Analysis of Chemical Weapons Decontamination Waste from Old Ton Containers from Johnston Atoll Using Multiple Analytical Methods

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Decontamination waste from chemical weapons (CW) agents has been stored in ton containers on Johnston Atoll since 1971. The waste was recently sampled and analyzed to determine its chemical composition in preparation for disposal. Due to the range of products and analytical requirements, multiple chromatographic and spectroscopic methods were necessary, including gas chromatography/mass spectrometry (GC/MS), gas chromatography/atomic emission detection (GC/AED), liquid chromatography/mass spectrometry (LC/MS), capillary electrophoresis (CE), and nuclear magnetic resonance spectroscopy (NMR). The samples were screened for residual agents. No residual sarin (GB) or VX was found to detection limits of 20 ng/mL, but 3% of the samples contained residual sulfur mustard (HD) at <140 ng/mL. Decontamination products of agents were identified. The majority (74%) of the ton containers were documented correctly, in that the observed decontamination products were in agreement with the labeled agent type, but for a number of the containers, the contents were not in agreement with the labels. In addition, arsenic compounds that are decontamination products of the agent lewisite (L) were observed in a few ton containers, suggesting that lewisite was originally present but not documented. This study was a prototype to demonstrate the level of effort required to characterize old bulk CW-related waste.

Introduction

In 1971, a stockpile of chemical weapons (CW) in ton containers was transferred to Johnston Island (JI), a U.S. territory located in the Pacific Ocean, from Okinawa, Japan. The CW agents, which included sarin (GB), sulfur mustard (HD), and VX, were transferred from the original ton containers into new ton containers. (The ton containers are high-strength, sealed steel barrels that are used for bulk storage of up to 900 kg of CW agent.) The old ton containers were filled with decontamination solution and stored on JI. According to records, the containers with GB residue were decontaminated with aqueous sodium carbonate solution, and the other containers were decontaminated with aqueous calcium hypochlorite (HTH) solution. Some ton containers contained laboratory or other wastes. A total of 241 ton containers contained aqueous waste (brine or caustic solutions), two contained ethylene glycol/water solutions (used for training purposes), two contained mineral oil (probably for use in fog generators as a battlefield or airfield obscurant), and one contained sand from sand-blasting.

As part of the effort to dispose of this waste, the ton containers were sampled. The samples were sent to the Edgewood Research, Development, and Engineering Center (ERDEC, recently renamed Edgewood Chemical Biological Center), Aberdeen Proving Ground−Edgewood Area, MD, for chemical analysis. The analyses requested were (i) to screen the samples for residual CW agents, (ii) to identify the principal components of the samples, and (iii) to relate the components to a chemical weapons agent to determine the original contents of the containers. Analysis for tests required for U.S. Environmental Protection Agency (U.S. EPA) Resource Conservation and Recovery Act (RCRA) hazardous waste classification were performed.

The decontamination products of CW agents have a range of polarity and volatility. A number of instrumental methods were necessary for the analyses. Gas chromatography/mass spectrometry (GC/MS) on nonpolar extracts of the samples was used to screen for CW agents and to detect nonpolar, volatile compounds. Gas chromatography/atomic emission detection (GC/AED) was used to quantify volatile compounds (*1*), including derivatized arsenic compounds related to lewisite (L). Chemical derivatization with GC/MS was used to identify polar and nonvolatile decontamination products (*2−6*). Capillary electrophoresis (CE) with indirect UV detection was used to quantify the alkyl methylphosphonic acids from nerve agent (GB and VX) decontamination (*7*). Liquid chromatography/mass spectrometry (LC/MS) with atmospheric pressure chemical ionization (APCI) was used to identify and quantify some of the decontamination products of HD. A similar approach has been reported previously with thermospray LC/MS (*8*). Nuclear magnetic resonance spectroscopy (NMR) was used for confirmation (*9*), although a number of the samples had high iron content, so significant sample preparation was required. The complementary chromatographic and spectroscopic techniques provided identification, quantitation, and confirmation of the results (*10*).

The analysis of the Johnston Atoll ton containers was a prototypical effort for future CW-related cleanups. Other military installations have repositories of waste that will also require disposal. The implications of characterization of waste will be discussed. This effort may be useful as a case study of the level of effort required to characterize other types of bulk waste.

