TOOELE CHEMICAL AGENT DISPOSAL FACILITY (TOCDF)

DEMONSTRATION TEST PLAN FOR THE

AUTOCLAVE SYSTEM

Revision 1

~~February 10, 2009~~Date to Be Determined

EXECUTIVE SUMMARY

The Tooele Chemical Agent Disposal Facility (TOCDF) was designed and built for the United States (U.S.) Army to destroy the chemical agent munitions stockpile at the Deseret Chemical Depot (DCD), located 20 miles south of Tooele, Utah. EG&G Defense Materials, Inc., (EG&G) operates the TOCDF under contract to the Army through the Chemical Materials Agency.

The U.S. Environmental Protection Agency (EPA) identification number for the TOCDF is UT5210090002. The facility operates under a Resource Conservation and Recovery Act (RCRA) Part B Permit, issued pursuant to the delegation of the State of Utah Department of Environmental Quality (DEQ), Division of Solid and Hazardous Waste (DSHW), under the Utah Administrative Code, Section 315 (R315). The TOCDF also operates under a Title V Air Permit administrated by the DEQ, Division of Air Quality (DAQ). Under these permit requirements; any system must demonstrate the ability to effectively treat hazardous wastes such that human health and the environment are protected.

The TOCDF secondary waste is generated as a result of demilitarization of the DCD chemical agent stockpile. Secondary wastes contaminated with chemical agent are treated on-site prior to shipment for final disposal at off-site facilities. The TOCDF proposes to use an autoclave to provide the on-site treatment to remove agent contamination from low-level-agent-contaminated wastes. Therefore, an Autoclave Demonstration Test (ADT) will be conducted to demonstrate treatment of secondary wastes in the autoclave by processing actual contaminated wastes to produce a treated residue that is not an agent vapor hazard [less than ~~1.~~0.5 Vapor Screening Limit (VSL)] or a 1 mg/kg agent practical quantitation limit or Waste Control Level~~contact hazard~~ (< 20 ppb VX)~~1 mg/kg~~).

The test performance will be measured by quantifying the amount of agent removed from the wastes by treatment. The removal will be determined by spiking samples with Agent VX and then analyzing the spiked samples after treatment in the autoclave. A successful test will demonstrate removal of 99 % of the agent from the spiked samples, an agent practical quantitation limit of the spiked sample of < 1mg/kg or less and an agent concentration in the headspace of less than ~~1.~~0.5 VSL.

Materials that will be treated in the autoclave include chlorinated polymer materials/~~,~~ non-chlorinated polymer materials (i.e., DPE suits), wood, and Life Support System (LSS) rubber hoses. The ADT will establish feed limits for treating wastes at below incineration temperatures using three waste streams. The Demilitarization Protective Ensemble (DPE) waste stream will include DPE suits along with polyethylene sheeting (DPE drum liner) and bags and possibly some DPE tape. The LSS air hose waste stream will include LSS air hoses and the metal fittings. The wood waste stream will be wood wastes ~~, plastics,~~ and possibly metal banding straps. ~~These three waste streams will be representative of the other wastes to be processed by the autoclave~~

~~with the exception of carbon wastes and metal drums.~~Other waste streams will be approved for treatment after a function test has demonstrated the treatment of the waste stream.

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LIST OF ACRONYMS AND ABBREVIATIONS

ACAMS	Automatic Continuous Air Monitoring System
~~ADAFC~~	~~ACAMS Dilution Air Flow Controller~~
ADT	Autoclave Demonstration Test
ASTM	ASTM International formerly American Society for Testing and Materials
AWFCO	Automatic Waste Feed Cutoff
CAL	Chemical Assessment Laboratory
CEMS	Continuous Emission Monitoring System
~~CHL~~	~~Contact Hazard Level~~
CFR	Code of Federal Regulations
CMA	Chemical Materials Agency
CPT	Comprehensive Performance Test
DAAMS	Depot Area Air Monitoring System
DAQ	State of Utah, Department of Environmental Quality, Division of Air Quality
DCD	Deseret Chemical Depot
~~DDAFC~~	~~DAAMS Dilution Air Flow Controller~~
DEQ	State of Utah, Department of Environmental Quality
DFS	Deactivation Furnace System
DPE	Demilitarization Protective Ensemble
DRE	Destruction and Removal Efficiency
DSHW	State of Utah, Department of Environmental Quality, Division of Solid and Hazardous Waste
DVS	Drum Ventilation System
EG&G	EG&G Defense Materials, Inc.
EPA	U.S. Environmental Protection Agency
ETL	Extreme Temperature Limit
GC	Gas Chromatography
GC/FPD	Gas Chromatograph/Flame Photometric Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
HAP	Hazardous Air Pollutant
HWMU	Hazardous Waste Management Unit
ICP/MS	Inductively Coupled Plasma/Mass Spectrometer
LIC	Liquid Incinerator
LOP	Laboratory Operating Procedure
LOQ	Limit of Quantitation
LSS	Life Support System

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

MACT	Maximum Achievable Control Technology
MDB	Munitions Demilitarization Building
MPF	Metal Parts Furnace

~~LIST OF ACRONYMS AND ABBREVIATIONS (continued)~~

OPL	Operating Parameter Limit
PLC	Programmable Logic Controller
POHC	Principal Organic Hazardous Constituent
PPE	Personal Protective Equipment
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QP	Quality Plant Sample
R315	Utah Administrative Code Section 315
RCRA	Resource Conservation and Recovery Act
SDS	Spent Decontamination Solution System
SEL	Source Emission Limit
STEL	Short Term Exposure Limit
SVOC	Semi-Volatile Organic Compound
SW-846	Test Methods for Evaluating Solid Waste, 3rd Edition including Update III, USEPA, SW-846, December 1996.
TAP Gear	butyl rubber coated garments
TC	Ton Container
TE-LOP	Tooele Laboratory Operating Procedure
TOCDF	Tooele Chemical Agent Disposal Facility
TSDF	Treatment, Storage and Disposal Facility
U.S.	United States
VOC	Volatile Organic Compound
VSL	Vapor Screening Limit
WCL	Waste Control Limit

