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Revised

Research for Investigating the Effectiveness of Solid Sorbents in Detecting Small Levels of Permeating Low-Volatility Organic Chemicals

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Final Report

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INTRODUCTION

The selection of chemical protective gloves is based on many factors, including barrier performance against chemicals, physical hazard resistance, effect on hand function, and cost. In nearly all instances of use, significant tradeoffs between worker protection and productivity are involved for any glove use as the wearing of gloves diminishes worker dexterity and tactility as well as significantly reducing hand comfort [1,2]. These tradeoffs can often result in improper wearing practices and failure to use gloves, when needed. Therefore, it is critically important that gloves provide the best fit, offer the greatest comfort, and create the least interference with hand function. The appropriate selection of gloves must therefore involve optimizing the human factor aspects for gloves against the need for providing minimum protection.

Part of the optimization process for glove selection must account for choosing the appropriate barrier protection against chemical exposure. The current practices for measuring glove material permeation resistance according to those established by test method American Society for Testing and Materials (ASTM) F739 do not always reflect this perspective of optimization. This is because this test method involves conditions that do not replicate actual wearer exposures and the types of measurements typically reported to do not allow end users to assess exposure. Instead, permeation testing is most often performed with ‘neat’ chemical over a relatively long-term exposure (usually up to 8 hours) and the testing does not entail evaluating all aspects of the glove performance, particularly as related to evaluating the entire exposure area accounting for repeated flexing, surface contact, and wearing degradation of gloves during use [3]. Limited research has shown that glove performance in use can be dramatically different than predicted by permeation testing [4,5]. Measurements of breakthrough time commonly used to support glove selection decisions through permeation testing are an arbitrary means to compare glove material performance against specific chemicals but offer no information about skin exposure to chemicals. A more useful measurement to report would be the cumulative permeation of a chemical that occurs over a given exposure period [6]. This measurement can then be related to levels of skin contact that could be permitted specific to the chemical.

The evaluation of glove performance from in-use measurements of permeation may offer a more appropriate means for determining the minimum necessary barrier performance of gloves and glove materials. This is especially true for organic chemicals that are not easily detected in conventional permeation tests. Many of these chemicals have low water solubility and low volatility but yet have been observed to permeate many types of gloves [7]. Thus, the availability of techniques to measure permeation of low volatile, low water soluble chemicals through gloves under conditions of actual use can offer the potential for not only monitoring worker exposure, but also provide the basis for determining the appropriate minimum protection.

This final report covers specific work requested by the National Institute for Occupational Safety and Health (NIOSH) for evaluating the effectiveness of absorbent materials used under gloves against specific chemicals and under defined exposure conditions, including the application of pressure. It is part of a comprehensive series of investigations sponsored by NIOSH to examine the use of solid sorbents and colorimetric indicators as a means for measuring glove material permeation resistance.

STUDY APPROACH

The technical approach shown in Figure 1 was used for carrying out this study. The study was broken into three primary tasks with each further divided into several related subtasks to establish the work breakdown structure shown in Figure 1:

This work structure was intended to provide a manageable approach to the work effort by specifically addressing separate, but related parts of the task assignments. Further detail on each task and subtask is described below.

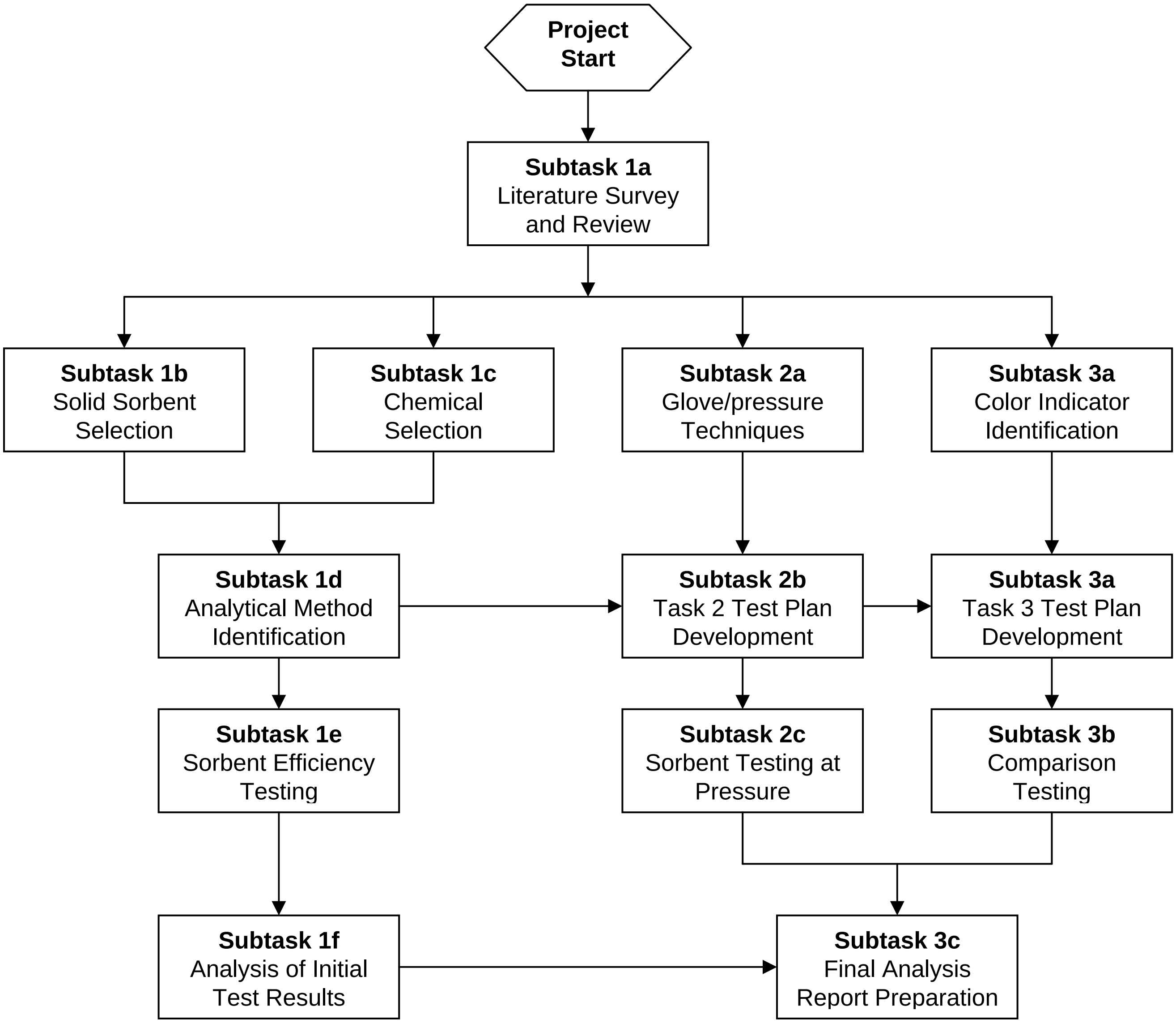

Figure 1 – Project Work Breakdown Structure

Task 1 – Evaluation of Solid Sorbent Efficiency

The first task involved a series of experiments to examine the efficiency and effectiveness of selected solid sorbent media in retaining selected semi-volatile chemicals. The following subtasks were established for this effort:

- Subtask 1a – Literature Review of Solid Sorbent Technologies
- Subtask 1b – Selection of Solid Sorbent Media
- Subtask 1c – Selection of Test Chemicals
- Subtask 1d – Identification of Analytical Methods
- Subtask 1e – Efficiency Testing of Solid Sorbents
- Subtask 1f – Analysis of Test Results

Literature Review of Solid Sorbent Technologies. Several literature sources were reviewed in the both the proposal preparation and during the early part of the project. An extensive literature search was conducted to collect information about different solid sorbent technologies and to account for past research for characterizing the effectiveness of solid sorbents in capturing low concentration exposures of semi-volatile chemicals. The objectives of the literature review were to:

1. Identify solid sorbent material candidates
2. Provide information for the selection of chemicals
3. Provide information to enable the development of procedures for using contact pressure
4. Identify colorimetric indicators

In conducting the literature survey, searches of key journals were made, including:

- American Industrial Hygiene Association Journal
- American Journal of Industrial Medicine
- American Society for Testing and Materials Special Technical Publications
- Applied Occupational and Environmental Hygiene
- Contact Dermatitis
- The Analyst
- Toxicological Letters

Literature information was collected through a variety of means, including the use of computerized literature searches, review of periodical indices, and direct solicitation of information through selected journals or publications. The results of this literature search are presented in the Literature Review Findings section of this report. Other results were used in forming the decisions in how the research in this study was to be conducted.

Selection of Solid Sorbent Media. A number of solid absorption materials were identified based on a review of the literature and suggestions provided in the NIOSH Statement of Work. For this study, three different solid sorbent materials were chosen for the study to permit an evaluation of their effectiveness against selected chemicals. The sorbents were selected to represent different sampling technologies and on the basis of prior success in their application for sampling under protective clothing.

Selection of Test Chemicals. Chemicals were selected in this study that are classified as semi-volatile. For the purpose of this study, semi-volatile chemicals were defined as liquid chemicals having vapor pressures at or below 5 mm Hg. As with the selection of sorbents, a strategy was employed to choose chemicals representing different chemical classes. This strategy was based on chemicals having known skin toxicity or sensitization properties, the types of analytical procedures used for their quantitative detection, the availability of colorimetric indicators for their qualitative detection, and the extent of permeation data for determining performance against a range of glove material products.

Identification of Analytical Methods. Following the selection of sorbents and chemicals, techniques were selected to evaluate the ability of the sorbents to adsorb the respective chemicals. These techniques included the manner in which the sorbents would be exposed to chemicals, the method of extraction, and the analytical procedures used for determining the mass of adsorbed chemical. In general, an attempt was made to use similar techniques for exposed sorbent materials and conducting their extraction to provide a consistent basis for comparing sorbent effectiveness. Analytical procedures were specific to the chemical, though a singular technique was found appropriate for each of the three chemicals evaluated in this study. The combination of chemical exposure techniques, extraction methods, and analytical procedures formed the test plan for conducting Task 1 testing.

Efficiency Testing of Solid Sorbents. Task 1 testing was carried out with three different sorbents, three chemicals, three chemical exposure (spiking) masses, and analytical techniques decided above forming a 3 x 3 x 3 test matrix. Replicate tests were conducted for each solid sorbent /chemical combination to assess precision of the selected techniques. Controls were also used to determine the appropriateness of study selection. Determinations were then made to establish the recovery of test chemicals from each sorbent material. The collection efficiencies and other findings were then tabulated and plotted to gain an understanding for lower and maximum limits of chemical exposures and the linearity of the sorbent material response.

Analysis of Test Results. The findings from the efficiency testing were made to determine the relative effectiveness of each sorbent as media that could be used underneath protective clothing for measuring exposure levels. This information was further used in designing experiments for Task 2 and Task 3 testing.

Task 2 – Determination of Contact Pressure Effects on Solid Sorbent Efficiency

Task 2 examined the application of the solid sorbent/chemical combinations to glove use and the effects of contact pressure. This task was divided into the following three subtasks:

- Subtask 2a – Selection of Pressure Application Method
- Subtask 2b – Development of Task 2 Test Plan
- Subtask 2c – Efficiency Testing of Solid Sorbents Under Pressure

Parts of Task 2 were conducted in parallel with Task 1.

Selection of Pressure Application Method. During the literature review, methods for ascertaining the effects of pressure on protective clothing use and specific analytical techniques for applying pressure during glove permeation testing were assessed. From this information, a specific technique to be utilized in the study was identified and decisions were made for the respective pressures to be applied through testing.

Development of Task 2 Test Plan. A test plan for evaluating the sorbents against the selected chemicals was established. This testing employed the same sorbents, chemicals, extraction methods, and analytical procedures selected in Task 1, but involved a different means for contacting the sorbent with the chemical. Research was conducted as part of the literature review to determine glove materials which would provide suitable permeation rates for each of the three chemicals. The test approach further established a means for providing chemical contact with a glove material over the selected sorbent with the application of pressure. Some initial experiments were conducted to assist in setting test parameters, such as the length of the testing that would yield quantifiable results.

Efficiency Testing of Solid Sorbents Under Pressure. Once the procedures were set, the solid sorbent/chemical combinations tested in Task 1 were evaluated at the three different pressures established in the test plan. Collection efficiencies and permeation determinations were then determined for each test.

Task 3 – Comparison of Solid Sorbents with Colorimetric Indicators

The last task involved comparing solid sorbents with colorimetric detectors. Specific subtasks for this task included:

- Subtask 3a – Identification of Colorimetric Indicators
- Subtask 3b – Development of Task 3 Test Plan
- Subtask 3c – Comparison Testing of Solid Sorbents with Colorimetric Indicators
- Subtask 3d – Preparation of the Final Report

Since the application of colorimetric indicators was independent of the Task 2 experiments, this work was done simultaneous with Task 2.

Identification of Colorimetric Indicators. The literature survey was used to help identify different colorimetric detection technologies that could be applied underneath gloves. While an attempt was made to identify different colorimetric technologies, the best prospects found the Perma-Tec™ sensor products from Colorimetric Laboratories, Inc. to offer the easiest application and most suitable use for future field studies. Other colorimetric indicator approaches were reviewed and discussed, but the use of the Perma-Tec™ sensor products offered a uniform approach for evaluating the effects of pressure against the solid sorbents.

Development of Task 3 Test Plan. To provide the same basis of exposure and permit comparison between the two media, nearly identical techniques were used for exposing colorimetric indicators as used for the selected sorbents. This work was done with the application of the same pressures selected in Task 2. Other than the use of the colorimetric detector in place of the sorbent and application of subsequent analytical determinations, the difference in approach used for Task 3 was that each colorimetric detector was specific to a single chemical in the study. This is in contrast to each of the sorbents being used for each chemical in Tasks 1 and 2

Comparison Testing of Solid Sorbents with Colorimetric Indicators. The Task 3 testing was carried out according to the test plan and the results were provided as detection or no detection on the basis of indicator color changes. This information was compared with the analytical results obtained in Task 2.

Preparation of Final Report. This report provides a summary of the methods and findings throughout the study. This report includes:

- Relevant literature review findings
- Basis for selection of solid sorbent materials and test chemicals
- Descriptions of analytical procedures
- Test results and discussion

Conclusions and recommendations are offered for the relative effectiveness of selected sorbents and colorimetric indicators under the conditions used in this study.

LITERATURE REVIEW FINDINGS

The literature review was undertaken to investigate prior research and practices as related to the use of solid sorbents for measuring permeation through protective clothing materials and other factors related to the design of the study. It was particularly important to determine the range of solid sorbents that have been used in past investigations, the conditions for their use, and the types of results that had been obtained for the evaluation of sorbent effectiveness against different chemicals. This information was then used to:

- Help select the types of solid sorbents to be used in the study
- Identify study parameters for the evaluation of the selected solid sorbents
- Provide criteria for the selection of semi-volatile chemicals to be considered
- Consider specific analytical techniques for quantifying sorbent capture of chemicals
- Establish pressure conditions to be applied to the sorbents

The findings from the literature review are organized in four sections:

1. Permeation testing practices and testing of semi-volatile chemicals
2. Use of sorbents in permeation testing
3. Use of sorbents for chemical detection for skin exposure
4. Application of pressure during protective clothing use

The pertinent literature reviewed is described below. Other findings are provided in the sections discussing specific methods later in the report.

Permeation Testing Practices and Testing of Semi-volatile Chemicals

In the United States, permeation testing is conducted according to ASTM F739, *Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact*. This test method was first established in 1981 and has been extensively applied by the protective clothing industry in reporting the chemical resistance of their products [8]. The method establishes a test cell where the clothing material specimen is mounted dividing the test cell into two hemispherical halves. One half of the test cell serves as the "challenge" side where chemical is placed for contacting the material chamber. The other half is used as the "collection" side that is sampled for the presence of chemical permeating through the material specimen. The basic procedure in each test is to charge chemical into the challenge side of the test cell and to measure the concentration of test chemical in the collection side of the test cell as a function of time.

Material permeation resistance is generally characterized using two test results: breakthrough time and permeation rate. Breakthrough time is the time that chemical is first detected on the 'interior' side of the material. As discussed below, its determination is strongly dependent on how the test is configured and the sensitivity of the detector. Permeation rate is a measure of the mass flux through a unit area of material for a unit time. Permeation rate is most commonly expressed in units of micrograms per square centimeter per minute ($\mu g/cm^2 min$). For a given material-chemical combination, the steady-state or maximum observed permeation rates are reported.

Figure 2 shows the typical permeation curve. From this illustration, two different approaches to interpret breakthrough time are shown. One is to simply record the time at which the chemical detection first occurs; while the other involves normalizing the breakthrough time at a specific permeation rate (usually to 0.1 µg/cm^{2}min) to yield different "breakthrough detection times," shown in the figure as BDT1 and BDT2, respectively. Actual breakthrough time is designated "BT," which is the time at which the first molecules penetration, though this may be below the ability of the analytical method to detect permeation.

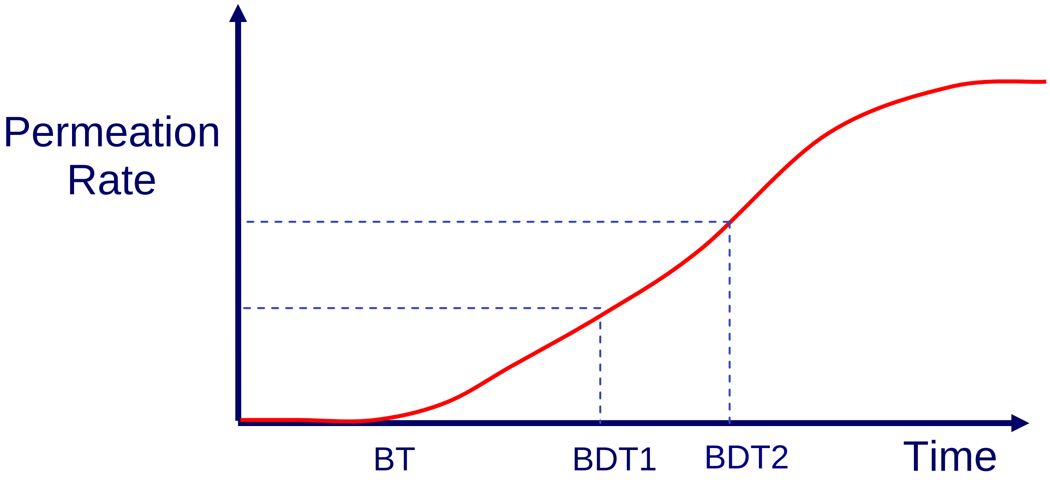

Figure 2 – Interpretation of Permeation Breakthrough Time

It is also possible to determine the cumulative permeation of chemical that occurs, although this practice is less followed in the industry. ASTM F 1383, *Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact,* is a variant of ASTM F739 that establishes procedures for intermittent contact for liquid and gaseous chemicals with clothing materials for permeation testing. The use of intermittent exposure conditions gives rise to permeation curves with a cyclic appearance (see Figure 3). As a consequence, breakthrough time with cumulative permeation is reported in lieu of permeation rate for these tests. Schwope et al. [9] illustrated this behavior for a number of material-chemical combinations and found the cumulative permeation to be proportional to the relative exposure time. Man et al. [10] compared permeation breakthrough times of protective clothing materials against specific chemicals using liquid contact, liquid splashes, and vapors. Their findings showed significant differences between the different exposure conditions for some combinations of materials and chemicals, but lesser changes in breakthrough time for other material-chemical sets. They postulated that the different wetting characteristics of the test materials contributed to this phenomenon indicating that materials easily wet by a chemical may show similar permeation for liquid splash exposures as with continuous liquid exposure.