Experimental Section

Sampling. Samples from the Johnston Atoll ton containers were collected by military technicians in appropriate protective equipment and using monitoring equipment, in accordance with established operating procedures. Two samples, each 1 L in volume, were collected from each ton

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container, one in an amber glass bottle and one in a polyethylene bottle. The samples were screened for high levels of CW agents at JI before shipment. The bottles were packed triply contained in cooled, sealed, insulated chests for shipment and refrigerated at 4 °C after receipt. Chain-of-custody documentation was maintained.

Chemical Standards. Chemical standards of the following compounds were obtained in diluted 2-propanol solutions from the Chemical Agent Standard Analytical Reference Material (CASARM) Program at ERDEC: *O*-ethyl *S*-(2-di-isopropylaminoethyl)methylphosphonothioate (VX, CAS Registry No. 50782-69-9); bis(2-chloroethyl)sulfide (sulfur mustard or HD, CAS Registry No. 505-60-2); *S*-(2-diisopropyl-aminoethyl)methylphosphonothioic acid (DAEMPTA, CAS Registry No. 73207-98-4); isopropyl methylphosphonofluoridate (GB, CAS Registry No. 107-44-8); and 2-chlorovinyl dichloroarsine (lewisite or L, CAS Registry No. 541-25-3). NOTE: These are regulated, acutely toxic compounds that must be handled in approved facilities with appropriate safety precautions to avoid risk to personnel.

Standards of the following chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI): methylphosphonic acid (MPA, 98%, CAS Registry No. 993-13-5); ethyl methylphosphonic acid (EMPA, 98%, CAS Registry No. 1832-53-7); thiodiglycol (TDG, or 2,2′-thiodiethanol, 99+%, CAS Registry No. 111-48-8); thiodiglycol sulfoxide (TDGO, or 2,2′-sulfinyl-diethanol); 1,4-dithiane (97%, CAS Registry No. 505-29-3); isethionic acid, sodium salt (HESA, 2-hydroxyethanesulfonic acid, 98%, CAS Registry No. 1562-00-1); vinylsulfonic acid, sodium salt (VSA, technical grade, 25% in water, CAS Registry No. 3039-83-6); triphenylarsine (97%, CAS Registry No. 603-32-7); 1,3-propanedithiol (PDT, 99%, CAS Registry No. 109-80-8); and arsenic(III) oxide (99.995%, CAS Registry No. 1327-53-3).

Standards of the following chemicals were obtained from Alfa AESAR (Ward Hill, MA): diisopropyl methylphosphonate (DIMP, 98+%, CAS Registry No. 1445-75-6) and thioxane sulfone (1,4-thioxane-1,1-dioxide, 99%, CAS Registry No. 107-61-9). The solvents dichloromethane (Burdick & Jackson B&J Brand, CAS Registry No. 75-09-2) and acetonitrile (Baker Ultra Resi-Analyzed, CAS Registry No. 75-05-8) were obtained from VWR (South Plainfield, NJ). The following derivatization reagent was purchased from Pierce (Rockford, IL): *N*-methyl-*N*-trimethylsilyl trifluoroacetamide (MSTFA, CAS Registry No. 24589-78-4). Standards of isopropyl methylphosphonic acid (IMPA, CAS Registry No. 5514-35-2) and 2-chlorovinyl arsenous acid (CVAA, CAS Registry No. 3088-37-7) were synthesized in-house.

Instrumentation. The following brands of equipment were used for the instrumental analysis: GC/MS, HP 5890 or 6890 GC with HP 5970, 5971, or 5973 MSD (Hewlett-Packard, Little Falls, DE); GC/AED, HP 5890 GC with HP 5921A AED; gas chromatography/flame photometric detection (GC/FPD), HP 5890 GC with HP 19256A FPD; LC/MS, HP 1090M HPLC with HP 5989A "MS Engine" and the APCI option G1075A (source manufactured by Analytica of Branford, Branford, CT, with no hexapole focusing stage); CE, HP [3]DCE; and NMR, Bruker (Billerica, MA) AC-250 MHz NMR. A few samples were screened on a Finnigan (division of ThermoQuest, San Jose, CA) LCQ ion trap mass spectrometer. The samples were analyzed for metals using inductively coupled plasma mass spectrometry (ICP/MS) using a Perkin-Elmer (Norwalk, CT) Elan 5000 ICP/MS at Chemical Solutions Ltd. (Mechanicsburg, PA).

