ABSTRACT

GABLER, WILLIAM. Adapting Air Sampling Methods for the Detection of Toxic Industrial Chemicals in NFPA 1994 Permeation Resistance Test. (Under the direction of Dr. Bryan Ormond, Dr. Roger Barker, Dr. Donald Thompson, and Dr. Keith Beck).

The NFPA 1994 Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents addresses the risk posed to first responders in situations involving the release of toxic industrial chemicals (TICs). It includes a test to evaluate the permeation resistance of ensemble fabrics to a list of five TICs (acrolein, acrylonitrile, dimethyl sulfate, chlorine, and ammonia) and defines a maximum allowable cumulative permeation for Class 2 and Class 3 ensembles. Testing parameters (temperature, humidity, collection air flow) cause challenges to conventional collection methods and care must be taken to control conditions.

This research identified experimental considerations in adapting air sampling methods for each of the five chemicals in the context of the permeation test. Existing Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) air sampling techniques were adapted and validated. The test procedure was evaluated for conditions which may lead to variability or analyte loss. Permeation testing for each chemical was performed on a set of three materials.

Results reveal that thorough validation procedures are needed to ensure collection, retention, and stability of certain analytes for a given method. Acrolein, an unsaturated aldehyde with high reactivity and vapor pressure, is found to be especially susceptible to potential under reporting and can exhibit high levels of analyte loss and sensitivity issues. Chlorine shows considerable loss in the test environment. Issues associated with collection flow rate and challenge concentrations are also detailed.

Adapting Air Sampling Methods for the Detection of Toxic Industrial Chemicals in NFPA 1994 Permeation Resistance Test

by
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DEDICATION

This thesis is dedicated to all the teachers that told me I could always amount to something; to all the people who supported me growing up; to everyone just livin' in the world we live in. It's all good baby, baby.

BIOGRAPHY

William John Gabler is an internationally unrecognized scientist, scholar, and student leader who specializes in analytical chemistry and protective clothing. William was born in Paris, France on a cool, foggy morning in September of the year 1987. He moved to Arlington, Virginia to pursue his elementary studies where he enjoyed a quiet childhood. Continually inspired by the promise of education, William decided to attend The College of William and Mary in Williamsburg, Virginia. He studied Chemistry under the guidance of Dr. Richard Kiefer and Dr. Robert Orwoll. Following his Bachelors he retreated to Arlington, Virginia spending time as a substitute teacher at Washington-Lee High School. In 2011 William unexpectedly ran off to graduate school, starting a Master's program at the North Carolina State University College of Textiles in Raleigh, North Carolina. He began working in the Textile Protection and Comfort Center in 2012, training with Dr. Bryan Ormond in the Chemical Protection Laboratory. Along with the evaluation of the NFPA 1994 permeation resistance test the Chemical Lab has also been researching test methods for protective ensemble closures, real-time permeation detection, and extraction techniques to detect chemicals on fabrics and other surfaces. Following his Masters research, William plans to pursue a Doctorate in Fiber and Polymer Science.

ACKNOWLEDGMENTS

This work would not have been possible without the support and direction of the Textile Protection and Comfort Center. Thank you Dr. Roger Barker for assembling such a dedicated group of people and for making an investment in the resources and capabilities needed to perform diverse and impactful research.

The following is largely a continuation of research started by Christopher Mekeel on factors impacting results in the NFPA 1994 permeation test. Further, the work is the result of the combined effort from a team who each contributed a large amount of knowledge, effort, and patience. Thank you to Dr. Bryan Ormond, Dr. Ashley Bradham, and Christopher Mekeel.

Thank you to Shawn, Kevin, Alex, John, Mark, Michelle, Julisha, Kyle, Candace, Marika, Emile, and Gail for making our office such a fun and welcoming place to work. Thank you for the support and motivation provided by my committee members Dr. Keith Beck and Dr. Donald Thompson.

Thank you to my family for being so supportive and for convincing me and every body else that Im much smarter then actually.

Thank you to all the friends I've made in Raleigh. It is great to have another place which feels like home.

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Chapter 1. Introduction

1.1 Purpose

Terrorism incidents and accidents involving the release of toxic industrial chemicals (TICs) are of serious concern. The garments worn by first responders in these situations must provide the necessary level of protection while minimally interfering with the ability to perform. Thus it is important to be able to accurately measure the chemical permeation resistance of protective clothing. The NFPA 1994 Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents exists to establish standards of testing and performance to certify such garments by defining test conditions, challenge levels, and maximum cumulative amounts of chemical permeation allowed within a test period (1).

Implementing the NFPA 1994 chemical permeation resistance test is an instructive exercise in the challenges of matching desired performance criteria to appropriate testing procedures. The test uses a high humidity air collection flow and dilute challenge concentrations intended to simulate use situations. Tests which more closely replicate real-world conditions should in theory give more accurate assessment of samples. However, each challenge chemical chosen must be considered individually with respect to the chemical analysis techniques required to implement such a test and the influence of test conditions. How do sample collection methods influence measured permeation? What test conditions alter results or cause variability?

An ideal permeation test uses challenge chemicals which represent a range of chemical classes; challenge levels representative of those expected in field use; sampling methods which

are verifiable, inexpensive, and accurate; and performance limits with toxicological meaning. The results of such a test should be reproducible, comparable, and applicable.

The purpose of this research is to identify protocols which may ensure that permeation tests used for certifying protective apparel are being performed in a consistent and accurate manner. What steps must be taken to improve sampling methods or permeation test protocols? Test standards should be designed both to certify materials for use in the field and provide a research tool for their improvement. Establishing a rigorous method of validating chemical permeation test procedures can lead to better analysis and design of garment components.

1.2 Research Objectives

The research objectives are to validate active air sampling methods used in chemical permeation resistance tests with available instrumental and analytical techniques. Each of the challenge chemicals used in NFPA 1994 were evaluated with the following objectives:

1) Survey options for collection and detection.

2) Validate chosen method by isolating the effects of test conditions.

3) Perform full test procedure using a variety of fabrics.

4) Evaluate method parameters which may lead to inconsistent results.

This information is meant to supplement the test standard, which does not define analytical method details. Components of the testing standard were also evaluated for ways in which differences in test implementation could cause variability. The significance of the challenge levels were also considered.

Chapter 2. Literature Review and Background

2.1 Toxic Industrial Chemicals

Toxic Industrial Chemicals (TICs) are chemicals manufactured or stored in large quantities which pose a risk for use by terrorists or as chemical warfare agents. Many different chemicals are considered TICs and present a wide variety of potential hazards including health effects (corrosives, poisons, carcinogens, reproductive hazards, respiratory effects) and physical hazards (flammable, combustible, explosive, and reactive chemicals). Agents can remain a risk for varying amounts of time after an attack depending on the physical properties of the released TIC (liquid, gas, aerosol) and the environment (temperature, weather conditions, terrain) (2).

The Department of Labor's Occupational Safety and Health Administration (OSHA) and many other organizations and government agencies offer guidelines highlighting the risks, exposure limits, and recommended protective equipment (PPE) for situations involving TICs (2). This information is especially crucial for first responders and military personnel who would be required to enter areas after an attack to rescue victims and perform military operations. Much of the information currently exists primarily to define and regulate workplace exposure limits (3)(4). The OSHA Technical Manual along with the Environmental Protection Agency (EPA) define Levels of Protection to help workers match necessary ensemble features to the hazard at hand (5). Multiple standards exist to classify and test the chemical protective levels of materials and garments. These are discussed more closely in 2.2.1.

There are some standards and guidelines specific to first responder equipment and activities. The National Institute of Justice offers the Guide for the Selection of Personal Protection Equipment for Emergency First Responders, which attempts to give an overview of available PPE products with technical specifications. However, this document does not appear to have been updated in recent years (6). The NIJ has also released a voluntary performance standard for certification of CBRN protective ensembles which is described in section Permeation Testing Standards 2.2.2 on permeation test standards (7).

More detailed information comes from the National Fire Protection Agency (NFPA) which offers multiple standards and publications providing information and setting certification procedures specifically for first responder equipment. These include NFPA 472 *Hazardous Materials/Weapons of Mass Destruction Response Handbook*, NFPA 1991 *Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies*, NFPA 1992 *Standard on Liquid Splash-Protective Ensembles and Clothing for Hazardous Materials Emergencies,* and NFPA 1994 *Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents.* These standards are unique because they define entire ensemble requirements for certification, attempting to take the guesswork out of choosing appropriate materials for emergency situations.

NFPA 1994 sets performance criteria for three classes of CBRN protective ensembles based on vapor and liquid hazard concentrations defined by the National Institute for Occupational Safety and Health (NIOSH) as Immediately Dangerous to Life and Health (IDLH) (1). Class 2 ensembles are intended for exposure levels above IDLH and Class 3 for levels below IDLH. Class 4 ensembles are not required to undergo permeation testing. The

NFPA standard was chosen as the focus of this project because it is a widely used certification standard which defines its own unique, applied permeation resistance test procedure. It uses a set of five TICs to challenge garment materials and components.

2.1.1 Overview of Toxic Industrial Chemicals

The physical properties of the TICs used in NFPA 1994 are summarized in Table 2-1 Toxic Industrial Chemicals Used in NFPA 1994 Chemical Permeation Resistance Test. All of these chemicals are considered common TICs by OSHA (2).

Table 2-1 Toxic Industrial Chemicals Used in NFPA 1994 Chemical Permeation Resistance Test (8) (3) (9)

TIC	Molecular Weight, g/mol	Boiling Point, ºC	IDLH, ppm	ACGIH TLV and OSHA PEL, ppm	Reported Effects through Skin Exposure
Dimethyl Sulfate	126.1	188, decomp	7	0.1 TWA *skin*	Severe blistering, poisoning, anticipated human carcinogen
Acrylonitrile	53.0	77	85	2 TWA 10 Ceiling *skin*	Irritates skin, toxic symptoms to central nervous system, lungs, liver, and kidneys
Acrolein	56.1	53	2	0.1 STEL *skin*	Skin burns, liver damage
Chlorine	70.9	-34	10	1 Ceiling	Inflammation of mucous membranes
Ammonia	17.3	-3.5	300	50 TWA	Reacts with moisture to form a corrosive, blistering of the skin

The levels listed are not those used to test the ensembles, which are listed in Table 2-3 Challenge Battery for NFPA 1994. The IDLH levels are used as the basis of selection logic in the NFPA standard. The NIOSH website states the following about the use of these values:

> "The purpose of establishing an IDLH value is (1) to ensure that the worker can escape from a given contaminated environment in the event of failure of the respiratory protection equipment and (2) is considered a maximum level above which only a highly reliable breathing apparatus providing maximum worker protection is permitted." (10)

The American Conference of Governmental Industrial Hygienists (ACGIH) values and OSHA values are also listed in the NIOSH IDLH handbook. The ACGIH defines Threshold Limit Values (TLV) of recommended occupational exposure limits. An additional *skin* notation is added for chemicals having a significant contribution to exposure through direct skin contact (8). OSHA defines Permissible Exposure Limits (PEL) which are legally enforceable limits for employee exposure. The levels are defined either as Ceilings, Short-Term Exposure Limits (STEL), or Time Weighted Averages (TWA). These are the average concentration which either cannot be exceeded at any time, over the course of 15-30 minutes, or over 8 hours, respectively. These values are not necessarily the source of the reported effects on the right side of the chart. Note that chlorine and ammonia do not have skin notations at their TLV values.

In order to be used as a chemical permeation challenge, each chemical must be able to be collected and analyzed from the air which passes through the collection side of the test cell. Information on the physical properties and detection methods of each chemical are given in the next sections. Test details are given in section 2.2.2 on permeation testing standards.

2.1.2 Ammonia

2.1.2.1 Uses and Properties

Ammonia, NH_3, is an ubiquitous biological chemical involved in the metabolic processes of nearly all plants and animals. Yet in large amounts it is a powerful toxin with dangerous physical properties. Excessive ammonia levels in tissue, called ammonia intoxication, causes convulsions and hyperventilation (11). Concentrations in air above 400 ppm can react with moisture to become corrosive and cause chemical burns on the skin. At the correct concentrations with oxygen it can become explosive in the presence of an ignition source (12). As a common, low-cost fertilizer and an important industrial compound, ammonia is a source of concern regarding air and waterway pollution, use in the manufacture of illicit drugs, release as a chemical weapon, and use as an explosive. Large storage tanks containing hundreds of pounds of liquid compressed anhydrous ammonia are often present in agricultural locations. Special precautions must be taken to prevent theft and misuse in these situations (13).

2.1.2.2 Collection and Detection Methods

Ammonia air sampling is readily achievable by its reaction with sulfuric acid (H_2SO_4) to form the stable ionic compound ammonium sulfate ($(NH_4)_2SO_4$). Ammonium sulfate is highly soluble in water and dissociates into conducting ions. OSHA lists two available methods. Method ID-164 uses a glass midget bubbler containing 0.1 N H_2SO_4 creating a solution which can be analyzed with an Ion Specific Electrode. The method is followed by ID-188 which instead uses carbon beads impregnated with H_2SO_4 and avoids problems with liquid sampling media. Similarly, the NIOSH method 6016 uses silica gel sorbent treated with H_2SO_4.

Sample rates up to 1 L/min are reported. Sample collection volume depends on the air concentration level being measured (14) (15) (16).

In both instances the sorbents can be extracted with deionized water and the ammonium ion can be analyzed using Ion Chromatography (IC) with a conductivity cell. These collection sorbents in the form of sampling tubes are commercially available and analysis with an IC system allows for fast and sensitive results down to part-per-billion sample concentrations. It is important to note for analysis with IC that ammonia is a weak base. In previous generation IC instruments, without suppression technology, ammonium gives a linear response between concentration and instrument response. Newer IC technology uses suppressors which remove anions in the eluent, so that the analytes pass through the detector in water. Suppressors reduce background conductivity and increase the detection range. However, for ammonium ions it causes a quadratic response between concentration and conductivity, because at higher concentrations in water fewer of the ammonium ions are protonated leading to a lower conductivity response. The quadratic response can be correlated with a coefficient of determination to over 0.999 (r^2) over four orders of magnitude (17).

Interference can be caused by ammonium salts in the air, by excessive amounts of sodium in the liquid sample, and by pH effects in the IC cause by excessive H_2SO_4. Ammonium sulfate can decompose to release ammonia, however this is reported to occur at temperatures exceeding 100^oC (18).

2.1.3 Chlorine

2.1.3.1 Uses and Properties

Chlorine, Cl_2, is the other gaseous challenge compound used in NFPA 1994. It is a widely used chemical, essential for a variety of purposes from disinfection and water purification to the synthesis of polymers, pesticides, and pharmaceuticals. It is the active agent in most swimming pool disinfection systems, at concentrations of up to 5 ppm in water. It is an irritating gas which primarily affects the respiratory system and mucous membranes. Exposures above 500 ppm in air can be fatal in the course of just 30 minutes without protective equipment (9). The release from a 1-ton tank of chlorine can cause respiratory discomfort over a 3-square-mile area. The same amount can be fatal to victims if concentrated in $1/10^{th}$ of a square mile area (19). Though it is a gas at standard temperatures, its high density makes it a persistent threat in release situations, where it accumulates in low lying areas.

Chlorine is reported to be the first chemical used in a large scale chemical warfare attack by Germany against Allied Forces in 1915 (20). It is a powerful oxidizer and in the presence of water forms hypochlorous acid and hydrochloric acid. These are capable of corroding metals, notably iron, carbon steel, and aluminum (21). Dry chlorine can be used in equipment made of most metals. However, in the presence of moisture it becomes highly corrosive and the use of glass, stoneware, or plastics is required (22).

2.1.3.2 Chlorine Chemistry

Chlorine detection is complicated by the chemical's reactivity in the presence of water, as shown in Figure 2-1. The primary reaction of chlorine gas is the disproportionation in the presence of moisture into two ionic species, chloride and hypochlorite. These species equilibrate between protonated and unprotonated forms depending on the pH of the solution.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$HOCl \leftrightarrow H^+ + OCl^- \text{ (pH dependent)}$$

Figure 2-1 Reaction of Chlorine in Water

Hydrochloric acid (HCl) is a strong acid which dissociates at low pH. The chloride ion (Cl^-) is fully reduced and very stable in water in the presence of counter ions. Hypochlorous acid (HOCl) is a weak acid. Both hypochlorous acid and hypochlorite ions (OCl^-) are present between pH of 6.5 and 8. The amount of dissociation relies on pH and temperature with hypochlorite favored at higher temperature and pH. Both forms are reactive oxidizers, making this the desired form of chlorine used as a disinfectant. The quantity of reducible chlorine present is referred to as available chlorine or percent active chlorine. Percent active chlorine is defined by the ratio of moles of available chlorine per unit mass in comparison to pure chlorine gas, which would be equivalent to 14.1 mol/kg and 100% available (19). Residual chlorine is a measure of all forms of chlorine present in a sample which are still available for oxidation. The hypochlorite ion is unstable and over time will itself disproportionate into chloride and chlorate (23).

Chlorine has very high solubility in water. There are multiple reactions which can lead to chlorine absorption in water besides the hydrolysis reaction described above, which itself is very fast. Chlorine reacts with many materials to reduce completely to chloride ions. One instance is the reaction with sulfite ions, which contain sulfur in the +4 oxidation state. The sulfite oxidizes to sulfate and the chlorine is reduced to chloride (Figure 2-2). Such a reaction has been explored as a possible trapping agent of chlorine from flue gas (24) (25). This

approach was adapted to the current research because of its ability to combine with ion chromatography for the detection of total chlorine in the form of chloride.

$$Cl_2 + Na_2SO_3 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

Figure 2-2 Reaction of Chlorine and Sodium Sulfite

2.1.3.3 Collection and Detection Methods

Two general approaches exist for the detection of chlorine. One approach is detection of chloride through conductivity reading. The other approach is an analysis of residual chlorine through the addition of a reducing agent, followed by titration of the derivative and detection using colorimetery or an electrochemical method.

NIOSH Method 6011 uses silver membrane filters held in a filter cassette. The silver reduces the chlorine to form silver chloride which can be rinsed in thiosulfate to release chloride. The chloride solution can be quantitated using ion chromatography (26) (27). This method has high sensitivity and it uses a compact and durable sampling device, capable of using flow rates up to 1 L/min. Interestingly, high humidity increases the collection capacity. However the sample preparation requires dilutions and the addition of reagents. The silver filters are relatively expensive (6$ each), though they can be cleaned and reused. Silver thiosulfate is strongly retained in IC columns, requiring strong mobile phase concentrations to elute which shortens column lifetime (27).

A combined Ion Chromatography and Electrochemical detection method has been used to detect hypochlorite, chloride, and chlorate. Hypochlorite is reduced to chloride by the ion exchange resins in IC thus it must be detected prior to the column. Sample flow is passed through an electrochemical flow cell first then directly through the anion column (23).

The other approach, detection of residual chlorine, is widely used to determine levels of active chlorine present as a bleaching agent or a contaminant in water. Integrated continuous monitoring systems exist for reading chlorine concentrations in water based on this principle. Multiple colorimetric methods, including two based on methyl orange and o-tolidine, are no longer common due to instability issues and chemical hazards (28) (29).

The current OSHA air sampling method uses a sulfamic acid solution in a bubbler, which reversibly stabilizes hypochlorite as active chlorine (30). Iodide and a buffer reagent are added. The iodide reacts completely with the chlorine to form iodine which is detected with an iodine specific electrode (31). This method requires preparation and dilution for each sample due to the small linear range of the electrodes. It is an indirect measure of chlorine atoms.

