Decontamination of a Mustard Gas Simulant (CEES) by Metal Oxide Powders

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KEYWORDS: metal oxide, 2-chloroethyl ethyl sulfide (CEES), decontamination, sulfur mustard, mustard gas, chemical agent, simulant.

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Contents

Contents 2

1 Background 3

2 Experimental Procedure 3

2.1 Materials and Instrumentation 3

2.2 Reaction of 2-Chloroethyl ethyl sulfide (CEES) with metal oxide powder 4

2.3 Extraction of CEES and its decontamination products 4

3 Results and Discussion 4

3.1 Effectiveness of metal oxides in decontaminating CEES 4

3.2 Desorbing CEES and its products from the metal oxides 6

3.3 Improving reproducibility 8

4 Conclusions 9

5 Acknowledgments 10

6 References 11

Figures

Figure 1: Chromatogram of cocktail extract from exposure of NanoActive™ Magnesium Oxide Plus to CEES for 24h……..… 6

Figure 2: Chromatogram of solvent extract from exposure of NanoActive™ Cerium Oxide to CEES for 24 h…….…… 7

Figure 3: Chromatogram of CEES extracted with ethanol showing formation of hydrolysis product in the absence of any metal oxides. ……..… 8

Tables

Table 1: Summary of results for all metal oxides exposed to CEES. Calculations are based on relative peak areas……..……5

Table 2: Recovery of CEES and its decontamination products from various metal oxide powders. Calculations are based on peak areas of CEES and decontamination products compared to peak areas of CEES in controls. ……..7

1 Background

Army vehicles and support equipment currently employ chemical agent resistant coatings (CARC) to repel chemical and biological environmental hazards. Likewise materials used in individual soldier protective clothing are designed to repel and/or absorb agents to protect from these threats. These types of materials systems presently provide passive protection, but have no inherent self-decontaminating ability. The ability for a material to decontaminate chemical agents *in situ* is highly desirable and may reduce weight and logistical footprints associated with decontamination operations.

Nanometal oxide coatings have been shown to decontaminate chemical agents and their simulants.[1-7] These findings often result from protocols that do not reflect conditions likely to be encountered in the field. This work explores the ability of several nanometal oxide powders to decontaminate 2-chloroethyl ethyl sulfide (CEES), a simulant for the blister agent sulfur mustard (HD) under ordinary atmospheric conditions.

2 Experimental Procedure

2.1 Materials and Instrumentation

NanoActive™ Aluminum Oxide Plus, Copper Oxide, Magnesium Oxide Plus, Cerium Oxide, Titanium Oxide, and Zinc Oxide, as well as FAST-ACT, were from NanoScale Materials, Inc. AlfaAesar titanium (IV) oxide, Aldrich bulk aluminum oxide, and Aldrich nanopowder alumi-

num oxide were also tested. Triton Systems, Inc., provided a series of magnesium oxide samples that had been heated at different conditions (described later). All solvents except for ethanol were DriSolv from EMD Chemicals, Inc. 2-Chloroethyl ethyl sulfide was from Aldrich.

Samples were analyzed using a HP5890 Series II gas chromatograph with a HP5972 Mass Selective Detector. The injector and detector temperatures were 250°C and 280°C, respectively. The column was a Phenomenex ZB-50 (30m x 0.25mm ID x 0.25µm FT). The column was maintained at 30°C for 3 min, then increased to 250°C at 10°C/min. The solvent delay was 3 min when tetrahydrofuran was the internal standard and 3.9 min when toluene was the internal standard.

2.2 Reaction of 2-Chloroethyl ethyl sulfide (CEES) with metal oxide powder

Approximately 0.025g CEES were added to 0.1g metal oxide powder. All samples were vortexed briefly to promote contact between the CEES and the powder. Samples then set at room temperature for 24 h. No efforts were made to control ambient light or humidity. Aliquots of CEES in an empty vial served as controls.

2.3 Extraction of CEES and its decontamination products

After 24 h, 3 mL of extraction solvent, usually methylene chloride, was added. Other solvents tried were ethanol, tetrahydrofuran, and a cocktail of methylene chloride/ethanol/tetrahydrofuran (1:1:1). Tetrahydrofuran (0.1% by volume) was added to methylene chloride and ethanol as an internal standard. For tetrahydrofuran and the solvent cocktail, the internal standard was 0.1% by volume toluene.

