CORRELATION OF CHEMICAL WARFARE SURROGATE TESTS ON AIR-PERMEABLE CHEMICAL PROTECTIVE UNIFORMS

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ABSTRACT:

Air-permeable chemical protective uniforms provide percutaneous protection against chemical liquids released as vapor and droplets by adsorbing the chemical in a layer of activated carbon. The air that flows through the uniform fabric evaporates sweat, providing cooling. The protective capacity of a material is tested by measuring the breakthrough time of chemical warfare agent (CWA) applied on a sample at a vapor concentration and wind speed representing average field conditions. Breakthrough time is many days for the dilute vapors of high-boiling percutaneous-threat agents and so testing has been reduced to one day using increased mass flow rate of the chemical vapor. CWA tests can only be carried out in a limited number of facilities equipped to handle toxic chemical warfare agents. Low toxicity surrogates are tested by the same procedure to see how well they mimic live agents. One-to-one correlation would enable the testing of CP uniform material in a standard chemistry laboratory setting. The properties of the CWA surrogate must mimic the properties of the CWA itself for a good correlation outcome between the surrogate test results and live agent resistance performance. Tests with a standard HD simulant were carried out in our laboratory to standardize sampling of activated carbon materials and procedures. Simulant and agent testing at low and high relative humidity was carried out at Calspan Univ. of Buffalo Research Center (CUBRC). Comparison of the results obtained from vapor permeation testing showed excellent correlation of permeation behavior between CWA's and simulants at high humidity. Liquid drop tests revealed a divergence for GD and DMMP (dimethyl methylphosphonate) only for early penetration results at both low and high relative humidity, where MeS provided the match. The effect of humidity is small for HD and MeS (methyl salicylate). The same effects are seen in thickened drops.

INTRODUCTION:

The testing of chemical protective materials will be more generally applied when it has been established that there is a close correlation between non-toxic simulants and chemical warfare agents in standard tests of breakthrough time and penetration as a function of time. Numerical correlation of less toxic simulants with chemical warfare agents can simplify the testing of military chemical protective uniforms. This paper contributes to the field of chemical protection testing by providing a study of such 'Alternate Testing Methods', funded under a Reliability Maintainability and Supportability / Operations Support Cost Reduction (RMS/OSCR) Program. The standard test methods for chemical protective uniforms were applied, as put forth in Test Operating Procedures (TOP) 8-2-501. Familiar HD and GD simulants, methyl salicylate (MeS) and dimethyl methylphosphonate (DMMP), were studied. Test conditions sample various field conditions, e.g. high and low relative humidity (RH), laminar and convective winds. Challenge conditions range from dilute vapor to small and large droplets, thickened with polymer. Techniques were employed to increase the reliability of the data obtained: near-neighbor

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sampling; continuous automated detection of vapor challenge and penetration, and of temperature, RH and flow velocity; one day or less test duration; automated liquid drop dispensing; and reproducible mounting of the 2-layer uniform samples.

VAPOR CHALLENGE TESTS:

In the Edgewood Arsenal Training Manual EATM311-3, 1967[1] and in updates in 1984[2] and 1997[3] the challenge for testing with HD agent vapor is 20 µg/L/min through a 100 sq cm Dawson cup. In TOP 8-2-501[3] (1997) either the Dawson cup or the tall form of the AVLAG cell which has 10 sq cm sample area and is designed for convective air flow test of liquid droplets can be used to run vapor tests. See Figure 1.

The Dawson vapor challenge takes several days to break through activated carbon fabric. In the small AVLAG cell we increased the vapor concentration 5x and used 5x faster face velocity to reach break-through within 24 hours. Liquid and thickened droplets of methyl salicylate (MeS), dimethyl methylphosphonate (DMMP), HD, and GD are tested with 1 Lpm dual air flow across the sample or a convective air flow that produces a pressure across the sample equal to 0.1" water.

The test plan is for CUBRC tests of HD, GD and MeS vapor and, with DMMP also, tests of liquid and thickened drops. Comparison between neighboring samples and different material swatches were carried out in- house by MeS vapor breakthrough tests.

The following "questions and answers" were treated:

Q. Vapor test: Fabric layers wrinkle in the AVLAG cell and vapor test sorption results are high.

A. Mounting the two fabric layers on a convex screen smooths the sample- lowers sorption/sq cm

Q. Liquid drop tests: Varied spacing between cover fabric and activated carbon layer causes inconsistent penetration results.

