PERMEATION OF VAPORS THROUGH POROUS MEMBRANES

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PERMEATION OF VAPORS THROUGH POROUS MEMBRANES

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A Thesis

Submitted To

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Master of Science

Auburn, Alabama
May 11, 2006

PERMEATION OF VAPORS THROUGH POROUS MEMBRANES

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VITA

Prithi Rao, daughter of Anathayya Vasudeva Rao and Indira Rao, was born on December 01, 1979, in Sharjah, UAE. She graduated high school from Indian High in the year 1997. She attended Fergusson College, Pune University, Pune where she graduated with a Bachelor of Science degree in Chemistry in August 2000. She also attended Nowrosjee Wadia College, Pune University, Pune where she graduated with a Master of Science degree in Polymer Science in the year 2002. She began her graduate studies in Integrated Textile and Apparel Science in Auburn University in August 2003.

PERMEATION OF VAPORS THROUGH POROUS MEMBRANES

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Master of Science, May 11, 2006
(MSc., N.Wadia College, Pune University, 2002)
(BSc., Fergusson College, Pune University, 2000)

88 Typed Pages

Directed by Gisela Buschle-Diller

Three types of microporous membranes have been investigated regarding their porsity and permeability for vapors. Permeation tests were carried out on membranes made from polypropylene and mixed polyethylene and polypropylene using β-pinene and dibutylsulphide as vapors. The membranes were characterized by scanning electron microscopy to evaluate their overall porosity. Vaporization experiments with β-pinene and dibutylsulphide were performed using a distillation set-up with the membrane intersecting the vapor flow. Permeation was determined as a function of weight of permeated vapor to the weight of the original specimen. The membrane made from polypropylene showed the highest permeability, while additives and filler particles present in membranes made from mixed polyethylene and polypropylene and UV treated Polypropylene membranes might have slowed the flow of vapor. The permeability of β-pinene for all the three membranes was higher when compared to experiments performed with dibutylsulphide.

ACKNOWLEDGMENTS

I would like to express my deepest sense of gratitude towards Prof. Gisela Buschle-Diller for her guidance through the entire investigation. I also would like to thank Dr Yasser Gowayed and Dr B.Lewis Slaten. Also thanks are due to my family for installing the necessary confidence in me to face and overcome challenges. Thanks to all my teachers over the years for the motivation provided to me to strive for excellence. Last but not the least, thanks to all my friends over the years for making me feel confident to face a challenge, by always pointing out my virtues rather than my flaws.

Style Manual Used is Guide to Preparation and Submission of Theses and Dissertation

Computer software used Microsoft word, Microsoft Excel, Chem Draw

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1. INTRODUCTION

1.1 Chemical Warfare Agents

Our history provides many instances where societies, religious groups and nations have tried to achieve political, religious and economic dominance. There have been many methods to achieve this kind of dominance, from swords and machine guns to the latest technology involving nuclear, chemical and biological warfare. The NATO definition of a chemical warfare agent is "A chemical substance which is intended for use in military operations to kill, seriously injure or incapacitate people because of its physiological effects"[1]. "The Chemical Weapons Convention defines chemical weapons as any chemical which through its chemical effect on living processes, may cause death, temporary loss of performance or permanent injury to people and animals" [2].

Chemical agents have been used as weapons from the beginning of the First World War up to the Gulf War. Nowadays, they are often used by terrorists as means to terrorize people, nations etc. This warfare technique requires small amounts of chemicals to bring about a mass destruction of a country and is also enough to bring a country's economy down.

The first use of chemical weapons was in the year 1915 during World War I when the Germans used them to cause panic among the Allied Forces. In this case they actually

played a psychological role to cause panic, fear, and unpredictable behavior among the allied forces that they might be attacked with gases. This set the stage for the United States, Great Britain, and France to probe into the research and development of a new class of gases. One of the important features of these gases was that the environmental conditions had to be favorable in order for them to be effective. Factors such as temperature, humidity, wind speed and its direction were important [3].

1.2 Effects of Chemical Warfare (CW) Agents

Chemical warfare agents cause psychological and physiological responses. In terms of the physiological responses, they cause nerve disorders, tremors, skin blisters, memory loss, depressions, hallucinations, loss of concentration, and sometimes even death. Besides their impact on humans they also contaminate food, water and kill animals [3].

The main psychological feature of these agents as mentioned above is to bring in the element of surprise amongst the soldiers and this in turn leads to fear, panic, and anxiety attacks causing a lot of chaos. Soldiers get paranoid and frightened at night. Conventional weapons do not have as much an impact on the human mind when compared with the CW agents. The sociopsychological responses to chemical warfare mostly show that the individuals are terrified of exposure to these classes of weapons [4].

1.3 Features of Chemical Warfare Agents

Physical, chemical and biological properties decide whether a chemical can be used for warfare. Some of the important properties that classify these chemical agents as

toxic are the vapor pressure, volatility, vapor density, freezing points, melting points and boiling points [5]. The vapor density determines whether the agent is heavier or lighter than air. Vapor pressure data determines the rate of evaporation and its volatility. The boiling point and the freezing point decide over the operational use.

1.3.1 Routes of Entry

There are many routes for these agents to enter the human body. From the respiratory tract the gases, vapors and aerosols can be inhaled through the nose and mixed in the body system through the lungs. Lungs and eyes which are moist tissues absorb the vapors. Also, the skin covered with sweat can readily absorb the vapors. Exposure to droplets of liquid can be dangerous as they can be easily absorbed by the eyes, skin and the mucous membranes [5].

Different chemical warfare agents have more than one way of route of entry, some being more effective than others. For example, the class of blood agents causes hazard to the person more by inhalation than by absorption through the skin and eyes. Blister agents are more effective when absorbed through the skin. Nerve agents have detrimental effects when absorbed through the eyes and the skin. The vomiting compounds and the choking agents are most effective when inhaled [5].

1.3.2 Duration of the Effectiveness of the CW Agents:

There are several factors that decide the period of effectiveness of CW agents. Physical properties of the chemicals, environmental conditions such as the outside temperature, wind speed, relative humidity, etc., and the target conditions like the

vegetation, soil, and contours all play a role. The method of dissemination, i.e., size of the particles, is also important. The form in which it is disseminated, i.e., the vapor form, is less persistent when compared to liquid droplet form. Gases, aerosols and highly volatile liquids disperse easily and are effective for a short period of time but large drops of liquids that are not volatile remain for a longer period of time in the land which increases their effect. Thus the instruments used to disseminate them, such as spray tanks and aerosol generators also modify the degree of the dispersion[6]. Higher surface temperature quickens the evaporation rate of chemical warfare in liquid form, whereas lower temperatures freeze the agent and leading to an increase in retention, although without immediate hazard to the soldiers. In a similar way, faster wind speeds increase the evaporation rate and also shift the chemicals around faster while low speed allows the chemical agents to remain longer in the air. Rains wash the agents from the ground into the water streams [6].

Areas with a lot of vegetation also increase the life time of the CW's as the liquid agents stick to the vegetation. In heavily wooded areas there is less wind speed and reduced temperatures; hence the vapors are retained for a longer period of time. Porous soils aid in soaking of the toxic liquids and this is dangerous as they are retained in the soil for a long time.

1.4 DOSAGE

The dose is the amount of the compound that the body takes in or absorbs. This is expressed as milligrams per kilogram (mg/kg).

The different types of dosages are explained is as follows [5]

Median Lethal Dosage of Liquid Agent (LD_{50}) of Liquid Agent

The LD_{50} of the liquid agent is the amount needed to kill 50% of the unprotected population exposed to it.

Median Incapacitating Dosage of Liquid (ID_{50}) Agent

This is the amount of the liquid agent expected to incapacitate 50% of the population. Dosages are based on the short exposures which are mainly 10 minutes or less.

Median Lethal Dosage (LCt_{50}) of a Vapor or Aerosol

This is the concentration of the vapor multiplied with time of exposure. It varies with the breathing rate and the degree of protection. An individual breathing faster will inhale more of the chemical, increasing the dose inside the body.

Median Incapacitating Dosage (ICt50) of a Vapor or Aerosol

This is the amount of the inhaled vapor that is sufficient to disable 50% of the exposed, unprotected individuals. This is expressed in mg-min/m^3. In some cases the signs or symptoms are more or less severe than expected and depend on factors such as the duration the individual held his or her breath during the short term exposure, the fit of the mask, how fast the individual was able to slip on his/her protective suit, whether the body absorbed the agent through the skin, the rate and depth of breathing of the person, etc.

1.5 Classification of Chemical Warfare Agents

Chemical agents are classified according to their volatility, and their lethal and incapacitating properties. They can also be classified according to the manner they attack the body: nerve agents, mustard agents, choking agents, blood agents and blister agents.

1.5.1 Mustard Agents

1.5.1.1 Background

These CW's have been used ever since World War I. They mainly belong to the class of blister agents, but were also called "Schwefellost" or "Yellow Cross" by the Germans and "Yperite" by the French. When compared with other chemical agents their lethality is especially high: 80-90% experience skin lesions, 86% experience eye lesions and 75% experience pulmonary damage [3]. In 1943, 100 tons of mustard gas was released into the water [3].

The use of mustard agents in Iran during the Iran-Iraq war by Iraq, caused 95% pulmonary problem and 92% eye damage in the Iranian people.Higher temperatures increased vaporization which resulted in causalities related to pulmonary damage.

In 1988, Saddam Hussein launched a chemical attack on Kurdish civilians using a mixture of mustard agent, tabun, sarin and VX. An estimate of 5000 immediate deaths occurred [7]. Additionally a number of the victims lost their eyesight or developed cancer. Even after years have passed the effects of these chemical agents are genetically transmitted to future generations.

1.5.1.2 Chemical Composition

There are basically two categories of blister agents namely the sulphur and the nitrogen mustards, both are alkylating agents. Sulphur mustard was first synthesized by Despretz in 1822. Its vesicant properties were recognized by Guthrie in the year 1860 and it was prepared in the pure form by Meyer in 1886. Hydrogen sulphide is treated with ethylene oxide to yield thiodiglycol which upon treatment with hydrogen chloride forms sulphur mustard [8] (see Fig. 1). It is a clear, colorless, oily liquid in the distilled form but

in its crude form it is a dark, oily liquid. It has a boiling point of 215-217˚ C and a freezing point of 14.4˚C. Mustard gas has a characteristic garlic or onion odor. The liquid vapor is readily soluble in oils, fats and organic solvents and soluble in water. Both the liquid and the vapor forms are capable of penetrating clothes. At normal temperatures and pressures it is stable. The mustard gas' main route of entry into the human body is through the skin as it has high lipid solubility and therefore can penetrate the lipid barrier easily. At higher temperatures, evaporation increases the concentration of this gas in the air [9]. The sulphur mustard agents include the H (Levinstein Mustard) and HD (Distilled Mustard) agent. These are chlorinated thioethers (Fig. 1). The nitrogen mustards include HN-1 (Fig. 2), HN-2 (Fig. 3), HN-3 (Fig. 4) are all made from ammonia. Out of all these HD and HN3 are the main gases that are used in the military.

Levinstein Mustard contains 30% sulphur impurities reducing the effectiveness of this compound. HD agent, i.e. distilled mustard, is prepared by purification and vacuum distillation of H agent. The liquid is usually colorless to amber colored and it has an odor which is more like garlic. When compared with the H agent, HD is more effective in causing blisters to the skin. This agent floats on water surfaces and hence can be more dangerous. Mustard gas on contact causes irritation to the tissue. Some of the early symptoms are inflammation of the eyes, nose, throat, trachea, bronchi and lung tissue, causing redness of the skin, blistering and ulceration.

At lower concentration it affects the eye and at higher concentrations it affects the skin. In hot and humid climate, the skin is moist with perspiration and hence there is more absorption of mustard gas which causes an increase in the casualty rate.

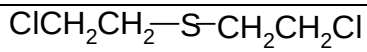


Fig. 1 Structure of Sulphur Mustard

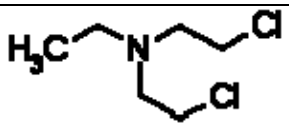


Fig. 2 Structure of Nitrogen Mustard (HN-1)

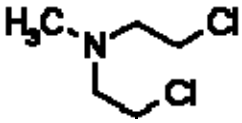


Fig. 3 Structure of Nitrogen Mustard (HN-2)

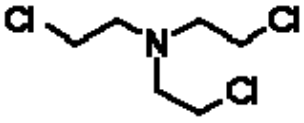


Fig. 4 Structure of Nitrogen Mustard (HN-3)

1.5.1.3 Mechanism of Action

The gas circulates in the blood and gets accumulated in the tissues. It is lipophilic in nature and gets easily accumulated in fat tissues and in the brain. Its main mechanism is through alkylation where it binds to the DNA strands [10]. Because of the fact that it is electrophilic in nature, it changes the structure of nucleic acids, cellular membranes and proteins.

Sulphur mustard is a bifunctional alkylating agent with two reactive chloroethyl groups interacting with cellular components by formation of intermediate products, namely ethylenesulfonium (sulphur mustard). The two reactive chloroethyl groups create cross- links with DNA altering the structure and resulting in error prone cellular repair mechanisms which can lead to erroneous DNA replication. The guanine base present in the DNA and RNA is affected the most. Cross-links between two strands, e.g. between 2 guanines, can inhibit DNA replication if it does not follow the proper mechanism [11].

1.5.2 Nerve Agents

The first nerve agent that was synthesized was tetraethyl pyrophosphate (TEPP) in Clermont in France by a German chemist. Schrader synthesized tabun (GA), sarin (GB) and soman (GD) [12]**.** At the end of the World War II, the nerve agent which is much more potent than sarin, was discovered and was named as VX. Nerve agents are relatively easy to produce from ordinary industrial chemicals. These agents like the other agents cause a lot of fear in the combat troops. They cannot be detected easily and these substances give no warning to the people around them. On March 20, 1995 the nerve

agent sarin was used by the Japanese cult Aum Shinrikyo to kill twelve people and injure 5500 people in the Tokyo subway [3].

Nerve agents are basically organophosphate ester derivatives of phosphoric acids which contain fluorine, cyanide or sulphur as the substituent group. These agents are mainly divided into the G agents and the V agents. They can also be classified as persistent agents or non-persistent agents. The G agents are the non-persistent agents as their physical characteristics allow them to vaporize and evaporate easily. V agents are more persistent as they are oily and non-volatile and therefore they remain in place for a long time [1].

