standards, which is a Proven DryCal® Technology volumetric piston prover of much higher accuracy (0.25 % or better) but of similar operating principles. For this purpose, a flow generator of ±0.10 % or less
stability is used. Our laboratory standards are qualified by direct measurement of their dimensions (diameter, length and time) using NIST-traceable precision gauges and instruments, such as depth micrometers and laser micrometers. Calibration Certificates for these gauges and instruments are available upon request. Rigorous analyses of our laboratory standards' uncertainties have been performed, in accordance with The Guide to the Expression of Uncertainty in Measurement (the GUM), assuring their traceable accuracy.

Technician Notes: _______

DWWilson

David W. Wilson, Chief Metrologist

Mesa Laboratories Inc. 10 Park Place Butler, NJ 07405 USA
(973) 492-8400 FAX (973) 492-8270 www.mesalabs.com Symbol "MLAB" on the NAS

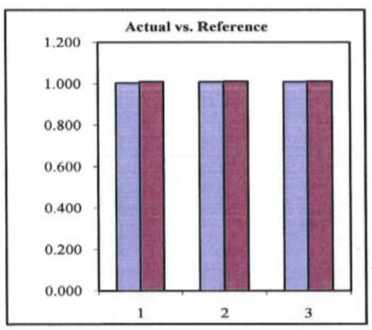
CERTIFICATE OF CALIBRATION

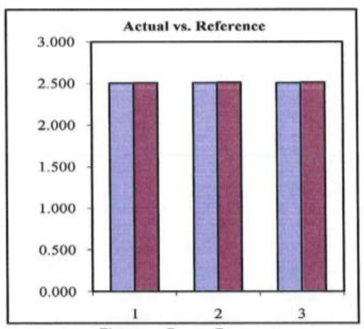
CIH EQUIPMENT COMPANY, INC.

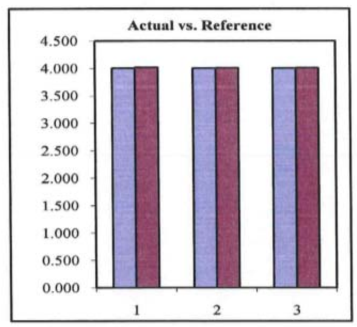
Primary Flow Calibrator

Manufacturer:	Bios	**Calibration Date:**	July 3, 2014
Model Number:	510M	**Date Due:**	July 3, 2015
Serial Number:	113727	**Temperature:**	72.9 °F
Service Order:	15889	**Relative Humidity:**	49 %
Reference Number:	15889-510M-113727	**Pressure:**	29.85 inHG

	Reference L/min	Actual L/min	Relative Difference	Percent Difference
@ 1.0 LPM				
1	1.004	1.0095	0.0055	0.54%
2	1.008	1.0102	0.0022	0.22%
3	1.008	1.0105	0.0025	0.25%
@ 2.5 LPM				
1	2.502	2.5082	0.0062	0.25%
2	2.508	2.5110	0.0030	0.12%
3	2.508	2.5120	0.0040	0.16%
@ 4.0 LPM				
1	4.006	4.0165	0.0105	0.26%
2	4.006	4.0114	0.0054	0.13%
3	4.005	4.0112	0.0062	0.15%







Standards

Manufacturer	Description	Model No.	Serial No.	Certificate No.	Due Date
TSI	Mass Flow Meter	4043	40430838004	00006880	10/11/2014

CIH Equipment Company, Inc. certifies that the instrument specified above meets the manufacturer specifications and was calibrated using standards traceable to National Institute of Standards and Technology (NIST) or have been derived from accepted values of natural physical constants or have been derived by the ratio type of self calibration techniques. The reported uncertainty of measurement is stated as the combined standard uncertainty multiplied by a coverage factor k = 2. The measured value and the associated expanded uncertainty represent the interval (y±U), which contains the value of the measured quantity with a probability of approximately a 95% confidence interval. The uncertainty was estimated following the guidelines of the ISO 17025 and the GUM. U = ±0.298%

Calibrated By: ______________ Date: 07/03/14

Albert Buca - Calibration Technician

1806 South Highland Ave • Clearwater, FL 33756-1762 • USA • PH: (727) 584-5063 • FX: (727) 581-5921
Toll Free: (888) 873-2443 • Website: http://www.cihequipment.com

Standard Order

Pine Environmental Services LLC
3902 Corporex Park Drive, Suite 450, Tampa, FL 33619
Toll Free (877) 259-7463 - Local (813) 620-1001
Fax (813) 620-4810
www.pine-environmental.com

PACKING

CONTRACT NUMBER: **F028701**
CONTRACT DATE: 9/9/2013
BEGIN DATE: 9/10/2013
TAKEN BY: LAA

SHIP DATE: **9/9/2013** **MON**

BILLED TO: 12-EN08540
ENVIRON INTERNATIONAL
ATTN: ACCOUNTS PAYABLE
10150 HIGHLAND MANOR DRIVE
SUITE 440
TAMPA, FL 33610

SHIP TO:
PINE ENVIRONMENTAL SERVICES
ATTN: MICHAEL KANIUGA
3902 CORPOREX PARK DR
STE 450
TAMPA, FL 33619

CONFIRM TO: **MICHAEL KANIUGA** LADKINS@PINE-ENVIRONMENTAL.COM (813) 376-8052

PROJECT #: **Comment:** 1 DAY RENTAL

CUSTOMER P.O.:	SHIP VIA:	SHIPPER ID:	TERMS:
DOE FT WALTON	Customer Pick Up		Net 30 Days

ITEM NUMBER	TYPE	WAREHOUSE	UNIT	ORDERED	SHIPPED	BACK ORDER
RAIR16105 IAQ- TSI Q-Trak	R	FL1	EACH	1.00	1	
GP10100 Cal Kit - Std -Regulator/Gas/Tedlar Bag	R	FL1	EACH	1.00	ϕ	

DUSIRAK