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Comparison of latex body paint with wetted gauze wipes for sampling the chemical warfare agents VX and sulfur mustard from common indoor surfaces

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ABSTRACT

Comparison of solvent-wetted gauze with body paint, a peelable surface sampling media, for the sampling of the chemical warfare agents VX and sulfur mustard from nine surfaces was performed. The nine surfaces sampled are those typical of interior public venues and include smooth, rough, porous, and non-porous surfaces. Overall, solvent-wetted gauze (wipes) performed better for the recovery of VX from non-porous surfaces while body paint (BP) performed better for the porous surfaces. The average percent VX recoveries using wipes and BP, respectively, are: finished wood flooring, 86.2%, 71.4%; escalator handrail, 47.3%, 26.7%; stainless steel, 80.5%, 56.1%; glazed ceramic tile, 81.8%, 44.9%; ceiling tile, 1.77%, 13.1%; painted drywall 7.83%, 21.1%; smooth cement, 0.64%, 10.3%; upholstery fabric, 24.6%, 23.1%; unfinished wood flooring, 9.37%, 13.1%. Solvent-wetted gauze performed better for the recovery of sulfur mustard from three of the relatively non-porous surfaces while body paint performed better for the more porous surfaces. The average percent sulfur mustard recoveries using wipes and BP, respectively, are: finished wood flooring, 30.2%, 2.97%; escalator handrail, 4.40%, 4.09%; stainless steel, 21.2%, 3.30%; glazed ceramic tile, 49.7%, 16.7%; ceiling tile, 0.33%, 11.1%; painted drywall 2.05%, 10.6%; smooth cement, 1.20%, 35.2%; upholstery fabric, 7.63%, 6.03%; unfinished wood flooring, 0.90%, 1.74%.

1. Introduction

The threat posed to people and the environment by intentional or unintentional chemical contamination of public venues is one that cannot be ignored. Following an event in which suspected toxic chemicals such as chemical warfare agents or pesticides have contaminated an area, samples will be collected to identify the nature of the poison and the extent of the contamination [1]. If such an event occurs in an enclosed environment (e.g., subway station, airport terminal, school), contamination will occur on the building interior surfaces and furnishings. These surfaces then become potential sample sources. In the case of building material surfaces, it is not always possible or desirable to remove and transport all or a portion of the surface to a laboratory. In these situations, a sampling technique that allows for sampling at the scene and is nondestructive to the surface is required. Here, we compare the use of a spread-and-peel surface sampling technique using body paint with that of a standard wipe sampling technique.

2. Contaminants

Two toxic chemicals that potentially could be used by terrorists are the nerve agent VX and the vesicant sulfur mustard (Fig. 1). VX [*S*-((2-diisopropylamino)ethyl) *O*-ethyl methylphosphonothioate] and sulfur mustard [bis(2-chloroethyl) sulfide] are both chemical warfare agents that are primarily skin contact hazards though both may be inhaled if aerosolized. VX is a potent cholinesterase inhibitor that is meant to kill (LD_{50}: 0.315 mg/kg administered onto human skin) [2]. In addition to being produced and stored by the U.S. military, VX was produced and used by Aum Shinrikyo in assassination attempts [3]. Sulfur mustard is a vesicant that is primarily meant to cause injury (LD_{50} 100 mg/kg administered onto human skin) though it may cause death if the injuries are great. As little as 5–10 $\mu g/cm^2$ of sulfur mustard on human skin can cause moderate injury (blisters) though hours may pass before any signs of injury occur [4]. Sulfur mustard was produced and used in World War I. It is estimated that the use of sulfur mustard caused more than 148,000 British casualties of which 2.6% resulted in death and 27,711

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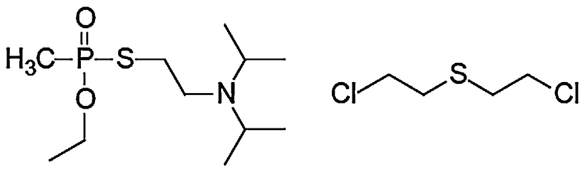

Fig. 1. Structures of VX and sulfur mustard.

casualties to soldiers of the American Expeditionary Force with 2.16% resulting in death [5,6].

For any sampling and analysis method, it is important that the methods possess suitable sensitivity and selectivity. While it is not possible to predict the amount of toxic material/agent resulting from a terrorist attack, the amount of the nerve agent sarin on the surfaces in the Tokyo subway car at the time of the 1995 attack was estimated to be 31 to 98 $\mu g/cm^2$ based on the amount released and assuming uniform distribution and deposition [7]. For the work reported here, the estimated amounts of contaminant, agent area density, is based on the median lethal dose of nerve agent VX and the amount of the vesicant sulfur mustard required to produce a blister. If VX was dispersed over an area in an amount sufficient to cause death to individuals within that area, then it is assumed that the surfaces in that area also would receive the same dose and be available for sampling. The amount of VX applied to surfaces in this study, 4.85 $\mu g/cm^2$, is within the range necessary to deliver a dose equal to the LD_{50} for average American adults if the VX is distributed uniformly over the entire body and assuming clothing offers some protection.

