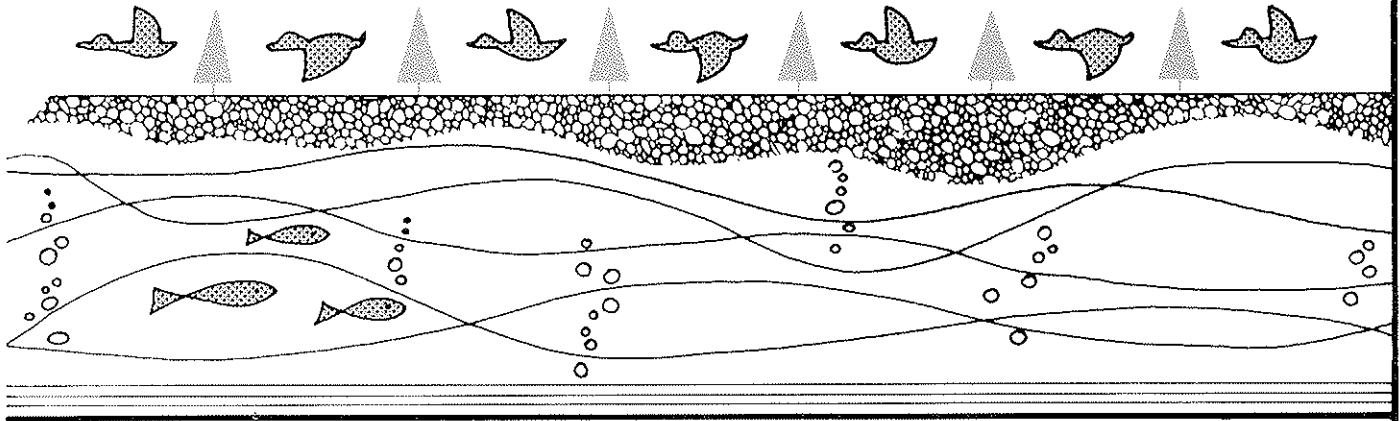




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SPILL TECHNOLOGY NEWSLETTER



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The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on oil spill countermeasures and other related matters. We now have over 2000 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of oil spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

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INTRODUCTION

This first issue of 1987 continues the new look introduced with the last issue of 1986. While the addition of colour has made the cover considerably more attractive, the most important change has been the marked improvement in the quality of typing and layout. Both improvements are thanks to a determined effort on the part of the staff of the Technology Transfer and Training Division who turn our manuscript version into the finished product. This issue also marks the start of our twelfth year of publishing and we see no sign of diminished need or interest.

The first article is by Rod Turpin and Philip Campagna who describe some of their spill response activities with the U.S. Environmental Protection Agency's Environmental Response Team. The article gives good practical lessons that are presented with the authors' well-known sense of humor. The second article is by Jeff Stull of the United States Coast Guard and is a review of current activities to improve chemical protective clothing.



"MONDAY MORNING QUARTERBACKS"

Submitted by: Rodney D. Turpin & Philip R. Campagna
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Introduction

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters, and Regional Offices, as well as other United States and foreign governmental agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

This paper briefly describes some of the more interesting learning experiences shared by the authors on various response activities. Although this paper is technical in nature, the subject is approached from the lighter side. The theme of each experience will be either occupational health and safety or air monitoring; and it will include such activities as train derailments, hazardous waste sites, and a malathion fire in Sri Lanka.

Experiences

1. "Hazardous Waste Site Activities Reduce Site Airborne Concentrations"

a. Drum Site: New England

Site Description: This site was located in a rural area of New England surrounded by both hardwood and evergreen trees. It consisted of approximately 5 000 to 7 000 drums containing various organic wastes. Although several of the drums were either rusted through or had been used as a 0.22 caliber pistol/rifle target by local resident(s), airborne organic concentrations were low due to ambient air temperatures.

ERT Support Function: In addition to ERT's on-site air monitoring function, we were involved in various other phases of the operation: compatibility testing; on-site mobile laboratory analysis; site safety protocols; and projectile opening of small lab pack bottles.

Air Monitoring Activity: The air monitoring operation was a very visible function since it monitored site conditions as well as private residential areas.

Since the site was located next to a major highway, it was decided to collect background samples up wind of the road when conditions were appropriate. The sampling activities took place in the late fall/early winter with background stations set up in a nearby public park surrounded by evergreen trees.

The real-time air monitoring instruments did not indicate elevated background concentrations within the park area where background samples were collected. However, on-site analysis of thermal desorption collection tubes did reveal that ambient background samples contained more organic contaminants than the site samples.

Obviously, background stations were relocated and did reflect a lower background level. However, the remaining questions were: Did the contaminants come from the evergreen trees or did the movement of air across the site remove the contaminants? The authors suggest that the trees were at fault and have not placed a background station in a park since this response.

b. Telephone Pole Treating Facility: Eastern Coastal Area

Site Description: This site was located within an industrial park on a small tidal river in a mid-Atlantic State. Even though the area was heavily industrialized, the citizens were concerned with their environment. Ten to fifteen years ago a nearby river had been contaminated by a pesticide manufacturing facility, which had an adverse impact on the fishing industry. Most of the river traffic was restricted to tugboats and barges. Drawbridges were the most popular way to transport automobile traffic across the river.

ERT Support Function: EPA Regional offices requested assistance in monitoring the site for potential on-site and off-site airborne contamination.

Air Monitoring Activities: Since some of the specific contaminants produced at this location could be potentially found in the surrounding atmospheric conditions, background data appeared to be more important for this site than for most others. Unfortunately, the most ideal ambient temperature conditions (summer) also meant the highest relative humidity and increased automobile activity.

After several months of planning and waiting for the right atmospheric conditions, the trip took place. However, "Mother Nature" was not totally cooperative. While ambient air temperatures and wind velocity were appropriate, wind direction was not optimum during the limited sampling period.

As luck would have it, the wind direction caused the background station to be set up near the drawbridge. While past experiences have revealed that automobile traffic will have an adverse impact on the background concentrations, wind direction would not permit any other options.

A survey of the area with handheld real-time instruments indicated an area below the drawbridge (3 to 3.7 m under the roadway) would be a suitable location for a background sample. Thus, the long awaited sampling commenced and within a four-hour sampling period something unscheduled happened. A tugboat passed by and the drawbridge raised -- not once but twice. In addition to this taking a long time (15 to 20 minutes), it occurred during two peak traffic periods -- 8:00 a.m.-9:00 a.m. and 11:00 a.m.-12 noon. This caused cars and trucks to back up for approximately 0.8 to 1.6 km on top of the background sampling station.

As you may have guessed, the on-site analytical gas chromatograph (GC) revealed that background levels were higher than site conditions. Once again, our air monitoring has shown that hazardous waste site activities reduce pollutants from the ambient air. At this point, we hope you agree that site monitoring is far easier than many background surveys.

2. "Ye Olde ERT Law: Murphy was an Optimist

a. Recycling Facility - Northwest Area

Site Description: This 13-acre (5.3-ha) site was located in the northwest portion of the West Coast in a residential/light industry area. The site was a recycling facility with various types of materials ranging from fly ash and scrap metal to organic waste contaminated with polychlorinated biphenyls (PCBs). The site consisted of approximately 70 storage tanks, 5000 drums, an incinerator, a laboratory, and waste lagoons just to name a few. What separates this site from other recycling facilities is that the acidity of some of the lagoons was below pH 1.