LIST OF UNITS OF MEASURE

acfm	actual cubic feet per minute
Btu/hr	British thermal units per hour
Btu/lb	British thermal units per pound
Btu/ft^3	British thermal units per ft^3
cfm	cubic feet per minute
°C	degrees Centigrade
°F	degrees Fahrenheit
dscf	dry standard cubic feet
dscfm	dry standard cubic feet per minute
dscm	dry standard cubic meter
ft	feet
ft^3	cubic feet
g	grams
gpm	gallons per minute
hr	hours
hp	horsepower
inHg	inches of mercury
inWC	inches of water column
lb	pounds
lb/hr	pounds per hour
L/min	liters per minute
µg	micrograms
µL	microliter
m^3	cubic meters
mg	milligrams
mg/dscm	milligrams per dry standard cubic meter
min	minutes
mL	milliliters
mL/min	milliliters per minute
mm	millimeters
ng	nanograms
ppm	parts per million
ppmdv	parts per million on a dry volume basis
psig	pounds per square inch gauge
scfm	standard cubic feet per minute
Wt%	weight percent
ΔP	velocity pressure

LIST OF CHEMICAL SYMBOLS AND FORMULAS

Agent GB	Sarin or methylphosphonofluoridic acid 1-methylethyl ester or O-isopropyl methylphosphonofluoridate
Agent VX	O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate
Al	aluminum
Ag	silver
As	arsenic
As_2O_3	arsenic oxide
B	boron
Ba	barium
Be	beryllium
Cd	cadmium
CdO	cadmium oxide
Cl^-	chloride
Cl_2	chlorine
CO_2	carbon dioxide
CO	carbon monoxide
Co	cobalt
Cr	chromium
Cu	copper
EA-2192	S-(2-diisopropylaminoethyl) methylphosphonothioic acid
H	Levinstein mustard
HD	distilled mustard
HT	mixture *bis*(2-chloroethyl)sulfide and *bis*[2-(2-chloroethylthio)ethyl] ether
HF	hydrogen fluoride
HNO_3	nitric acid
H_3PO_4	phosphoric acid
Hg	mercury
HCl	hydrogen chloride
Mn	manganese
NaOH	sodium hydroxide
H_2SO_4	sulfuric acid
mustard	*bis*(2-chloroethyl)sulfide
Ni	nickel
NO_x	nitrogen oxides
O_2	oxygen

LIST OF CHEMICAL SYMBOLS AND FORMULAS (continued)

Pb	lead
PbO	lead oxide
PbCl	lead chloride
PCBs	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofurans
Q	1,2-*bis*(2-chloroethylthio)ethane
Sb	antimony
Se	selenium
SO_2	sulfur dioxide
Sn	tin
T	*bis*[2-(2-chloroethythylthio)ethyl]ether
TCDD	tetrachlorodibenzo-p-dioxins
Tl	thallium
V	vanadium
Zn	zinc

LIST OF IDENTIFICATION CODES FOR AUTOCLAVE INSTRUMENTS MONITORING REGULATED OPERATING PARAMETERS

A10-TIT-244	Autoclave Bin 1 Temperature Thermocouple
A10-TIT-243	Autoclave Bin 2 Temperature Thermocouple
A10-TIT-242	Autoclave Bin 3 Temperature Thermocouple
A10-TIT-241	Autoclave Bin 4 Temperature Thermocouple
A10-TIT-201	Autoclave Headspace Temperature
A10-PIT-203	Autoclave Vacuum Pressure
A10-PSH-203	Autoclave Pressure Switch High
TEN-083G *	Autoclave Agent GB Headspace Monitoring
TEN-083V *	Autoclave Agent VX Headspace Monitoring
TEN-083H *	Autoclave Agent Mustard Headspace Monitoring

* Only the Automatic Continuous Air Monitoring System (ACAMS) monitoring the agent contaminating the secondary waste will be on line during operation.

1.0 INTRODUCTION

The Tooele Chemical Agent Disposal Facility (TOCDF) was designed and built for the United States (U.S.) Army to destroy the chemical agent munitions stockpile at the Deseret Chemical Depot (DCD). EG&G Defense Materials, Inc. (EG&G), operates the TOCDF under contract to the U.S. Army through the office of the Chemical Materials Agency (CMA). The U.S. Environmental Protection Agency (EPA) identification number for the TOCDF is UT5210090002. The facility operates under a Resource Conservation and Recovery Act (RCRA), Part B Permit issued pursuant to the delegation of the State of Utah, Department of Environmental Quality (DEQ), Division of Solid and Hazardous Waste (DSHW), under the Utah Administrative Code, Section 315. The TOCDF also operates under a Title V Air Quality Permit administrated by the State of Utah, DEQ, Division of Air Quality (DAQ) and the Hazardous Waste Combustors Maximum Achievable Control Technology (MACT) rules. Under the requirements of these permits, the treatment systems must successfully demonstrate treatment of hazardous wastes while protecting human health and the environment.

The current TOCDF incinerators used to destroy the chemical weapons in the DCD stockpile are two Liquid Incinerators (LICs), a Deactivation Furnace System (DFS), and a Metal Parts Furnace (MPF). Secondary wastes are generated from the demilitarization of the DCD chemical stockpile. Secondary wastes contaminated with chemical agent are treated on-site prior to shipment for final disposal at off-site facilities. These secondary wastes include Personal Protective Equipment (PPE) such as Demilitarization Protective Ensemble (DPE) suits or butyl rubber coated garments (TAP Gear), packaging material (dunnage), plastic sheeting, spill absorbent, Life Support System (LSS) air hoses, spent activated carbon, and other miscellaneous wastes. Large amounts of wastes are currently being placed in storage, so the quantity of secondary wastes in permitted storage will continue to grow.