Cumulative permeation measurements are often reported when evaluating highly toxic chemicals, such as chemical warfare agents. Specific test protocol have been established by the U.S. Military to measure chemical agent permeation where the cumulative mass per unit area is used as the basis for establishing acceptable material performance [11]. This practice has been further implemented as part of the National Fire Protection Association standards on emergency protective clothing [12].

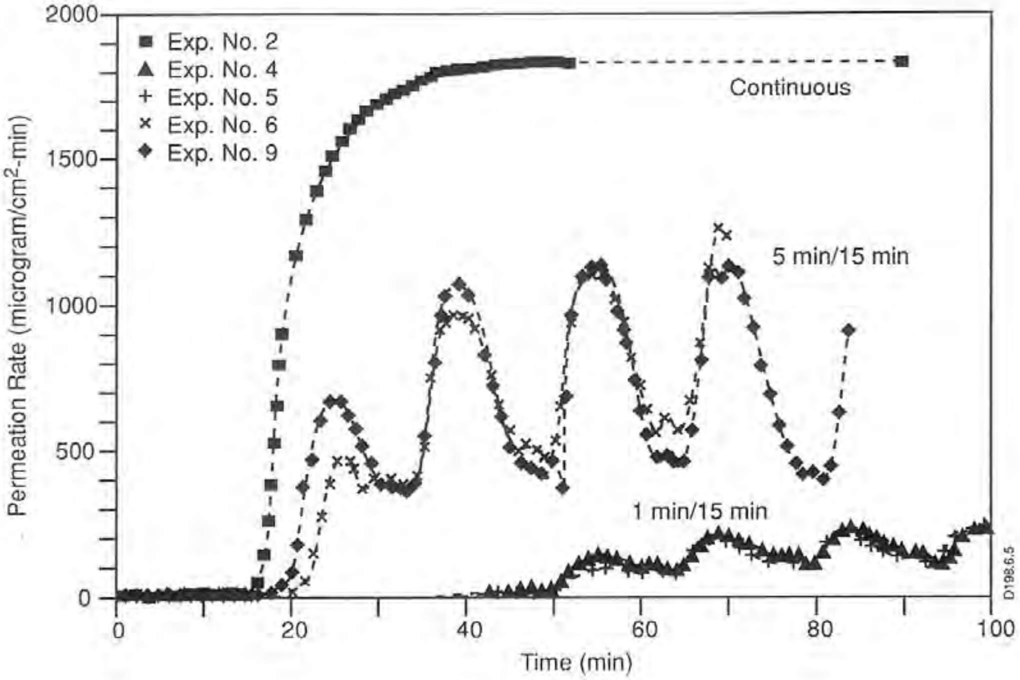

Figure 3 – Cyclic Permeation Observed During Permeation Testing Involving Intermittent Contact [9]

While the ASTM F739 establishes a number of parameters for the test, the method permits flexibility in the choice of test system configuration, the collection medium, sampling rate, and analytical methods. Tests may be conducted either in an open loop (with a gas or liquid collection medium passed through the collection side of the test cell directly to the test system) or closed loop configuration, where the collection medium is maintained inside the collection side of the test cell. Closed loop permeation systems tend to provide an easier means for assessing cumulative permeation. Air, nitrogen, helium, and water are common collection media. In general, these collection media have no effect on the clothing material and are amenable to most analytical techniques. However, in cases where the test chemical has a relatively low vapor pressure, gaseous collection media may have inadequate capacity for the permeant requiring a different choice of collection medium. Similar concerns arise for test chemicals having low water solubility when water is the collection medium. These situations have been addressed by circulating large volumes of fresh gas or water through the collection chamber; however, this practice dilutes permeant concentration in the collection medium and reduces test sensitivity [13].

Some test chemicals exhibit both low water solubility and vapor pressure. Chemicals with these characteristics generally include pesticides and higher molecular weight chemicals such as polynuclear aromatics and polychlorinated biphenyls. One approach for conducting permeation tests with these chemicals has been to use solid collection media [7,14,15]. This technique involves placing a solid, highly absorbent film directly against the material specimen. Ehntholt [14,15] designed a special test cell using a silicone rubber material for collection of pesticides. Unfortunately, the silicone rubber was reported to be a poor sorbent and the technique was considered labor-intensive, involving multiple replicates to determine breakthrough times, and subject to cross-contamination [16]. In addition, swelling of the test material can prevent uniform contact of the specimen with the solid collection medium. An alternative approach described by Pinnette and Stull [16] and Swearengen et al [17] used a liquid splash collection. In these approaches, a solvent media is briefly contacted with the material specimen on the collection side and the extract evaluated for the chemical(s) of interest. This approach is also considered labor intensive and its overall collection efficiency has not been fully validated. When this approach is followed, it first must be demonstrated that the solvent does not affect the barrier properties of the test material. For example, absorbance of the splash solvent from the collection medium into the test material can cause sample swelling and affect challenge chemical permeation. A third approach was used by Spence [18] for permeation testing with halogenated pyridines. His technique employed a technique for concentrating the permeant in the collection medium. Other researchers have used radioisotope labeled chemicals to assist in determining permeation of low volatile, low water soluble chemicals [19].

Use of Sorbents in Permeation Testing

Difficulties in correctly quantifying permeation of semi-volatile chemicals have resulted in further research for using sorbents as collection media. Palmes and Johnson examined a technique involving permeation of lindane through a thin polyethylene membrane with capture of the pesticide by polyurethane foam for later analysis [20]. While specifically not used for permeation testing, this research showed the potential for using a solid sorbent media for measuring permeation.

A series of investigations have demonstrated the efficacy of using specially created sorbent pads from Colorimetric Laboratories (Des Plaines, IL) for the determination of permeation of different chemicals through protective gloves. Vo and Berardinelli performed permeation testing against triethylamine using Perma-Tec™ aliphatic amine pad in combination with a microwave-extraction technique coupled with gas chromatographic analysis [21]. They were able to demonstrate recoveries of 63 to 90% over the range of 0.2 to 1.0 µL of chemical applied to the pads and successfully measured permeation of triethylamine with this technique for six different glove styles yielding breakthrough times of 40 seconds to greater than 4 hours. Permeant concentrations were found to be approximately 100 µg/cm^2. A similar study involved a quantitative study of aniline through gloves using Perma-Tec™ aromatic amine pads [22]. Recoveries ranging from 65 to 89% percent were found for volumes of 1.1 to 1.9 µL, while the use of the pads was able to discriminate breakthrough times from 182 seconds to 82 minutes with cumulative permeation measuring at 0.53 to 0.55 µg/cm^2. More recently, Vo evaluated a new pad specifically developed for the detection of organic and inorganic acids through glove materials [23]. The new acid-based pads, which use a reagent responding to acid contamination by exhibiting a color change, were demonstrated against propionic acid, and acrylic acid for a number of gloves. The adsorbent pads showed recoveries of 52-72% over a spiking volume range of 0.2 to 1.8 µL and provided breakthrough detection as low as 260 and 270 µg/cm^2 cumulative permeation for propionic acid and acrylic acid, respectively. Vo et al then evaluated the new indicator pads in conjunction with a thermo-hand system, which simulated material flexing and provided acid exposure replicating skin temperature and humidity conditions [24].

The use of 3M Empore sorbent filters (porous polymer extraction disks) based on a C18 resin was evaluated for determining chemical permeation for four different solvents against five protective glove materials [25]. The researchers were able to demonstrate that the filters adsorbed better than 98% solvent and show solvent recoveries ranging from 72 to 94 percent for all solvents for applied volumes ranging from 0.2 to 1.8 µL. By using infrared (IR) spectroscopy as the standard method to determine the breakthrough time of the different solvents, the simultaneous exposure of the sorbent filters at breakthrough was used to compare sensitivity to permeating chemical. The study showed sorbent filter detection of permeation at cumulative permeations ranging from 150 to 580 $\mu g/cm^2$ at the time IR detection occurred. This information was able to establish the advantage of the sorbent filters as a collection media for a number of low volatility chemicals.

Use of Sorbents for Chemical Detection for Skin Exposure

A variety of different methods have been used to characterize levels of skin exposure for workers involved in chemical handling. Dermal exposure methods have involved exposure patches, patches from worker clothing, skin swabs, and hand washes to measuring chemical deposition on skin. A number of investigations have involved the use of cotton materials, particularly for the quantification of pesticide exposures. Creely and Cherrie [26] used cotton gloves to collect samples of a permethrin-based pesticide. Their approach involved the determination of protection factors as a ratio of outside to internal concentration as determined by known exposures and measurements of recovered pesticide on the cotton gloves. From this investigation, they were able to discriminate failure modes of the gloves due to pesticide application practices and problems. Another study by Keeble et al used α-cellulose pads to quantify exterior exposure patterns and protection levels offered by work clothing and three different protective garments against Guthion (azinphos-methyl) [27]. In this testing, the pads were extracted with 100 mL of cyclohexane with the extract analyzed by gas chromatography with electron capture detection. Popendorf created a cotton gauge "dosimeter" by backing surgical gauze with aluminum foil and placing the assembly inside a glassine coated paper envelope with a 6-cm hole cut from its face to control the exposure area of the gauze pad [28]. Using this technique he was able to quantify skin exposure for orchard workers applying a pesticide containing 80% captafol. Another form of skin detection device for pesticides involved the sandwiching of an ethylene glycol impregnated glass filter paper between two layers of surgical gauze [29]. This approach was used for measuring the deposition of 2,4-D during individual pesticide spraying operations.

Sorbent media consisting of charcoal cloth has also been applied to the measurement of skin exposure to various solvents. Hirayama and Ikeda first used different prepared charcoal cloths to monitor exposure to mixed vapors of organic solvents, including hexane, ethyl acetate, and toluene [30]. While a number of the investigated charcoal felts failed to absorb or quantify some chemicals due to humidity effects, two of the prepared felts succeeding in quantifying vapor concentrations proportional to exposure duration. Cohen and Popendorf used an activated carbon cloth for collecting ten different solvents, including toluene and dichloropropene, as a method for skin exposure dosimetry [31]. Over the range of solvents investigated, they found retention to be between 36% and 87%. They further discovered that the charcoal cloth dosimeter's accuracy and precision were optimal in situations involving possible dermal exposure to toxic materials with low to moderate volatility or with low vapor concentration. Perkins and Vescial evaluated charcoal cloth as a potential field monitor for the efficacy of chemical protective clothing [32]. Perkins and Rainey later fashioned a glove using the charcoal felt as a means for detecting permeation through whole gloves following repeated flexing [33].

Skin exposure assessments have also employed a number of other materials. Vaananen et al used pads fabricated from polypropylene filters that were cut to fit into filter cases for monitoring road pavers for dermal exposure to polycyclic aromatic hydrocarbons (PAHs) [34]. In this investigation, PAH contamination on the pads was isolated using a cyclohexane/methylene chloride extract followed by concentration in an evaporator and analysis by gas chromatography with mass spectral detection. Similar work was carried out by Jongeneelen et al and Van Rooij et al for quantifying PAH exposure among different workers [35-36]. Souter et al described a number of specific approaches to dermal sampling involving the use of patches [37].

Lorberau and Pride [38] compared two different solid sorbent media for assessing dermal exposure to pesticides. In this study cotton gauze pads and 3M Empore filters were specifically employed to measure collection of two insecticides (chlorpyrifos and diazinon) and five herbicides (atrzaine, alachlor, metochlor, cyanazine, and 2-4 D ethylhexyl ester) using gas chromatography with flame ionization detection. Their study examined the detection limits and recoveries for both media with findings showing greater stability for recovery of the semi-volatile chemicals from the Empore filters with respect to temperature and humidity conditions. A related study followed one year later, involving the determination for a related series of herbicides in hand washes, on dermal patches, and in air [39]. The study involved using dermal patches consisting of polyurethane foam where recovery of adsorbed herbicides involved an isopropanol extraction. The technique was shown to be effective for collecting 6 of the 8 herbicides.

Rowell, Fletcher and Packham used commercial sorbent-based pads (Perma-Tec™ for solvents) to examine the recovery of common volatile solvents using a thermal desorption method involving gas chromatography [40]. They were able to demonstrate recoveries of better than 90% for 0.5 to 5.0 µL spiking volumes for acetone, d-limonene, methanol, methyl ethyl ketone, trichloroethylene, toluene, and m-xylene. These solvents represent a range of boiling points spanning from 56 to 175^{o}C. They were further able to demonstrate the ability to detect 16 to 60 ng of each solvent when solvent mixtures were applied to the pads with the exception of d-limonene. A related study [41] determined the efficiency of solvent adsorption using the same Perma-Tec™ solvent pads and chemicals, with the addition of tetrachloroethylene, but applied a microwave-solvent extraction method to determine chemical recoveries. The best recoveries (> 90%) were obtained with solvents having boiling points below 110^{o}C, while recovery efficiencies were between 80 and 90% for the lower boiling point chemicals.

Other research has been performed with different semi-volatile chemicals. For example in a study of hexamethylene diisocyanate (HDI) skin exposure in auto body shops, wipe sampling techniques were able to show the inadequacy of latex gloves for protecting workers [42]. The employed techniques involve a skin SWYPE™ wipe sampling patch (Colorimetric Laboratories, Des Plaines, IL) that employed a colorimetric based solid sorbent. Solid phase extraction disks involving reverse phase sorbent based on C18, octyldecyl-bonded silica have been used to determine chlorpyriphos, malathion, diazinon, and acephate recovery from foliar residues dislodged from plant matter. These disks have also been used to assess potential worker exposure to pesticides [43].

Standard chromatographic adsorbents have also been encapsulated into special devices for evaluating clothing performance against chemical warfare agents. For the purpose of measuring warfare simulants into full body ensembles, a passive sampler was developed to specifically monitor for methyl salicylate [44]. The sampler consists of an adsorbent that is placed in a package consisting of a high density polyethylene film over an aluminum foil laminate. The packet includes medical grade double adhesive tape to secure the device to the wearer's skin, and provides an exposure area of 4.8 cm^2. The development of the sampling device included a review of different sorbents, including Ambersorb and Tenax, with Tenax TA showing the least variation of adsorption with increasing humidity. While the HDPE film over the adsorbent does not simulate the permeability of skin, it does lessen the effects of humidity. The samplers have been shown effective for a number of chemical warfare simulants, including chloroethyl ethyl sulfide, dimethyl methyl phosphonate, diisopropyl methyl phosphonate, and methyl salicylate.

Twenty or more of these samplers are positioned over the wearer's body as part of a Man-in-Simulant Test (MIST) that was devised by the U. S. Army Research, Development and Engineering Center. Device placement is shown in Figure 4. During the MIST evaluation, the analysis of these devices is used to determine both localized penetration for blister agents and the overall effectiveness (protection factor) of the full ensemble using a body region hazard analysis.

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

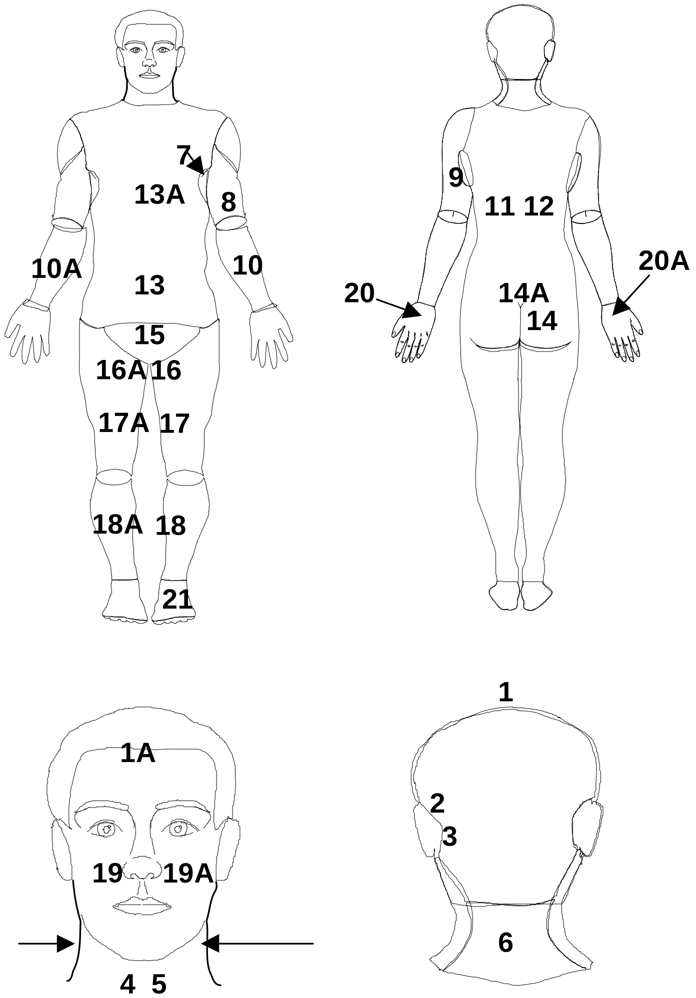

Figure 4 – Passive Dosimetry Device Location for MIST Evaluations

Application of Pressure during Protective Clothing Use

No specific references were identified that have examined the effects of pressure on the chemical resistance of protective clothing materials. The majority of comprehensive reviews of permeation have not included pressure as a significant factor affecting clothing performance [6,13]. Nevertheless, it is understood that pressure can have an impact on the contact of clothing surfaces on the wearer and that wearer activity that creates contact points between clothing and skin surfaces has a higher likelihood of causing mass transfer (chemical exposure) to the skin. While the body may be subject to a number of forces which cause compression of clothing against the wearer, such as through kneeling, crawling, or leaning, the area of most interest to this study is distribution of pressure over the hands during glove use.