A. Test swatches 2 ways - measure droplet penetration both with convex dome and with a net spacer inserted between layers. This is not a test of the swatch performance on average, but permits comparison of the behavior of simulant and agent liquid drops.

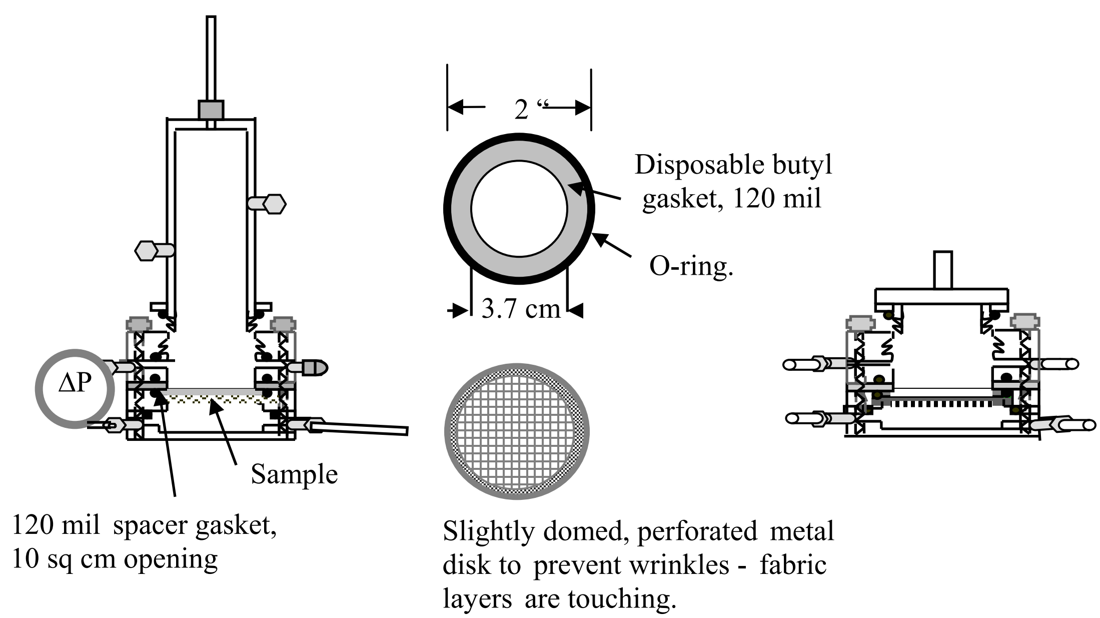

Fig. 1 AVLAG cell with perforated dome support and gap-filling gasket (convective & dual flow).

Typical tests with HD and GD vapor at low and high relative humidity (RH) are shown in Fig.2. and summarized in Figures 3 and 4.