Sarin (Fig. 6) is highly volatile in comparison with tabun (Fig. 5) and soman (Fig. 7). These agents can be made persistent by adding thickening agents. Tabun contains a cyanide functional group, sarin a fluorine group and VX (Fig.8) a sulphur group. 1 mg of these agents is sufficient to kill humans.

1.5.2.1 Physical and Chemical Properties

Agent tabun (GA) is a colorless to brown colored liquid which has a molecular weight of 162.1 g and a vapor pressure of 0.07 mm Hg at a temperature of 25 degrees Celsius. The vapor concentration in air is around 610 mg/m^3 (this is the concentration of any airborne chemical in air). In water it undergoes hydrolysis and therefore it is not persistent in aqueous systems. Its way of entry into the human body is primarily through the respiratory tract. Sarin (GB) is a colorless liquid which has a molecular weight of 140.1 g. The vapor pressure of sarin is 2.9 mm Hg at 25 degrees Celsius which makes it more volatile. The vapor concentration in the air is around 22 gm/cm^3. It is more miscible

with water and more persistent at low temperatures. The rate of hydrolysis is dependent on temperature, pH and can be accelerated in the presence of the ions.

Soman (GD) is a colorless liquid which has the molecular weight of 182.2 g and camphor like odor. This has a vapor pressure of 0.4 mm Hg. In air, it is easily dispersed due to its low volatility. In water hydrolysis to non-toxic products occurs. The thickened form of GD is TGD or also known as VR-55. VX is a colorless to a straw-colored liquid which has a rotten fish smell due to the presence of the amine groups [13].

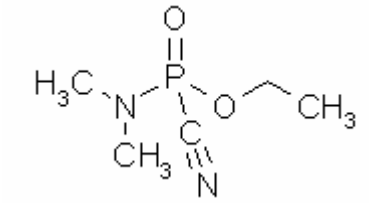


Fig. 5 Structure of Tabun (GA)

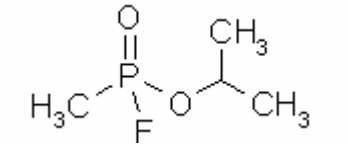


Fig. 6 Structure of Sarin (GB)

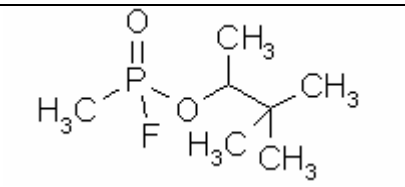


Fig. 7 Structure of Soman (GD)

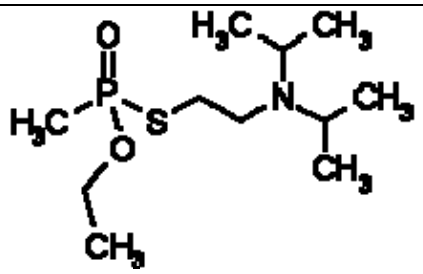


Fig. 8 Structure of VX

The common symptoms that are shown by the individuals exposed to this type of nerve gas are difficulty in breathing, drooling, excessive sweating, nausea, vomiting, twisting, jerking, confusion, drowsiness, and coma. Again, the severity of these symptoms depends on the dose and duration of exposure to the agents [14]. When the gas enters through the skin, the symptoms appear slowly. Death can occur in one to two hours. Repeated exposure to these agents with low concentrations shows the aforementioned symptoms. Lethal doses can kill a person in less than 15 minutes.

1.5.2.2 Mechanism of Action

To understand the mechanism of these agents, it is important to understand the function of the neurotransmitter, the acetyl choline (ACh), present in the cholinergic portion of the nervous system [15]. This neurotransmitter is released by the nerve impulse at the axon terminal and diffuses through the synaptic cleft and then binds with the receptor, producing a postsynaptic action potential to initiate activity in the organ. Acetylcholine esterase (AChE) blocks the action of acetyl choline by binding with it. AChE has two active sites, the anionic and esteratic sites. The anionic site is represented by glutamate ion. The esteratic site is composed of serine, histidine and tyrosine residues.

ACh forms a reversible complex with the active site of the enzyme where the ACh transfers the acetyl group to the serine group in the enzyme and releases the choline group. The acetylated enzyme undergoes hydrolysis to produce the acetate ion and regenerated enzyme to block the action of another ACh molecule.

The acetylcholine enzyme is not able to function normally when the body is exposed to the nerve agents as these agents block the enzymatic action [15]. This is done by irreversibly inhibit the AChE by phosphorylating the serine hydroxyl present at the active site of the enzyme. The inhibition leads to an accumulation of the ACh group at the receptor site. These agents bind with the enzyme at a very rapid rate. At high doses this can cause death. The toxic effects of the organophosphorous compounds all depends on their stability, rate of absorption through different routes, rate of reaction with the AChE and their individual selectivity with the enzyme [16].

Toxicity: The LCt_{50} for tabun is 400 mg.min/m^3, for sarin the values are 100mg.min/m^3 for sarin, for soman it is 50 mg.min/m^3, and 10 mg.min/m^3 for VX. The LD_{50} for tabun is 1000 mg, 1700 mg for sarin, 100 mg for soman, and 10 mg for VX [13].

Nerve agents are dangerous both as a liquid and as a vapor. As a vapor they cause local effects in the organs of the unprotected face (eyes, nose) while as a liquid they produce local effects in the organs under the skin (sweat glands, muscle).

Effects of Nerve Agent as Vapor: The nerve agents are easily absorbed by the lungs and the eyes. Changes occur in the smooth muscles of the eye and also in the secretory glands of the bronchi which results in bronchial constriction and excessive secretions in the upper and lower airways.

After exposure to the minimum dose of the nerve agent vapor, nasal discharge which is watery, nasal hyperemia, and tightness in the chest are observed. Within minutes of exposure redness of the eyes occurs due to conjuctival hyperemia, heaviness behind

the eyes, not complete blindness but dimness [1]. At high vapor concentrations, nerve agents cause systemic effects as the nerve agents is transferred from the lungs to the circulatory system.

Effects of Liquid Nerve Agent

The effect of liquid nerve agent causes localized sweating near the site of the exposure and localized twitching. Upon ingestion of the liquid nerve agent it causes diarrhea, cramps, and vomiting [1].

1.5.3 Organo-arsenic Chemical Warfare Agents

Organo-arsenic agents have been used since World War I. They were first introduced by the Germans in 1917 as the Blue Cross Agent (diphenylchloroarsine), a mask breaker, to destroy the masks used by the Allied Countries. These irritating agents were developed to penetrate the gas masks and cause soldiers to remove the masks. Lewisite and Adamsite, which belong to this group, were later developed in the US [2].

Diphenylcyanoarsine, which is a red/sneeze/nausea gas, was produced in a chemical weapon factory in Okunoshima, Japan [17]. Blue Cross was the name given because of the markings on the shell case that were mixed with high explosives. The shell was designed to release fine particles of the gas used to penetrate the masks. However this was not very successful as it did not produce sufficiently high concentrations of the finely powdered agent [18].

Inorganic arsenic compounds have also been used as poisons for centuries but they are nonvolatile and therefore they are not suitable for the chemical warfare. Arsine (AsH_3) is a very toxic gas but very flammable making it unsuitable for use on the battle

field for this reason. As a consequence of this, a number of organic arsenic compounds were produced by the chemists as a part of the 'chemist's war' [19]. Derivatives of arsenic trichloride were developed including diphenylchloroarsine (DA) [Fig. 9] and diphenylcyanoarsine (DC) [fig. 10]. The British used pieces of cheese cloth in the mask to protect themselves against the agent [2].

1.5.3.1 Chemistry

In the 1940's, biochemists Stocken and Thompson from Britain proposed that the toxicity of arsenic compounds was due to their high affinity for sulfhydryl groups in enzymes [20]. The organo-arsenic compounds are mostly alkyl and aromatic derivatives of arsenic trichloride.

The chemicals that belong to this class are mustard/lewisite (blister agent), phenyldichloroarsine (blister and vomiting agent), ethyldichloroarsine (blister agent), methyldichloroarsine (blister agent), diphenylchloroarsine (vomiting agent), adamsite (vomiting agent), and diphenylcyanoarsine (vomiting agent). The latter compounds can be made by reacting an alkyl halide or diazobenzene with sodium arsenite. The resulting alkyl or arylarsonic acid is then reduced with sulphur dioxide to give the corresponding dichloroarsine.

Lewisite (Fig. 12) is prepared by reacting arsenic trichloride with acetylene in the presence of aluminum trichloride catalyst, resulting in a mixture of mono-, di-, and tri-substituted vinyl arsines. Lewisite undergoes rapid hydrolysis under moist conditions to give 2-chlorovinylarsine oxide [21]. Adamsite (Fig. 11) is prepared by reacting arsenic

trichloride with N,Ndiphenylamine. This compound is rapidly hydrolyzed when it is used in aerosols.

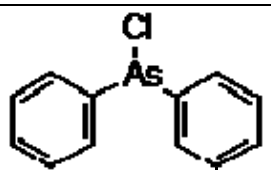


Fig. 9 Structure of diphenylchloroarsine (DA)

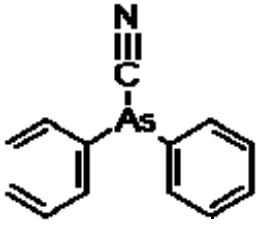


Fig. 10 Structure of diphenylcyanoarsine (DC).

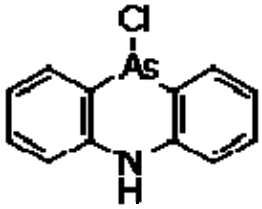


Fig. 11 Structure of Adamsite (DM).

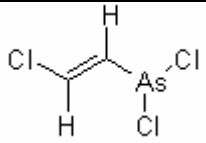


Fig. 12 Structure of Lewisite.

1.5.3.2 Mechanism of Action

Organoarsenic agents mainly attack the cellular respiratory system by inhibiting the action of the enzymes [3]. Lewisite can penetrate the skin rapidly as it can easily bind to proteins and thiols, which are mainly present in skin and hair [22]. Lewisite causes injury to cells and tissues by forming a stable arsenical ring with two thiol groups present in the protein group [23]. A variety of enzyme systems such as pyruvate dehydrogen complex, succinic oxidase, and hexokinase are all inhibited by Lewisite. The function of the pyruvate dehydrogenase complex function is to catalyze the oxidative decarboxylation of pyruvate to acetyl CoA in the citric acid cycle via the intermediate product dihydrolipoamide. When exposed to lewisite, the 1,3 thiol groups of the intermediate product form a stable structure with the As (III) which is present in lewisite. The trivalent form of arsenic which is present in lewisite and other organoarsenic agents is highly reactive in biological systems which makes these agents highly toxic [22].

Adamsite and ethyldichloroarsine are good in inhibiting cholinesterase. The organo-chloroarsines are alkylating agents. Phenyldichloroarsine can interact with red blood cells and they can form bonds with glutathione [3].

1.5.3.3 Primary affects on the human body

Lewisite is a lipophilic substance and its primary route is through the absorption of the skin [22]. This causes painful blistering of the skin just like sulphur mustard and nitrogen mustard. Reddening of the skin occurs after 30 minutes of exposure and within 13 hours blister formation can be seen. The effect is less severe when compared with the mustard agents but occurs four times faster than mustard agents. Lewisite is absorbed

through the skin but has the same effects as the mustard agents. Further symptoms are pulmonary edema, diarrhea, weakness, low blood pressure [22]. Lewisite produces lesions at a higher rate than the mustard agents but after 24 hours both the agents produced similar lesions [3].

Methyl and ethyl dichloroarsine cause severe respiratory pain due to the presence of the chlorine. This also causes damage to the lungs and eye discomfort. The methyl arsenic group helps in penetrating to in the body. The arsenic component can lead to subsequent bone marrow destruction. Methyl dichloroarsine in comparison with the ethyl and phenyl dichlorarsines has a higher volatility and can evaporate quickly. Phenyldichloroarsine damages the throat and the lungs and will have a longer persistency period in the body if it is not hydrolyzed which can lead to bone marrow destruction [24].

Arsenical irritants in liquid and vapor form can be absorbed by the skin and causes systemic poisoning. The capillary permeability is changed leading to the loss of fluid from the blood stream and causing shock and eventually death. Erythrocytes can undergo haemolysis leading to hemolytic anemia [3].

1.5.4 Cyanide Agents

1.5.4.1 History

Cyanide Agents are well known potent poisons/toxins which have been known for over 200 years. Cyanide gas and its properties make it ideal to be used as a chemical weapon as it kills rapidly, dissipates quickly and does not leave any toxic residue. Cyanide gas and its effects were first discovered by the Swedish chemist Scheele in 1782 [25]. Also he was its first victim due to inhalation of the gas in 1786. Cyanide inhalation causes the

cessation of breathing, although the heart of the person keeps beating, but the heart beat and the blood circulation get weakened. Therefore, there is a deficiency of the blood flow to the respiratory center in the brain which in turn contributes to the lethal effect of this agent. It was used in World War I and in the Iran-Iraq war [26] due to its properties, and it was also found suitable for local terrorist action. Hydrogen cyanide (AC) [Fig. 13] has a faint odor and the taste of bitter almonds. Signs of cyanide poisoning can be seen by the pink color of the affected person's lips, fingernails, and skin [2].

Fig. 13 Structure of Hydrogen Cyanide

1.5.4.2 Common Effects of Cyanide Exposure

Hydrogen cyanide is less persistent when compared with other blood agents. Exposure to higher concentrations instantly leads to unconsciousness and death. Failure of the nerve function is the primary action of cyanide as the muscles are more resistant to cyanide [3]. Cyanide can also cause heart failure by releasing catecholamine in the blood which has a powerful effect on the blood vessels eventually leading to an increase in blood pressure and hence heart failure.

1.5.4.3 Biochemistry of Cyanide

Cyanides are strong nucleophiles and show higher affinity for carbonyl groups which represent a major biological active group. Cyanide reacts with these carbonyl

group through nucleophilic addition to form cyanohydrins, present in different enzymes, coenzymes and substrates and block or inhibit their normal activity [2]. They also react with the enzymatic sulfhydryl compounds. Thus they are mainly considered metabolic poisons which block the mitochondrial enzyme, cytochrome oxidase, which is in the electron transport chain [28].