2.1.4 Dimethyl Sulfate

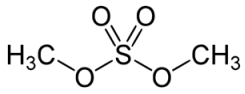


Figure 2-3 Structure of Dimethyl Sulfate

2.1.4.1 Uses and Properties

Dimethyl Sulfate (DMS) is a colorless liquid with a faint onion-like odor. It is a low cost and high reactivity alkylating agent. This means it is able to transfer its methyl groups to other compounds, making it useful in the manufacture of many chemicals across industries. It is notably used to cleave DNA in sequencing laboratories. DMS is reported to have been used as a chemical warfare agent during World War I, and it has recently been investigated as a theoretical chemical weapon in US Military terrorist attack training exercises (32). It is listed by the Department of Health and Human Service's Report on Carcinogens as a reasonably anticipated human carcinogen. It has been studied for its ability to react with nucleic acids in the body. DMS hydrolyzes in wet environments into methanol and sulfuric acid. Inhalation can lead to difficulty breathing, symptoms of methanol intoxication, followed by cytotoxicity in vital organs. It has a high density and low vapor pressure, meaning it will remain as liquid in most environmental situations. It reacts with the skin to cause severe blisters, sometimes with delayed onset of multiple hours, making it very similar in action to the chemical warfare agent Sulfur Mustard (HD) (33).

2.1.4.2 Collection and Detection Methods

DMS has the highest boiling point and molecular weight of the NFPA 1994 chemicals. It is more easily trapped by sorbent materials, soluble in most organic solvents, and can be detected with multiple detectors. Two methods published to collect DMS at the Permissible Exposure Limit (PEL) use Poropak Q and Poropak P sorbents followed by extraction and analysis with a Gas Chromatograph (GC). OSHA PV2147 uses 200 mg Poropak Q glass tubes, extraction with acetone and analysis on a GC with a Flame Photometric Detector. The method has a reported detection limit of 0.05 ppm sampling at 0.1 L/min (34). NIOSH 2524 uses 200 mg Poropak P sorbent tubes with 100-mg front and 50-mg back sections, extraction with diethyl ether, and analyzed on a GC using an electrolytic conductivity detector in sulfur mode. It has a reported detection limit of 0.25 ppm at a sampling rate of up to 0.2 L/min (35). DMS can also be detected with Flame Ionization Detection, Mass Spectrometry, and in Liquid Chromatography with a UV detector after derivatization.

2.1.5 Acrylonitrile

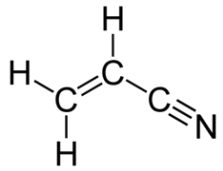


Figure 2-4 Structure of Acrylonitrile

2.1.5.1 Uses and Properties

Acrylonitrile (vinyl cyanide) is an olefin containing the cyanide functional group. It can be polymerized, which is useful in the production of resins, fibers (acrylic), coatings, and

as a synthetic intermediate. It is highly flammable and can form explosive vapors in air. It has a high vapor pressure, 83 torr at 20^{o}C. VCN is a serious health hazard, exhibiting toxicity through all forms of exposure. It is mutagenic, teratogenic, and a carcinogen in test animals. Absorption through the skin causes toxic symptoms in the entire body, affecting the nervous system, gastrointestinal tract, liver, kidneys, and causing skin peeling (9). VCN is present in cigarette smoke. Exposure can be monitored in the body as hemoglobin adducts after it reacts with terminal amines in the blood. This method has been used to measure exposure in factory workers and in mothers who smoke and their newborn babies. Correlation was found between the smoking frequency of mothers and the levels in their children's hemoglobin, indicating trans-placental transfer (36).

2.1.5.2 Collection and Detection Methods

Acrylonitrile has multiple established analytical methods. NIOSH 1604 suggests the use of coconut shell charcoal sorbent as a collection medium, extraction with 2% (v/v) acetone in carbon disulfide, and detection on a GC with a Flame Ionization Detector (FID). Charcoal sorbent extracted with carbon disulfide is a common method for small molecular weight organic compounds due to charcoal being inexpensive and readily available and carbon disulfide's ability to displace molecules from the carbon surface as well as its low signal response in FID. The addition of small amounts of polar solvent optimizes the extraction by increasing its affinity for polar analytes (37) (38). However, carbon disulfide is a highly toxic chemical and is used as a challenge chemical in some permeation testing. NIOSH 1604 was reportedly validated with samples up to 1.91 mg per 200 mg of carbon and showed no breakthrough up to 36.7 L when sampling 8 mg/m^3 air at 0.2 L/min. However the same

evaluations stated that lower level samples (8.5 µg) showed an average of only 79% recovery. The method was validated using liquid standard spikes prepared in hexane and vapor phase spikes created by mixing a standard with 5 L of 80% RH air in a sample bag. Extractions were performed at high and low levels, 8.5 µg and 16.5 µg (39) (40). To address the drawbacks of low level recovery and the effect of humidity on charcoal, porous polymer adsorption tubes paired with thermal desorption have also been shown to be effective (41).

2.1.6 Acrolein

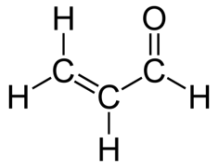


Figure 2-5 Structure of Acrolein

2.1.6.1 Uses and Properties

Acrolein is a volatile unsaturated aldehyde with highly reactive electrophilic properties. It has a very high vapor pressure, 214 torr at 20^{o}C making it similar in volatility to acetone. It is naturally occurring in certain foods and as a combustion product of organic materials such as wood, cooking oil, tobacco products, and polymeric substances such as polyethylene making it a likely respiratory hazard to firefighters. Inhalation leads to irritation and choking. Significant eye irritation has been reported at 0.06 ppm exposure to human subjects (42). As a widespread environmental pollutant it is especially toxic to aquatic life. It is used industrially as a slimicide (a chemical which prevents the growth of organisms which produce slime during

paper production), a microbiocide, and as an important chemical precursor to acrylic acid (9) (42).

Acrolein binds to nucleophilic amino acid residues in the body and in acute exposure leads to cell death and other complex molecular effects (43). It can be absorbed through the skin and skin contact can lead to chemical burns, respiratory effects, and produce delayed pulmonary edema (9). Acrolein can react in a variety of ways. It is stored with hydroquinone which acts as a stabilizer to prevent free-radical polymerization. Acrolein typically can only be purchased in 90% purity with up to 10% present in the form of the acrolein dimer, 3,4-dihydro-2H-pyran-2-carboxyaldehyde, which forms under heat. This reaction is optimized at 170^{o}C (44). In the presence of water, acrolein forms 3-hyroxypropionaldehyde (3-HPA) which can further react to form multiple derivatives (45).

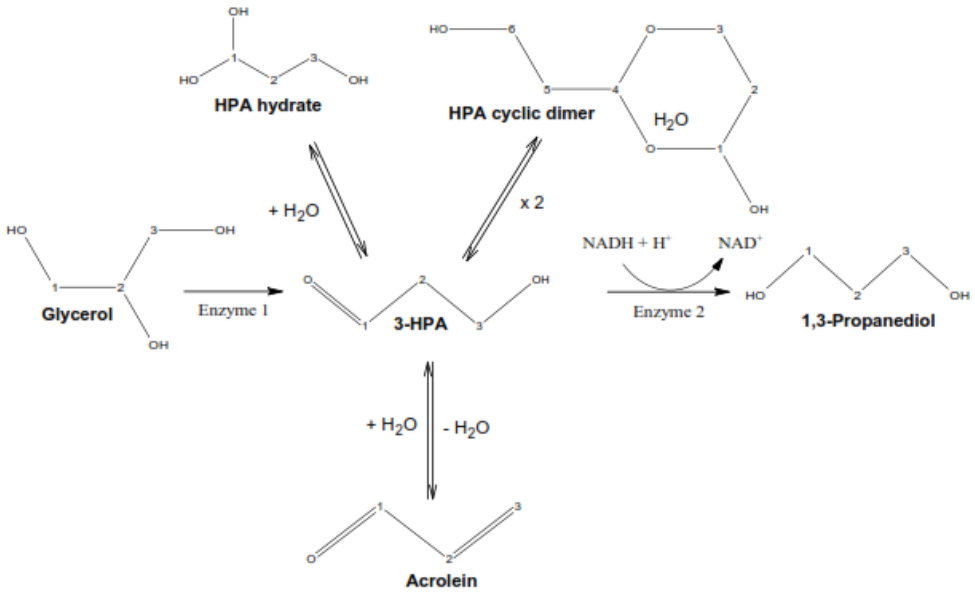


Figure 2-6 Reactions of Acrolein in Water

2.1.6.2 Collection and Detection Methods

Due to acrolein's reactive nature it has proven difficult to collect and characterize in environmental air samples. Methods usually rely on derivatization with the carbonyl group followed by solvent extraction.

EPA TO-11A uses 2,4-dinitrophenylhydrazine (DNPH) coated sorbents. This method has a high sample capacity and is capable of collecting at flow rates up to 2 L/min (46). However, in 2000 the EPA amended the standard to remove acrolein from the list of target analytes (47). It was found that the acrolein-DNPH derivative reacts into multiple additional adducts over time (48). Additionally, the cartridges are expensive compared to most single use active sampling sorbent cartridges.

EPA TO-15 is the current accepted method for collecting environmental samples of acrolein. It uses steel canisters to collect pressurized samples, which are not easily applicable to collection in test situations and has recently been under scrutiny for carryover contamination (49).

Another derivatization approach uses the reagent 2-(hydroxymethyl)piperidine to create acrolein-oxazoladine. It is either coated on a sorbent (50) (51) or mixed in a solution. However these methods are limited in multiple ways. The method capacity is only 30 µg and the reaction rate is notably slow. The standard preparation requires at least 4 hours to react acrolein with the reagent. Both methods utilize collection flows drastically lower than the NFPA 1994 test collection flow (0.05 – 0.2 L/min compared to 1 L/min). The detection limit is sensitive enough however the methods require the use of a Nitrogen-Phosphorus Detector (NPD).

Polymeric sorbent followed by thermal desorption have been used for the collection of acrolein from air, however no recovery efficiency was reported (41). Acrolein is detectable with a Photo-Ionization Detector (PID) with an 11.7 eV or 10.6 eV lamp, though the latter requires a correction factor of 3.9. A novel approach using a bisulfite adduct "mist chamber" to trap acrolein has been reported, followed by derivatization for detection in LC (52). It requires a rather large collection apparatus and has not been independently verified.

2.2 **Chemical Protective Clothing**

2.2.1 Classification Standards

Chemical Protective Clothing (CPC) design and construction is targeted toward use situations. These situations can be characterized by the concentration and toxicity of chemical

exposure, duration of use, and physical environment (53). The EPA's Levels of Protection publication has established simple outlines to link equipment components with situations, ordered from Level A (highest protection) through D (lowest protection). As a brief example, the suspected presence of substances with a high degree of skin hazard requires the use of a Level A suit which has a limiting criteria of being fully-encapsulating and requires a self-contained breathing apparatus (SCBA). Meanwhile, if the concentrations do not represent a severe skin hazard but vapors and gases at levels Immediately Dangerous to Life and Health (IDLH) are present then a Level B suit is prescribed, for which SCBAs are still required but only clothing providing splash protection is required. These levels only provide basic differentiation in construction but do not specify minimum performance (54).

The International Organization for Standardization (ISO) provides a more extensive grouping of chemical protective clothing in ISO 16602 Protective Clothing for Protection against Chemicals - Classification, Labeling and Performance. It groups clothing into six Types, sets mechanical, barrier, and flammability criteria, and defines Classes within each Type based on ranges of performance for these key properties (55) (56). The six types, summarized below, use similar language to the EPA Levels of Protection.

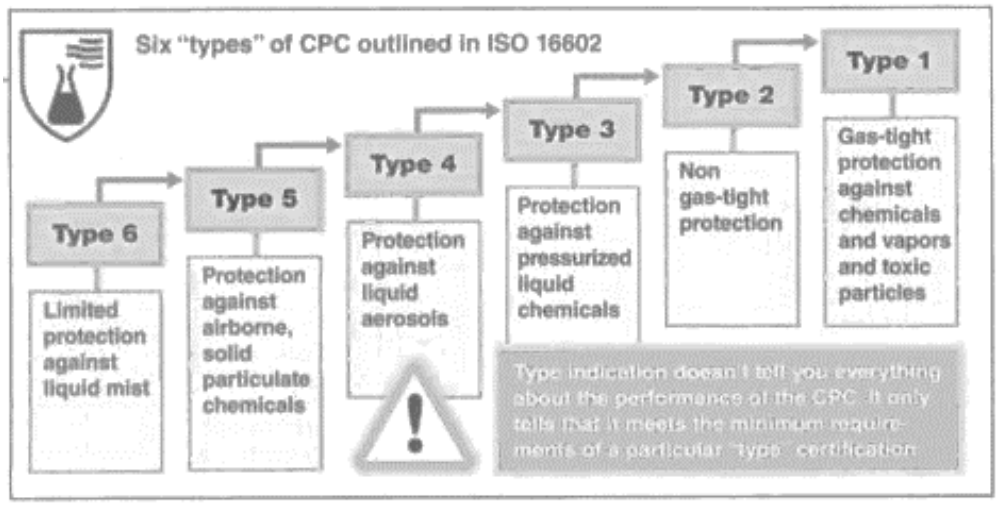


Figure 2-7 CPC Type Classifications in ISO 16602 (56)

An example of the Classes used to distinguish materials' permeation resistance within a Type is shown in Figure 2-8 CPC Class Classifications in ISO 16602. It can be seen that Type 1 Class 6 clothing would provide the highest level of protection against permeation of liquids and vapors.

Table 4 — Classification of permeation resistance according to time to cumulative permeation of 150 µg/cm²

Class	Time to cumulative permeation of 150 µg/cm² min
6	w 480
5	w 240
4	w 120
3	w 60
2	w 30
1	w 10

Figure 2-8 CPC Class Classifications in ISO 16602 (55)

ISO 16602 provides detailed language for defining and testing chemical protective clothing performance. It is already widely implemented and provides the opportunity for international harmonization, including labeling requirements (56). However the standard only addresses clothing and does not directly specify performance for boots, face protection, gloves, or respiratory devices nor does it contain information on biological, radiological, or thermal hazards (55).

The American National Standard Institute and the International Safety Equipment Association have published ANSI/ISEA 103-2010 American National Standard for Classification and Performance Requirements for Chemical Protective Clothing which is consistent with the ISO standard (57).

Following similar guidelines the NFPA defines performance based classifications for protective clothing with the comprehensive focus of addressing entire ensembles for risks specific to first responders facing chemical and biological hazards. These are defined in separate standards which provide performance criteria, again based on use situation. They include Vapor-Protective (NFPA 1991), Liquid Splash Protective (NFPA 1992), and Chemical/Biological Terrorism Threats (NFPA 1994). NFPA 1991 references an ASTM International standard, ASTM F739, to implement permeation testing. NFPA 1994 defines its own permeation resistance method which is derived from a military Test Operating Procedure (TOP) 8-2-501. The NFPA method provides more specific use guidelines as well as specifications intended directly for first responders and military personnel.

NIJ Standard-0116.00 is similar to NFPA 1994 in that it adopts the permeation methods from other test standards and additionally defines a list of performance criteria for ensembles

including ergonomic, mechanical, and thermal testing. The standard defines four Law Enforcement Response Levels (LERLs) for CBRN incidents with criteria roughly matching NFPA Class 1-4 ensembles. The LERL 2-4 permeation test uses identical challenge chemicals mimicking Class 3 evaluation in NFPA 1994-2007 and gas challenges at a range of concentrations (7).

2.2.2 Permeation Testing Standards

Current standardized procedures for performing chemical permeation resistance tests include NFPA 1994, ASTM F739, ISO 6529, EN374, and TOP 8-2-501. Table 2-2 Comparison of Permeation Standard Test Requirements summarizes test conditions and performance criteria. The TOP standard and an additional NIOSH standard designed for the permeation resistance of chemical warfare agents are published but not widely used (58). It should be noted that none of the methods specify analytical procedures or method validation procedures. ISO 6529 and ASTM F739 contain information about calibrating and determining sensitivity for a permeation test system (59). They do not cite toxicological data outlining acceptable exposure limits either.

It can be said that most of these methods seek to test for an optimized permeation condition where the test surface is submerged in the challenge and the collection side is continuously swept clear, achieving a maximum concentration gradient in the material. The ISO, EN, and ASTM methods are written in general terms which allow multiple approaches to permeation test setups, collection, and analytical methods. They also encourage testing outside the suggested chemical battery, which allows manufacturers to publish permeation data for their materials against chemicals of interest. Only NFPA 1994 uses diluted challenge

concentrations and specified test conditions. It also includes tests against chemical warfare agents (CWA) and biological agents. The challenge batteries for each permeation standard are located Table 2-3, Table 2-4,

Table 2-5, and Table 2-6.

Table 2-2 Comparison of Permeation Standard Test Requirements

Standard	Cell	Condition	Challenge	Sensitivity	Measure
ASTM F739	Suggested glass cell 25.4 mm diameter exposure ~15 mL sweep volume	27 °C	Suggested: ASTM F1001	0.1 µg/cm^2/min	Time to detection of 0.1 µg/cm^2/min
ISO 6529	Suggested glass cell 25.4 mm or 51 mm diameter exposure	any	Suggested: ISO 6529 Annex A	0.1 µg/cm^2/min	Time to detection of 150 µg/cm^2 cumulative
EN 374	Suggested glass cell	any	Suggested: EN 374 Challenge Battery	1.0 µg/cm^2/min	Time to detection of 1 µg/cm^2/min
NFPA 1994	Required TOP 8-2-501 metal cell 35.5 mm diameter exposure 13.3 mL sweep volume	32 °C and 80% RH air collection medium	Required: NFPA 1994 TICs	0.1 µg/cm^2	Ceiling of 6 µg/cm^2 cumulative over 60 min

2.2.2.1 NFPA 1994 Chemical Permeation Resistance Test Challenge History

The NFPA 1994 test concentrations have been changed with each revision of the test standard. There have been three editions: 2001, 2007, and 2012. The original method did not require vapor permeation testing for Class 3 garments and the test included cyanogen chloride, carbonyl chloride, and hydrogen cyanide as challenges. In 2007 acrylonitrile and acrolein replaced those three challenges because they posed more of a threat from skin exposure. They

were added as liquid challenges with the same test concentration as dimethyl sulfate. Ammonia and chlorine remained in the test because they were deemed to be such likely real world threats, but their challenge concentrations were also changed from 1,000 ppm for the vapors to the 350 ppm and 40 ppm concentrations used today. These numbers apparently come from the NIOSH Statement of Standards used to evaluate respirators for CBRN use. The concentrations match the challenge concentration of sarin vapor - 2,000 mg/m^3 and 210 mg/m^3 - used to test permeation resistance of SCBAs and Air Purifying Respirators (APRs), respectively (60) (61). This follows the logic that the respirator is the most fundamental line of defense so a higher concentration challenge would not be acceptable for an ensemble using such a respirator. However the same standard for APRs contains a canister test for ammonia at a concentration of 2,500 ppm and formaldehyde at 500 ppm. In 2012, acrylonitrile and acrolein were changed to vapor challenges with the same concentration as ammonia and chlorine because, due to their high vapor pressure, they would exist as vapors in the test conditions.

Table 2-3 Challenge Battery for NFPA 1994

Challenge Chemical	NFPA Class 2	NFPA Class 3
Acrolein	350 ppm	40 ppm
Acrylonitrile	350 ppm	40 ppm
Ammonia	350 ppm	40 ppm
Chlorine	350 ppm	40 ppm
Dimethyl Sulfate	10 g/m^2	10 g/m^2

Table 2-4 Chemical Battery for EN 374

Predefined chemical in EN 374	Class	CAS* number	Code letter
Methanol	Primary alcohol	67-56-1	A
Acetone	Ketone	67-64-1	B
Acetonitrile	Nitrile compound	75-05-8	C
Dichloromethane	Chlorinated paraffin	75-09-2	D
Carbon disulphide	Sulphur containing organic compound	75-15-0	E
Toluene	Aromatic hydrocarbon	108-88-3	F
Diethylamine	Amine	109-89-7	G
Tetrehydrofurane	Heterocyclic and ether compound	109-99-9	H
Ethyl acetate	Ester	141-78-6	I
n-Heptane	Saturated hydrocarbon	142-85-5	J
Sodium hydroxide 40%	Inorganic base	1310-73-2	K
Sulphuric acid 96%	Inorganic mineral acid	7664-93-9	L

Table 2-5 Chemical Battery for ISO 6529 (59)

A.2 List of recommended liquid test chemicals

Reagents are listed by common name, synonym, and Chemical Abstract Registry Service (CAS) number given in square brackets:

— acetone (2-propanone) [67-64-1],

— acetonitrile (cyanomethane, methyl cyanide) [75-05-8],

— carbon disulphide [75-15-0],

— dichloromethane (methylene chloride) [75-09-2],

— diethylamine [109-89-7],

— ethyl acetate [141-78-6],

— *n*-hexane [110-54-3], or *n*-heptane,

— methanol (methyl alcohol, carbinol) [67-56-1],

— sodium hydroxide (40 % by mass), r = 1,33 kg/l [1310-73-2],

— sulphuric acid (96 % by mass), r = 1,83 kg/l to 1,84 kg/l [7664-93-9],

— sulphuric acid (18 % by mass),

— tetrahydrofuran (THF, 1,4-epoxybutane) [109-99-9], and

— toluene (toluol) [108-88-3].