10% RH　　　　80% RH

HD VAPOR
DRY & 80%RH

CUMULATIVE
SORPTION
AT 3% PENETRATI

Challenge 0.1 mg/L
@ 50 cm/min

GD VAPOR
DRY & 80% RH

CUMULATIVE
SORPTION
AT 3%
PENETRATION

Challenge 0.1 mg/L
@ 50 cm/min

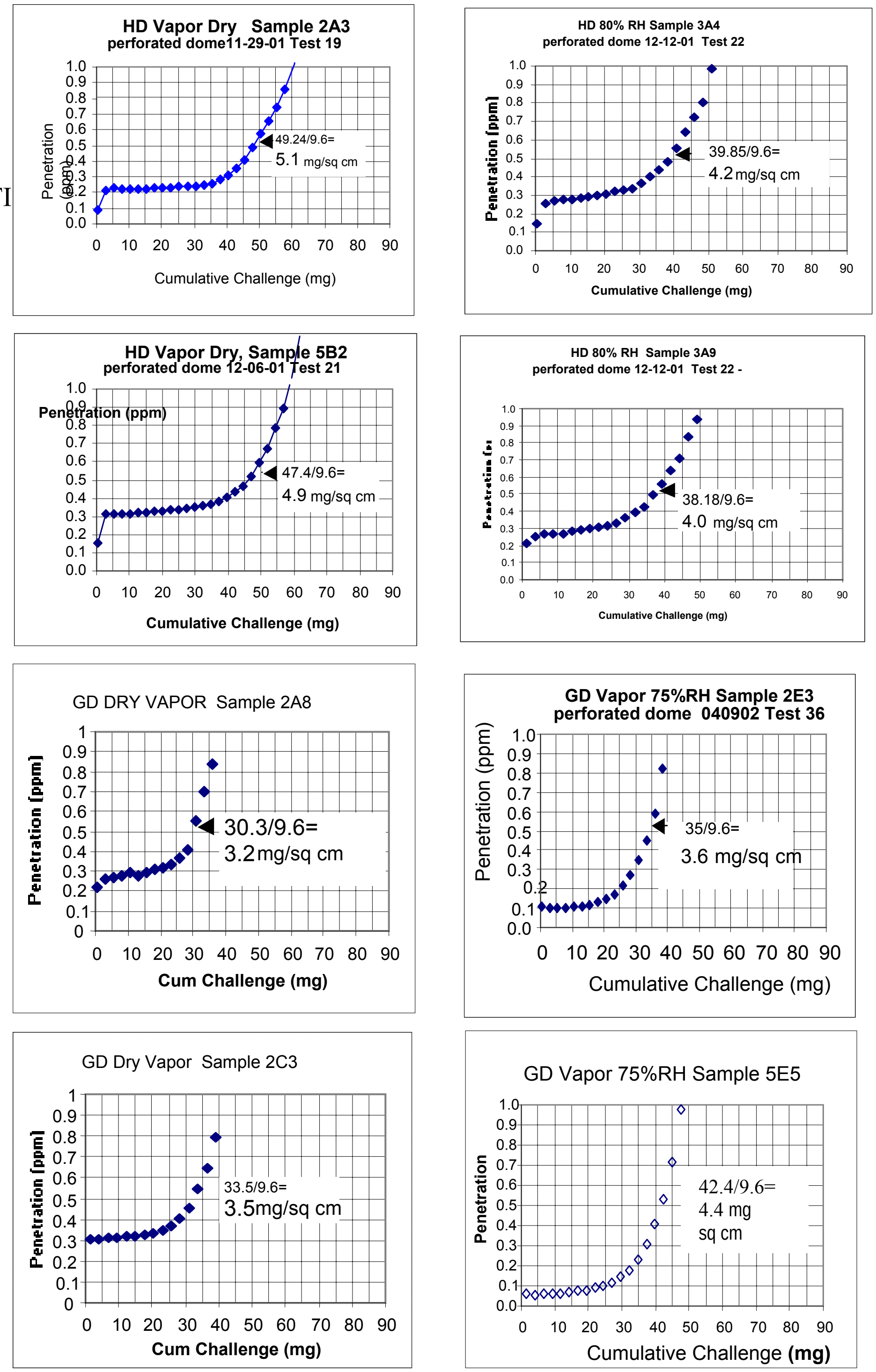

Figure 2. Vapor HD and GD challenge tests at low and high RH.

DYNAMIC SORPTION TEST DATA
Vapor Challenge 0.1 mg/L at 50 cm/min face velocity

Cumulative Challenge at 3% breakthrough (mg/sq cm)				
	%RH	**MeS**	**HD**	**GD**
VIRGIN	swatch:	A B C D E 2	A B C D E 2	A B C D E 2
	0	4.8_5 4.4_5 4.2_5 3.7_3 4.9_5 4.7_4		
	10	4.0_1 3.8_2 4.0_2	5.1_1 4.7_6	3.3_2 3.1_2 3.9_2
				4.0
	80	4.5_2 4.1_2 4.6_2	4.1_4 4.3_2	4.4 1.7_2 4.0_2 3.7_2
REGEN'D		+/-0.6 +/-0.8 +/-0.4		
	0	5.3_2 4.8_2 4.6_2 4.0_2 4.2_2		
	10	6.5_1	5.2_2 4.8_1	
	80	5.6_1 5.5_1	3.5_3 3.2_3	

Figure 3. Vapor sorption test data on replicates of six swatches. a. Tested with dry MeS vapor, 4 of 6 swatches match well, 2 are slightly less sorptive. b. Regeneration (three 1-hour washes with acetone, 48 hr drying in 95°C air-flow oven) after tests with dry MeS: on same or neighbor samples regeneration increases MeS sorptivity 10%, dry tests, and 20% at high RH, and decreases HD sorptivity at high RH.