1.5.5 Lung Damaging Agents

1.5.5.1 Introduction

Lung damaging agents attack the lung tissue causing pulmonary edema [29]. From this group, the most toxic and dangerous is phosgene agent (Fig. 14). About 80% of the injured casualties were caused by lung damaging agents during World War I. When the Allied troops used chlorine during World War I the Germans used phosgene to counteract this chemical. In the 1920s phosgene was manufactured by many countries for its use as chemical warfare agent. Diphosgene (Fig. 15), which is an improved form of the phosgene agent, was produced after World War I. During World War I, chemical filters were employed to filter out phosgene gas but with the advent of diphosgene gas, these chemical filters were not very useful since diphosgene decomposes to chloroform and phosgene and chloroform could destroy the filters [30].

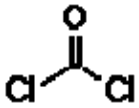


Fig. 14 Structure of Phosgene

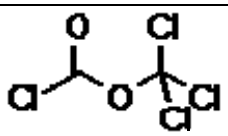


Fig. 15 Structure of Diphosgene

1.5.5.2 Chemical Characteristics

Phosgene is a colorless gas which has a molecular weight of 98.92 g and liquefies at a temperature of 8°C. At high concentration it has a pungent odor and in dilute concentrations the odor is often described as the smell of moldy hay or green corn. It is slightly soluble in water and can get easily hydrolyzed to carbon dioxide and hydrochloric acid.

This agent can more easily react with amine, hydroxyl, and sulfhydryl groups than when compared with water. Phosgene causes lung injury after inhalation [31, 32]. Its mechanism of action is not completely known. It may attack by inhibiting the enzymes or by producing hydrochloric acid in the alveoli. It increases the permeability of the alveolar capillaries which interferes with the pulmonary gaseous exchange and leads to hypoxia, resulting in cardiac failure [31].

1.5.5.3 Symptoms

Exposure to lung damaging agents immediately results in coughing, choking, feeling of tightness in the chest, nausea, vomiting, and headache. These symptoms can be of little value as some victims that develop severe cough, fail to develop any lung injury while other victims that have slight lung irritation can develop fatal pulmonary edema. Therefore the severity cannot be measured with the immediate symptoms. With exposure to very high concentrations this can result in death within several hours [33].

1.6 Basic Behavior of Chemical Warfare Agents

Warfare agents, as discussed previously, are categorized as persistent or non-persistent. The persistent types of CW are more hazardous as they remain for a longer duration on any surfaces and by vaporizing, become an inhalation hazard. A non persistent agent can also be an inhalation hazard as it disperses as quickly as gases and airborne particles but its lifetime is shorter. In the battle field individuals are exposed to CW's for a longer period of time and the human body is able to detoxify these agents only to a limited extent. At lower concentration agents like hydrogen chloride or cyanogen chloride are detoxified by the human body very quickly compared to other agents. Nerve agents like tabun, sarin and soman are persistent from 10 minutes to 24 hours at higher ambient temperature and from two hours to three day's at lower temperature. V-agents are more persistent than the other nerve agents with life times from two days to one week at higher temperature and from two days to some weeks at lower temperature. Blister agents are persistent from three days to one week in warm weather and for several weeks in cold weather. Lewisite has a faster rate of action when compared

to the mustard agents and persists for one to three days or even weeks during cold weather [5].

1.7 Medical Support for Military

Medical operations especially in a chemical warfare environment are complex. It is very important to understand and recognize the type of gas that the victim has been exposed to and to treat the individual accordingly. Immediate care is essential. One of the most difficult aspects of a battle field situation in which chemical warfare agents have been used is that these agents remain in the atmosphere for extended periods of time.

There are three types of environments that exist in a battle field, the uncontaminated area where no chemical gases exist, a contaminated area where the chemical agents exist in the liquid and also probably in the vapor form, and a third with a vapor only environment. To decontaminate the entire environment is not possible, but there are different ways in which the exposed environment can be sufficiently decontaminated. It is also necessary that the equipment is cleaned so that there are no further contact hazards.

In the first step of decontamination against CW agents, there should be individual and collective protection. Individual protection means gloves, boots, gas masks, and protective overalls which are important for persistent agents and those that can penetrate the skin easily. For those that pose a threat against the eyes and the face, the respiratory mask is important.

Collective protection is difficult to achieve. All equipments should be kept in sealed containers. Collective protection makes it possible to treat the injured and affected

individuals, with the medical personnel taking precaution by wearing protective clothing. Medical units have to be well prepared to receive any number of victims and to have enough equipment and the necessary facilities to treat affected persons [1].

1.8 Currently Available Antidotes

1.8.1 Aerosolized Atropine

For immediate help against nerve agent poisoning, atropine solution in a pressurized container with an inhaler is useful. A mixture of 0.43 mg of atropine sulphate which is equivalent to 0.36 mg of atropine can be used against tabun, sarin, soman, cyclosarin and the V-agents in case the victim shows respiratory symptoms [5].

1.8.2 Convulsant Antidote for Nerve Agents (CANA)

CANA is used against soman (GD). CANA is employed in form of an auto injector which contains 10 mg of diazepam to control convulsions and to prevent brain and cardiac damages [5].

1.8.3 British Anti-lewisite or BAL (Dimercaprol)

British Anti Lewisite is given by injection and it displaces the arsines that are bound to the enzymes and the enzymes are then reactivated to resume their biological activity. This does lead to some alarming side reactions once it is injected, but these seem to pass within a few hours [2].

1.8.4 Nerve Agent Pretreatment Pyridostigmine (NAPP)

NAPP is used against soman (GD) and tabun (GA). This treatment contains 21 30 mg of pyridostigmine bromide tablets sealed in a blister pack. In military this is used only under an “activated contingency protocol” [2]. Only when it is known that soman and tabun are

an actual threat to the soldiers they are given permission to use these tablets. This treatment has a lot of side effects but they are insignificant compared to the kind of effect nerve agents have on soldiers [2]. These tablets are given every eight hours and 42 tablets of NAPP (pyridostigmine bromide) are issued to all the personnel.

1.8.5 Nerve Agent Antidote Kit (NAAK OR Mark I)

This kit is used against all the nerve agents like tabun, sarin, soman, cyclosarin, and VX. It consists of an atropine auto injector (2mg) and a pralidoxime chloride auto injector.

1.8.6 Antidote Auto-injector

The concept of an antidote auto-injector was introduced by Meridian Medical Technologies to the medical military group [2]. In the case of an attack involving CW's the responders should effectively administer the antidotes. These auto-injectors are compact and have self-contained antidote delivery systems unlike the syringe which is slow. This company is the only FDA-approved supplier of these nerve agent antidotes to the Department of the Defense.

Some of the nerve agent antidote auto-injectors are AtroPen which contains 2mg of atropine sulphate. ComboPen is another kind of auto injector which contains 600 mg of pralidoxime chloride in 2ml. They are disposable, have a concealed needle and the speed of the injection is quick and easy. It is possible that CW agents are a mixture of two or more agents, simultaneously chemical and biological. A mixture will make it more difficult to identify the agents and to determine the antidotes that might be effective. Once exposed, affected persons should be decontaminated from the chemical agents immediately, since some CW can cause serious effects within seconds.

2. CHEMICAL PROTECTIVE CLOTHING

The main purpose of chemical protective clothing is to shield the individuals from chemical and biological hazards. Chemical protective clothing mainly consists of the gloves, boots, a suit, and gas masks. Additionally the following components of the chemical protective ensemble are essential: respiratory equipment (SCBA, combination SCBA/SAR, air purifying respirators), cooling system (ice vest, air circulation, water circulation), communications device, head protection, eye and ear protection, inner garment, and outer protection (over gloves, over boots, flash cover). The face mask covers the whole face. It has an air tight seal against the valve, speech transmitter and nose cup. The gas masks made of rubber materials and containing a charcoal filter protect the face, respiratory tract, and eyes. Air is drawn in to the mask via the filter canister [34].

Chemical protective clothing can be classified according to three factors, namely, design, performance and service life. Classifying by design specifies the areas of the body that are protected by the suit. They consist of gloves for the hands, boots for the legs, aprons, protective jackets, coveralls, and full body suits for the body. Performance classifies chemical protective clothing according to the function of the suit. Service life indicates whether the protective clothing is reusable i.e. that is for multiple wearings, or it can be a one time use i.e. disposable. For example, the Saranex/Tyvek garment is a disposable coverall that is used for liquid splash protection [34]

2.1 Suits for vapor, liquid splash and particular protection

Vapor protective suits (NFPA Standard 1992) are made for situations where there is no direct contact with the chemical. This is the highest protection level which provides the "gas-tight" integrity and protects the individual from any kind of contact from liquid and vapor form of chemical agent. Liquid-splash protective suits offer protection against liquid chemical agents but do not protect against the vapors of the chemicals as they are not gas-tight [35].

Resistance to CW agents can be described through permeation, penetration, degradation and breakthrough time. Permeation is the process by which a chemical passes through the protective clothing material on a molecular basis. In case the composition of the material has been changed due to degradation, the chemical agent is able to pass more freely through it. Penetration of the chemical can also occur through the zippers, at seams and pinholes. Generally degradation includes all physical changes that the material experiences on contact with the chemical such as discoloration, swelling, loss of strength, and deterioration. The breakthrough time is the time it takes for a chemical to permeate the material completely. It is an indication for the useful life time of the material.

Some of the common barrier materials against toxic chemicals that are used for clothing are polyvinylchloride, a fairly resistant polymer, and Tyvek, a spun bonded nonwoven protective material made of olefin which is used for disposable clothing [35].

2.2 Development of Reactive Materials for Chemical Protective Clothing

Polyurethane based elastomeric material is suitable for use as a face mask in protective clothing as it resists penetration to chemical warfare agents [36]. Decontamination of chemical warfare agents can also be made by incorporating reactive sorbent materials into the protective clothing. The most common reactive sorbents are made of two types of materials, one being dehydroxylated aluminum oxide and the other porous carbon impregnated with the reactive solution. Both types of sorbents can detoxify CW's. Activated aluminum oxide is a highly porous form of aluminum oxide which has the capacity to adsorb moisture from gases, vapors and liquids [37].

There have also been efforts in developing materials which can neutralize toxins through the help of enzymes [38]. Scientists have developed polyurethane foam which contains toxin-neutralizing enzymes. This can be used against nerve agents in the near future. The enzyme used is the phosphortriesterase which is covalently bonded to the polyurethane foam. These sponges can be reactivated and renewed by dipping the sponge in an oxime solution and do not have to be disposed off. Repeated generation could lead to a small loss of enzyme activity after the enzymes destroy the nerve agents by hydrolyzing the organophosphate bond.

The enzyme could be incorporated in any form and can be used in fabrics for protective clothing. The advantage of using this in production of the protective suit is that it will be lighter in weight than the three layered suit which is currently being used by the US soldiers [38].

2.3 Deactivation Mechanisms (Decontamination through Detoxification).

Deactivation reactions are aimed at eliminating the chemical warfare agents by breaking them down into products which are harmless and nontoxic. However the decontamination process is most effective when it is performed instantly upon exposure to CW agents. Many factors have to be considered in this process, for example the nature of the surface where the warfare agents are most likely to be deposited and the surface-agent interaction, which is in direct relationship to the extent to which the chemical agents penetrate into the surface [43]. The Chemical Warfare agents react with the decontaminants and in the process can get detoxified to nontoxic products.

2.3.1 Deactivation reactions using bleach and other oxidizing agents

The first decontaminants that were used were bleaching powders and potassium permanganate [42]. The reaction with the excess bleach is more effective as it converts the agents into less or even non toxic products.

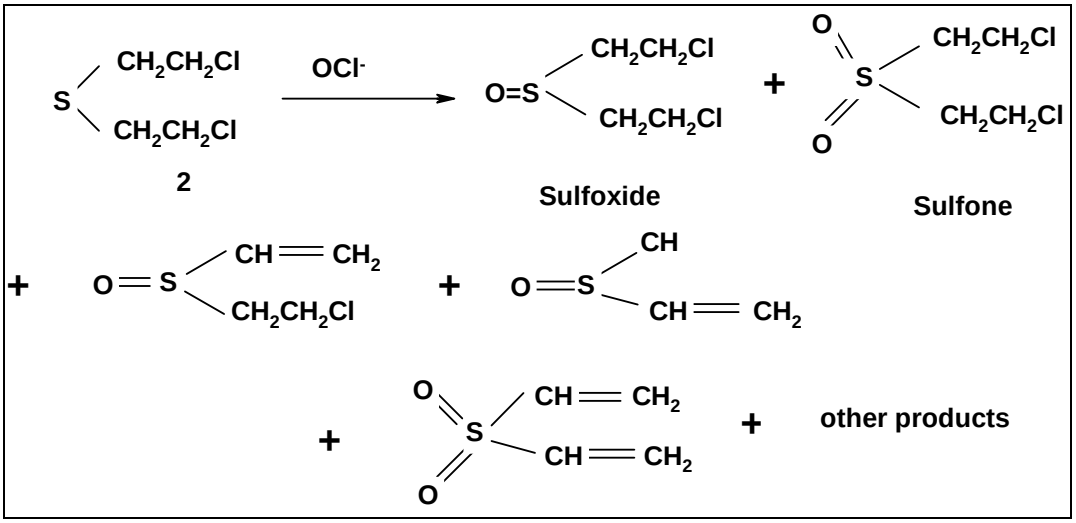


Fig. 16 Decontamination of Sulphur Mustard

In Fig. 16 the reaction of sulphur mustard is slower. Sulphur mustard is first converted into sulfoxide and subsequently into sulfone (both products are nontoxic). These products then undergo a series of elimination reactions to form monovinyl and divinyl sulfoxides and sulfones [42].

2.3.2 Deactivation mechanisms of VX agent.

Chlorine containing bleach can also be used for the decontamination of the VX agent [44]. In this reaction sulphur is rapidly oxidized with $HClO^-$. The protonated nitrogen undergoes oxidation releasing chloride (Fig. 17).