Methods for Agent Detection. A primary goal of this effort was to screen the decontamination samples for residual chemical weapons agent to the lowest detectable levels. Analysis of the agents GB, VX, and HD to concentrations of 20 ng/mL was done using liquid−liquid extraction with methylene chloride followed by GC/MS in SIM mode. In most cases, all three agents could be screened in one GC run, although occasionally pH adjustment was necessary prior to extraction. Typical GC conditions included an HP-5MS column (or equivalent) with an oven ramp from 35 to 280 °C at 15 °C/min, using helium with a flow of 0.7−1.0 mL/min.

Analysis of agents, particularly VX, to lower concentrations was not only instrument limited but also limited by the presence of chemically similar interferences in the decontamination solution samples. For nine of the samples, GC/MS did not give unequivocal identification of VX, even when comparing a spiked with an unspiked sample. In these cases, two alternative methods were used: (i) VX was reacted in solution with silver fluoride to form ethyl methylphosphono-fluoridate, which was detected by GC/MS; and (ii) samples were analyzed by an MS/MS method for VX on a Finnigan LCQ ion trap mass spectrometer after sample cleanup. The MS/MS used a parent ion of m/z 268 (M + H$^+$ for VX) and the m/z 128 fragment ion, using isocratic LC with 70% aqueous buffer and 30% methanol on a Hypersil ODS column.

For detection of lewisite (L), derivatization with PDT and hexane extraction was done. L tends to decompose during gas chromatography, so analysis without derivatization is not recommended. The PDT derivatization reaction is fast and goes to completion (*11, 12*). In aqueous solution, L rapidly hydrolyzes to CVAA, although both are derivatized and detected by the method. Arsenic- and sulfur-specific detection by GC/AED were done using standards of triphenylarsine and 1,4-dithiane, respectively, giving detection limits of 8 ng/mL.

Detection of Volatile Decontamination Products. Volatile, nonpolar decontamination products of the agents were identified using GC/MS in scan mode by comparison to EI MS libraries and known standards. Some were quantified using GC/AED with a phosphorus- or sulfur-specific calibration curve. By using element-specific quantitation, similar detection limits were obtained for all related compounds. However, no extraction efficiencies were measured for any compounds except for the agents, so quantitation is approximate. The results are used to show that there were orders of magnitude variations in the concentrations of analytes.

Detection of Nonvolatile Decontamination Products. Many of the primary decontamination products of the agents are not volatile and cannot be detected directly by GC. A number of instrumental methods were used to identify and quantify these compounds: (i) analysis of trimethylsilyl (TMS) derivatives using GC/MS by evaporating the samples to dryness and adding MSTFA; (ii) analysis by CE; and (iii) analysis by LC/MS.

CE with indirect UV detection was used for nerve-agent-related alkyl methylphosphonic acids (*7*), providing quantitation limits of 100 μg/mL before dilution. LC/MS was primarily used for analysis of HD-related compounds due to the complexity of the mixtures and to quantify thiodiglycol and related compounds. Positive ion APCI was used for detection of TDG, TDGO, thiodiglycol sulfone, and related polar compounds. Negative ion APCI was used for detection of isethionic acid, vinyl sulfonic acid, and other sulfonic acids that were not identified by CE or derivatization GC/MS. Typical LC conditions used a gradient run from 100% aqueous ammonium acetate buffer to 95% acetonitrile on a 2.1 × 100 mm Hypersil ODS column (or similar), with a flow rate of 0.25 mL/min.

NMR Confirmation. NMR for the nuclei ^{31}P, ^{1}H, and ^{13}C was done on selected samples to confirm the product identification, determine the product distribution in unprepared samples, and search for any other products that could be missed by other methods. In some cases, samples could be analyzed with no preparation. However, a considerable amount of iron and iron oxide was dissolved or

suspended in some samples from corrosion of the container, broadening the NMR peaks and requiring additional filtering or use of a complexing agent (*13*).

Results and Discussion

Residual Agent. None of the samples contained residual GB or VX for detection limits of 20 ng/mL.