Samples were vortexed briefly after the solvent was added. Samples were set in the hood for two hours or shaken for two hours on a wrist-action shaker. All samples were filtered through Acrodisc 0.45µm PTFE syringe filters prior to GC/MS analysis.

3 Results and Discussion

3.1 Effectiveness of metal oxides in decontaminating CEES

Various metal oxide powders were reacted with CEES. Only the NanoActive™ Aluminum Oxide Plus and Magnesium Oxide Plus showed appreciable decontamination of CEES after 24 h. The same metal oxides from other manufacturers did not produce similar levels of decon-

tamination, perhaps due to the preparation of these materials.[1,2] However, even the highest decontamination observed was below what would be needed to effectively decontaminate a vehicle exposed to a chemical agent in the field. Results for all metal oxides tested are summarized in Table 1.

Metal Oxide	%CEES	% elimination product	% hydrolysis	% enchained product
NanoActive™ MgO[a]	87 ± 2.9[e]	5.3 ± 0.72	8 ± 2.7	0.3 ± 0.13
NanoActive™ MgO[b]	87 ± 1.5	6.1 ± 0.10	6 ± 1.5	0.4 ± 0.11
NanoActive™ Al_2O_3[a]	74 ± 31[e]	18 ± 7.3	24 ± 10	0.046 ± 0.05
NanoActive™ Al_2O_3[b]	57 ± 4.2	16 ± 1.0	26 ± 5.2	0
Adrich bulk Al_2O_3[a]	99.2 ± 0.26	0.6 ± 0.22	0.21 ± 0.036	0
Aldrich nanopowder Al_2O_3[a]	99.6 ± 0.10	0.3 ± 0.10	0	0
NanoActive™ CeO_2[a]	99.9 ± 0.19	0.1 ± 0.10	0	0.06 ± 0.081
NanoActive™ CuO[a]	99.2 ± 0.018	0.53 ± 0.042	0.24 ± 0.015	0.030 ± 0.0088
NanoActive™ ZnO[a]	99.0 ± 0.22	0.62 ± 0.086	0.3 ± 0.13	0
NanoActive™ TiO_2[a]	98 ± 1.7	0	2 ± 1.7	0
AlfaAesar TiO_2[a]	100 ± 0	0	0	0
NR3-121 MgO[c]	98.5 ± 0.22	1.4 ± 1.6	0.15 ± 0.059	0
NR3-122 MgO[d]	98.8 ± 0.40	1.2 ± 0.40	0	0

Table 1. Summary of results for all metal oxides exposed to CEES. Calculations are based on relative peak areas. Zeros indicate that no peaks were seen. [a]Extracted in methylene chloride without shaking. [b]Extracted in methylene chloride with shaking. [c]Extracted in cocktail with shaking. This sample was prepared by heating at 80°C for 12 h by Triton Systems, Inc. [d]Extracted in cocktail with shaking. This sample was prepared by heating at 250°C for 24 h by Triton Systems, Inc. [e]Average of four trials for this substance. All other substances were tested in duplicate.

Typical decontamination routes[3] were elimination of the chlorine to yield CH_2=CH-S-CH_2CH_3 (retention time 4.8 min) or hydrolysis to produce $HOCH_2CH_2$-S-CH_2CH_3 (retention time 10.6 min). Chromatograms are shown for NanoActive™ Magnesium Oxide Plus (Figure 1) and NanoActive™ Cerium Oxide (Figure 2). A late-eluting peak at 14.9 min was also seen, consistent with previous results from this lab.[4] The proposed structure for this compound, Cl-CH_2CH_2-S-CH_2CH_2-S-CH_2CH_3, is consistent with mass spectra. However, synthesizing this compound to establish its retention time would be necessary to verify this structure.

