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EPA Project Summary

Evaluation, Development and Verification of Field Methods for Rapid, On-Site Determination of Appropriate Chemical Protective Clothing

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Personnel involved in chemical spill emergency response and hazardous waste site activities often have the need to make on-site decisions regarding the effectiveness and limitations of their available chemical protective clothing. While there are many existing test methods for assessing the chemical resistance of clothing materials, none has been packaged, tested, and accepted as a field kit. The purpose of this effort was to develop a prototype kit. Three gravimetric test methods, which are typically used in the laboratory, were evaluated for their applicability and overall usefulness in field kit form. The methods evaluated were: an immersion test, a degradation test, and a permeation cup test. Baseline data for comparison were obtained using ASTM Method F739-85–Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases. Each method was evaluated using a test matrix comprised of four neat chemicals; three two-component mixtures thereof; and two common protective materials. The permeation cup was selected as the preferred method for field application. The underlying principle of the permeation cup is that chemical contained in a cup that is covered by the clothing material will permeate and evaporate from the clothing material. As this occurs, the weight of the cup will decrease and from measurements of the weight loss as a function of time, the breakthrough

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time and permeation rate of the chemical through the material can be calculated. Three prototype permeation cup field kits were fabricated and subjected to preliminary user trials. The method is also being considered for standardization by ASTM. Preliminary results from these trials were favorable; additional laboratory and field testing is recommended in order to establish the validity and limitations of the method.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA and EPA contractor personnel involved in emergency spill response and hazardous waste site activities normally wear some form of chemical protective clothing (CPC). Commercially available CPC is fabricated from a wide variety of polymeric materials. The effectiveness of these materials as barriers to the chemicals or mixtures to which exposure may occur is of primary interest to those responsible for worker protection. The chemicals and mixtures may be of known or unknown composition.

Test data on the chemical resistance of chemical protective materials are available for only a small fraction of the virtually infinite number of possible chemical and material combinations. In addition, essentially all of the data generated to date are for neat chemicals. The likelihood of finding data on the exact chemical mixture/material combination of interest is very small. The need exists, therefore, for a field test method that will enable field personnel to rapidly determine the barrier effectiveness of their available CPC to the chemicals or mixtures at hand.

ASTM Method F739-85 and analogous procedures have been developed and are widely applied for measuring the barrier properties of protective materials. In general, these tests are designed for and are performed in the laboratory under controlled conditions by skilled personnel. Typical analytical techniques include: gas chromatography, infrared spectrometry, and atomic absorption. These methods have allowed for significant advances in clothing development and selection but do not provide a useful means for field personnel to assess CPC chemical resistance in the field.

To meet the need for assessing the chemical resistance of clothing materials in the field, the applicability of three candidate gravimetric test methods was evaluated. They were an immersion test, a degradation test, and a permeation cup test. These tests are routinely used in the laboratory for measuring the performance of polymeric materials. Baseline data for comparison were obtained using ASTM Method F739-85–Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases.

Procedure

The applicability of the three gravimetric methods was judged according to six criteria:

- The test should provide an estimate of the breakthrough time (BT) and steady state permeation rate (SSPR). It is not necessary that the test actually measure the BT or SSPR if good correlations exist between these parameters and the results of the test.
- The test method should be nonspecific in that the permeation of any chemical or mixture would be interpreted as a breach of the material being tested.
- The kit should be durable, portable and self-contained, requiring no external power.

- The method should be simple to learn and to perform. Minimal calibration should also be required.
- The method development should require a minimal amount of time and cost.
- The method should, at a minimum, be applicable to a wide variety of liquid, organic chemicals and clothing materials.

Each test method was evaluated using seven chemical challenges (acetone, hexane, methanol, toluene, and three two-component mixtures of acetone and hexane) and two clothing materials (nitrile rubber and butyl-coated nylon). Triplicate runs were made for each test for each chemical/material combination except for the case of ASTM F739-85 where the known precision of the method and past experience with these chemicals and materials made only duplicate testing necessary.

Immersion Test

In the immersion test, a specimen of the clothing material was weighed, then completely immersed in the chemical or chemical mixture, and at specified time intervals removed, patted dry, and reweighed. The test duration was 48 hours. Percentage weight changes were calculated and visual observations recorded. In many of the tests, the weight change reached a maximum value and then fell off slightly. The peak or highest percentage weight increase measured during the test was reported, along with the time to reach the peak.