Nine samples had higher detection limits for VX with GC/MS analysis because of interfering compounds that did not allow identification of a distinct GC peak for the spiked agent. Two alternative methods were used for these samples. Derivatization with AgF was successful for screening seven of the nine samples. LC/MS/MS was successful in screening all nine samples. In all cases, both a sample and the same sample spiked at 20 ng/mL were prepared and analyzed.

Residual HD was detected in some samples: 3% had detectable levels, mostly in the range of 20−30 ng/mL, but one sample was measured at 140 ng/mL. These samples had high concentrations of HD-related decontamination products, so the possibility exists that HD was reformed in the GC injection port from one or more of the compounds, but this issue was not studied. HD was not detected in many samples that had high product concentrations. Due to the low concentrations, the HD could not be confirmed by other techniques.

The existing records of the ton containers did not indicate that any of them contained L. However, analysis for L was done after samples were observed to contain high concentrations of arsenic(III) oxide, found as a tris(trimethylsilyl) derivative with MSTFA. Arsenic(III) oxide is a decontamination product of L, although it could originate from other sources. About 7% of the samples had detectable concentrations of CVAA ranging from 10 to 2400 ng/mL. The only known source of CVAA is from L. CVAA is not volatile, although it is a vessicant and may be the active agent of L in biological tissue (*14, 15*).

The nonaqueous samples were also screened for agents. No agents were found in the sand, rust, two ethylene glycol, or two mineral oil samples. CVAA was detected in one ethylene glycol sample. Detection limits were higher than 20 ng/mL because of matrix effects. Detection limits for the sand and rust samples, using a dichloromethane extraction, were nearly as good as the aqueous samples. The two ethylene glycol solutions were extracted with hexane rather than methylene chloride, and the detection limits were 400 ng/mL for GB, 250 ng/mL for HD, and 500 ng/mL for VX. The most difficult matrix for agent detection was the mineral oil. These samples were miscible with the nonpolar solvent and so could not be extracted for agent analysis. They also could not be run on the GC/MS without dilution, since the large number of compounds in the samples overloaded the detector. The agent screen was performed using GC/FPD with P and S detection and retention time matching. No agent was detected, but the detection limits were found to be 1 μg/mL for GB, 50 μg/mL for HD, and 50 μg/mL for VX.

Decontamination Products. Decontamination products for all agents were analyzed for in all samples. The decontamination products that were found in the samples did not always correspond to the labels in the existing documentation. Overall, 74% of the samples had decontamination products that corresponded to the labeled CW agent. Some of the containers had nondescript labels that did not indicate the type of agent, and 16% of the ton containers were actually mislabeled, indicating one agent but containing the products related to another. Most of the samples contained products related to a single agent, but a few had mixtures.

GB Decontamination Products. GB gave the simplest mixture of decontamination products. The major GB product was IMPA. DIMP is a typical impurity in GB at relatively low concentrations, but it is much more stable to degradation,

so it is usually characteristic of GB. MPA was always in significantly lower concentrations than IMPA. Tributylamine and dibutylamine were observed in many samples since tributylamine is used as a stabilizer for GB.

VX Decontamination Products. The major phosphorus-containing decontamination product of VX is EMPA. MPA, which is a degradation product of both IMPA and EMPA, was also observed at lower concentrations than EMPA.

EMPA was not always detected by derivatization GC/MS in samples containing VX decontamination products, even when it was identified by CE and ^{31}P NMR. In some samples, it was observed but with lower signal intensity than IMPA in GB-related samples with comparable concentrations. MPA also gave a lower signal in VX-related samples than GB-related samples.

In a previous study, it was found that EMPA is derivatized as completely as IMPA, and it can be detected about as efficiently by GC/MS (*1*). The studies have suggested that MPA, a divalent ion, is derivatized more efficiently in acidic solution than in basic solution (*2*), suggesting that metal ions in basic solution could form salts with the anion, which could hinder derivatization (*1*). This effect was also noted previously for IMPA and EMPA, which are monovalent anions (*17*). The observation is consistent with the difference in the decontamination solutions used for the two agents. GB was decontaminated with sodium carbonate solution, which had high sodium content but little or no calcium. VX was decontaminated with HTH solution, which had high calcium content. It is possible that the anions formed salts with calcium were not efficiently dissolved and derivatized in MSTFA. This problem illustrates the importance of having multiple, complementary analytical methods for determining priority analytes.

