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An Evaluation of Charcoal Cloth as a Potential Field Monitor for the Efficacy of Chemical Protective Clothing

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Generally the results of manufacturers' permeation tests are used to select chemical protective clothing. However, these test results are subject to several sources of error. In addition, certain conditions, such as temperature, exposure time and duration, immobility of the garment, and sample thickness, which is dependent on the location from which the garment is sampled for testing, are controlled in the experiment in ways which may not reflect actual use conditions. The only way to accurately determine the efficacy of a garment is to monitor its permeation resistance in the field. For volatile permeants this is difficult, since the most obvious way to trap these compounds after permeation is with a sorbent, and the efficiency of this process is not certain given the natural ventilation that occurs during use of protective clothing, especially gloves. In this study charcoal cloth was made into gloves and used beneath polyvinylchloride gloves to monitor permeation. The glove system was flexed at rates of 0, 30, or 50 times per minute. The weight loss of the system was monitored as an indicator of the permeation through the glove, and the charcoal gloves were assayed via gas chromatography for the heptane permeant. Under no-flex conditions the charcoal cloth was near 100 percent effective at trapping the heptane. Under conditions of flex, 61 to 86 percent of the heptane was captured. Given the inexact nature of the clothing selection process, these appear to be acceptable results. However, a few other factors, such as the polarity of the permeant, need to be considered. PERKINS, J.L.; VESCIAL, K.: AN EVALUATION OF CHARCOAL CLOTH AS A POTENTIAL FIELD MONITOR FOR THE EFFICACY OF CHEMICAL PROTECTIVE CLOTHING. APPL. OCCUP. ENVIRON. HYG. 12(5):362–366; 1997.

The development of two permeation test methods[1,2] by the American Society for Testing and Materials Committee F-23 has led to the publication of a great many permeation test results. Many of these results are provided by the manufacturers of the garments and provide a screening technique for selecting the chemical protective clothing (CPC) which appears to be most effective against permeation of the chemical(s) in question and subsequent exposure to the skin. However, it is known that a number of variables, controlled in the laboratory but uncontrolled in use conditions, may affect the permeation efficacy of CPC. Variables include small (10°C) temperature changes,[3] batch to batch variability,[4] thickness differences,[5] flexing or tool use,[6,7] and intermittent use.[8–10] Therefore, the most certain way to test the final efficacy is through field monitoring techniques. Field evaluation of CPC allows one to compare the relative efficacy of two CPC polymers, to determine the actual permeation rates in the field for use in skin exposure estimates and risk assessments, and to determine if a less expensive and less effective CPC may nonetheless be effective enough to limit exposures to below some target value (i.e., aid in the selection process).

Only a few studies of field assessment of CPC have been performed. In one study cotton gloves were worn beneath neoprene gloves to measure the permeation of polychlorinated biphenyls (PCBs).[11] In this study cotton could be used as an adsorbent for PCBs since they are essentially nonvolatile. The study showed that the less expensive neoprene gloves could be substituted for Viton® gloves and still give acceptable protection. In another study, fluorescent, amine-based permeants, monitored on the skin using ultraviolet light, were used to show that the use of screwdrivers and other tools had an effect on permeation, which was measured by looking at the fluorescence on the hand.[6] Other studies[12–14] have used swatches composed of gauze to measure the penetration of pesticides through clothing used by farm workers. In these studies some permeation is measured, but for the most part liquid penetration through seams and openings in typical farm clothing is measured. Nevertheless, they provide useful information about the actual exposures to farm workers' skin. None of the above techniques can be applied to monitoring volatile permeants.

Previous Work

Cohen and Popendorf[15] first studied the use of charcoal cloth as a field monitor for skin exposure to volatile compounds. The emphasis of that study was on monitoring skin exposure to liquids rather than monitoring permeation through CPC. Thus they were concerned about retention of charcoal cloth given liquid doses of various sizes which would affect the estimate of the skin exposure, and the propensity of the cloth to adsorb vapors from the air leading to an overestimate of skin exposure. While neither problem is directly related to the monitoring of vapors beneath CPC, other aspects of the study, such as the effects of layering, surface area, temperature, and relative humidity are, and will be discussed later.