SIMULANT/AGENT VAPOR TEST DATA SUMMARY
Variation in 6 swatch materials is measured in 0% RH by MeS vapor sorption at 3% breakthrough.
Sorption relative to swatch **A**$_5$**:** **E**$_5$ =1.02**A;** [**2**]$_4$**=**0.98**A**; **B**$_5$ = 0.92**A**; **C**$_5$ = 0.88**A**; **D**$_2$=0.85**A**.
Normalized values of simulant and agent sorption on the various swatches is shown:

Cumulative Challenge @ 3% Penetration of 0.1mg/L Vapor Challenge (@CUBRC)

	MeS	HD	GD	
10%RH	C=4.0(2)->4.5	A=5.1(1)->5.1	A=3.3(2)->3.3	
	A=4.0(1)->4.0	B=4.7(6)->5.2	B=3.1(2)->3.4	
	B=3.5(2)->3.8	Avg = **5.2**	C=3.9(2)->4.4	
	Avg = **4.2**		Avg = **3.7**	
				RH
80%RH	A=4.5(2)->4.5	A=4.1(4)->4.1	C=4.4(1)->5.0	65%
	B=4.1(2)->4.5	B=4.3(2)->4.7	omit D=1.7(2)->2.0	80%
	[2]=4.6(2)->4.6	Avg =**4.3**	D=4.0(1)->4.7	65%
	Avg =**4.5**		E=4.0(2)->3.9	75%
			[2]=3.7(2)->3.8	77%
			Avg =**4.2**	

Figure 4. At low relative humidity HD is sorbed 20% more than MeS, and GD is sorbed 12% less than MeS. At ~75% relative humidity sorption is the same for all three vapors MeS, HD, GD. Is GD sorption reduced at 80% RH? Lower GD penetration detection at higher RH suggests hydrolysis.

LIQUID DROP TESTS:

Test drops are 2 x 5 mg, polymer-thickened, or 8 x 1 microliter (8 x 1.2 mg) on a 10 sq cm area. Comparison of breakthrough time and penetration at 1 , 6, and 12 hours for MeS, HD, DMMP and GD is shown in the tables, Figures 5-7.

THICKENED DROPS TESTS AT LOW (10%) RH; CONVECTIVE AND DUAL FLOW

DP=0.1"	CONVECTIVE TESTS AT LOW (10%) RH					1 Lpm DUAL FLOW TESTS AT LOW RH					
	Sample	BT (hrs) 4ug/sqcm	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm	Sample	BT (hrs) 4ug/sqcm	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm	24hr pen ug/sqcm
TGD 2x5 uL	**7E6**	**0.6**	**13.9**	**94**	**110**	**9B6**	**no brk**	**0.25**	**0.580**	**0.71**	**0.86**
	8E4	**0.7**	**13.7**	**74**	**82**	**9B5**	**no brk**	**0.20**	**0.829**	**1.10**	**1.33**
	6C6	**0.7**	**13.8**	**102**	**110**	**8C6**	**no brk**	**0.38**	**1.243**	**1.57**	**1.89**
	4C7	**0.7**	**11.1**	**81**	**85**	**2E8**	**no brk**	**0.05**	**0.229**	**0.37**	**0.47**
TDMMP 2x5 uL	**3C4**	**0.8**	**8**	**~52**	**~60**	**7B2**	**no brk**	**0.13**	**0.260**	**0.420**	**0.83**
	5C5	**0.8**	**6**	**~80**	**~90**	**7B3**	**no brk**	**0.11**	**0.364**	**0.60**	**1.22**
	6C9	**0.8**	**7**	**76**	**90**	**7B4**	**no brk**	**0.10**	**0.199**	**0.29**	**0.44**
	8C7	**0.5**	**20**	**130**	**150**	**7B5**	**no brk**	**0.11**	**0.516**	**0.83**	**1.26**
TMeS 2x5 uL	**5B1**	**3.7**	**0.62**	**23**	**~110**						
	2C6	**4.5**	**0.42**	**13**	**~75**						

No break-through for dual flow tests.

Figure 5. DMMP can be used instead of GD in Thickened Drop Tests at low RH.

