

Evaluation of Chemical Protective Clothing: A Comparative Study of Breakthrough Times with Sulphur Mustard and a Simulant, 1,3-Dichloropropane

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ABSTRACT

Carbon-coated non-woven fabrics were evaluated against vesicant sulphur mustard and 1,3-dichloropropane (DCP). Breakthrough times of these chemicals were compared and fitted in a linear equation. A correlation, better than 95 per cent was obtained. It is recommended that DCP be used in the evaluation and quality control of fabric in the chemical protective clothing manufacturing industries to reduce the exposure and risks of handling lethal chemicals. However, the clothing may be challenged with actual CW agents to determine their protective potentials, in the laboratory. Diffusion coefficients for DCP were also computed from the breakthrough data for carbon-coated fabric of different grades.

1. INTRODUCTION

For protection of the whole body against toxic chemicals which manifest their effect by absorption through skin, chemical protective clothing (CPC) is used. Apart from elastomer- or polymer-coated impermeable shields, carbon-containing permeable clothing is in vogue. Permeable type of clothing is preferred over impermeable type due to low heat stress and comfort, enabling use for a longer duration. The carbon-containing material developed so far includes carbon-coated non-woven fabric, carbon-impregnated polyurethane foam, hard carbon microsphere-adhered woven fabric and activated charcoal cloth. The performance of permeable type

of fabric is governed by the surface properties of activated carbon, quantity of carbon available per unit area of the fabric and its distribution pattern. The so-called air permeability (AP), quantified in terms of the volumetric flow of air per unit area at a given positive pressure, is a measure of comfort. AP depends upon the distribution pattern of the coating and structure of the base fabric. Scanty reports about the performance evaluation of breathable fabric available in literature¹⁻⁷ reveal that invariably highly toxic di (2,2-chloroethyl) sulphide, commonly known as sulphur mustard and abbreviated as HD in military literature, is used for this purpose. Breakthrough time (BTT) measurements of HD at 20 °C are an essential part of most of the military

specifications. However, use of (HD) at the production site for quality assurance and quality control poses problems of handling due to its toxic nature, more so in the absence of trained personnel and later decontamination. A method based on 1,3-dichloropropane (DCP) penetration is described in the British specification which is claimed to be analogous to HD BTT test. The use of comparatively non-toxic (DCP) as a simulant for HD in this method, and gas chromatography (GC) as a monitoring technique offer many advantages, such as accuracy, speed and non-subjectivity. However, full potential of this method could not be exploited in the absence of systematic correlation studies.

In this paper, the authors present details of a comparative study on BTTs of HD and penetration time of DCP through protective clothing. The protection potential of CPC is inversely proportional to the diffusivity of the chemical to which CPC is exposed. CPC, consisting of a high surface area absorbent, resists penetration of the toxic chemicals and gives protection for long periods. Sometimes, certain chemicals take days for penetration through CPC. Thus, in the case of a good quality coated fabric, the measurement of a single important parameter BTT, becomes a constraint in the bulk production of CPC.

It would therefore, be preferable, if a substitute simulant for HD in CPC evaluation at industrial establishments could be found for quality control and quality assurance. Through a substitute like DCP, because of its high diffusivity and a very rapid BTT compared to HD, rapid evaluation of CPC is facilitated. The experimental data confirmed its suitability.

2. EXPERIMENTAL WORK

2.1 Materials

CPC samples were prepared by coating active carbon (characteristics given in Table 1) using polychloroprene as a binder on the reinforced non-woven fabric (100 ± 5 gsm). The coating dough comprising compounded neoprene dissolved in toluene and powdered carbon was prepared in a Sigma mixer. A highly porous non-woven fabric was made