ERT Support Function: ERT's support consisted of the following on-site activities: occupational health and safety protocols; air monitoring; compatibility testing; removal/disposal techniques; on-site mobile laboratory protocols/support; and off-site analytical protocols/support.

Occupational Health and Safety Protocols: The specific site safety plan followed the guidelines given in the U.S. EPA, OERR, Standard Operating Safety Guides (November, 1984) and was modified to meet the specific needs of this site. The various site activities were conducted in Levels "B" and "C".

Since all of the waste materials were required to be shipped out of the particular state for disposal, solidifying the organic liquid waste present in the lagoons was a necessity. Recognizing the location of the northwest site, sawdust was selected as the natural cellulose material to accomplish this task. The actual mixing of the sawdust caused more of an occupational health and safety problem than did the engineering aspects.

A front-end loader was selected as the mixing device and the operator used modified Level B protective equipment. The clothing consisted of the chemical-resistant type, while the respirator was a supplied-air type with the air tank affixed to the cab.

After several days of monitoring the breathing zone of the front-end loader, the cleanup contractor's industrial hygienist reduced the respirator protection from air-supplied to an air-purifier respirator.

In this case, the operator was subsequently hospitalized for several hours when the front-end loader punctured a drum which released a toxic plume. This plume engulfed the operator and penetrated the air purifier. The concentrations were such that the individual was overcome and collapsed.

While the contractor's practice of selecting respirator protection is applicable for other industrial settings, it is not applicable for hazardous waste site operations. The U.S. EPA, OERR Standard Operating Safety Guide (November, 1984), calls for the selection of respirators to be based on several factors, one of which is potential exposure.

b. Sanitary Landfill Sampling - Northeast Area

Site Description: This site was located on the East Coast and was bordered on the south by the Atlantic Ocean and on the east by a canal. The site was surrounded by single and multiple family dwellings.

The site was an active sanitary landfill which included a small municipal waste incinerator. A short period before the monitoring was performed there were news stories in the local papers concerning the illegal disposal of hazardous waste into sanitary landfills in the metropolitan area. Residents of the area had also complained of odours from the landfill.

ERT Support Function: ERT's task was to perform air sampling/monitoring at the landfill and community. Air samples were collected at the landfill from gas vents, from possible leachate seeps, and in the community. The plan consisted of collecting air samples on various types of media (i.e., carbon, tenax, silica gel, etc.), and in air bags, and real-time monitoring with a mobile mass spectrometer (MS/MS) unit.

The air samples were collected over a six- to eight-hour period using personal sampling pumps at various flow rates with carbon, tenax, and silica gel collection tubes. In addition, air bag samples were collected from various sampling locations. The air bag samples were analyzed for methane gas using an organic vapour analyzer-flame ionization detector (OVA-FID) and for vinyl chloride using a photoionization detector - gas chromatograph (PID-GC). Standards for the vinyl chloride were prepared by diluting a certified vinyl chloride air standard cylinder using zero air and air bags.

It was during the analysis for vinyl chloride that Murphy's Law first appeared during this activation. Instead of shipping the vinyl chloride cylinders, it was decided to place the standard in 5-litre air bags and to make the field dilution from these. During the first day of analysis, the analyst observed that the peak area of diluted standards decreased over time. It was determined that the vinyl chloride was either bleeding from the bags or was decomposing. Therefore, an emergency call was placed back to the office and the air cylinder was immediately shipped to the site.

High Tide or Low Tide: Murphy's Law struck again. Note that some of the sampling team was born and raised around the Great Lakes area where the effect of the tides on water level is minimal. On the third day, the sample plan called for sampling the areas where vapours might be emitted from the leachate. This was done by stationing pumps equipped with various media over possible leachate seeps. It was during the second inspection of pump locations that the effect of tidal activity was observed by the sampling team....the stations were gone. The pumps were found the next day during low tide....not working.

c. Abandoned Incineration Operation: Great Lakes Area

Site Description: This site was located in a suburban area and consisted of contaminated soil and sludge. In addition, the site consisted of lagoons and a 2-acre (0.8-ha) area of buried drums. The sludge and soil contained C-46, C-56, C-58, C-48 and other chlorinated organics. The cleanup activities were being performed by a responsible contractor.

ERT Support Function: The ERT was requested by the region to develop and implement a community air monitoring plan and emergency action plan in case of a release. The ERT was also asked to review the cleanup contractor's air monitoring plan, and the health/safety practices of on-site workers.

Air Monitoring Activity: The air sampling consisted of three downwind stations in the yards of residences, two stations downwind of the site at the site fence line, two background stations, and one mobile station. Each station consisted of various personal sampling pumps equipped with a variety of collection media tubes --carbon, porapak-T Tenax/chromosorb (for GC/MS analysis), and GC-Tenax for on-site thermal desorptions GC analysis. The plan also called for performing real-time monitoring for organic vapours with hand-held instruments.

The on-site GC analysis was used to screen samples and to assist site personnel in determining if site activities were causing releases into the community. In addition, this information was used to select which tubes would be sent to an analytical lab for analysis. Lab samples were kept cool with the use of cool packs, which use an endothermic reaction for cooling. The chemicals are mixed by hand crushing the bags. But after long hot days, using various types of protective clothing and equipment, the easiest jobs become difficult. One of the bags just would not crush, so one of the samplers put the bag between his knees and with both hands and legs tried to crush the bag. The bag not only crushed but ruptured, spraying his groin with the endothermic solution. The individual ran the 90 m to the decon station in a world record pace. In addition to the burning sensation, the individual had to face the fact that he is the team's health and safety expert.

d. Train Derailment: Gulf States

Site Description: This response activity was located in a rural area in one of the Gulf of Mexico States. It consisted of approximately 40 derailed chemical tank cars, which were on fire, leaking and/or exploding.

ERT Support Function: In addition to the ERT's air monitoring and occupational health and safety function, the team was also involved in evaluating soil and groundwater contamination, as well as cleanup techniques.

Air Monitoring and Occupational Health and Safety Activities: While this response left many memorable experiences, the following three are still dear to the authors' hearts.

1. Weather Balloons: The problem was that the air surveillance team was not able to get close enough to the air plume because of the explosion potential.

Two small weather balloons were obtained from a nearby airport to lift the air collection pumps and tubes approximately 60 m to get above the pine trees and into the plume. The two small weather balloons, however, did not provide enough lifting power, so latex rubber gloves were filled with helium for assistance. Imagine if you will, the gloves expanded to the size where they resembled cow udders. Yes, the press had a good time.

Unfortunately, the balloon/glove stations were set out at approximately 6:30 a.m. and left out for four hours. When the sampling team returned, the helium had expanded and exploded the gloves which brought the pumps crashing to the ground. The good news was that after approximately a 60 m free fall, the pumps "kept on ticking".

2. 110 Electric Generators: Since air monitoring at a derailment is often a 24-hour effort, the air surveillance team decided not to use the battery capabilities of the field gas chromatographs (GCs). Instead, the instruments were run off of the command post's gas generator. A surge occurred in the electricity, and blew out one of the two available field GCs. After this response, our analytical instruments have never been run off of generated power.
3. Eye Protection: One of the chemical tank cars had leaked into a nearby drainage ditch. The material was very acidic and small pools were being cleaned up.