The application of pressure by the hands on gloves has been investigated in a number of studies. Fellows and Freivalds measured grip force distribution using force sensing resistors, electromyography, and subjecting ratings, and found that during a grip, grip force is distributed very unevenly [45]. The base of the forefinger sustains the largest force with the based of the thumb and the tips of the four fingers maintaining lesser amounts of force. A later study, again using force sensing resisters, determined force distribution over the hands for different types of implements including knives, hammers, and power tools [46]. In particular, the tips of the third and fourth digits and the base of the first digit registered forces in excess of 100 gm/cm^2, while other areas like the thumb, base of the second digit and the thenar region (base of the hand) registered forces greater than 75 gm/cm^2. The distribution of these areas is shown in Figure 5.

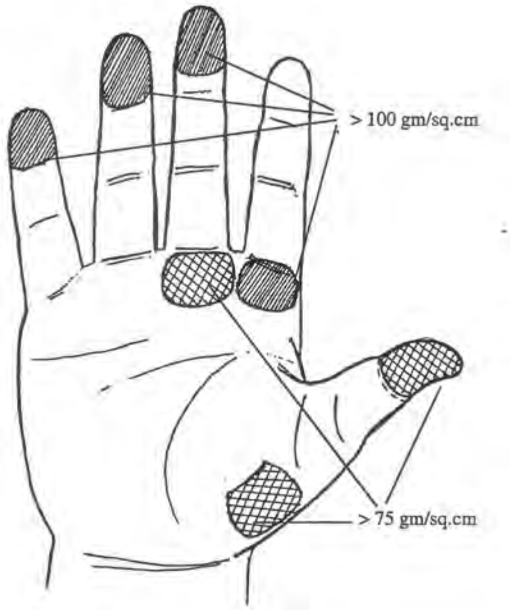

Figure 5 – Force Distribution on Hands as Determined by Fellows & Freivalds [45]

The hands can be subject to different pressures other than tool use as experienced in pushing and carrying heavy objects. Some references [47-49] report that pressures up to 10 kg/cm^2 can be transmitted to the hands during strenuous activity. Some of these activities, particularly when work is conducted around contaminants, can involve gloves.

EVALUATION OF SOLID SORBENT EFFICIENCY

The principal factors of the study design were undertaken as part of the first task to evaluate solid sorbent efficiency. In this first part of the study, the objective was to identify a number of sorbents suitable for semi-volatile chemicals, which could be used underneath gloves or other protective clothing. The specific choices of solid sorbents, chemicals, and the design of testing procedures affected the evaluation of sorbent effectiveness in the second and third parts of the study for investigating the effects of pressure and analog colorimetric detectors.

The following subsections provide:

- The rationale for sorbent selection
- Criteria used in selecting semi-volatile chemicals
- The design of analytical techniques for measuring sorbent chemical collection and recovery
- Results for the collection (recovery) efficiencies for the selected sorbents and chemicals

Solid Sorbent Media Selection

Several solid absorption materials potentially viable for the study were identified in a review of the literature and by contacting various suppliers. Additional suggestions were provided in the NIOSH Statement of Work for this study. For the sorbents considered in this study, the sorbents can be classified into the following categories:

- Activated charcoal or charcoal-based material fabrics
- Adsorbents bound onto filter media
- Silicone rubber-based films or polyurethane-based foams
- Special sorptive devices

Charcoal Fabrics. Activated charcoal represents one of the more common forms of chemical sorbents. These sorbents are commonly used in air sampling devices and for control of odors, usually as packed beds in tubes or other geometries that permit air flow for the intended application. When constructed into fabrics, the activated carbon is formed into filaments and fibers that are then bundled with other textiles for physical support. Alternatively, the activated charcoal is formed into tiny spheres that are then fixed onto textile carrier fabrics or porous foam materials. Typically, these fabrics have a carbon density between 180 to 220 g/m^2. A number of activated charcoal fabrics have been developed over the past decades principally as materials used in defense clothing for protection against chemical warfare agents. These materials are increasingly liquid resistant while permitting water vapor transport for comfort without significant loss of vapor sorption properties [50-51]. These products are now being used in a number of consumer applications ranging from hunting clothing to daywear. Fabric longevity remains a problem as continued use will saturate the capacity of the fabrics to adsorb contaminants. Fabric effectiveness is also questioned for a number of smaller volatile chemicals [52]. A variety of charcoal fabrics have been used for skin dosimetry with varying levels of effectiveness; however, charcoal fabrics that have been prepared to limit the effects of humidity have shown relatively high recoveries of semi-volatile chemicals. [30-33]. Example suppliers include Calgon, Gentex, Lantor, Lanx, and Saratoga.

Filter Media-Based Adsorbents. Another class of sorbents includes adsorbents that are bound into filter media. This technology is also sometimes referred to solid phase extraction (SPE). This type of sorbent is also commonly used for air sampling tubes and also as chromatographic columns and other separation devices. The sorbents are loaded as particles onto a membrane or disk. These particles are then tightly held together within an inert matrix of a textile or plastic material, which provides the supporting structure for the particles (see Figure 6). A typical supporting material is polytetrafluoroethylene (PTFE) constructed in the form of fibrils. Typical particle loadings range from 5 to 25% of the overall product weight with particle sizes from 10 to 50 µm. Example of particle loaded membrane are the Empore disks available from 3M. These disks are commonly used in water sample analyses to extract organic chemicals. Empore disks based on C8 (octyl) and C18 (decaoctyl) bonded silica technologies have proven effective in the sorption of several different organic contaminants [53-56]. The majority of methodologies and research has been specific to the C18 technology and includes several different groups of semi-volatile chemicals of interest to the study including aromatic amines, phenols, pesticides, and polynuclear aromatic hydrocarbons. Details on the filter technology are provided in Appendix A along with sample methods for using the 3M Empore disks for different organic chemical extraction and analysis. Related membrane-based sorbent materials are also available from Higgins Analytical (Hiasil and Kromasil), J. T. Baker (Bakerbond Speed Disks), and Varian (SPEC).

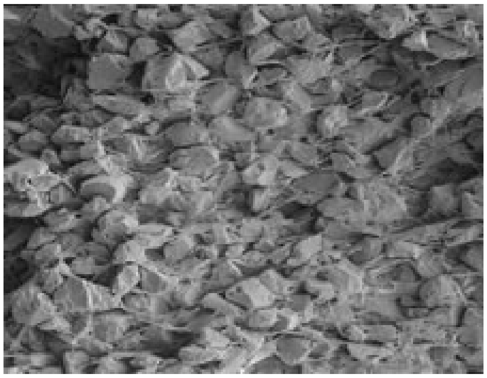

Figure 6 – Electron Micrograph of 3M Empore C18 Disk

Film and Foam Sorbents. Silicone rubber-based films were used by Entholt et al [14-15] in the evaluation of pesticide permeation through protective clothing fabrics. Films of different thickness (2.5 and 5.1 mm) have been evaluated based on Dow-Corning's Silastic. The use of polyurethane foams as a potential sorbent media was also reported in two separate studies and indicated in general as an appropriate sorbent for dermal sampling [20,37,39]. The reviewed literature did not report other specific film or foam collection media for chemical collection underneath clothing, but several studies involved various forms of filter paper, gauze, or other textile materials as collectors for chemicals through clothing materials [26-29,34]. A significant consideration in the use of solid films and polyurethanes is the potential swelling of polymer during chemical adsorption (as noted in [16]) in addition to concerns about maintaining intimate contact with exposure surfaces.

Special Adsorbent Devices. A fourth type of sorbent considered in this study was a specific device created for evaluating clothing effectiveness to inward leakage by chemical warfare agent simulants. Known as passive adsorbent devices, these sorbents are used on individuals wearing protective clothing in environments containing the simulant (usually methyl salicylate and other chemicals) to measure the specific doses received at the portion of the body where placed [44]. Passive Adsorbent Devices are small packets that are filled with an adsorbent, Tenax™ TA. The top layer of the packet is HDPE film that provides the sampling surface. The back of the packet is an impermeable plastic-coated foil. Medical grade double-coated adhesive is affixed to the back of the packets enables the devices to be attached to the skin of the test subject. A photograph of these devices is provided in Figure 8.

Figure 7 – Passive Adsorption Devices

Tenax™ TA is a porous polymer resin based on 2, 6-diphenylene oxide. It has been specifically designed for the trapping of volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrices. It is primarily used as a column packing for chromatography but is also used in detection tubes as referenced in NIOSH and EPA test methods. The specific form of Tenax™ TA used in passive adsorbent devices is a 60-80 mesh size with a density of 0.25 g/cm^3, pore size of 200 nm, and pore volume of 2.4 cm^3/g.

For this study, the selection of specific solid sorption media was based on the following characteristics:

- Known information about sorptive properties
- Availability of information on use and handling
- Availability in a form that permits glove contact
- Compatibility with extraction solvents and ease of extraction

Specific solid sorption media were reviewed to account for their characteristics based on both analytical properties and practical considerations. For example, sorbents were selected that provided some evidence for efficiency in adsorbing low volatile chemicals or specific classes of chemicals. It was also important that procedures existed to permit the extraction of the sorbent and analysis of the extract.

In addition, the selected sorbents needed to be in a form that permits use for detecting permeation underneath glove or other clothing materials. Lastly, it was decided that the selected sorbents represent a range of characteristics to demonstrate sorbent technology for use with protective clothing. Table 1 provides a list of sorbent materials that were considered for this study.

Table 1 – Candidate Sorbent Materials and Proposed Extraction Methods

Sorbent System	Technology	Source	Range of Chemical Sorbent
Activated charcoal cloth (Zorflex)	Activated charcoal impregnated into fabric system	Calgon Carbon Corporation (Pittsburgh, PA and UK)	Indicated to adsorb a wide range of chemicals; limited information on low-volatility chemicals
Bakerbond Speed Disks	Adsorbent particle-loaded membrane bound with PTFE fibrils (C8 or C18)	J. T. Baker (Phillipsburg, NJ)	Represented for extraction of slightly polar to non-polar industrial samples
C-Tex	Woven, knitted and nonwoven fabrics with carbon fibers	Carbon Cloth Mast Carbon AP (UK)	Indicated to adsorb a wide range of chemicals; limited information on low-volatility chemicals
Empore Sorbent Disks	Adsorbent particle-loaded membrane bound with PTFE fibrils (C8 or C18)	3M (St. Paul, MN)	Demonstrated effectiveness and methods for wide range of semi-volatile chemicals
Hiasil 100 (C8 or C18)	Resin based system	Higgins Analytical (Mountain View, CA)	Used as chromatography packing material; also made as extraction disks similar to 3M Empore products
Kromasil 100 (C8 or C18)	Resin based system		
Lanx Fabric	Polymerically encapsulated activated carbon integrated into fabric	Xymid LLC (Newark, DE)	Demonstrated effectiveness against chemical warfare agents and pesticides
Life-Tex CD-2000	Activated carbon fibers sandwiched between layers of knit or woven fabrics	Gentex (Carbondale, PA)	Demonstrated effectiveness against chemical warfare agents and pesticides
Passive Adsorbent Devices	Tenax TA adsorbent sealed into packet with HDPE film cover	Syon/ITW Devcon (Danvers, MA)	Used in man-in-simulant tests (MIST) of full ensembles; commonly employed in environment containing MeS
Polyurethane Foam	Ultrapure foam material	Supelco (Bellafonte, PA)	Some studies showed use of polyurethane foams for detecting various pesticides
Saratoga™	Activated carbon spheres encased in foam or textile materials	Blucher GmBh (Dusseldorf, Germany)	Demonstrated effectiveness against chemical warfare agents and pesticides
Silastic™	Silicon-based rubber	Precision Silicones, Inc. (Chino, CA)	Previously used against various pesticides and low volatility chemicals

A final selection of sorbents included:

- Charcoal impregnated cloth (C-Tek supplied by Colorimetric Laboratories and represented as from a Carbon Cloth, UK)
- 3M Empore C18 Extraction Disks
- Passive Adsorption Devices

The selected charcoal cloth was chosen on the basis of its availability (including use as part of the solvent Perma-Tec™ colorimetric indicators) and literature findings suggesting utility against a range of volatile and semi-volatile chemicals. The material used in this study has a thickness of 0.90 mm, unit area weight of 210 g/m^2, surface area of 1200 m^2/g, and surface density of 100 to 120 g/m^2. The 3M Empore C18 Extraction Disks were selected given prior research demonstrating specific adsorption and high recovery for different semi-volatile chemicals. The C18 disks were preferred over C8 disks because of more extensive methodology that had been developed by 3M for applying the C18 to the extraction of different analytes (only one EPA method had been developed for the C8 extraction disks; C8 is also considered applicable to more polar compounds). Passive adsorption devices were included since these sorbents were being used in the specific detection of volatile and semi-volatile chemicals. Their recent specification as part of an ASTM test method for whole ensemble testing combined with the range of chemicals that can be adsorbed by Tenax TA offered a different alternative sorbent for investigation. Specifications for 3M Empore Disks and passive adsorbent devices are provided in Appendix A.

Test Chemical Selection

General Selection Criteria. The selection of chemicals for this study was based on achieving a range of different chemical characteristics, including:

- Molecular weight
- Functional type (chemical class)
- Vapor pressure
- Industrial significance
- Known skin toxicity or sensitivity
- Methods for analytical detection
- Available colorimetric indicators
- Permeation data for selected glove materials

To be selected in this study, chemicals had to be classified as semi-volatile, having vapor pressures at or below 5 mm Hg. Since only a few chemicals were used in the study, it was also important to select chemicals from different chemical classes to demonstrate the utility of sorbents and colorimetric indicators for assessing glove permeation. A starting point for chemical selection was the *NIOSH Pocket Guide of Chemical Hazards.* Using this reference, a list of low vapor pressure chemicals having known skin toxicity or sensitivity was compiled to create the first set of candidate chemicals. The list included a number of heavier molecular weight, cyclic chemicals, as well as insecticides and other known skin toxic chemicals. The list and relevant characteristics for each chemical is presented in Table 2.

Table 2 – Candidate Study Chemicals

Chemical	Mol. Wt.	Chemical Class[1]	Vapor Pressure[2] (mm Hg)	Industrial Uses[3]	Perm. Data[4]
Acetone cyanohydrin*	85.1	Not classified	0.8	Insecticide, organic intermediate	No
Acrylamide*†	71.1	Acrylimide	0.007	Dyes, water treatment	Lim.
Acrylic acid*	72.1	Aliphatic carboxylic acid	3	Monomer	Yes
Adiponitrile*	108.2	Aliphatic nitrile	0.002	Nylon intermediate	Lim.
Aniline*†	93.1	Aromatic amine	0.6	Rubber accelerator, dyes, isocyanates	Yes
Bromoform*†	252.8	Aliphatic halogen compound	5	Organic intermediate	Yes
2-Butoxyethanol†	118.2	Glycol ether	0.8	Solvent, paint remover	Yes
Chlordane*†	409.8	Alicyclic halogen compound	0.00001	Insecticide	Lim.
m-Cresol*	108.2	Alicyclic hydroxyl compound	0.14	Disinfectant, organic intermediate	Yes
Cyclohexanone*†	98.2	Alicylic ketone	5	Organic intermediate	Yes
Demeton*	258.3	Organophosphorous compound	0.0003	Insecticide	No
Dichlorvos*‡	221.0	Organophosphorous compound	0.01	Insecticide, fumigant	No
Dichrotophos*	237.2	Organophosphorous compound	0.0001	Insecticide	No
Diethylenetriamine*	103.2	Polyaliphatic amine	0.4	Solvent, dyes	Yes
Dimethylacetamide*	87.1	Aliphatic amide	2	Solvent, catalyst	Yes
Dimethylformamide*	73.1	Aliphatic amide	3	Solvent, catalyst	Yes
Dimethyl sulfate*†	126.1	Sulfur compound (sulfate)	0.1	Methylating agent	Lim.
Dinitrotoluene*†	182.2	Nitrogen compound	1	Organic intermediate	Lim.
Dioxathion*	456.6	Organophosphorous compound	Unknown	Insecticide	No
Disulfoton*	274.4	Organophosphorous compound	0.0002	Insecticide	No
2-Ethoxyethanol*	90.1	Glycol ether	4	Solvent, paint remover	Yes
2-Ethyoxyethanol acetate*	132.2	Glycol ether	2	Solvent, paint remover	Yes
Fenthion*	278.3	Organophosphorous compound	0.00003	Insecticide	No
Malathion*	330.4	Organophosphorous compound	0.00004	Insecticide	Lim.

Chemical	**Mol. Wt.**	**Chemical Class[1]**	**Vapor Pressure[2] (mm Hg)**	**Industrial Uses[3]**	**Perm. Data[4]**
Methyl demeton*	230.3	Organophosphorous compound	0.0004	Insecticide	No
Methylene bisphenyl isocyanate‡	250.3	Aromatic isocyanate	0.000005	Polyurethane intermediate	Yes
4,4’-Methylene dianiline*†‡	198.3	Aromatic amine	<0.00001	Hardening agent, dye intermediate	Yes
Nicotine*	162.2	Heterocyclic nitrogen compound	≈ 0	Insecticide, fumigant	Lim.
Nitrobenzene*†	123.1	Nitrogen compound	0.3	Solvent, organic intermediate	Yes
Nitrotoluene*	137.1	Nitrogen compound	0.1	Organic intermediate	Lim.
Parathion*	291.3	Organophosphorous compound	<0.00001	Insecticide	Lim.
Pentachlorophenol*†	266.4	Aromatic hydroxyl compound	0.001	Fungicide, bactericide	Yes
Phenylhydrazine*†	108.1	Hydrazine	0.04	Reagent, organic intermdiate	No
Phorate*	260.4	Organophosphorous compound	0.008	Insecticide	No
TEDP*	322.3	Organophosphorous compound	0.0002	Insecticide	No
1,1,2,2-Tetra-chloroethane*†	167.9	Aliphatic halogen compound	5	Solvent, paint remover	Yes
Toluene 2,4-diisocyanate‡	174.2	Aromatic isocyanate	0.05	Polyurethane foams and elastomers	Yes
Tolidine*†	107.2	Aromatic amine	1	Organic intermediate	No

NOTES

* Skin notation in ACGIH TLV book (2004)

† Suspected or actual human carcinogen; animal carcinogen based on ACGIH TLV book (2004)

‡ Sensitizing chemical based ACGIH TLV book (2004)

[1] Chemical classes were based on ASTM F1186, *Standard Classification System for Chemicals According to Functional Groups*, 2004.

[2] Vapor pressures compiled from *NIOSH Pocket Guide of Chemical Hazards,* U.S. Department of Health and Human Services, NIOSH, June 2004.

[3] Industrial Uses from RL Lewis, Sr.,*Hawley’s Condensed Chemical Dictionary,* 12th Edition, Van Nostrand Reinhold, 1993.

[4] Determination of permeation data availability based on K Forsberg and LH Keith, *Chemical Protective Clothing Permeation and Degradation Compendium,* Lewis Publishers, 1995; Lim. – limited data (determined if data available for 3 or less materials); other industry sources were also checked for data availability.