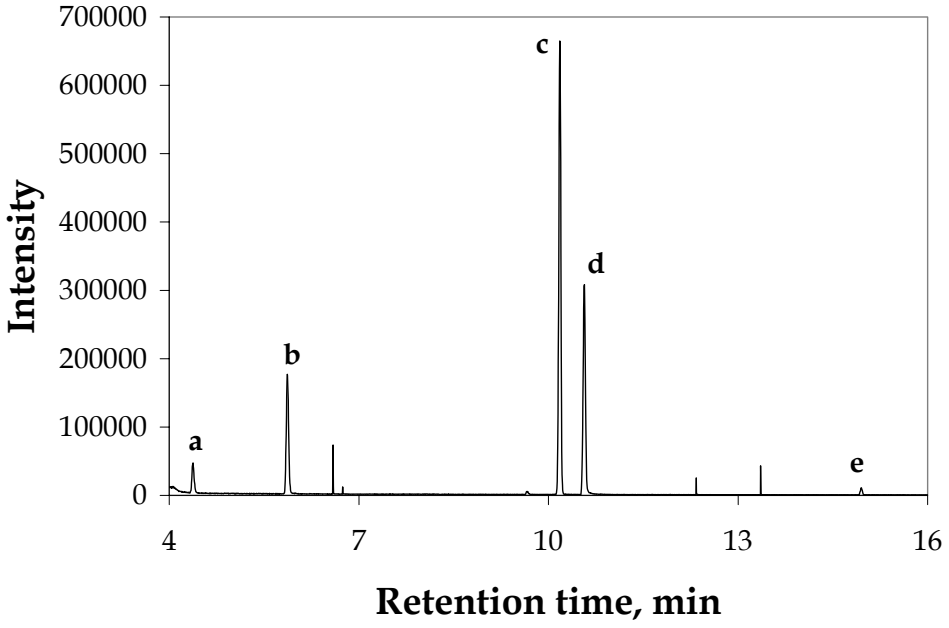

Figure 1. Chromatogram of cocktail extract from exposure of NanoActive™ Magnesium Oxide Plus to CEES for 24 h. Peak a is the elimination product, CH_2=CH-S-CH_2CH_3. Peak b is the internal standard, toluene. Peak c is CEES. Peak d is the hydrolysis product, $HOCH_2CH_2$-S-CH_2CH_3. Peak e is the enchained product, Cl-CH_2CH_2-S-CH_2CH_2-S-CH_2CH_3.

3.2 Desorbing CEES and its products from the metal oxides

Recovery of CEES and its decontamination products, as compared to control, sometimes varied widely for the same metal oxide (see Table 2). Some of this variability may be attributed to adding the CEES directly to the solid metal oxide powder. Although samples were vortexed to mix the reactants, it is unlikely that the two reactants were uniformly mixed. A solvent would facilitate contact between the reactants, and some solvents have been shown to significantly increase the rate of decontamination.[5] However, the addition of a solvent does not simulate realistic field conditions. For this reason, no solvents were added to the reaction until the extraction step.

Originally, samples were extracted without any agitation. Transferring the vials to a shaker during extraction yielded moderate improvements in recovery. Therefore, this modification was incorporated into the procedure.

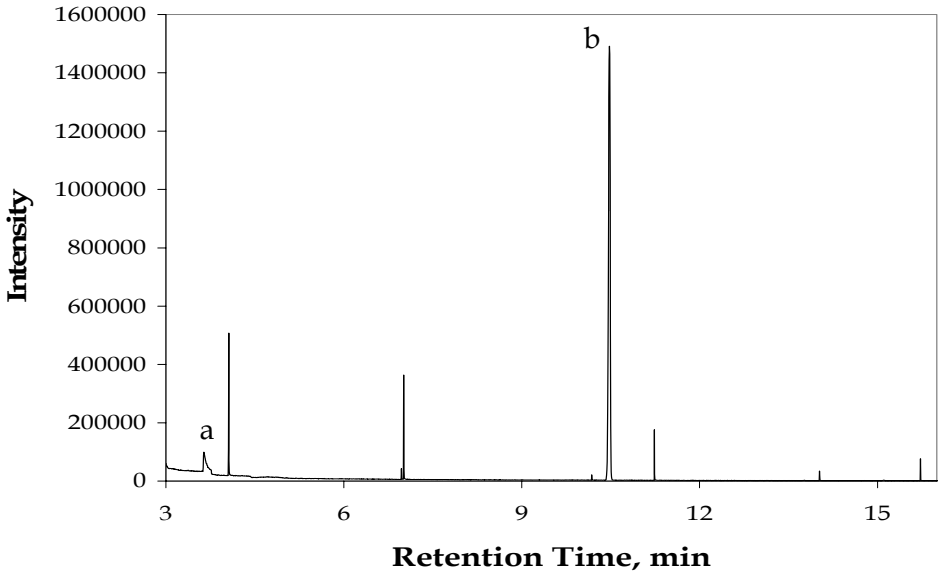

Figure 2. Chromatogram of solvent extract from exposure of NanoActive™ Cerium Oxide to CEES for 24 h. Peak a is internal standard, tetrahydrofuran. Peak b is CEES.