The authors had not only advised but were demanding that the ditch cleaners wear full-face respirators. Of course, the railroad's cleanup contractor's industrial hygienist did not agree, and the issue of EPA's authority to enforce health and safety protocols during a state lead responsible party cleanup was being debated. During this 24-hour heated discussion, a ditch cleaner, who was wearing a 1/2-face respirator with no eye protection, lost his balance. In losing his balance, the shovel fell into the muddy pool containing the waste material, and he received a chemical burn to one eye.

3. Malathion Fire: Sri Lanka

Site Description: It was two weeks before Christmas and all through the office not a hazard was stirring, not even a spill.

The quietness was broken when a call came over the hotline. The call was from the state department AID office. They requested information on malathion, because a warehouse fire had just occurred in Colombo, Sri Lanka. The warehouse contained approximately 20 million pounds (9×10^6 kg) of malathion. This malathion was a wetttable powder stored in corrugated cardboard boxes.

ERT Support Function: Initially, they wanted information on possible breakdown products, adverse health effects, and disposal options. A report containing this information was prepared immediately. We also informed them that the fire was probably smouldering at the bottom of the piles, since the boxes were stacked 6 m high.

After the information was reviewed by the AID office, it was determined that ERT personnel were needed to perform an on-site inspection to assist the Sri Lankan government in determining if the fire was still smouldering, whether vapours were still being released, and the appropriate disposal options.

Response Activity: The travel itinerary for the two-man team consisted of a morning flight to Washington, D.C., for a briefing, and an evening flight to Sri Lanka.

The minor problems which occur with many responses started almost immediately. The 12-piece sampling equipment had to be carried as luggage. The equipment consisted of temperature probes, cannister air purifying respirators, disposable protective clothing, air sampling and monitoring equipment, hand augers, and reference material. During the trip to Sri Lanka this luggage had to be transferred between four planes (New York - Washington - New York - Switzerland - Sri Lanka). Only one piece of luggage was lost during this part of the trip.

Upon arriving at the airport on Friday morning the team found that no reservations were made and seats were not available on the 7:00 a.m. flight. Next, the flight from New York to Switzerland was changed by the airlines at the last minute to a flight to Hamburg, Germany with a connection to Switzerland. This minor change caused a five-hour delay in the teams' arrival in Sri Lanka. During the briefing, the team had learned that some terrorist problems existed in the country. Upon arrival in Sri Lanka the team members observed that army personnel were guarding the airport and government offices. After talking to a local official, they learned that the head of State of Pakistan was visiting and the soldiers were an honour guard.

Even with these minor problems, the overall response went very well. The team was able to core into the pile to obtain temperature readings and measure vapour levels. The temperature probe showed that some of the piles were still smoldering, and the vapour readings revealed that no immediate health threat existed. The team also provided recommendations for disposal of the waste materials. The Sri Lankan people were extremely cooperative and cordial to the team during their stay.

Acknowledgement

The authors express their appreciation to all members of the U.S. EPA Environmental Response Team, U.S. EPA-ERT's TAT and U.S. EPA EERU contractors for their many contributions and constant updating of our response activities.

Conclusion

The authors hope you have enjoyed their efforts to share those situations which have added to their learning experience. As in other fields, there is no substitute for hands-on experience in the hazardous materials response field.

PERFORMANCE STANDARDS FOR CHEMICAL PROTECTIVE CLOTHING IN EMERGENCY RESPONSE*

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Introduction

Federal, state, local, and commercial response organizations use a variety of protective clothing items to protect their personnel during chemical spill incidents. These items range from outfits of overalls, gloves, and boots to totally-encapsulating suits. Chemical protective suits offer the highest level of protection and are used when the greatest chemical toxicity hazards are encountered. Despite the widespread use of chemical protective suits, few standards have been developed which are directly related to chemical protective clothing. The American Society for Testing and Materials (ASTM) has introduced new test methods for protective clothing. For example, the ASTM F23 Committee on Protective Clothing has established a testing procedure for measuring the chemical permeation resistance of clothing materials. Nonetheless, there are no comprehensive standards which specify garment and material performance requirements.

The consequences for this lack of standards are multifold. Protective clothing users are faced with a myriad of products in selecting the "right" garment. Many times, smaller organizations have limited resources to procure chemical protective clothing. These organizations often must rely on a single type of chemical protective suit to meet their chemical response needs. Users also need some level of confidence that their selected clothing will perform as intended, or according to the manufacturer's claims. Furthermore, it is difficult to compare products when manufacturers report data or features of their suits differently. Even chemical data taken using the same standard test method cannot easily be compared because of differences in reporting documentation. More importantly, however, protective clothing can be manufactured which does not provide adequate protection due to poor construction or quality assurance.

Comprehensive protective clothing standards are clearly needed. On August 12, 1983, a tank car loaded with dimethylamine located on an industrial railroad track in Benicia, California began leaking product. Firefighters, wearing chemical protective suits, responded to the leak. Shortly after working on scene; however, the visors of their protective suits became cloudy and one visor eventually shattered and exposed the wearer to large concentrations of the chemical⁽¹⁾. Information available to the fire department about the particular chemical protective suit led the firefighters to believe that the suits offered adequate protection for the hazardous dimethylamine environment. Upon investigating the accident, the United States National Transportation Safety Board (NTSB)

* The opinions in this paper are those of the author, and do not necessarily represent the views of the U.S. Coast Guard, American Society for Testing and Materials, or National Fire Protection Association.

recommended that several federal agencies work together in this area to promote a consensus of standards that would lead to improved products and greater confidence in using them⁽²⁾.

The U.S. Coast Guard together with the Environmental Protection Agency, Federal Emergency Management Agency, and the National Institute for Occupational Safety and Health and the Occupational Safety and Health Administration, have formed a working group to comply with the NTSB recommendation. The role of this working group is to coordinate U.S. federal agency research in the area of chemical protective clothing. This also involves reporting progress on federal research and development outside the U.S. government, and actively participating in both ASTM's F23 Committee on Protective Clothing and a newly established subcommittee of the National Fire Protection Association to pursue standards for chemical protective suits.

Types of Standards and Standards Development Philosophy

In general, there are three types of standards which can be applied to chemical protective suits: documentation, performance, and design. Documentation standards direct manufacturers to perform specific tests and to report certain data from those tests to users. These type of standards may also require manufacturers to provide information to users about their products, such as a complete description of the materials used in fabricating a garment. In a performance standard, a property or characteristic of the product is measured and a required level of performance is set that the manufacturer's product must meet. For example, the garment material in a chemical protective suit might have to possess a tear resistance of at least a certain value. These standards are also called minimum performance requirements because the product must attain a minimum level of performance. The most rigorous standards are design-oriented. Design standards specify to the manufacturer the exact way a product must be constructed. These standards are generally avoided because they are design-restrictive, i.e., they do not allow manufacturers latitude to devise innovative designs for their products.

