Permeation Measurements of High-Concentrations of VX Standards Through Butyl Gloves

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Abstract

A research study was conducted to investigate the potential for high concentrations of VX nerve agent in solvent to breach the butyl rubber protective gloves used in laboratories. There was a safety concern that the solvent could help drive the VX through the gloves. The study incorporated gloves from multiple manufacturers challenged with VX in several common laboratory solvents, covering a range of solvent properties. The ECBC-designed test method is currently undergoing a formal transition to the testing and evaluation community as an official method for programs of record, under the auspices of the Deputy Under Secretary of the Army for Test and Evaluation (DUSA-TE).

Introduction and Goals

- Safety study conducted to investigate the potential for solvents to promote permeation of VX through protective gloves.
- The permeation of various neat contaminants has been studied, and standards of protection have been established for military and domestic uses.
- The impact of solvents working as a vehicle is a research topic that has not been deeply explored.
- Goals were to explore the permeation of VX at the concentration level of 1 mg/mL.
- Three solvents were chosen to investigate a wide range of solvent properties.

Materials

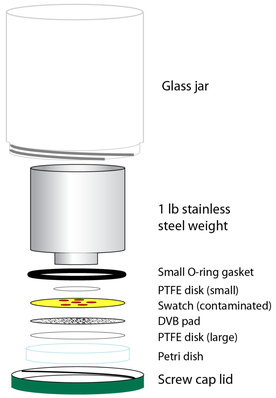
- 7 mil butyl gloves, manufactured IAW MIL-DTL-43976D.
  - Honeywell Safety Products [previously North Butyl Rubber]
  - Guardian Manufacturing
- 10 mil medium-soft (40 A) durometer natural latex, positive control material.

Solvent	Category	Comment	Used for these Experiments
Isopropyl alcohol (IPA)	Polar-protic alcohol	Most common solvent for VX standard preparations. The highest priority solvent candidate.	Yes
Acetonitrile (ACN)	Polar-aprotic	Common solvent for standard preparation. Used as mobile phase in LC analysis.	
$MeCl_2$	Non-polar, halogenated	Used by some groups for sample extraction. Less commonly used now as compared with previous experiments, as other solvent choices are more compatible with LC analytical methods. Is the only halogenated solvent candidate.	
Acetone	Polar-aprotic	Common solvent for standard preparation but used less frequently than ACN.	No
Hexanes	Non-polar	No longer used as a common solvent for standard preparation. Has some solubility challenges at higher concentrations.	
MeOH	Polar-protic alcohol	Used by some groups for sample extraction. Not typically used for primary standard preparation because of evaporation complications. IPA was a higher priority alcohol because of initial testing.	

Methodology

The low-volatility agent permeation (LVAP) fixture and method were used in this test to better approximate the contact scenario in a laboratory. The LVAP was used to apply pressure to a contaminated swatch to ensure good contact between the swatch and a contact sampler pad underneath, as shown.

- The swatch was contaminated with six 1 µL drops and photographed.
- Swatch was covered with 28 mm diameter PTFE disk and an O-ring gasket.
- Vapor control samples had an additional sheet of aluminum foil between the swatch and divinylbenzene (DVB).
- The weight was applied, covered with an inverted jar, and placed in an incubator.
- After the timed contact period, the cell was taken out of the incubator and the weight removed.
- The cell was photographed again and disposable forceps were used to remove the DVB pad for a 30 min extraction in acetone.
- Aliquots were then taken for LC-MSMS analysis.



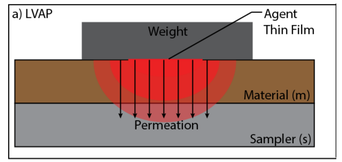
US Government Patent Pending

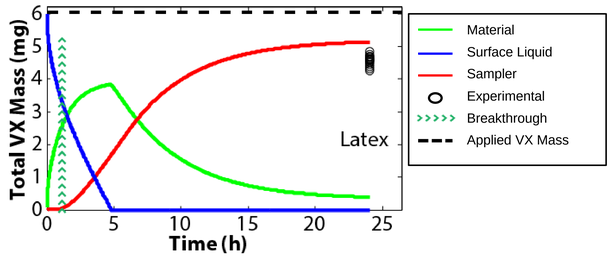
Method Validation and Physics-based Model

The LVAP method is undergoing a formal transition to the test and evaluation community under the auspices of the Deputy Under Secretary of the Army Test and Evaluation (DUSA-TE). The method has recently completed a verification and validation (V&V), demonstrating the variability in the results. For the V&V tests, neat VX was used on standard reference materials, including the same latex used as a positive control for the solvent glove study.

The test method performance was characterized through calculation of the intermediate-precision standard deviation (IPSD) via a single-laboratory study at ECBC, following ISO 5725-3 (1994). The 24 h IPSD for VX on latex was 8.2%, representing the expected variability that the method would have within a single laboratory.

As part of the V&V study, a physics-based model was developed to predict neat agent permeation through the test materials. This was based on a Fickian diffusion model with the diffusivity and solubility of VX in the latex material estimated by correlation with published values. The model was successful in predicting the measured permeation for VX through latex at the 24 h and 48 h time points, prior to the experiments being conducted. An example of the output from the model is shown.





Controls

- Analytical permeation testing was conducted under ISO 17025 quality controls.
- Multiple quality control steps were used, including: stock concentration analysis, verification of deposited mass, logging of environmental conditions, positive-control samples, negative-control samples, pre- and post- sample photographs, and analytical quality control.

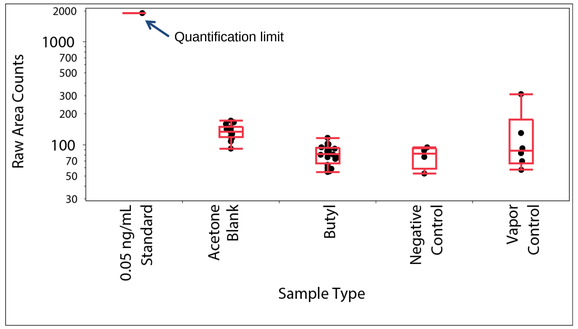
Results

- None of the butyl glove samples tested had measureable permeation.
- All positive control samples had measureable permeation.
- None of the negative control samples or vapor control samples had permeation levels above the quantification limit.

Solvent	Manufacturer	*n*	Average (ng)
$MeCl_2$	Honeywell	4	BQL (<1 ng)
	Guardian	4	BQL
ACN	Honeywell	4	BQL
	Guardian	4	BQL
IPA	Honeywell	4	BQL
	Guardian	4	BQL

Discussion

- All quality-control criteria were satisfied, providing additional confidence.
- The plot shows the raw area counts vs. sample type.
  - The analytical solvent blanks, the butyl glove samples, the negative control samples, and the vapor control samples were all approximately 1 order-of-magnitude below the lowest analytical standard.
  - Unable to demonstrate a statistical difference between these groups.



Conclusions

For the given test scenario of 4 h and 6 µL of 1 mg/mL of solution in the specific solvents, the gloves seemed appropriate for providing protection to laboratory operators. No breakthrough was measured. It must be stressed that all workers should change their gloves if they suspect the gloves have become contaminated.

The LVAP method is appropriate for a contact scenario and the physics-based model was successful in predicting the permeation of VX through a standard material.

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