Degradation Test

A modification of a draft ASTM degradation test procedure was used in this study. The normally outside surface of the clothing material was exposed to the challenge chemicals for one hour. The weight, thickness, and elongation of the material were measured before and after the chemical exposure. The percentage change in these parameters was calculated and reported along with any visual observations.

Permeation Cup Test

The permeation cup test was modelled after ASTM Method E96–Moisture Permeability of Polymeric Films. The CPC material is secured over the mouth of a shallow cup containing the chemical of interest and the cup inverted. From measurements of the cup's weight as a function of time, an estimate of the BT and SSPR can be made.

ASTM Method F739-85

Baseline data for comparison of the results from the immersion, degradation, and permeation cup tests were obtained using ASTM F739-85. In this test, the clothing material separates two chambers of a test cell. The chemical of interest is charged into one chamber and the concentration of the permeant in the other chamber is monitored as a function time. BT and SSPR are calculated from the concentration data according to the appropriate procedure specified in ASTM F739-85.

Results and Discussion

Immersion Test

The immersion test satisfied five of the six design criteria. The method is easily learned and quickly performed. It is nonspecific, applicable to a wide variety of chemicals, and readily adaptable to a field kit. Neither BT nor SSPR, however, are easily determined from immersion test data. Furthermore no validated correlation exists between weight change and BT or SSPR. Use of the test in the field would require field personnel to understand and depend upon rules of thumb relative to the interpretation of weight change data. For example, as seen in Table 1, short BTs and high SSPRs are typically associated with large percentage changes in the weight of the clothing material. There is also remarkably good agreement between the rankings of the results from the two tests, i.e., the sequence of the chemicals in the leftmost and rightmost columns.

Note in Table 1, however, that for the same approximate weight changes, the BT and SSPR are considerably different for the two materials. The fact that there is no general quantitative relationship between weight change and permeation test results is one major drawback of the immersion test. Some materials exhibit little or no weight change and yet have short BT and high SSPR. Others such as polyvinyl chloride can lose weight due to the immersion. Effective interpretation of immersion test results requires a knowledge of how specific materials perform. Such knowledge is unreasonable to expect of field personnel. The test, moreover, is inappropriate for an important category of clothing materials. These materials include multilayer structures and coated fabrics in which only the outer layer is designed to be chemically resistant. High weight gains with such materials could result from chemical absorption by the inner layers which would not likely be exposed to chemical in the actual use of the garment.

Degradation Test

The degradation test is, for all practical purposes, a single-sided immersion test. Consequently the test is applicable to multilayer or coated clothing materials. Compared to the immersion test, the method is somewhat but not significantly more difficult and time consuming to perform. The data in Table 2 again show the general relationship between high weight change and low BT and high SSPR. Greater changes in thickness also seem to correlate with lower BT and high SSPR. No correlation was found between the change in elongation and BT or SSPR.

Similar to the immersion test, the key drawback of the test is the difficulty in data interpretation. Virtually all of the issues mentioned for the immersion test apply to the degradation test.

Table 1. Comparison of Immersion Test Results with ASTM F739

Nitrile

Immersion Test				ASTM Test		
Chemical	% Weight [a]	Time [b]	Resistance	BT [c]	SSPR [d]	Chemical
Acetone	178	< 1	Least	4.5	8680	Acetone
Ace:Hex, 75:25 (v/v)	163	< < 1	↓	5.4	3280	Ace: Hex, 75:25 (v/v)
Toluene	148	< 1	↓	6	1860	Ace:Hex, 50:50 (v/v)
Ace:Hex, 50:50 (v/v)	99	< < 1	↓	12	1330	Toluene
Ace:Hex, 25:75 (v/v)	52	< < 1	↓	11	650	Ace:Hex, 25:75 (v/v)
Methanol	52	1	↓	39.4	86	Methanol
Hexane	6	< 1	Most	nd [e]	nd	Hexane