THICKENED DROP TESTS AT 80% RH; CONVECTIVE AND DUAL FLOW

DP=0.1"	CONVECTIVE TESTS AT 80% RH					1 Lpm DUAL FLOW TESTS AT 80% RH					
	Sample	BT (hrs) 4ug/sqcm	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm		Sample	BT (hrs) 4ug/sqcm	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm
TGD 2x5 uL	2C2	0.8	13	33	40	TGD 2x5 uL	8D4	no brk	0.21	0.391	0.42
	5E7	2.5	2.0	7	10		3D5	no brk	0.07	0.140	0.17
	3E4	1.3	6.0	26	30		827	no brk	0.58	0.67	0.79
	4E3	0.9	10	35	40		828	no brk	0.07	0.143	0.17
TDMMP 2x5 uL	7E8	8	0.03	0.4	~20	TDMMP 2x5 uL	7B6	no brk	0.01	0.02	0.05
	7E4	7	0.03	0.1	~20		8B4	no brk	0.02	0.04	0.17
	8E7	8	0.17	1.6	38		9B4	no brk	0.03	0.07	0.10
	521	5	0.8	28	89		2C9	no brk	0.04	0.05	0.10
TMeS 2x5 uL	4D3	2.8	0.60	47	160	TMeS 2x5 uL	2D1	7.5	0.44	2.7	6.1
	4D8	2.0	1.0	58	150		3D2	no brk	0.12	0.65	1.20

Figure 6. At 80% RH thickened GD penetration is generally between TDMMP and TMeS.

A true comparison between thickened agent and simulant requires identical polymer mixing and aging of thickened solutions. At 80% RH TDMMP can be considered a good simulant for TGD, although a good measure of breakthrough will require controlled polymer preparation and ageing. In contrast to the high 12-hour cumulative penetration from TMeS, hydrolysis of GD and DMMP in 12 hours may limit their detection.

DUAL FLOW LIQUID DROP TESTING TESTING:

At dual flow of 1 Lpm air over top and bottom of sample, neat 8 x 1 μL drops of neat HD, GD, and DMMP and 2 x 5 μL drops of TGD and TDMMP did not produce breaklevel cumulative penetration (4 $\mu g/cm^2$). The same minute penetration concentrations were detected for agents and simulants. The tests were run with dry air (10% RH) and at 80% RH.

CONVECTIVE FLOW LIQUID DROP TESTING:

In Figure 7. is illustrated enhancement of the differentiation among swatches found by dry vapor sorption testing when they are tested with neat HD drops in convective air flow (ΔP=0.1 iwg) at low relative humidity. Striking, consistent differences between some swatches are evident. Note: new swatch K is twice as effective while J is less so. Variation between samples of the same swatch is usually small. The liquid drop tests were not as accurate as planned due to variation in drop size. Although drop dispensing was automated (TRIDAK), some data was not used when HD clogging of the tip (smaller drops) or tip contact after release of drops (dragging) was noticed. Manual stepping was used. Nevertheless with two simulants, MeS and DMMP, the behavior of GD and HD is well bracketed for assessment of breakthrough penetration of activated carbon material by agents.

CONVECTIVE FLOW DP=0.1" PAST NEAT DROPS

at 10% RH	Sample	BT (hrs) @4ug/cm^2	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm
Neat HD 8x1 uL drops	6D9	1.5	3.2	44	125
	8D6	2.0	4.5	40	118
	7E3	3.5	1.7	14.0	38
	2E6	4.0	0.6	12.0	36
	J3	2.1	1.9	14.1	22
	J4	2.6	1.5	10.7	18.6
Neat MeS 8x1 uL drops	1J6	1.5	2.7	6.0	6.5
	1J8	2.3	1.9	5.0	5.3
	1J2	2.7	1.8	4.9	5.4
	5E6	no brk	0.8	2.8	3.2
Neat GD 8x1 uL drops	3210	0.3	19	25	28
	8B5	0.7	8	13	14.4
	5J7	0.5	6.4	7	7.5
	4K5	13.8	3.1	3.6	3.9
Neat DMMP	1J9	0.0	14.9	23	29
	1J7	0.7	11.5	43	54

Figure 7.
7a. Dry: Early penetration of HD and MeS, and later penetration of HD and DMMP, match up. GD penetration is between MeS and DMMP.

at 80%RH	Sample	BT (hrs) @4ug/cm^2	1 hr Pen ug/sq cm	6 hr Pen ug/sq cm	12 hr Pen ug/sq cm
Neat HD 8x1 uL drops	4J9	2.1	2.1	9.3	38
	4J11	2.5	1.7	9.7	54
	326	1.5	2.8	10.6	12.4
	529	1.7	2.6	10.7	14.1
Neat MeS 8x1 uL drops	1K1	2.0	1.8	6.5	8.1
	1J10	1.3	3.4	8.5	9.6
	727	1.2	3.8	8.5	9.5
	1B3	1.5	2.9	8.5	9.1
Neat GD 8x1 uL drops	3K2	11.0	2.8	3.6	4.1
	3K1	10.3	2.4	3.5	4.1
	5J10	1.0	4.0	19.5	23.1
	5J11	1.3	3.4	12.8	15.1
Neat DMMP	2A1	8.5	0.7	3.1	4.6
	1A7	7.2	0.5	2.6	6.1

7b. 80% RH: Penetration of MeS matches HD. DMMP matches GD.