The current estimate of secondary wastes generated by TOCDF operations is 1,000 tons. The Mustard Campaign requires the munitions to be processed in the MPF; therefore, only a limited time is available for the processing of secondary wastes in the MPF. This will result in significantly extending TOCDF closure to allow processing of both the munitions and the secondary wastes in the MPF. To minimize this impact, TOCDF intends to install and operate an autoclave for the purpose of treating secondary waste. ~~with a headspace agent concentration greater than or equal to (≥) 1.0 Vapor Screening Limit (VSL) as determined by an Automatic Continuous Air Monitoring System (ACAMS) and a Depot Area Air Monitoring System (DAAMS).~~

Secondary wastes will be sorted based on the waste evaluation conducted in the Drum Ventilation System (DVS). Those ~~wastes~~drums containing DPE suits with an ACAMS reading that is < 1.0 VSL ~~will~~may be shipped offsite to a Subtitle C Treatment, Storage, and Disposal

Facility (TSDF) per Condition 2.2.2.21. ~~Those~~The DPE suit wastes with an ACAMS agent concentration ≥ 1.0 VSL ~~and other wastes~~ are candidates for treatment in the autoclave.

An autoclave is a sealed vessel into which pressurized steam is injected. The elevated pressure at which the autoclave is operated allows the steam to reach temperatures > 212 ºF, the boiling point of water. These increased temperatures and steam from the autoclave will result in the hydrolysis of the chemical agents to non-toxic compounds that result in waste decontamination without waste incineration. Then these decontaminated wastes can be shipped off-site to a licensed Subtitle C TSDF for disposal as hazardous wastes.

A test is proposed to demonstrate the performance of this miscellaneous treatment unit. This test will be referred to as the Autoclave Demonstration Test (ADT). A set of samples will be collected to characterize the autoclave effluent streams, and a set of process data will also be collected to document the performance of the autoclave under the test conditions. Spiked samples will be recovered and analyzed to document the treatment effectiveness of the autoclave; and agent ~~emissions~~concentration in the headspace gas of the autoclave will be monitored ~~during~~at the ~~ADT~~completion of each run to ensure it is safe to open the autoclave.

EG&G will conduct the ADT, and collect the effluent stream-samples. At the conclusion of the process cycle, the headspace above the treated wastes will be monitored for agent to ensure there is not a vapor hazard when opening the autoclave. Two process samples will be collected; the condensate samples from the condensers that cool the exhaust from the autoclave, and the spiked samples. ~~The spiked samples will demonstrate the treatment of the agent in the wastes.~~ Spiked samples will be recovered and analyzed for agent to determine how much spiking agent and break-down products remain~~s~~ after treatment. The condensate samples will be analyzed by the TOCDF Chemical Assessment Laboratory (CAL) and a Utah Certified subcontractor laboratory for each parameter. ~~Spiked samples will be recovered and analyzed for agent to determine how much spiking agent remains after treatment.~~ Continuous headspace monitoring of the HVAC carbon filtration system midbeds and stack will be analyzed during the testing period. ~~No~~ E~~e~~xhaust gas samples (DAAMS) will be collected in addition to the headspace agent monitoring during the cooling/drying cycle of the autoclave. The analytical methods used to analyze the condensate samples will be from SW-846 (1) and Tooele Laboratory Operating Procedures (TE-LOPs). All procedures not currently in the permit must be approved per R315-2-15 prior to use.

1.1 BACKGROUND CHEMISTRY DISCUSSION

Autoclave processing was selected for secondary wastes because the environment it creates causes the chemical agents to undergo hydrolysis. Hydrolysis causes a substituent element in the compound to be replaced by a hydroxide group (-OH). However, this reaction proceeds at different rates for different compounds, and some compounds do not undergo hydrolysis reactions. In the case of mustard, the chlorine (the substituent element) is replaced with the hydroxide group, producing thiodiglycol. There are three different forms of Lewisite and

Lewisite L1 and L2 are easily hydrolyzed, however, Lewisite L3 does not hydrolyze because it does not have a chlorine atom available for the hydroxide group to replace.

Nerve agents GB and VX are compounds that can undergo hydrolysis reactions. They are both phosphonate esters that undergo substitution reactions at phosphorus to yield substituted compounds that are much lower in toxicity than the original compounds. Agent GB will undergo hydrolysis by the hydroxide group replacing the fluorine atom to yield isopropyl methylphosphonic acid.
Agent VX can undergo two different substitution reactions and yield either ethyl methylphosphonic acid (EMPA) or S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA-2192). The reaction that produces EMPA will also produce diisopropylaminoethanethiol. The EMPA can undergo further hydrolysis to produce methylphosphonic acid (MPA). The reaction products are dictated by the reaction conditions (2).

1.1.1 Agent Hydrolysis Studies

Table 1-1 shows the relative reaction rates for hydrolysis in aqueous solutions for the chemical agents treated at TOCDF based on data from the literature (3, 4, 5). This table shows the relative reaction rates as measured by the hydrolysis rate data and the thermal decomposition rate. The autoclave will operate at elevated temperatures and pressures, which will increase the reaction rate for the hydrolysis reaction. The thermal decomposition temperature shown in Table 1-1 is the temperature at which the autoclave will operate.