Metal Oxide	% recovery
NanoActive™ MgO[a]	41 ± 19[e]
NanoActive™ MgO[b]	81 ± 21
NanoActive™ Al_2O_3[a]	12 ± 6.6[e]
NanoActive™ Al_2O_3[b]	131 ± 2.6
Adrich bulk Al_2O_3[a]	84 ± 11
Aldrich nanopowder Al_2O_3[a]	96 ± 17
NanoActive™ CeO_2[a]	85 ± 26
NanoActive™ CuO[a]	74 ± 6.8
NanoActive™ ZnO[a]	99 ± 13
NanoActive™ TiO_2[a]	49 ± 49
AlfaAesar TiO_2[a]	88 ± 6.8
NR3-121 MgO[c]	101 ± 11
NR3-122 MgO[d]	101 ± 5.2

Table 2. Recovery of CEES and its decontamination products from various metal oxide powders. Calculations are based on peak areas of CEES and decontamination products compared to peak areas of CEES in controls. Zeros indicate that no peaks were seen. [a]Extracted in methylene chloride without shaking. [b]Extracted in methylene chloride with shaking. [c]Extracted in cocktail with shaking. This sample was prepared by heating at 80°C for 12 h by Triton Systems, Inc. [d]Extracted in cocktail with shaking. This sample was prepared by heating at 250°C for 24 h by Triton Systems, Inc. [e]Average of four trials for this substance. All other substances were tested in duplicate.

Tetrahydrofuran and ethanol were tried as extraction solvents to see if these solvents were more effective at dissolving CEES and its decontamination products than methylene chloride, the initial extraction solvent (data not shown). Results for these trials were mixed, with different solvents yielding different ratios of products. A cocktail of all three solvents mixed in equal proportions was subsequently tried, with most recoveries in the range of 60-90%.

In trials with ethanol as the solvent, some hydrolysis of CEES was observed in the controls without any metal oxides (Figure 3.) Although this was never observed in any controls extracted with the cocktail, it is recommended that ethanol be avoided as an extraction solvent.

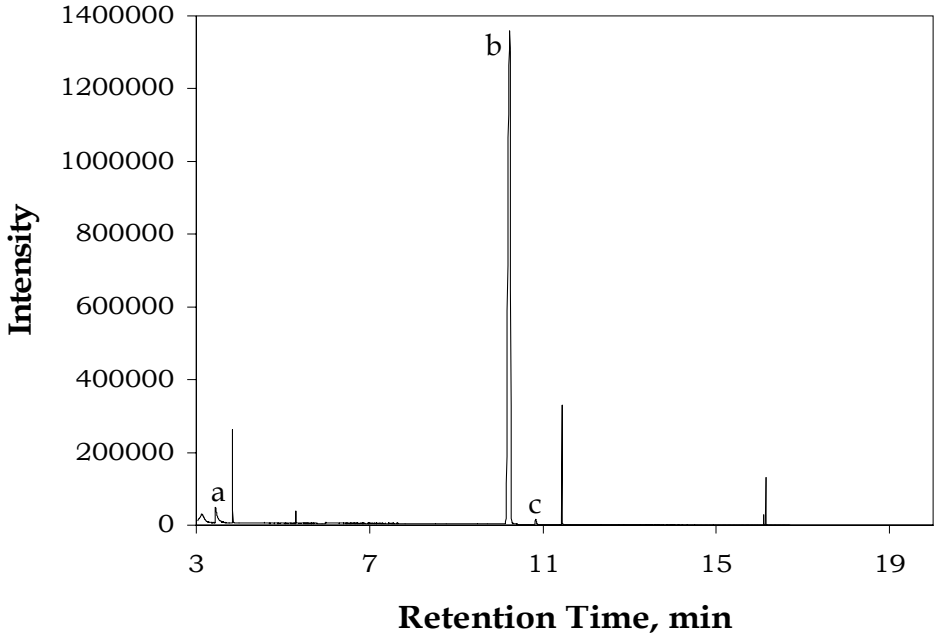

Figure 3. Chromatogram of CEES extracted with ethanol showing formation of hydrolysis product in the absence of any metal oxides. Peak a is the internal standard, tetrahydrofuran. Peak b is CEES. Peak c is the hydrolysis product, $HOCH_2CH_2$-S-CH_2CH_3. No elimination product, CH_2=CH-S-CH_2CH_3, and no enchained product, Cl-CH_2CH_2-S-CH_2CH_2-S-CH_2CH_3 were observed.