The other primary decontamination product of VX is 2-(diisopropylamino)ethanethiol, the nitrogen- and sulfur-containing product of VX hydrolysis. This product reacts to give rise to secondary products. The major sulfur-containing products that were observed were methyl diisopropylamino-ethyl sulfide, ethyl diisopropylaminoethyl sulfide (CAS Registry No. 110501-59-2), bis(diisopropylaminoethyl) sulfide (CAS Registry No. 110501-56-9), and bis(diisopropylamino-ethyl) disulfide (CAS Registry No. 65332-44-7). These products were observed at concentrations of 1−5 μg/mL or less, which is much less than the concentration of EMPA in the same samples (200−2000 μg/mL). It is possible that additional higher molecular weight products formed over time are not water-soluble. It is also possible that, in basic solution, the sulfur-containing amines formed a separated organic layer that was not sampled from the ton containers. The compounds *N,N*-dicyclohexylurea or *N,N*-diisopropylurea were also commonly observed since they are hydrolysis products of the stabilizers in VX.

A basic hydrolysis product of VX is DAEMPTA (*10*), which is toxic (*16*). Due to the length of time and the environmental conditions under which the ton containers have been stored, the presence of this compound was not expected. It is soluble in the brine solutions at all pH levels and produces decontamination products identical to those of VX. Five samples with the highest concentrations of EMPA were analyzed for DAEMPTA using an LC/MS method similar to one reported previously (*10*). It was not observed to detection limits of 10 μg/mL.

HD Decontamination Products. The decontamination solutions of HD contained a large number of products. Table 1 shows a selection of samples with HD and/or L decontamination products. The concentrations and pH values covered a wide range. In most samples, the major decontamination product of HD was TDG. A few samples had as much as 5.5% TDG. On the other hand, several samples had <10 μg/mL of TDG and no other significant decontamination

TABLE 1. Selection of Some Samples Containing HD and L Decontamination Products Showing the Types and Amounts of the Products[a]

sample	pH	TDG	TDGO	dithiane	thioxane	Th-O2	HD	AsO₃	CVAA
D-13469	6.12	29000	7600	180	450	340			0.1
D-14036	3.76	D,<10						500	0.33
D-1524	4.94	D,<10		0.2					
D-20635	4.0							1800	0.29
D-23882	4.20	26000	14000	110	D, <10	1000			
D-34389	4.83	228	2500	0.2	D,<10	280		X	0.07
D-35323	8.76	D,<50	52	0.45	0.1	1400		X	0.28
D-44815	3.93	55	170	260	320	66			
D-48714	2.78	55000	3500	540	310	1100	0.14		
D-49530	12.32	4040	6200	42	100	1300			0.03
D-49726	4.78	D,<10						D,<10	0.01
D-56656	3.90	10200	3600	28	95	760			
D-57064	4.65	12000	5500	147	5.8	430			0.01
D-57301	12.20	19000	930	310	740	1600			
D-57348	6.31	1240	1600	16	230	650			
D-77143	4.5							25	0.03
D-77157	11.49	1020	1800	7.1	76	2000	0.014		
D-79544	9.67	4260	2800	38	120	1200		X	0.17

[a] All concentrations in μg/mL. An "X" indicates that the compound was detected but not quantified. A "D,<" indicates that the compound was detected by derivatization GC/MS, but it was present below the quantitation limits.
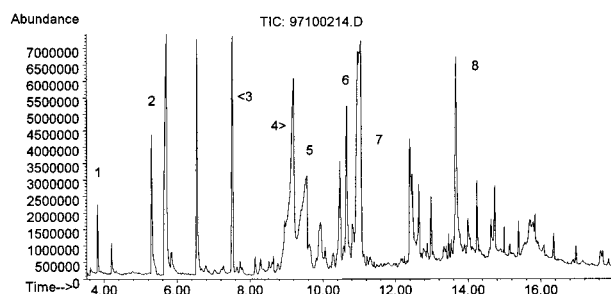