TABLE 1-1. RELATIVE REACTION RATES FOR CHEMICAL AGENTS

AGENT	VAPOR PRESSURE		VOLATILITY		HYDROLYSIS	THERMAL DECOMPOSITION
	@ 0 °C (torr)	@25 °C (torr)	@ 0 °C (mg/m^3)	@25 °C (mg/m^3)	**Rate** (Half Life)	**Rate** (Half Life)
VX	4.20E-05	8.78E-04	0.662	12.6	40 days @ 25 °C & pH = 7	35 hours @ 150 °C
GB	0.41	2.48	3,370	18,700	47 hours @ 25 °C & pH = 6	2.5 hours @ 150 °C
HD		0.106		906	8.5 minutes @ 25 °C & pH = 7	Decomposes @ 149 - 177 °C

An evaluation of the data in Table 1-1 and a review of literature on the hydrolysis of chemical agents (3, 4, 5) indicated that the chemical agents present in the secondary wastes can be successfully decontaminated in an autoclave. Agent VX is the most difficult agent to hydrolyze based on the hydrolysis rates of the three chemical agents. Mustard is hydrolyzed in minutes,

Agent GB in hours, and Agent VX only after 40 days of treatment at room temperature. This shows that Agent VX will be by far the most difficult agent to treat in the autoclave. It also indicates that elevated temperatures in the autoclave will be necessary to effect the destruction of Agent VX in a timely manner.

A 1985 study conducted by Battelle also investigated the use of steam to decontaminate rooms and whole buildings as a preparation for closure of facilities (6). A 120-minute reaction time was used for GB and VX, and the treatment conditions reduced the Agent GB ~~and mustard~~ concentrations below the detection limit, with only a trace of Agent VX detectable. A 20 minute reaction time was used for mustard with concentration below the detection lmit. These demonstrations showed destruction of greater than 99.5 % of the chemical agents. The reaction rate data for Agents GB, VX, and mustard are shown in Table 1-2.

TABLE 1-2. STEAM TREATMENT OF CHEMICAL AGENTS

PARAMETER	REACTION TIME (MIN)	RESIDUAL MASS OF AGENT (MG)	% DESTRUCTION
Agent GB	120	<0.2 ~~PQL~~	> 99.8
Agent VX	120	0.5	99.5
Mustard	~~1~~20	< 0.2~~PQL~~	> 99.8

A study conducted for the Centers for Disease Control determined that the reaction rate for the hydrolysis of Agent VX in a nearly-neutral pH solution was very dependent on the temperature of the reaction (7). The autoclave provides a unique environment that allows the temperature of the steam to exceed the normal boiling point of water through higher pressures in the vessel. This higher temperature will make the treatment of Agent VX possible in a reasonable amount of time. Figure 1-1 shows the exponential dependence of the reaction rate on temperature.

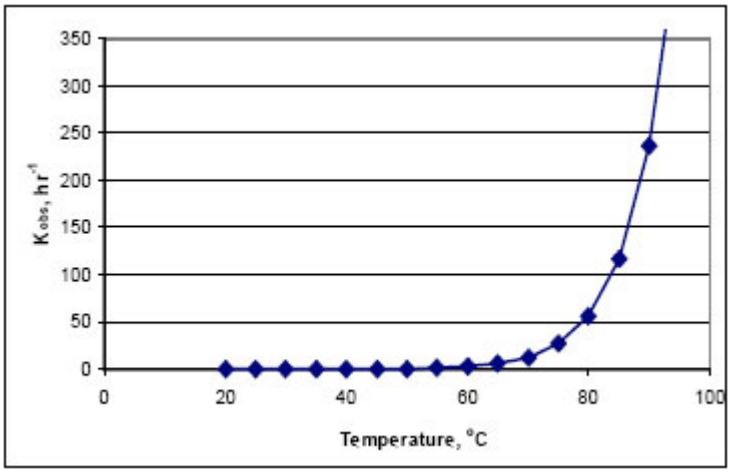

Figure 1-1. Temperature Dependence of Apparent Rate Constant for VX Hydrolysis at a pH of 7.7 (7).

1.1.2 Autoclave Studies

An initial study was conducted at the Bondtech factory in North Carolina and it showed that the treatment of secondary wastes in an autoclave is possible. This first study used a direct steam autoclave 3-feet in diameter, which demonstrated that the plastics melted but the DPE suits and rubber items remained intact (8).

The second series of tests was undertaken to show the ability of the autoclave to treat actual chemical agents. This series of tests was undertaken using Agent VX to demonstrate the compound that is most resistant to hydrolysis (based on the literature cited above). The data have shown that > 99 % of the agent was destroyed or removed from the spiked samples, but agent concentrations were found in the aqueous streams from the treatment process. The tests using wood as a waste stream showed that a lower amount of agent was removed from the spiking matrix, but lower concentrations remained in the headspace gas and the aqueous effluents. The other information developed by the second series of tests was the absence of EA-2192 in the spiked matrices and the effluent streams from the autoclave (9).

The third series of tests demonstrated of the treatment of DPE suits in plastic drums. It was conducted in a 6-foot diameter autoclave at the Bondtech Factory in North Carolina. Bondtech and EG&G personnel conducted the tests using 55-gallon (gal) plastic drums (10). Moisture sensitive packets were placed within the wastes to demonstrate if steam had penetrated the wastes. In addition, thermocouples were placed within the wastes to determine the inside temperatures of the wastes in the autoclave. The plastic drums and plastic bags that held the DPE suits both melted allowing the steam to access the DPE suits. The series of tests included some tests that did not adequately thermally treat the wastes as evidenced by plastic bags that did not melt and thermocouple temperatures that did not reach the treatment temperatures. However, the end result was that conditions could be modified to allow all the wastes to reach the required treatment temperatures, and steam did penetrate to the moisture sensitive packets. Therefore, the tests were very successful in demonstrating the full scale treatment of DPE suits in an autoclave.