In calculating the hypothetical VX area density, it is assumed that the only exposed skin of an average adult American is that presented by the head and hands. If clothing allows 7.5 to 24% of the agent to penetrate through to the skin, as described for pesticide workers wearing a cotton shirt, trousers, and boots or gym shoes, then a VX area density of 4.1 to 7.4 $\mu g/cm^2$ is required to deliver one LD_{50} (0.315 mg/kg) for average American adults[1] [8,9]. Another study predicted the penetration through a single layer of clothing to be between 0.2% and 14.1% when the external loading was 5 to 10 $\mu g/cm^2$ [10]. Under these conditions, the required surface area density for VX to deliver an LD_{50} dose ranges from 5.46 to 11.5 $\mu g/cm^2$. If clothing and hair offer no protection to average American adult females and males, then an area density for VX of only 1.28 $\mu g/cm^2$ to 1.36 $\mu g/cm^2$, respectively, is required to deliver the 0.315 mg/kg LD_{50} [2,8]. These surface density values are much less than the 160 to 320 $\mu g/cm^2$ of VX required to deliver the full median lethal dose to adult Americans from contact by one hand (palm only or palm and fingers) with an escalator handrail [11]. In this situation, it is likely that an even greater amount of VX would be needed because other factors may limit the transfer efficiency from surface to hand [12–14].

It has been reported that only 20% of sulfur mustard in contact with human skin is likely to penetrate, the remainder evaporating, and that 12% of that which does penetrate becomes bound and causes cellular damage [4]. Further, it is estimated that as little as 0.1 to 1.0 $\mu g/cm^2$ of sulfur mustard bound within the skin is required to cause a mild, visually observable injury. The amount of sulfur mustard applied to the surfaces in the tests reported here (5.22 $\mu g/cm^2$) is that which may cause injury as it would result in an amount near the low end of the range required to cause injury (0.13 $\mu g/cm^2$ bound within the skin). If no evaporation from the skin occurs, such as when a hand is placed directly onto the surface, then the amount of sulfur mustard bound within the skin would be near the middle of the range (0.63 $\mu g/cm^2$). Total body surface area contamination by sulfur mustard at 5.22 $\mu g/cm^2$ with no protection by clothing or hair would result in a total dose of 97 mg or 1.3 mg/kg for the average adult American female and 108 mg (1.2 mg/kg) for the average adult American male. These values are significantly less than the reported LD_{50} for humans when sulfur mustard is administered to the skin (LD_{50} 100 mg/kg).[2]

3. Wipes and peelable media sampling

Wipe sampling has become the most often used method for collecting contaminants from surfaces for subsequent analysis and different media have been used for wipe sampling [15,16]. It has been noted that sampling from different types of surfaces, smooth or textured, requires good contact [17].

Wipe samples have been used to collect pesticide residues and chemical warfare agent-related chemicals from surfaces to assess the extent of contamination [16,18,19]. Because of the problems associated with insufficient contact and contaminant penetration into porous surfaces, wipe sampling has generally been considered useful only for non-porous surfaces. Wipe sampling, according to ASTM D6661-10, is recommended for use for hard non-porous materials such as metal, glass, painted or sealed surfaces, tile, pipes and tanks in and around buildings but not for rough or porous surfaces such as upholstery, carpeting, brick, concrete, ceiling tiles, and bare wood [18].

In an attempt to overcome the problem of sampling porous or rough surfaces with wipes, the use of a peelable spread-on or spray-on sampling media was tested and demonstrated for pesticides and chemicals related to chemical warfare agents (precursors and degradation products) for a variety of surfaces including metal, upholstery, flooring, plastic, drywall and glass [7,20,21]. The sampling media were rubber cement, body paint, Vinnol E15/45, Floorpeel 4000, and UCAR 451. In addition to being commercially available, these media offer prolonged contact with the surface, may be used on non-horizontal surfaces, and may be left in place for extended periods, if desired. Simple solvent extraction of the dried sampling medium provides a solution which then can be analyzed directly. These characteristics make this sampling technique potentially applicable to sampling numerous large and small surface areas. This is important because of the potential requirement to collect and analyze a large number of samples after an event involving contamination of a building interior.

Rubber cement and the body paint are based on natural rubber latex. Rubber cement contains heptane, and the body paint is water based. Vinnol E 15/45 is a vinyl chloride-vinyl acetate copolymer [22]. Suitable solvents for Vinnol E 15/45 are acetone, 2-butanone and ethyl acetate. Floorpeel 4000 is a water-based vinyl acetate/acrylic copolymer and is designed to protect non-porous surfaces such as painted or sealed concrete, sealed wood floors, metals, glass, and plastic [23]. UCAR Latex 451 is a styrene-acrylic copolymer [24]. Unlike the Vinnol E15/45, Floorpeel 4000, and UCAR 451, body paint and rubber cement do not peel the paint from drywall. Rubber cement and Vinnol E15/45 contain flammable solvents, and this may be a concern, either in transporting them or using them in some environments. There is a concern that the solvents could damage some finished surfaces [17,19]. These qualities, along with the data showing body paint provided better recoveries from surfaces than rubber cement [7], led to the selection of body paint for sampling of the chemical warfare agents.

[1] Calculations assume an average skin surface area of the head and hands to be 0.203 m^2 and total body surface area (BSA) of 1.85 m^2 with a weight of 75.4 kg for adult American females (age $\geq$ 20 yr) and skin surface area of head and hands to be 0.243 m^2 with total BSA of 2.06 m^2 with a weight of 88.7 kg for adult American males (age $\geq$ 20 yr).