Available Analytical Methods and Colorimetric Indicator for Selected Chemicals. Excluding the chemicals where there were limited or no permeation data, the remaining chemicals were reviewed for the recommended analytical methods, including suggested sampling media, extraction solvents, and detection methods together with the availability of colorimetric indicators. This information is presented in Table 3.

Table 3 – Analytical Methods and Colorimetric Indicator Availability for Selected Chemicals

Chemical	**Recommended Analytical Method[1] (NIOSH Method Number)**	**Colorimetric Indicator Availability[2]**
Acrylic Acid	XAD; Methanol/water extraction; HPLC/UV detector (28)	Unknown
Aniline	Silica gel; Ethanol extraction; GC/FID (2002)	Perma-Tec™ (aromatic amine)
Bromoform	Charcoal; CS_2 extraction: GC/FID (1003)	Unknown
2-Butoxyethanol	Charcoal; Methanol/$CHCl_2$ extraction; GC/FID (1403)	Perma-Tec™ (solvent)
m-Cresol	XAD; Methanol extraction; GC/FID (2546)	Perma-Tec™ (phenol)
Cyclohexanone	Charcoal; CS_2 extraction; GC/FID (1003)	Perma-Tec™ (solvent)
Diethylenetriamine	XAD; DMF extraction; HPLC/UV detector (2540)	Perma-Tec™ (aliphatic amine)
Dimethylacetamide	Silica gel; Methanol extraction; GC/FID (2004)	Perma-Tec™ (solvent)
Dimethylformamide	Silica gel; Methanol extraction; GC/FID (2004)	Perma-Tec™ (solvent)
2-Ethoxyethanol	Charcoal; Methanol/$CHCl_2$ extraction; GC/FID (1403)	Perma-Tec™ (solvent)
2-Ethyoxyethanol acetate	Charcoal; Methanol/$CHCl_2$ extraction; GC/FID (1403)	Perma-Tec™ (solvent)
Methylene bisphenyl isocyanate	Bubbler; Acetylate/Methanol; HPLC/UV/ECD (5521)	Perma-Tec™ (aromatic isocyanate)
4,4'-Methylene dianiline	Filter; KOH/Methanol extraction; HPLC/UV/ECD (5029)	Perma-Tec™ (aromatic amine)
Nitrobenzene	Silica gel; Methanol extraction; GC/FID (2005)	Unknown
Pentachlorophenol	Filter; Methanol extraction; HPLC/UV Detector (5512)	Perma-Tec™ (phenol)
1,1,2,2-TCE	Charcoal; CS_2 extraction; GC/FID (1019)	Unknown
Toluene 2,4-diisocyanate	Coated glass wool; Methanol extraction; HPLC/UV Detector (2535)	Perma-Tec™ (aromatic isocyanate)

[1] Analytical methods compiled from *NIOSH Pocket Guide of Chemical Hazards*, U.S. Department of Health and Human Services, NIOSH, June 2004.

[2] Availability based on information from Colorimetric Laboratories website and private communications with Tom Klingner of Colorimetric Laboratories, 2005.

The information in Table 3 showed that a variety of chemicals could be detected using common analytical methods and extraction techniques (on conventional media). The exceptions were some of the isocyanate chemicals that required derivatization or other more complicated analytical procedures. The only commercially available colorimetric detectors configured to be used under gloves were identified as being available from CLI Laboratories (Des Plains, IL). The company offers seven different types of Perm-Tec™ detectors that are for use underneath gloves or other protective clothing. A new phenol-based detector was only recently made available to address detection of phenol-type chemicals.

Review of Permeation Data for Selected Chemicals. A more detailed analysis was made for availability of permeation data for the respective chemicals. Permeation data were compiled for the selected chemicals for a couple of common glove polymers (natural rubber, nitrile rubber, and Neoprene rubber) that were likely to provide some barrier performance against the chosen chemicals. Unfortunately, most data compilations are out of date or do not have chemical resistance information that is product specific. Owing to the detail provided by Ansell Professional, their on-line Specware chemical resistance data program was used to acquire chemical resistance data for the selected chemicals. This information is shown in Table 4.

Table 4 – Chemical Resistance Data for Selected Chemicals[1]

Chemical	**Degradation**			**Breakthrough Times**			**Permeation Rates**		
	N.R.	**Nitr.**	**Neop.**	**N.R.**	**Nitr.**	**Neop.**	**N.R.**	**Nitr.**	**Neop.**
Aniline	E	NR	E	25	NR	145	<9	NR	<900
2-Butoxyethanol									
m-Cresol	G			11			<9		
Cyclohexanone	P	F	P	Unk	103	30	Unk	<90	<900
Diethylenetriamine									
Dimethylacetamide	E	NR	NR	15	NR	NR	<90	NR	NR
Dimethylformamide	E	NR	E	25	NR	45	<9	NR	<900
2-Ethoxyethanol	E	G	E	25	210	128	<9	<90	<90
2-Ethyoxyethanol acetate	E	F	G	10	90	75	<90	<90	<9
Methylene bisphenyl isocyanate									
4,4'-Methylene dianiline									
Pentachlorophenol	NR	E	E	NR	>360	151	NR	<0.9	<900
Toluene 2,4-diisocyanate	G	NR	NR	7	NR	NR	<9	NR	NR

[1] Data were provided from AnsellPro Specware on line (2005). Degradation ratings are based on visual effects (E – excellent, G – good, F – fair, P – poor, NR – not recommended); breakthrough times are reported in minutes; permeation rates are reported in µg/cm^2/min. Unk – information is unknown; blanks indicate that no information was available.

It was important to select chemicals where glove materials existed with appropriate chemical resistance characteristics. Suitable glove materials were those with chemical resistance meeting the following parameters:

1. Known permeation data should show that material degradation does not occur (ratings of good or excellent).

2. Recorded permeation breakthrough times should be less than an hour with low to moderate rates of permeation (0.9 to 9.0 µg/cm^2/min).

The lack of degradation was considered important because a material surface that exhibited too much swelling or deterioration would interfere with the contact of the chemical with the exposure surface during the application of pressure. The targeted permeation breakthrough times and permeation rates were selected because a rate of permeation was desired which would approximate the expected detection limits for both the selected sorbents and colorimetric detectors.

Final Chemical Selection. In order to employ three different colorimetric indicators, aniline, m-cresol, and 2-ethoxyethanol were selected as the study chemicals. Aniline was chosen over methylene dianiline because a straightforward analytical technique could be used for its detection and permeation data were available. Of the solvents, 2-ethoxyethanol was found to be the best choice owing to its permeation characteristics, common industrial usage, and ease of analysis. The selection of m-cresol was based on availability of permeation information and simpler analytical procedures. The three selected chemicals provide a range of vapor pressure from 0.14 to 4 mm Hg and can each be analyzed using gas chromatography with flame ionization detection.

Analytical Methods

The choice of chemicals and solid sorbent materials affected the selection of analytical methods that could be used for spiking, extracting, and analyzing for test chemicals extracted from sorbent materials. Analytical procedures were chosen that achieved the following:

- Determination of analyte collection efficiency at different sorbent loadings
- Linearity of collection efficiency
- Nominal lower limit in range of interest
- Establishment of an upper sorbent capacity

Separate techniques were needed for each step. The procedures used for each step are described in the subsections below.

Spiking Procedures. As previously described, the geometry of each selected sorbent media was different. In order to provide a uniform area of exposure, sorbent sample size was consistent with the area for the sampling surface of the passive adsorbent devices at 4.8 cm^2 (3/4 in x 1.0 in). For the purpose of sorbent efficiency (recovery) determinations, samples of sorbents were prepared by cutting to this size. A modification of these devices was necessary because the application of chemical directly to the film surface resulted in liquid beading and non-uniform exposure of the sorbent. In spiking the device sorbent, the Tenax TA sorbent was removed from the device, placed in a vial, and spiked. Three different volumes were used for spiking sorbents at 0.2, 1, and 5 µL. This range of volume was chosen as similar to previous studies where solid sorbents were used for the measurement of glove material permeation resistance [21-25]. Spiking was performed in a disposable aluminum dish.

Extraction Procedures. The spike media were allowed to sit uncovered for 1 hour, after which the sorbents were placed in a vial and desorbed with 1 mL of methanol/methylene chloride solvent (the 5 µL spiked media were extracted with 2 mL of extraction solvent). This extraction solvent is recommended for 2-ethoxyethanol and was found to cover the range of recommended extraction solvents (ethanol is recommended for aniline while methanol is recommended for m-cresol). The vials were then sonicated for one hour. The desorb solvent was then drawn off and analyzed immediately. Under these procedures, poor recoveries were obtained for the passive adsorbent device Tenax TA sorbent (approximately 10%). Therefore, subsequent techniques were applied where the Tenax TA sorbent was allowed to remain in the desorb solvent overnight (approximately 16 hours) and subjected to analysis in the morning. This technique significantly improved the recoveries of the study chemicals, though it is unknown if any of the analyte evaporated during this period.

Analysis Procedures. A modified version of NIOSH Method #1403 (Alcohols IV) was applied for analysis. In this method, gas chromatography with flame ionization detection is used. Some adjustment of the chromatography conditions were provided to obtain clear separation of the three selected chemicals (see Figure 8). Elution (retention) times for aniline, m-cresol, and 2-ethoxyethanol were found to be approximately 6.3, 7.6, and 1.7 minutes.

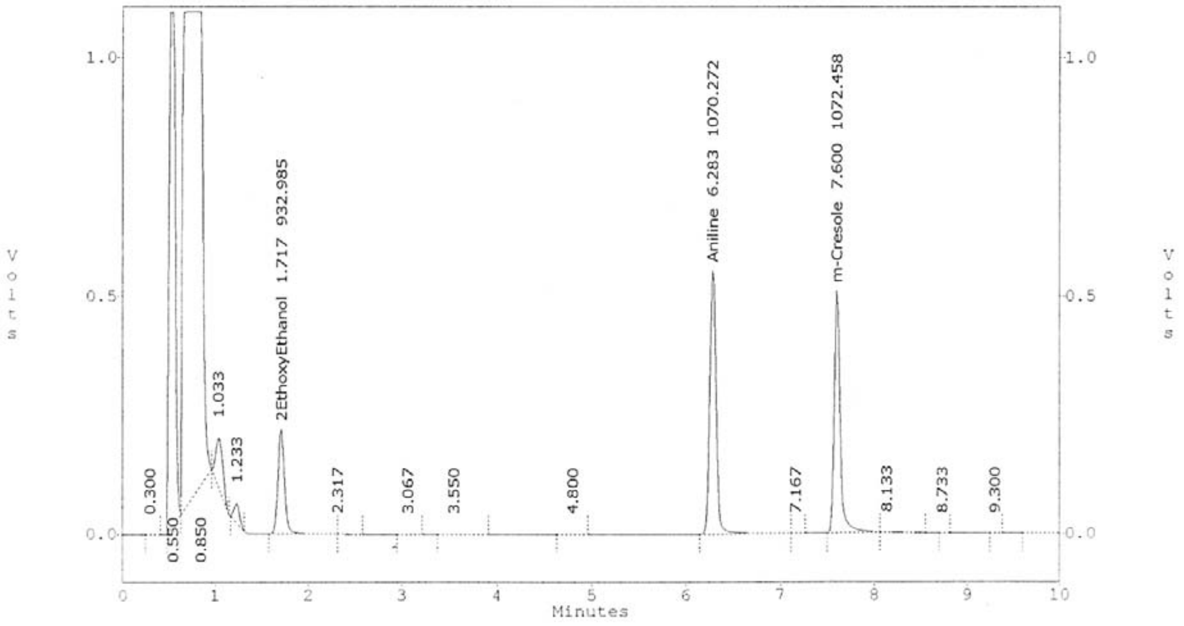

Figure 8 – Example Chromatogram Showing Separation of Selected Chemicals

Parameters used in the analysis of the test chemicals are specified in Table 5. Six different standard solutions were used to determine analytical response for each analyte over a range of 0.1 to 250 µg. The calibrations curves for each chemical are presented in Figures 9-11. Blanks were also run on each sorbent and an analysis was conducted for the extraction solvent as a control.

Table 5 – Analytical Measurement Parameters

Technique	Gas chromatography; flame ionization detection
Equipment	HP 5980
Analytes	Aniline, m-cresol, 2-ethoxyethanol
Desorption solvent	methanol/methylene chloride
Injection volume	1 µL
Temperature **Injection** **Dectector** **Column**	 200^{o}C 300^{o}C 80^{o}C (4 minutes) - 200^{o}C (15^{o}C/minute)
Carrier gas	Helium, 3 mL/min
Column	Capillary, polyamide-coated fused silica composition, RTX1

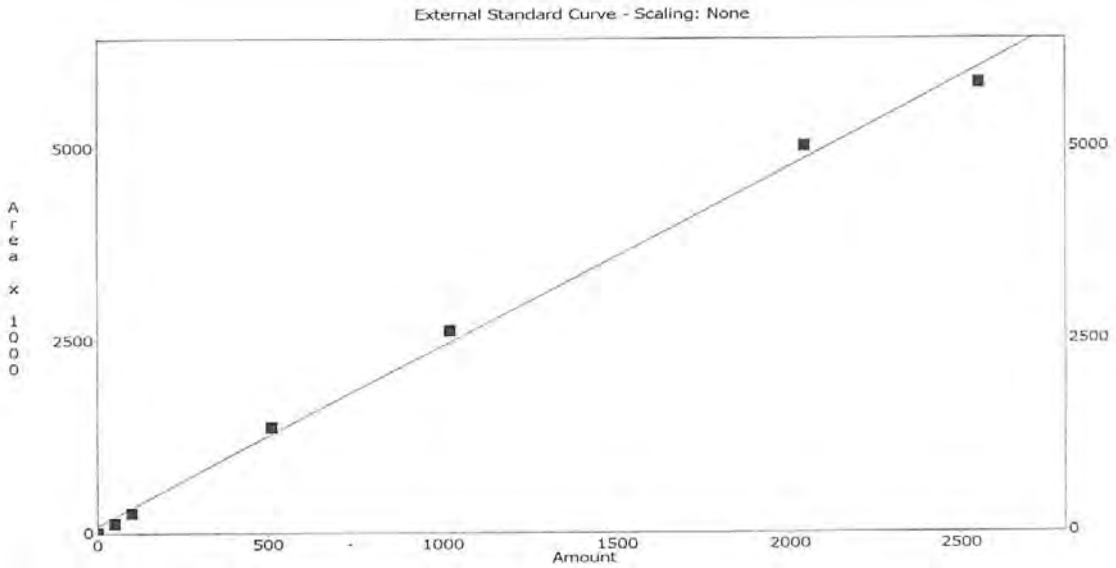

Figure 9 – Calibration Curve for Aniline

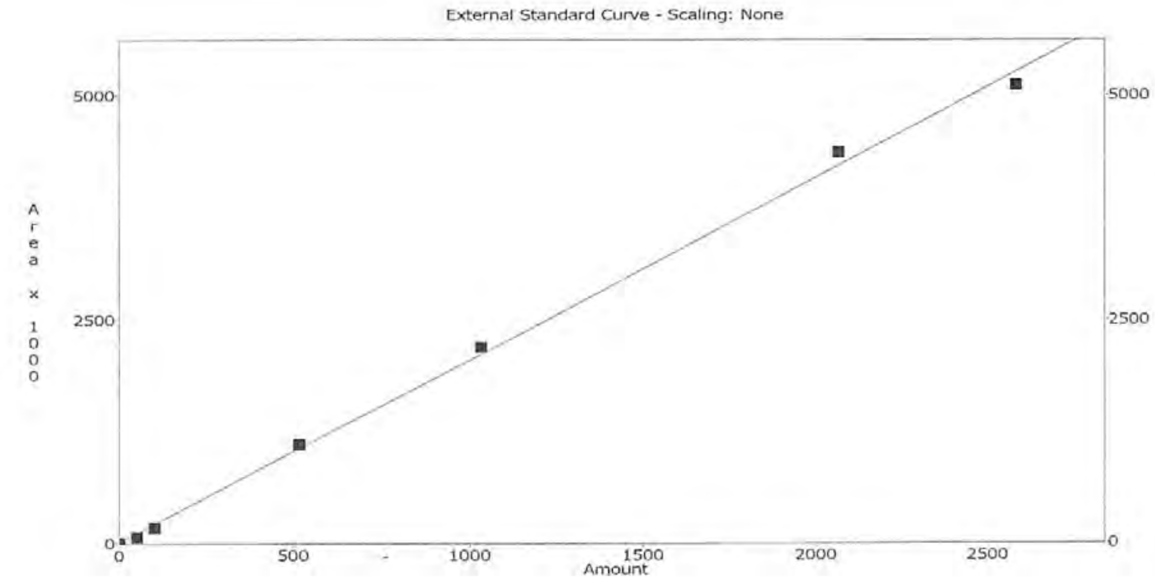

Figure 10 – Calibration Curve for m-Cresol

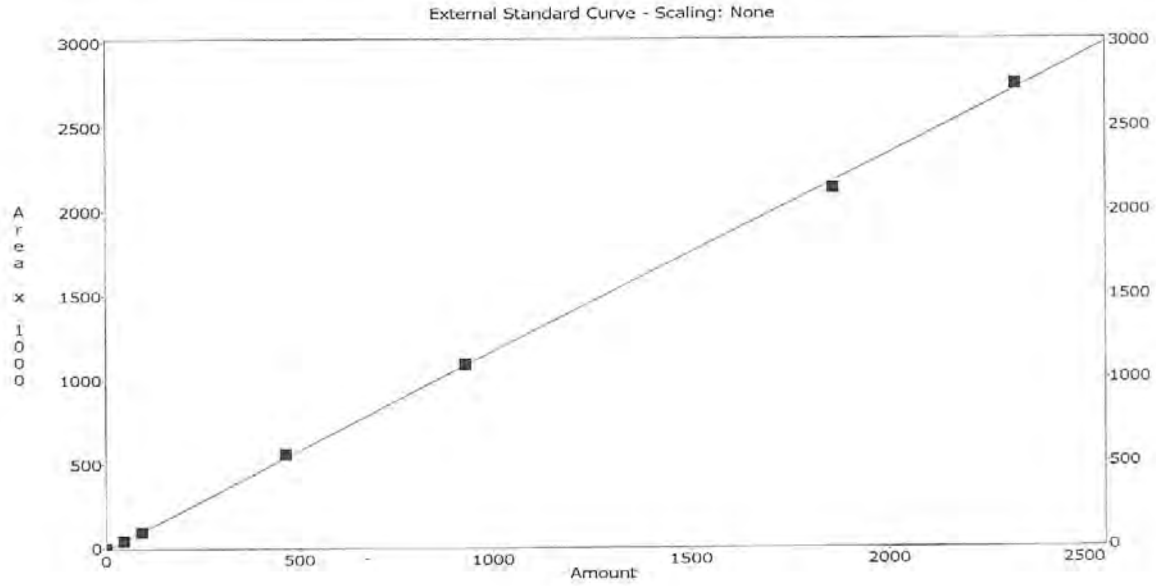

Figure 11 – Calibration Curve for 2-Ethoxyethanol

Results for Testing of Solid Sorbents

Testing was carried out for the three selected solid sorbent, three selected chemicals, and 3 spiking volumes. For each solid sorbent/chemical combination, three replicate tests were conducted to assess precision of the selected techniques. Determinations were then made to establish the recovery of test chemicals from each sorbent material. These collection (recovery) efficiencies are presented in Table 6. Linearity of sorbent recovery by chemical is shown in Figures 12 through 14.