Butyl Nylon

Immersion Test				ASTM Test		
Chemical	% Weight [a]	Time [b]	Resistance	BT [c]	SSPR [d]	Chemical
Toluene	103	< 1	Least	7	529	Toluene
Hexane	72	< 1	↓	3.7	463	Ace: Hex, 25:75 (v/v)
Ace:Hex, 25:75 (v/v)	59	< 1	↓	6	328	Ace:Hex, 50:50 (v/v)
Ace:Hex, 50:50 (v/v)	22	< < 1	↓	16	95	Ace:Hex, 75:25 (v/v)
Ace:Hex, 75:25 (v/v)	13	< < 1	↓	13.2	83	Hexane
Methanol	11	1	↓	nd	nd	Methanol
Acetone	8	< 1	Most	nd	nd	Acetone

[a] Percent weight change, average of three tests.
[b] Time (hours) to peak % wt. gain, average of three tests.
[c] Breakthrough time (minutes), average of two tests.
[d] Steady state permeation rate ($\mu g/cm^2$ -min), average of two tests. SSPR is the basis for ranking Resistance.
[e] None detected in 6+ hours.

Table 2. Comparison of Degradation Test Results with ASTM F739 Results

Nitrile

Degradation Test[a]			ASTM Test		
Chemical	WT/TH/ELON	Resistance	BT[b]	SSPR[c]	Chemical
Toluene	103/19/250	Least	4.5	8680	Acetone
Acetone	79/16/571	↓	5.4	3280	Act:Hex, 75:25 (v/v)
Ace:Hex 50:50 (v/v)	54/13/308		6	1860	Ace:Hex, 50:50 (v/v)
Ace:Hex, 25:75 (v/v)	4/11/233		12	1330	Toluene
Ace:Hex, 75:25 (v/v)	2/17/350		11	650	Ace:Hex, 25:75 (v/v)
Methanol	2/6/244		39.4	86	Methanol
Hexane	0.2/-0.1/25	Most	nd[d]	nd	Hexane

Butyl Nylon

Degradation Test			ASTM Test		
Chemical	WT/TH/ELON	Resistance	BT[b]	SSPR[c]	Chemical
Hexane	59/60/nd	Least	7	529	Toluene
Ace:Hex, 25:75 (v/v)	40/46/nd	↓	3.7	463	Ace:Hex, 25:75 (v/v)
Toluene	31/31/nd		6	328	Ace:Hex, 50:50 (v/v)
Ace:Hex, 50:50 (v/v)	14/15/nd		16	95	Ace:Hex, 75:25 (v/v)
Ace:Hex, 75:25 (v/v)	10/10/nd		13.2	83	Hexane
Acetone	6/5/nd		nd	nd	Methanol
Methanol	4/2/nd	Most	nd	nd	Acetone

[a]Percentage changes in weight (WT), thickness (TH), elongation (ELON), averages of three tests.
[b]Breakthrough time (minutes), average of two tests.
[c]Steady state permeation rate ($\mu g/cm^2$ -min), average of two tests. SSPR is the basis for ranking Resistance.
[d]Non detected.

Permeation Cup Test

From the limited number of laboratory tests performed to date, the cup method appears to satisfy all six of the criteria for the field kit. BT and SSPR are readily estimated/calculated from the data and, as is evident from Table 3, there was good agreement between BT and SSPR for the permeation cup test and ASTM F739-85. The cup test is not capable of

Table 3. Comparison of Permeation Cup Test Results with ASTM F739

Nitrile

Cup Test				ASTM Test		
Chemical	BT[a]	SSPR[b]	Resistance	BT	SSPR	Chemical
Acetone	2.7	2590	Least	4.5	8680	Acetone
Ace:Hex, 75:25 (v/v)	4.7	1760	↓	5.4	3280	Ace: Hex, 75:25 (v/v)
Ace:Hex, 50:50 (v/v)	6.7	1170		6	1860	Ace:Hex, 50:50 (v/v)
Toluene	13	727		12	1330	Toluene
Ace:Hex , 25:75 (v/v)	9.3	560		11	650	Ace:Hex, 25:75 (v/v)
Methanol	50	45		39.4	86	Methanol
Hexane	nd[c]	nd	Most	nd	nd	Hexane

