Efficient and quick method for evaluation of carbon-coated breathable protective clothing for toxic chemicals

V S Tripathi, Darshan Lal & A K Sen
Defence Materials & Stores Research & Development Establishment, DMSRDE P.O., G T Road, Kanpur 208 013, India

Received 18 March 1996; revised received 16 October 1996; accepted 12 December 1996

An efficient and quick method for evaluation of breathable fabric is described. The method is based on measurement of penetration time of 1,3-dichloropropane (DCP) using the portable diffusion test equipment (DTE) developed at DMSRDE. DTE comprises of a diffusion cell, a single-flame flame ionisation detector (FID), a digital millivoltmeter and a timer. All these components are fitted in a 25x50x10 cm box along with the required controls. The calibration procedure and the working of the instrument are described in some details. The results obtained using the conventional method and the new method/apparatus developed have shown better than 99.5% correlation on regression analysis. Air permeability of different fabrics has also been recorded.

Keywords: Carbon-coated breathable protective clothing, Dichloropropane, Diffusivity, Air permeability, Protective clothing

1 Introduction

Due to comparatively low-heat stress, breathable carbon-coated fabric is preferred over impermeable polymer-coated fabrics for protection against toxic chemicals which cause injury by adsorption through skin. Various methods adopted worldover for evaluation of breathable fabric make use of live agents, e.g. mustard, and are time consuming. In most of the test methods, colour development in a detector paper is used for monitoring the breakthrough of chemical agent and this induces an element of subjectivity. Moreover, the use of toxic chemicals at production site for fixing and optimization of operating conditions of the plant and quality control creates safety problems. It may also be pointed out that due to non-uniform distribution of the carbon particles and presence of binder, the characterization methods based on equilibrium adsorption techniques, such as surface area measurement and pore size distribution, do not indicate the performance of the fabric.

In view of these problems, a portable diffusion test equipment has been developed in this laboratory for rapid quality control of the breathable fabric using a simulant and gas chromatographic technique. The breathable fabric used is active carbon-coated fabric and the simulant used is 1,3-dichloropropane (DCP) in lieu of S-mustard used in standard methods. DCP is chosen as a simulant because it has some similarity in structure with S-mustard, e.g. two terminal chloro groups. DCP has a low boiling point and is easy to detect by gas chromatographic detectors. Important properties of mustard and DCP are shown in Table 1. It may be seen that the DCP penetration time correlates fairly well with mustard breakthrough time. This equipment has been particularly useful for quality control, at the production site, of carbon-coated fabric.

<table>
<thead>
<tr>
<th>Property</th>
<th>Mustard</th>
<th>1,3-Dichloropropane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>S</td>
<td>CH₂Cl</td>
</tr>
<tr>
<td>Size (diam.)</td>
<td>6.97 Å</td>
<td>6.40 Å</td>
</tr>
<tr>
<td>Density at 20°C</td>
<td>1.186 g/cc</td>
<td>1.275 g/cc</td>
</tr>
<tr>
<td>Boiling point</td>
<td>118°C</td>
<td>217°C</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>159.08</td>
<td>112.99</td>
</tr>
</tbody>
</table>

Table 1—Physical properties of HD mustard and 1,3-dichloropropane
In this paper, the design of diffusion test equipment, its method of calibration, correlation of mustard breakthrough time with DCP penetration time and its advantage in rapid and accurate evaluation of carbon-coated fabric are described.

2 Materials and Methods

The diffusion test equipment is based on gas chromatographic technique. The GC column separating the components of a vapour by partition is however replaced by a diffusion cell. Penetration time of the simulant 1,3-dichloropropane across the polyethylene film and breathable carbon-coated fabric is detected and measured by flame ionisation detector.

2.1 Materials

Pure dry nitrogen (Indian Oxygen Limited, India) was used for primary calibration and as carrier for secondary calibration and testing. 1,3-dichloropropane (Aldrich Chemical Co, USA) of 99.5% purity was used for measuring penetration time. Low-density polythene blow films of 13 μm and 50 μm thickness were procured locally. Protective clothing samples were made by coating dough (carbon + neoprene binder) using knife on roller technique on nonwoven fabric. Base fabric comprised of polyester wadding and plane weave polyester/cotton scrim attached together by needling. Base nonwoven fabric (95±5 g/m²) had air permeability of 250 cm³/cm²/s at 5 mm water head. Fabric samples A-G having different carbon contents were prepared by varying the operating parameters such as carbon to binder ratio, dough viscosity, traverse rate of fabric, etc. The details of method and materials of coating are not reported here as a patent application has been filed on the process of coating.