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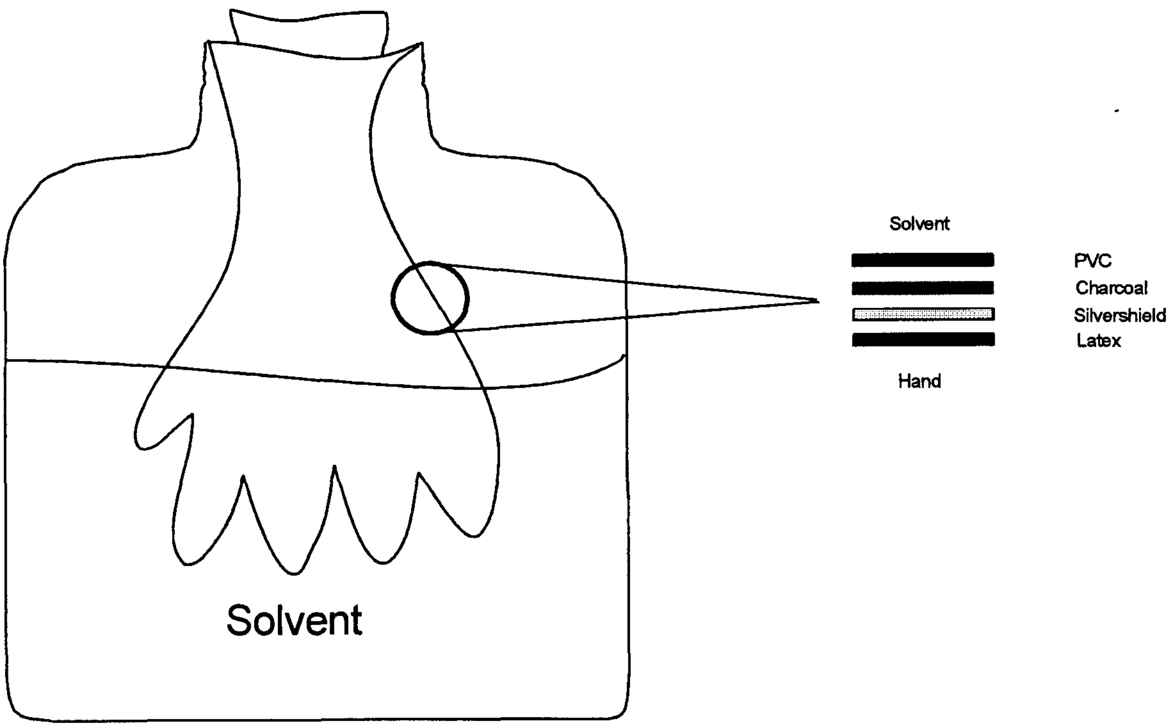

FIGURE 1. Depiction of the test system and detail of glove layering.

Purpose

The purpose of this study was to evaluate charcoal cloth as a monitor for volatile compounds such as heptane after they have permeated CPC. If charcoal cloth is efficient in adsorbing the permeating vapors before they escape the CPC (e.g., out the cuff of a glove or through the dump valve of a fully encapsulating suit), then a good field monitor for CPC effectiveness will have been demonstrated. Gloves were used as the most stringent test of capture efficiency, and the hand was flexed to create a high ventilation rate of the glove.

Materials and Methods

Overview

Two factors that may affect the efficiency of adsorption and retention by the charcoal cloth include water vapor from the person's hand and rapid ventilation of the glove, which may prevent adequate contact time between the permeated solvent and the charcoal cloth. Temperature may also be important in terms of its effect on both permeation and adsorption processes. In this study temperature was controlled at 24° to 26°C and water vapor was kept from the charcoal cloth by use of a latex glove over the experimenter's hand. The experimenter's hand was flexed to simulate ventilation of the glove under field conditions.