Table 1. Characteristics of carbon-coated non-woven fabric

Active carbon	Origin	Surface area (N ₂ BET) (m ² /g)	Total pore volume at P/P ₀ =0.9861 (cm ³ /g)	Particle size (μm)	Bulk density (g/cm ³)
A	Casurina wood	1680	1.2	42	0.3
B	Coconut shell	150	0.9	63	0.4

by needle punching polyester wadding on a cotton/polyester scrim. The coating was done on scrim side on a spreading machine by 'knife on roller technique' and add-on was varied by controlling the viscosity of the coating composition, traverse rate of the fabric and/or gap between knife and the roller. The carbon to binder ratio was kept at 60:40. The coated fabric was cured at 120 °C for 8 hr after initial evaporation of the solvent on a coating plant. Active carbon used for coating was obtained from Active Carbon India, Ltd., Hyderabad. Chemicals used in penetration studies and BTT measurements were of AR grade. A small quantity of HD was synthesised and double distilled before use.

2.2 Sulphur Mustard Breakthrough Time Measurements

The method for HD breakthrough time measurements is described in detail². In this method, a specially designed brass assembly, two discs of coated fabric (charcoal sides facing each other) are exposed to an atmosphere saturated with mustard vapours at 20 °C. A detector paper prepared using a congo red-impregnated filter paper spotted with SD reagent (2,4-dichlorophenyl benzoyl chloroimide) was kept on top of the samples to follow the BTT of HD. First appearance of blue colour on the detector paper indicated BTT, the protection time against HD.

2.3 1,3-Dichloropropane Penetration Measurement

The details of the diffusion test equipment and procedure adopted are given elsewhere⁸. The apparatus consists of a diffusion cell, a single flame ionisation detector (FID), and an 1mV recorder or digital millivoltmeter with time. The diffusion cell comprises

milivoltmeter with time. The diffusion cell comprises two 100 mm full solid brass cylinders, the upper one having 52 mm through hole and the lower one a 3 mm deep groove of 2.5 cm diameter. The upper cylinder acts as a housing for the test cup in which the test specimen, the DCP source and spacers are mounted. The groove in the lower cylinder is continuously swept by carrier gas nitrogen stream at a given flow rate, which is fed to the FID. A separator made of 13 μm polythene film covered with a fine wire mesh is sandwiched between the two cylinders. The cell is maintained at a constant temperature of 30 ± 0.05 °C through cartridge heaters, precision temperature controller and proper insulation. In the test cup, the sample is placed at the bottom followed by a 3 mm spacer. A disc of Whatman No.1 filter paper is placed over the first spacer on which two drops of DCP are dispensed using a 10 μl syringe. The filter paper is secured in its place using a 1mm spacer and a glass stopper which also prevents fast evaporation of DCP to the atmosphere. It may be noted that in both the above tests, the coated fabric is exposed to the atmosphere saturated with the test agent vapours.

The apparatus is first calibrated before use, such that 1mV reading on the strip chart recorder corresponds to 1 $\mu\text{g}/\text{min}$ flow of DCP through the FID. This condition is obtained via adjustment of

flame height, attenuation and backing voltage, etc. DCP penetration time is the time taken to reach 1 mV reading in the presence of a given sample in a standardised apparatus.

In blank tests, no coated fabric is used and the rest of the test cup is assembled, as described above. The time taken for reaching 1mV reading after placing DCP on the filter paper in the present case was 13 s (average of 10 readings) and standard deviation 0.48 s

2.4 Data Reduction

In the case of polymeric films, the diffusivity of a permeating material can be computed from the time lag of the S-shaped breakthrough curve (Fig. 1) using the following relationship obtained by solving Fick's equation⁸⁻¹⁰:

$$6D_A$$

where L is the time lag in seconds obtained by extrapolation of the straight line portion of the S-shaped curve, l is thickness of the film in cm and D_A is diffusivity in cm^2/s . However, in the present case, the time lag is not only due to diffusivity (surface, intragranular and Knudsen) but also due