The ASTM and NFPA appear to have distinctly different but compatible approaches in their development of protective clothing standards. The current focus of ASTM is to develop standards which measure the properties of materials used in chemical protective clothing, or to establish test methods to measure the performance of complete protective garments. Already, several standards exist which specify methods for making these measurements. Moreover, standards from other ASTM committees, like those of D-11 on Rubber, can be applied to protective clothing. Therefore, ASTM's direction is one of providing performance measurement techniques which will standardize product documentation. To this end, the ASTM F23 committee has a task group working on a comprehensive documentation standard for chemical protective suits which will require manufacturers to specify certain information and conduct particular tests on their respective products.

In contrast, NFPA is working on performance standards which will set specific requirements for chemical protective suits. A Subcommittee on Hazardous Chemical Protective Clothing under NFPA's Technical Committee on Protective Equipment for Firefighters is developing several standards of this type. For these standards, manufacturers will not only have to conduct certain tests and report the results, but also meet the

required minimum performance. To be compliant, a manufacturer's product must meet all requirements of the standard. As with ASTM specifications, manufacturers completely complying with a standard are able to label their product as compliant. Many standards specify the wording and type of compliance label to be issued.

Classification of Chemical Protective Suits

Several classification schemes exist for chemical protective clothing. Some are based on design while others are related to the function or application of the protective clothing. One of the better known classification systems was developed by the U.S. Environmental Protection Agency using levels of protection to distinguish between types of protective clothing⁽³⁾. Four levels, A to D, were established using the degree and type of toxicity hazard to select the appropriate protective clothing, breathing apparatus, and other associated equipment. These levels and the recommended criteria for using them are listed in Figure 1. While this scheme lends itself to classifying protective clothing systems, it was not designed to categorize chemical protective suits. Certain areas are subject to interpretation. For example, it is not clear whether a Level A suit must completely enclose the user and his/her respiratory protection, or if the respiratory equipment can be worn outside the suit. Additionally, the selection of the garment based on its "durability" is left to the judgement of the user. These distinctions are essential to the development of various chemical protective clothing standards.

A classification system under consideration by the NFPA uses the EPA's "Level of Protection" as its basis. The highest level, Level A, dictates the use of a totally-encapsulating suit primarily in those cases where any dermal exposure to the chemical(s) is not permissible. The NFPA proposes to classify this type of clothing as "vapour-protective". Chemical protective suits recommended for both Levels B and C include one- or two-piece chemical "splash suits". The NFPA proposes to define this type of clothing as "liquid-protective". The reason for this distinction is to provide a means for verifying the performance of each protective clothing type. Therefore, classification of a chemical protective suit can be based on whether the suit can meet a performance test, as opposed to its design attributes (performance-oriented versus design-oriented definition).

Another part of the proposed NFPA classification scheme would further subdivide the vapour- and liquid-protective chemical protective suits by clothing durability and function. Here the intent is to discriminate between "disposable" or "limited-use" and "rugged" protective suits. Again, the actual distinction would be based on a battery of performance tests or perhaps different performance requirements. The end result would be a two-by-two matrix of chemical protective suits differentiated by performance. In reality, it is highly probable that each type of chemical protective suit would have a number of standard requirements in common and form the "core" requirements for each of the four chemical protective suit standards.

Chemical Resistance Requirements

One of the most difficult areas in developing standards for chemical protective clothing is the measurement of clothing chemical resistance. The ASTM F23 Committee has made significant advances in establishing standard methods for measuring the permeation

LEVEL OF PROTECTION	EQUIPMENT	PROTECTION PROVIDED	SHOULD BE USED WHEN:	LIMITING CRITERIA
A	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Fully-encapsulating, chemical-resistant suit. • Inner chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Cooling unit. • Coveralls. • Long cotton underwear. • Hard hat. • Disposable gloves and boot covers. 	<p>The highest available level of respiratory, skin, and eye protection.</p>	<ul style="list-style-type: none"> • The chemical substance has been identified and requires the highest level of protection for skin, eyes, and the respiratory system based on either: <ul style="list-style-type: none"> — measured (or potential for) high concentration of atmospheric vapors, gases, or particulates or — site operations and work functions involving a high potential for splash, immersion, or exposure to unexpected vapors, gases, or particulates of materials that are harmful to skin or capable of being absorbed through the intact skin. • Substances with a high degree of hazard to the skin are known or suspected to be present, and skin contact is possible. • Operations must be conducted in confined, poorly ventilated areas until the absence of conditions requiring Level A protection is determined. 	<ul style="list-style-type: none"> • Fully-encapsulating suit material must be compatible with the substances involved.
B	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Chemical-resistant clothing (coveralls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Coveralls. • Disposable boot covers. • Face shield. • Long cotton underwear. 	<p>The same level of respiratory protection but less skin protection than Level A.</p> <p>It is the minimum level recommended for initial site entries until the hazards have been further identified.</p>	<ul style="list-style-type: none"> • The type and atmospheric concentration of substances have been identified and require a high level of respiratory protection, but less skin protection. This involves atmospheres: <ul style="list-style-type: none"> — with IDLH concentrations of specific substances that do not represent a severe skin hazard; or — that do not meet the criteria for use of air-purifying respirators. • Atmosphere contains less than 19.5 percent oxygen. • Presence of incompletely identified vapors or gases is indicated by direct-reading organic vapor detection instrument, but vapors and gases are not suspected of containing high levels of chemicals harmful to skin or capable of being absorbed through the intact skin. 	<ul style="list-style-type: none"> • Use only when the vapor or gases present are not suspected of containing high concentrations of chemicals that are harmful to skin or capable of being absorbed through the intact skin. • Use only when it is highly unlikely that the work being done will generate either high concentrations of vapors, gases, or particulates or splashes of material that will affect exposed skin.
<i>(Based on EPA protective ensembles.)</i>				
C	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Full-facepiece, air-purifying, canister-equipped respirator. • Chemical-resistant clothing (coveralls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Coveralls. • Disposable boot covers. • Face shield. • Escape mask. • Long cotton underwear. 	<p>The same level of skin protection as Level B, but a lower level of respiratory protection.</p>	<ul style="list-style-type: none"> • The atmospheric contaminants, liquid splashes, or other direct contact will not adversely affect any exposed skin. • The types of air contaminants have been identified, concentrations measured, and a canister is available that can remove the contaminant. • All criteria for the use of air-purifying respirators are met. 	<ul style="list-style-type: none"> • Atmospheric concentration of chemicals must not exceed IDLH levels. • The atmosphere must contain at least 19.5 percent oxygen.
D	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Coveralls. • Safety boots/shoes. • Safety glasses or chemical splash goggles. • Hard hat. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Gloves. • Escape mask. • Face shield. 	<p>No respiratory protection. Minimal skin protection.</p>	<ul style="list-style-type: none"> • The atmosphere contains no known hazard. • Work functions preclude splashes, immersion, or the potential for unexpected inhalation of or contact with hazardous levels of any chemicals. 	<ul style="list-style-type: none"> • This level should not be worn in the Exclusion Zone. • The atmosphere must contain at least 19.5 percent oxygen.

FIGURE 1

U.S. ENVIRONMENTAL PROTECTION AGENCY LEVELS OF PROTECTION

(ASTM F739), penetration (ASTM F903), and degradation (Draft ASTM F23.30.03) resistances for protective clothing materials. These phenomena relate to the different types of chemical interaction with the protective material and are well documented^(4,5). Measurement of permeation resistance is a likely requirement for vapour-protective clothing, where the clothing materials should prevent any intrusion of the hazardous chemical. This method can show the effects of material chemical degradation as well. Liquid-protective clothing materials, on the other hand, should be tested for penetration resistance. This distinction is important because the qualifying test for liquid-protective clothing permits vapour penetration. The ramification of this proposal is that users should only select liquid-protective clothing if exposure to vapours of the subject chemical(s) is permissible and considered non-hazardous.

