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Physics-based agent to simulant correlations for vapor phase mass transport

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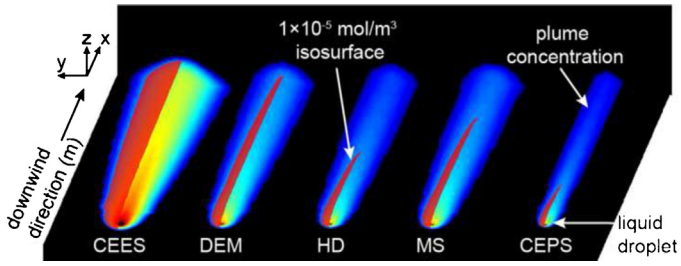
HIGHLIGHTS

- Determination of agent and simulant transport parameters.
- Vapor phase transport in diffusion and advection dominant conditions simulated.
- Simulant-to-agent correlation and corresponding validity criteria.
- Guidelines provided for chemical warfare agent simulant experimental design.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical warfare agent simulants are often used as an agent surrogate to perform environmental testing, mitigating exposure hazards. This work specifically addresses the assessment of downwind agent vapor concentration resulting from an evaporating simulant droplet. A previously developed methodology was used to estimate the mass diffusivities of the chemical warfare agent simulants methyl salicylate, 2-chloroethyl ethyl sulfide, di-ethyl malonate, and chloroethyl phenyl sulfide. Along with the diffusivity of the chemical warfare agent bis(2-chloroethyl) sulfide, the simulant diffusivities were used in an advection-diffusion model to predict the vapor concentrations downwind from an evaporating droplet of each chemical at various wind velocities and temperatures. The results demonstrate that the simulant-to-agent concentration ratio and the corresponding vapor pressure ratio are equivalent under certain conditions. Specifically, the relationship is valid within ranges of measurement locations relative to the evaporating droplet and observation times. The valid ranges depend on the relative transport properties of the agent and simulant, and whether vapor transport is diffusion or advection dominant.

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1. Introduction

1.1. Background

Chemical warfare agent (CWA) simulants are intended to mimic a given CWA as accurately as possible in a specific environment without toxicological hazards. Due to many factors, including limited access to surety facilities for CWA work, it is paramount that accurate replicates of CWAs be used to increase the scope, depth, and applicability of research directed at protection, neutralization/decontamination, and assessment of risk with respect to CWA exposures. Numerous studies have addressed the measurement of different physical and chemical properties and behavior in specific environments for established simulants of CWAs, including blistering agents like distilled mustard (HD) and lewisite (L) as well as nerve agents from VX to G series compounds [1]. Historically,

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CWA simulants have been selected based on similarity of key physical–chemical properties, particularly macroscopic quantities such as molecular weight and size, density, viscosity, solubility, and thermodynamic quantities associated with changes in physical state. Alongside chemical intuition, database mining through cheminformatics has been employed to confirm choices of simulants and generate new candidate surrogates [2].

The spectrum of agent related phenomena to be considered and then simulated in different environments includes mass transport, hydrolysis, photolysis, and biodegradation processes. Additionally, depending on the process or environment to be studied, simulants also serve as accurate representations of their CWA counterparts for a specific property or behavior. Consequently, work has been directed at evaluating specific physical and chemical properties of agent surrogates and determining which simulants best match these agent properties. As an example, the phenolic functionality of the HD simulant methyl salicylate (MS) has been shown to react stoichiometrically with hypochlorite-containing neutralization solutions and serve as an effective reactivity simulant for decontamination processes in porous fabrics [3]. Multiple simulants for organophosphorus compounds used in traditional nerve agents were studied in aqueous systems to show varying redox chemistry that would make certain simulants be better indicators for development of pathways for detection, decontamination, and destruction of CWAs in aqueous solutions [4]. Lastly, reactivity of simulants for both VX and HD were studied in ionic solutions as an alternative to organic solvents to promote rapid oxidation, alcoholysis, and hydrolysis [5].

In addition, it is important to determine how a simulant can be used to approximate transport of that agent through a specific environment. To this end, the transport of simulants has been investigated in different media of varying porosity and physical state, from common building construction materials to personal protective equipment, with measurements of breakthrough time, sorption/uptake, and permeability [6–9]. The determination of agent concentration profiles or gradients facilitates the prediction of exposure to potential toxicological threats and the development of decontamination and neutralization techniques.