Butyl Nylon

Cup Test				ASTM Test		
Chemical	BT	SSPR	Resistance	SSPR	BT	Chemical
Toluene	8.7	282	Least	530	7	Toluene
Ace:Hex, 25:75 (v/v)	7.3	323	↓	460	3.7	Ace: Hex, 25:75 (v/v)
Ace:Hex, 50:50 (v/v)	6	200		330	6	Ace:Hex, 50:50 (v/v)
Ace:Hex, 75:25 (v/v)	13.7	76		83	13.2	Hexane
Hexane	30	51		95	16	Ace:Hex, 75:25 (v/v)
Methanol	nd	nd		nd	nd	Methanol
Acetone	nd	nd	Most	nd	nd	Acetone

[a] Breakthrough time (minutes), average of three tests for cup test and two tests for ASTM test.
[b] Steady state permeation rate ($\mu g/cm^2$ -min), average of three tests for cup test and two tests for ASTM test. SSPR from the ASTM test is the basis for ranking Resistance.
[c] None detected in 1 hour for cup test or 6 hours for ASTM test.

distinguishing the identity of the permeant. The values reported in the table are for total permeant, independent of composition.

For eight of the eleven chemical/material combinations for which BT was detected, the values for the permeation cup were within ± 25% of those for the ASTM test. SSPR from the cup test were typically lower than but within 50% of those from ASTM F739-85. When the permeation cup results are ranked from high to low SSPR, as in Table 3, only one chemical/material combination falls out of place when compared to the ASTM F739-85 results. These findings led to the conclusion that the permeation cup was the most promising of the candidate methods for the field kit.

One recognized limitation of the permeation cup procedure, as with any permeation test in which a gas acts as the collection medium, is that it may not be applicable to chemicals having low volatility. Evaporation of the chemical from the surface of the clothing that is exposed to the ambient air is required if permeation is to be deduced from weight loss data. If the volatility is low, then evaporation could be the controlling step and a true assessment of the barrier properties of the CPC would not be obtained. One solution to this problem is to physically remove by wiping or other procedure the chemical from the surface. Neither the limits of applicable vapor pressure nor alternative approaches for removing surface chemical were explored in this study. A plan for doing so was suggested.

Field Kit Development

The favorable results from the laboratory investigation of the permeation cup test method led to the development of a permeation cup field kit. Three prototype, self-contained field kits were fabricated and included the following: three permeation cups and stands; a 100 gram capacity, battery-powered balance; instruction manual; and assorted paraphernalia.

The accuracy and precision of the cup test are principally determined by the accuracy and precision of the balance and the evaporation rate of the permeant. Since the results of the cup test are obtained from weight differences, a balance with good precision is preferred over one having high accuracy. At the time of this study, the most precise, battery-powered balance with the necessary capacity (100 grams) had a precision of ± 0.01 gram. More precise, battery-powered balances are expected in the future. Also if the criterion that the kit be totally self-contained were dropped, then balances powered by alternating current could be used and precision to four or five decimal places would be attainable.

User Trials

Three groups of EPA or EPA contractor field personnel have tested the kit, with mixed results. In one case the contractor discontinued the use of one type of CPC material after measuring a more rapid breach of the barrier than was acceptable.

Conclusions and Recommendations

Gravimetric methods are expedient and useful means for providing field personnel with information on the likely chemical resistance of protective clothing materials. Of the three methods evaluated, that based on the permeation cup method was chosen for the field kit. The permeation cup test is simple and easy to perform, produces BT and SSPR, and is readily conformed into a durable, self-contained kit for field application.

In addition to its utility as a user kit, the permeation cup test appears to be an attractive alternative to the more costly and time-consuming ASTM Method F739-85. With the availability of analytical balances in the laboratory, this method can produce results remarkably similar to results generated using F739-85. The test can also be used to identify the most promising materials for subsequent testing with ASTM F739-85 and to help establish the intervals for sampling in that test. It is, however, essential that the limitations of the method imposed by the volatility of the permeant be considered.

The initial laboratory and field results of the permeation cup field kit are promising but have been obtained under a narrow set of conditions. The continued investigation of the permeation cup test method in both the laboratory and in the field is recommended. The range of limitations and applicability of the method must still be investigated before the method can be completely validated and recommended for field implementation. In addition to the volatility of the permeant, the effects of environmental conditions such as temperature and air velocity across the cup face must be quantified.

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The complete report, entitled "Evaluation, Development and Verification of Field Methods for Rapid, On-Site Determination of Appropriate Chemical Protective Clothing," (Order No. PB 89-118 673/AS; Cost: $28.95, subject to change) will be available only from:
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