FIGURE 1. GC/MS chromatogram of the dichloromethane extract of sample 56656. The numbered peaks are assigned as follows: (1) 1,1,2-trichloroethane; (2) 1,4-thioxane; (3) 1,4-dithiane; (4) thiodiglycol (TDG); (5) 1,4-thioxane-1,1-dioxide (Th-O2); (6) dithiane oxide; (7) Q-related product; (8) T-related product.
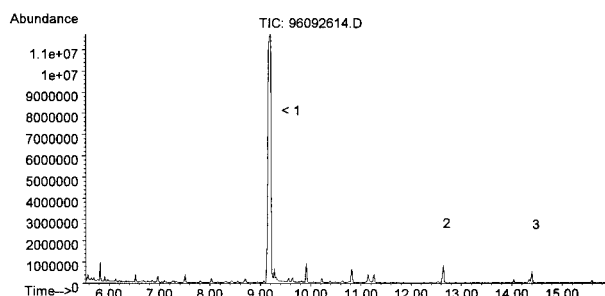

FIGURE 2. GC/MS chromatogram of MSTFA derivative of residue of sample 56656 after evaporation. The numbered peaks are assigned as follows: (1) bis(trimethylsilyl) derivative of thiodiglycol; (2) bis-(trimethylsilyl) derivative of the diol of agent Q; (3) bis(trimethylsilyl) derivative of the diol of agent T.
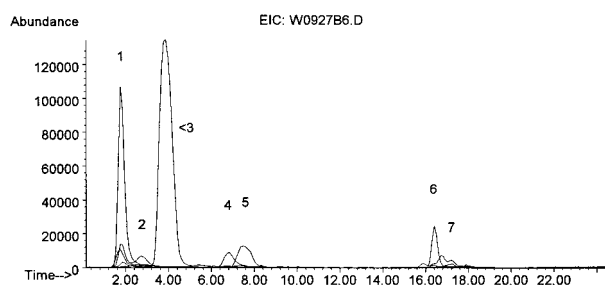

FIGURE 3. LC/MS extracted ion chromatogram of sample 56656 using positive ion APCI and gradient elution. The numbered peaks are assigned as follows: (1) thiodiglycol sulfoxide (major peak at m/z 139); (2) thioxane sulfoxide (m/z 121); (3) thiodiglycol (m/z 123, 105, 87); (4 and 5) two compounds related to agent Q; (6 and 7) several compounds related to agent T.

products. The concentration of products in the GB- and VX-related samples covered a much narrower range of concentrations, from 200 to 2000 μg/mL.

Some samples had TDGO as the major product. In other samples, thioxane sulfone was the major product, unexpectedly. These observations suggest that the TDG was oxidized to other products in these samples over time. The samples containing high levels of thioxane sulfone were typically strongly basic, although there were some exceptions, and there was no definitive pattern that explained why it formed in some samples but not others.

A large number of other products were observed in the HD decontamination samples that could be due to impurities in the original HD or secondary reaction products. Figure 1 shows a GC/MS chromatogram of the dichloromethane extract of a sample with a high concentration of HD decontamination products, with some of the peaks labeled. Figure 2 shows the GC/MS chromatogram of the MSTFA derivative of the same sample. By far the largest peak in this chromatogram is from the derivative of thiodiglycol. Figure 3 shows the LC/MS chromatogram with positive ion APCI. The compounds 1,4-dithiane and 1,4-thioxane are commonly observed nonpolar impurities easily detected by GC. Some of the additional compounds that have been tentatively assigned from MS library searches or spectral interpretation include thioxane sulfoxide, dithiane oxide, dithiane dioxide, thiodiglycol sulfone, divinyl sulfone, diethyl sulfone, ethyl thioethanol, methyl thioethanol, and 1,1,2-trichloroethane, along with unassigned peaks.

Oxidation of TDG produces HESA and other alkyl sulfonic acids. VSA was observed in many samples. Occasional samples also contained hydroxychloroethyl sulfonic acid, dichloromethyl sulfonic acid, chlorovinyl sulfonic acid, and chloroethyl sulfonic acid. These compounds were identified by the M − H⁻ ion and the Cl isotope peak distribution using negative ion APCI LC/MS, although standards of some of the compounds were not available and the compounds were not confirmed with other methods. Figure 4 shows a LC/MS chromatogram showing these peaks.