In the limit of using simulants in place of agent, the challenge is to determine what observables are accurate predictors of actual agent mass transport in a particular environment. For the specific treatment of mass transport of an agent like HD due to evaporation or volatilization from liquid in air at atmospheric pressure, it is intuitive to consider simulants with similar vapor pressure, P_{vap}, and Henry's law constant, K_H (HD $P_{vap} = 0.11$ Torr, $K_H = 9.8 \times 10^{-3}$ at 25 °C) [1]. However, to accurately determine the transport of HD and resulting distribution of agent in air, a direct comparison between HD and its simulants is necessary. This study involves the time resolved measurement via dynamic contact angle (DCA) of sessile droplets of common HD simulants (methyl salicylate (MS), 2-chloroethyl ethyl sulfide (CEES), di-ethyl malonate (DEM), and chloroethyl phenyl sulfide (CEPS)) on impermeable substrates to obtain their mass diffusivity in air using a previously described physics-based model with an inverse parameter estimation algorithm [10]. The transport properties are then employed in an advection-diffusion model to compare the vapor concentrations from an evaporating sessile droplet of each of the simulants and HD under various atmospheric conditions, from which a simulant-to-agent correlation is developed.

2. Experimental procedures, materials, and equipment

The experimental setup and procedures have been described previously [10]. A 1 μL droplet of agent was dispensed onto an impermeable material placed in a DCA analyzer (FTA 1000C, First Ten Ångstroms, Portsmouth, VA) environmental chamber with a stagnant air environment at temperatures between 20 and 40 °C. The substrate materials had low surface energy, resulting in a sessile droplet with minimal spreading. Images of the droplet were recorded until the droplet evaporated. Image analysis was performed to determine the droplet volume evolution for the duration of the experiment.

The chemicals used in this study were Chemical Agent Standard Analytical Reference Material (CASARM, 98.0% purity) grade bis(2-chloroethyl)sulfide (distilled mustard, or HD), Reagent Plus, ≥99%-grade methyl salicylate (MS, Sigma–Aldrich), 98%-grade 2-chloroethyl ethyl sulfide (CEES, Sigma–Aldrich), 99%-grade diethyl malonate (DEM, Sigma–Aldrich), and 98%-grade 2-chloroethyl phenyl sulfide (CEPS, Sigma–Aldrich). Purity information was obtained from either NMR or GC–MS analyses and maintained on file. Chemical agents and other select contaminants are used only in properly certified surety facilities, capable of handling such chemicals safely. The personnel handling the chemical agents for this study were fully trained and certified for such operations.

3. Mathematical models and methods of analysis

3.1. Transport parameter estimation

The mathematical system of interest and the parameter estimation procedure has been described previously [10] for the determination of the temperature-dependent diffusivity of HD in air. The mathematical model is comprised of a 2D axi-symmetric geometry that couples agent distribution within the air and a moving boundary condition that describes the droplet shape evolution over time. The parameter estimation code (COMSOL v. 3.4) predicts the drop volume evolution for a guessed value of the diffusivity of the compound in air, D_{air}, which is iteratively updated using a gradient descent algorithm until the mean-square error of the predicted droplet volume evolution is minimized compared to the experimentally measured volume evolution.

3.2. Comparison of agent and simulant vapor phase mass transport

The effective use of a simulant to assess the vapor concentration of agent requires an agent-to-simulant concentration relationship. Here, attention was limited to the case of a droplet evaporating on an impermeable substrate with the concentration measured downwind. The local vapor concentration depends on the environmental conditions (i.e., air velocity and temperature), and the time elapsed after droplet deposition. The relationship between the measured simulant and agent concentrations under identical conditions depends on the relative evaporation rates of the liquids and subsequent transport of the vapor.

The agent-to-simulant vapor concentration relationship was explored over a range of temperatures and velocities at different measurement locations. A three dimensional advection-diffusion finite element model (COMSOL v. 4.3) for an evaporating droplet (initial volume 1 μL, initial contact angle 40°) on an impermeable substrate was constructed with identical initial droplet conditions for all cases, ensuring that the effects of transport properties were isolated for the purposes of this analysis. However, it is recognized that the initial droplet shape can vary depending on the particular chemical. The impermeable substrate was placed in the center of a region of interest (2.2 m per side). Time evolution of the vapor concentration was monitored at three measurement positions (MP) downwind from the evaporating droplet (MP1 and MP2 were 0.1 and 1 m respectively from the trailing edge of the substrate, and MP3 was 0.1 m crosswind from MP2). Symmetry was utilized to