Table 2-6 Chemical Battery for ASTM F739 (62)

Challenge Chemicals	Description	CAS number
Acetone	Common Solvent, ketone	67-64-1
Acetonitrile	Nitrile compound	75-05-8
Anhydrous ammonia	Basic gas, high volume chemical commodity	7664-41-7
1,3-Butadiene	Hydrocarbon gas	106-99-0
Carbon disulfide	Sulfur containing organic compound	75-15-0
Chlorine	Acid gas, high volume chemical compound	7782-50-5
Dichloromethane	Chlorinated paraffin	75-09-2
Diethyl amine	Amine	109-89-7
Dimethyl formamide	Amide	68-12-2
Ethyl acetate	Ester	141-78-6
Ethylene oxide	Heterocyclic ether gas	75-21-8
Hexane	Saturated hydrocarbon	110-54-3
Hydrogen chloride	Inorganic acid gas	7647-01-0
Methanol	Primary alcohol	67-56-1
Methyl chloride	Chlorinated hydrocarbon gas	74-87-3
Nitrobenzene	Nitro compound	98-95-3
Sodium hydroxide	50% w/w, largest production volume base	1310-73-2
Sulfuric acid	93.1 %, 66° Be', largest production volume mineral acid	7664-93-9
Tetrachloroethylene	Chlorinated olefin	127-18-4
Terahydrofuran	Heterocyclic ether compound	109-99-9
Toluene	Aromatic hydrocarbon	108-88-3

2.2.3 Materials and Construction

It is important to understand the variety of materials used in the construction of chemical protective clothing. Material compatibility leads to a variety of permeation characteristics. Protective clothing can be made of a combination of components consisting of woven and knit textiles, rubbers and plastics, porous films, adsorbent materials, and plastic laminates (53). The barrier properties required for chemical permeation resistance also have considerable effect on the physiological conditions of the wearer. Studies have indicated that

the climate under an impermeable protective garment can reach temperatures generally 10^{o}C above the outside temperatures and relative humidity above 90% during normal use (63).

Climatic conditions can directly impact permeation rate and alter material barrier characteristics. It is also important because it highlights an underlying motivation of permeation testing. It is possible to over protect, to create garments which impede in the ability of the user to perform tasks and remain comfortable. Applied permeation testing seeks to evaluate for minimum performance criteria so that more comfortable and versatile chemical protective clothing can be made available to those who need it.

2.3 **Permeation**

2.3.1 Theory of Molecular Permeation

Permeation is defined as the movement of chemical through a material on the molecular level. It consists of three steps whereby the chemical (referred to below as the "solvent") adsorbs onto, diffuses through, and desorbs from the material (referred to below as the "polymer") (53) (59). Penetration is a different phenomenon which involves bulk flow of chemical through the material. Some materials are impenetrable to liquids, but nearly all polymeric films and fabrics will allow molecular permeation of solvents given enough time. Permeation is a more sensitive measure of barrier properties and provides an important quantitative measure of a fabric's chemical protection (64).

2.3.1.1 Solubility and diffusion

The first step in permeation involves solvent-polymer interaction which varies depending on the solubility of the two substances and molecular interaction forces. Solubility parameters are based on the free energy of mixing for the two substances or from the cohesive

energies of each chemical (53). Each solvent and polymer pair will have a unique solubility coefficient, S, which can be thought of as the amount of permeant that is capable of dissolving into a material. Solubility can be determined on its own using an immersion method and tracking the weight increase of a material sample over time (58). The solubility step is a significant factor of a polymer's ability to protect against a given solvent and the reason that inclusive challenge batteries are necessary.

The diffusion step proceeds by the random motion of solvent molecules through the material. This movement is largely dependent on the solvent's molecular volume. Diffusion would eventually lead to evenly distributed solvent in a closed system, but if the opposing side of a material is constantly being swept clear, a concentration gradient forms across the material and diffusion continues to occur. The most fundamental description of diffusion follows Fick's Law which defines the mass flux, J ($mg/cm^2/min$) as a gradient solvent concentration (dc) across the thickness of the material (dx, distance from surface) times a unique diffusion coefficient, D (cm^2/min).

$$J = -D \frac{dc}{dx}$$

Equation 1 Ficks' First Law

The solubility coefficient and diffusion coefficient can be multiplied to equal a permeability coefficient, P. Molecular models have been made which attempt to predict permeation parameters, such as mass flux, breakthrough time, and steady state permeation from solubility factors.

2.3.2 Factors Affecting Chemical Permeation

2.3.2.1 Conditions

The diffusion coefficient will vary depending on factors such as the solubility, challenge molecular weight, temperature, and challenge concentration at the surface. Higher temperatures lead to substantially increased permeation rates. Attempts have been made to characterize the effect of temperature on permeation characteristics using hose materials submerged in solvent, with the goal of predicting altered permeation (breakthrough and steady state permeation) at temperatures which differ from test temperatures (65).

Humidity can also alter transport properties but has a much greater impact on selectively permeable membrane materials which can allow small molecules and gases to permeate (66). Polymer membranes can swell in the presence of water and become more permeable to water vapor and organic chemical vapors. Sample conditioning must be maintained before and during testing for consistent permeation. If test components are not conditioned to test conditions in the NFPA standard, it is possible to form condensation within the test cell and in air collection lines due to the high humidity used.

2.3.2.2 Cell Construction

Cell geometry can alter permeation characteristics. Flow characteristics of the collection media and different challenge techniques can impact permeation rate. Exposure area changes the amount of permeant, but this a relative change.

It has been shown that high backpressure caused by air flow on the collection side of a cell can lead to material distention, causing a higher effective exposure area and possible material thinning (67). Air flow characteristics within the cell can also lead to poor mixing with collection media, resulting in suppressed permeation. Air flow studies which analyze the

efficiency of different sweep geometries of cells have been performed. It has been shown that efficiency is best achieved by decreasing the collection side volume to increase sweep velocity (68) (69). This would decrease the required amount of collection medium and lead to increases in sampling sensitivity.

Another factor in cell design is the method of challenge chemical delivery. The TOP 8-2-501 test cell, called the Aerosol, Vapor, Liquid Assessment Group (AVLAG) cell, as well as ones used by the Natick Soldier Center were designed for applying chemical warfare agents, either as a flooded surface or liquid droplets. The most desirable design for this task uses a horizontally oriented, small area material and a screw top which can quickly be resealed (58).

2.3.2.3 Challenge Concentration

As stated, the permeation rate depends on the challenge concentration. Applied permeation tests like NFPA 1994 seek to determine permeation characteristics at concentrations below the worst possible exposure. There are different approaches to testing with lower concentration challenges such as intermittent contact with a challenge chemical, applying liquid droplets, challenging with premixed air concentrations, or using a simulated vapor.

Intermittent contact causes different permeation patterns (69). Liquid droplets are unique because they consist of localized areas of high concentration challenge for compounds and the concentration changes during the duration of the test depending on the chemical's vapor pressure. Premixed dilute vapors are difficult to prepare and involve large amounts of contaminated air. Another approach to dilute chemical challenges is to invert the typical cell construction, fill the bottom with a liquid and using the vapor pressure of the challenge to

create a vapor. Another option is to use an additional barrier membrane with a predetermined permeation rate between the challenge and the test material (68). These methods make it difficult to achieve specific challenge concentrations.

2.3.3 Permeation Indices

Multiple ways exist to measure or characterize permeation. These include nominal breakthrough time (the time to reach a certain permeation rate), time to steady state permeation, steady state permeation (the permeation rate at equilibrium, where cumulative permeation increases linearly), and cumulative permeation (a measure of the total amount of permeant at a given time after exposure), each of which can be seen in Figure 2-9.

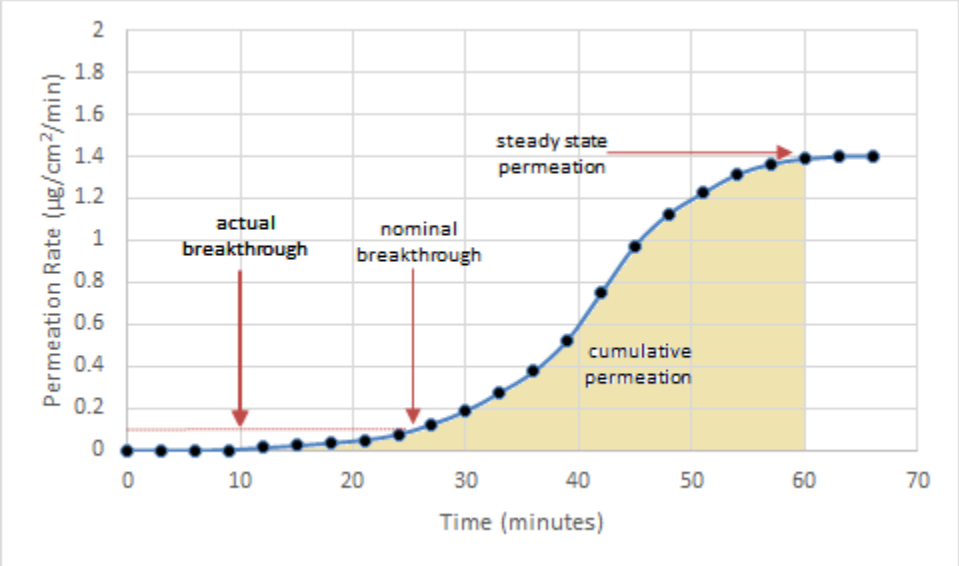


Figure 2-9 Permeation Indices Displayed on a Representaive Permeation Rate Curve

ISO 16602 Annex E describes the significance of the alternative measures of permeation. It states that time to a defined mass of chemical permeant is the best measure of

chemical protection because it equates to the "time to failure" of a material. Breakthrough times, on the other hand, do not equate to "safe wear time" because it is possible for extended harmful amounts of chemical to permeate through a CPC material at a rate below such an arbitrarily defined rate. The ASTM benchmark of 0.1 μg/cm^2/min is only meant to be a realistic threshold for detection methods, not a meaningful toxicological mark. ASTM F739 contains a note stating that "limited quantitative information exists about acceptable levels of dermal contact with most chemicals. Therefore, the data obtained using this test method cannot be used to infer safe exposure levels" (62). This is clear when considering the other arbitrarily set breakthrough rate of 1 μg/cm^2/min used in the EN standard.

ISO considers 150 μg/cm^2 a conservative estimate, located between the 0.1 and 1 μg/cm^2/min over the course of a 480 minute (8 hour) exposure time for the highest level of protection. Such a level can be defined without the need to consider the permeation curve of a material (55). There is some concern of the possibility of permeation spikes, where the permeation rate would suddenly jump to dangerous levels above the threshold for short periods. The ISO standard requires minimum sampling rates to address this, but it is a possibility for methods which only take a single cumulative measure. NFPA 1994 coincides roughly with the ISO and ASTM measure by setting its pass/fail limit at 6 μg/cm^2 cumulative over the course of 60 minutes, roughly equal to the ASTM and ISO threshold rate of 0.1 μg/cm^2/min. However, the test uses diluted chemical challenges making a determination of "time to failure" different.

Another approach has also been to define breakthrough times and permeability coefficients normalized for sample thickness. These values could be compiled for materials

using reference challenge chemicals and a reference material, allowing a comparison of a material's performance and applicability for a given CPC application (58).

One more approach is the determination of Lag Time, which is the intercept of the asymptotic line along the steady state permeation slope of a cumulative permeation plot. It has no direct physical significance however it can be accurately measured and exists independently of the sampling sensitivity, removing a major source of variability across different implementations of a permeation test (69). Though it was in fact one of the first metrics used for the determination of permeability parameters, it is no longer widely used, nor included in standard performance requirements.

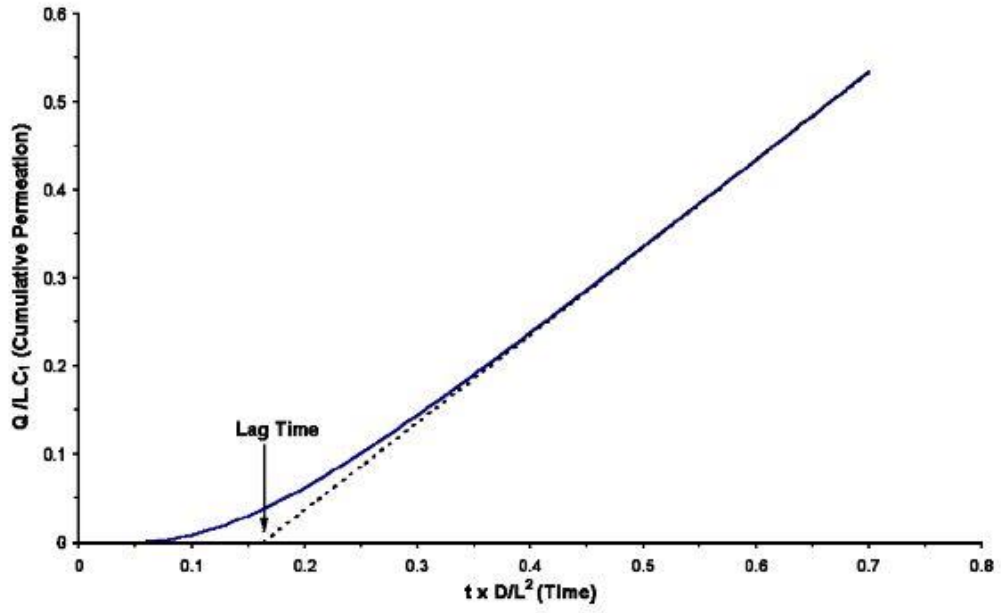


Figure 2-10 Typical Cumulative Permeation Curve with a Representaion of Lag Time Measurement (69)

2.4 **Air Sampling Methods**

Air sampling methods are relevant to chemical protective clothing for two reasons. One is to determine the concentrations present in situations to assess risks and predict the level of personal protection required. The other use, more relevant to this research, is to determine the amount of chemical as it permeates through test samples. Test situations typically involve small amounts of analyte and require high sensitivity.

The main variables in implementing air sampling methods depend on the amount of chemical expected, the chemical properties, and the detection limit of the method. A given method is limited at a minimum by the detection limit of the analytical system and at a maximum by the adsorptive capacity of the sampling material. Chemical quantities are determined by extraction from collection media and detection on analytical instruments, by direct reading detectors such as photo-ionization detectors, or by use of colorimetric reactions (70).

2.4.1 Passive Air Sampling

Sampling methods can either be active or passive. Passive sampling uses the diffusion of chemicals from higher concentration to lower concentration to trap chemicals from the air. The diffusion occurs at a predictable rate, defined as a diffusion constant, which can be used to calculate concentration in air. The ambient vapor concentration, geometry, and size of the sampler determine the amount of vapor transferred into the sampler. These methods have the advantage of not requiring any power source for collection and a general ease of use during sampling. Examples include the passive dosimeter badges used to monitor industrial exposure, Passive Adsorbent Dosimeters (PADs) used in the Man-In-Simulant-Test, and Solid Phase

Microextraction (SPME) techniques which can quickly collect small amounts of analyte from a sample or atmosphere.

2.4.2 Active Air Sampling

Active sampling involves passing environmental or industrial air samples through a sorbent material or into a collection apparatus (bag, impinger, or canister) with the use of a sampling pump. The concentration of a chemical atmosphere is calculated simply using the amount of analyte detected divided by the sampled air volume (sampling rate x sampling time). Active sampling is more applicable to the test methods in this research because: 1) the continuous air flow required by the NFPA test standard, and 2) the ability to collect and account for the entire cumulative amount of permeant.

Environmental air samples are often complex and may include multiple sampling components to control conditions and gather a range of analytes. Sensitivity and interference can be an issue. Collection times of 24 hours are often used. Occupational samples are usually in more controlled environments. These samples are collected to test for exposure compliance and can vary from 15 minutes to 8 hours depending on the sensitivity of the collection method and if short term exposure limits (STEL) or time weighted average (TWA) are being tested (70).

Information on sampling methods and equipment is available through many sources. Commercial retailers of sampling supplies (e.g. SKC, Restek, Waters, Supleco and commercial testing service companies) and governmental organizations (e.g. NIOSH, OSHA, WHO, EPA) release methods and technical publications.

2.4.3 Variables in Active Air Sampling

The environmental conditions, the chemical properties of the analyte, and the collection media all play a factor in the detection range of an active air sampling method. In order to achieve the desired sensitivity for an analyte the temperature, humidity, collection volume, collection rate, sorbent/solution selection, and extraction technique must be carefully considered. The primary concern with active air sampling is the possibility of analyte loss through breakthrough: the pass-through or release of analyte from the collection media.

2.4.3.1 Breakthrough

The OSHA validation guidelines consider 5% breakthrough through the sampler to be the acceptable threshold for a sampling method (71). Other sources suggest a benchmark of 25% breakthrough to the back section of a sorbent tube as a valid indicator (70). Breakthrough can be defined for a method based on the air volume sampled to reach the breakthrough limit. Thus a method can have a defined allowable sampling volume until capacity is reached. Figure 2-11 shows an example of sample breakthrough data when collecting from a generated controlled test atmosphere. It is possible to calculate the maximum volume for a certain mass of sorbent and a given flow rate before breakthrough occurs (70).

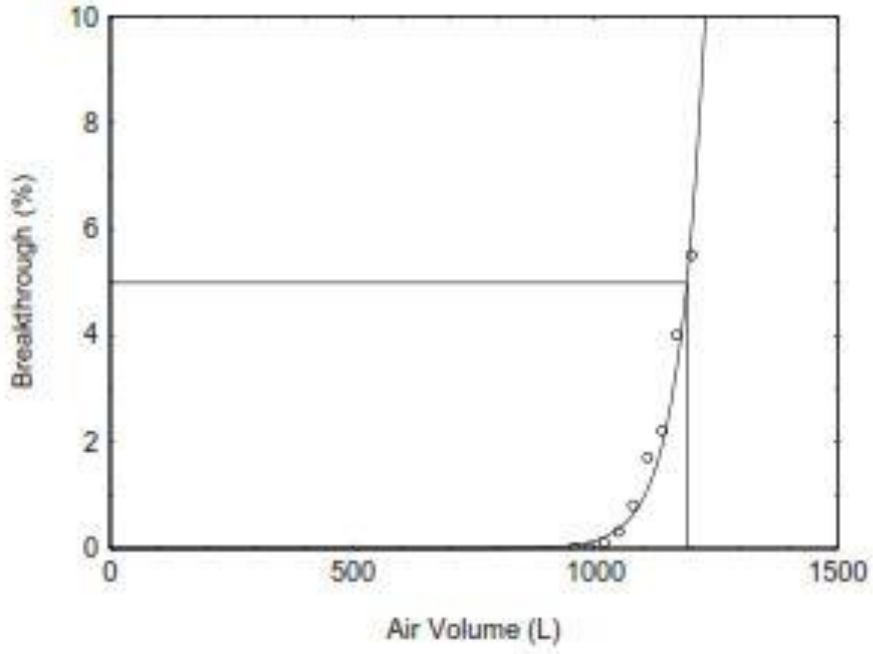


Figure 2-11 Breakthrough Determination for Sampling from a Generated Test Atmosphere (71)

Another approach to determining the suitability of a sampling condition is to measure the air required to displace an analyte from the sorbent. These retention studies are available for many sorbents and highlight the effect of temperature. Figure 2-12 shows the breakthrough volumes of aldehydes and ketones on Tenax TA ® (72). These breakthrough volumes are defined as the volume of air required to displace the analyte from one gram of Tenax TA® (a relatively large amount of resin). Increasing molecular weight increases the volume needed for breakthrough. The low molecular weight compounds with less than four carbons have very low temperature thresholds for breakthrough.

Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300
Acetaldehyde	2.20	0.650	0.200	0.070	0.031	0.014	0.007	0.004	0.002	0.001						
Propanal	25.0	5.00	1.30	0.375	0.125	0.043	0.018	0.009	0.004	0.002	0.001					
Acetone	28.0	6.00	1.40	0.405	0.127	0.047	0.019	0.009	0.004	0.002	0.001					
2-Methyl Propanal	100	17.0	3.50	0.985	0.291	0.086	0.033	0.015	0.007	0.003	0.002	0.001				
Butanal	190	30.0	6.00	1.60	0.441	0.124	0.045	0.019	0.008	0.004	0.002	0.001				
2-Butanone	251	40.0	7.10	1.90	0.483	0.151	0.058	0.023	0.009	0.004	0.002	0.001				
3-Methyl Butanal	500	67.0	12.5	3.00	0.960	0.264	0.087	0.034	0.014	0.006	0.003	0.002	0.001			
Pentanal	795	112	22.0	5.00	1.20	0.396	0.132	0.047	0.018	0.008	0.004	0.002	0.001			
2-Pentanone	1,500	180	30.0	6.00	1.30	0.417	0.129	0.046	0.019	0.009	0.004	0.002	0.001			
3-Pentanone	1,600	200	32.0	6.30	1.50	0.432	0.137	0.049	0.021	0.009	0.004	0.002	0.001			
Hexanal	4,000	500	79.0	16.0	3.50	1.00	0.342	0.105	0.036	0.016	0.007	0.004	0.002	0.001		
2-Hexanone	10,000	1,000	141	25.0	5.00	1.20	0.343	0.107	0.038	0.016	0.006	0.003	0.002	0.001		
Gluturaldehyde	7,800	1,000	180	35.0	8.40	2.50	0.800	0.270	0.110	0.050	0.025	0.013	0.007	0.003	0.002	0.001
Benzaldehyde	7,900	1,100	185	35.0	9.00	2.50	0.900	0.320	0.120	0.058	0.028	0.012	0.006	0.004	0.002	0.001
4-Heptanone	40,000	3,500	400	60.0	12.0	2.60	0.738	0.203	0.065	0.024	0.010	0.004	0.002	0.001		
2-Methylcyclohexanal	25,000	2,500	350	63.0	14.0	3.40	1.00	0.371	0.130	0.050	0.021	0.009	0.005	0.003	0.001	
3-Heptanone	45,000	4,000	450	70.0	13.0	3.00	0.827	0.229	0.072	0.028	0.010	0.005	0.002	0.001		
Heptanal	40,000	3,500	447	65.0	14.0	3.00	0.876	0.238	0.080	0.027	0.011	0.005	0.003	0.001		
3-Methylcyclohexanal	30,000	3,000	400	68.0	16.0	4.00	1.10	0.402	0.135	0.052	0.022	0.010	0.005	0.003	0.001	
4-Methylcyclohexanal	40,000	4,000	500	90.0	20.0	5.00	1.30	0.431	0.144	0.055	0.023	0.010	0.006	0.003	0.001	
2-Heptanone	50,000	5,000	500	76.0	15.0	3.20	0.867	0.243	0.077	0.029	0.011	0.005	0.002	0.001		
3-Octanone	71,000	5,800	650	100	19.0	4.10	1.00	0.328	0.103	0.038	0.014	0.006	0.003	0.001		
Octanal	158,000	12,500	1,400	210	35.0	6.30	1.90	0.544	0.168	0.050	0.019	0.008	0.004	0.002	0.001	
2-Octanone	250,000	20,000	2,000	250	40.0	7.80	2.00	0.556	0.154	0.052	0.019	0.008	0.004	0.002	0.001	
5-Nonanone	500,000	32,000	3,200	400	63.0	13.0	3.20	0.900	0.260	0.081	0.028	0.011	0.005	0.002	0.001	
2-Nonanone	790,000	50,000	4,400	550	90.0	16.0	3.80	1.00	0.311	0.095	0.031	0.012	0.006	0.003	0.001	
Nonanal	1.00E+06	63,000	5,000	530	90.0	18.0	4.00	1.00	0.320	0.090	0.033	0.013	0.006	0.003	0.001	

Figure 2-12 Breakthrough Volume to Displace Aldehydes and Ketones per gram of Tenax TA (72)

Humidity is another factor relevant to breakthrough. High humidity can cause water to collect in the sorbent, blocking active sites, displacing analyte, and competing with analyte. Many studies exist comparing water uptake characteristics of different sorbents (73). The OSHA standard requires testing the breakthrough with the generated atmosphere at 80% RH. The point is clear that breakthrough must be characterized at the desired use conditions and will vary for a given compound and sorbent pair. Excessive sampling rates decrease the ability of a sorbent to collect analyte.

2.4.4 Collection Media for Active Air Sampling

Sorbent materials can be grouped as either carbon-based, inorganic, or porous polymeric materials. Within each category a variety of types exist with different surface areas, particle sizes, surface characteristics, and polarity. These include silica gel, zeolites, molecular sieves, aluminum oxide, activated carbon, carbon black, graphitized carbon, styrene-divinylbenzene copolymers, ethylenebenzene/divinylbenzene copolymers, polyvinylpyrrolidinone, polyphenylene oxides, and polyurethane foams (74). An overview of sorbent properties is given below. All sorbents operate on the same principle. They consist of high surface area particles filled with pores and intermolecular spaces which provide a surface for analytes in the air to adhere. The distinguishing factors in choosing a sorbent to collect an analyte are the size, polarity, and boiling point of the analyte.

Sorbent selection guides are commonly provided by commercial suppliers. There are many studies conducted testing the retention properties of selected sorbents against a group of test compounds (75) (76) (77). An overview of materials used as solid sorbents is shown in

.

Table 1.1 Properties of some solid sorbents according to Quintana, Uribe and Arbeloa (1992), ECA (1994), Zielinska and Fujita (1994), Figge, Rabel and Wieck (1987) and ISO (2001).

Type	Structure	Surface area (m^2/g)	Products	Desorption	Compounds tested (Starting at b.p.)	Polarity	Thermal stability	Water affinity
Inorganic	Silica gels	1–30	Volasphere, Florisil	Solvent	PCBs, pesticides	High	–400 °C	High
	Molecular sieves	500–800		Solvent	Permanent gases	High	<400 °C	High
	Aluminum oxides	~300	Alumina F1	Solvent	Hydrocarbons	High	300 °C	High
Carbon based	Activated Charcoal	800–1200		Solvent	Non-polar and slightly polar VOCs (>50 °C)	Medium	>400 °C	High
	Carbon molecular Sieves	400–1200	Carbosieve, Ambersorb, Spherocarb Carboxen	Solvent/ Thermal	Non-polar and slightly polar VOCs (>– 80 °C)	Low	>400 °C	Low–medium
	Graphitized carbon blacks	12–100	Carbotrap, Carbopack, Carbograph	Thermal	Non-polar VOCs (>60 °C)	Low	>400 °C	Low
Porous polymers	Styrene, divinylbenzene or polyvinylpyrrolidone polymers	300–800	Porapak Q/N, Chromosorb 106/102,	Thermal/ solvent	Non-polar and moderately polar VOCs (>40 °C)	Variable	<250 °C	Low
	Phenylphenylen oxide polymers	20–35	Tenax	Thermal	Non-polar VOCs (>60 °C)	Low	<350 °C	Low
	PU-Foams			Solvent	Pesticides	Low	<200 °C	Low

Remarks: Tenax® is a registered trademark of Buchem B.V., NV, NL; Carbotrap®, Carbopack®, Carbograph®, Carbosieve® and Carboxen® are registered trademarks of Sigma-Aldrich Co., USA; Chromosorb® is a registered trademark of Johns-Manville Corp, USA; Porapak® is a registered trademark of Waters Associates Inc., USA; Spherocarb® is a registered trademark of Analabs Inc., USA.; Volasphere®: E.Merck KGaA, Germany; Florisil® is a registred trademark of U.S. Silica Co., USA.

Figure 2-13 Overview of Materials Used as Solid Sorbents (74)

2.4.4.1 Carbon

Carbon can take many different forms as a sorbent material. The most common is activated charcoal which has a high surface area to weight ratio, low price, and high capacity. As a testament to its ability, activated charcoal is the primary material used in air-purifying respirator (APR) filters. It is of medium polarity, it is prone to react with certain analytes, and has a high water affinity, making it less than ideal in high humidity situations. It is commercially available as Anasorb®.

Carbon molecular sieves are the carbon framework remaining after pyrolysis of a high carbon material (70). Depending on the initial material, a wide variety of pore sizes and structures can be achieved. They are capable of trapping very high volatility compounds and can be made more impervious to humidity. As a result they are often significantly more expensive. They are commercially known as a variety of materials named Carboxen® and Carbosieve® (77).

2.4.4.2 Tenax

Tenax TA® is a widely used sorbent material composed of 2,6-diphenyl-p-phenylene oxide. It is known for its high temperature stability, making it useful for thermal desorption, as well as its low affinity for water vapor. It is capable of collecting low concentrations of volatile compounds. It is well suited for higher boiling point compounds and aromatics. It has low reactivity and can be cleaned and reused with solvent washing or heating. A variation exists, Tenax GR®, which contains 30% graphitized carbon and has reduced moisture uptake. (70)

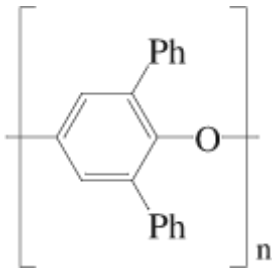
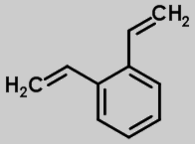
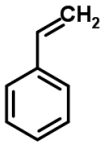
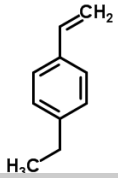
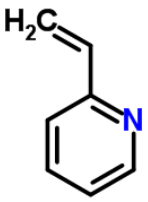
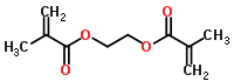


Figure 2-14 Repeat Structure of 2,6 diphenyl-p-phenylene oxide (78)

2.4.4.3 Porapak

Porapaks are a class of crosslinked materials based on copolymers of divinylbenzene. They are named in order of increasing polarity from P through T, with the exception of Porapak N which is the most polar. The variety comes from the inclusion of copolymers making a range of sorbents targeted towards varying polarity of analytes. They have lower reactivity and less water uptake than activated charcoal. They are common packing materials for gas chromatography columns. All variations are subject to limited thermal stability and surface area (79) (77) (70). They are directly comparable to the range of polymers under the commercial names Chromosorb ® and HayeSep ®, which were not utilized in this research.

*Table 2-7 Structural Units of Polymers used as Adsorbents under the Commercial Name Porapak ® (79)**

Comonomer	Monomeric Structure	Polarity	Porapak
Divinylbenzene		Least Polar	P,Q,R,S,N
Styrene		Least Polar	P
Ethylvinylbenzene		Moderately Polar	Q
Vinyl pyridine		Polar	S
Vinylpyrolidinone		Most Polar	N
Ethyleneglycol-dimethacrylate		Most Polar	T, N

*All structures formed in ChemSpider Software

2.4.4.4 Sorbent Tubes

Sorbent tubes are typically constructed from glass containing front and back sections of sorbent separated by polyurethane foam or glass wool. The smaller back section is intended to measure breakthrough and ensure that the tube was not sampled over capacity. The amount of sorbent in a tube determines its capacity. The glass tubes are flame sealed and the tips are broken off when ready to sample. Sorbent can also be purchased in bulk and tubes, such as the steel tubes used in thermal desorption, can be prepared individually,.

All of the above sorbents are available in different particle sizes or "mesh sizes". Particles are sifted through two meshes to give a range. The mesh numbering system is inversely related to particle size so a 60/80 mesh consists of larger particles than 80/100. Smaller particles and longer, narrower tubes lead to increased back pressure or pumping pressure but higher collection efficiency.

2.4.4.5 Impingers

Impingers are glass sampling devices which direct an air flow path through a liquid collection solution. The air passes through a submerged glass tube to force the air to mix with the liquid. Some impingers use fritted glass tips which split the air into small bubbles; these are referred to as bubblers. The bubbles increase the surface area of contact between the analytes in the air and the solution. Impingers (25-mL) are used in multiple OSHA sampling methods, typically at a flow rate of 0.3 to 1 L/min. It is important to consider the rate of absorption of the analyte into the absorbing solution because insufficient absorption leads to breakthrough. Reagents can be added to trap sorbents, for example with aldehydes in EPA

Method TO5. If the volatility of the absorbing solution and analyte are too high the analyte may be released or the solution concentration could change over the course of sampling (70)

.

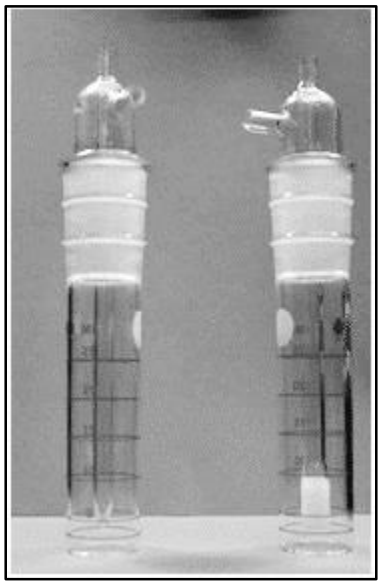


Figure 2-15 Midget Impinger and Bubbler (5)

2.4.5 Sorbent Extraction

Many advanced extraction techniques are available for removing analytes from samples. These techniques include Soxhlet, Pressurized Fluid, Microwave Assisted, and Supercritical Fluid extraction. However for the controlled collection of volatile organic compounds onto solid sorbents, simple extraction techniques are sufficient by use of an organic solvent or with heat (thermal desorption) (80).

Thermal desorption has the advantage of not requiring a solvent and can be automated to pair directly with a Gas Chromatograph. It requires specialized equipment and is not

compatible with thermally labile compounds. A thermal desorption sample can only be analyzed once, and if low desorption temperatures are used compounds will have broad, poorly resolved peaks (80).

Solvent desorption can be as simple as mixing solvent with a sorbent sample in a capped vial. There are various parameters to consider when optimizing solvent extraction of an analyte from a sorbent material. These include solvent selection, solvent volume, temperature, time, filtering, and agitation required to reach the desired extraction efficiency. The choice of the proper solvent can reduce the need for excess time and agitation and reduce volume of solvent needed, increasing method sensitivity by increasing sample concentration.

The extraction of analyte from a solid phase sorbent relies on the main factors of solubility and equilibrium. According to the Nernst Distribution Law, a partition coefficient (K_D) exists for a given system, defined by the concentration of analyte in one phase [S_1] to the other [S_2]. $K_D = [S_1]/ [S_2]$, is a measure of analyte affinity for the stationary phase versus the mobile phase (81).

The principle relates to stationary phase and mobile phase interaction in liquid chromatography. In order for the analyte to move it must be soluble in the liquid, or the liquid must be able to displace the analyte from the sorbent surface. Solvents can be ranked for their ability to displace solute from a given adsorbent. The "eluent strength" relates to the solvent's adsorption energy. Adsorption is an exothermic process, a higher adsorption energy of an eluent means that it will preferable displace the analyte on the sorbent surface (82). The goal is to choose the solvent or solvent mixture which has the highest eluent strength and in which the analyte has sufficient solubility. Some analytes can become irreversibly trapped on a

sorbent surface if the forces holding the analyte on the sorbent (polar, dispersion, dipole, hydrogen bonding, steric effects, entropic energy) cannot be overcome.

Additional factors important for solvent selection include: 1) Solvent reactivity – The solvent should not react with the analyte or degrade the stationary phase, 2) Interference – The solvent should not interfere with the signal of the analyte in the chosen analytical method. Examples of interference are overlapping elution time in gas chromatography and high UV cut off in HPLC, and 3) Toxicity and cost – Toxic solvents should be avoided if possible (38).

2.5 **Method Validation Procedures and Techniques**

2.5.1 OSHA Validation Guidelines

OSHA has published Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis (71). It provides a step by step process (Figure 2-16) to form and validate analytical methods and sampling procedures. It also provides a method writing template. The procedures for instrument calibration, testing capacity, retention efficiency, and extraction efficiency were adapted for use in this research. The only changes were to use the NFPA test conditions and target concentrations instead of those suggested in the guidelines. Interference and storage studies were not necessary because of the laboratory setting of the sampling. Sampling rate is set by the NFPA 1994 standard to 1 L/min.

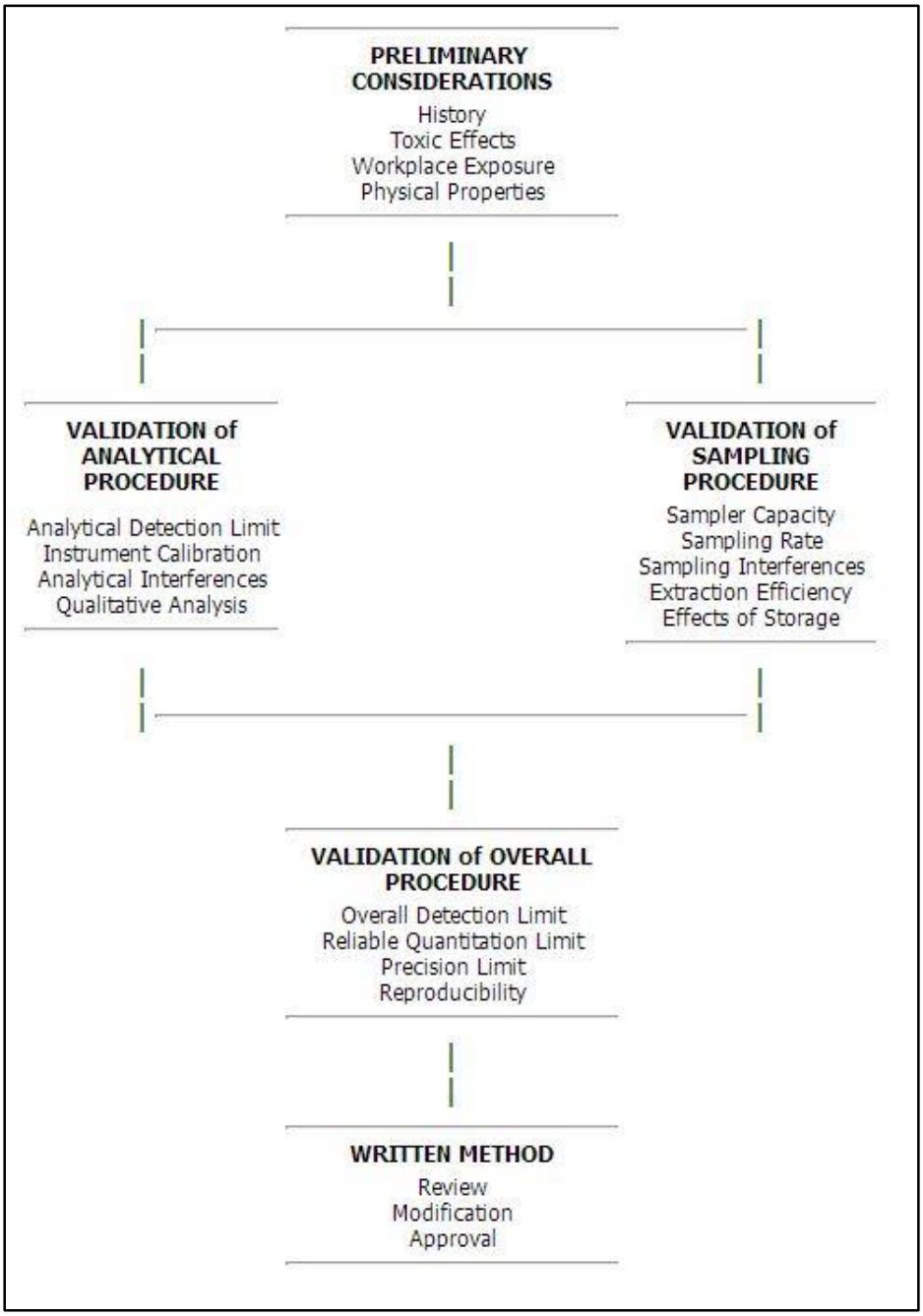


Figure 2-16 Procedural Approach to Method Validation in the OSHA Validation Guide (71)

2.5.2 Instrument Calibration

The foundation of an analytical technique is the detection method and standard calibration. It helps ensure the accuracy and precision of judging the quantity of an analyte in an experimental sample. Standards can be purchased from many commercial sources or prepared from chemical samples. Standards should be prepared with high-quality reagents. It is important to take into account chemical purity, for instance acrolein is commonly available only up to 90% purity, which must be considered when making standard solutions.

