Assessing Chemical Agent Decontamination Efficacy of a Nanostructured Fabric using Headspace and Split/Splitless Injection Gas Chromatography and Mass Spectrometry (GC-MS)

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ABSTRACT

Warfighter protection is of substantial concern for the military. We developed a multifunctional and nanostructured decontamination material with the capabilities to adsorb and photocatalytically degrade chemical agents. We envision our material being incorporated into personal protective equipment and uniforms. The decontamination material is photo-active and upon exposure to ultraviolet (UV) light readily degrades the target simulant into a simple non-lethal chemical compound. Adsorption of the chemical agent simulant, reactivity, degradation, and formation of resultant degradation products were all monitored by Gas Chromatography and Mass Spectrometry (GC/MS). We developed a reproducible method to monitor the efficacy of the decontamination material with GC/MS using a split/splitless liquid injection technique. This technique is superior to direct injection of headspace vapors which does not allow determination of whether analyte vapors are sufficiently and homogenously partitioned into the headspace. Liquid injections allow us to assess optimal linearity of chemical simulant and response factor. This technique allows direct quantification of unknown concentration amounts based on the calibration curve of the analyte.

Keywords: GC/MS, nano-structured material, decontamination

1 INTRODUCTION

Chemical agent exposure continues to be a persistent threat to the warfighter on the battlefield. Exposure to chemical agents can result in a myriad of rapidly deteriorating health conditions, up to and including death, as soon as ten minutes post exposure.

As terrorists evolve into more organized successful groups, the probability of chemical agent exposure increases for both warfighters and first responders. With the ever increasing possibility of an exposure event, there is an urgent need for agent detection and mitigation of both biological and chemical agents. One such mitigation tactic for chemical agents that has been explored is decontamination immediately following exposure to such agents. Chemical decontamination is considered to be the conversion of toxic chemicals into harmless products either by degradation or detoxification. [1]

Few technologies exist in the area of chemical agent decontamination. Most of the decontamination methods employed are for decontamination of the environment or other surfaces. Mahato et al. reported the use of nanocrystalline zinc oxide aero-gels in the decontamination of Sarin, a well know chemical agent.[2] Sarin is hydrolyzed to form a surface bound non-toxic species on zinc oxide. Mahato et al. proposed the same principle of simulant hydrolysis with the use of nanosheets formed into nanobelts. [3] Another technique for chemical agent degradation and decontamination is through the use of Titanium Dioxide (TiO_2) nanoparticles. TiO_2 has the ability to absorb UV light and undergo photochemical oxidation to generate highly reactive hydroxyl radicals. In turn the hydroxyl radical degrades the chemical agent or simulant into a less lethal compound.[4] To the author's knowledge, no reports of decontamination of personal protective gear or other clothing with the use of TiO_2 have been made.

If clothes have been exposed to contamination, extreme care must be taken when undressing to avoid transferring chemical warfare agent to the skin. There may be particular problems when caring for injured persons as their clothes may have to be cut off of them. [5] The technology we developed is for warfighter protection, as well as the first responder, as the first line of defense. We developed a multifunctional and nanostructured decontamination material using a combination of nanotechnology and photochemical agent degradation. When our multifunctional and nanostructured decontamination material is exposed to a chemical agent simulant and ultraviolet (UV) light, the photocatalytic degradation of the chemical simulant occurs

due to the active nanostructured material, titanium dioxide (TiO_2). In this study, we developed a test method to monitor the efficacy of the decontamination material by Gas Chromatography and Mass Spectrometry (GC/MS).

EXPERIMENTAL

2.1. Materials

Diisopropyl methyl phosphonate (DIMP, Alfa Aesar), 2-chloroethyl-ethyl sulfide (CEES, Sigma-Aldrich). Ethyl Acetate (EA, Sigma-Aldrich), Chloroform (CH_2Cl_2, Honeywell/ B&J). All the materials were used as-received.