Table 6 – Recovery Efficiencies for Sorbent/Chemical Combinations

Solvent	**Spiking Volume (µL)**	**Average Recovery Efficiency**		
		Charcoal Cloth	**Empore Disk**	**Passive Ads. Device**
Aniline	0.2	113	76.5	72.3
	1	97.0	77.7	77.5
	5	89.9	87.0	90.1
m-Cresol	0.2	104	99.8	94.4
	1	78.2	94.6	85.4
	5	89.5	93.5	95.3
2-Ethoxyethanol	0.2	111	93.2	116
	1	94.3	94.3	85.2
	5	73.0	92.7	99.9

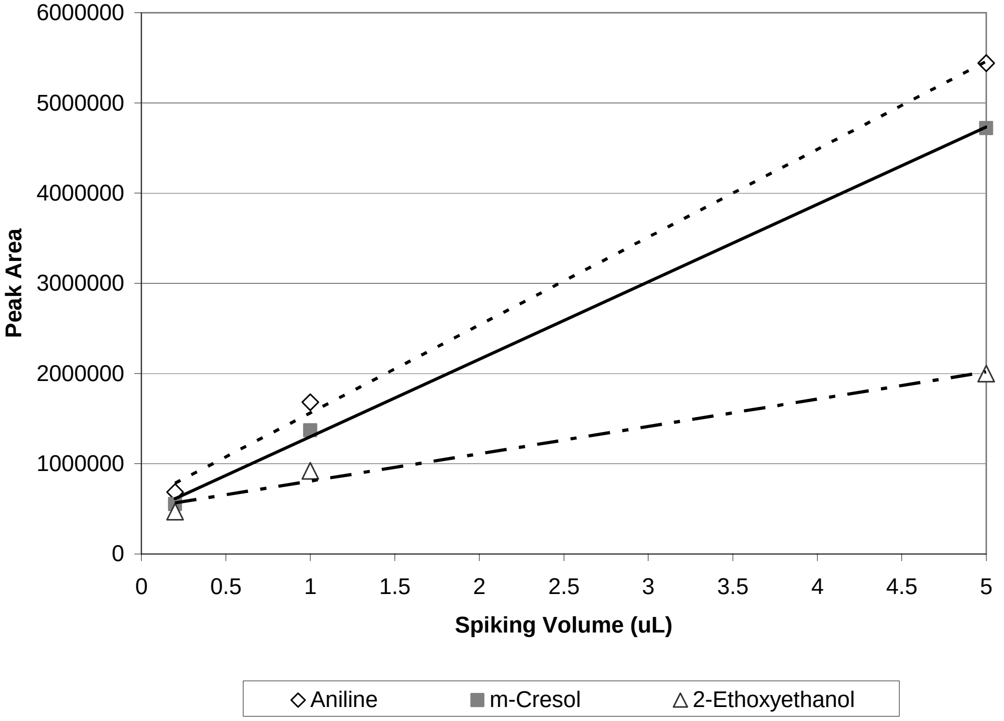

Figure 12 – Peak Area versus Volume of Chemical Added for Charcoal Cloth

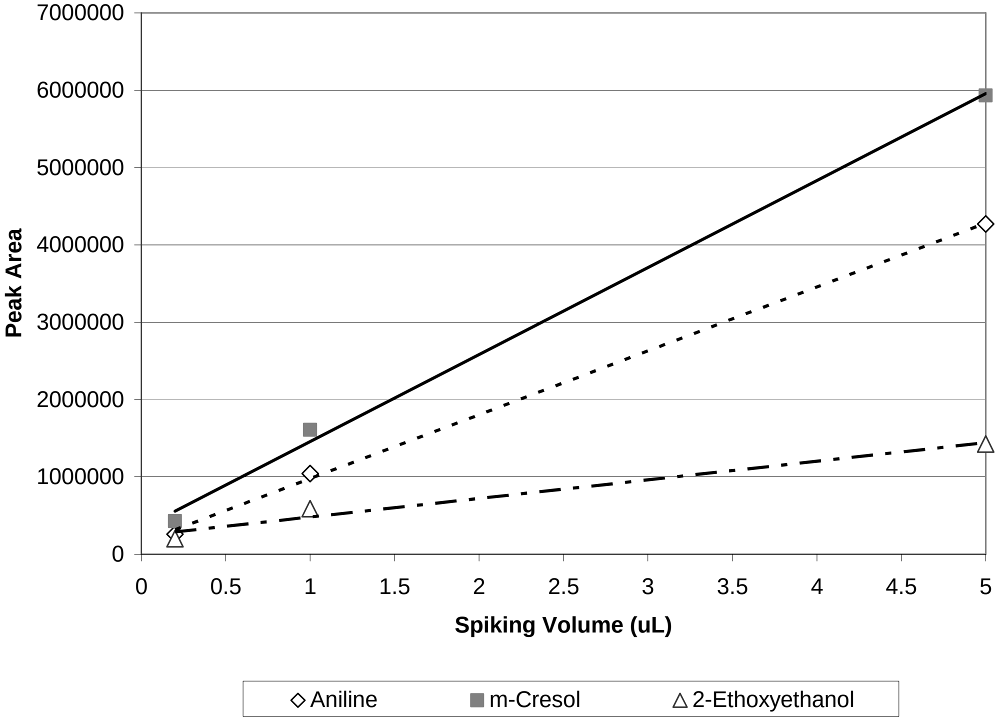

Figure 13 – Peak Area versus Volume of Chemical Added for Empore Disks

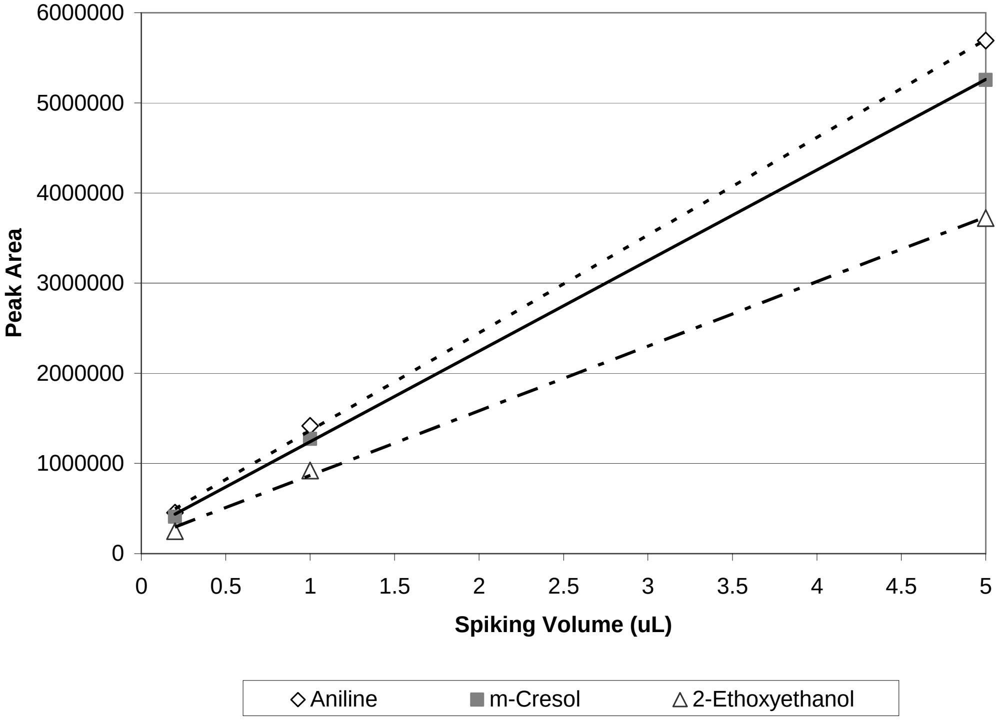

Figure 14 – Peak Area versus Volume of Chemical Added for Passive Adsorbent Devices

Analysis of Results

Chemical recoveries varied with both the sorbent and the chemical. The most consistent results were observed for the Empore disks where percent recoveries for both m-cresol and 2-ethoxyethanol were in the mid-90s. A lower recovery was found for aniline. In the case of the charcoal cloth and passive adsorbent device sorbents, chemical recoveries were less consistent. The charcoal cloth exhibited recovery percentages better at lower spiking volumes than higher volumes for two of the three chemicals. The passive adsorbent devices showed relatively varied recoveries that may have been due to need for longer desorption times being required. It is suspected that the longer extraction times for the passive adsorbent devices may have contributed to some volatilization of the spiking solvent, partly explaining the inconsistent trend in measured recoveries.

The relative response of each sorbent to different extraction volumes over the range of 0.2 to 5.0 µL was found to be linear. Correlation coefficients were calculated for each sorbent-chemical combination and ranged from 0.949 to 0.993.

PRESSURE EFFECTS ON SOLID SORBENT EFFICIENCY

Selection of Test Pressures

During the literature review, several sources were identified to determine the pressure applied on gloves to the hand while gripping and handling hand tools. Generally these pressures ranged upward to 75 and 100 grams per square centimeter [46]. While there was literature where solid sorbents were used as collection media in permeation testing, the specific pressures were not reported, but assumed to be near ambient.

A total of three different pressures were used. The maximum pressure corresponded to the maximum pressure specified in the NIOSH Statement of Work at 200 grams per square centimeter (2.8 psi). An applied pressure of 100 g/cm^2 (1.4 psi) was used as an intermediate pressure for testing. The last pressure was set near ambient (the minimum pressure that can be reproducibly applied at 6.8 g/cm^2 (0.10 psi).

Selection of Test Glove Material

As part of the chemical selection process, it was determined that natural rubber glove materials would provide a suitable glove medium for evaluating the pressure effects of solid sorbents and colorimetric detectors. A more detailed investigation was made for deciding on which type of specific natural rubber glove to choose. Since the data initially relied on for discerning chemical permeation through glove materials was from Ansell Professional, various natural rubber gloves of that manufacturer were identified. These gloves consist of several styles in various thickness, surface textures, and interior treatments. Gloves that included interior flocking could not be considered because of the interference with making contact with the solid sorbent. It was further found that the generic chemical resistance data represented for unsupported natural rubber were based on a product known as "Canners and Handlers." Additional permeation tests were conducted for the three chemicals against this glove to ascertain that the selected glove provide degradation resistance and permeation resistance in the desired range. Table 6 provides the results of this testing.

Table 7 – Commercial Permeation Test Results for Selected Glove Material

Chemical	Weight (g/m^2)	Thickness (mil)	Breakthrough Time (min)		Permeation Rate (µg/cm^2-min)
			Actual	Normalized	
Aniline	452	17	24	31	6.8
m-Cresol	440	17	9	15	8.8
2-Ethoxyethanol	465	18	20	24	15.5

Notes – all values are the average of three replicates; actual breakthrough times determined at limit of detection for analytical system; normalized breakthrough times determined when permeation rate is equal to 0.1 µg/cm^2-min; reported permeation rate is maximum permeation rate indicated during 3 hour test.

It was important that the glove provide a uniform surface for sorbent contact on the material interior and chemical transfer layer on the material exterior. For this reason, portions of the glove gauntlet were used for glove material samples. The finger area exhibited curvature while the palm side of both the fingers and glove palm had embossing for affecting glove grip. The thickness of all glove samples was measured and found to vary no more than a mil (0.43 mm ± 3 mm).

Test Approach

A relatively simple approach was employed to evaluate sorbent effectiveness as a function of pressure. Several preliminary experiments were required to select the appropriate technique and conditions for testing. Specific considerations will include:

- The concentration of test chemical for exposing solid sorbent materials
- The type of chemical transfer material
- The manner of applying pressure (most likely through a dead weight)
- The length of time that the exposure under pressure is conducted

For the purposes of this study, the following steps were used:

1. The solid sorbent material providing 4.8 cm^2 (approximately 2.2 x 2.2 cm) of exposed surface was placed inside a disposable aluminum pan on a flat, solid surface.

2. A sample of the selected glove material measuring 3 cm square (9.0 cm^2) was placed directly over the sorbent material such that the sorbent material was centered underneath the glove sample.

3. A chemical transfer material was then placed on top of the glove material sample. In this study, a Whatman filter paper was used as the chemical transfer material. The filter paper was cut to approximately the same dimensions of the sorbent material. Prior to the experiment, the filter material was soaked in the chemical for a period of one hour. Care was exercised to prevent any contamination to other surfaces during the placement of the doped filter paper on top of the glove material sample.

4. A second disposable aluminum pan was placed over top of the chemical transfer material/glove material/solid sorbent sandwich. This procedure partly sealed the sandwich between the aluminum pans to minimize evaporation or chemical transfer to other surfaces.

5. A suitably sized glass vessel containing water or metal shot was then placed directly inside the top aluminum pan. The glass vessel was filled with water or metal shot to achieve the desired pressure on the sample. For the condition of ambient pressure, the glass vessel was not used.

6. The experiment was begun with the assembly of all layers and the application of the weight on top of the assembly. Test exposures of 1 hour were used as this period was found consistent with expected permeation of each test chemical through the selected glove.

7. Following the 1-hour exposure time, the weight and upper layers on top of the solid sorbent were carefully removed and the sorbent was extracted and analyzing according to the previously described procedures.

The proposed assembly is shown in Figure 15. A mock up of the experimental assembly is shown in Figure 16.

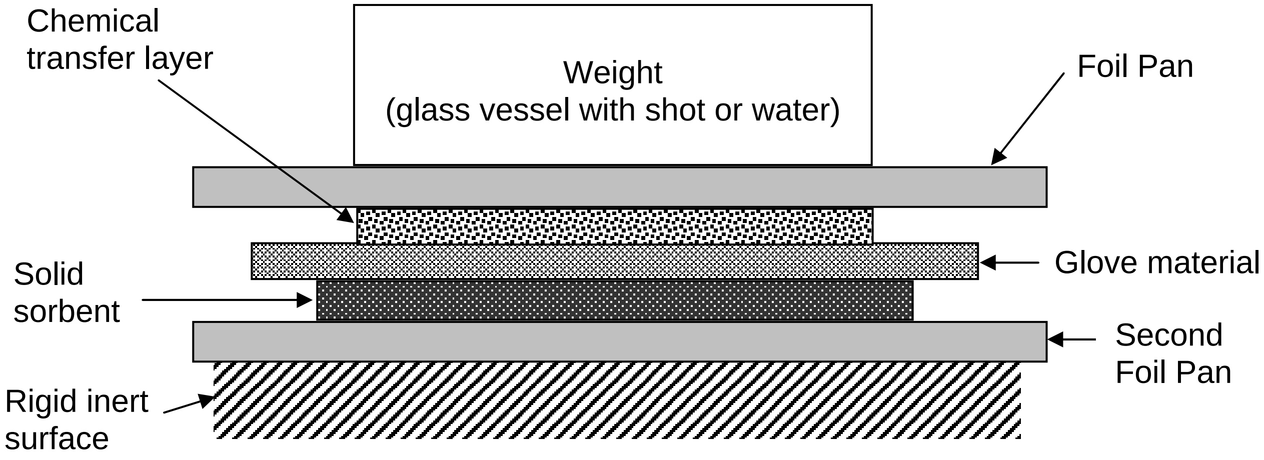

Figure 15 – Diagram of Approach to Study Sorbent Efficiency Under Pressure

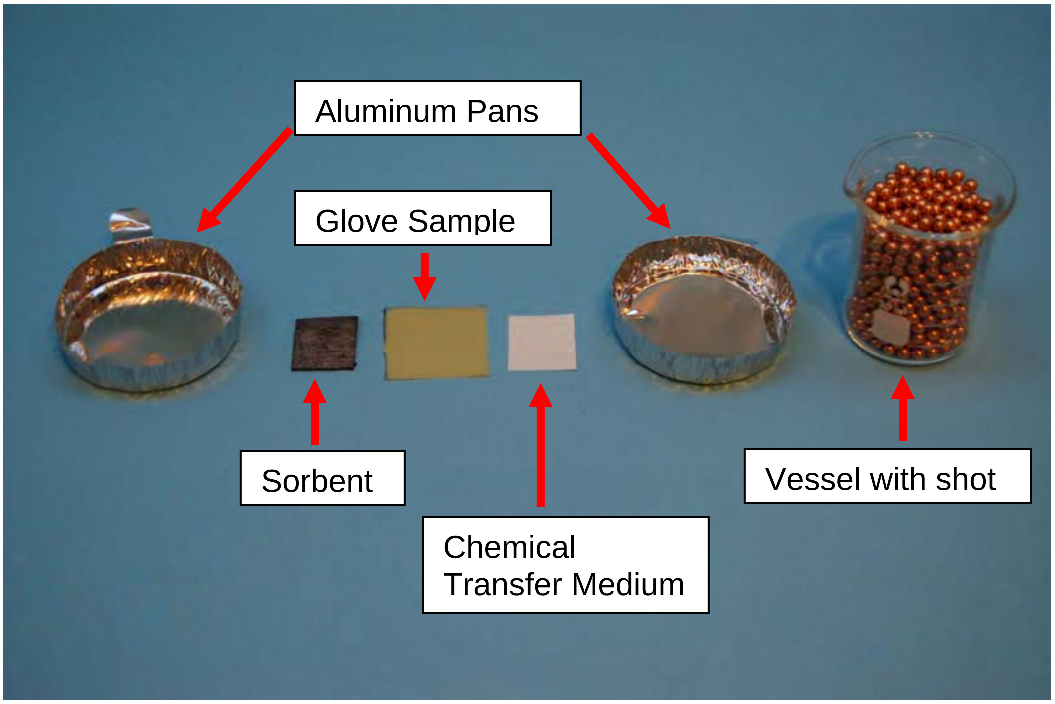

Figure 16 – Assembly of Pressure Testing Apparatus

Permeation results were reported as µg/mL. However, these values were converted to cumulative permeation masses on the basis of the exposed sorbent surface area in contact with the glove material.

Results for Testing of Solid Sorbents under Pressure

Table 8 shows the results for the glove permeation testing with solid sorbents under pressure. These are also presented graphically in Figures 17 to 19.