Test Apparatus

The experimental apparatus is composed of a 1-gallon (3.78 L) jar which contains approximately 2 L of heptane (see Figure 1). A submerged thermometer is used to monitor solvent temperature. The cuff of the outside or exposed glove is folded over the rim of the jar opening and sealed with Teflon® tape, and then a metal ring seal is used to tightly crimp the glove against the jar so that any solvent that escapes the system must escape by permeating the glove. Moving from the exposed glove toward the experimenter's hand are other gloves of the system. In succession these are the charcoal glove, a North Silvershield® glove to protect the experimenter from exposure, and a latex examination glove to keep perspiration out of the system. The test system consisted of the test cell, the solvent, the thermometer, and all gloves excluding the latex examination glove.

Materials

Heptane was used as the permeant. Polyvinylchloride (PVC) gloves (Pioneer V-20, unsupported, 20-mil or 0.51-mm thickness) were used as the outside or exposed CPC. This combination was chosen so as to give a maximum challenge to the charcoal cloth. Up to 4 g of heptane was expected to permeate, depending on flex rate and total exposure time at an expected steady-state permeation rate of around 150 $\mu g/cm^2/min$.[7]

The charcoal gloves were fabricated from activated charcoal cloth (Charcoal Cloth Ltd., Maidenhead, Berkshire, England). Activated charcoal cloth is 100 percent activated carbon derived from cellulose fabric. The cloth is very light (120 g/m^2), but is not very strong. The breaking strength is less than most other fabrics (1.5 kg/cm). Thus it can be cut and sewn into gloves, but it frays easily and individual fibers tend to unravel and break with use. It has been used for military applications and has a considerable absorptive capacity.[16]

A double layer of charcoal cloth was used as preliminary experiments indicated a slightly greater efficiency. Other researchers found that up to four layers increased the retention of liquid doses, but that six layers made no additional difference.[15] The total weight of each charcoal glove was approximately 19 g. Thus the total surface area was about 1.7 ft^2 (1580 cm^2) based on an approximate weight per area of 0.012 g/cm^2.

Flexing Protocol

A set of experiments was conducted under static conditions with no flexing. In this experiment the hand was inserted into the glove system for a total of 1 minute to allow the glove to form, pushing the charcoal against the PVC and leaving a space in the center of the Silvershield glove. The hand was then removed. At the end of 1 hour the test apparatus was reweighed.

To simulate the ventilation of a glove in normal use conditions which might lead to less adsorption by the charcoal, differing flexing protocols were used. A latex-gloved human hand was inserted into the test system, and the hand was flexed at a rate of 30 flexes per minute (low flex) or 50 flexes per minute (high flex).

Three replicates were run for each of the three experimental conditions. Three low flex experiments were run for 1 hour, and in the third test a tear occurred between the thumb and forefinger. This replicate was repeated for a period of only 40 minutes. The high flex experiments were run for a period of 20 minutes to avoid this degradation.

Assay

Two measurements were made. First, the test system was weighed before and after the exposure and flexing period. Since the charcoal cloth glove was included in the system, any weight change would be due to permeant which had left the system and was not trapped by the charcoal cloth. It is possible that some solvent could escape from around the ring seal; however, the results show that most of the solvent could be accounted for through the assay process (see below).

The second assay was performed on the charcoal cloth. 100 ml of carbon disulfide was added to a 2-L container which contained the exposed charcoal cloth glove. The container was shaken vigorously for 1 minute, and desorption was allowed to take place for 30 additional minutes. The solution was analyzed by gas chromatography-flame ionization detector (Hewlett Packard 5890). Injection volumes of 5 μL were used. A stainless steel column of 10 percent SP 2100 on 100/120 mesh Supelco Port® was used.

Spiking Experiments

To determine the desorption recovery efficiency, gloves were spiked by placing a glove and a petri dish in a large jar. A heptane spike volume of either 5 or 7 ml was added to the petri dish and the jar was closed. After an overnight sorption period the gloves were desorbed with carbon disulfide and analyzed.