Permeation Resistance Testing. Permeation resistance is the currently recommended method for measuring material chemical resistance. ASTM F739 specifies procedures for measuring permeation resistance by gases and liquids of protective clothing materials using the apparatus pictured in Figure 2. This method is the most complex of the three and its measured parameters -- breakthrough time and permeation rate -- are subject to variations produced by the environment, equipment, material, and testing chemical. As a consequence, results from the test are not easily compared between laboratories. Yet, a number of organizations use permeation breakthrough times as the basis for recommendations on using chemical protective suits. Also inherent in the method, is the difficulty of relating data on a pristine material to exposure conditions encountered in the field for an entire suit.

Specification of key test parameters and procedures can help further standardize the ASTM permeation resistance test. Foremost among these, is the minimum detection limit of the analytical device used to detect breakthrough time. For the same material, chemical, and test conditions, a poor analytical detection limit can result in a relatively longer breakthrough time than one obtained using a very sensitive analytical technique. In some cases, the results can be rather dramatic. On a new material, the breakthrough time for carbon disulphide was reported to be in excess of eight hours using flame ionization gas chromatography, whereas the same material-chemical combination with an electron capture detector yielded a breakthrough time of 30 minutes⁽⁶⁾. Testing laboratories cannot be expected to choose the same detection methodology for each chemical. If a minimum detection limit was set for all permeation resistance testing, then many of these disparities might be avoided.

Similarly, the configuration of the test apparatus can affect the permeation breakthrough results. Depending on the type of analytical detector chosen, systems can be either "open" or "closed". Open systems are typically used for continuous sampling of the permeation cell collection medium; closed systems for discrete sampling. In closed systems, the chemical permeate accumulates in the collection side of the permeation cell until the concentration can be detected by the analytical device. Breakthrough times measured in this way are shorter than those for open systems where there is no accumulation. It is conceivable that the rate of permeation can be so small that permeation can be detected in a closed-loop system but not in the analog open configuration. Specifying open or closed permeation system configurations, however, would reduce the testing laboratory's flexibility in choosing analytical detectors. One way of overcoming this problem is to measure detector sensitivity independent of the

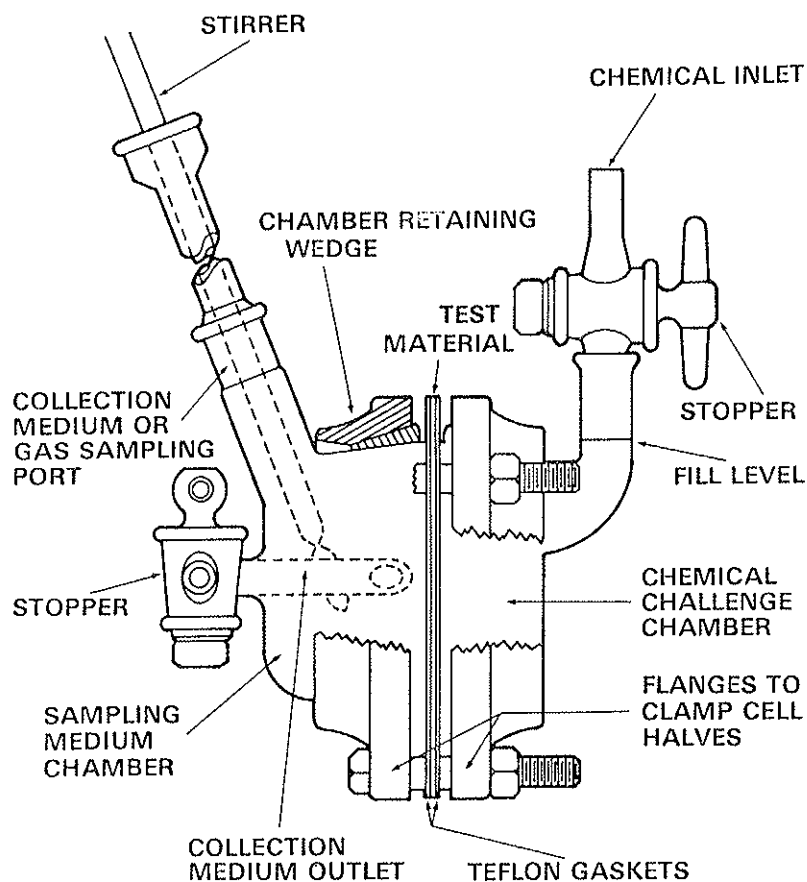


FIGURE 2 PERMEATION TEST CELL

permeation system configuration. Measurement of a minimum permeation rate may provide a workable approach.

The length of the test is decided by the testing laboratory but is most often related to the expected use time of the protective clothing. For chemical protective suits, testing periods range from one to eight hours. However, many suit use recommendations are based on the criterion of no breakthrough of the respective chemical within one hour. The supporting reasoning is that most users in emergency response wear a chemical protective suit for less than one hour due to the limitation of air from the self-contained breathing apparatus, and the severe physiological demands imposed by wearing the suit for that length of time⁽⁷⁾. Some researchers believe that this one-hour period includes a large safety factor because testing involves constant liquid (or gas) contact with material over the entire test period⁽⁸⁾. Both the ASTM and NFPA are considering a minimum test period of three hours; for NFPA, a performance requirement of one hour is being proposed.

Penetration Resistance Testing. ASTM F903 specifies the procedures for measuring the liquid chemical resistance of materials. This method involves subjecting the material to

the liquid at a specified pressure head of 2 psi (13.8 kPa) and noting the time when visible penetration of the liquid occurs. In the penetration test apparatus, the clothing material acts as a partition separating the hazardous liquid chemical from the viewing side of the test cell. This apparatus is pictured in Figure 3. The ASTM method is used to identify protective clothing materials and constructions that limit the exposure to hazardous liquid chemicals. The method is not applicable for measuring vapour penetration. Significant amounts of the chemical may permeate the specimens that pass penetration tests.