Table 8 – Summary of Average Test Results for Sorbent Collection at Different Pressures

Chemical	Sorbent	Applied Pressure (g/cm^2)	Extraction Result* (µg/mL)	Cumulative Permeation (µg/cm^2)
Aniline	Charcoal cloth	6.8	<1.0	0.42
		100	16.6	6.72
		200	178	74.8
	Empore disk	6.8	11.8	4.96
		100	197	82.7
		200	420	100
	Passive Adsorbent Device	6.8	Not detected	Not applicable
		100	Not detected	Not applicable
		200	Not detected	Not applicable
m-Cresol	Charcoal cloth	6.8	Not detected	Not applicable
		100	3.1	1.3
		200	7.1	3.0
	Empore disk	6.8	Not detected	Not applicable
		100	140	58.8
		200	226	94.9
	Passive Adsorbent Device	6.8	Not detected	Not applicable
		100	Not detected	Not applicable
		200	Not detected	Not applicable
2-Ethoxyethanol	Charcoal cloth	6.8	1810	760
		100	1980	832
		200	4040	1700
	Empore disk	6.8	Not detected	Not applicable
		100	1170	491
		200	3260	1370
	Passive Adsorbent Device	6.8	3.9	1.6
		100	5.5	2.3
		200	10.8	4.54

* Extraction results are on the basis of an extraction volume of 5 mL.
** The cumulative permeation are based on the total chemical in the extraction volume accounting for the exposure areas of the sorbent in contact with the glove specimen.

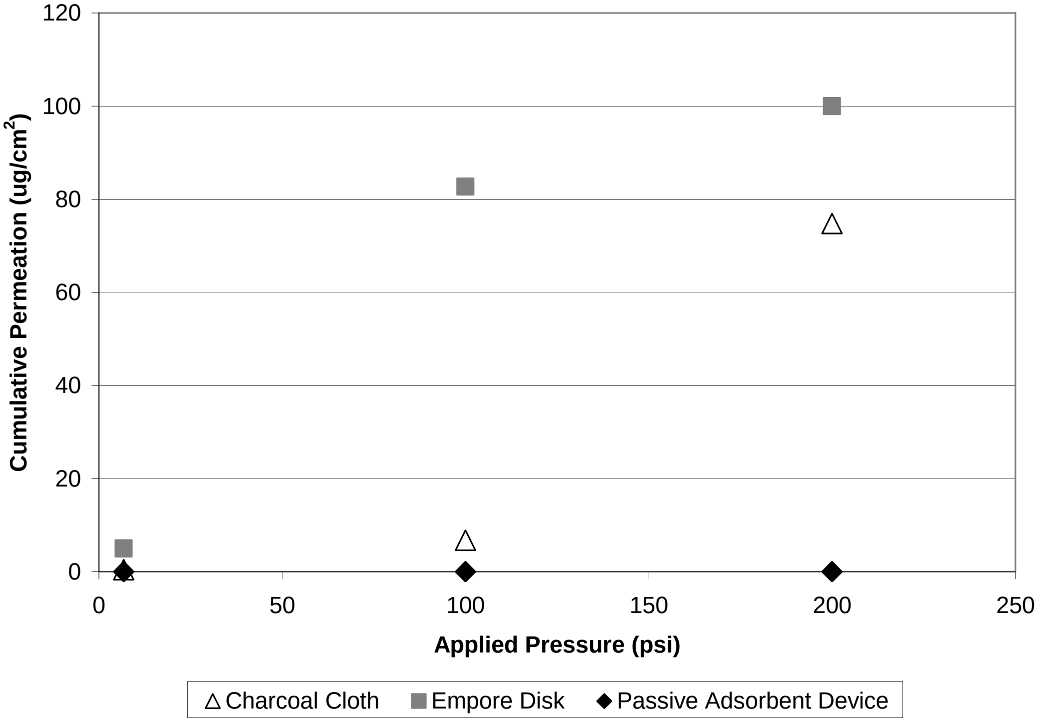

Figure 17 – Cumulative Permeation at Different Pressures for Aniline

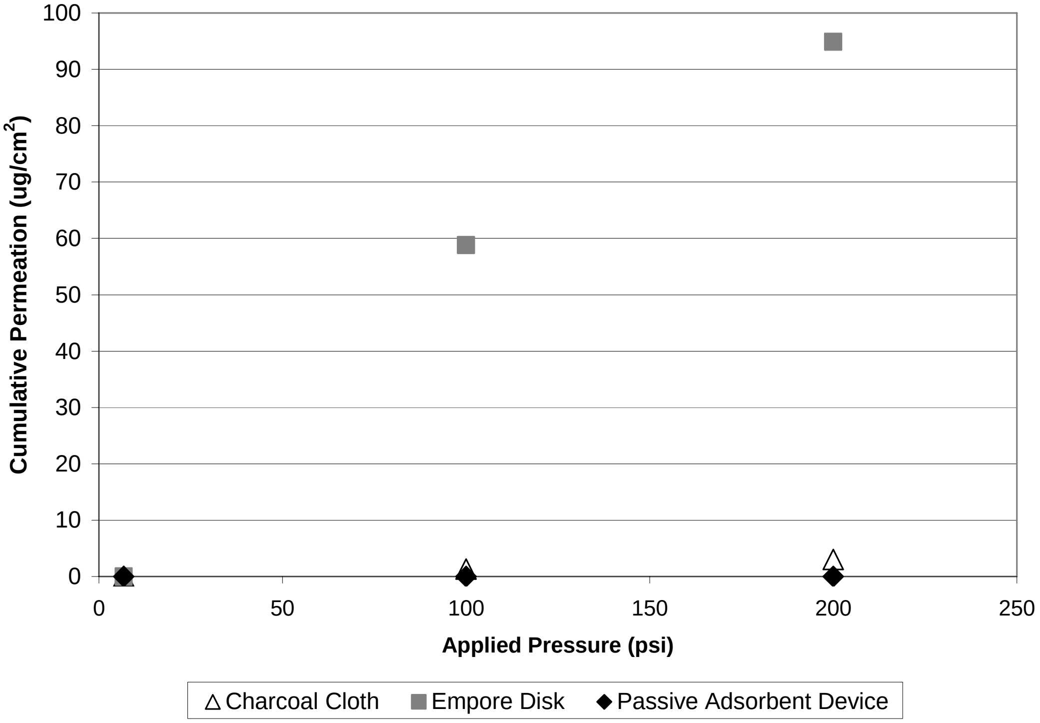

Figure 18 – Cumulative Permeation at Different Pressures for m-Cresol

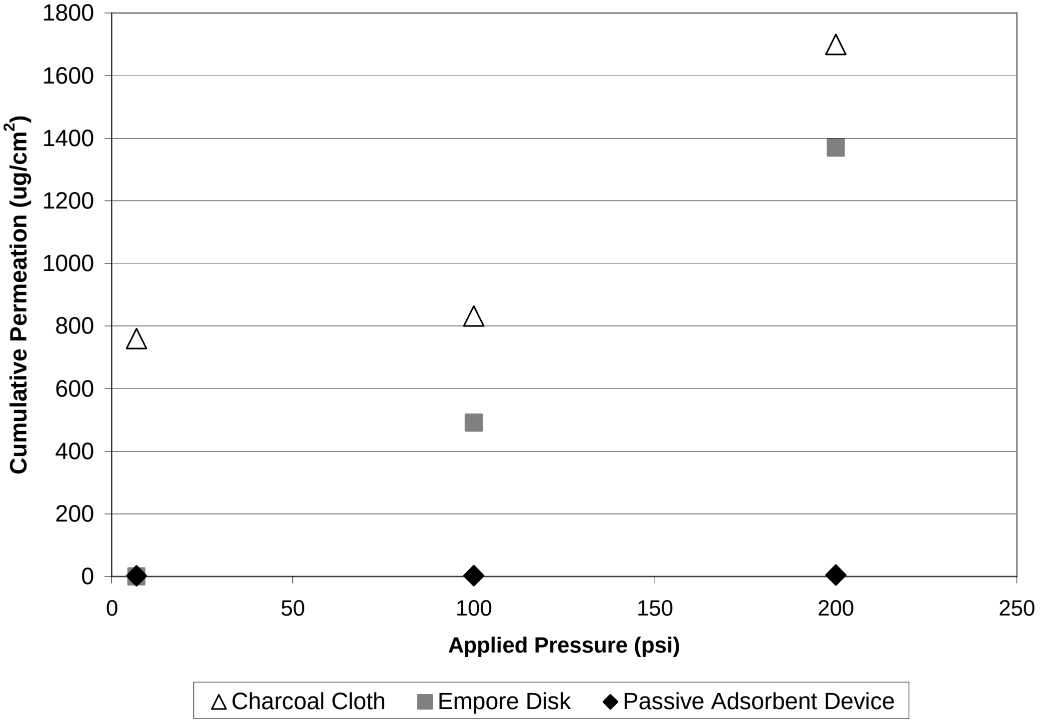

Figure 19 – Cumulative Permeation at Different Pressures for 2-Ethoxyethanol

Findings for Sorbent Pressure Tests

In general, the detection of permeating chemical improved with increasing pressure in most cases. This is undoubtedly the result of improved contact with the sorbent with the glove material. In several instances, no permeation was detected by the respective sorbent in the ambient pressure condition. For two of the chemicals (aniline and m-cresol), the passive adsorbent device sorbents did not detect any chemical at any pressure. This may be due to the fact that chemical must permeate both through the glove material and through the thin layer of HDPE that covers the sorbent and that is intended to protect the sorbent from high humidity as part of the device.

The responses of sorbents in detecting permeation appeared to be consistent with the commercial permeation data, which show different permeation rates through the selected glove material. For example, larger cumulative permeation masses were reported for 2-ethoxyethanol, which exhibited the higher permeation rate in standardized permeation testing.

Given the failure of some sorbents to detect chemical permeation at some pressures and in some cases not at all, no specific trends could be discerned. With the limited data, it was not possible to determine if a linear or other type of relationship existed.

COMPARISON OF SORBENTS WITH COLORIMETRIC INDICATORS

Identification of Colorimetric Indicators

During the literature review, the principal colorimetric indicators identified were those developed and commercially available from Colorimetric Laboratories (Des Plaines, IL). A colorimetric detection kit was identified for the pesticide chlorpyrifos available from EnviroLogix (Portland, ME). This kit uses an enzyme-linked immunosorbent assay (ELISA). In the test, the pesticide residues compete with the enzyme (horseradish peroxidase) for a limited number of antibody binding sites on the inside surface of the test wells. After a wash step, the results are visualized with a color development step. The manufacturer indicates that the kit can also be applied to related pesticides, including chlorpyrifos-methyl, diazinon, quinalphos, azinphos-ethyl, axinphos-ethyl, pirimiphos-ethyl, pirimiphos-methyl, parathion, parathion-methyl, fenitrothion, and malathion. Limits of detection are indicated as part per billion levels of the pesticides in water and soil samples. Another approach to colorimetric detection that was investigated included chemical warfare agent detection papers. Chemical agent detection papers incorporate two different dyes and a pH indicator. Upon contact with an aerosol containing chemical agent through blotting on suspected surfaces, the M8 (military) paper turns dark green for vesicants (e.g., VX agent), yellow for G nerve agents (e.g., Sarin), and red for blister agents (e.g., Distilled Mustard). The M9 paper is similar but uses a single indication of agent being present; it also has an adhesive backing allowing detector papers to be placed on clothing or skin. There have also been color strips that have been developed for hazardous materials operations that provide a range of colorimetric detection capabilities. One provider, Smart Strip (Boynton Beach, FL), has created a card like device that includes reagent-agents to react with contaminants and claims detection limits at ppm levels for arsenic, chlorine, cyanide, fluoride, sulfide, oxidizers and nerve agents. Neither the pesticide or agent color indicator approaches were used due to the sensitivity of the indicators and choice of chemicals used in the study.

In the selection of chemicals, a specific colorimetric indicator was selected for each chemical. Each of the indicators was specific to the one chemical and was provided by Colorimetric Laboratories. Colorimetric Laboratories has developed a series of different detectors for a range of chemicals, including polar solvents, aliphatic amines, aromatic amines, aliphatic isocyanates, aromatic isocyanates, acids and bases, hydrazines, and phenols. The indicators rely on reagents that turn color when encountered by the specific chemicals for which the reagent chemistry was selected. The reagents are encapsulated so that the chemicals must first permeate the barrier before the color change. Some indicators require special procedures for their development. These indicators have been used as part of several studies that were identified in the literature review [20-22]. A separate development has taken place for an inorganic/organic acid indicator by NIOSH [23,24]

Test Approach

Similar procedures developed in Task 2 were applied to the evaluation of selected colorimetric detectors at the respective pressures. The same experimental procedures were used. The colorimetric indicators were prepared for use in the study by cutting off the adhesive areas such that the pad portion of the indicator was present. The indicators were then substituted for the position of sorbent as previously described.

Instead of extraction and analysis, the colorimetric indicators were observed for color changes after following the manufacturer instructions for their development (see above). When color changes were observed, the results were reported as positive, whereas if no change was discernable, the results were reported as negative.

The procedures for each colorimetric indicator were followed.

- The aromatic amine colorimetric detector required color development by the addition of 3-5 drops of tap water to the indicator following the exposure. The indicator pad, originally pale yellow, turned a pink color in the areas where the water was absorbed in the presence of aromatic amines (see Figure 20).

- For the relatively new phenol based colorimetric indicator, a special development solution was added to the exposed pad. The white pad turned a bright red color in the area where the developing solution was added when m-cresol was present (see Figure 21).

- The solvent based Perma-Tec™ indicators did not require specific development. The indicator consists of a charcoal fabric piece with an over lain white strip. With the addition of 2-ethoxyethanol, the white strip turned pale gray which intensified approximately one hour after exposure. Figure 22 shows examples of an unexposed and exposed solvent based Perma-Tec™ indicators.

Figure 20 – Unexposed and Exposed Aromatic Amine Perma-Tec™ Indicators (Aniline)

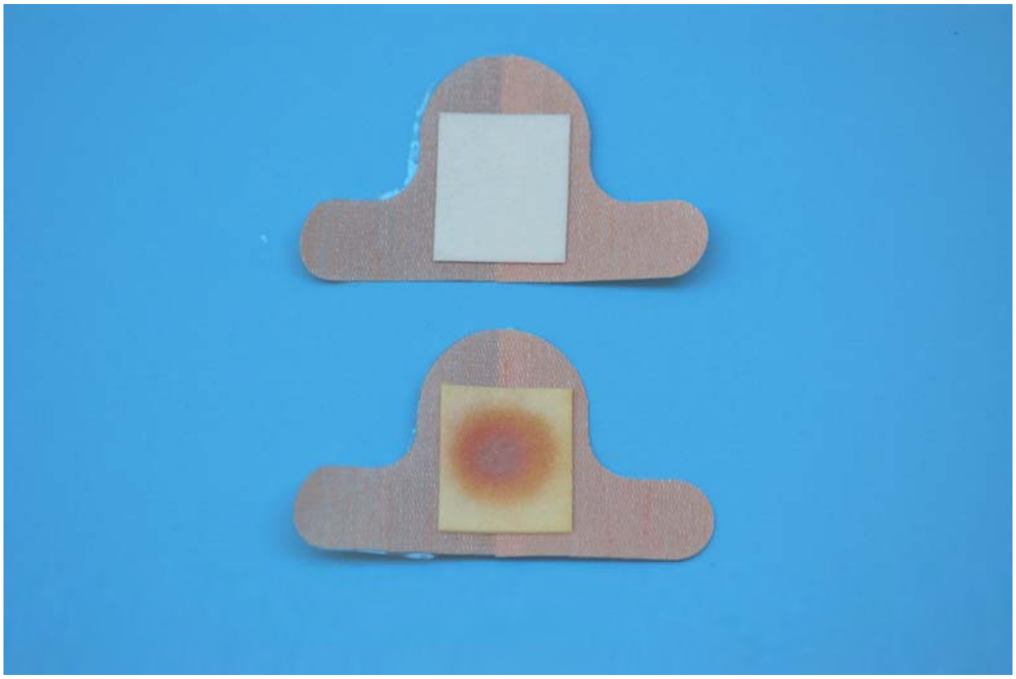

Figure 21 – Unexposed and Exposed Phenol Perma-Tec™ Indicators (m-Cresol)

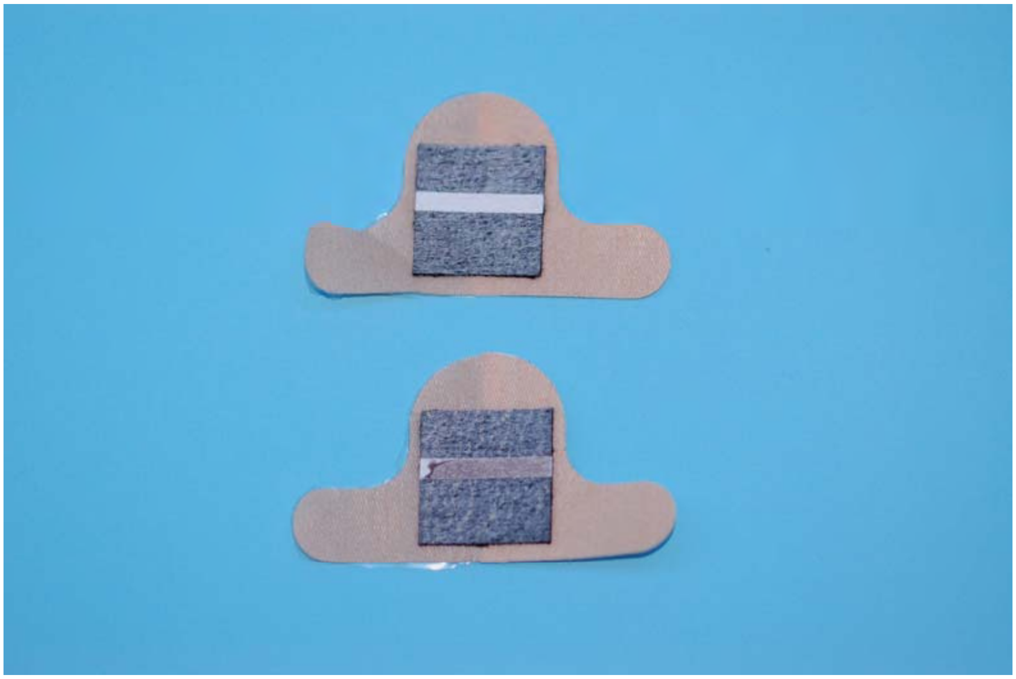

Figure 22 – Unexposed and Exposed Solvent Perma-Tec™ Indicators (2-Ethoxyethanol)

Comparison of Solid Sorbents with Colorimetric Indicators

Tests were carried out with each chemical and colorimetric indicator at the three pressures for multiple replicates. Test results are provided in Table 9. An indication of detection using the three sorbents (detected – positive; not detected – negative) is also provided in the table for comparing solid sorbent performance with the colorimetric indicators.