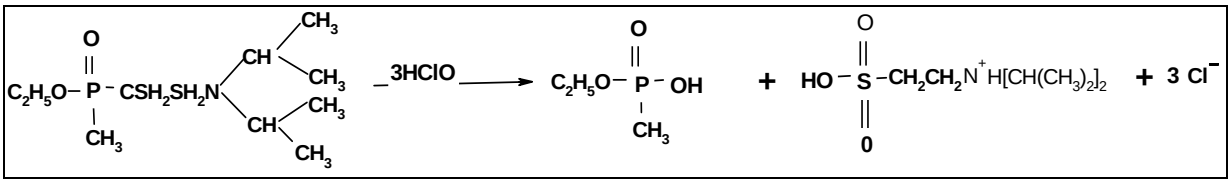


Fig. 17 Reaction products from VX agent and hypochlorite anion

VX agent can be easily detoxified through an oxidation mechanism using hydrogen peroxide or other "per" compounds. Common bleach NaO^+Cl^- and other super chlorinated bleach are the most commonly used oxidants.

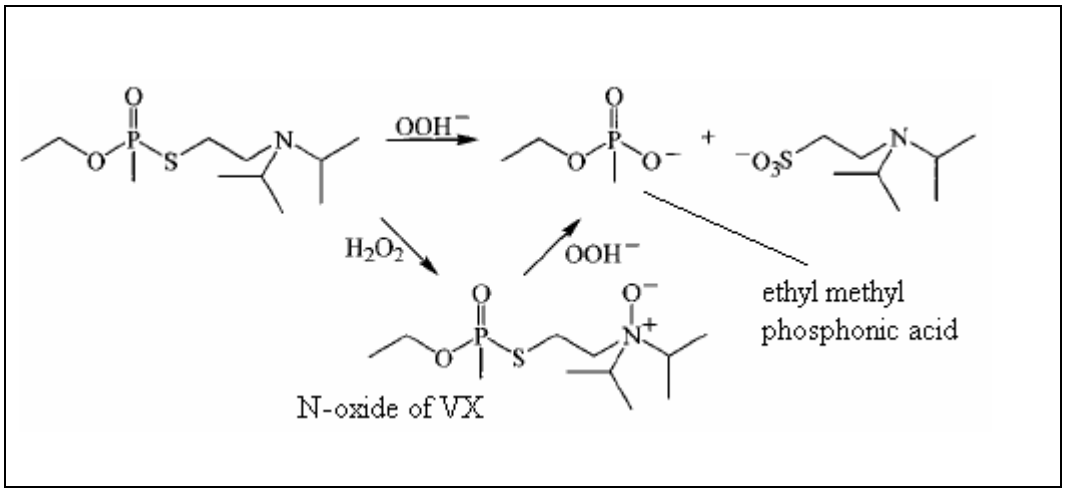


Fig. 18 Reaction between VX with peroxide.

VX [(O-ethyl-S-[2-(diisopropylamino) ethyl]-methylphossphonothioate can undergo rapid perhydrolysis to obtain ethyl methyl phosphonic acid (EMPA) via the formation of N-oxide of VX (VX-NO) [43].

Alternative hydrolysis reactions for VX include nucleophilic substitution reactions which cause cleavage of the P-S bond. VX agents easily react with the anionic nucleophiles which displace the S-alkyl and the O-alkyl group. Sarin (GB) can easily be decontaminated with basic peroxide [43]. Fig. 19 shows a schematic of its reaction with hydrogen peroxide.

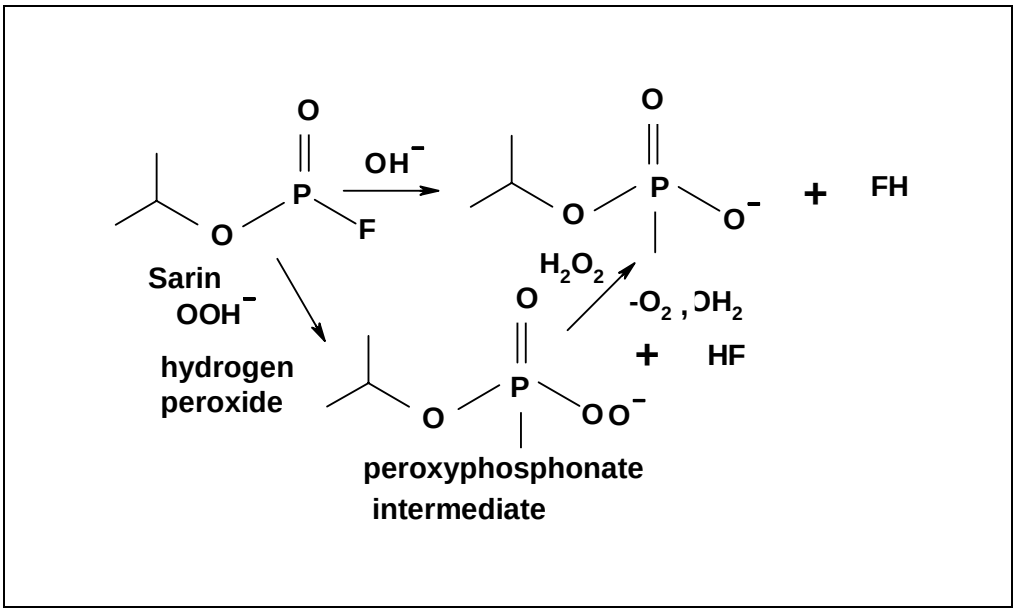


Fig. 19 Reaction of sarin with basic peroxide

Tabun is rapidly hydrolyzed in basic solutions which contain sodium carbonate, sodium hydroxide and potassium hydroxide.

2.3.3 Deactivation Mechanism of Lewisite

British anti-lewisite (BAL) was discovered by biochemists at Oxford University and distributed in the form of an ointment during the World War II [44]. Its structure is shown in Fig. 20. This antidote is very important for emergency cases during the chemical warfare attack.

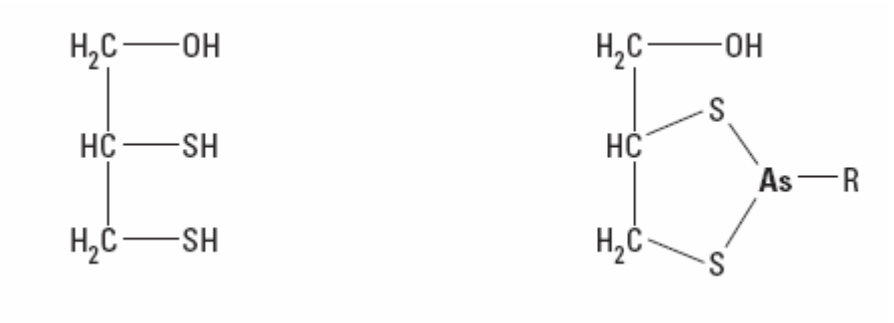


Fig. 20 Structure of BAL (2, 3 dimercaptopropanol)

Lewisite reacts with British anti lewisite (BAL) to form a stable cyclic non-toxic arsenic derivative [44].

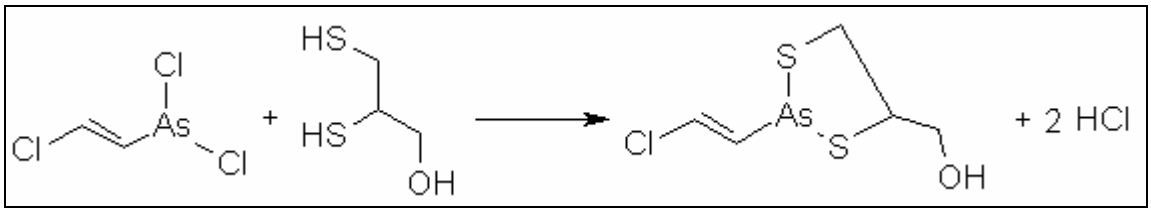


Fig. 21 Reaction of Lewisite with BAL (British Anti Lewisite)

2.4 Simulants for Chemical Warfare agents

It is very important to understand the effects of chemical warfare agents on the human body. By mimicking CW agents, a basis for evaluating the protective materials in a regular chemical laboratory is provided. Using nontoxic mimics it is possible to test the chemical warfare agents for their permeation through the barrier materials. Thus mimics must have similar physical and chemical properties as CW agents, but are non toxic.

The focus must be on those properties that can give the most reliable and decisive information regarding the agent's permeation through and their possible reaction with the barrier materials. In a permeation study mustard simulants have been used such as the 1, 6 dichlorohexane DCH), di-n-butyldisulphide (DBSS), bis 4-chlorobutyl ether (BCBE), 2 chloroethylphenylsulfide (CEPS), 2-chloroethyl cyclohexyl sulfide (CECS), dibutyl sulfide (DBS). These simulants have been selected based on the molecular weight and their solubility [39].

Chemical simulants have also been used to understand the CW agent's chemistry. Monofunctional derivatives of mustard such as $RSCH_2CH_2Cl$ where R is ethyl, methyl or phenyl react in the same way as the mustard agent. $RSCH_2CH_2X$ with X being tosylate, brosylate, bromine, iodine and other leaving groups also react similar as the mustard agent [41]. Accordingly for G agents, which are the nerve agents, a number of organophosphorous esters could be used such as the DMMP (dimethyl methylphosphonate), and DIMP (diisopropyl methylphosphonate), DFP (diisopropyl phosphorofluoridate) [41]. It has to be understood though that simulants can only imitate some aspects of the warfare agents and not all, therefore the results may not apply entirely to the agents.

The mimics listed in Table1 were used to understand the detoxification process of VX. Most of these simulants mimic some of the properties of the chemical warfare agent. For example, O,S-diethyl methylphosphonothioate, O,S-diethyl phenylphosphonothioate simulate the intermolecular substitution and oxidation of VX [41].

Table1: A list of VX simulants

Examples of VX simulants	
Chemical Name	**Structure**
diethyl methylphosphonate(DEMP)	**$CH_3P(O)(OC_2H_5)_2$**
tri-n-butyl phosphate	**$P(O)(O\text{-}n\text{-}C_4H_9)_3$**
O,S-diethyl methylphosphonothioate	**$CH_3P(O)(OC_2H_5)(SC_2H_5)$**
O,S-diethyl phenylphosphonothioate	**$C_6H_5P(O)(OC_2H_5)(SC_2H_5)$**
thiophenyl diphenylphosphinate	**$(C_6H_5)_2P(O)(SC_6H_5)$**
thiophenyl diethylphosphate	**$(C_2H_5O)_2P(O)(SC_6H_5)$**
p-nitrophenyl diethyl phosphate	**$(C_2H_5O)_2P(O)(OC_6H_4NO_2\text{-}p)$**
p-nitrophenyl diethylphosphorothioate	**$(C_2H_5O)_2P(S)(OC_6H_4NO_2\text{-}p)$**
S-[2-(ethylthio)ethyl]o,o-diethylphosphorothioate	**$(CH_3CH_2O)_2P(O)(SCH_2CH_2SCH_2CH_2)$**
S-[2-(ethylthio)ethyl]O,O-dimethylphosphorothioate	**$(CH_3O)_2P(O)(SCH_2CH_3SCH_2CH_3)$**
S-(1,2-dicarbethoxylethyl) O,O-dimethyl dithiophosphate	**$(CH_3O)_2P(S)(SCH(CH_2C(O)OC_2H_5)(C(O)OC_2H_5))$**
S-phenyl O-ethyl ethylphopshonothioate	**$(C_2H_5)P(S)(OC_2H_5)(SC_6H_5)$**

2.5 Standard Tests to Evaluate Gas Permeability

2.5.1 Standard Test Methods for Permeability Experiments

Standard Test Method for Air Permeability if Textile Fabrics, D 737-96

This test method has been developed for the measurement of air permeability of textile fabrics which include woven fabrics, nonwoven fabrics, air bag fabrics, and knitted fabrics. The values for this test method are stated in SI units. The testing apparatus consists of the test head which is a circular test area of 38.3 cm^2. A clamping system is used to secure the test specimens (a 55 type A durometer hardness polychloroprene clamping ring of 20 mm in width and 3mm in thickness). A pressure gauge or manometer and a flowmeter control the sir flow. Air flow passes perpendicularly through a known area of fabric and is adjusted to obtain a prescribed air pressure differential between two fabric surfaces. The air permeability of the fabric is determined through the rate of air flow [45].

2.5.2 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact, F 739-99

This test method is used for the measurement of the resistance of protective clothing materials from liquids or gases performed under the condition of continous contact with the clothing material. This method has been designed for volatile liquids and gas. The resistance of the protective clothing is measured through the breakthrough detection time, normalized breakthrough detection time and permeation rate. In this permeation test apparatus the protective clothing specimens partitions the test chemical from the collection medium. The collection medium which consists of the liquid or the

gas, is analyzed quantitatively for its concentration of the chemical to observe the amount of chemical that has permeated the protective clothing material [46].

2.5.3 Standard Test Method for Measurement of Diffusivity, Solubility, and Permeability of Organic Vapor Barriers Using a Flame Ionization Detector, F 1769-97

This test method has been assigned to test the permeability of volatile organic vapor barriers consisting of films, plastic sheeting, coated papers, and laminates. A planar sample is exposed to a mixture of a specific gas at one side through means of constant gas flow in a controlled temperature cell. The gas can consist of one gas or different compounds including moisture. The compounds that diffuse through the sample are analyzed by a flame ionization detector. In this test method, the material is assumed to show Fickian behavior and Fick's Law is used to calculate the permeability of the planar surfaces [47].

2.5.4 Standard Test Method for Oxygen Gas Transmission Rate through Plastic film and Sheeting a Coulometric Sensor, D 3985-95

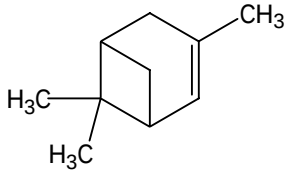
With this test method, the steady-state rate of transmission of oxygen gas through plastics which are in the form of film, laminates, coextrusions, sheeting or plastic-coated papers or fabrics is evaluated. The oxygen transmission rate and the permeability of the film to the oxygen gas are measured. The samples are equilibrated in a dry test environment where the relative humidity is less than 1%. A sealed semi-barrier is placed between two chambers where the specimen is mounted. One of the chambers contains nitrogen and the

other contains oxygen gas. The oxygen gas passes through the film and into the nitrogen carrier gas where it is transported to the coulometric detector resulting in a signal proportional to the amount of oxygen [48].

3. EXPERIMENTAL

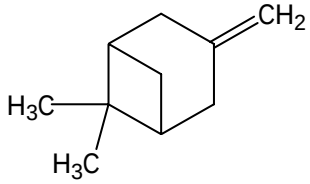
3.1 Materials

Compounds used as mimics, such as dibutylsulphide, (1S)-(-)-β-pinene (99% purity) and (1R)-(+)-α-pinene (99+% purity), were obtained from Sigma-Aldrich Chemicals. Their chemical structures are shown in Figures 22-24. All other chemicals were supplied from Acros Organics.