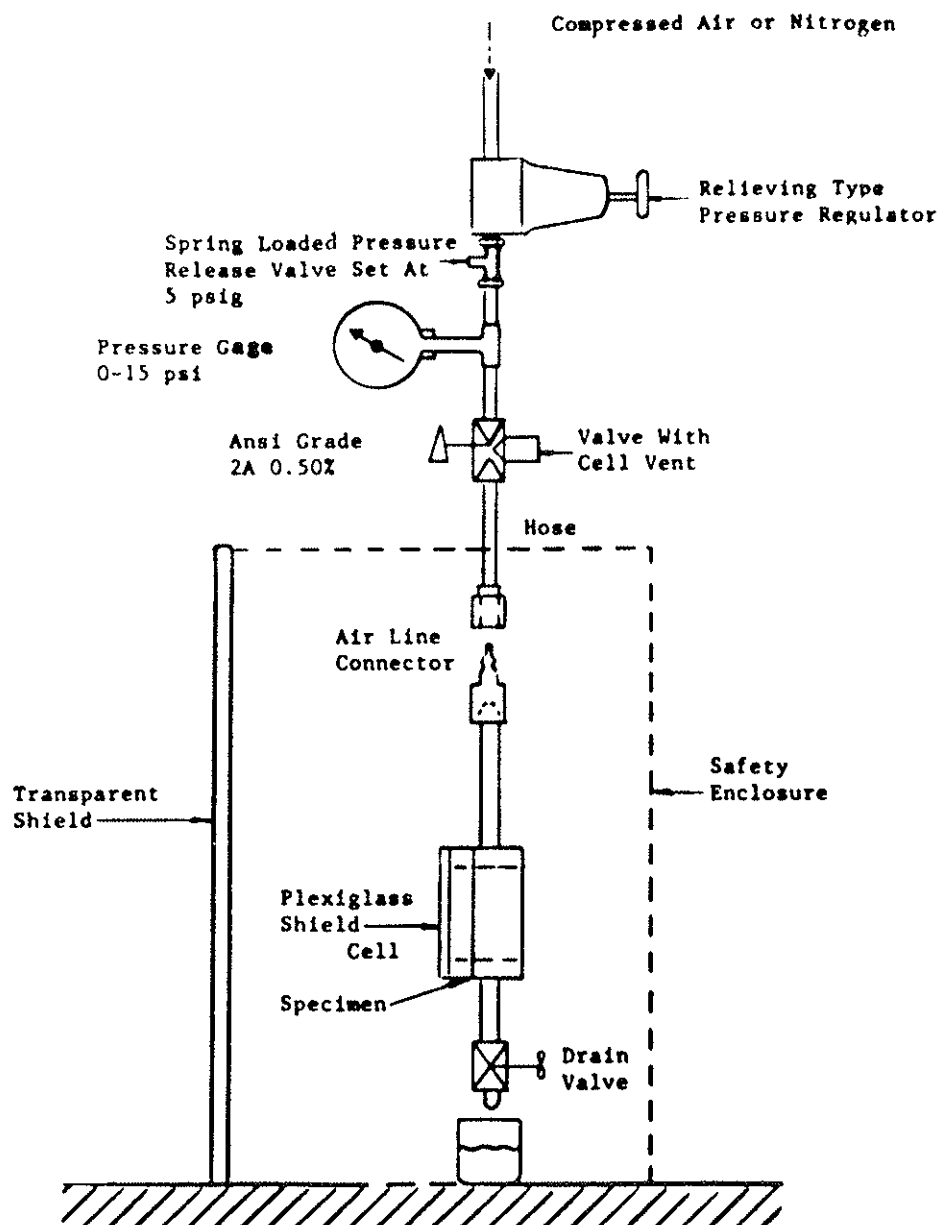


FIGURE 3 PENETRATION RESISTANCE TEST APPARATUS

Selection of Chemicals. To fully evaluate a chemical protective suit's chemical resistance, it would be necessary to conduct testing of all suit materials for all the chemicals a response organization had the possibility of encountering. For the Coast Guard, this would amount to over 1100 chemicals listed in its Chemical Hazard Response Information System⁽⁹⁾. A number of these chemicals can be eliminated by taking into account their chemical state and toxicity. Yet, it is still a nearly-impossible task to test all material and chemical combinations. In order for a standard to be useful, some means of selecting priority chemicals must be adopted.

Both the ASTM and NFPA are engaged in devising standard chemical batteries for testing the chemical resistance of protective clothing materials. ASTM F1001 specifies a standard list of 15 chemicals which represent a wide range of chemical classes and hazards (Table 1). NFPA is considering using the ASTM list with the addition of ammonia and chlorine. Requiring permeation or penetration test results on a minimum number of chemicals would allow comparison of the general chemical resistance performance between different products. However, the chemical resistance limitations of a chemical protective suit must still be determined by testing against the priority chemicals for each respective response organization.

TABLE 1 STANDARD CHEMICALS FOR EVALUATING PROTECTIVE CLOTHING MATERIALS*

Chemical	Chemical Class
Acetone	Ketone
Acetonitrile	Nitrile
Carbon Disulphide	Sulphur Organic Compound
Dichloromethane	Chlorinated Hydrocarbon
Diethyl Amine	Amine
Dimethylformamide	Amide
Ethyl Acetate	Ester
Hexane	Aliphatic Hydrocarbon
Methanol	Alcohol
Nitrobenzene	Nitrogen Organic Compound
Sodium Hydroxide (50%)	Inorganic Base
Sulphuric Acid (93.1%)	Inorganic Acid
Tetrachloroethylene	Chlorinated Hydrocarbon (Olefin)
Tetrahydrofuran	Heterocyclic Ether
Toluene	Aromatic Hydrocarbon

* These chemicals are recommended in ASTM F1001, "Standard Guide for Test Chemicals to Evaluate Protective Clothing Materials"

Selection of Suit Materials. In the past, the practice has generally been to test the primary or garment material of chemical protective suits exclusively. This has resulted in suit use recommendations based on the garment material only without consideration for

the other materials making up the suit. Visors, faceshields, gloves, boots, and garment material seams are areas of chemical protective suits also likely to be exposed during a chemical incident. The dimethylamine spill in Benicia illustrates this point. Other major materials used in the construction of the suit or together with the suit must be evaluated in the same manner as the garment material. Thus, recommendations for using chemical protective suits must be based on the chemical resistance of all major materials with the chemical resistance of the weakest material being the limiting factor. If a breathing apparatus is worn outside the chemical protective suit, or if airline hoses are employed, the external materials of these items should be subjected to the same tests as the suit materials.

Proposed Documentation and Performance Requirements. Documentation requirements for chemical resistance testing should include either permeation or penetration testing as appropriate against a limited number of representative chemicals. Standards must go on to specify how the different tests are conducted. For example, ASTM F739 could be recommended for measuring permeation resistance with the qualification of a minimum detection limit of 1 ppm and three-hour test period for each material-chemical combination tested. These tests should be performed for every major material used in fabricating the garment including at least the garment, visor (faceshield), glove, and boot materials. The main purpose of such a documentation requirement is to allow users to compare products with the same information. This would also let users assess a chemical protective suit's ability to resist mixtures and unidentified chemicals.

Performance requirements for chemical protective suits should be chemical specific. If standards are used to support the quality of products used in chemical spill response, the chemical resistance performance requirements should reflect the needs of response organizations. Furthermore, it should be left to the users and the manufacturers to determine the chemicals for which a suit must meet the performance requirements. For these reasons, a generic performance requirement is recommended such as "no permeation breakthrough (for vapour-protective suits) or detectable penetration (for liquid-protective suits) in one hour". Like the documentation standard, the performance requirement must define the test method and parameters (i.e., minimum detection limit). In this manner, the manufacturers can logically choose which chemicals to test their products against based on expected performance and user demand. Additionally, incentive is provided to manufacturers to test as many chemicals as possible to market their products. Following this approach, the end result will be a list of chemicals associated with each chemical protective suit with compliance based on standardized testing.

Additional chemical resistance requirements apply to other suit components which are not flat sheet materials that easily lend themselves to the methods previously discussed. These include suit seams, the suit closure, gaskets, and vent valves. Suit seams can be tested for both permeation and penetration using the standard methods; however, special gaskets must be used with the permeation test cell to prevent leakage along the non-uniform profile of the suit seam. Suitably sized specimens and test cells must be fabricated to perform penetration testing on the suit closure. Suit gasket materials may be tested as sheet materials. As with other materials, the performance of these components should be considered in understanding the limitations of chemical protective suits. Suit seams should possess chemical resistance at least equal to the garment material itself.