Table 9 – Summary of Results for Evaluation of Colorimetric Indicators at Different Pressures

Chemical	Colorimetric Indicator	Applied Pressure (psi)	Indicator Result	Solid Sorbent Result		
				Charcoal Cloth	Empore Disk	Passive Ads. Dev.
Aniline	Perma-Tec™ Aromatic Amines	6.8	Positive	Positive	Positive	Negative
		100	Positive	Positive	Positive	Negative
		200	Positive	Positive	Positive	Negative
m-Cresol	Perma-Tec™ Phenols	6.8	Positive	Negative	Negative	Negative
		100	Positive	Positive	Positive	Negative
		200	Positive	Positive	Positive	Negative
2-Ethoxyethanol	Perma-Tec™ Solvent	6.8	Negative	Positive	Negative	Positive
		100	Negative	Positive	Positive	Positive
		200	Negative	Positive	Positive	Positive

Analysis of Results

Surprisingly, no discernable pressure effects were observed with the colorimetric indicators in contrast to findings for the solid sorbents for the two chemicals where colorimetric changes were observed (aniline and m-cresol). It may be speculated that sufficient chemical permeated over the time period to cause a change in the colorimetric indicators that was within the indicator's limit of detection at each pressure. While the phenol-based Perma-Tec™ indicators were relatively new, a detection limit of less than 0.1 mg was presented as being possible by the manufacturer. Colorimetric Laboratories indicated that the limit of detection for the Perma-Tec solvent indicators was at 0.5 to 5.0 mg for the solvent version of this product. Later tests of with direct contact of 2-ethoxyethanol with the detector strip of the indicator yielded no reaction at the spiking volumes used in the study until a volume of 0.05 mL (approximately 50 mg) was applied. This observation could explain the lack of detection by the solvent colorimetric detectors for 2-ethoxyethanol.

CONCLUSIONS

This study was able to demonstrate that different solid sorbents can be used for the efficient detection of semi-volatile chemicals, having vapor pressures below 5 mm Hg. The selected sorbents offer potential for use under protective clothing based on their design and prior demonstrated use for measuring chemical permeation. The relative effectiveness of the solid sorbents was characterized with the 3M Empore C18 extraction disks providing the greater consistency of results over the spiked volume range used in the study (0.2 to 5 µL). The analytical techniques developed to extract and quantify the selected analytes proved linear with increasing volume. The study showed that increasing pressure (up to 200 g/cm^2, consistent with tool use) increases the ability of the selected sorbents to detect semi-volatile chemicals. While the mechanism for these observations has not been fully investigated, it is suspected that the increased pressure provides more uniform contact of the permeating chemical with the sorbent material. In comparing the performance of the selected solid sorbents with commercially available colorimetric indicators, correspondence was generally achieved between solid sorbent and colorimetric indicators for detection of permeating chemical. Exceptions included the colorimetric indicator that did not show detection of the selected solvent (2-ethoxyethanol). In this case, the indicator sensitivity to the chemical may have been at higher level than achieved in the permeation of the sample glove material. However, colorimetric detectors showed indications of permeation in all cases for the selected aromatic amine (aniline) and phenolic chemical (m-cresol). While the findings of this study are limited to a few chemicals and solid sorbents under specific conditions, the results suggest the potential for using solid sorbents and colorimetric indicators as an effective media under protective clothing to quantify or indicate permeation, respectively. A practice of using solid sorbents can provide a more meaningful basis for measuring permeation in terms of cumulative dose to the individual worker under the conditions of use.

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APPENDIX A

Specifications for Sorbents Used in Study

Appendix A

Specifications for Preparation of Passive Adsorbent Devices

A.1 General Description. Passive adsorbent devices are small packets that are filled with an adsorbent, Tenax TA. The top layer of the packet is high-density polyethylene (HDPE) film that provides the sampling surface. The back of the packet is an impermeable plastic-coated foil. Medical grade double-coated adhesive is affixed to the back of the packets enables the devices to be attached to the skin of the test subject.

A.2 General Device Specifications: The general specifications for passive adsorbent devices are provided in Table A1.

Table A.1 – General Device Specifications

Characteristic	Specification
Outer dimensions	25 mm x 35 mm (1 in. x 1 3/8 in.)
Film sampling surface dimensions	18 mm x 25 mm (3/4 in. x 1 in.)
Film sampling surface area	450 mm^2 (3/4 $in.^2$) ± 2.5%
Edge dimensions	0.68 mm (1/8 in.) sides; 0.19 mm (3/16 in.) ends
Corners	Trimmed 0.1 mm (3/32 in.) at 45 degree angle
Adsorbent	40 mg ±10% Tenax TA

The devices are assembled and packaged in FDA certified cleanroom. Adsorbent exposure is kept to a minimum. The devices are kept free of contamination from human contact or vapors in air that can be detected using analytical technique used to measure device adsorption of Methyl Salicylate. Devices are packaged as soon as feasible after assembly to minimize potential for contamination.

A.3 Materials of Construction

A.3.1 Barrier Film. The thickness of the barrier film is 0.025 mm (0.001 in.) ± 5%, with the thickness measured every 1 meter. The color of the barrier film is natural. The barrier film is subject to a heat soak treatment at 95°C for 4 days. The barrier film is high density polyethylene (HDPE) meeting the specifications provided for the resin in Table A.2 and film in Table A.3.[1]

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[1] The Finathene HDPE 1285 product meets these specifications. This product is available from FINA Oil and Chemical Company, 8350 North Central Expressway, P. O. Box 2159, Dallas, TX 75221 USA, Phone: 214-750-2400.

Table A.2 – Resin Properties of HDPE

Property	**Typical Value**	**Test Method**
Melt Flow Index, g/10 min		ASTM D 1238
190^{o}C, 2.16 kg	0.07	
190^{o}C, 5kg	0.31	
130^{o}C, 21.6 kg (HLMI)	9.0	
Density, g/cm^3	0.950	ASTM D 792
Melting Point, ^{o}F	260	ASTM D 3417

Table A.3 – Properties of the Barrier Film

Property	**Typical Value**	**Test Method**
Dart Impact, g	350	ASTM D 1709, Method A
Elmendorf Tear Resistance, g	24 Machine direction 120 Transverse direction	ASTM D 1922
Tensile Strength at Yield, psi	5,300 Machine direction 5,000 Transverse direction	ASTM D 882, 20 in./min
Tensile Strength at Break, psi	8,900 Machine direction 8,500 Transverse direction	ASTM D 882, 20 in./min
Elongation at Break, %	300-500 Machine direction 300-500 Transverse direction	ASTM D882, 20 in./min
Secant Modulus of Elasticity, psi @ 2% strain	122,000 Machine direction 132,000 Transverse direction	ASTM D882, 20 in./min
Water Vapor Transmission at 100^{o}F, g/24 hr/100 in./mil	0.8	ASTM E96

A.3.2 Nylon/Foil Barrier Film. The nylon/foil barrier film is a material meeting Mil-B-131H, "Barrier Materials, Water vapor proof, Greaseproof, Flexible, Heat-sealable" for Type 1, Class 1. The film consists of four layers, from outside to inside, consisting of a 60 gauge Nylon, low density polyethylene, 0.003 in. foil and 0.002 in. polyethylene layer. Specifications for the nylon/foil barrier film are provided in Table A.4.[2]

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[2] The nylon/foil barrier film meeting these specification is available from Syon, ITW Devcon, Danvers, MA 01923 USA, Phone: 508-881-8852 (6030 Nylon/Foil Barrier Bag material)

Table A.4 – Specifications for Nylon/Foil Barrier Film

Property	Typical Value	Test Method
Thickness, in.	0.005	
Moisture vapor transmission rate, g/100 in.^{2}/24 hrs	< 0.02	MOCON
Oxygen transmission rate, cm^3/m^2/24 hr	< 0.01	MOCON
Tensile strength, at break, lbs	22 Machine direction	TAPPI T404 TS66
	22 Transverse direction	
Breaking strength, grab, lbs	62	Federal Standard 101
Bursting strength, psi	65	TAPPI T403 TS63
Puncture resistance, lbs	17.5	Federal Standard 101
Heat seal conditions, single bar heat	400^{o}F/40 psi/2 sec	

The nylon/foil barrier film is evaluated for oil resistance in testing according to Federal Standard 101, Method 3014 and Mil-B-131H by pouring 5 mL of oil (TT-S-735, Type 6) into 3 in. x 3 in. pouches that are then sealed. The pouches are then placed in an oven set at 160^{o}F ± 2^{o}F for 24 hours. Oil resistance is demonstrated when no leakage is observed.

The nylon/foil barrier film is evaluated for water resistance in testing according to Federal Standard 101, Method 3028 and Mil-B-131H. Sample materials measuring not less than 6 in. x 6 in. are immersed in distilled water for 48 hours. After the water exposures, the samples are then placed in an oven set at 160^{o}F ± 2^{o}F for 24 hours. Water resistance is demonstrated when samples do not delaminate more than 1 in. in length along the edge and ½ in. in depth from the edge.

A.3.3 Adhesive Backing. The adhesive backing is a double coated tape that consists of a 3 mil transparent polyethylene film, coated on both sides with a hypoallergenic, pressure sensitive adhesive. The adhesive backing is of medical grade and provides adhesive to steel of 30 oz/in. (8.3 N/in.) minimum, a tape caliper without liner of 0.12 mm (4.9 mil), tensile strength of 4.5 lbs/in. (20 N/25 mm) minimum, elongation of 200%, minimum, and a liner removal of 50 g/in. (0.49 N/in,) maximum.[3]

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[3] The adhesive backing meeting these specifications is available from 3M Medical Specialties, 3M Center, Building 275-5W-05, St. Paul, MN 55144-1000 USA, Phone: 800-228-3957(3M Double Coated Medical Tape Cat. No. 1509)

A.3.4 Adsorbent. The sorbent is Tenax TA of 60 to 80 mesh size that is free of fines and interfering contaminants. A PAD amount of 40 mg ±10% is used. Chemical cleanliness of the Tenax TA has been found to be a major concern when analyzing PADs. Tenax TA must be washed to remove fines and preconditioned to remove materials that interfere with the gas chromatographic determination of MeS. Analytes collected by the samplers may be removed from the Tenax TA by either solvent extraction or thermal desorption prior to analysis.

A.3.4.1 Cleaning Procedure. The following procedure is used for cleaning the Tenax TA adsborbent:

(1) Use HPLC grade methanol (MeOH).
(2) Transfer Tenax to Pyrex (or equivalent) container, cover with MeOH, place under vacuum (10 to 15 torr) until gas bubbles cease forming, maintain vacuum for 5 min, and increase pressure to ambient.
(3) Reduce pressure and increase pressure two more times.
(4) Wash with MeOH to remove fines.
(5) Heat in oven to 75 to 80°C for 1 to 2 hr or until dry.

A.3.4.2 Preconditioning Procedure. The cleaned Tenax TA adsorbent is preconditioned by heating adsorbent to 340°C under N_2 (six 9s purity, 20 mL/min) overnight.

A.3.4.3 Storage Procedure. The preconditioned Tenax TA is stored in an air-tight receptacle to minimize any exposure to the air.

A.3.4.4 Procedures for Determiniation of Cleanliness. The adsorbent must be free of contaminants that interfere with the analytical detection of MeS. Tenax TA suppliers are required to provide chromatograms and supporting documentation to demonstrate cleanliness for each lot of adsorbent. The test parameters provided in Table A.5 are used to determine cleanliness of the adsorbent.

Table A.5 – Test Parameters for Determining Cleanliness of Adsorbent

Analytical method	Thermal desorption, GC/FID
Tenax TA sample size	40 mg
Instrument sample desorption	250^{o}C, 6 min
Instrument trap desorption	274^{o}C, 4 min
Instrument column	0.53 mm id x 15 m x 1 µm df Stabilwax or equivalent
Oven temperature	120^{o}C, isothermal
FID temperature	250^{o}C

The maximum interfering peak overlap or background level cannot be more than 3 ng at the MeS retention (elution) time.

3M

PRODUCT Information

Empore™

High Performance Extraction Disk Products

Standard and High Density Membranes

General Information

3M™ Empore™ Extraction Disk Products are available in two membrane formats:

The standard density (SD) Empore disk products are designed for use with biological matrices and are recommended as the first choice for most bioanalytical applications. The high density (HD) Empore disk products are intended for smaller elution volumes and relatively clean sample matrices.

Product Information

Both SD and HD membranes are made using a 3M patented technology which entraps sorbent particles within an inert matrix of polytetrafluoroethylene. The resulting particle-loaded membrane (90% particles: 10% PTFE, by weight) results in a denser, more uniform extraction bed than can be achieved in a traditional SPE cartridge made from loosely packed particles.

3M™ Empore™ Extraction Disk
45-55 µm particle size

3M™ Empore™ Extraction Disk
8-16 µm particle size

The dense particle packing and uniform distribution within SD and HD Empore disks provide efficient and reproducible sample preparation. The diffusion distance between particles is minimized, adsorption is more efficient, and extraction can be accomplished using less sorbent mass to provide the following performance gains:

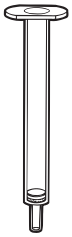
- Small elution volumes
- Reduced time for solvent evaporation or elimination of this step completely
- Channeling effects eliminated
- Excellent reproducibility/low CVs

Product Characteristics

Feature	Standard Density (SD)	High Density (HD)
Applications	For a wide range of samples and volumes including plasma and urine	Suggested for clean samples and when lower elution volumes are desired
Sorbent particle size	Standard, 45-55 µ	Small, 8-16 µ
Membrane thickness	0.75 mm approx.	0.5 mm approx.
Vacuum requirements	5-10 inches Hg, (0.17-0.34 bar), depending on sample viscosity	Requires strong vacuum of 15-20 inches Hg, (0.68-0.68 bar) or greater

Product Formats

A selection of Empore SD and HD membranes is available in four sizes of extraction disk cartridges: 4 mm/1 mL, 7 mm/3 mL, 10 mm/6 mL and 20 mm/40 mL. Empore SD membranes are also available in 96-well microtiter plate format, which is ideal for sample preparation prior to LC/MS and other high throughput applications. Each well of the 3M™ Empore™ Extraction Disk Plate has an effective membrane diameter of 5.5 mm and reservoir volumes of 1.2 or 2.5 mL. Methods can be easily transferred from disk cartridges to disk plates.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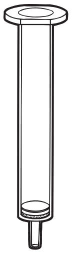
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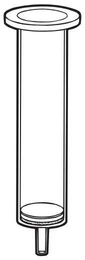
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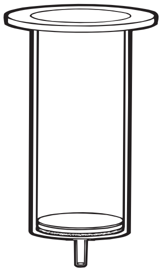
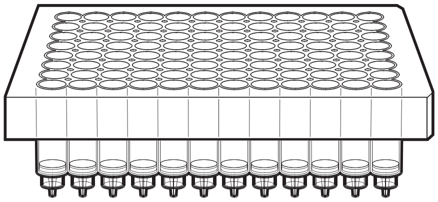

40 ml


96 well plate (standard 1.2 ml)

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Extraction Disks

Method Summary

EPA Method 525.2
Revision 1.0

Determination

Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry

Method promulgation was announced in the Federal Register Volume 59, No. 232 on December 5, 1994. Method authors: J.W. Eichelberger, T.D. Behymer, W.L. Budde; Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

This Drinking Water Methods document is not currently published in an NTIS document and is available directly from US EPA: Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268. Telephone: (513) 569-7586.

Summary of Method

A one liter water sample is passed through a 47mm C18 Empore™ disk and eluted with ethyl acetate and methylene chloride, the extract dried and reduced in volume to 1.0 mL and analyzed by GC/MS.

Analytes

The analyte list for this method is comprised of 110 compounds representative of several classes of pesticides, polynuclear aromatic hydrocarbons, PCBs, phthalates and adipates. Method detection limits (MDLs) as published in the method range from 0.03-2.4 µg/L and recoveries from 20 - 180%. Refer to the published method for compound specific MDLs and recoveries. By compound class, average recoveries are:

Pesticides	108%
PCBs	108%
Phthalates & Adipates	116%
PAHs	112%

The validation data presented herein were determined on three independent lots of C18 disks. MDLs were not determined as part of this validation. In addition to the listed method analytes, recovery data for an extended list of analytes is also included.