These tests also demonstrated that wastes like DPE suits represent a worst-case example of the effect of packing density on the treatment of wastes. The voids within the drums are minimized by firmly packing the suits into the drums (rather than just setting them in), thereby increasing the packing density of the drum. Other wastes such as LSS hoses and wood will have more

voids within the drums, allowing better access of steam to the wastes, which in turn improves the effectiveness of agent treatment.

1.1.3 Headspace Monitoring Studies

A study was conducted by Battelle, at their Columbus, Ohio, research facility, on the applicability of headspace monitoring for secondary waste contaminated with chemical agents (11). The study looked at monitoring for Agent GB, Agent VX, and mustard. The objective of the test was to determine whether wastes contaminated at the Waste Control Limit (WCL) would have a detectable concentration using an ACAMS at the VSL level. The study used DPE suits, butyl rubber aprons (TAP Gear), wood, and charcoal. It concluded that the vapor pressure of the agents allows the agent concentration in the headspace to exceed ~~the~~ 1.0 VSL ~~alarm~~ for Agent GB and mustard regardless of the material contaminated, with the exception of the charcoal. The measurements were made at 4 hours after spiking the materials. Agent VX was detected between the 0.2 and 0.5 VSL concentrations~~, but not at the 1.0 VSL concentration~~.

The study also looked at concentrations on an accelerated monitoring schedule of 15 minutes and 45 minutes. These data indicated that the data collected at 15 minutes were higher in concentration than the data collected after that. These data indicate that monitoring the autoclave headspace should be performed within the first hour. Based on this, TOCDF proposes to sample the headspace at 15 minutes after completion of the drying and cooling cycle of the run.

The final point from the Battelle study was the evaluation of headspace concentrations at the contact hazard level (CHL), which was defined as the Negligible Severity (low-level) Effect Level for Percutaneous Liquid Exposure (11). The matrices were contaminated with 0.55 mg of Agent GB and Agent VX. The GB results exceeded the 1.0 VSL limit by 400 to 500 times. The VX results exceeded the limit by a factor of 7 to 27.

The conclusion is that if waste is contaminated at the WCL or CHL, an ACAMS is capable of detecting the agent in the headspace of the container or vessel being monitored.

A second study was conducted to determine if the headspace reading on a drum differed from readings in the individual bags inside the drum. A total of 30 drums were tested and it was found that all the bags inside the drum had been cut open before being placed in the drum. The drums were rotated on a drum roller to determine if the first reading was the same as the reading collected after mixing the drum and it was determined that there was no statistical difference in the two readings. ~~Therefore, the agent concentrations in the headspace of the drums represented the agent concentration throughout the drum.~~ It was also found that 26 of the 30 drums tested had an agent concentration that was < 1.0 VSL indicating that the decontamination of the contents before being placed in the bags was effective (12).

1.2 AUTOCLAVE DEMONSTATION TEST PLAN ORGANIZATION

This plan describes the operating ~~conditions,~~conditions; samples collected, and sample analyses for the ADT. The Quality Assurance Project Plan (QAPP) (see Appendix A) describes the sampling and analyses to be conducted. Appendix B provides the Shakedown Plan that will be used to prepare the autoclave for the ADT. Appendix C provides additional supplemental information.

1.3 FACILITY INFORMATION

The TOCDF is located in EPA Region 8, and the TOCDF EPA Identification Number is UT5210090002, which is also the DSHW RCRA Permit number. The DCD Title V Operating Permit Number is 4500071001.

The ADT points of contact are:

Thaddeus A. Ryba, Jr., TOCDF Site Project Manager
11620 Stark Road
Stockton, UT 84071
(435) 833-7439

Mr. Gary McCloskey, TOCDF General Manager
EG&G Defense Materials, Inc.
11600 Stark Road
Stockton, UT 84071
(435) 882-5803

Mr. Steven Brow, ADT Test Director
EG&G Defense Materials, Inc.
11600 Stark Road
Stockton, UT 84071
(435) 882-5803

1.4 SECONDARY WASTE SORTING PROCESSES

The TOCDF secondary wastes are generated from the demilitarization of chemical munitions and bulk containers. They are typically single-use items, discarded process equipment, or agent-

contaminated dunnage. These secondary wastes were generated within the TOCDF Munitions Demilitarization Building (MDB) and were exposed to liquid chemical agent or chemical agent vapors within the MDB. Therefore, a high probability exits that secondary wastes are contaminated with chemical agent, which requires on-site treatment.

The secondary waste will be sorted in the DVS/DVSSR (Igloo 1632) and treated in the autoclave (Igloo 1631), if applicable~~necessary~~. Containerized secondary waste will initially be moved from its current storage location in Area 10 to
Igloo 1633, which was permitted as a Container Storage Hazardous Waste Management Unit (HWMU). Igloo 1633 will serve as a staging area to hold drums of secondary waste that are to be sorted, and sorted drums of waste that are being held to accumulate a sufficient quantity to support autoclave operations.

Drums of secondary waste are sorted into two waste categories at the DVS/DVSSR (Igloo 1632). Each waste drum is placed into the DVS, where the headspace of the drum is monitored for chemical agent using an ACAMS. Secondary wastes will be treated in the autoclave, once the waste stream has been approved by the Executive Secretary for processing. ~~with headspace ACAMS results that are ≥ 1.0 VSL are candidates for additional on-site treatment in either the autoclave or in the MPF.~~

1.5 AUTOCLAVE SECONDARY WASTE MANAGEMENT SUMMARY

Drums of secondary waste (DPE, LSS and Wood)~~with ACAMS results of ≥ 1.0 VSL~~ will be moved to Igloo 1631 for autoclave treatment. The autoclave will be installed in Igloo 1631, which is located in DCD Area 10. This igloo was previously used to sample the DCD Mustard Ton Container (TC) Stockpile. The gloveboxes that were used to sample the TCs have since been removed in anticipation of the autoclave installation.