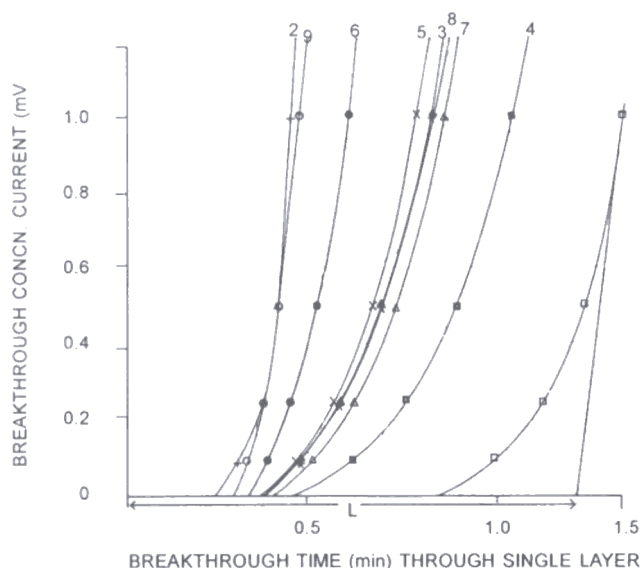


Figure 1. 1,3-Dichloropropane breakthrough time curves

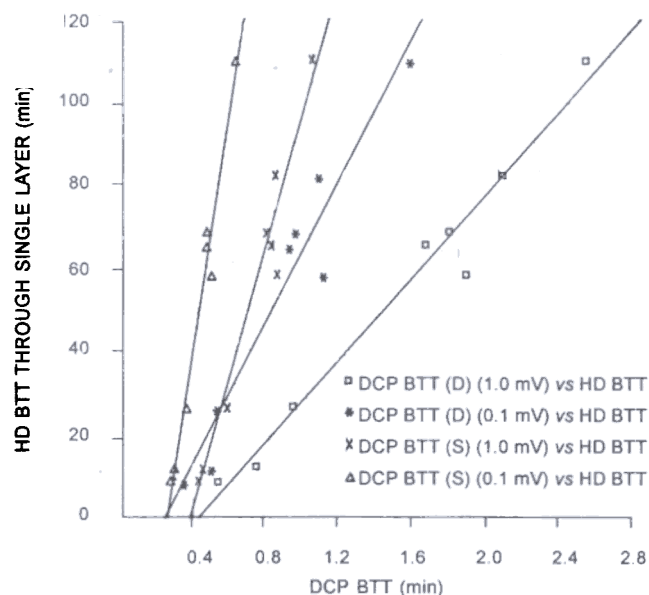


Figure 2. Correlation between DCP BTT and HD BTT

The diffusivity calculated is only the apparent diffusivity. Nevertheless, Eqn (1) can still be applied for calculating apparent diffusivity (D_A). In calculating D_A from Eqn (1), time lag of the blank run 13 s was subtracted from the observed value of permeation time to obtain the true time lag caused by the sample.

The following equation was used to calculate D_A of HD through the carbon-coated non-woven fabric⁴:

$$t = l^2 / \pi^2 D_A \quad (2)$$

where t is the breakthrough time and l , thickness of the membrane.

2.5 Thickness of Coated Fabric

The average thickness of the coating on non-woven fabric was determined using scanning electron microscope. The coated fabric was carefully cut and mounted on the sample holder for the measurement

Table 2. Characteristics of carbon-coated non-woven fabric* (single layer)