In addition to these products corresponding to HD, there are also hydrolysis products corresponding to agent Q and
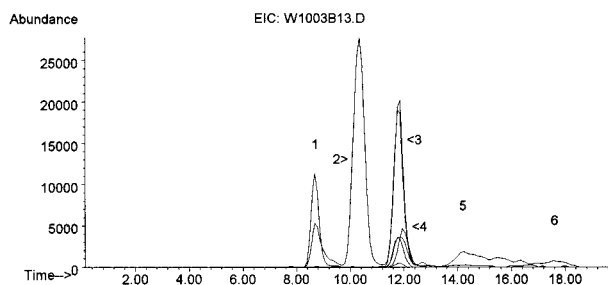
FIGURE 4. LC/MS extracted ion chromatogram of sample 56656 using negative ion APCI. The numbered peaks are assigned as follows: (1) hydroxyethane sulfonic acid (major ions at m/z 125, 107, 95, and 80); (2) vinyl sulfonic acid (m/z 107); (3) hydroxychloroethane sulfonic acid (m/z 159, 161, 107, 123, 141, and 80); (4) chloromethane sulfonic acid (m/z 129, 131, and 80); (5) chlorovinyl sulfonic acid (m/z 141 and 143); and (6) dichloromethane sulfonic acid (m/z 163, 165, 167, 128, and 80).

agent T, which are longer chain analogues of HD that were sometimes mixed with HD. Agent Q (sesquimustard) is 1,2-bis(2-chloroethylthio)ethane (CAS Registry No. 3563-36-8), and agent T (O-mustard) is bis(2-chloroethylthioethyl) ether (CAS Registry No. 63918-89-8). The corresponding diols for these compounds were observed by GC/MS and LC/MS, as shown in Figures 1–3, but quantitative standards of the compounds were not available.

Perchloroethene (tetrachloroethylene, CAS Registry No. 127-18-4, RCRA U-210), which is a volatile, toxic compound on the RCRA list, was detected in at least 10% of the samples. This compound may originate from decontamination of HD. Hexachloroethane (CAS Registry No. 67-72-1, RCRA U-131), another RCRA volatile chemical, was detected in one sample. That sample also contained several other chlorinated compounds, suggesting that this one ton container was a general repository for chlorinated waste in addition to the decontaminated agent. Several other samples also contained some unidentified chlorinated compounds at low concentrations.

Most, but not all, of the samples with high concentrations of HD decontamination products also had an orange precipitate. Some also had green, black, or gray precipitates. These precipitates were not soluble in the solvents used for this study, so they were not characterized. They may be metal salts from corrosion of the container and reaction with the decontamination solution.

L Decontamination Products. There was a good correlation between the presence of CVAA and high arsenic determinations in the samples by ICP/MS. The highest concentration of arsenic in all the samples measured by ICP/MS was 7800 μg/mL. The arsenic compound arsenite, As(OH)$_3$ or arsenic(III) oxide, appeared to be the major arsenic-containing species.

Characterization of Other Samples. The contents of two ton containers labeled "Lab Waste" were found to be organic liquids. The major component was mineral oil, identified by NMR and GC/MS. The identity of these samples was unknown prior to analysis. Other aromatic compounds were detected in low concentrations, but no CW-related compounds or polychlorinated biphenyls were detected. Mineral oil is used in fog-generating equipment.

Two samples were an ethylene glycol matrix. They were labeled as "antifreeze" and were used for training purposes. One of the samples contained 1.4 μg/mL of CVAA. A sample of sand that remained from sand-blasting a container and two sample bottles that contained rust from one rusted ton container were screened for agent and analyzed for decontamination products.

Other Analyses for RCRA Hazardous Waste Classification. A few other tests were run to meet the requirements of the U.S. EPA RCRA for classification of the waste: (i) The pH values of aqueous samples were measured, and they varied from acidic (pH 4) to very basic (>pH 13). Fourteen samples are classified as corrosive based on the pH > 12.5. In comparison, freshly prepared, concentrated HTH solutions have pH > 12.5. In fact, 14 samples were water with no decontamination reagent present. (ii) Heavy metals, analyzed using ICP/MS, had concentrations over the RCRA limit in 50% of the samples. A few had high arsenic levels, but most had lower levels (1–50 μg/mL) of lead, cadmium, arsenic, or mercury. (iii) Samples were analyzed for flashpoints using a Pensky-Martens closed cup flashpoint tester. All samples had flashpoints above 140 °F. (iv) All samples were examined for reactivity with both water and dichloromethane during sample preparation, and none were reactive. (v) Samples were tested for inhibition of the cholinesterase enzyme, which is characteristic of nerve agents, and no inhibition was observed.