The autoclave system includes:

- an autoclave,
- the boiler to provide steam to the autoclave and vacuum systems,
- chillers to cool the gas stream and condense water vapor,
- an air blower that supplies cooling air to the autoclave after the thermal treatment,
- a transfer ~~holding~~ tank to collect the condensate until it can be pumped to storage,
- a Programmable Logic Controller (PLC), and

- ~~two~~Two 1,000-gal Spent Decontamination Solution System (SDS) Tanks to store aqueous wastes until shipment offsite.

Waste is fed to the autoclave in poly drums and the drums are placed in 64.7-cubic-foot (ft^3) waste bins. The autoclave can hold up to four waste bins. A liner is placed in the bin prior to placing multiple drums of secondary waste into the bin. The drum size will vary between 1~~2~~ gallon to 110 gallons, but the majority of the drums are 55-gal in size. The number of drums placed in the bin is a function of their size and waste density and four 55-gal drums can be placed in each bin. It is anticipated that there will not be very many drums larger than 55-gal, but in those instances where they are encountered, they will be handled on a case-by-case basis. This may include placing a single drum in the center of the bin, or two drums on their sides in the bin. The physical dimensions will dictate the placement of the drums, but in no cases will four drums larger than 55-gal be placed in one bin.

Drum weights will be~~have been~~ recorded for each drum of secondary wastes. The drum weights will be compared to the maximum allowable drum weights before the drum is placed in the bin. Drums used during shakedown and the ADT will be repacked for specific tests or the placement of thermocouples or spiking assemblies. These drums will be weighed before they are placed in the bins. All drums will have a weight and weight density recorded before they are loaded in the bins.

Drums are moved to the opening of the autoclave and a minimum of one thermocouple ~~is~~will be placed in a minimum of one drum in each bin. Placement and number of thermocouples will be optimized during the shakedown period. DSHW will be notified 7 days in advance when thermocouple testing will be performed. These thermocouples will monitor the temperature of the wastes during the treatment process. Placement of the thermocouple and any other necessary waste preparations ~~will~~may occur in the DVS/DVSSR (Igloo 1632) or at a location determined during shakedown.~~ or next to a fume hood, which is located on one side of the autoclave vessel to allow the air flow from the worker side, across the waste, and into the fume hood~~. ~~Exhaust gas from the fume hood is ducted to the carbon filter system, which supports autoclave and DVS operations that will occur concurrently in adjacent Igloo 1632.~~ ~~The autoclave load/unload door is hinged on the side opposite the fume hood.~~

The autoclave bins are loaded into the autoclave using a lift and internal chain conveyor so no confined space entry will be required. The leads from the thermocouples are connected to the PLC system or data logging system if more than four thermocouples are required and the door to the autoclave is closed and sealed~~ closed~~.

A steam eductor draws a vacuum on the autoclave interior down to 10 inches of mercury (inHg). The air drawn from the autoclave and the eductor steam are mixed at the eductor resulting in a water-saturated gas. This gas passes through two condensers and ~~a demister that remove~~a demister that removes most of the moisture from the gas stream before the gas exhausts to a carbon filter system. The condensed water vapor is drained to a 175-gallon transfer~~ holding~~

tank. When the transfer~~holding~~ tank contents reach about 150 gal, it will be pumped to one of two 1,000-gal SDS tanks.

After the autoclave pressure reaches 10 inHg, the steam eductor is stopped, and steam is directed from the boiler to the autoclave. The autoclave is a direct-steam design, so the steam injected into the autoclave contacts the secondary waste material inside (as opposed to an indirect-steam design where the steam passes through tubes that run through the autoclave). The maximum operating pressure and temperature of the autoclave are 85 pounds per square inch gauge (psig) and 330 ºF, respectively.

Autoclave operations are controlled by a dedicated PLC. The PLC will record the autoclave pressure, temperatures of the autoclave headspace thermocouple and the four waste thermocouples as a function of time, and the treatment time at the treatment temperature. The waste tracking form will record the run number, date, time run started, time run ended, the differential pressure of the carbon filtration system, the wastes treated in the run, and the weights and contents of the drums. The operator can select and control the operating temperature and duration of temperature soak. Once the temperatures inside the waste bins, as measured by the thermocouples, reach the setpoint, a timer starts with a predetermined time, and the temperature and pressure within the autoclave is maintained for that time period.

The autoclave will have a minimum of two cycles where a vacuum is drawn on the vessel followed by the addition of steam to the vessel. These cycles help the waste reach the minimum treatment temperature in a reasonable time and facilitate the movement of steam throughout the waste load. During the heating of the wastes, the plastic bags will melt and open the wastes to treatment of the agent by the steam. When the minimum temperature is reached, the soak timer will start and will run until the set time is reached. If at any time one of the four thermocouples falls below the minimum treatment temperature, the timer will stop until the thermocouple temperature increases above the minimum temperature.

When the process timer expires, steam is once again directed to the eductor, and the interior of the autoclave is evacuated. This post-treatment evacuation step is intended to dry and cool the treated waste inside the autoclave. The water vapor removed from the autoclave is condensed and collected in the transfer~~holding~~ tank, which will be emptied at the end of the run.