Sample No.	Carbon loading (g/m ²)	Thickness (cm)	Air permeability (cm ³ /cm ² /s)	Diffusivity (cm ² /s)	
				DCP	HD
	Nil	0.0050	Nil	7.18×10 ⁻⁸	1.26×10 ⁻⁹ (c)
	Nil	0.0050	Nil	7.18×10 ⁻⁸	1.99×10 ⁻⁹ (d)
	Nil	0.0013	Nil	2.17×10 ⁻⁸	6.01×10 ⁻¹⁰ (c)
	Nil	0.0013	Nil	2.17×10 ⁻⁸	1.33×10 ⁻⁹ (d)
2 ^a	51.4	0.0400	>100.0	2.42×10 ⁻⁵	3.18×10 ⁻⁷
3	94.8	0.0440	16.0	1.15×10 ⁻⁵	4.98×10 ⁻⁸
4	137.6	0.0570	13.5	1.43×10 ⁻⁵	4.99×10 ⁻⁸
5	181.5	0.0620	9.5	2.51×10 ⁻⁵	5.87×10 ⁻⁹
6	130.5	0.0550	10.3	2.88×10 ⁻⁵	1.95×10 ⁻⁷
7	102.1	0.0550	32.8	1.68×10 ⁻⁵	8.77×10 ⁻⁸
8	170.8	0.0590	5.0	2.19×10 ⁻⁵	7.15×10 ⁻⁸
9 ^b	246.4	0.0950	28.0	11.14×10 ⁻⁵	1.29×10 ⁻⁶

a In samples 2 to 8, carbon A of casurina wood origin (Table 1)

b Carbon B of coconut shell origin (Table 1)

c Vapour challenge

d Liquid challenge

1 Polyethylene film for standardisation.

2 Roto cured; carbon - 60 %

3* Roto cured; carbon - 70 %,

4 to 9 Chamber cured: carbon-60 %

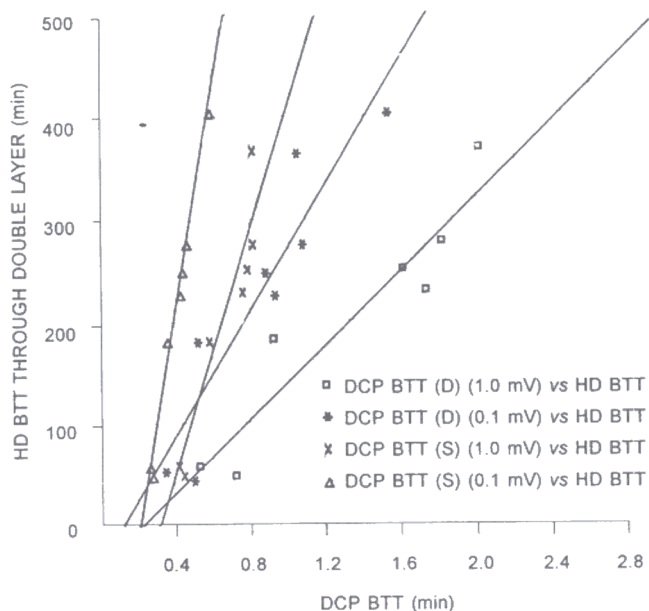


Figure 3. Correlation between DCP BTT and HD BTT of thickness.

2.6 Air Permeability of Coated Fabric

AP of coated fabric was measured using SEARLE air permeability apparatus. The data given is for AP at 10 mm water head pressure. AP of uncoated base non-woven fabric at 10 mm pressure was beyond the range of apparatus used for measurement.

3. RESULTS & DISCUSSION

Breakthrough curves for all the nine samples for permeation of DCP through carbon-coated fabric and polythene (50 μm) are shown in Fig. 1. The initial curvature in the breakthrough curve is caused due to many processes, such as mass transfer, permeation through the binder, surface diffusion, intragranular diffusion, adsorption and desorption. The straight line portion signifies equilibrium conditions. The final plateau of the curve is not shown in the figure. Straightway, one is tempted to choose time lag as the characteristic parameter for quality control. However, studies revealed that time lag does not correlate well with HD BTT. It was observed that after the first point of inflection, the rate of advancement of the straight line portion denoting concentration rise varied significantly with the quality of the coated fabric. Thus, 1 μg/min DCP flow through FID adjusted equivalent to 1mV was fixed arbitrarily.