2.2 Methods

2.2.1 Preparation of calibration standards

A calibration curve was performed to determine linearity of a series of DIMP samples in EA, and CEES in CH_2Cl_2. The concentrations chosen after determining the limit of detection for each simulant using GC/MS were 0.05, 0.1, 0.25, 0.5, and 1.0 mg/mL. These amounts were also prepared to cover the expected concentration range for DIMP and CEES samples after exposure to our decontamination material. Headspace samples were injected as 10µL samples using a gas tight syringe. Liquid samples were injected as 1µL samples also using a gas tight syringe.

2.2.2 Photocatalytic degradation of chemical agent simulants

The decontamination material was placed in a 20 mL headspace vial and a known amount of the simulant (DIMP or CEES) was added. The vapors were allowed to form in the headspace vial overnight. Vials were then exposed to a UV light source, with a wavelength of 395nm. Headspace gases were removed from each vial and injected in the Gas Chromatograph.

Alternatively, 5mL of either CH_2Cl_2 or EA was added to each vial containing the simulant vapors and simulant vapors with decontamination material to extract the simulant and its degradation products. Liquid samples were filtered to remove any particulates prior to injection. Figure 1 shows the schematic of the test method developed to monitor the efficacy of the decontamination material by GC/MS.

The photocatalytic degradation of DIMP was performed by exposing the headspace vial to UV light for one hour. On the other hand, the photocatalytic degradation of CEES was performed as a time lapse study. Vials were exposed to UV light for 0, 1, and 2 hours.
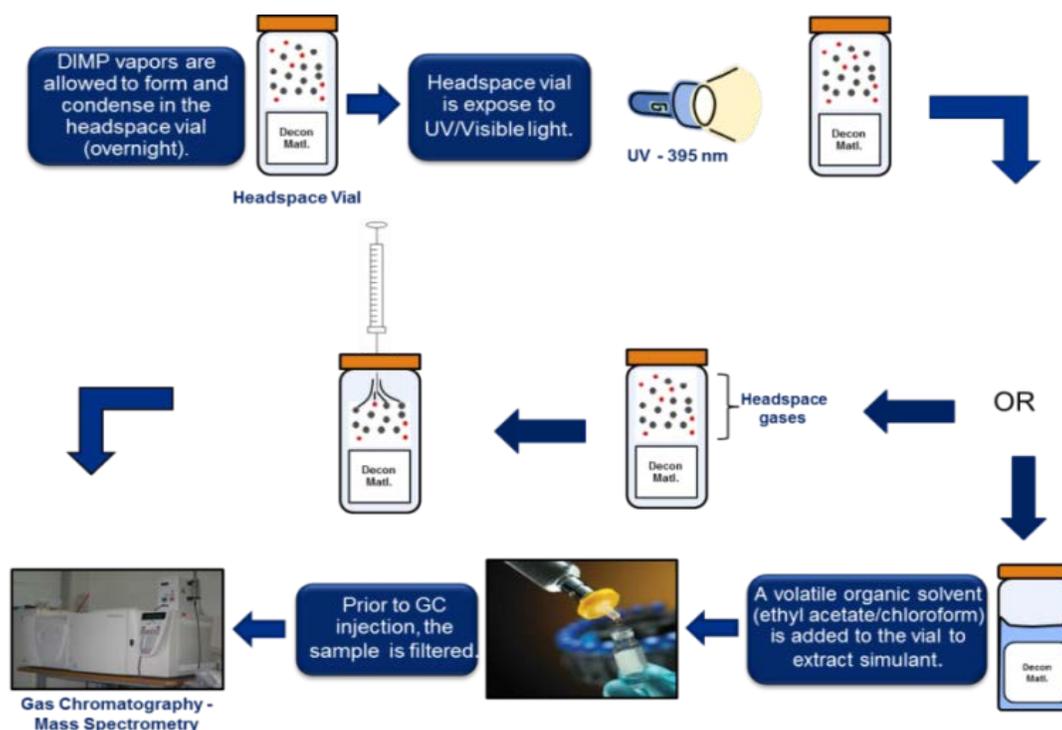
Figure 1: Schematic of test method developed to monitor the efficacy of the decontamination material by GC/MS.