Non-linear and quadratic relationships require at least five standards to characterize a curve (83). Standard concentrations should be evenly spaced to avoid points which have excessive leverage to influence the regression line. Regression analysis is important to ensure the correlation of the calibration (84).

2.5.3 Method Detection Limits

Detection limit is an important part of any analytical method and especially important as a criteria in certifying chemical protection. ISO and ASTM define a minimum detection limit based on permeation rates of 0.1 μg/cm^2/min while NFPA has a lower limit of 0.1 μg/cm^2 over the course of 60 minutes. This equates to a minimum amount of analyte that must be able to be collected and detected on the analytical instrument. It will vary depending on how the sample is prepared and other factors such as cell exposure area, collection flow rate, sample volume, extraction method, and sampling time.

For instance, consider a hypothetical 10 cm^2 test cell collecting at 1 L/min. A direct reading photo-ionization detector sampling from this air line at 0.5 L/min would have to be able to detect air concentrations of 0.5 μg/L (mg/m^3); a system using continuous sampling gas

chromatography which analyzes pre-concentrated samples every 2 minutes using FID would have to detect 2 µg on the column; a bubbler sampling solution which is collecting the air flow into a 10 mL solution over the course of 10 minutes would have to detect 1 µg/mL (ppm) samples in liquid; a system using a sorbent tube collecting the air flow for 10 minutes which is desorbed with 4 mL of solvent would have to detect 2.5 µg/mL (ppm) samples.

On the instrument, the detection limit, also called Detection Limit of the Analytical Procedure (DLAP) or Method Detection Limit (MDL), is the ability to distinguish a sample from a blank. The limit depends on the noise associated with signal detection and is generally accepted as being three standard deviations away from the blank response (Equation 2) (71). Once a detection method is chosen the detection limit can be determined by choosing a low level concentration, preparing at least seven replicates of the sample, and measuring the statistical variation of its signal response. This method provides a detection limit which has a 99% probability of being greater than a blank. One source suggests that the spike level be chosen such that it is greater than the resulting detection limit but less than ten times the resulting detection limit, and has a signal-to-noise ratio (sample mean divided by standard deviation) between 2.5 and 10 (83). The OSHA validation guidelines use a different method using ten equally spaced samples to determine the Detection Limit of the Analytical Procedure (DLAP) and the Reliable Quantitation Limit (RQL), which is ten standard deviations away from a blank.

$$L_D = \frac{3S_{Y \cdot X(DLAP)}}{A}$$

where L_D is the DLAP
$S_{Y \cdot X(DLAP)}$ is the standard error of estimate for the DLAP
A is the analytical sensitivity (slope)

$$L_{RQL} = 10\frac{S_{Y \cdot X(DLOP)}}{A}$$

where L_{RQL} is the reliable quantitation limit
$S_{Y \cdot X(DLOP)}$ is the standard error of estimate for the regression line for DLOP
A is the analytical sensitivity (slope)

Equation 2. Limit of Detection and Limit of Quantitation Equations

2.5.4 Method Validation

The goal of validating a chemical collection method is to show that a method will collect and transfer a verifiable amount of an analyte from the test environment to the detection instrumentation without significant analyte loss. Many tests can be designed to check for the conditions which lead to breakthrough, decomposition, decreased sensitivity, and interference.

2.5.4.1 Liquid Spike

This test is performed by spiking a high concentration liquid standard directly onto the collection medium - liquid, sorbent in a vial, or sorbent in the collection tube. The sorbent can be extracted immediately to see if any analyte loss occurs in the extraction procedure. The spiked tube may also be allowed to sit in a chosen environment to see if certain conditions affect recovery.

This is a simple procedure and allows accurate spiking of analyte. However it does not replicate collection because the analyte is concentrated in solvent. It is important to use a solvent which evaporates quickly to ensure immediate sorption of the analyte onto the sorbent

and prevent flow of analyte out of the sorbent. For a liquid collection solution a liquid spike will alter the sample volume.

2.5.4.2 ATIS Spike

This procedure uses a Supelco® Adsorbent Tube Injector System to spike sorbent tubes with a challenge chemical in vapor form. The system consists of a glass tube with an injection septum. The tube is mounted on a heater plate capable of controlling temperature from ambient to 190^{o}C. The system comes with a carbon air filter and pressure control valve to pass a steady flow of nitrogen or any other inert gas through the glass tube, at a recommended flow of up to 0.1 L/min. Various adapters are available to attach adsorbent tubes or sampling media to the outlet of the tube. The heated tube and inert gas allow rapid vaporization of a sample and efficient transfer onto the sorbent material. It does not replicate the NFPA test conditions but it offers a different form of introducing the analyte, albeit with a greater potential for analyte loss.

2.5.4.3 Mixed Vapor Bag Spike

This method uses sampling bags to individually mix a vapor sample by spiking a known amount of analyte into bag then adding a certain volume of air to create a vapor. One advantage of this method is creating a vapor with a desired relative humidity and temperature. However there is a large amount of uncertainty and variability with the use of bag samples due to interaction with bag material, carryover, difficulty accurately filling or emptying an air volume, and special equipment required to control spiking rate.

2.5.4.4 Pressurized Cylinder Gas Spike

This test is performed by passing a gaseous sample of the analyte at a pre-mixed concentration from a pressurized cylinder through the collection medium. Flow rate and time

determine the spike level. The sample flow is controlled using a flow controller validated with a flow meter. In order to further ensure the accuracy of the total flow an additional sealed vessel containing liquid with a submerged outlet can be placed in-line after the collection tube or impinger. As the gas is sent through the system, air entering the vessel displaces an equivalent amount of liquid. The change in the level of the liquid can be measured (24). Corrections in calculating the molar equivalent of the air may be needed if high pressure is involved in moving air through the system.

This test provides the most realistic imitation of conditions in a permeation test because the analyte is in vapor form and can be introduced at similar concentrations and conditions by mixing with a conditioned air flow. However it also difficult to measure gas as accurately as liquid. There are specialized gas sample bags which can be used to capture or introduce gas samples, however these require special equipment to fill accurately and are susceptible to analyte loss. Though sample challenges may not be performed reproducibly they still provide important information. By challenging at an approximate level the collection method can be tested for breakthrough at the desired flow rate and challenge concentration.

2.5.4.5 Retention Test

Retention is the ability of the collection medium to retain the analyte while sampling an air stream (not to be confused with "retention time" used in analytical methods to describe the time it takes for an analyte to elute from a chromatographic column). It can be tested by placing the collection tube or bubbler, spiked with a known amount of analyte, into the air flow path. Retention efficiency is equal to the amount recovered divided by the original spike amount. The liquid spike can be applied directly onto the head of the sorbent or, for volatile

compounds, onto a piece of glass wool at the head of the sorbent tube (71). This is a way to measure breakthrough and to see if larger sorbent tubes or multiple sorbent tubes are needed. The retention efficiency can depend on the spike level, flow rate, flow volume, and air conditions.

2.5.4.6 Extraction Test

Extraction efficiency must be tested to ensure that the method and procedure chosen to desorb analyte from the sorbent results in sufficient recovery of the analyte. This test can be performed by preparing a spiked standard in liquid and a spiked sorbent sample. Both samples should undergo the same conditions involved in extraction (heating, agitation, sitting time). The amount of recovered analyte and the amount of analyte detected in the liquid spiked sample should then be compared to a standard to ensure that the extraction procedure does not lead to analyte loss or sample concentration changes. Then the analyte recovered from the extraction should be divided by the amount of analyte in the standard to give the extraction efficiency, given as a percentage. Ideally, no less than 90% of the analyte should be lost during extraction (71).

2.5.4.7 Storage Stability Test

It may be necessary to test the stability of a stored sample before or after extraction. This test is common for environmental samples which must be transported from the sampling site to an analytical laboratory. It consists of testing the concentration of a sample after a period of time at certain conditions (typically 24 hours to 7 days with or without refrigeration) to see if changes in the detected concentration occur. Changes should not be more than 10% (38).

2.5.4.8 Positive Control Test

The purpose of all the methods listed above is to isolate test factors which may cause insufficiencies in the chosen collection method. Within the context of detecting a failure in a chemical permeation resistance test, a positive control or "forced fail" is an attempt to prove that, at a minimum, the chosen method is able to identify the amount of chemical permeant defined as the pass/fail limit considering all aspects of the test implementation.

Chapter 3. Experimental

3.1 Experimental Approach

The experimental approaches below describe the development of the sampling, extraction, and analysis procedures of each of the challenge chemicals. The construction and operation of the permeation test apparatus is also detailed. Together the document provides all the experimental procedures necessary to implement an evaluation of the permeation resistance of protective clothing.

3.2 Chemicals and Instrumentation

3.2.1 Chemicals

The chemicals used in this study include 99.99% carbon disulfide, 99.5% GC Resolv™ acetone, 99.9% Optima™ acetonitrile, Certified ACS methanol from Fisher Scientific; 99%+ acrylonitrile and dimethyl sulfate from Acros; 90% acrolein with 1-2 w% hydroquinone, 99% crotonaldehyde, 99% trans-cinnamaldehyde, 95% trans-2-pentenal, 97% 2-piridinemethanol from Aldrich; Certipret 1,000 mg/L ammonium and 1,000 mg/L chloride standards from Spex;

sodium sulfite anhydrous from Kodak; Type 1 18 MΩ*cm deionized water from a Siemens Purelab ® Ultra Analytic purification system.

Certified standards of the challenge gases in pressurized cylinders were obtained from Speciality Gases of America (350 ppm acrylonitrile, acrolein, ammonia and chlorine and 40 ppm ammonia and chlorine in an air balance) and Praxair (acrolein (41.99 ppm) and acrylonitrile (40.99 ppm) in air balance).

3.2.2 Collection Media and Sample Preparation

The following collection media and sample preparation tools were used: SKC Inc 226-115 Porapak Q sorbent tubes, 226-10-6 Treated Silica Gel sorbent tubes, 226-09 Anansorb CSC sorbent tubes, 226-01 Anansorb CSC sorbent tubes, 226-118 Treated XAD-2 sorbent tubes; Supelco 6-4834 25-mL fritted glass bubbler; Analytical syringes from Hamilton and SGE in 10-µL, 100-µL, and 1000-µL volumes were used as well as Eppendorf Repeater ® Combtip pipettes; and Branson 1510 sonicator was used for some sample extractions. All standards were made in Class A volumetric flasks.

3.2.3 Analytical Instrumentation

The analytical instruments used include: Dionex ICS-2000 in Cation Mode using a CS12a 2mm x 250mm column with guard column, CSRS-300 2mm suppressor, DS6 Heated Conductivity Cell, and EGC III MSA Eluent Generator Cartridge, and 25-µL sample loop; Dionex ICS-2000 in Anion Mode using an AS12a 2mm x 250 mm column with guard column, ASRS-300 2mm suppressor, DS6 Heated Conductivity Cell, and EGC III KOH Eluent Generator Cartridge, and 25-µL sample loop; Agilent 6890N Gas Chromatograph with 5875C Mass Spectrometry Detector with a Restek RTX-1701 280^{o}C 30m x 250µm x 0.25µm; Agilent

1260 Infinity Liquid Chromatography instrument with a Diode Array Detector and Agilent Poroshell 120 EC-C18 2.7µm, 3.0mm x 100mm; Orion 5 Star Bench top Meter with a 9770BNWP Residual Chlorine Electrode.

3.3 **Test Chamber and Components**

3.3.1 Permeation Cell

The six test cells used were editions of the TOP 8-2-501 AVLAG cells constructed from stainless steel (Aerospace Tooling and Machining, Salt lake City, Utah). They consisted of two compression plates using 5 Viton O-rings to compress the sample, seal the compression plates, and seal the screw top. The fabric sample sits between the two middle compression plates. An image of the unassembled cell can be seen in Figure 2-1Figure 3-1. A schematic image representing the collection flow can be seen in Figure 3-2.

Figure 3-1 Permeation Test Cell

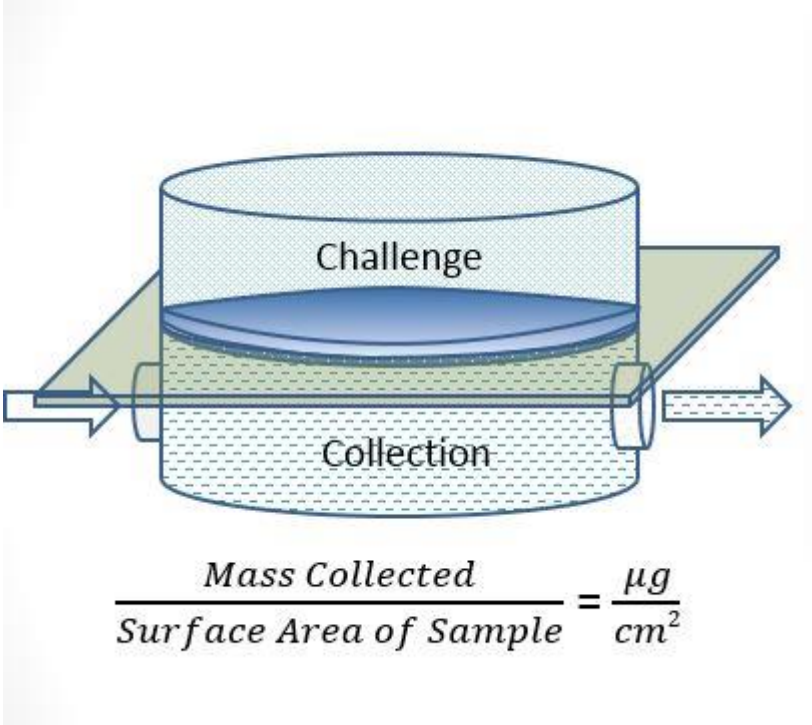


Figure 3-2 Schematic Representation of Permeation Cell

3.3.2 Air Flow and Conditioning Components

An experimental test chamber was constructed to maintain climatic conditions and air flow conditions. A box, which is capable of fitting within a fume hood and constructed of clear solvent-welded acrylic sheets is used to house the test cells and maintain components at the required test temperature. A pressure-regulated hydrocarbon free air source from a Parker Balston HPZA-3500 Zero Air Generator is fed into the test chamber through ¼" inner diameter stainless steel tubing. The air first passes through a Perma Pure® MH-110-24S humidifying tube supplied with deionized water. An Omega® proportional-integral-derivative (PID) controller with humidity and temperature probe is used to control a heating tape wrapped around the humidifying tube and a heater block located within the chamber. The humidity

probe is mounted in a housing in the air line directly before one of the test cells. A manifold splits the flow to four separate air lines, regulated by MKS 1179A flow controllers, which deliver 1 L/min to each test cell. Flow controllers were calibrated using an Aalborg GFM17 flow controller calibrated for air.

Figure 3-3 and Figure 3-Figure 3-4 display a labeled flow diagram and an image of the test chamber.

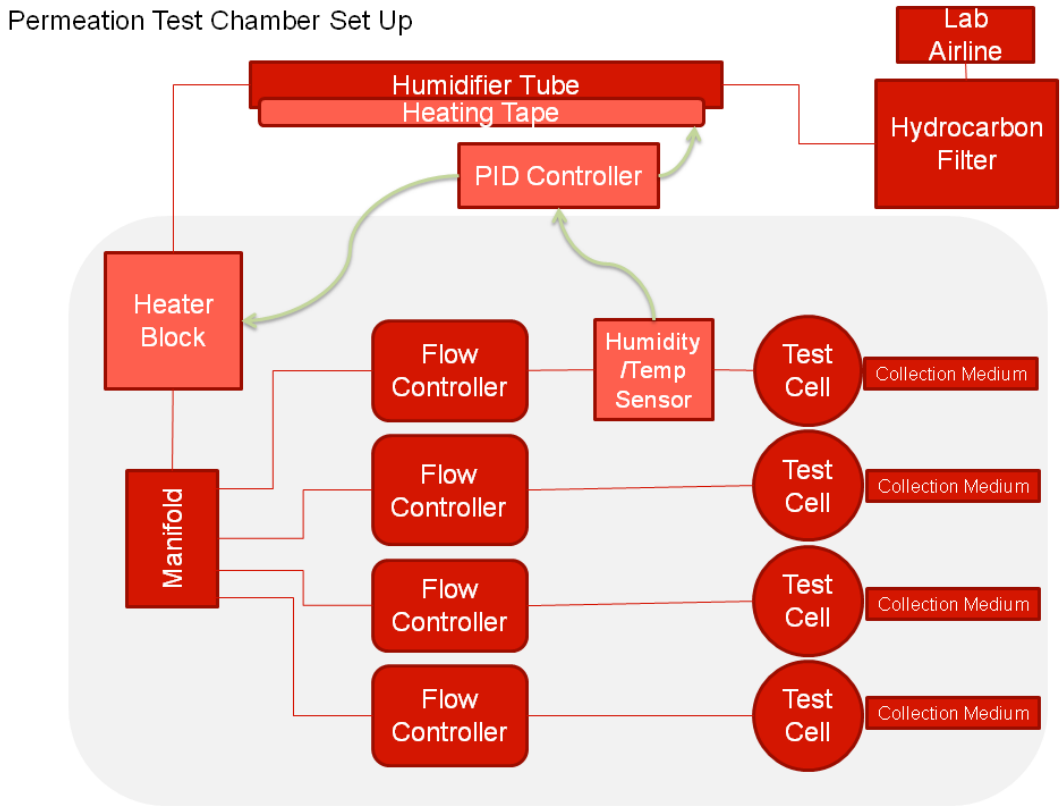


Figure 3-3 Permeation Test Chamber Flow Diagram

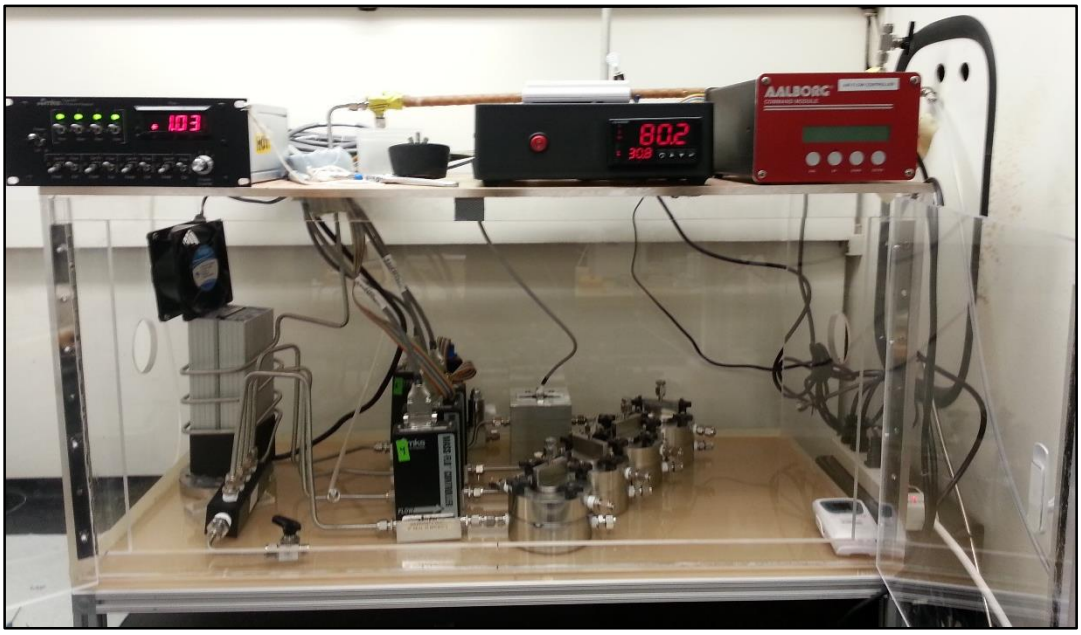


Figure 3-4 Test Chamber

3.3.3 Chamber Validation

The chamber was evaluated to ensure its ability to maintain test conditions. The PID controller settings must be adjusted to optimize the heating rate of the heating tape and heating block and reduce fluctuations of the test conditions.