In the sample studied, this eventually indicated as some point on the equilibrium portion of the curve. It was surprising to see that DCP breakthrough curve for 50 µm polythene film was similar to that for a good quality carbon coated fabric. However, the analogy can not be extended further, as the two systems are quite different.

Some of the important characteristics of the sample used in the correlation studies are given in Table 2 along with AP, and HD and DCP diffusivities

Table 3. Penetration data for 1,3-dichloropropane and sulphur mustard for single layer of carbon-coated non-woven fabric

Sample No.	BTT and SD for (DCP BTT) ^a				SM BTT (HD BTT) ^b
	(min)				
	(SD)				
	0.1mV	0.25mV	0.5mV	1.0mV	
	0.97	1.10	1.21	1.31	33.42 ^c
	(0.04)	(0.05)	(0.07)	(0.06)	(0.12)
					21.18 ^d
					(0.02)
					4.75 ^c
					(0.02)
					2.15 ^d
					(0.02)
2	0.28	0.35	0.38	0.42	8.50
	(0.02)	(0.02)	(0.05)	(0.05)	(0.71)
3	0.45	0.55	0.66	0.79	65.60
	(0.04)	(0.06)	(0.06)	(0.08)	(12.73)
4	0.60	0.73	0.86	1.00	110.16
	(0.02)	(0.03)	(0.03)	(0.03)	(7.35)
	0.44	0.54	0.64	0.75	68.67
	(0.05)	(0.05)	(0.07)	(0.08)	(10.73)
6	0.36	0.42	0.49	0.57	26.16
	(0.01)	(0.02)	(0.02)	(0.03)	(2.40)
	0.48	0.59	0.70	0.82	58.33
	(0.03)	(0.03)	(0.04)	(0.06)	(4.08)
8	0.45	0.59	0.70	0.82	82.33
	(0.03)	(0.03)	(0.04)	(0.05)	(11.37)
9	0.30	0.35	0.39	0.44	11.83
	(0.03)	(0.03)	(0.03)	(0.02)	(2.85)

a Average of 10 samples

b Average of 10 samples

c Vapour challenge

d Liquid challenge

l Polythene film (50 µm) for standardisation

lⁱ Polythene film (13 µm)

at 20 and 30 °C, computed using Eqns (1) and (2), respectively. One would expect that AP will decrease with increase in loading. However, this does not hold good for the the present system due to its complex nature. It was observed that small changes in viscosity, gap between roller and knife and/or curing process affected the distribution pattern and consequently AP significantly. Due to inherent nature of the samples, the thickness measurements cannot be made very accurately; hence these values at best give the general trend of change in D_A according to loading and quality of carbon. It may be seen that diffusivity of DCP at 30 °C does not change much from samples 2 to 8, in which the same grade of carbon was used for coating, though loading is quite different in these samples and curing process is also not the same. However, in the case of sample 9, in which comparatively low surface area carbon was used, the diffusivity is quite high compared to other samples. This suggests that adsorption/desorption in micropores is probably the key mechanism responsible for attenuation of challenge concentration. As expected, HD diffusivity values at 20 °C are

Table 4. Penetration data for 1,3-dichloropropane and sulphur mustard for double layer of carbon-coated non-woven fabric

Sample No.	BTT and SD for (DCP BTT) ^a				SM BTT (HD BTT) ^b
	(min)				
	(SD)				
	0.1mV	0.25mV	0.5mV	1.0mV	
2	0.35	0.42	0.47	0.52	57.00
	(0.01)	(0.02)	(0.02)	(0.03)	(24.47)
3	0.89	1.15	1.36	1.61	249.00
	(0.07)	(0.09)	(0.11)	(0.13)	(25.76)
4	1.52	1.89	2.13	2.46	403.00
	(0.12)	(0.16)	(0.17)	(0.20)	(54.14)
5	0.93	1.20	1.43	1.74	226.63
	(0.08)	(0.12)	(0.12)	(0.03)	(26.18)
6	0.52	0.65	0.77	0.92	180.63
	(0.05)	(0.06)	(0.07)	(0.10)	(21.35)
7	1.07	1.33	1.56	1.83	275.25
	(0.09)	(0.11)	(0.13)	(0.16)	(24.64)
8	1.04	1.35	1.65	2.02	365.28
	(0.06)	(0.10)	(0.12)	(0.16)	(24.967)
9	0.50	0.57	0.64	0.72	47.00
	(0.04)	(0.02)	(0.03)	(0.03)	(9.68)