Glove Reuse

To determine the conditions under which charcoal gloves could be reused, gloves were spiked with heptane as above and then desorbed with 100 ml carbon disulfide. They were then air dried, desorbed twice in two separate volumes of carbon disulfide, air dried again, and desorbed a final time. After a final air drying, the gloves were ready for reuse. (This is a total of four desorptions and three air drying periods.) Although fewer combinations of air drying and desorption were tried, a residue of heptane was found, while the above combination did not leave a detectable residue of heptane. However, the technique did take a toll on the gloves in that it caused some loss of carbon fibers.

TABLE 1. Heptane Mass (Milligrams) Recovered from Charcoal Cloth (M_C), Found by Weight Difference Before and After Experiment (M_D), Total Mass Permeated (M_T), and Efficiency (M_C/M_T) in 20- to 60-Minute Experiments

Flex	Time (min)	M_C	M_D	M_T	Eff (%)
No	60	1634	110	1744	94
No	60	1554	40	1594	97
No	60	1694	350	2044	86
Low	60	3250	370	3620	79
Low	60	2530	400	2930	86
Low	40	1170	320	1490	79
High	20	531	180	711	75
High	20	315	200	515	61
High	20	306	170	476	64

Data Reduction

Two pieces of information were determined from the two assays. The weight difference before and after the experiment conveyed the amount of heptane that had been lost from the system and not adsorbed by the charcoal. The assay of the charcoal glove indicated the amount of the heptane that permeated through the PVC glove and was adsorbed by the charcoal. The combination of these two amounts indicated the total amount of permeation that had occurred through the PVC. Thus, the collection efficiency of the charcoal cloth under the differing conditions could be determined by the equation

$$\frac{M_C}{M_T} \times 100\%$$

where:

M_C = mass found on the charcoal
M_T = mass found on the charcoal plus mass determined by the weight difference

Results

The four spike desorption recovery experiments yielded recoveries of 91 to 98 percent. Therefore, no corrections were made to the amounts recovered in the flex and no-flex experiments.

The main experimental results are shown in Table 1. Under static conditions the charcoal cloth adsorbed between 86 and 97 percent of the heptane that permeated the PVC glove. Since these results are in virtual agreement with the efficiencies from the spiking experiment, it is likely that the Teflon tape and ring seal performed their functions well.

Under low flex conditions the adsorption efficiency range was 79 to 86 percent. A *t*-test showed no statistical difference in the low and no-flex results. However, it might be expected with a larger sample size that a difference of minimal importance might be discerned. At the high flex rate the adsorption efficiencies dropped to 61 to 75 percent. These high flex results were statistically different from the other two treatments ($p < 0.05$).

Discussion

The spike experiments indicated that the charcoal cloth had adequate capacity to adsorb up to 7 ml of heptane (4.75 g) and that this heptane could be desorbed from the charcoal cloth with acceptable efficiency. Similarly, the flexing experiments indicated that the charcoal cloth used beneath a CPC glove under field conditions could be a reasonable field monitor certainly under a condition of low flex. At higher flex rates the efficiencies dropped off to as little as 61 percent. The reason for the loss of efficiency could actually be twofold. Flexing was an important factor in that it caused greater ventilation of the glove and therefore potential for loss of heptane through the glove cuff. On the other hand, previous work[7] has shown that flexing also causes higher permeation rates for the heptane/PVC system. Thus a greater mass of heptane was entering the area of the charcoal cloth and as a consequence the charcoal cloth may not have been able to absorb it rapidly enough. Permeation rates increase with flex.

Regardless of whether the loss of efficiency was due to increased permeation, increased flex, or both, the test conditions for both variables represent extreme conditions relative to what one normally would expect. First, the permeation of heptane through PVC occurs at very high rates (about 150 $\mu g/cm^2/min$ as determined in Reference 7) relative to a CPC system that one would expect to use under actual worker exposure conditions. Indeed, most manufacturers would recommend against the use of PVC for exposures to heptane over long periods of time (more than a few minutes). Furthermore, even 30 flexes per minute, or one every 2 seconds, sustained over a period of 1 hour, represents a high mobility for the hand. No doubt such mobility would lead to other physiologic problems if sustained over any long period of time such as weeks or months.