In general, this study indicates that the characterization of old, poorly documented CW wastes can require a considerable laboratory effort. The most important effort for regulatory and transportation documentation was the screening for residual agent, done by GC/MS. A significant number of instrumental methods were needed to identify and quantify the major products. There was also a significant amount of time needed for methods development on the unfamiliar matrices and reanalysis for validation and confirmation. The two mineral oil and two glycol samples required a significant effort for agent screening, even though they were only a small fraction of the total number of samples. Although all of this information is not necessarily required by U.S. EPA regulations, it is useful for proper safety precautions, handling, and disposal of the waste, particularly if it is CW related. This study should be helpful in allowing an appropriate amount of time and equipment to perform the analyses before the waste is moved for disposal.

A report containing all the tabulated analytical results and methods is available from the authors (*18*).

Literature Cited

(1) Creasy, W. R.; Rodríguez, A. A.; Stuff, J. R.; Warren, R. W. *J. Chromatogr. A* **1995**, *709*, 333–344.

(2) Black, R. M.; Clark, R. J.; Read, R. W.; Reid, M. T. J. *J. Chromatogr. A* **1994**, *662*, 301–321.

(3) D'Agostino, P. A.; Provost, L. R. *J. Chromatogr.* **1992**, *589*, 287–294.

(4) D'Agostino, P. A.; Provost, L. R. *J. Chromatogr.* **1993** *645*, 283–292.

(5) Tørnes, J. A.; Johnsen, B. A. *J. Chromatogr.* **1989**, *467*, 129–138.

(6) Shih, M. L.; Smith, J. R.; McMonagle, J. D.; Dolzine, T. W.; Gresham, V. C. *Biol. Mass Spectrom.* **1991**, *20*, 717–723.

(7) Cheicante, R. L., Jr.; Stuff, J. R.; Durst, H. D. *J. Cap. Electrophoresis* **1995**, *2* (4), 157–163.

(8) Wils, E. R. J.; Hulst, A. G. *Fresenius J. Anal. Chem.* **1992**, *342*, 749–758.

(9) Mesilaakso, M.; Tolppa, E.-L. *Anal. Chem.* **1996**, *68*, 2313–2318.

(10) Creasy, W. R.; Stuff, J. R.; Williams, B.; Morrissey, K. M.; Mays, J.; Duevel, R.; Durst, H. D. *J. Chromatogr. A* **1997**, *774*, 253–263.

(11) Logan, T. P.; Smith, J. R.; Jakubowski, E. M.; Dolzine, T. W. *Proceedings of the 1992 ERDEC Scientific Conference on Chemical and Biological Defense Research*, November 17–20, 1992, Aberdeen Proving Ground–Edgewood Area, MD; 1992, pp 843–850.

(12) Albro, T. G.; Durst, H. D.; Simak, R. *Proceedings of the 1993 ERDEC Scientific Conference on Chemical and Biological Defense Research*, November 16–19, 1993, Aberdeen Proving Ground–Edgewood Area, MD; 1993, pp 219–225.

(13) Brickhouse, M. D.; RaghuVeer, K. S.; Durst, H. D. *Proceedings of the 1996 ERDEC Scientific Conference on Chemical and Biological Defense Research*; ERDEC-SP-048; Aberdeen Proving Ground–Edgewood Area, MD, November 19–22, 1996; pp 637–641.

(14) Fowler, W. K.; Stewart, D. C.; Weinberg, D. S.; Sarver, E. W. *J. Chromatogr.* **1991**, *558*, 235–246.

(15) Waters, W. A.; Williams, J. H. *J. Chem. Soc.* **1950**, 18–22.

(16) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K. *J. Am. Chem. Soc.* **1990**, *112*, 6621–6627.

(17) Kataoka, M.; Tsunoda, N.; Ohta, H.; Tsuge, K.; Takesako, H.; Seto, Y. *J. Chromatogr. A* **1998**, *824*, 211–221.

(18) Durst, H. D.; et al. *Report on the Analysis of Johnston Atoll Ton Container Decontamination Solution Samples*; EAI Report A202/97/001F; EAI Corporation: Abingdon, MD, November 1997.