2.2.3 Gas Chromatography/Mass Spectrometry

Samples were tested using a Shimadzu 17A GC with a tandem 5050 Quadrupole Mass Spectral Detector. The mode used was Electron Impact with a full scan completed from 40amu-500amu. The temperature of the source was set to 240°C. The injection port was set up for a split/splitless injection at a temperature of 280°C. Separation was performed on a 30m x 0.25mm x 1.00µm thick Agilent DB5-MS general screening capillary column. The split was set at 36:1. The oven temperature program was 60°C isothermal for a 2 min hold, then ramped from 60ºC to 250ºC at 19.7ºC/min with a 250ºC hold for 3.50 min. The carrier gas was helium controlled at a flow rate of 1.0 mL/min.

3   RESULTS AND DISCUSSION

3.1 Calibration Curves

Calibration curves established with CEES in CH_2Cl_2 and DIMP in EA proved to be linear with a coefficient of determination, for the best fitted line, to be 0.999 for CEES (Figure 2) and 0.990 for DIMP (data not shown). The optimal technique for assessing the linearity is with liquid injections of the calibration samples. Headspace injections were performed for calibration standards and samples. Results of our headspace injections were not reliable or reproducible. Two limitations of the headspace technique are: consistently sampling in the same location for each vial; and homogeneous partitioning of the analyte in the headspace vapors. Results of the liquid injections were used to assess the efficacy of the decontamination material.
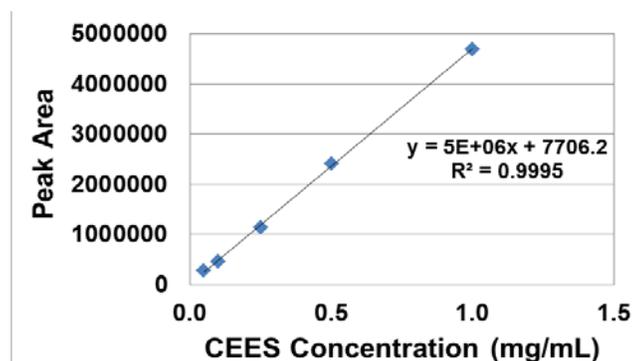
Figure 2: CEES calibration curve showing linearity and best fitted line.

3.2 Photocatalytic degradation of DIMP

Table 1 shows DIMP concentration for DIMP simulant, as well as DIMP simulant with decontamination material both unexposed and exposed to UV light. The determination of the unknown DIMP concentration from the vial with our decontamination material was calculated using the calibration curve and the DIMP peak area response from that sample. The results showed no degradation of DIMP by UV light (Table 1). Comparison between the vial of simulant without UV exposure, and the vial of simulant with decontamination material that was exposed to UV light shows a 52% reduction in concentration for the latter. This result showed and confirmed the photocatalytic degradation of DIMP using the decontamination material containing TiO_2. DIMP degradation products, isopropyl alcohol (IPA) and methyl phosphoric acid were not quantifiable by GC/MS in this study. IPA was not formed in a sufficient quantity to be observed, and methyl phosphoric acid is not volatile, the first step in being analyzed by GC/MS. For DIMP, this limits the capability of the GC/MS technique to measure the decontamination material's effectiveness by the appearance of any degradation product.

Table 1
DIMP concentration for DIMP simulant unexposed and exposed as well as DIMP simulant/decontamination material unexposed and exposed to UV light for 1 hour.