An important factor in the operation of the test set up is pressure. The flow controllers constantly adjust air flow based on the pressure in the supplied air. The absolute pressure of a system changes the relative humidity. Increasing pressure will increase the relative humidity and cause larger fluctuations in relative humidity with a given temperature change. Pressure makes it more difficult for the PID to control humidity and may lead to condensation in the air lines which can damage the flow controllers. Different collection media cause different back-pressure in the air supply system. For each collection media the back pressure was measured

as outlined in section 3.4.7 and the system was tested for its ability to maintain temperature and humidity over the duration of a test.

Cell pressure leak tests were conducted according to instructions located in NFPA 1994. Pressure leak tests were also performed on the air supply system, specifically around the temperature/humidity probe housing. Before each permeation test, flow rates were checked in front and behind the collection media.

3.4 **Procedures**

All method development and validation procedures were focused on proving that the analytical techniques and collection methods were capable of meeting the minimum test requirements outlined in NFPA 1994 which uses a 6 µg/cm^2 cumulative threshold and a 0.1 µg/cm^2 method detection limit (1). Thus amounts near those collection limits were used to evaluate extraction, breakthrough, and retention.

3.4.1 Dimethyl Sulfate

3.4.1.1 Method Development

For DMS, the NIOSH 2524 (35) sampling method was adapted to the available laboratory equipment. Poropak Q sorbent tubes (SKC 226-115) 50/80 Mesh Size were used or sample collection. Sampled tubes were opened and the sorbent was transferred to 4-mL glass vials. The sorbent was soaked in 2 mL of acetone for one hour, then filtered with a 2- micron polyvinyl difluoride sample filter upon loading GC auto-sampler vials. Samples were analyzed using GC-MS.

3.4.1.2 Recovery

Three samples of sorbent were spiked with a 6 µL liquid spike of stock solution equivalent to 84 µg of DMS then extracted to test extraction efficiency.

Four sorbent tubes were spiked with a liquid spike of stock solution equivalent to 84 µg of DMS then attached to an air flow of 1 L/min at 80% RH and 32°C to test retention. Samples were removed after 15, 30, 45, and 60 minutes then extracted and analyzed to see if retention changed over time. A liquid spike of stock solution equivalent to 53 µg of DMS was also used on three additional samples which were placed in the air line for 60 minutes.

3.4.2 Acrylonitrile

3.4.2.1 Method Development

For acrylonitrile, the NIOSH 1604 (40) sampling method was adapted to the available laboratory equipment. Charcoal sorbent tubes, SKC 226-09 (400-mg front and 200-mg back sections) and SKC 226-01 (100-mg front and 50-mg back sections), were used for sample collection. All samples were filtered with 2-micron polyvinyl difluoride filters upon loading sample vials, then analyzed using GC-MS.

3.4.2.2 Recovery

Acrylonitrile is volatile and the NIOSH method uses carbon disulfide as an extraction solution, which is an undesirable due to its toxicity, volatility, and flammability. For these reasons additional steps were taken to alter the sampling method to establish extraction and retention.

A 6-µL liquid spike of stock solution equivalent to 58 µg of acrylonitrile was spiked directly onto 600mg of charcoal sorbent in a 4-mL vial in triplicate. Three milliliters of carbon

disulfide containing 2% acetone was added then the samples were agitated and allowed to sit at room temperature for one hour.

Retention tests were performed using a liquid spike of stock solution equivalent to 58 µg of acrylonitrile spiked directly into sorbent tubes. Sorbent tubes were attached to an air flow of 1 L/min at 80% RH and 32°C. Four 600-mg tubes were attached for 0, 30, 45, and 60 minutes with an additional sorbent tube attached directly behind to detect breakthrough. Three 200-mg tubes were attached for 60 minutes each. Each tube section was extracted individually and analyzed using GC-MS.

3.4.3 Ammonia

3.4.3.1 Method Development

For ammonia, OSHA standard ID-188 and NIOSH standard 6106 (15) (14) were adapted to the available laboratory equipment. Sorbent tubes containing silica gel coated with sulfuric acid (SKC 226-10-06) were used for sample collection. Extractions were performed using 20 mL of 18 MΩ*cm water added to the sorbent in 20-mL glass vials. Samples were placed in a sonicator for 45 minutes then filtered upon injection using IC Acrodisc 13-mm syringe filters with 0.2-µm Supor (PES) membrane.

3.4.3.2 Collection and Recovery

Three samples of sorbent were spiked with a 60-µL liquid spike of stock solution equivalent to 60 µg of ammonia then extracted to test extraction efficiency.

Sorbent tubes were spiked with a liquid spike of stock solution equivalent to 60 µg of ammonia, then attached to an air flow of 1 L/min at 80% RH and 32°C for 60 minutes. Four additional samples were spiked with 10 µL of stock solution equivalent to 10 µg of ammonia then attached to the air flow and removed after 15, 30, 45, and 60 minutes.

A gas cylinder spike was used to evaluate collection capacity and breakthrough. Two tubes were attached in sequence to detect breakthrough. A measured volume of air from a 350-ppm ammonia cylinder was passed through the tubes. The air flow was measured using a liquid displacement system. The end of the sorbent tube was attached to the outlet of a 500-mL fritted bubbler filled with water. As the air flow entered the bubbler it displaced water out of the bubbler into a collection vessel. The bubbler was marked on the exterior to show a displacement of 350 mL. The process was timed and the air pressure was adjusted to reach air flow of roughly 1 L/min. This was meant to deliver approximately 80 µg of ammonia to the collection tube, however a large margin of error was found to be associated with the process, possibly due to leaks in the air system.

3.4.4 Chlorine

3.4.4.1 Method Development

A new method was designed for collection of chlorine based on the principle outlined in NIOSH Method 6011 (26) and an experiment conducted by Askew and Morisani (24). A 25-mL bubbler containing 10 mL of 0.1 mM sodium sulfite (Na_2SO_3) was used for collection. All chlorine absorbed is converted to chloride and the liquid collection media allows samples to be directly injected into the IC system for analysis. Samples were filtered upon injection using IC Acrodisc 13-mm syringe filters with 0.2-µm Supor (PES) membrane. The impinger body and the fritted tube were then rinsed with at least three volumes of deionized water and dried before reuse. Air was used to purge and dry the fritted end.

3.4.4.2 Method Validation

Samples of chlorine bleach, collected chlorine air samples, and spiked chloride samples were prepared in deionized water and in 0.1 mM sodium sulfite solution. The samples were

compared side by side using the ion chromatography instrument and using a Residual Chlorine Electrode (RSE). All samples in the sodium sulfite showed no signal when prepared and analyzed using the RSE. All samples analyzed in the IC matched concentration readings to those prepared in water and analyzed on the RSE.

3.4.4.3 Collection and Recovery

A gas cylinder spike was used to evaluate collection capacity and breakthrough. Two bubblers were attached in sequence to the outlet of the chlorine cylinder regulator. A measured volume of air from a 350-ppm chlorine cylinder was passed through the bubblers following the method described in 3.4.3.2. This method was meant to deliver approximately 350 µg of chlorine to the collection bubblers. Six samples were prepared this way.

One 10-mL sample of sodium sulfite solution in bubblers was spiked with 60 µL of stock solution equivalent to 60 µg of chloride, then attached to an air flow of 1 L/min at 80% RH and 32^{o}C for 60 minutes to test retention.

3.4.4.4 Cylinder Priming

Pressurized cylinders containing chlorine and air mixtures may require "priming" due to chlorine, which has a high density, collecting at the bottom of the cylinder. Before any chlorine tests were performed, the cylinder was allowed to run for 20-30 minutes to ensure uniform chlorine delivery. No literature sources were found to support this claim, however it was suggested by the cylinder provider and was observed in the gas spiking experiment above.

3.4.4.5 System Loss Tests

Chlorine continually showed inconsistent values when attempting to use the gas cylinders for standard spiking. Knowing the reactivity of chlorine in the presence of moisture

and metals, a test was devised to probe potential chlorine loss to the air flow system (Figure 3-5).

A test cell was placed in the test chamber with the collection air flow passing through the bottom of the cell. No sample was placed in the cell and one of the connections on the challenge side of the cell was capped. On the other challenge side connection the 350-ppm cylinder of chlorine was attached through a length of stainless steel tubing. The outlet of the collection side of the test cell was attached to a collection bubbler with a flow meter at the end of the test set up. The collection air flow was set to 0.9 L/min. The cylinder flow was opened and increased until the flow meter at the outlet of the bubbler read 1 L/min. The air flow was sampled for 60 minutes using bubblers, replaced every 15 minutes then analyzed on the IC.

A chlorine permeation test was also performed according to Class 2 procedures using an ASTM F739 glass cell and plastic fittings and the EMS fabric. The conditioned air was used as a collection medium as well as 15 mL of the 0.1 mM sodium sulfite solution.

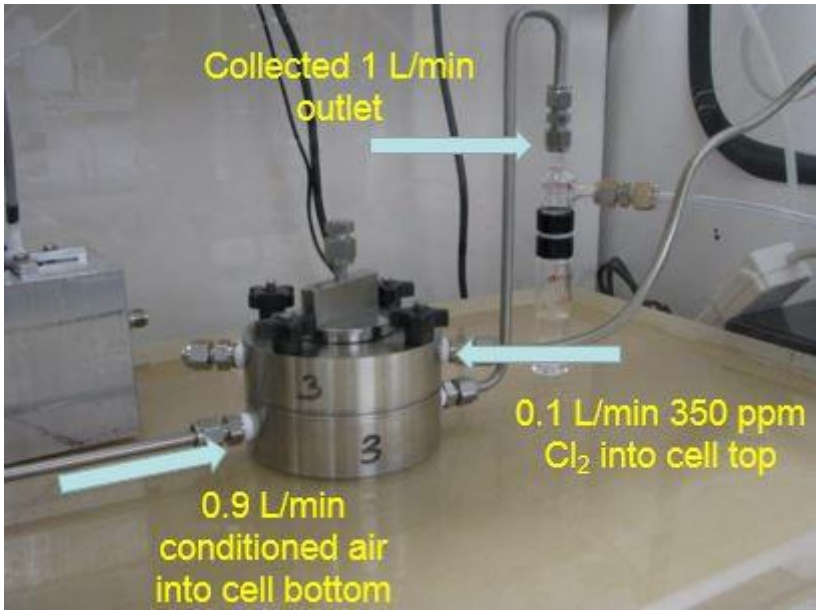


Figure 3-5 Chlorine Positive Control

3.4.5 Acrolein

3.4.5.1 Method Development

As stated in 2.1.6.2 the published sampling methods for acrolein appear to not be applicable to collection in NFPA 1994. The detection of the acrolein-HMP derivative was evaluated, but produced an insufficient signal on the GC-MS system and the reaction rate requires a significantly lower sampling rate. Though acrolein is known for its high reactivity and thus is usually collected using a derivatizing agent, this research sought to assess the possibility of collecting acrolein directly onto solid sorbent materials without derivatization.

3.4.5.2 Retention and System Loss Tests

Multiple sorbents were chosen to compare the retention of acrolein. The largest concern was the loss of acrolein through its reactivity with moisture and heat. A stability test was performed where 6 µL of stock solution equivalent to 60 µg of acrolein was spiked into a charcoal sorbent tube then was capped and allowed to sit in the chamber at 32°C for 60 minutes.

Retention was also tested by attaching three spiked tubes to an air flow of 1 L/min at 80% RH and 32ºC for 15, 30, and 60 minutes. Extraction tests were performed using five different sorbents as possible collection media: Activated Charcoal, Tenax TA®, Tenax GR®, Carboseive S-III, and Carboxen 569. The Tenax ® tubes were hand packed in ¼" stainless steel thermal desorption tubes using 200-mg of sorbent, 100-mg of glass beads, and glass wool to hold the sorbent in place.

3.4.5.3 Alternative Tests

Three other unsaturated aldehydes, crotonaldehyde, 2-pentanal, and cinnamaldehyde, were screened as possible alternatives or simulants for acrolein. Each chemical was subjected to extraction tests using the five different sorbents and the stability test using the activated charcoal sorbent to test for their stability in the test environment. Cinnamaldehyde, which contains an aromatic group, showed high stability and recovery value so it was also subjected to retention tests and a permeation test as a comparison to acrolein.

3.4.6 Permeation Tests

3.4.6.1 Materials

Three fabrics were chosen as test samples for permeation testing. These consisted of samples cut from a commercially available NFPA 1994 certified Class 2 suit, a commercially available Emergency Medical Services (EMS) garment consisting of a woven fabric with a laminated moisture barrier layer, and a laboratory bench protective liner material consisting of a polyethylene based film.

3.4.6.2 Procedure

All of the chemical challenges, including cinnamaldehyde applied as a 10 g/m^2 liquid challenge, were used to evaluate the permeation resistance of the three test materials. The

NFPA 1994 standard test procedures were followed for the evaluation of Class 2 materials with the exclusion of sample flexing and abrading. The challenge flow rate for the gas and vapor challenges was kept constant throughout the test at 0.3 L/min. The outlet of the cell challenge flows was fed through a high volume carbon filter to collect the TICs then into a fume hood. Three replicates were run for each material/chemical combination except for cinnamaldehyde which was only used once for each material.

3.4.7 Back Pressure Tests

The effect of back pressure was evaluated using a materials distention test similar to that designed by Bromwich (69). The back pressure in-line and the material distention were measured for each collection method and the EMS fabric. The distention was measured using a caliper suspended above the test cell with the screw top removed (Figure 3-6). A thin rubber septum was placed between the depth probe and the fabric to distribute the pressure of the thin metal probe resting on the center of the fabric. The caliper was zeroed when resting on top of the compression plate. The measured distention plus the plate thickness and minus the septum thickness equals the actual distention. The measurement was taken with an air flow of 1 L/min through the cell. The new effective surface area was calculated using the equation for the surface area of a spherical cap.

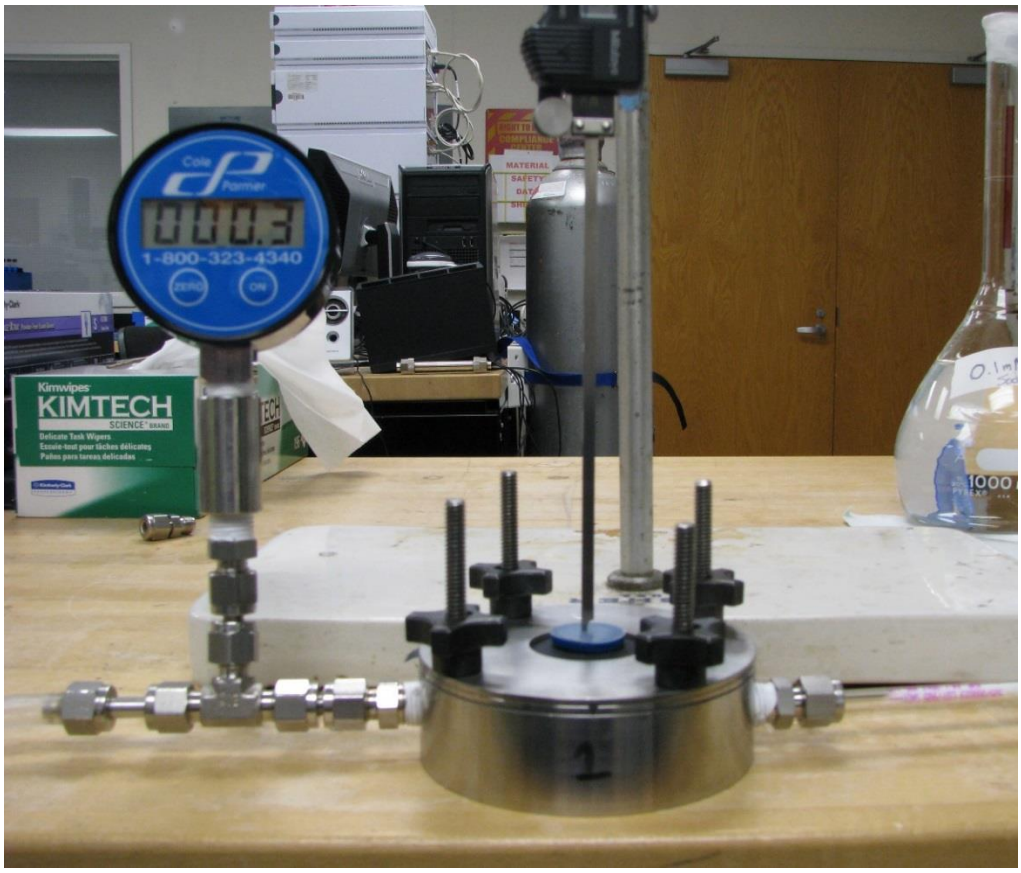


Figure 3-6 Material Distention Test Setup

Chapter 4. Results and Discussions

4.1 Analytical Methods

The following analytical methods were developed to ensure that each analyte could be detected below the required limit of detection specified in the NFPA standard.