525.2 METHOD PERFORMANCE

Analyte	Ave %R(RSD) (n=9)
Acenaphthylene	109(3.2)
Alachlor	113(2.3)
Aldrin	113(3.7)
Ametryn	123(6.5)
Anthracene	120(3.4)
Atraton1	44(22)
Atrazine	123(4.6)
Benz[a]anthracene	105(3.4)
Benzo[b]fluoranthene	112(4.8)
Benzo[k]fluoranthene	109(10)
Benzo[g,h,i]perylene	120(3.9)
Benzo[a]pyrene	106(2.8)
BHC, alpha	122(4.2)
BHC, beta	112(4.3)
BHC, delta	119(3.4)
BHC, gamma (Lindane)	118(2.7)
Bromacil	115(7.1)
Butachlor	105(2 7)
Butylate	115(6.0)
Butylbenzylphthalate	121 (3.4)
Carboxin	100(4.9)
Chlordane, alpha	97(3.1)
Chlordane, gamma	119(3.5)
Chlordane, bans nonachlor	98(4.2)
Chlorneb	123(4.7)
Chlorobenzilate	107(2 8)
Chlorpropham	100(3 2)
Chlorpyrifos	120(5.9)
Chlorthalonil	110(3.2)
Chrysene	104(3.1)
Cyanazine	77(3.2)
Cycloate	124(3.1)
DCPA	122(4 1)
4,4'-DDD	112(3.8)
4,4'-DDE	99(7 0)
4,4'-DDT	110(7.4)
Diazinon	98(13)
Dibenz[a,h]anthracene	124(3.7)
di-n-butylphthalate	125(4.4)
Dichlorvos	109(10)
Dieldrin	98(2.9)
di(2-ethylhexyl)adipate	111 (4.0)
di(2-ethylhexyl)phthalate	122(3.7)
Diethylphthalate	106(3.5)
Dimethylphthalate	113(4.8)
2,4-dinitrotoluene	79(11)
2,6-dinitrotoluene	84(9.8)
Diphenamid	1 08(2.8)
Disulfoton	115(7.6)
Disulfoton sulfone2	164(2.8)
Disulfoton sulfoxide2	136(8.9)
Endosulfan I	102(5.2)
Endosulfan II	118(3.4)
Endosulfan sulfate	117(3.3)
Endrin	126(3.0)
Endrin aldehyde	119(9.2)
EPTC	112(8.4)
Ethoprop	110(4.2)
Etridiazole	116(3.7)
Fenamiphos	99(2.2)
Fenarimol2	150(5.5)
Fluorene	108(3.0)
Fluridone2	114(4.5)
Heptachlor	112(4.1)
Heptachlor epoxide	109(2.9)
Hexachlorobenzene	104(4.1)
Hexachlorocyclopentadiene	103(7.5)
Hexazinone	125(4.6)
Indeno [I,2,3, c, d] pyrene	121 (3.7)
Isophorone	87(11)
Methoxychlor	107(2 1)
Methyl paraoxon	106(4 2)
Metolachlor	109(2 2)
Metribuzin1	81 (6.0)
Mevinphos	108(7.9)
MGK 264	116(4.0)
Molinate	121(5.6)
Napropamide	97(3.2)
Norflurazon2	141(4.2)
Pebulate	119(5.4)
Pentachlorophenol	81 (4.9)
Permethnn, cis	110(4.4)
Permethrin, trans	114(3.8)
Phenanthrene	113(1.9)
Prometon1	49(37)
Prometryn	110(5.2)
Pronamide	120(4.7)
Propachlor	120(5.6)
Propazine	118(4.4)
Pyrene	109(2.4)
Simazine	92(7.3)
Simetryn	103(15)
Stirofos	106(4.3)
Tebuthiuron2	100(11)
Terbacil	108(6 8)
Terbufos1	124(3.0)
Terbutryn	113(5.5)
Triademefon	117(13)
Tricyclazole2	137(12)
Trifluralin	113(5.6)
Vernolate	102(4.8)

PCB Congeners	
2,3-Dichlorobiphenyl	116(3.6)
2-Chlorobiphenyl	99(2.3)
2,2',3,3',4,4',6-heptachlorobiphenyl	110(5.6)
2,2',4,4',5,6'-hexachlorobiphenyl	106(3.3)
2,2',3,3',4,5',6,6'-octachlorobiphenyl	106(6.2)
2,2',3',4,6-pentachlorobiphenyl	105(3.2)
2,2',4,4'-tetrachlorobiphenyl	114(2.9)
2,4,5-trichlorobiphenyl	114(3.1)

1 n=3

2 Analyte recovery reported is from EPA published method. It was not included in the independent validation.

Spike levels = 2.0 µg/L

Method

1. Assemble an all glass filtration assembly using a 47 mm C18 Empore™ disk. Use of a manifold for multiple extractions is acceptable.
2. Wash the extraction apparatus and disk by adding 5 ml of a 1:1 mixture of ethyl acetate (EtAc): methylene chloride (MeCI2) to the reservoir. Pull a small amount through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.
3. Condition the disk by adding approximately 5 ml of methanol to the reservoir, pulling a small amount through the disk then letting it soak for about one minute. Pull most of the remaining methanol through the disk, leaving 3 to 5 mm of methanol on the surface of the disk.
4. Add 5 ml of reagent water to the disk and using the vacuum pull most through, again leaving 3 to 5 mm of water on the surface of the disk.
5. Add 5 ml of methanol to the water sample and mix well. Add the water sample to the reservoir and, under vacuum, filter as quickly as the vacuum will allow. Drain as much water from sample bottle as possible.
6. Remove filter assembly and insert suitable sample tube for eluate collection.
7. Add 5 ml of EtAc to the sample bottle. Rinse bottle thoroughly and transfer solvent to the disk with dispo-pipet, rinsing sides of filtration reservoir in the process.
8. Pull half of solvent through disk then release the vacuum. Allow the remaining solvent to soak the disk for about one minute, then draw remainder through under vacuum.
9. Repeat the solvent rinse of the sample bottle and apparatus using 5 mL of $MeCl_2$.
10. Using a disposable pipette, rinse down the sides of the filtration glassware with two 3 mL aliquots of 1:1 EtAc/$MeCl_2$.
11. Dry the combined eluant with 5-7 grams granular anhydrous sodium sulfate. Rinse the collection tube and sodium sulfate with two 3 mL portions of 1:1 EtAc/$MeCl_2$ and place combined solvent into a concentrator tube.
12. Concentrate extract to 1 ml under gentle stream of nitrogen (may be warmed gently). Do not concentrate to <0.5 ml or loss of analytes could occur.
13. Analyze by GC/MS.

Additional compounds validated by this method include:

Analyte	Ave %R (RSD)[1]
Aspon	121(3.8)
Azinphos-methyl	93(3.2)
Benfluralin	115(4.5)
Bolstar	117(4.1)
Chloropropylate	103(3.0)
Clomazone	104(4.1)
Coumaphos	100(2.3)
Demeton	61(4.5)
Desethylatrazine	26(3.0)
Desisopropylatrazine[2]	102(NA)
Dichlobenil	99(7.2)
Dichlofenthion	123(3.2)
Dichloran	114(12)
Dyfonate	104(3.5)
Ethelfluralin	97(2.3)
Ethion	115(3.6)

Analyte	Ave %R (RSD)[1]
Famphur	107(5.3)
Fenthion	124(4.1)
Fluazifop-butyl	123(3.1)
Fluchloralin	123(3.5)
Fluometuron	99(3.9)
Malathion	113(3.9)
Merphos	100(17)
1-methyl Naphthalene	93(4.5)
MGK-326	120(5.1)
Oxadiazon	115(2-9)
Pendimethalin	123(7.1)
Phorate	97(4.1)
Profluralin	127(11)
Propanil	100(4.2)
Tribufos (DEF)	107(3.8)

1 Spike levels 2.0 µg/L, n=9

2 n=2

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Extraction Disks

January 1996

Method Summary

SW-846 Method 3535 Solid Phase Extraction Test Methods for TCLP Leachates

A solid-phase extraction disk method (Method 3535) has been validated for extraction of the semivolatile organic analytes from Method 1311 Toxicity Characteristic leachates. The validation data have been reviewed and accepted by the EPA SW-846 Workgroup and are scheduled for inclusion in the proposed 4th Update to SW-846 (anticipated early 1996). Copies of the draft method are available from the Methods Section Office at (202) 260-4761, until the time they are proposed officially by an announcement in the Federal Register.

Once accepted by the workgroup, draft methods may be used in most RCRA applications – the only exceptions being those analyses for which the use of SW-846 methods is mandatory. Applications considered “mandatory” are: hazardous waste characterizations, delisting programs, characterization of free liquids, emissions monitoring from trial burns, and determining air emissions from process equipment. This method pertains to the first two of these applications in which the solids are subjected to acidic buffers to “leach” potentially toxic materials which are then quantified. The leachate preparation must follow Method 1311; the sample preparation of that leachate for the semi-volatiles analyses can be done by any reliable method (including the proposed method 3535, which is detailed herein) according to EPA sources. Technical questions regarding specific RCRA applications and methods can be directed to the EPA Methods Information Communication Exchange (MICE) at (703) 821-4690.

This method summary is an extension of the Method 3535 application note. As additional analyte groups or matrices are validated by this method, specific conditions will be outlined in a similar document.

Method Summary

TCLP leachates are prepared according to the procedure outlined in EPA Method 1311. The leachates are filtered with 0.6-0.8 micron glass fiber filters as directed in the method, and specific aliquots are prepared for each of the semivolatile organic analyte groups: organochlorine pesticides, herbicides, base/neutral and acid extractables. For each analyte group, a measured volume of sample is extracted using a 3M Empore™ Extraction Disk with SDB-XC (47mm). With the exception of the acid herbicides (extracted at pH 1.0), all other analytes were extracted without modifying the buffer pH. The analytes are eluted with acetone/ethyl acetate (acid herbicides with acetonitrile), dried with sodium sulfate, and concentrated or diluted to the desired final volume for analysis by the determinative method.

TCLP Validation Study

The validation data summarized herein were generated in a single laboratory by a single operator. Multiple operator data and two additional laboratories’ data sets were submitted to the EPA in the validation data package.

Buffer solutions were prepared according to EPA Method 1311. With the exception of the acid herbicides fraction, all samples were extracted without pH modification. The buffers (Buffer #1 pH = 2.88, Buffer #2 pH = 4.93) were spiked as is at low and high levels, and recoveries were determined for evaluation of the extraction efficiency. Soils were then leached with each buffer as per Method 1311, and the leachates fortified at both low and high levels to assess matrix effect on extraction efficiency. A third data set was generated using soils containing ethylene glycol at 1% and 10% levels. The leachates from these soils were spiked with the analytes of concern at action levels to determine the efficacy of extraction in the presence of other organic matter. (See *Fortification Levels* below.)

Fortification Levels:

	Low mg/L	Action mg/L	High mg/L		Low mg/L	Action mg/L	High mg/L
Organochlorine Pesticides				**Base/Neutral Extractables**			
Toxaphene	0.25	0.5	1.0	1,4-Dichlorobenzene	3.75	7.5	15.0
Chlordane	0.015	0.03	0.06	2,4-Dinitrotoluene	0.065	0.13	0.26
Endrin	0.01	0.02	0.04	Hexachlorobenzene	0.065	0.13	0.26
Heptachlor[1]	0.004	0.008	0.16	Hexachlorobutadiene	0.25	0.5	1 .0
Lindane	0.2	0.4	0.8	Hexachloroethane	1.5	3.0	6.0
Methoxychlor	5.0	10.0	20.0	Pyridine	2.5	5.0	10.0
				Acid Extractables			
Acid Herbicides				Cresol[1] (o,m,p-)	100	200	400
2,4-D	5.0	10.0	20.0	2,4,5-trichlorophenol	200	400	800
2,4,5-TP	0.5	1.0	2.0	2,4,6-trichlorophenol	1.0	2.0	4.0
				Pentachlorophenol	50	100	200

[1] Heptachlor/Heptachlor Epoxide and the cresols were spiked in the combined totals indicated.

Methods

Organochlorine Pesticides

1. **Prepare Sample.** Measure a **250 mL** aliquot of the leachate and set aside. The validation data were generated without modifying pH of the leachates.
2. Using a 6-place stainless steel manifold, place a 47mm SDB-XC disk on the glassware base. Wet the disk with acetone (about 1 ml) to preswell this polymer material. Place the reservoir atop the base and clamp in place. The vacuum source should be capable of pulling about 20-25 inches Hg.
3. **Prewash.** Add about 5 mL acetone to the reservoir, rinsing down the sides in the process. This should be done with a receiving vial in the reservoir to capture the waste solvent. Turn on the vacuum momentarily until a few drops of solvent are seen coming through the disk, then release the vacuum and allow the solvent to soak for one minute. Resume the vacuum to draw all of the solvent through the disk, and allow to air-dry with vacuum on. Repeat the prewash with 5 mL ethyl acetate. Remove the receiving vial and dispose of the solvent as appropriate.
4. **Condition.** Add 5 mL methanol to the reservoir. Apply vacuum until a few drops appear below the disk, then release the vacuum. Allow the disk to soak for about 1 minute. From this point until the extraction is completed, it is critical to leave a layer of liquid atop the disk to keep the sorbent from drying and returning to a hydrophobic state. Apply vacuum and draw the methanol level down until 1-2 mm remain atop the disk.
5. Add about 15 mL reagent water to the remaining methanol in the reservoir. Apply vacuum and again draw through most of the water – leaving about 2-3mm of water above the disk.

6. **Extraction.** Add the 250 mL leachate sample to the remaining water in the reservoir and turn on the vacuum. Allow the entire sample to filter. Allow the disk to air-dry with the vacuum on after the sample extraction has been completed.
7. Add 4 mL of acetone to the sample bottle that contained the spiked leachate. Swirl thoroughly to dissolve any residue which might be adsorbed to the container. Set aside.
8. **Elution**. With a receiving vial in place, transfer the acetone from the sample bottle to the reservoir, rinsing down the sides in the process. Add an additional 2 mL acetone, rinsing down the sides of the reservoir. Allow to soak for 1 minute. Apply vacuum momentarily until a drop appears on the drip tube, then release the vacuum. Allow to soak for one minute, then turn on full vacuum and draw all of the acetone through and into the receiving vial.
9. Repeat the bottle rinse and elution in the above step using 5 mLs ethyl acetate.
10. Add a second 5 mL aliquot of ethyl acetate directly to the reservoir, rinsing down the sides. Collect all the aliquots in the same receiving vial.
11. Remove the elution-receiving vial from the manifold. Dry the solvent with anhydrous granular sodium sulfate. Transfer solvent to glassware suitable for the concentration step. Rinse the sodium sulfate twice with additional ethyl acetate and add the solvent to the concentrator tube.
12. Proceed to concentration step followed by analysis as per Method 8081 or equivalent.

Base/Neutral and Acid Extractables

Base/Neutral Fraction:

1. **Prepare sample.** Measure a 250 mL aliquot of leachate and set aside. The pH was not adjusted for the validation studies.

   The extraction procedure is identical to that of the OCP's detailed above. The buffers were extracted as is, with no pH adjustment or other modifiers.

Acid Fraction:

1. **Prepare sample.** Measure a 25 mL aliquot of leachate and set aside. These should be extracted without pH adjustment.

The extraction for this fraction is, again, the same as the OCP method.

Eluants may be combined from both fractions for GC/MS analysis.

Acid Herbicides

NOTE: The validation study incorporates a modification to EPA Method 8321 (HPLC/UV for the determinative method). Method 8321 uses a diethyl ether liquid/liquid extraction of the chlorinated phenoxyacid compounds, then solvent-exchanges to acetonitrile. This method uses acetonitrile as the elution solvent and eliminates diethyl ether altogether.

As part of the interlaboratory validation, one laboratory used the HPLC method; the other used GC/ECD for the determinative method (EPA Method 8150). Sample preparation directions for both determinative methods are outlined herein.

1. **Prepare sample** – Measure a 250 mL aliquot of leachate. Adjust the pH to 1.0 with sulfuric acid (1:1) and set aside.
2. Using a 6-place stainless steel manifold, place a 47mm SDB-XC disk on the glassware base. Wet the disk with acetone (about 1 mL) to preswell the polymer material. Place the reservoir atop the base and clamp in place.

3. **Pre-wash** the glassware and disk by adding about 5 mL of acetonitrile to the reservoir, rinsing down the sides in the process. This should be done with a receiving vial in the reservoir to capture the waste solvent. Turn on the vacuum momentarily until a few drops of solvent are seen coming through the disk, then release the vacuum and allow the solvent to soak for two minutes. Resume the vacuum to draw all of the solvent through the disk, and allow to air-dry with vacuum on. Remove the receiving vial and dispose of the solvent as appropriate.

4. **Condition** the SPE disk. Add 5 mL methanol to the reservoir. Apply vacuum until a few drops appear below the disk, then release the vacuum. Allow the disk to soak for about 1 minute. From this point until the extraction is completed, it is critical to leave a layer of liquid atop the disk to keep the sorbent from drying and returning to hydrophobic state. Apply vacuum and draw the methanol level down until 1-2 mm remain atop the disk.

5. Add about 15 mL reagent water to the remaining methanol in the reservoir. Apply vacuum and again draw through most – leaving about 2-3mm of water above the disk.

6. **Extraction** – Add the 250 mL leachate sample to the remaining water in the reservoir and turn on the vacuum. Allow the entire sample to filter. Allow the disk to air-dry with the vacuum on after the sample extraction is completed.

7. Place 5 mL of acetonitrile in the sample container that contained the spiked sample. Rinse the container and set aside.

8. **Elution** – Place a receiving vial in the manifold to capture the elution solvent. Using a pipette, transfer the acetonitrile from the container rinse to the reservoir, rinsing down the sides. Apply vacuum until a few drops appear on the drip tip, then release the vacuum. Let soak one minute, then draw through into the receiving vial.

9. Repeat this step with a second 5 mL aliquot of acetonitrile.

10. Elute with a third 5 mL aliquot of acetonitrile dispensed directly into the reservoir.

11. **Concentration:**

    HPLC (EPA Method 8321) – Place the elution vial in a warm water bath and using a gentle stream of nitrogen, decrease the volume to less than 10 mLs. Transfer the solvent to a 10 mL volumetric flask and adjust to a 10 mL final volume with acetonitrile.

    GC/ECD (EPA Method 8150) – Follow the above directions through step 10. Add approximately 3 grams granular anhydrous sodium sulfate to the vial and allow to sit for about 15 minutes. Transfer the solvent to an appropriate vial and add 2 mL diazomethane solution. Allow the derivitization to proceed for 30 minutes. Concentrate to less than 10 mLs as detailed above, and adjust to a 10 mL final volume.

12. Analyze by HPLC/UV (Method 8321) or GC/ECD (EPA Method 8150).

RECOVERY STUDIES

	Average Percent Recovery								
						1% Organic		**10% Organic**	
	BLH n=28	**SB1L n=7**	**SB1H n=7**	**SB2L n=7**	**SB2H n=7**	**SB1A n=4**	**SB2A n=4**	**SB1A n=4**	**SB2A n=4**
Organochlorine Pesticides									
Chlordane	102	80	97	91	97	86	96	90	98
Endrin	89	106	106	124	81	97	103	97	100
Heptachlor	95	88	104	71	70	93	97	95	85
Heptachlor Epoxide	96	92	110	118	91	98	90	96	88
Lindane	107	104	126	74	92	99	101	101	99
Methoxychlor	95	107	109	73	87	92	96	94	93
Toxaphene	89	75	82	87	97	74	79	83	89
Base/Neutral Extractables									
1,4-Dichlorobenzene	66	51	56	50	65	65	62	66	53
2,4-Dinitrotoluene	97	89	90	86	92	87	89	93	76
Hexachlorobenzene	93	84	88	86	94	76	79	85	70
Hexachlorobutadiene	68	53	43	57	50	71	64	65	57
Hexachloroethane	58	50	65	51	66	71	69	72	57
Nitrobenzene	86	80	94	80	105	84	81	81	71
Pyridine*									
Acid Extractables									
o-Cresol	88	86	90	97	103	94	81	88	88
m- & p-Cresol	87	77	83	83	96	95	88	82	96
2,4,5-Trichlorophenol	90	93	99	94	96	94	86	96	87
2,4,6-Trichlorophenol	94	106	115	104	101	96	110	99	108
Pentachlorophenol	79	79	110	81	80	80	111	94	97
Acid Herbicides									
2,4-D	92	93	90	101	98	89	78	95	94
2,4,5-TP(Silvex)	92	98	91	75	112	79	99	78	91

B1 = pH 2.886; B2 = pH 4.937
BLH = Average %R for buffers 1 and 2 spiked at low and high levels
SB1 = Soil leach with buffer #1
SB2 = Soil leach with buffer #2
low (L) and high (H) level spikes

Organic Effect: 1% & 10% Ethylene glycol:
SB1A = Soil leach, buffer 1, action (A)level
SB2A = Soil leach, buffer 2, action (A)level

* Pyridine recoveries using the SDB sorbent membrane are low. The EPA workgroup stated this was not considered to be a problem since pyridine recoveries by the standard method are extremely variable.

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