To this point, all recommended testing has been proposed for virgin materials. Users need to know how the materials will perform following actual use. One way of providing an indication on how suit material chemical resistance changes with wear is to test the materials after some form of physical abuse. Early proposals recommended creasing materials, then subjecting the creased materials to either the permeation or penetration resistance tests. More recent ideas include the use of standard material flexing devices which perform reproducible mechanical actions such as the Gelbow tester specified in U.S. Federal Standard 101C, 2017. The chemical resistance performance of the flexed garment material could then be compared with pristine samples. A radical decrease in performance would indicate the high probability of material failure in the field. Crude testing of this nature has already been performed for a number of materials against methyl isocyanate. In one case, a virgin material sample demonstrated a permeation resistance of eight hours, but this fell to ten minutes when the samples had been creased⁽¹⁰⁾.

Physical Property Requirements

Both ASTM and NFPA are only in the early stages of identifying which physical properties are meaningful to users. Several standard methods for measuring material physical properties are available in the form of ASTM, NFPA, and U.S. Federal Standards. Most of these test standards involve testing particular material types (textiles, elastomers, plastics, and coated fabrics) as opposed to materials for specific applications. The difficulty in using many existing methods is relating test results to expected field conditions. For example, the way in which material tensile (or breaking) strength is measured is by noting the force required to pull the material apart in tension. This action may or may not have an equivalent phenomenon in the field. Therefore, physical property test methods must be chosen which simulate the wear conditions expected by chemical protective suit users.

Efforts are underway in both ASTM and NFPA to classify physical properties in categories of material strength, integrity, and durability. One recommended battery of tests is provided in Table 2. Different materials in the chemical protective suits will have certain properties associated with the function of the material in the design of the suit, such as light transmission characteristics for suit visors. Of great concern to suit users is the ability of protective suits to withstand field hazards such as tears, cuts, punctures, and abrasion. Material integrity may be examined by testing materials for tensile or bursting strength, and hydrostatic resistance. These same integrity tests should be applied to suit seams and closures which should demonstrate at least the same performance as the garment material. Material aging might be evaluated through methods for measuring resistance to UV light, ozone, and heat degradation. Other properties such as stiffness can be measured under varying temperature to determine low or high temperature performance. Flame resistance is another important property of concern to users.

A single method for each of the relevant properties that can accommodate the different types of materials used in chemical protective suits should be identified. Selection of a single method encourages standardization of physical property testing by manufacturers and material suppliers. It also allows users to compare material characteristics of various similar products. Nonetheless, the choice of a single method for each physical property is difficult. Chosen methods must not only allow testing of different material types

TABLE 2 RECOMMENDED BATTERY OF PHYSICAL PROPERTY TESTS FOR CHEMICAL PROTECTIVE SUIT MATERIALS

Physical Property	Test Method
Garment Material	
Abrasion Resistance	ASTM D3386
Bursting Strength*	ASTM D3786
Cut Resistance	ASTM F23.20.01 (draft)
Flammability	ASTM D568
Flexural Fatigue	FED STD 101C, 2017
Hydrostatic Resistance	ASTM D751
Puncture Resistance	ASTM F23.20.02 (draft)
Stiffness (with temperature dependence)	ASTM D1043
Tear Strength	ASTM D751
Tensile Strength*	ASTM D751
Visor Material	
Distortion	ASTM D881
Impact Strength	ASTM D3029
Light Transmission and Haze	ASTM D1003
Scratch Resistance	ASTM F548

* these tests can also be used to determine the strength of suit seams and closures.

(plastic film versus coated fabric), but must also discriminate between the qualities of each material. For example, some protective clothing materials become stiff and brittle in cold temperatures. The application of a cold temperature bend test (ASTM D2136) shows these materials passing at -25°C . In this case, the method does not support the observed phenomena and does not discriminate material cold weather performance. However, two methods (ASTM D1043 and FED STD 191A, 5202) show significant cold temperature differences in material performance and can be related to field experience⁽¹¹⁾. Test methods can only be chosen by comparing test results for a number of different representative materials. In this manner, problems with the test method can be noted and modifications made for measuring the appropriate parameters.

The choice of performance requirements versus documentation requirements for material physical properties depends on how relevant the material characteristic is to field performance and how much the property varies among materials. Most current material physical property specifications are found in military standards for related types of clothing. The basis for many of these requirements is unclear. Minimum material performance in terms of physical properties should only be established when the material characteristic is closely related to physical phenomena that the method attempts to measure. In any case, most material physical property requirements are arbitrary. One benefit of their use is to encourage improvement of materials in terms of strength, durability, and other characteristics.

Component Function Tests

Suit exhaust valves are used in most vapour-protective suits to allow venting of exhaust air from the self-contained breathing apparatus worn inside the suit. These valves are constructed of materials with relatively poor chemical resistance and uncertain performance. Manufacturers employ valves with cracking pressures ranging from 0.025 to 0.75 kPa (0.1 to 3.0 inches water gauge pressure) on totally-encapsulating chemical protective suits to maintain a small positive pressure inside the suit. It is assumed that this positive pressure prevents the diffusion of hazardous vapours into the suit via poor seams, closures, or worn material. Little testing has been conducted to determine the performance characteristics of suit exhaust valves. It is not known, for example, whether different types of valves are truly one-way, preventing negative pressures in the suits and the backflow of chemical through the valve(s), and how different operating pressures may affect this performance. Understanding the performance of these components requires that standard techniques be established. The Coast Guard is sponsoring a study to examine the performance differences between valves using a two-chambered test apparatus with a breathing machine⁽¹²⁾. One side of the chamber acts as the outside environment with a challenge chemical, while the other side represents the interior of the suit. This testing will provide the basis for both comparing and improving suit exhaust valves.

Other component functional tests may be applied to suit closures, fittings, or accessories. Suit closures, like seams, should offer the same protective qualities as the garment material. As previously described, closure performance can be ascertained through chemical resistance and physical integrity testing. This testing, however, should also be performed after the closure has been operated several times because of wear that can change the performance characteristics of the closure. Many manufacturers employ splash covers for both suit exhaust valves and closures. These covers are either flaps of materials or inverted pockets which protect sensitive suit components from direct impingement of liquid splashes. Specification of splash covers to protect these components may be one area where design requirements are justified.

Overall Suit Testing

Only a few methods exist for evaluating the complete protective garment. These methods can be classified in the categories of garment pressure (inflation) testing, qualitative leak testing, and manned suit functionality testing. Variations in the methods for each category exist; some methods are more quantitative than others. Only draft standards have been proposed for garment pressure testing and qualitative leak testing. These methods are only applicable to vapour-protective clothing. There are no current tests for evaluating the integrity of liquid-protective clothing in preventing liquid penetration through the total garment. Possible tests include using chambers outfitted with nozzles to spray liquid (water) against a suit ensemble dressed on a mannequin. Penetration might be qualitatively measured by using a dye in the liquid to stain special garments worn on the mannequin underneath the suit, or water (moisture) sensors in the mannequin itself.