It is important to realize that even under such extreme conditions the charcoal cloth still managed to capture over half of the permeated heptane. For field studies of the efficacy of CPC, a charcoal efficiency of 50 percent is probably adequate. For example, if one were wishing to compare the field efficacy of two different types of CPC, one of which was considerably cheaper and presumably less effective than the other, then errors in determining the actual permeation in the field of up to 50 percent are probably not significant. Since in most cases we are not aware of the actual effects of permeated materials on the skin, we are prone to err on the safe side. Thus our selection process tends to build in large safety margins which should be robust enough to absorb such errors as would be presented by the efficiency of the charcoal cloth. The real purpose of field studies is to gain a better understanding of the permeation process in the field versus the laboratory. While a laboratory study may indicate a steady-state permeation rate of 100 $\mu g/cm^2/min$, a field study might indicate that over a 4-hour period a worker is exposed to a mass of permeant that is 1/10 or even 1/100 of that expected from extrapolating the steady-state rate over the entire exposed surface area of the CPC. Certainly if a field study indicated that actual permeation rates in the field were 10 percent or even 50 percent different from what one might have expected, this should not prompt one to change the CPC that is used. Rather, there are so many other uncertainties in the CPC selection process that such an error is likely to be inconsequential in the overall problem of dermal exposure risk management.

Before actual field studies are performed, a few precautions should be given relative to variables that were not examined in this study. Temperature could be a factor that would cause increased loss of solvent due to increased volatility and decreased adsorption potential. Cohen and Popendorf[15] found that temperature changes from 20° to 30°C had no significant effect on adsorption and retention of liquids onto charcoal cloth. They found a twofold effect on retention caused by relative humidities ranging from 30 to 100 percent. Thus it is important to use the perspiration barrier even in cold environments. If this is done it might be expected that the moisture inside the CPC at the charcoal cloth is similar to the moisture level in the outside environment. It does not seem likely that the diffusivity of the vapor is important. A fast-diffusing molecule would diffuse to the charcoal rapidly, and thus be more likely to be adsorbed. The path between the CPC and the charcoal is considerably shorter than from the region of permeation to the cuff. Thus, diffusion of the molecule is likely to be to the charcoal. The concentration between the two gloves might affect efficiency: the higher the concentration, the greater the likelihood that some molecules will escape. However, it has already been mentioned that the permeation rate of heptane through PVC (and thus the concentration between the two gloves) is higher than normally would be recommended for use. Thus any effects of concentration are not likely to be greater than those seen here.

The most important variable is polarity. Solvents with greater polarities than heptane would be expected to escape the interior of the glove more easily because they would be adsorbed and retained less efficiently for a given concentration. Essentially the same physical–chemical rules can be applied to this problem as to the problem of charcoal tube air sampling. However, simple vapor spiking experiments at loadings that one expects to collect under the CPC should shed light on the potential for polar compounds to be poorly adsorbed. First the spiking experiment will give a good indication of recovery from the charcoal. If the recovery is not good (say $<90\%$), then the head space above the charcoal should be monitored to determine if the capacity has been exceeded at that particular spiking level. If the capacity is adequate, it is likely that the polar molecule will be adsorbed efficiently.

Conclusion

It is concluded from this preliminary work that activated charcoal cloth might be utilized as an effective field monitor for volatile compounds permeating through CPC. The user should take care to isolate the charcoal cloth from the worker's skin so as not to allow perspiration to interfere with the absorptive capacity of the charcoal. The experimenter should estimate the amount of permeant which is expected under the CPC in field conditions so as to make certain that the capacity of the charcoal cloth is adequate. The capacity should be verified in a spiking experiment to determine adsorption and desorption efficiency of the cloth for the chemical in question.

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