Upon completion of the final evacuation process step, the interior of the autoclave is backfilled with ambient air at atmospheric pressure. Ambient air is passed through the autoclave using an external blower introducing about 300 cubic feet/minute (cfm) to dry and cool the wastes for a minimum of 30 minutes. The duration of this cooling/drying cycle will be optimized during shakedown. After the drying/cooling cycle, the autoclave will be sealed and allow any agent present in the wastes to off-gas and develop a headspace agent concentration. After a minimum of 15 minutes, the ACAMS and DAAMS will be used to determine the headspace agent concentration. The 15 minute time period was based on the Battelle study on headspace monitoring (11) that determined that 15 minutes was the optimum time period for the agent concentration to stabilize, but the time will be set by testing during the shakedown period. The

ACAMS will determine the agent concentration in the head space using a minimum of one complete ACAMS cycle to determine the agent concentration. If the ACAMS agent concentration is indicated to be in greater than or equal to ~~excess of~~ ~~1.~~0.5 VSL, the DAAMS tubes will be analyzed. The DAAMS result will be the confirmation of the agent concentration. If the DAAMS tubes are analyzed, their result will be the agent concentration used to determine the handling of the wastes. Each batch QPs must be in control. If the agent concentration is < ~~1.~~0.5 VSL, the treatment of the secondary waste to remove agent contamination is complete, and the treated wastes are removed from the autoclave, placed in a rolloff, and shipped to a Subtitle C TSDF. If the confirmed agent concentration is ~~≥ 1.~~
≥ 0.5 VSL, then the waste is treated by another autoclave cycle.

The liner that was initially placed in the waste bins will be sealed to enclose the secondary wastes by collecting the sides of the bag to the center and securing the liner closure with plastic or wire ties. The bin is taken outside the igloo, and the bin's contents are transferred into a roll-off, which will be filled until the weight limit or volume limit are reached. The roll-off will then be covered and shipped off-site to a Subtitle C TSDF as hazardous waste.

Note that the temperature at which the autoclave is operated does not result in a reduction in the ~~volume~~mass of the waste treated. In other words, autoclave operations do not incinerate the wastes it treats, and therefore, does not result in the generation of ash. The polyethylene bags (in which secondary waste is typically packed) melt, exposing the wastes inside to the steam, which hydrolyzes the agent compounds into non-toxic compounds.

In addition, the wastes treated in the autoclave are classified as F999 hazardous waste ~~only~~ because they are residues from the treatment of chemical agent contaminated items. ~~The secondary~~Other wastes ~~(e.g., plastic or wood) do not include chemical compounds or elements that would categorize the items as hazardous waste when discarded. An example is the DPE suits; the plastic is not hazardous~~codes may apply and ~~would not~~will be ~~a danger if it had not been exposed to chemical agents~~added when the waste is shipped offsite.

1.6 AUTOCLAVE DEMONSTATION TEST OBJECTIVES

The objectives for the TOCDF ADT are to:

- Demonstrate the ability of the autoclave to treat ~~a~~ DPE, LSS hoses and Wood~~variety of~~ secondary wastes to agent concentrations that allow the safe handling of the wastes until they can be shipped to a Subtitle C TSDF. The demonstration that the agent has been destroyed will be based on spiked samples and the amount of agent remaining on the spiked samples after treatment.

- Establish operating conditions governing the treatment of secondary wastes in the autoclave that establish an operating envelope for~~that allows the~~ treatment of the secondary wastes based on waste temperatures and treatment times.

- Characterize the condensate samples to include Agent VX, agent hydrolysis compounds, Volatile Organic Compounds (VOCs), Semi-Volatile Organic Compounds (SVOCs), polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), and metals, to establish the final treatment for the condensate waste stream.

- Monitor for Agent VX in the autoclave headspace after treatment to ensure no agent is present before opening the autoclave.

- Monitor for Agent VX (DAAMS) in the gases exiting the autoclave during the cooling/drying cycle for the ~~compliance test~~ADT. ~~.~~ The Executive Secretary may waive this requirement after review of the monitoring data collected during shakedown.

1.7 PROPOSED ADT PROGRAM

This ADT will establish ~~permit limitations for~~ Operating Parameter Limits (OPLs) for the autoclave for treatment of Agents GB, VX, and mustard contaminated secondary wastes. The OPLs will include a minimum treatment temperature, maximum drum weight/weight density for each waste stream~~type~~, and treatment time at the treatment temperature. The ADT will demonstrate treatment of a secondary waste feedstock to demonstrate worst-case agent contamination for secondary waste treatment. Three types of waste in drums will be treated in the ADT. Since the autoclave is a batch feed treatment system, the shakedown period will be used to determine the optimum charge volume, maximum individual drum weight, and ~~charge interval~~treatment time at the treatment temperature for these secondary wastes. The system pressures will vary between a vacuum of about 10.0 inHg to a positive pressure less than 85 psi under steam treatment. ~~Operating Parameter Limits (OPLs) for the autoclave will be established by the ADT~~The temperature and pressure are directly related, but they both will be recorded.

The drums used for the ADT will be specially prepared to demonstrate the maximum individual drum weight/weight density and the destruction of chemical agent. The maximum individual drum weight will be demonstrated by hand packing the drums to reach the desired weight in each drum. This may involve adding wastes from different drums into one drum. The chemical agent destruction will be measured -using spiked samples placed in the bottom third of the drums. A minimum of three spiked samples will be placed in a minimum of three drums of each type of waste. This will result in a minimum of nine spiked samples for each run. The number of spikes will be determined during shake-down. DSHW will be notified seven days in advance of spike testing. The spiked samples will be recovered after the run and they will be returned to the CAL for analyses.

Samples of the condensate draining from the condensers will be collected at the beginning of the run when the autoclave is first evacuated, two more condensate samples will be collected when the autoclave is evacuated during the heat up of the wastes, and then a final sample will be collected during the final evacuation of the autoclave and the drying cycle. These samples will be analyzed for for the parameters listed in Section 1.6.

Agent concentration of the air exiting the autoclave during the cooling/drying cycle will be monitored using DAAMS for VX at the 0.5 VSL. The Executive Secretary may waive this requirement for this ~~compliance~~ test~~long term operation~~s after review of the monitoring data collected during shakedown. The DAAMS tubes will include a QP sample for each run to verify that the sampling would not affect the retention of the G-Analog of Agent VX on the DAAMS tubes.