Garment Pressure Testing. The most widely used methods for assessing chemical protective suit integrity involve the practice of inflating the suit to determine leakage.

Pressure testing measures the integrity of the suit and visor material, suit seams, and suit closures for gas-tightness. In the test, the suit is inflated to a specified pressure and either the pressure drop is measured over time, or a soap solution is applied to the outside of the suit for observing the appearance of bubbles (to detect leaks). The suit exhaust valves must be closed (or plugged) to perform the test, and a provision must be made for attaching a pressure gauge. Some manufacturers specify the pressure to which the suit should be inflated. The proposed ASTM method (F23.50.01) specifies a maximum inflation pressure 0.75 kPa (three inches water gauge pressure), a test pressure 0.5 kPa (two inches water), and an allowable pressure drop (20%) over a three minute period. It also requires using the soap solution to locate leaks if the suit does not meet the pass/fail criteria. The method is illustrated in Figure 4 and appears very sensitive to small leaks in the garment. Tests with representative suits show that suits failing the ASTM pressure test give high protection factors from qualitative leak testing described in the following⁽¹³⁾. Pressure testing is well suited as a performance requirement for individual suit quality assurance by manufacturers.

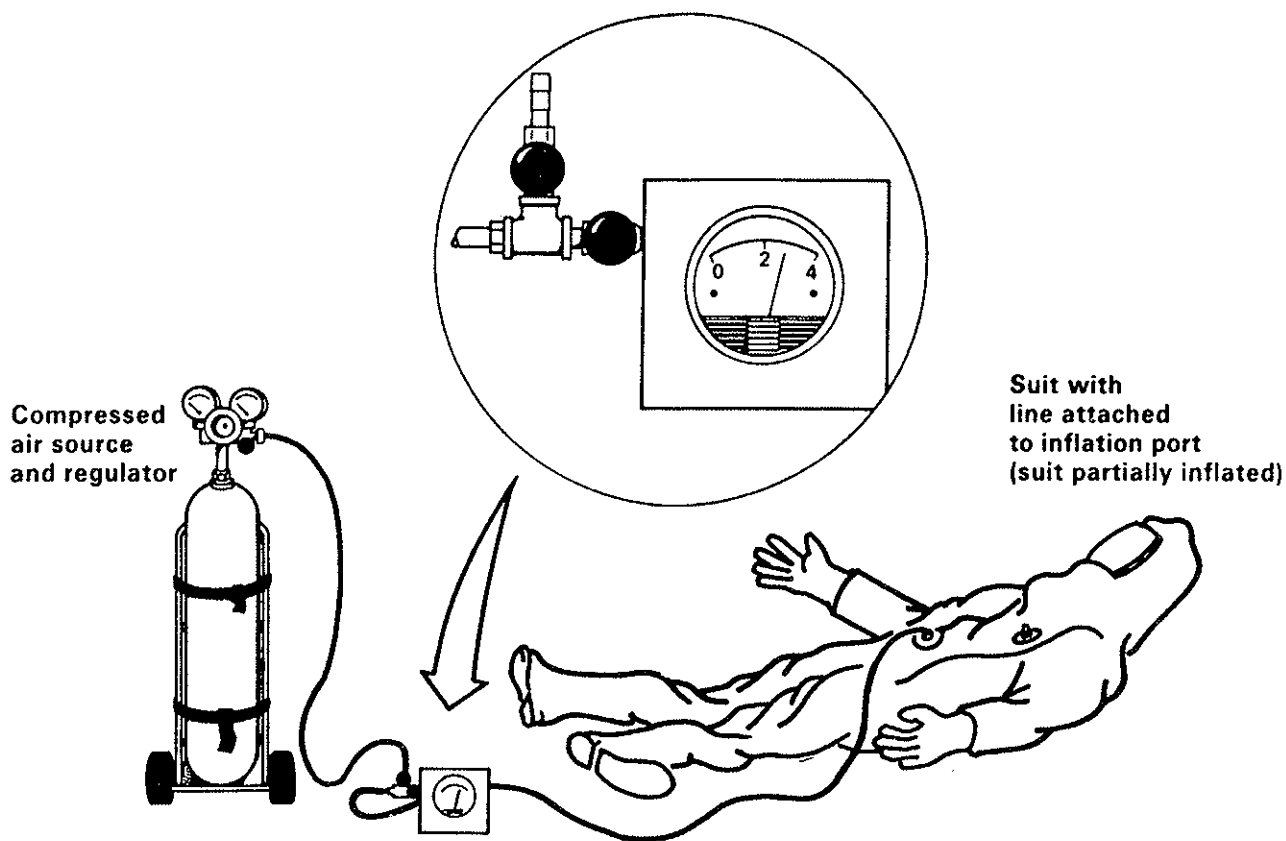


FIGURE 4 RECOMMENDED PRESSURE TEST APPARATUS AND TYPICAL TEST CONFIGURATION

Qualitative Leak Testing. Qualitative leak testing measures the integrity of the entire chemical protective suit to a gaseous or aerosol challenge agent in a manner simulating actual use. This testing involves the exposure of a test subject wearing the suit and a self-contained breathing apparatus in a closed chamber, and measuring the gas challenge agent concentration both inside and outside the suit. The proposed ASTM method (F23.50.02) employs ammonia gas at a concentration of 1000 to 2000 ppm and lengths of stain detection tubes. The test subject also engaged in a series of exercises to test the suit under dynamic conditions. This test was principally designed as a field test and would be difficult to use in manufacturing quality control because of its qualitative nature.

Other variations of this method may use different gases or aerosols (at non-toxic concentrations) and the appropriate methods. Dependent on the means used to measure the concentration of the gas, the test can be qualitative, semi-quantitative, or quantitative. When the concentration methods are both precise and extend over a large detection range, the results can be used in a semi-qualitative manner by rationing the external to internal challenge agent concentrations to calculate a "protection factor". Large protection factors are indicative of high suit integrity. The measurement of protection factors is a widely used practice for assessing breathing device integrity. During these tests suit pressure can also be monitored to determine if relative pressures become negative to allow penetration of the challenge agent.

Manned Functionality Testing. Manned suit testing is often performed to determine the range of activities that a user can do while wearing the chemical protective suit and a breathing apparatus. These may include different types of exercises or tasks which simulate the end application of the chemical protective suit. Results from these tests are generally subjective regarding the design, comfort, and fit of the garment. Measurements of the wearer's physiological condition (e.g., core temperature, skin temperature, heart rate, and blood pressure) during this testing serve as a means for quantifying the physical stress on the wearer when compared to the same tests of the subject not wearing the suit. One study of this type has already demonstrated significant physiological differences for the wearing of different chemical protective suits⁽¹⁴⁾. These tests are subjective and not reproducible; therefore, they are not appropriate for manufacturing performance standards. Nevertheless, this testing is ideal for user acceptance testing or evaluations to compare different products.

Conclusions

Once standards are developed, protective clothing users will be able to examine a garment for compliance labels and know if the garment meets the minimum requirements of either ASTM or NFPA. The ASTM documentation standard will allow a user to compare chemical protective suits with the same information from product to product. The NFPA minimum performance standard would provide a suit user with some confidence that the product "passes" specific tests to provide a minimum level of performance. Collectively, the standards should provide incentives to manufacturers to improve their products and allow a framework within the marketplace to encourage competition.

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