4.1.1 Gas Chromatography

The GC-MS method developed for dimethyl sulfate was as follows:

Column: Restek RTX-1701 30m x 250µm x 0.25µm
Injection: 10-1 split ratio at 160^{o}C

Flow: 1.5 mL/min, 19.5 mL/min total Helium
Temperature Gradient: 50°C hold 3 min, 100°C/min to 200°C, Total: 9.5 min
MS Transfer Temperature: 250°C
Selected Ion Mode: 45, 66, 95, 96, and 125 m/z
Analyte Chromatographic Retention Time: 4.9 min

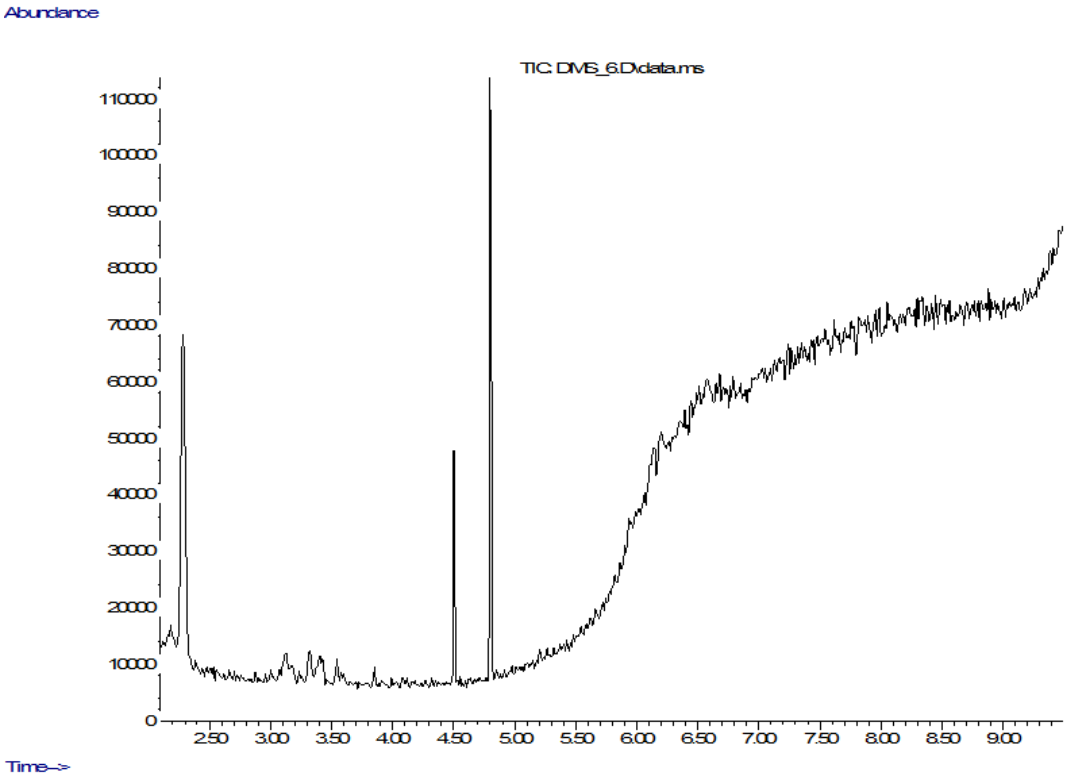


Figure 4-1 Chromatogram of DMS

The GC-MS method for acrylonitrile was as follows:

Column: Restek RTX-1701 30m x 250µm x 0.25µm
Injection: 20-1 split ratio at 250°C
Flow: 1 mL/min, 24 mL/min total Helium
Temperature Gradient: 35°C hold 2 min, 25°C/min to 200°C, Total: 8.6 min
MS Transfer Temperature: 250°C
Selected Ion Mode: 53, 52, 51, 50, 38, 26 m/z
Analyte Chromatographic Retention Time: 2.4 min

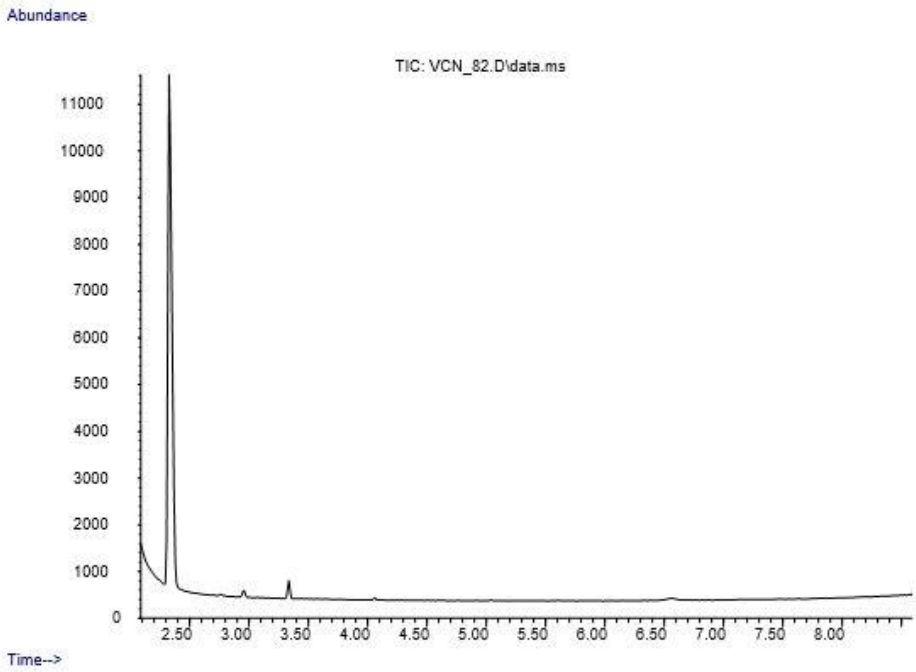


Figure 4-2 Chromatogram of Acrylonitrile

Table 4-1 Summary of DMS and Acrylonitrile Methods and Calibrations

	Dimethyl Sulfate	**Acrylonitrile**
Sorbent	Porapak Q, 200-mg	Activated Charcoal, 600-mg
Desorbing Solution	Acetone, 2 mL	Carbon Disulfide, 3 mL
Calibration Range (ng/µL)	0.13 – 131	0.095 – 95.7
R^2	0.9999	0.9998
Slope	5941	5754
Intercept	-2469	2046
Standard Deviation of Low Level Spike	320	564
Limit of Quantitation (ng/µL)	0.64	0.97
Limit of Detection (ng/µL)	0.19	0.29
NFPA Required Limit of Detection (ng/µL)*	0.48	0.32
** Method LOD defined as 0.1 µg/cm^2 permeation rate, which is equivalent to a resulting sample concentration depending on desorbing solution volume*		

4.1.2 Ion Chromatography

The IC method developed for ammonium was as follows:

Column: CS12a 2mm x 250mm with guard column
Suppressor: CSRS-300 2mm suppressor
Detector: DS6 Heated Conductivity Cell
Eluent: EGC III MSA Eluent Generator Cartridge
Manual injection, 25-µL sample loop
Flow rate: 0.25 mL/min
Suppressor Current: 15 mA
Eluent Concentration: 20 mM
Analyte Chromatographic Retention Time: 5 minutes

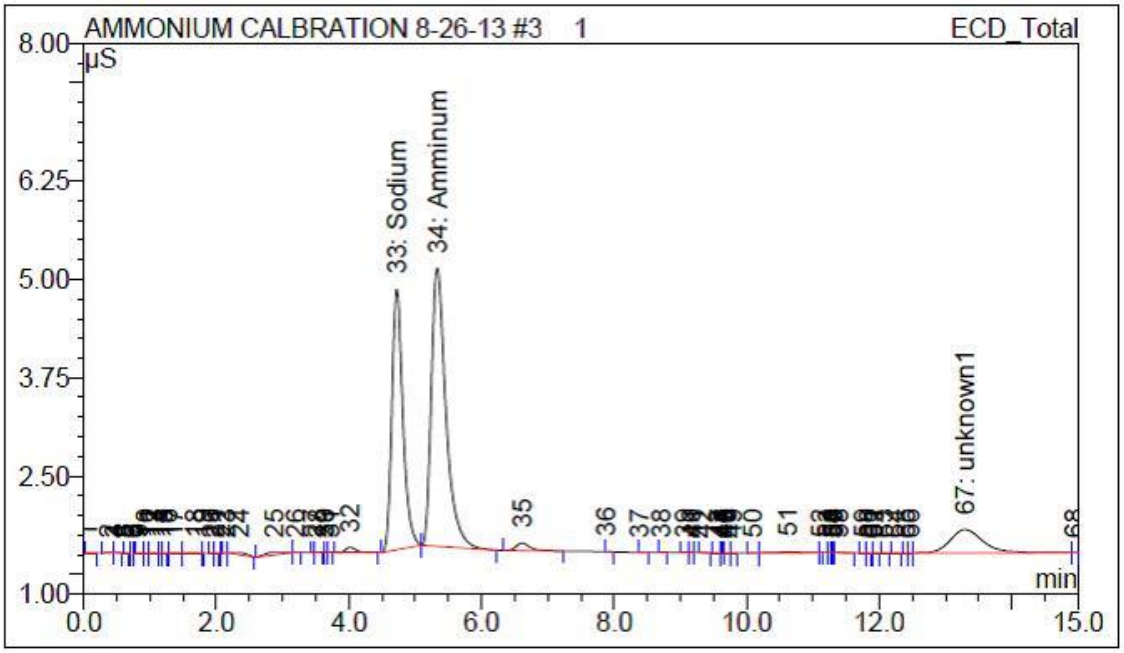


Figure 4-3 Chromatogram of Ammonium

The IC method developed for chloride was as follows:

Column: AS12a 2mm x 250mm with guard column
Suppressor: ASRS-300 2mm suppressor
Detector: DS6 Heated Conductivity Cell
Eluent: EGC III KOH Eluent Generator Cartridge

Manual injection, 25 µL sample loop
Flow rate: 0.25 mL/min
Suppressor Current: 15 mA
Eluent Concentration: 23 mM
Analyte Chromatographic Retention Time: 5 minutes

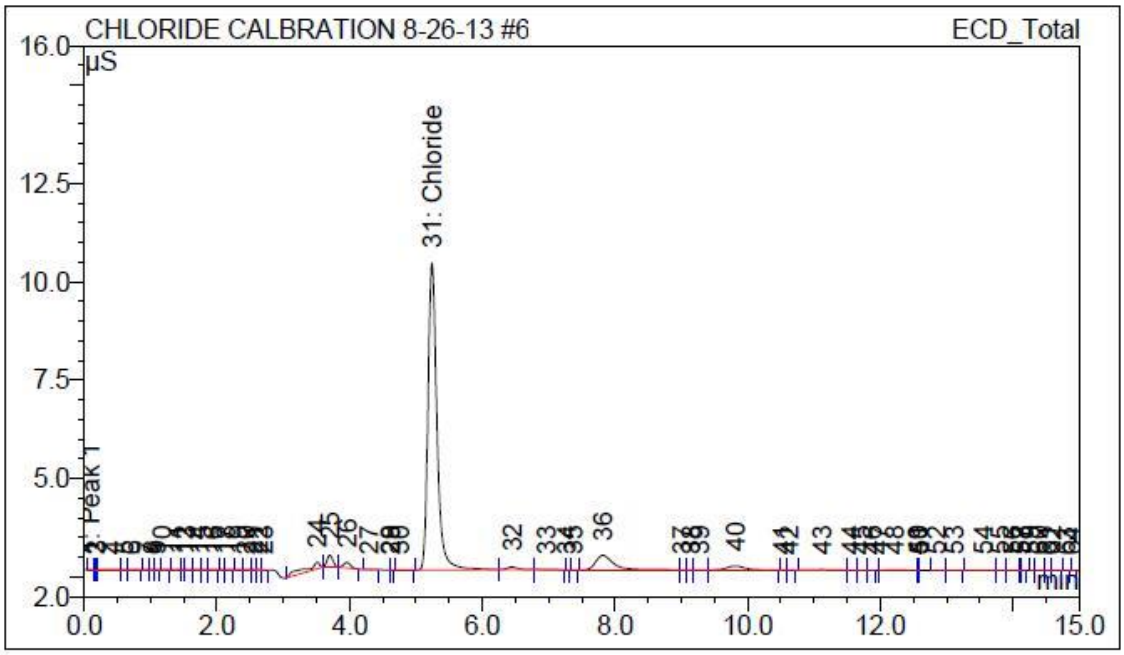


Figure 4-4 Chromatogram of Chloride

The method calibrations and the limits of detection and quantitation are summarized below in Table 4-2.

Table 4-2 Summary of Chloride and Ammonium Methods and Calibrations

	Chloride	**Ammonium****
Collection	25-mL Bubbler	Silica Gel Coated with Sulfuric Acid
Desorbing Solution	10 mL 0.1 mM Sodium Sulfite	20 mL DI H_2O
Calibration Range (ng/µL)	0.05 - 8	0.1 - 5
R^2	0.9996	0.9994
Slope	1.305	Quadratic Constants: -0.0675 0.8653 0.0749
Intercept	-0.039	-
Standard Deviation of Low Level Spike	0.005	0.0069
Limit of Quantitation (ng/µL)	0.04	0.08
Limit of Detection (ng/µL)	0.01	0.02
NFPA Required Limit of Detection (ng/µL)*	0.096	0.048

** Method LOD defined as 0.1 µg/cm^2 permeation rate, which is equivalent to a resulting sample concentration depending on desorbing solution volume*
***Ammonium shows a quadratic response, the LOD and LOQ were determined using a linear correlation fit to the lowest 3 points*

4.1.3 Liquid Chromatography

4.1.3.1 Acrolein

The HPLC method developed for acrolein was as follows:

Column Specifications: Agilent Poroshell 120 EC-C18 2.7µm, 3.0mm x 100mm
Flow: 0.5 mL/min
Gradient: 80:20 H2O:ACN 0-0.5 min
20:80 H2O:ACN 0.5-5 min
80:20 H2O:ACN 5-12 min
Wavelength: 215 nm
Analyte Chromatographic Retention Time: 3.1 min

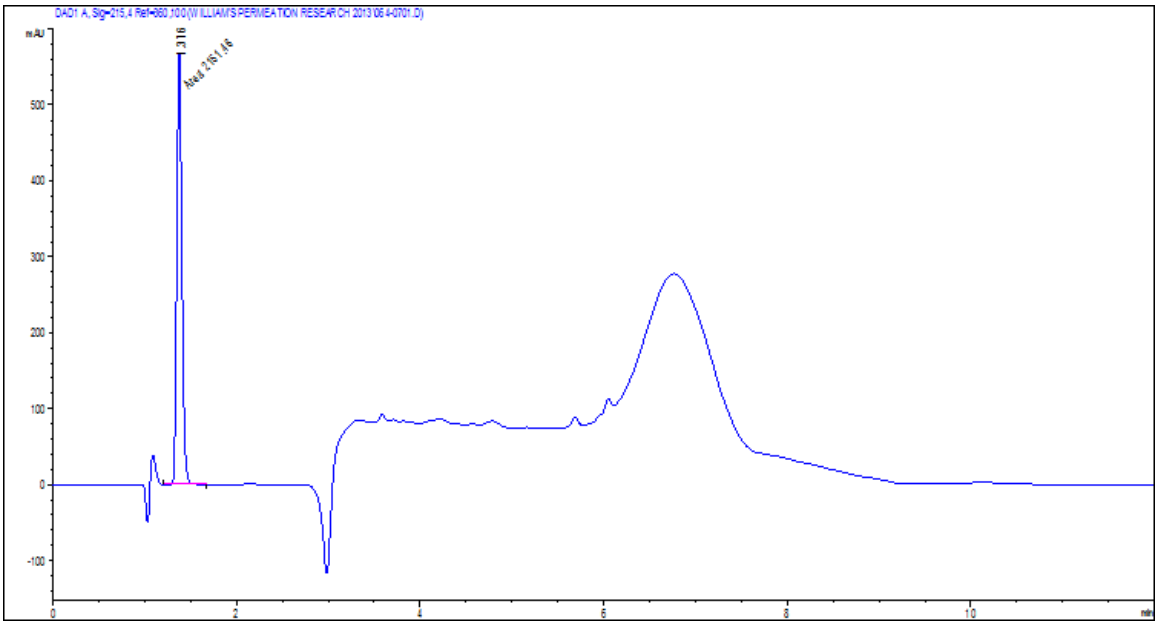


Figure 4-5 Chromatogram of Acrolein

The HPLC method developed for cinnamaldehyde was as follows:

Column Specifications: Agilent EC18 2.7µm, 3.0mm x 100mm
Flow: 0.5 mL/min
Gradient: 60:40 H2O:ACN 0-0.5 min
20:80 H2O:ACN 0.5-5 min
60:40 H2O:ACN 5-12 min
Wavelength: 285 nm
Analyte Chromatographic Retention Time: 3.3 min

The method calibrations and the limits of detection and quantitation are summarized below in Table 4-3.

Table 4-3 Summary of Acrolein and Cinnamaldehyde Methods and Calibrations

	Acrolein	**Cinnamaldehyde**
Collection	Activated Charcoal, 600-mg	Tenax TA, 200-mg
Desorbing Solution	4 mL Acetonitrile	4 mL Acetonitrile
Calibration Range (ng/µL)	0.095 – 95.7	0.99 – 29.9
R^2	0.9995	0.99997
Slope	151.33	120.8
Intercept	-66.3	-1.17
Standard Deviation of Low Level Spike	1.663	-
Limit of Quantitation (ng/µL)	0.11	-
Limit of Detection (ng/µL)	0.03	-
NFPA Required Limit of Detection (ng/µL)*	0.24	-
** Method LOD defined as 0.1 µg/cm^2 permeation rate, which is equivalent to a resulting sample concentration depending on desorbing solution volume*		

4.2 **Method Validation Results**

Each collection and extraction technique was verified to ensure sufficient recovery.

4.2.1 Sorbent Extractions

The sorbent extraction efficiencies are summarized in Table 4-4.

Table 4-4 Method Extraction Efficiencies

TIC	Method Adapted	Collection	Desorption	Extraction
Ammonia	OSHA ID188 NIOSH 6106	Silica Gel w/ H_2SO_4 200-mg	20 mL DI H_2O	94.6%
Dimethyl Sulfate	NIOSH 2524	Porapak® Q 200-mg	2 mL Acetone	94.7%
Acrylonitrile	NIOSH 1604	Activated Charcoal 600-mg	4 mL CS_2 w/ 2% acetone	95.8%
Acrolein	None	Activated Charcoal 600-mg	3 mL Acetonitrile	90%

4.2.2 Retention and Collection Capacity

The retention efficiency and collection capacity values for each collection method are summarized below.

The dimethyl sulfate retention values (Table 4-5 and Table 4-6) showed sufficient retention and negligible decrease in analyte over time. The 84-µg sample had an average recovery of 83% and the 57-µg samples had an average recovery of 93%.

Table 4-5 DMS Retention Over Time

Time (min)	µg recovered	% retained
15	71.6	85%
30	74.3	88%
45	65.7	78%
60	67.9	81%

Table 4-6 DMS Retention

Time (min)	µg recovered	% retained
60	50.4	95%
60	47.4	89%
60	46.8	88%

The acrylonitrile retention values showed extremely low retention on the smaller 200-mg tubes, with an average retention of only 6% (Table 4-7). The larger 600-mg tubes showed sufficient retention with an average of 99%, though the second tube showed increasing breakthrough over time (Table 4-8).

Table 4-7 Acrylonitrile Retention On Smaller Sorbent Tubes

Time (min)	µg recovered	% retained
60	3.46	6%
60	3.52	6%
60	3.19	5%

Table 4-8 Acrylonitrile Retention on Larger Sorbent Tubes

Time (min)	µg recovered	% Breakthrough onto second tube	Total % retained
0	52.3	0	91%
30	54.1	5%	94%
45	60.1	8%	105%
60	57.1	11%	99%

The acrolein retention tests showed significant analyte loss but not significant breakthrough on the activated charcoal sorbent (Table 4-9). It can be seen that a steadily increasing amount of acrolein is not recovered through the retention test. This is likely due to reaction in the test conditions and possibly with the sorbent material itself.

Table 4-9 Acrolein Retention over Time

Condition	% Breakthrough on second tube	Average % Recovery
Sorbent Spike Immediate Extraction	0%	90.48
Capped at 32ºC for 60 min	0%	86.94
Retention 15 minutes	1.52	71.89
Retention 30 minutes	2.65	66.07
Retention 60 minutes	2.50	58.74

The three other unsaturated aldehydes were tested for extraction against a variety of sorbents (Table 4-10) and analyzed for retention on activated charcoal (Table 4-11). Cinnamaldehyde was tested on hand-packed Tenax TA® tubes because this sorbent is widely used for aromatic analytes. 2-Pentenal was not tested against multiple sorbents because it showed similar retention data to crotonaldehyde. None of the aldehydes showed breakthrough, meaning the analyte is being lost in the collection medium. Only cinnamaldehyde showed stability in the test conditions. The retention values in Table 4-11 incorporate the extraction efficiencies of each analyte. In terms of using these aldehydes as a comparison to acrolein, cinnamaldehyde has the largest molecular volume and highest boiling point which does not make it a likely simulant. However, it had the highest stability in the testing environments, indicating it could be collected most reliably.

Table 4-10 Aldehyde Extraction from Various Sorbents

	Acrolein	Crotonaldehyde	2-Pentenal	Cinnamaldehyde
Activated Charcoal	88%	73%	76%	0%
Carboseive S-III	101%	N/A	N/A	N/A
Carboxen 569	86%	91%	N/A	N/A
Tenax GR	106%	98%	N/A	102%
Tenax TA	107%	100%	N/A	100%
Porapak N	N/A	96%	N/A	N/A

Table 4-11 Retention of Aldehydes on Carbon and Tenax Tubes in Test Conditions

	Acrolein	Crotonaldehyde	2-Pentenal	Cinnamaldehyde
Front	58%	85%	88%	101%
Back	0%	0%	0%	0%

The ammonia retention tests showed high retention with an average of 105.6% (Table 4-12). The values are above 100% indicating a positive bias in the calibration at this sample concentration or inaccuracy in dilutions.

Table 4-12 Ammonia Retention over Time

Time (min)	µg recovered	% retained
30	10.7	107.2
45	10.6	106.20
60	10.5	104.6

The gas collection tests with ammonia showed good collection capacity and low breakthrough at the challenge levels (Table 4-13).