TESTS WITH A SPACE BETWEEN LAYERS:

The same set of agent-simulant tests was carried out with a small teflon net circle between the cover fabric and activated carbon liner layers to examine the effect of a space between the layers.

Neat drops: The reduction/delay in penetration with a net spacer between the layers is a factor of 2 for neat 1 microliter drops of dry HD; MeS penetration was unaltered; and DMMP penetration was reduced to 1/6th. At 80% RH HD penetration from neat drops is the same as when dry for 6 hours, but then rises for lower sorbing material unless there is a space, that is the net prevents a delayed increase typical of HD. MeS penetration was slightly reduced by the net; and the penetration from DMMP drops, already

lowered by a factor of 10 at 80% RH was reduced further by the net. Penetration after 6 hours usually starts to level off but HD behavior is unique in increasing (to a lesser extent for the higher capacity material) and this late upward trend of HD was not changed by 80% RH.
Thickened drops: Dry or at 80% RH, TGD penetration is delayed/reduced by a factor of 3 by a net spacer. 80% RH already reduces penetration from TGD drops by a factor of 3 but doubled TMeS penetration. TMeS penetration is reduced to 1/4th by the net when either dry or wetted. Unlike neat MeS, TMeS penetration does not level off after 6 hours and remarkably the thickened drops challenge 2 x 5 μL of TMeS mimics neat 8 x 1 μL HD in penetration. The net is a little more effective in reducing penetration of TMeS than of neat HD.

CONCLUSIONS

Mounting a test sample of chemical protective material consisting of cover fabric and activated carbon liner on a convex screen smooths out wrinkles that form when the sample edge is tightened in the cell. Wrinkles add area to a vapor test sample, artificially raising the calculated value of sorption/sq cm by equating sample area to cell area. Reproducibility was achieved in 24-hour MeS dry vapor challenge tests, providing a means for comparing the sorptive capacity of different activated carbon materials. The vapor sorption capacity (challenge accumulation at the time of 3% breakthrough) was found to be the same for the three chemicals MeS, HD, GD tested at 75% relative humidity. MeS is a good simulant for both agents HD and GD in vapor tests. At low relative humidity HD is adsorbed 20% more than MeS, and GD is adsorbed 12% less than MeS and the coincidence at high RH is due to different mechanisms - ability to displace the water in the activated carbon pores, and partial hydrolysis of GD - nevertheless there is good reproducibility in the vapor tests at high RH to support the assignment of equal measured capacity for all three chemicals.

For tests with liquid drops of agent or simulant, smooth, close contact of the fabric layers mounted on a perforated dome provided consistent testing information from the fast-breaking strong challenge that convective flow presents; this can be supplemented with gapped fabric layers to test the effect of wrinkles. At low relative humidity DMMP and GD show the same early breakthrough and subsequent penetration for 12 hours. There is little detected penetration of DMMP and GD in convective flow of 80% (only at breaklevel in 12 hours) perhaps due to hydrolysis. MeS matches HD until after about 6 hours when levelling off fails to occur for HD both at low and 80% RH. However the same upswing occurs with thickened MeS so that a very close match in penetration behavior is unexpectedly found between neat 8 x 1 μL HD drops and 2 x 5 μL TMeS drops.

Wrinkles could introduce a variation in the drops' vapor penetration path that is a realistic happening but the overall behavior of which requires statistically significant sampling. Chemical protective uniform tested with HD drops without attention to the presence of wrinkles can vary by a factor of 2 in break-time and 6 in accumulated penetration. Surprisingly the gap between the fabric layers did not have the same effect on all three, producing less penetration for HD and DMMP, while MeS penetration is unaffected.

There is little penetration from liquid drops in dual flow tests; the simulants mimic agents well.

REFERENCES

1.Dawson, Gilchrist EATM311-3 1967; 2.Mary Jo Waters CRDC-SP-84010 1984; 3.TOP 8-2-501 Army Dugway Proving Ground 1997