3.3 Improving reproducibility

All reactions were conducted at ambient conditions for light, temperature, and humidity. These conditions were chosen since field conditions will be similarly unpredictable. Some literature references use metal oxides prepared or maintained at specific temperature or humidity.[6,7] These procedures may make the metal oxides more uniform and give

more reproducible results. For the magnesium oxide samples from Triton Systems, Inc., this effect was not observed (see Table 2).

In chromatograms where THF was used as the internal standard, the THF peak shows tailing (Figures 2 and 3). This poor peak shape can lead to increased variability in the area of the peak, corresponding to an increase in the variability of the data for the analytes. To overcome this, toluene was selected as the new internal standard. As shown in Figure 1, toluene displays a good symmetrical peak shape.

Absolute and relative recoveries were based on one or two controls prepared and analyzed with the metal oxide samples. The control contained only CEES, so quantitation assumed that the products and the parent compound produced equivalent responses in the detector. This may not be true. Obtaining or synthesizing samples of the elimination and hydrolysis products would be helpful in addressing this question.

The control also served as a one-point calibration in these experiments. Preparing a calibration curve from standards of known concentration—for all compounds of interest—would provide more reliable quantitation.

All mass spectra were full scans, showing total ion current in the chromatograms. Full scans are helpful in analyzing samples with unknown analytes, so full scanning was useful at the beginning to see what decontamination products would form. At this point, enough data have been collected to determine the expected products and their retention times. Subsequent analyses with selected ion monitoring would now be appropriate. Since monitoring specific ions is more selective than full scanning, this may also help reproducibility.

As mentioned above, treating solid samples with CEES may itself cause fluctuations in the data. Maintaining realistic conditions while developing a robust assay will likely require some compromises.

4 Conclusions

Thirteen different metal oxides were compared for their ability to decompose CEES, a simulant for sulfur mustard. Most metal oxides showed little to no decomposition of CEES. NanoActive™ Plus MgO and Al_2O_3 demonstrated the highest ability to degrade CEES. However, even these materials after 24 hours still contained 60-90% of the original CEES applied. These results are lower than some results obtained by other researchers under conditions unlikely to be found in the field.[4,5] In this work, samples were maintained at ambient temperature and light, and no solvents were added to facilitate the reaction.

The realistic conditions may have contributed to the reproducibil-

ity challenges recurring throughout these studies. Since the liquid CEES was added to solid metal oxide powders, the CEES was unlikely to diffuse uniformly through the solid reactant. The extent of CEES decomposition would depend on the amount of contact between the CEES and the metal oxide powder.

Although the extent of mixing of the two components is difficult to change, some parameters of the assay can be modified. Single or duplicate controls were used for quantitation, but three- or five-point calibration curves should yield more reproducible results.

These initial studies were also done with full scan mass spectrometry. Since we were initially unsure which decontamination products might form, this was a good starting place. However, now that we know the reactions that happen, better specificity in the analysis would be obtained with selected ion monitoring. This detection is less susceptible to interference or contamination from other substances, and should yield more reproducible results.

Finally, remember that CEES is only one chemical agent simulant. Different chemical agents, especially those with different modes of action, have very different chemical structures. Low levels of decomposition of CEES gives no indication of the ability of metal oxides to decontaminate other chemical agents. Metal oxide powders might still be effective against compounds which troops might encounter in the field.

5 Acknowledgments

Funding for this work was provided by the ARL/USMA Faculty Outreach. We thank COL David Allbee, COL Garrett Lambert, and Mark VanLandingham for arranging this opportunity. We also thank Triton Systems, Inc. for preparing several metal oxide powders, as well as the Active Coatings group in the Multifunctional Materials Branch of the Weapons and Materials Research Directorate for their assistance with this project.

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