2.2 Diffusion Test Equipment (DTE)

Portable DTE assembly comprises of a diffusion cell, single-flame FID, mass flow controllers, digital millivoltmeter, and a timer built in the apparatus. If ultra pure hydrogen is used as fuel and nitrogen as carrier, single flame FID gives adequate sensitivity. The usual recorder/integrator has been replaced by a digital millivoltmeter and a timer built in the apparatus. Timer used in DTE has been designed in such a way that it stops as the digital millivoltmeter reaches one millivolt reading. Mass flow controllers are used for fine control of carrier and fuel gas flow. The DTE assembly can be packed in a 24 in. suitcase and can be carried to the test site as and when required.

The diffusion cell (Fig. 1) comprises of two brass cylinders having 52.0 mm hole at the centre. The upper cylinder has a through hole and acts as housing for test cup containing DCP source. The lower cylinder having 3 mm deep groove provides the area to be swept by the carrier gas. A 13 μm polythene film covered with wire mesh is sandwiched between the two cylinders. The diffusion cell is connected to FID with 1/16 in. stainless steel tubing. The test cup comprises of 3 mm thick spacer placed over breathable fabric followed by Whatman No. 1 filter paper and 1 mm thick spacer. The diffusion cell is installed in the DTE apparatus casing to retain the portability of the equipment. The cell is heated to 30°C using cartridge heater and temperature controller and is properly insulated to maintain temperature during testing.

2.3 Calibration

The set-up used for primary calibration is shown in Fig. 2. Pure dry nitrogen stream from cylinder was split in two parts and passed through precalibrated capillary flow meters. One stream of
nitrogen was passed through a bubbler (containing DCP) maintained at 0°C at the flow rate of 1 mL/min. The saturated stream was further diluted with the second stream at the rate of 1 L/min. This mixed stream after homogenisation in 2 m long column was sent to FID at the ratio of 10 mL/min. The rest of the stream was vented out. This flow rate corresponds to 1 µg/min of 1,3-dichloropropane. The sensitivity of the instrument was then adjusted in such a way that it gave 1 mV reading consistently while DCP laden nitrogen flew through FID. The DCP concentration was calculated using following equation:

\[ g = \frac{PM}{vRT} \]

where \( g \) is the DCP present (in grams) in \( v \) ml of nitrogen; \( P \), the saturated vapour pressure of DCP at \( T^\circ K \); \( M \), the molecular weight of DCP; and \( R \), the gas constant.

Once the primary calibration was achieved, the arrangement used in Fig. 2 was disconnected and a polythene film of 50 µm thickness was placed in the sample holder without changing the sensitivity of instrument. DCP penetration time was then measured through the film by the timer at 1 mV reading. A set of polythene films from different places of the same roll was chosen and penetration time of different films recorded (Table 2). The mean of six readings was taken for a film, and the film which was found to have penetration time nearest to 85 s was taken as standard for secondary calibration for subsequent day to day work.

Permeation time of different films samples cut from the same roll varied widely due to the variation in thickness of polythene films from point to point. However, the standard deviation for the same film was quite small and DCP penetration time was quite reproducible.

After calibration, the apparatus was ready for testing of protective breathable fabric. The parameters of primary and secondary calibration and the procedure of testing of breathable fabric is as per the UK specification. Acceptability criteria for a roll of fabric is also laid in the specification. Accordingly, the average of DCP penetration time for six samples in the given set of conditions should not be less than 45 s and no single reading should be less than 40 s.

2.4 Procedure

The instrument was switched on and the flow rate of \( H_2 \) and \( N_2 \) measured carefully. Compressed air after passing through air purifier was fed to FID for burning the flame. The apparatus was kept on for an hour for stabilization before use.

As it has been mentioned that primary calibration is not possible in routine testing, as such secondary calibration was carried out. Previously tested 50 µm thick polythene film was placed in the test cup and then kept in the diffusion cell for 5-10 min to attain temperature equilibration.

Five micro-litre of 1,3-dichloropropane was then dropped over the filter paper and covered with a stopper to minimise loss of DCP from the cell. When the average of six readings was around 85 s, the apparatus was considered calibrated and ready for testing. A piece of breathable fabric was then placed in place of 50 µm polythene film and DCP penetration time measured in the same way.