Table 4-13 Ammonia Gas Collection

Sample	µg recovered	% breakthrough to second tube
Gas Spike 1FT	40.4	-
Gas Spike 1BK	0.5	1.19
Gas Spike 2FT	64.9	-
Gas Spike 2BK	1.2	1.78
Gas Spike 3FT	66.9	-
Gas Spike 3BK	0.9	1.33

The chlorine retention test showed a 97% recovery. The gas collection tests showed good collection capacity and low breakthrough at a variety of challenge levels (Table 4-14).

Table 4-14 Chlorine Gas Collection

Sample	µg recovered	% breakthrough
Gas Spike 1FT	375.4	-
Gas Spike 1BK	23.1	6%
Gas Spike 2FT	421.3	-
Gas Spike 2BK	5.5	1%
Gas Spike 3FT	239.1	-
Gas Spike 3BK	1.7	1%
Gas Spike 4FT	12.6	-
Gas Spike 4BK	1.4	3%
Gas Spike 5FT	85.2	-
Gas Spike 5BK	5.8	5%
Gas Spike 6FT	18.7	-
Gas Spike 6BK	2.1	5%

4.2.3 Chlorine Positive Control

The chlorine positive control showed very low recovery (Table 4-15). The cylinder was delivering 100 µg of Cl_2 per minute so the expected sample recovery was up to 1,500 µg. Some faint green cell corrosion was observed on the surface of the compression plates. This test does not replicate a true permeation test. The air mixing inside the cell is different and the cylinder delivery was seen to be unreliable, however the test was conducted at very high concentrations. It appears that a large amount of analyte was lost simply from the test environment.

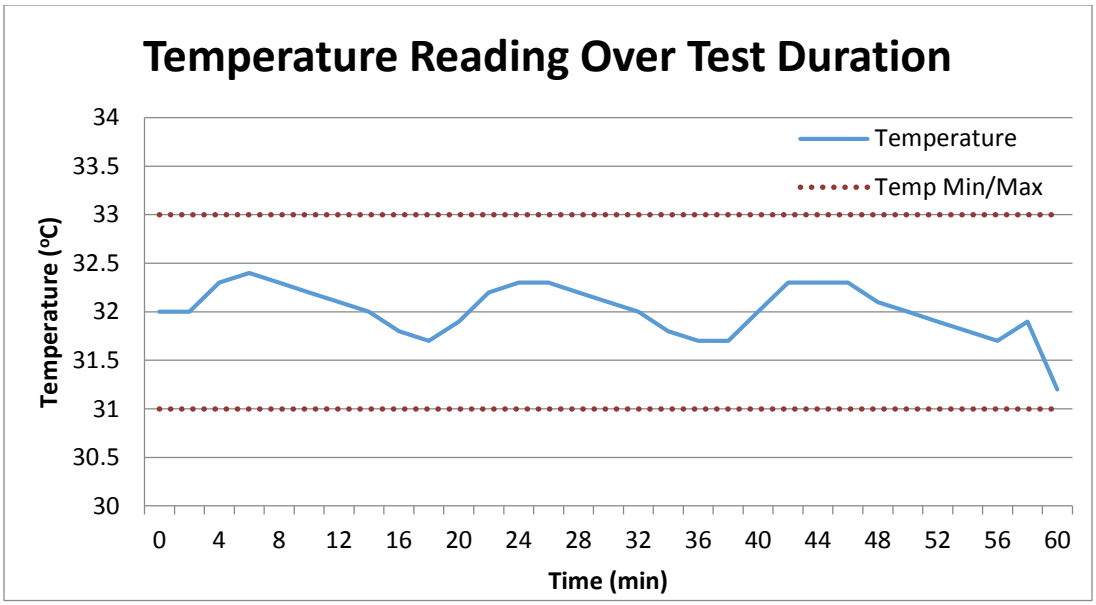
Table 4-15 Chlorine Collection in Positive Control Test

Time	µg Recovered	Theoretical % Recovered
15	26	1.7 %
30	42	2.8 %
45	59	3.9 %
60	93	6.2 %

4.3 **Permeation Tests**

4.3.1 Conditions

The chamber humidity and temperature readings were recorded every 2 minutes to ensure conditions stayed within the required range. The data from one such test are displayed in Figure 4-6. The temperature inside the chamber shows gradual cycling in response to the controller. The humidity is prone to more erratic changes but generally shows very good control.



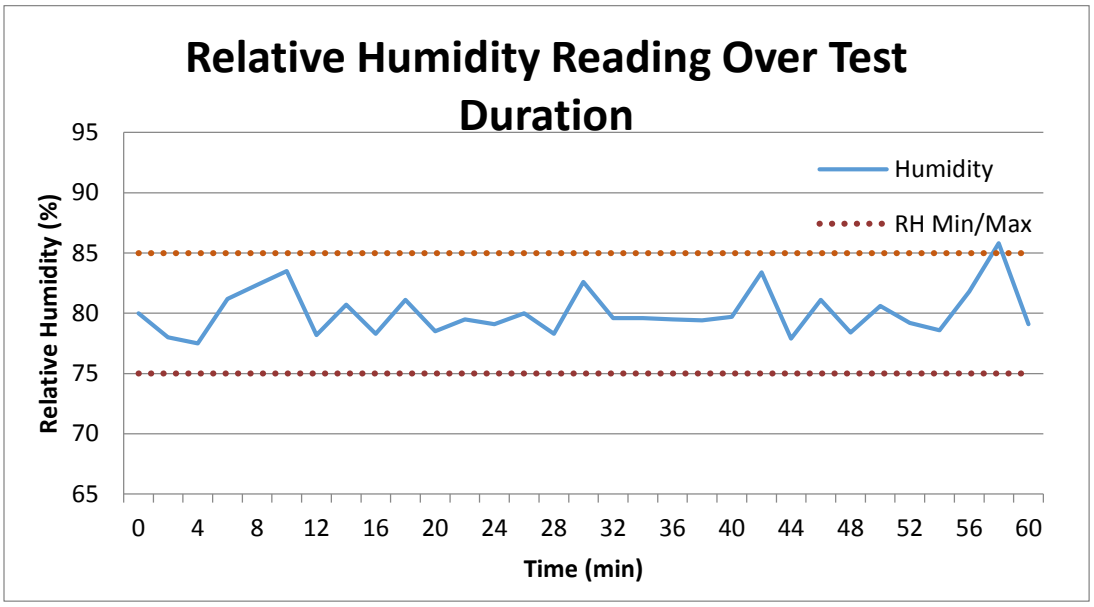


Figure 4-6 Air Condition Readings Over Test Duration

4.3.2 Permeation Data

The cumulative permeation test results for each chemical and fabric tested as Class 2 samples are given in Table 4-16. The results are presented as the total amount of permeant detected divided by the sample exposure area.

The NFPA certified material did not show any permeation indicating it performs well beyond the certification standard. The results from the other two materials are instructive. One reason is they show the variation which is possible for different material and challenge matches. The EMS fabric shows much more permeability to most of the challenges than the PE bench liner. For both samples DMS showed the highest level of permeation. Back pressure played a notable role in the permeation results of the PE bench liner test against cinnamaldehyde. The packed tubes for collection of cinnamaldehyde caused the PE bench liner material to irreversibly stretch and distort, possibly causing much higher levels of permeation. Chlorine was not detected in any of the tests.

Table 4-16 Permeation Test Results for Class 2 Evaluation of Sample Materials

Challenge	**1994 Class 2 µg/cm²**	**EMS µg/cm²**	**PE Bench Liner µg/cm²**
DMS	N/D	600.00	84.52
Acrylonitrile	N/D	39.61	1.23
Ammonia	N/D	7.48	0.06
Chlorine	N/D	N/D	N/D
Acrolein*	N/D	6.87	0.83
Cinnamaldehyde	N/D	6.18	358.83[+]

** Acrolein data has been extrapolated using a recovery efficiency of 60%.*
[+] Sample showed excessive amounts of distention and distortion from back pressure

The chlorine permeation test results using an ASTM F739 glass cell with plastic fittings are presented in Table 4-17. Changing to a glass cell and using Teflon® plastic tubing did lead to detectable chlorine permeation, showing that chlorine is a valid chemical challenge depending on the test conditions. The effect of collection medium is also strikingly clear. The liquid collection showed nearly 100 times more permeation. This is strongly dependent on the type of fabric used. The EMS fabric has a moisture barrier which likely allows some level of moisture vapor through or is able to saturate with moisture, altering the permeation characteristics.

Table 4-17 Alternate Chlorine Permeation Test Results for EMS Fabric

Method	**Permeation, µg/cm^2**
NFPA Cell, metal fittings	N/D
ASTM Cell, plastic tubing and fittings, air collection	2.3
ASTM Cell, liquid collection	96

4.4 **Analysis of Testing Conditions**

4.4.1 Challenge Levels

The NFPA 1994 standard defines vapor and gas challenge concentrations in parts-per-million (ppm) but does not specify if this is by volume or by weight. Parts-per-million by weight is not commonly used but this is a possible source of confusion which should be clarified.

The standard defines a flow of 0.3 L/min of humidified air for the challenge side during open-top testing of Class 3 ensembles with the liquid challenge. However, a flow rate for the vapor and gas challenges is not specified. The standard only states that the challenge concentration must be maintained over the course of the test. The importance of this is highlighted in Table 4-18. This table shows the amount of chemical in micrograms which would actually occupy the cell top for each challenge using the AVLAG cell which has a volume in the top half of the cell of 13 mL and an exposure area of 9.89 cm^2. If flow was not maintained over the course of the test there would not be enough challenge present to cause a failure.

Table 4-18 Challenge Amounts in Filled Top Cell

Challenge	**ppm, v**	**mg/m^3**	**Filled Cell Top (µg)**
Acrolein	40	90	1.16
Acrylonitrile	40	85	1.10
Ammonia	40	28	0.36
Chlorine	40	113	1.47
Challenge	**ppm, v**	**mg/m^3**	**Filled Cell Top (µg)**
Acrolein	350	784	10.19
Acrylonitrile	350	742	9.64
Ammonia	350	242	3.14
Chlorine	350	991	12.89
Failure at 59 µg total permeant using 9.89 cm^2 exposure area 13 mL cell volume			

To maintain the challenge concentration, one would need an idea of the permeation rate. The minimum permeation rate to reach the failure level of 59 µg would be a constant 0.1

µg/cm^2/min or approximately 1 µg/min. This equates to a needed challenge flow rate of 13 mL per minute at minimum for Class 3 tests. However permeation does not reach a steady state immediately and often increases exponentially for a period. If the permeation rate were to begin increasing rapidly and the supplied challenge was not sufficient to maintain that permeation, the chemical gradient would decrease and the permeation rate would be depressed. Thus the standard must account for a higher possible rate. Assume instead that the permeation rate suddenly increased to 6 µg/cm^2 or 60 µg/min at the end of the test, which would result in a failure within one minute (the acceptable error range for time of the test). The minimum flow rate for the challenge would be 780 mL/min for Class 3 challenges and 89 mL/min for Class 2 challenges for most of the challenges. Ammonia which has a much lower molecular weight would require an even higher supply. This is likely an overestimate of a realistic jump in permeation rate, but it highlights a point of possible variation in how the test is implemented. One drawback of using these challenge gases and vapors worth mentioning is the large amount of waste gas which must be used and disposed of to implement a test.

A final and more difficult issue to address is the underlying significance of the challenge concentrations chosen. NFPA 1994 is unique for defining diluted vapor challenges. As stated in Section 0 the challenges have evolved across different editions of the standard. The largest change occurred when acrylonitrile and acrolein were changed from liquid to vapor challenges. The challenge concentration was also reduced substantially when this occurred. Table 4-19 shows the equivalent concentration of the two chemicals as vapors if they were to be applied as liquid according to the previous standard edition. The concentrations were

previously 1,000 times higher than the current test. The only challenge applied as a liquid, DMS, is a significantly higher challenge than the other chemicals.

Table 4-19 Challenge Concentrations for Acrolein and Acrylonitrile as Liquid Spikes

Challenge	Liquid (mg)	Vapor (mg/m3)	ppm
Acrolein	9.89	760,769	339,735
Acrylonitrile	9.89	760,769	358,943
Liquid spike challenge of 10 g/m^2			

This raises the question of what the challenge levels, which are clearly under continued consideration, are meant to accomplish. The dilute gas and vapor challenges are meant to equate to more "moderate" permeation resistance compared to vapor tight Class 1 suits (85).

4.4.2 Flow Rate and Back Pressure

The back pressure test results are listed in Table 4-20. Increased back pressure caused an increase in material distention resulting in 6% to 12% larger effective exposure areas. The deformation of the material can be seen in Figure 4-7. The sorbent tubes had higher back pressure than the bubbler. The Porapak® tube and the individually packed Tenax® tubes used for DMS and acrolein have smaller particle sizes, and therefore have the highest back pressure and highest amount of material distention.

Table 4-20 Results of Back Pressure Test

Challenge	Back Pressure (psi)	Distention (mm)	New Surface Area (cm^2)	Percent Increase (%)
Ammonia	0.70	4.1	10.43	8.41
DMS	0.74	4.6	10.57	9.86
Chlorine	0.32	3.6	10.31	7.12
Acrylonitrile 1 Tube	0.32	3.4	10.26	6.62
Acrylonitrile 2 Tubes	0.92	4.2	10.44	8.55
Cinnamaldehyde	2.64	5.5	10.83	12.63

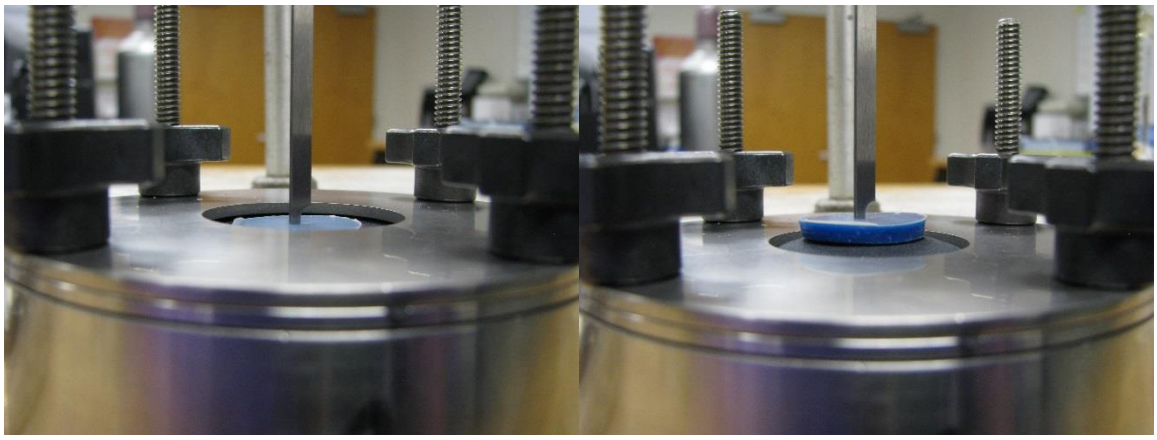


Figure 4-7 Image of cell top removed to show no air flow (left) and air flow (right) causing backpressure and material distention

The distention values are only for the EMS fabric and will be unique for other fabrics. Measurements were not taken with the bench liner material, however it is supported by only a thin non-woven layer and stretched significantly during testing. It is not clear if material thinning occurred however some material damage can be observed in Figure 4-8 which shows

the underside of the EMS fabric after testing with the hand packed Tenax® tubes. The outer two rings are caused by the compression O-rings which seal the material. However the inner ring is caused by the material pushing upward against the edge of the opening on the challenge side compression plate. This thinned material would be on the exposed area.

As discussed in the literature, the flow characteristics on the collection side of a permeation cell are important in optimizing collection of permeant. The flow rate must be high enough to clear the cell and maintain the concentration gradient but it must not have any effects which may alter the measured permeation rate. When the air flow rate of 1 L/min defined in NFPA 1994 is used with active air sampling media material distention, breakthrough, and air leaks around collection media can occur.

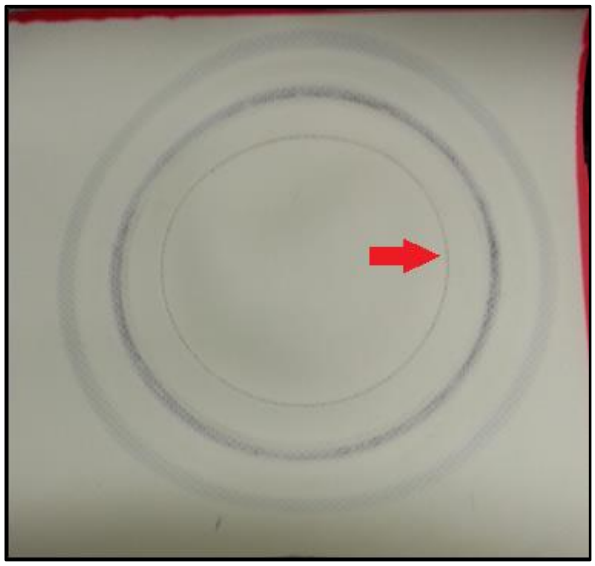


Figure 4-8 Material damage caused by back pressure

Chapter 5. Conclusions

This research provides examples of guidelines and considerations for implementing the chemical permeation resistance test in a repeatable and reliable manner. It shows that active air sampling methods are a viable option for the collection of cumulative amounts of chemical in permeation resistance tests using air as the collection media. However, there are some drawbacks associated which must be considered. Validation methods are needed to confirm the capacity and recovery of sorbents in the test conditions. Effects from the flow rate and challenge reactivity lead to variability between different implementation approaches. Active air sampling provides the easiest method to account for the entire amount of cumulative permeant and allows each chemical to be quantitated on the analytical instrument best suited for its detection and identification. Four of the five chemicals used in the NFPA 1994 Chemical Permeation Resistance Test had collection methods, which were modifiable for implementation in this laboratory, in existence.

Acrolein faced significant collection issues and indicated signs of degradation in the test environment. A suitable sorbent was not found. This raises questions about the ability to meaningfully quantify acrolein as a chemical challenge. Chlorine also showed multiple possibilities for inconsistent implementation as a challenge chemical. No material tested showed significant chlorine breakthrough at the challenge levels. A "forced fail" test showed high levels of loss and reactivity in the test conditions.

The most challenging test condition in regards to implementing the NFPA 1994 Chemical Permeation Resistance Test is the collection flow rate. Most air sampling methods are not intended for such volumes of air because of the increase of analyte breakthrough. Back

pressure associated with sampling media causes different levels of material distention. Additionally the test does not accommodate selectively permeable fabrics which may allow air to pass through the material while still providing chemical permeation resistance. Some changes in the standard could clarify aspects of implementation, for instance with the challenge flow rate or how to handle data variability around recovery efficiency and backpressure. These results show that each chemical chosen as a challenge must be considered in regards to its chemical properties, reactivity, and detection method.

Chapter 6. Recommendations

There is still considerable work which can be performed to evaluate and develop permeation test methods for chemical protective equipment and to further define "safe wear times." From the findings above the following changes to the standard should be considered. The standard should include a minimum challenge flow rate. Chlorine should not be used as challenges if there is no way to ensure it poses its intended challenge in the test conditions. Acrolein should not be used as a challenge if it cannot be collected reliably.

Further work should focus on addressing future needs of fabrics being developed and on more clearly defining the relationship between the bench level test and the challenges faced in the field. One important issue to address is the change in permeation characteristics using different challenge concentrations. What is the significance of choosing more diluted permeation challenge vapors? Is it the best way to evaluate materials which are meant to provide "moderate" chemical vapor resistance? What other failure mechanisms may exist for CPC? Is there a simpler way to screen fabrics against a battery of chemicals?

Methods must be developed to test unconventional fabrics and components such as selectively permeable membranes and closures which do not fit in current test cells. Skin permeation studies and specific toxicological data can be used to clarify exposure thresholds and predict what occurs as toxic chemicals actually enter the chemical suit microclimate. The effects of other use conditions such as high moisture or a wetted surface should be investigate. The sophistication of permeation data must increase to include solubility data and more sensitive detection limits.

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