a Average of 10 samples

b Average of 10 samples

values at 20 °C are much lower than DCP, and D_A values at 30 °C. However, due to variance in experimental method and lack of precision in identifying the end point in HD BTT test, not much importance can be attached to HD diffusivity values.

Table 5. Correlation matrix for breakthrough times of sulphur mustard and 1,3-dichloropropane(min)

Correlation between	Regression equation	Correlation coefficient	Standard error	t_{lab}
DCP BTT(S) (for 0.1mV) & HD BTT (S)	$Y = -84.4+329.3X$	0.958	40.041	8.2
DCP BTT (D) (for 0.1 mV) & HD BTT (S)	$Y = -23+90.2X$	0.965	10.0456	8.98
DCP BTT (S) (for 1.0 mV) & HD BTT (S)	$Y = -65.7+171.3X$	0.971	17.1124	10.01
DCP BTT (D) (for 1.0 mV) & HD BTT (S)	$Y = -22.1+5.15X$	0.985	3.7194	13.85
DCP BTT (S) (for 0.1 mV) & HD BTT (D)	$Y = -259.7+1155X$	0.933	182.4657	6.33
DCP BTT (D) (for 0.1 mV) & HD BTT (D)	$Y = -40.4+311.9X$	0.925	52.3998	5.95
DCP BTT (S) (for 1.0 mV) & HD BTT (D)	$Y = -198.7+601.1X$	0.955	76.7358	7.91
DCP BTT (D) (for 1.0 mV) & HD BTT (D)	$Y = -42.2+181.2X$	0.961	21.3585	8.48
HD BTT (S)	Sulphur mustard breakthrough time for a single layer			
HD BTT (D)	Sulphur mustard breakthrough time for a double layer			
DCP BTT (S)	1,3-dichloropropane breakthrough time for a single layer			
DCP BTT (D)	1,3-dichloropropane breakthrough time for a double layer			
X	DCP BTT			
Y	HD BTT			

The average DCP penetration time under a standard set of conditions when plotted against HD BTT at 20 °C gave a straight line for both single and double layers (Figs 2 and 3). The correlation was always better than 95 per cent. These results encouraged to see if an equally good correlation exists between HD BTT and DCP penetration time corresponding to 0.1, 0.25 and 0.5 mV. The data are given in Tables 3 and 4 and the correlation matrices are given in Table 5. As may be seen, correlation is always quite good. Plots for 0.1 mV are included in Figs 2 and 3. This suggests that as long as a portion of equilibrium part of the breakthrough curve is included in DCP penetration time, good correlation is obtained.

DCP penetration time depends significantly on the nature and precise thickness of the separating film and GC conditions. In view of this, though in the present study the average HD BTT value at 20 °C laid down in British specifications for acceptable fabric (160 min) corresponds to 30 s instead of the specified 45 s, one does not wish to suggest changes in the specified values.

4. CONCLUSION

The present study demonstrates that as suggested in the British specifications, DCP penetration time under standard set of conditions can be used as an alternative to HD BTT measurements. The comparatively non-toxic nature of DCP and use of instrumental method for monitoring the penetration of the test agent makes the method more accurate, unambiguous and non-hazardous. The rapidity of this method makes it still more attractive for routine quality control and quality assurance. Eventually, HD BTT test can be done on a few samples in the laboratory for final clearance of the lot.

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