α-pinene

Fig. 22 Chemical structure of α-pinene.



β-pinene

Fig. 23 Chemical structure of β-pinene.

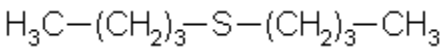


Fig. 24 Chemical structure of dibutylsulfide

The microporous membranes used were B130, Aptra Classic, and Aptra UV8. B130 is composed of polyethylene and polypropylene. Aptra Classic and Aptra UV8

consist mainly of polypropylene. The difference between the Aptra Classic and the Aptra UV8 is that the Aptra Classic membranes were exposed to UV radiation.

3.2 Characterization of the Mimics

3.2.1 Gas Chromatography (GC)

1 mL of (1S)-(-)-β-pinene (99%) was diluted with 30 mL high purity acetone and mixed well in a vial. 0.2 µL were injected for each GC run using a 1µL Hamilton syringe. The syringe was first rinsed with beta-pinene-acetone solution for about 7 to 8 times. A gas chromatograph (Agilent Technologies GC 6890N) equipped with a FID (Flame Ionization Detector) was used with SPB-608 column packed with fused silica. The dimensions of the columns were 15mx0.53mmx0.5µm. The temperature range for β-pinene and α-pinene was set from 35ºC to 55ºC. The temperature was increased at a rate of 5ºC per min. The procedure was repeated with the same parameters for (1R)-(+)-α-pinene (99+ % purity) and the distilled β-pinene which was obtained from the pure (1S)-(-)-β-pinene (99% purity).

3.2.2 Differential Scanning Calorimeter (DSC)

The DSC analysis was carried out under nitrogen atmosphere using a DSC 2920 Modulated Differential scanning calorimeter. A sample of β-pinene was weighed into an aluminum sample pan and the pan placed into the instrument. The heating ramp was set to 10ºC per min to a maximum temperature to 220°C. The flow rate of nitrogen to the DSC and the (Refrigerator Cooling System) RCS was adjusted to 50 and 110 cc/min for heating and cooling, respectively. Only heating curves were recorded.

3.2.3 Scanning Electron Microscopic (SEM) Evaluation

The membranes were cut into small pieces and attached to SEM stubs using double-sided carbon tape. The samples were then sputter-coated with gold. A Zeiss DSM 940 scanning electron microscope with digital imaging was used to examine the samples at 10 kV. SEM pictures were taken at magnifications of up to 2000x.

3.2.4 Vaporization Experiments

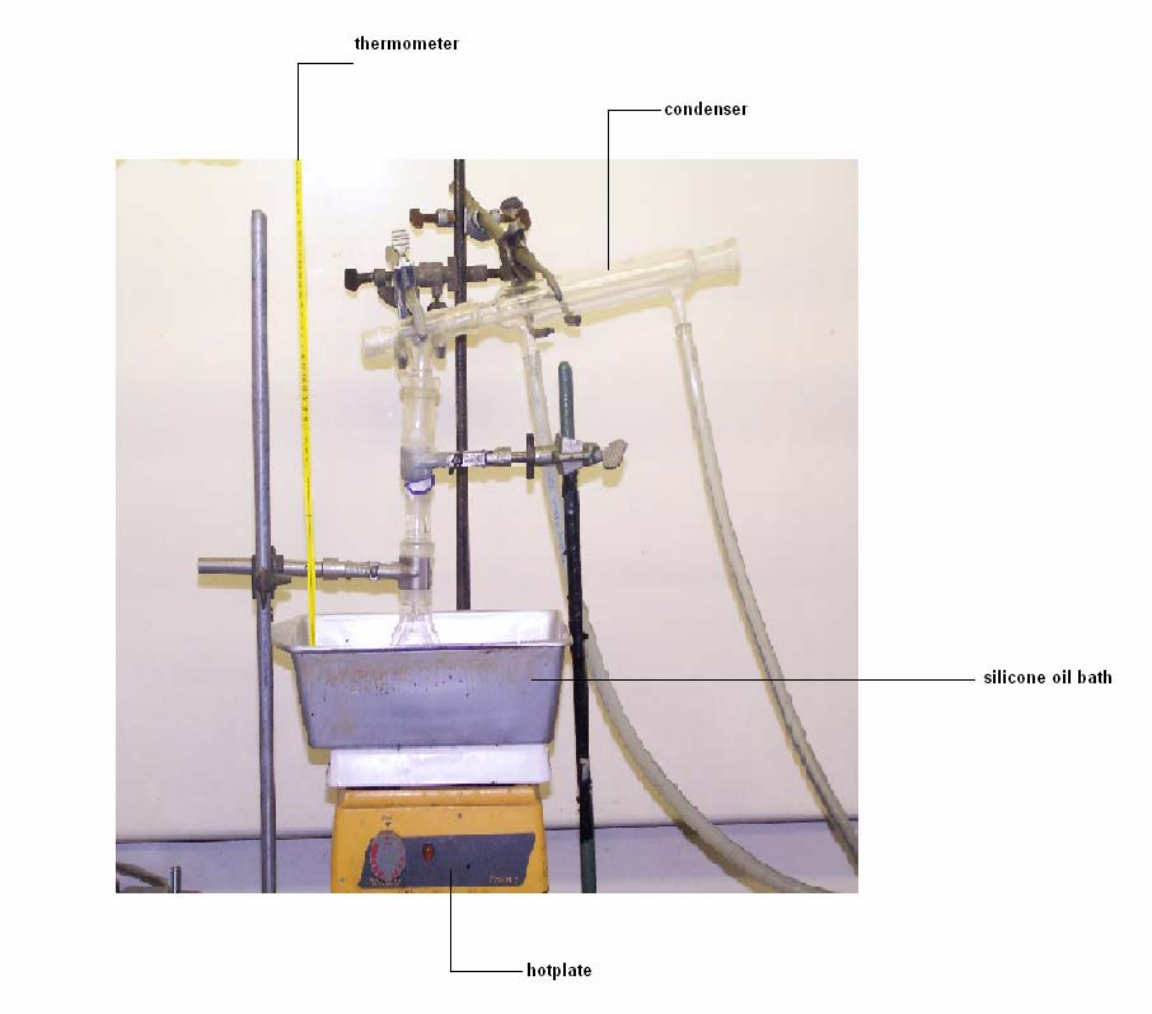


Fig. 25 Experimental set up for permeability tests

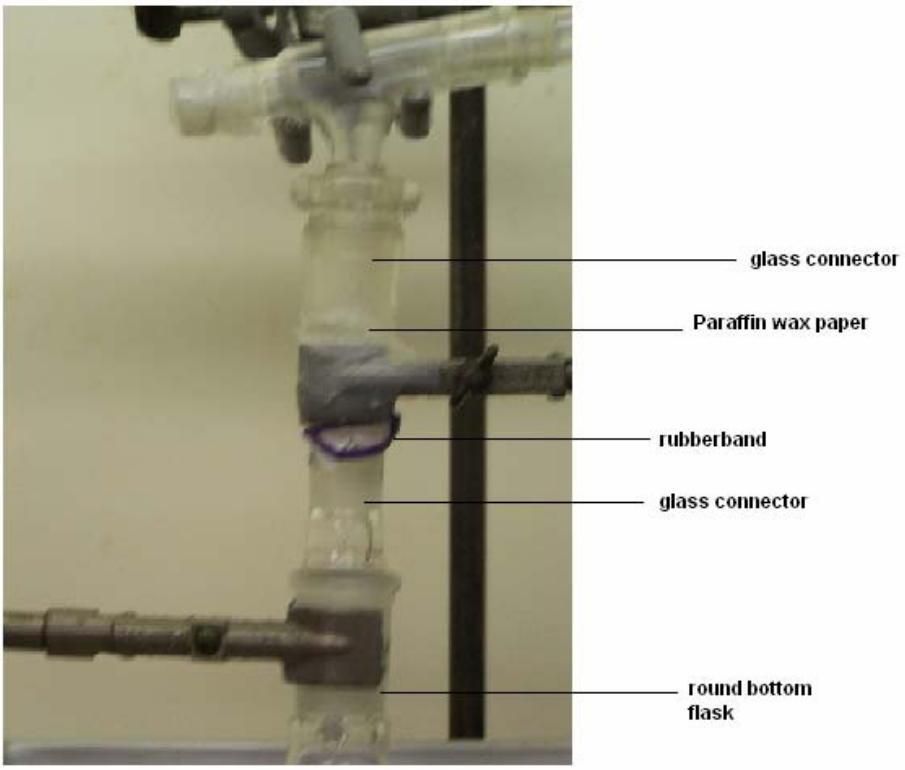


Fig. 26 Close up view of the glass connector-membrane-glass connector

Samples of 2 g of β-pinene were weighed in round bottom flasks. The flask was immersed in a silicone oil bath. The following procedures were followed.

1) A blank reading was taken by heating 2grams of beta pinene for 45 minutes.

2) One of the three membrane types at a time was placed between the flask and a condenser and held in place with the help of a clamp taped with paraffin paper. The flask was heated for 20, 30 and 45 min. After cooling, the flask was weighed and compared to the weight before heating.

3) B130, Aptra classic and Aptra UV8 membranes were individually weighed and placed on the glass connector and the same procedure was followed as in the second step. But this was heated for 45 minutes. The flask was cooled and the membranes were weighed and recorded. The diameter of the glass connector was recorded as two centimeters.

The above three steps were performed for dibutylsulphide with the same three membranes. The experimental set up is shown in fig. 25 and fig. 26

4. RESULTS AND DISCUSSIONS

In this research, the chemical warfare agents are being mimicked by gases that are not toxic. The main goal of this research is to detoxify the chemical warfare agents upon contact with the protective suit. In order to achieve this goal it is necessary to first mimic the chemical warfare agents with gases that are less toxic, and present no danger to workers or the environment.

The gases are being simulated on the basis of the physical properties of the chemical warfare agents; two important properties being vapor pressure and the molecular weight. These characteristics were selected to investigate whether the permeability of the mimicking gases is comparable to the permeability of the CW agents. In previous experiments the simulants have been selected based on properties such as molecular weight, solubility, volatility and vapor pressure [39]. In this project the chemical compounds that were used for mimicking have been selected based on vapor pressure and volatility properties of the CW agent.

The chemical compounds that were chosen were from a group of aroma chemicals used in the flavor and perfume industry. Aroma chemicals are derived from essential oils, natural extracts, and fruit juices. They have a wide range of polarities, volatility, and solubility. The essential oils are present mainly in flowers, fruits and leaves, and sometimes in the wood of plants (for example, sandal wood). Essential oils are

hydrocarbons which contain a mixture of chemicals that impart a particular smell. The essential oils can be classified in to terpenes, alcohols, esters, aldehydes and ketones. The terpenes are further divided into monoterpene hydrocarbons and sesquiterpenes.

4.1 Characteristics of the Mimics

4.1.1 Beta-pinene

This chemical belongs to the monoterpene family. It is used as an aroma chemical in the fragrance industry and as a flavoring agent for ice cream and ices, candy and baked goods. Commercial β-pinene is a colorless transparent liquid. The molecular weight of β-pinene is 136.24 g; its vapor pressure is 2.93 mm Hg at 25°C; and its density is 0.860 kg/m^3. β-pinene has a boiling point of 166° where as sarin has a boiling point of 147-158°C.

β-pinene was selected as a simulant for nerve agent sarin. Sarin has a vapor pressure of 2.9 mm Hg at 25°C and a molecular weight of 140.1 g. Due to these similarities in vapor pressure, molecular weight and boiling point, the essential oil β-pinene seemed to be a promising compound as a mimic.

4.1.2 Dibutylsulphide:

Dibutylsulphide has been used as mimic for mustard gas. Unlike β-pinene, this compound was chosen as a simulant for mustard gas based on its chemical structure being similar to the structure of the chemical agent. It has a molecular weight of 146.29 g and a boiling point of 182°C. The vapor pressure is 0.816 mm Hg at 25°C.

Dibutylsulfide is available in form of a liquid. It is used as a chemical intermediate in many industries.

4.2 Results of Gas Chromatography Experiments

Gas chromatography (GC) can be used as a tool for chemical analysis. The principle of GC is that the gas passes over a solid or liquid surface. The gas will be slowed down if it has some tendency to interact with the solid or liquid surface. The time it takes for it to pass through the column is measured as retention time. Each component produces a spectral peak specific to the compound under investigation. Since the mimics, such as β-pinene, were selected with the goal to evaluate permeation through membranes, the important question was raised whether β-pinene would decompose or isomerizes into α-pinene upon exposure to heat.

In the case of β-pinene which was diluted with acetone (Fig. 27) the first spectral peak that appeared on the chromatogram was that of the solvent, i.e. acetone (Fig. 28), and the second peak was that of β-pinene. The retention times for acetone and β-pinene were 0.41 min and 6.04 min, respectively. A very small double peak between 3 and 4 min appeared which could indicate some impurity in the compound.

Thus, in order to differentiate between α-pinene and β-pinene, commercial α-pinene was diluted with acetone, injected in to the GC column and graphs compared. From the Fig. 29 it can be seen that the retention time for α-pinene was 2.9 min.

The chromatogram of distilled β-pinene solution in acetone is shown in Fig. 30. There were three peaks, the first peak being acetone, the second, smaller peak similar to the main peak shown in Fig. 27 but shifted to higher retention times, and the third peak

identified as β-pinene. The retention time for the second peak was 3.84 min which does not match the peak of α-pinene. As can be expected, the various pinene isomers show some differences in their physical properties. For example, (1S)-(-)α-pinene has a boiling point of 155-156°C and a slightly lower melting point than (+)-α-pinene. It is possible that the condensed product is a mixture of different isomers, thus the observed gas chromatographic peak was shifted to slightly longer retention times without separating the compounds.

Acetone elutes first from the column as the solvent has a high volatility. Also the area under the curve was smaller than the area under the peak for β-pinene. From this we can say that the concentration of α-pinene was far less when compared with β-pinene. Thus from this analysis it can be concluded that α-pinene was also present in the distilled pinene solution. This might be largely due to the fact that β-pinene on heating isomerizes to α-pinene. β-pinene occurs in essential oils with alpha pinene and is very hard to separate. β- pinene does not exist in a pure form.