Sample	DIMP Concentration (mg/mL)
Simulant –UV	0.10
Simulant +UV	0.12
Decon. Matl. –UV	0.12
Decon. Matl. +UV	0.05

3.3 Photocatalytic Degradation of CEES

In Table 2 the CEES concentrations for CEES simulant alone as well as CEES simulant with decontamination material, both unexposed and exposed to UV light are reported. Similar to DIMP, CEES does not degrade by UV light. CEES alone is not photo-active and will not self degrade under UV light. A reduction of 90%, in comparison to the vial containing simulant with out UV exposure, of the initial concentration of CEES was observed when CEES was exposed to UV light in combination with the decontamination material. Figure 3 shows the CEES and CEES degradation product chomatograms as a function of time. The time lapse study showed the appearance of CEES degradation products (i.e. 2-mercaptoethanol and 2-ethylthio ethanol) after 1 hour of UV exposure as well as the faith of the simulant. The volatility of the CEES degradation products enable monitoring using GC/MS.

Table 2

CEES concentration for CEES simulant alone as well as CEES simulant with decontamination material both unexposed and exposed to UV light for 1 hour.

Sample	CEES Concentration (mg/mL)
Simulant –UV	0.29
Simulant +UV	0.24
Decon. Matl. –UV	0.23
Decon. Matl. +UV	0.03
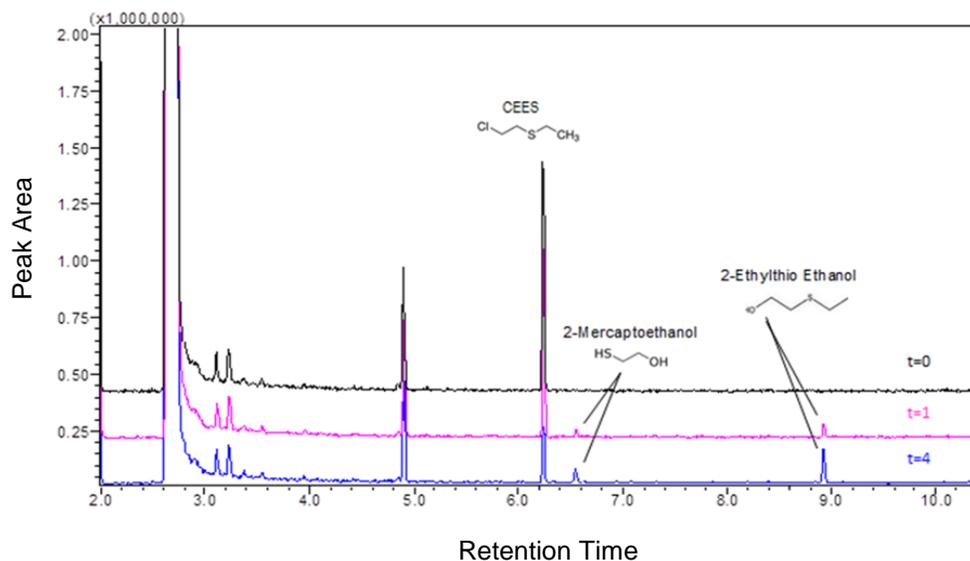
4 CONCLUSION

In this study, we developed a method to monitor the efficacy of the decontamination material with GC/MS using a split/splitless liquid injection technique. This technique is superior to direct injection of headspace vapors because of the inability of the latter to determine if analyte vapors are sufficiently and homogenously partitioned into the headspace. Liquid injections allow us to assess optimal linearity of chemical simulant and response factor. This technique allows direct quantification of unknown concentration amounts based on the calibration curve of the analyte.

Additionally, the multifunctional and nanostructured decontamination material has the capability to adsorb and photocatalytically degrade chemical agent simulants due to the active nanostructured material, TiO_2. In this study, the photocatalytic degradation of two simulants, CEES and DIMP, and the efficacy of our decontamination material were assessed by GC/MS. The volatile nature of the simulants and its degradation products, combined with rapid

GC/MS analysis allows us to determine that our decontamination material is able to significantly reduce simulant concentration following UV exposure.

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