3 Results and Discussion

Carbon-containing fabrics should have two important properties. Firstly, it should reduce the challenge concentration of CW agent such that cumulative dose never crosses intermediate incapacitating dose in say 24 h (ref. 7). Secondly,
the air permeability of fabric should be high so that physiological stress is minimum.

In case of bis (dichloro-diethylsulphide), the agent recommended for testing, the median incapacitating dosage (IC50) is 2000 mg min/M3. Accordingly, for exposure to air saturated with vapour of above agent a sample should give breakthrough time (BTT) of around 3 h at 20°C. On the other hand, the air permeability should be minimum 30 mL/cm²/min. The binding of carbon particle on the fabric substrate should also be proper for the retention of functional properties as well as for aesthetics. The carbon-coated fabric is a complex system and the characteristics of carbon particles, nature of base fabric, the type of the binder and the coating conditions are to be properly optimized to get the desired properties in the fabric. The retention of pollutants on the fabric is determined mainly by surface properties of carbon, its particle size, concentration of binder and the distribution pattern of carbon on the fabric. The binder is usually an elastomer. For selecting a simulant, its nature of permeability through the elastomeric binder is an important consideration. Thus, any chemical used as simulant should have the same type of interaction with binder and mechanism of removal by carbon should also be physical adsorption without any specific interaction as in case of actual agents. The test agent 1,3-dichloropropane meets both these requirements. However, due to low molecular weight its adsorbability is low and hence breakthrough occurs in much shorter time compared to that for mustard, the usual test agent. A typical breakthrough curve obtained from DTE apparatus using the timer is shown in Fig. 3. Some results of DCP penetration test conducted during development work are given in Table 3. It may be seen from the data that standard deviation in DCP values is very low. The mustard breakthrough time for the same pieces of fabric is also given in Table 3. The result shows that the standard deviation in mustard BTT value is quite high, probably due to subjectivity in the estimation of time of colour development.

According to the British specification3, in case of acceptable fabric the average of 6 readings should be 45 s in the standard conditions and no single specimen should give less than 40 s reading. The value of minimum DCP penetration time in our correlation exercise was slightly lower than this value, probably due to the differences in the

---

**Table 3—Comparison of mustard and DCP vapour diffusion tests**

<table>
<thead>
<tr>
<th>Fabric No.</th>
<th>Air permeability at 10 mm water head cm²/cm²/s</th>
<th>Mustard test</th>
<th>DCP test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean penetration time, min</td>
<td>SD min</td>
<td>Mean penetration time, s</td>
</tr>
<tr>
<td>A</td>
<td>62.2</td>
<td>13.2</td>
<td>17.2</td>
</tr>
<tr>
<td>B</td>
<td>78.6</td>
<td>16.3</td>
<td>19.0</td>
</tr>
<tr>
<td>C</td>
<td>145.6</td>
<td>18.5</td>
<td>33.7</td>
</tr>
<tr>
<td>D</td>
<td>164.6</td>
<td>14.6</td>
<td>51.8</td>
</tr>
<tr>
<td>E</td>
<td>107.2</td>
<td>31.9</td>
<td>23.3</td>
</tr>
<tr>
<td>F</td>
<td>90.3</td>
<td>46.6</td>
<td>18.3</td>
</tr>
<tr>
<td>G</td>
<td>172.2</td>
<td>15.2</td>
<td>74.8</td>
</tr>
</tbody>
</table>

---

Fig. 3—Typical permeation curve of DCP through polythene and carbon fabric
polythene films used as barrier to separate the two parts of diffusion cell. The regression analysis of mustard BTT and DCP penetration time of different fabrics given in Table 3 leads to following regression equation:

\[
\text{HD BTT} = 0.4477 \times \text{DCP penetration time} - 18.4472
\]

Correlation coefficient = 0.99158

It may be stated from above that DCP penetration time can be used as a parameter for evaluation of breathable fabric with full confidence.

### 4 Conclusion

The portable DTE apparatus, used successfully in development work of breathable fabric, involves diffusion across the breathable carbon-coated fabric and polymer barrier. It could be used for diffusion measurements of various organic compounds through variety of barriers. Use of FID for quantification after diffusion enhances the speed and accuracy of the instrument.

### Acknowledgement

The authors are thankful to Prof G N Mathur, Director, DMSRDE, for encouragement during the course of this work. They are also thankful to Nucon Engineers, India, for assembling the apparatus.

### References