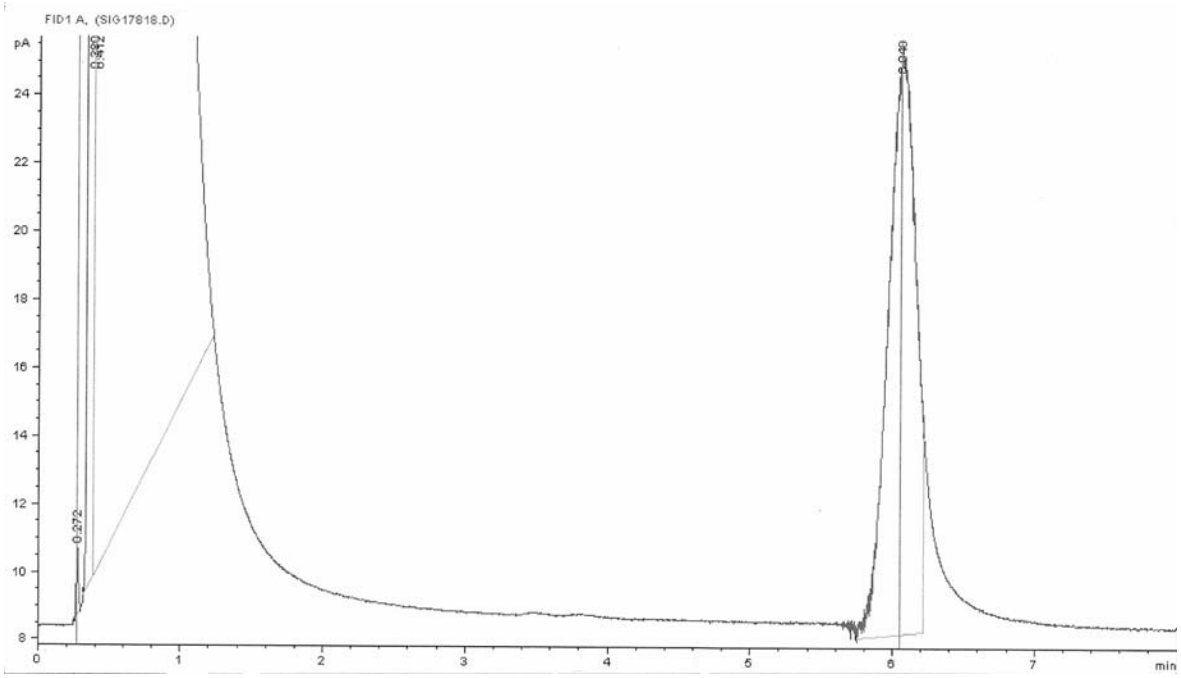


Fig. 27 Gas Chromatogram of pure β-pinene in acetone.

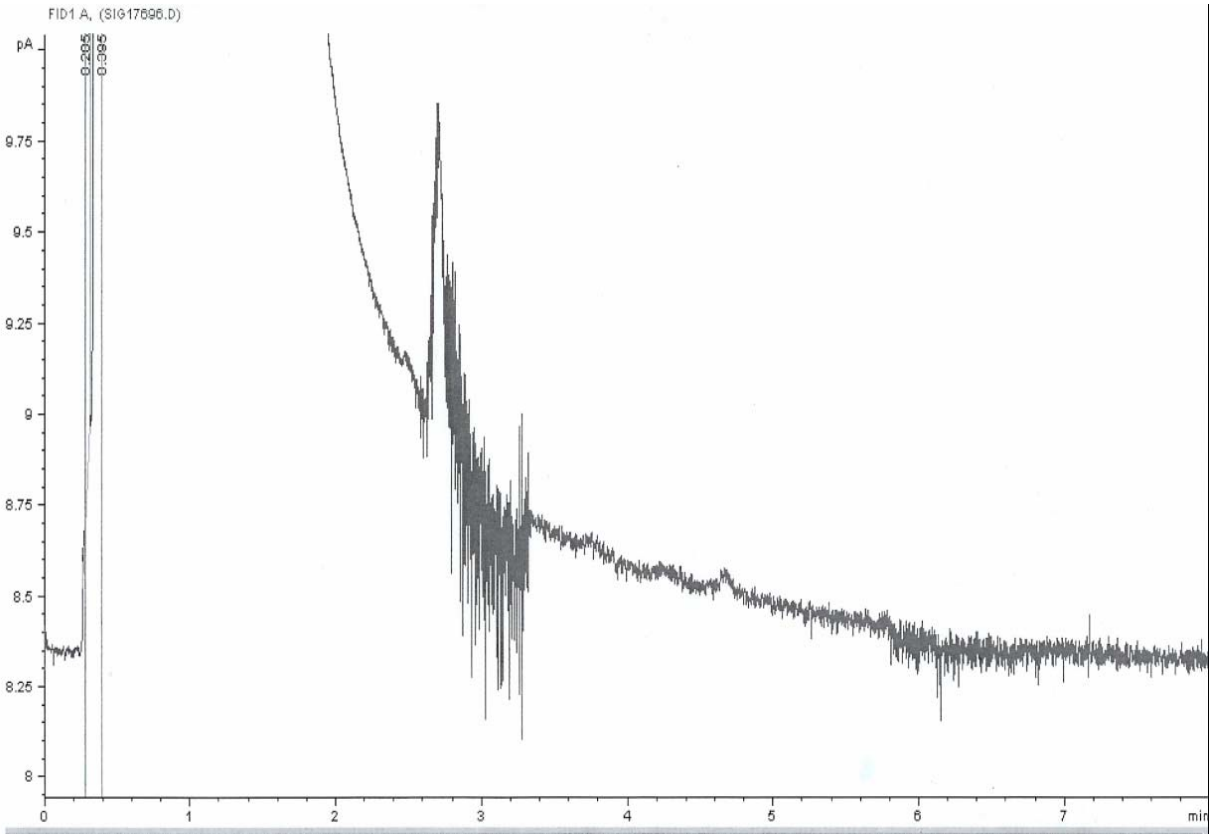


Fig. 28 Gas chromatogram of acetone.

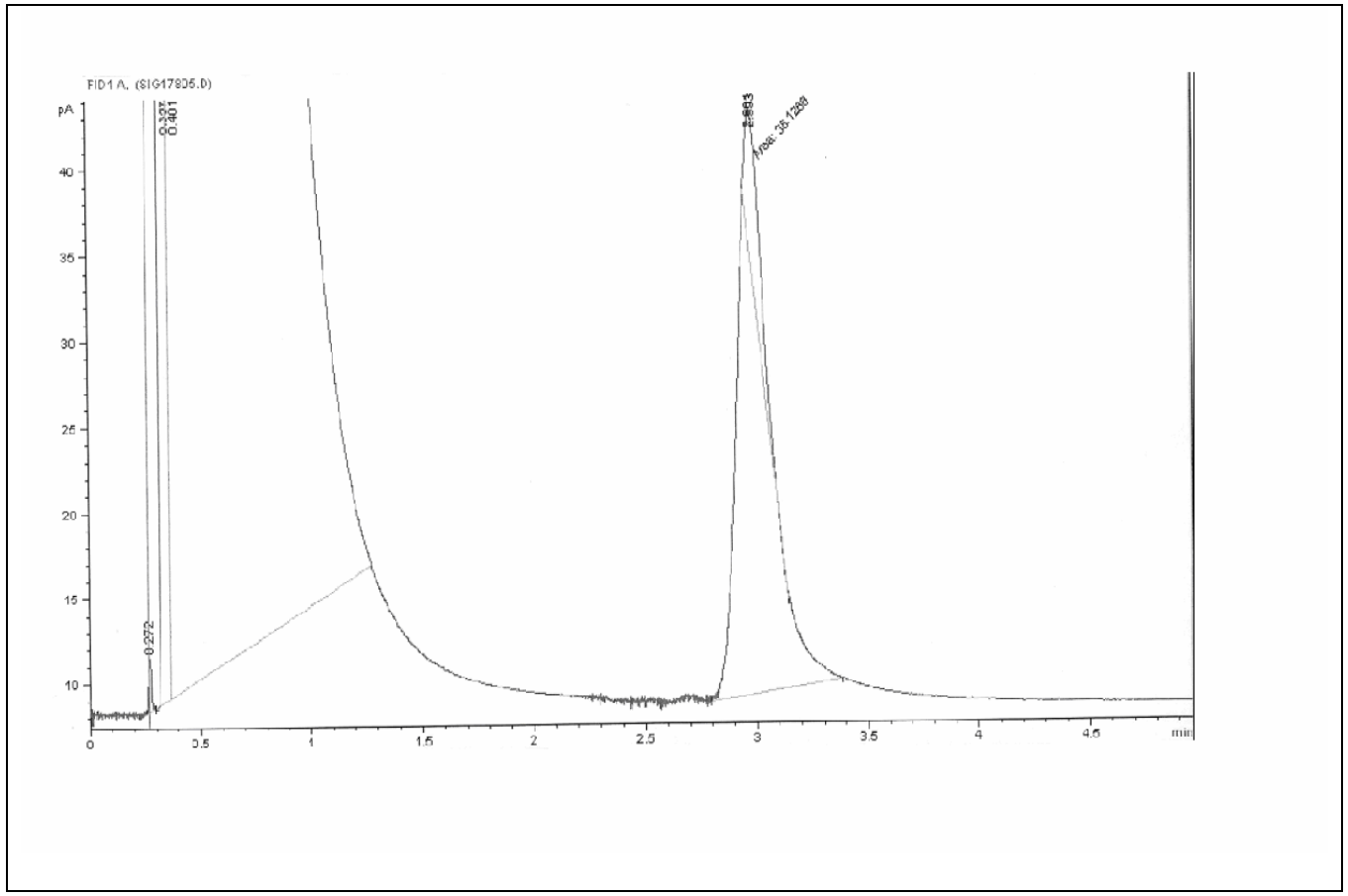


Fig. 29 Gas chromatogram of α-pinene in acetone.

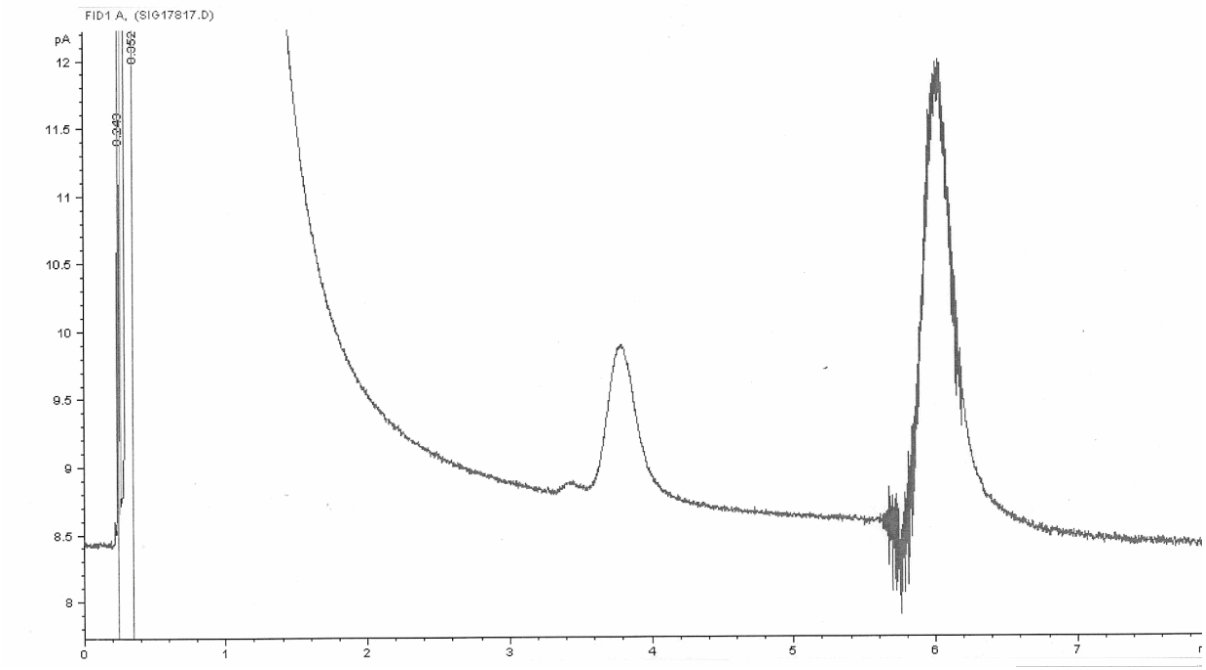


Fig. 30 Gas chromatogram of distilled β-pinene in acetone

4.3 Differential Scanning Calorimetry (DSC)

DSC is a universal tool for study of the physical and chemical transformation for systems where heat changes are involved. Thus, with DSC the specific heat capacity and the heat of transition, phase changes and melting points of a compound can be determined. The purpose of performing a DSC experiment with β-pinene was to investigate at which temperature vaporization would occur.

The DSC graphs recorded were inconclusive (Fig. 31). Two peaks of vaporization were observed. The on-set of first peak most probably indicates the vaporization of α-pinene and the second peak that of β-pinene. However, the DSC graphs did not allow for a clear identification of either pinene isomer or the isomerization temperature. No further DSC experiments were performed.

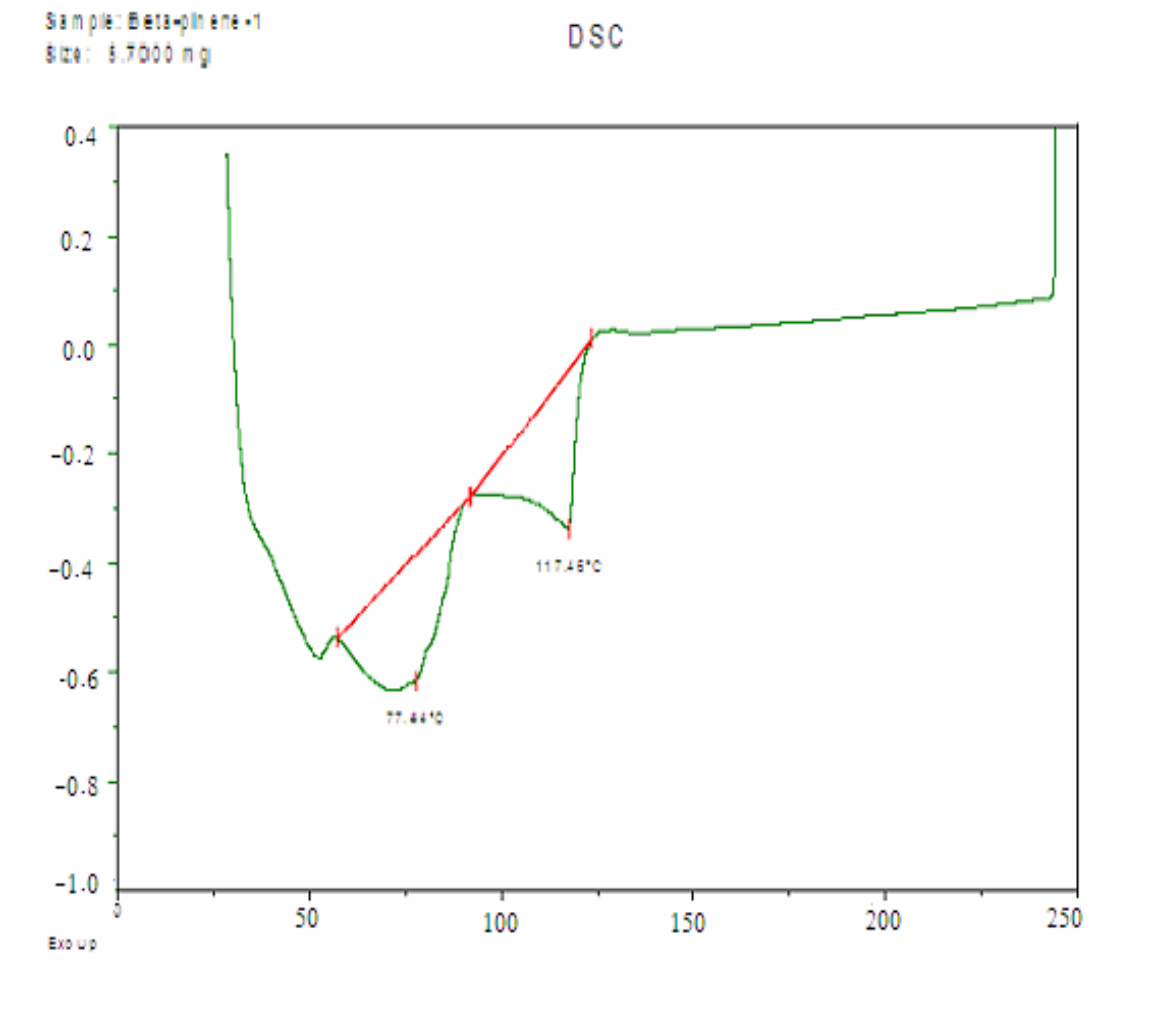


Fig. 31 Thermogram of β-pinene.

4.4 Permeability Tests

Before assessing the barrier characteristics of three different membranes a blank experiment was performed without a membrane interfering with the evaporation of either β-pinene or dibutylsulfide to show maximum vaporization of the liquids. For β-pinene there was a maximum percentage weight loss of 7.91% and for dibutylsulfide 6.27%.

The three membranes B130, Aptra Classic, and Aptra UV8 were tested for permeability using β-pinene and dibutylsulphide. All three membranes are microporous membranes. As mentioned before, B130 membranes are made of polyethylene and polypropylene whereas the Aptra Classic and Aptra UV8 membranes consist of polypropylene. The pores for these membranes were created using calcium carbonate as filler materials. These filler materials are responsible for creating tortuous pathways in the membranes and make it difficult for the gas molecules to permeate through the membranes. The thickness of the B130 membrane is 30 microns and for the other two it is 45 microns. Scanning electron micrographs of the membrane surfaces are shown in Figures 32-34.

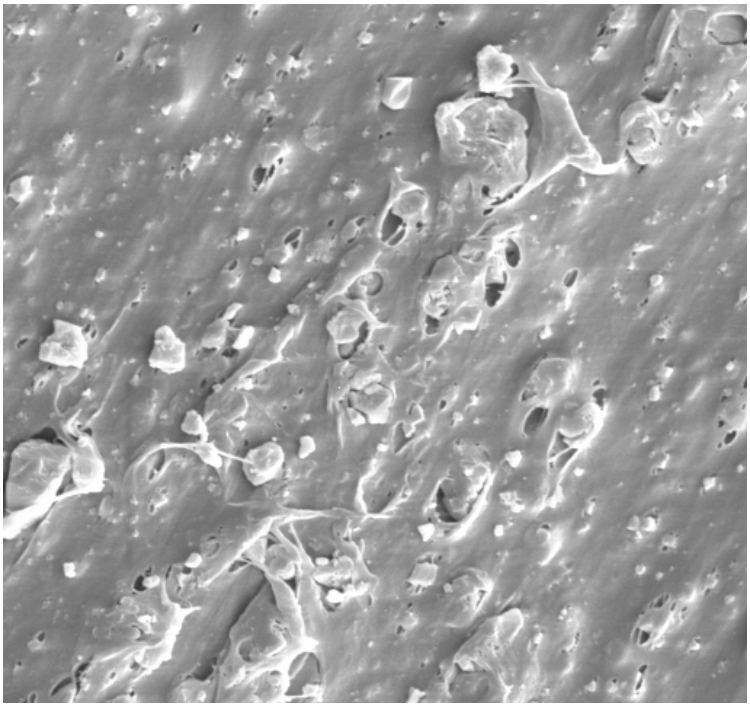


Fig. 32 SEM picture of B130 membrane (x2000).

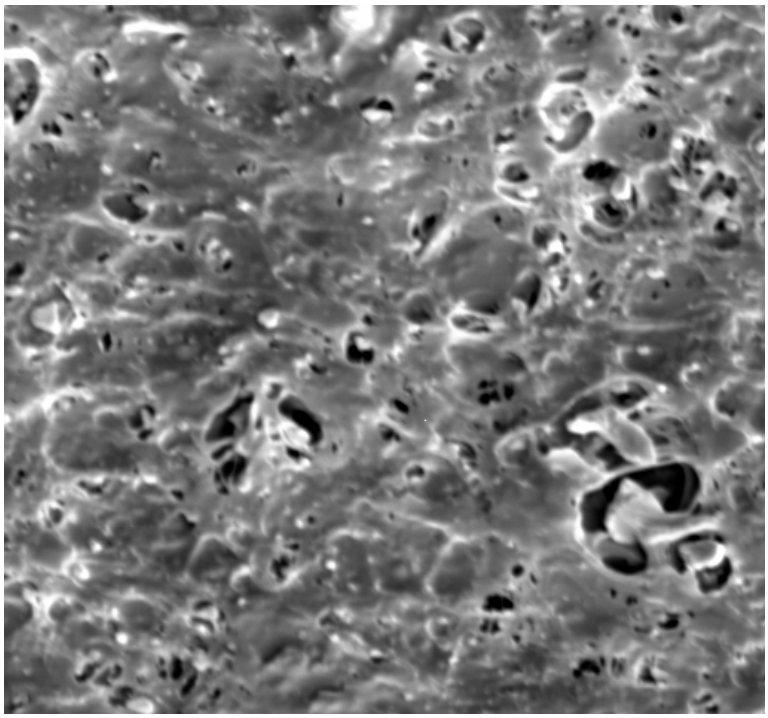


Fig. 33 SEM picture of Aptra Classic membrane (x2000).

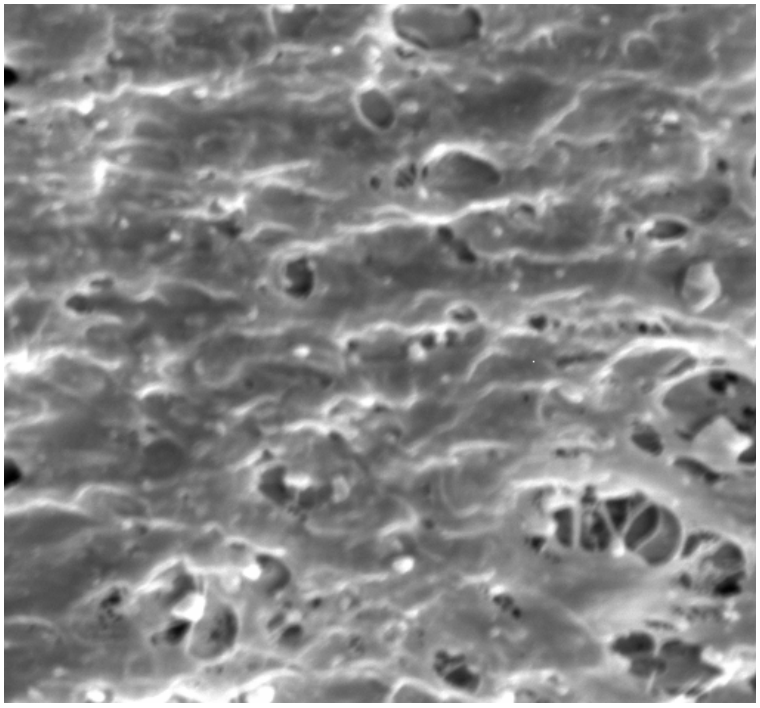


Fig. 34 SEM picture of Aptra UV8 membrane (x2000)

The results obtained from permeability tests using liquid β-pinene are shown in Table 2. Permeability is expressed as weight loss (compound weighed in flask) as a result of the vaporization of the mimic. From the readings Figures 35-37 show the results graphically related to the membrane types for β-pinene. It can be seen that there was no considerable difference in percent weight loss between the three types of membranes. After heating the flask for 20 minutes with either Aptra Classic or Aptra UV8 blocking the passage of the mimic, very little difference in weight loss of unevaporated compound was observed while B130 showed slightly higher permeation. The similarity between the two Aptra membranes might be based on the fact that they were both made of polypropylene and manufactured in the same way with the only exception that Aptra UV 8 had been treated with UV stabilizers.

The data for 30 minutes showed that Aptra Classic and Aptra UV8 allowed slightly higher permeation than the B130 membrane. Here again the values for Aptra Classic and Aptra UV8 were very similar. The pores of the B130 membrane could have been blocked somewhat due to the presence of fillers. β-pinene molecules might have been adsorbed to a certain extent, expressed in lower membrane permeability. The B130 membrane is less porous than the other 2 membranes, as can be seen in Figures 32-34.

The data for 45 min (Table 2) show that the Aptra Classic membrane had a higher permeability than B130 and Aptra UV8. It could be argued that Aptra Classic membranes have more pores which might have widened with time and temperature making it easier for β-pinene molecules to permeate. Aptra UV8 membranes are less porous when compared to Aptra Classic. In addition the presence of the UV stabilizers in the membranes could have some impact. B130 membranes are not only not very porous but also stretched in only one direction.

Overall, the highest permeation was observed when the membranes were subjected to β-pinene vapors for 45 min. This shows that there is a strong interdependence of permeation with time and temperature. It is possible that the pores of the membrane dilate with time at high temperature. This might have allowed the permeant molecule to more easily penetrate.

The results obtained from permeability tests using liquid dibutylsulfide are shown in Table 3. Figures 38-40 show the results graphically related to the membrane types for dibutylsulfide. Aptra Classic showed higher permeability than the other two membranes when compared for an experimental time period of 20 min. Dibutylsulfide has a slightly higher molecular weight than β-pinene. The molecular structure of the dibutylsulfide

might also be playing a role in its permeation into the membrane. Dibutylsulfide appears to be more rod-like while β-pinene is almost spherical. Aptra Classic might have the more suitable pore shape so that permeability is higher. As mentioned previously, Aptra Classic membranes had been stretched in two directions, thus affecting the pore size, possibly shape and the number of pores present. Aptra UV 8 had been made in the same way but due to the presence of UV stabilizers, it might be showing lesser permeability to this mimicking compound. After 30 min permeation time, B130 allowed for higher permeation, whereas the Aptra Classic and Aptra UV 8 membrane showed similar readings. For the experiments at 45 min, there was no significant difference between the three membranes regarding permeability. All three membranes showed the highest weight loss at this time interval.

When the two mimicking compounds were compared, B130 membranes when subjected to dibutylsulfide showed overall higher permeability than when subjected to β-pinene vapors. The heat necessary for evaporation of dibutylsulfide had to be maintained at a higher level (188ºC) while β-pinene only needed 166ºC. The difference in temperature could have had some effect on the membranes.

Vapors of β-pinene seemed to pass through Aptra Classic membranes easier than dibutylsulfide. The reason could possibly be found in the difference in structure and molecular shape: being more spherical β-pinene molecules could more easily penetrate through the membranes. The same reason could be implied for Aptra UV 8 membranes. However for longer permeation experiments (45 min) dibutylsulfide seemed to pass easier. Thus, the results of the permeability experiments were inconclusive and their interpretation cannot solely be based on differences in membrane pore structure.

For a further series of experiments the membrane used in each case was carefully weighed before and after evaporation of the mimicking compound to examine whether some of the compound might have been adsorbed. The results are presented in Table 4. A clear weight gain could be observed indicating adsorption or compound condensation within the pores of the membrane. Aptra UV 8 membranes seemed to be especially prone to adsorption showing the highest weight gain (between 7 and 8%), followed by Aptra Classic (4-5%). B130 membranes increased the least in weight. The same trend was observed for both β-pinene and dibutylsulfide. From these data it can be concluded that the entire vapor did not pass completely through the membranes. Instead a portion had been held back by the membranes. It is possible that the UV-stabilizers contained in Aptra UV 8 are responsible for retaining these chemicals. Aptra Classic showed less adsorption probably due to the lesser number of pores and somewhat smaller pore size.

In conclusion it can be said that at extended exposure to heat and the vapor of either β-pinene or dibutylsulfide all membranes became fairly permeable compared to the blank experiment without membrane as barrier. Aptra UV 8 retained a large portion of the vapor while the pores of B130 membranes probably increased to a certain extend without adsorbing as much vapor as the other membranes.

Table 2 Permeability Test Results for β-pinene.

Initial Weight of β-pinene = 2.00 g

Time (min)	Blank (%)	Weight loss (%) B130					Weight loss (%) Aptra Classic					Weight loss (%) Aptra UV8				
		Test 1	Test 2	Test 3	Mean	Std	Test 1	Test 2	Test 3	Mean	Std	Test 1	Test 2	Test 3	Mean	Std
20		2.9	2.825	3	2.91	0.07	1.875	1.95	2.025	1.95	0.06	1.83	1.935	1.77	1.845	0.07
30		3.15	3.01	3.405	3.19	0.16	4.31	4.375	4.23	4.305	0.06	4.325	4.245	4.315	4.295	0.04
45	7.91	5.765	5.735	5.785	5.76	0.02	6.23	6.295	6.25	6.26	0.03	5.505	5.485	5.52	5.50	0.01

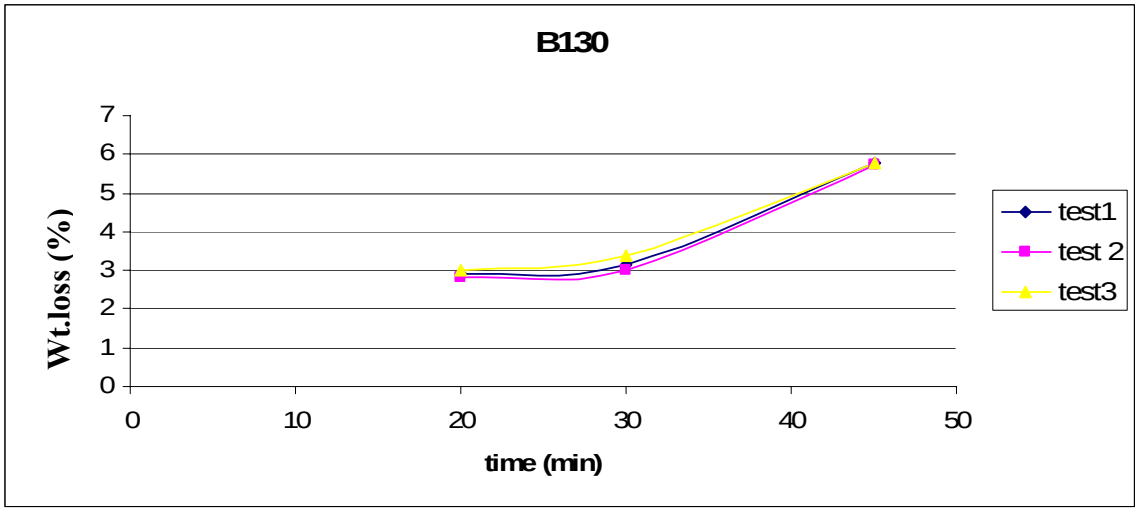


Fig. 35 Permeability of B130 Membrane using β-pinene

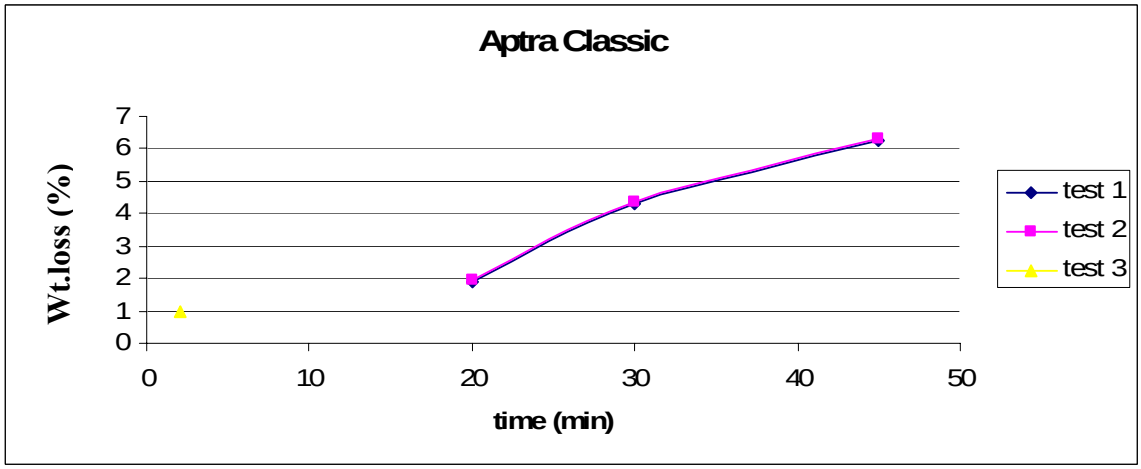


Fig. 36 Permeability of Aptra Classic membrane using β-pinene

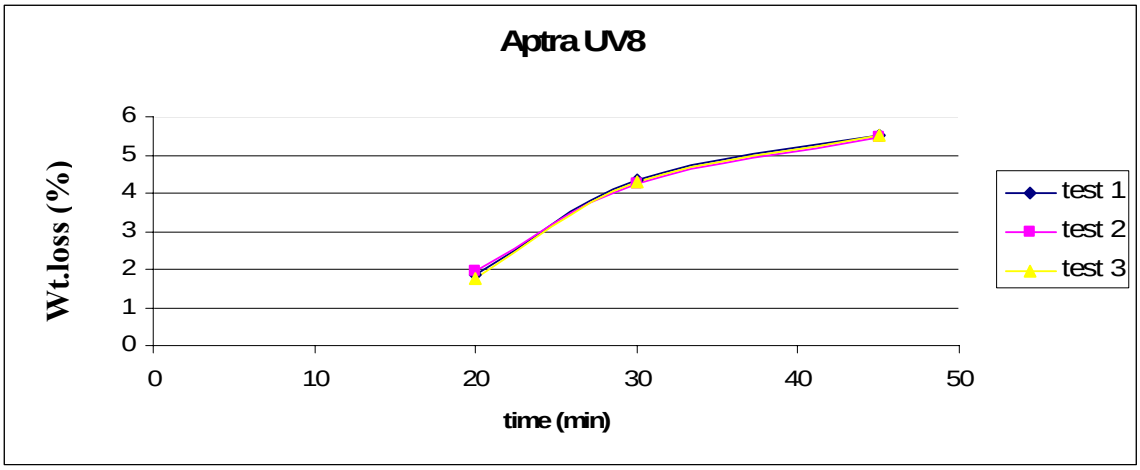


Fig. 37 Permeability of Aptra UV8 membrane using β-pinene

Table3 Permeability Test Results for dibutylsulfide

Initial weight for dibutylsulfide = 2.00g

Time (min)	Blank (%)	Weight loss (%) B130					Weight loss (%) Aptra Classic					Weight loss (%) Aptra UV8				
		Test 1	Test 2	Test 3	Mean	Std	Test 1	Test 2	Test 3	Mean	Std	Test 1	Test 2	Test 3	Mean	Std
20		1.405	1.44	1.465	1.44	0.02	2.445	2.405	2.46	2.44	0.02	1.735	1.76	1.695	1.73	0.03
30		4.01	3.995	4.26	4.09	0.12	3.605	3.595	3.59	3.6	0.01	3.57	3.61	3.575	3.585	0.02
45	6.27	5.885	5.605	5.87	5.79	0.13	5.4	5.355	5.42	5.39	0.03	5.575	5.64	5.605	5.61	0.03

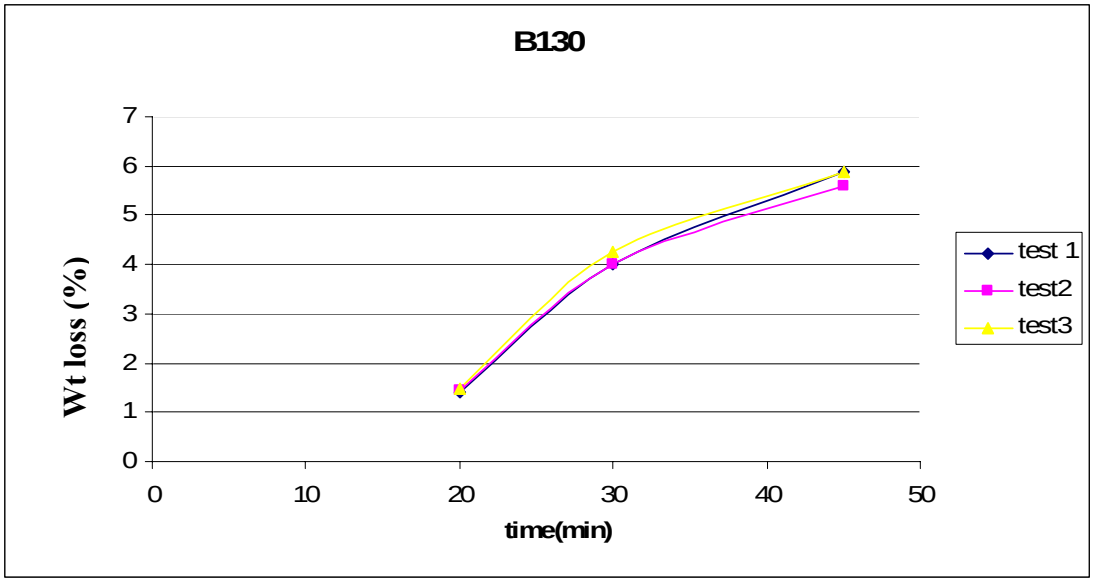


Fig. 38 Permeability of B130 membrane for dibutylsulfide

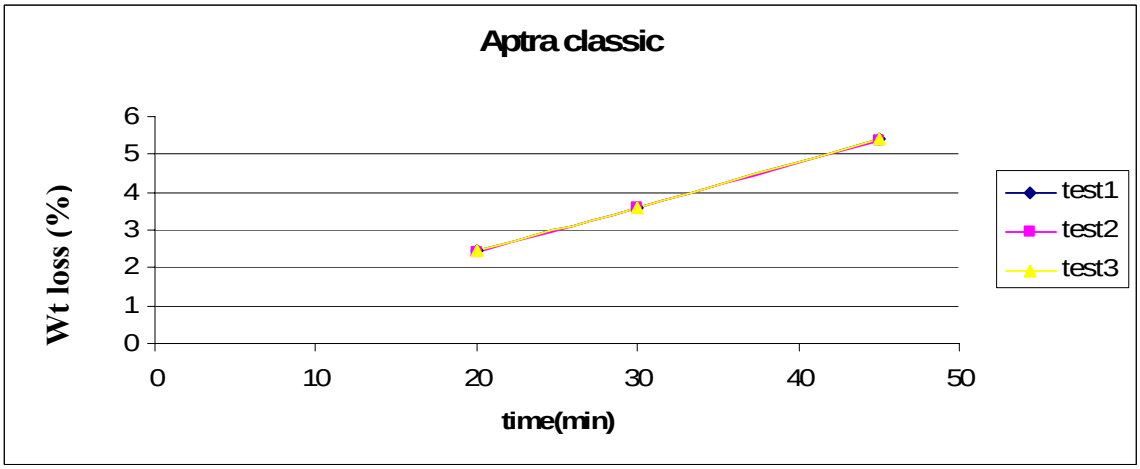


Fig. 39 Permeability of Aptra Classic membrane for dibutylsulphide.

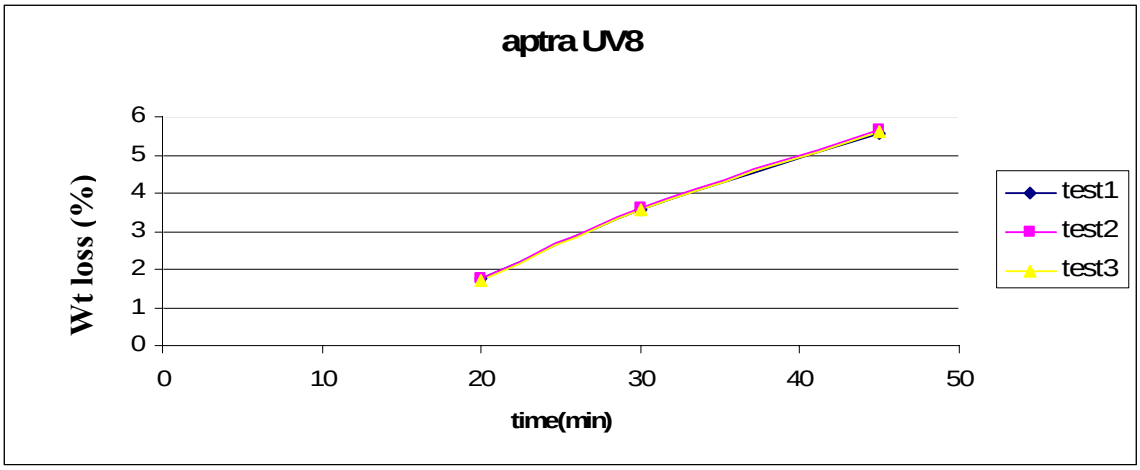


Fig. 40 Permeability of Aptra UV 8 membrane for dibutylsulfide

Table 4 Membrane weight gain (%) after heating for 45 minutes

Initial weight of membranes was between 0.0708-0.0745 g

	Membrane Weight Gain (%) after 45 min		
	B130	Aptra Classic	Aptra UV8
β - pinene	2.14	5.18	8.05
dibutylsulfide	1.88	4.49	7.04

Table 5 % of solution absorbed in membranes in terms of total solution weight for 45 minutes

	B130	Aptra Classic	Aptra UV8
β - pinene	0.08003	0.184926	0.28497
dibutylsulfide	0.07003	0.1602	0.24992

5. CONCLUSIONS

Three types of membranes, namely B130, Aptra Classic and Aptra UV8, were investigated in regard to their permeability. The B130 membrane is made of polyethylene and polypropylene while the other two are made of polypropylene, the difference being that the Aptra UV8 membrane was additionally treated with UV stabilizers. From scanning electron microscopic images it was observed that the Aptra Classic and Aptra UV8 membranes were more porous than the B130 membrane. Permeability tests for these membranes were carried out using the β-pinene and dibutylsulphide in vapor form. These chemicals were selected based on molecular weight, shape and vapor pressure.

For longer exposure to the vapors at higher temperature all three membranes showed fairly high permeability with only minor difference between the three types and without significant differentiation between the two chemical compounds used to test their permeability. It could be argued that extended exposure to heat might impact, i.e. widen, the pore structure of the membranes and thus allow for increased permeability. It was found however that the membranes considerably differed in their adsorption behavior towards the chemical vapors. B130 retained the least amount of vapor compound while Aptra UV 8 adsorbed the most. Thus, the permeation characteristics of the membranes cannot solely be explained by the observed slight differences in their pore structure but must also be seen in light of their physical or chemical sorption behavior. Obviously the membrane types differed clearly with regard to this property. It will have to be

determined whether this characteristic could be used to further enhance the barrier properties of these membranes.

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