Agent concentrations in the autoclave headspace will be monitored using ACAMS and DAAMS. The headspace of the autoclave will be monitored after treatment is completed, but an agent concentration in the waste will not be determined before treatment; therefore, a Destruction and Removal Efficiency (DRE) based on agent emissions cannot be calculated. The success of the test is based on the demonstration of agent removal from the spiked samples.

The agent monitoring will occur after the steam treatment of the wastes and the cooling/drying step. The blower will use room air from the igloo to blow through the autoclave to reduce the temperature and moisture content of the autoclave before agent monitoring. Removing the moisture will allow the agent monitoring to take place with minimum interference from the moisture during sampling. The agent monitoring will follow the sequence: The ACAMS and DAAMS will have the V/G pads changed, the ACAMS will be challenged, then the agent ~~monitoring of the~~ headspace monitoring will take place, and then the sample line will be challenged. If the ACAMS agent concentration is greater than or equal to ~~1.~~0.5 VSL, then the DAAMS tubes will be analyzed, otherwise the DAAMS tubes will not be analyzed.

1.8 ADT SAMPLING AND ANALYTICAL PROTOCOLS

Discussions of the sampling and analysis procedures are provided in Appendix A. The structure of the ADT is designed to meet the objectives in Section 1.6. The ~~exhaust gas sampling and~~ analytical methods to be used to quantify specific ADT parameters are taken from SW-846 (1) and TE-LOP. These methods are described by the following:

- The Agent VX will be monitored in the headspace in the autoclave to determine whether Agent VX remains unhydrolyzed in the wastes by the ACAMS (TE-LOP-524) and the DAAMS (TE-LOP-522). The DAAMS tubes will be analyzed for Agent VX (TE-LOP-562).

- Spiked samples will be analyzed after treatment to demonstrate that an agent detection limit of less than 1 mg/kg was achieved~~at least 99 % of the agent has been removed from the spiked samples~~. The spiked samples will be extracted and then analyzed (TE-LOP-572). ~~And will be approved per R315 prior to use.~~

- Condensate samples will be analyzed by the CAL for Agent VX, and its hydrolysis products ~~by the CAL.~~ (EA-2192, EMPA, and MPA) using TE-LOP-572.

- A subcontractor laboratory will analyze the condensate samples for VOCs using SW-846, Method 8260B; for SVOCs using SW-846, Method 8270D~~C~~; for PCDDs/PCDFs using SW-846, Method 8290A, and for metals using SW-846, ~~Method~~ Methods 6020A and 7470A (1).

- TOCDF shall monitor/analyze the gases exiting the autoclave to the HVAC for VX (0.5 VSL), with DAAMS tubes ((TE-LOP-522/TE-LOP-562) , for the cooling/drying cycle. The Executive Secretary may waive this requirement for this ~~compliane~~ test~~long te~~rm ~~operation~~ after review of the monitoring data collected during shakedown.

1.9 FINAL WASTE FEED LIMITS

Three types of secondary wastes will be demonstrated during the ADT~~, but other~~ to establish the operating parameters for the autoclave. Other secondary wastes listed in Tables 5-1, 5-2, and 5-3 may~~wil~~l be qualified for treatment in the autoclave based on the results of ~~this test and this is discussed in Section 5.~~the ADT and the results of function tests that are required by the Permit Modification. The four bins will be filled with drums of the three types of secondary waste. One bin will be filled with DPE suits, a second with LSS hoses, a third with wood, and the fourth with contain drums with the three types of waste. ~~Any secondary~~Weight limits on the wastes to be ~~containing sludge~~processed will ~~only~~ be ~~treated in the MPF. Although not all secondary~~by individual drums maximum allowable weight~~s~~/weight density by waste ~~types will be~~type based on the weights demonstrated during the ADT~~, each will be approved for processing in the autoclave as a result of this ADT, with the exception of carbon and contaminated soils, which will be demonstrated in separate demonstration tests.~~ .

2.0 ENGINEERING DESCRIPTION OF THE AUTOCLAVE TREATMENT SYSTEM

The autoclave will be installed in Igloo 1631, which is located in DCD Area 10. This igloo was previously used to sample the DCD Mustard TC Stockpile. The glove boxes that were used to sample the TCs have since been removed in anticipation of the autoclave installation. The entire installation includes:

- A direct steam autoclave;
- A boiler and associated water treatment system;
- A conveyor system to load the bins into the autoclave;
- A vacuum system;
- A two stage condensing system;
- Air blower to cool and dry autoclave contents;
- A demister to remove water droplets after the condenser.
- One 175-gallon transfer ~~holding~~ tank and transfer pump;
- A PLC; and
- Two 1,000-gal SDS Tanks.

2.1 AUTOCLAVE DESCRIPTION

The autoclave was built by Bondtech Corporation of Salisbury, North Carolina. The autoclave is 6 feet in diameter and 20 feet long with a capacity to hold four waste bins or 16 55-gal drums. The waste bins are made from stainless steel and they are 4 feet 6 inches wide by 4 feet 8 inches deep by 3 feet 1 inch tall. The autoclave is a direct steam autoclave, which means that the steam comes into direct contact with the waste in the autoclave and does not provide heat to tubes located inside the autoclave. The planned autoclave operating temperature will be 305 °F which is equal to a pressure of about 60 psig. The maximum pressure to the autoclave is 85 psig and the dual pressure relief valves on the autoclave vessel are set to vent at 85 psig. The temperature and pressure are directly related; therefore, the maximum temperature is 330 °F based on a

pressure of 85 psig. The autoclave vessel is pressure rated to 163 psi. Therefore, the relief valves will release well before the vessel is in danger of bursting.

The autoclave vessel will be located inside Igloo 1631 and the air within the igloo will be vented to the carbon filter system. This will result in the igloo being under engineering control and any agent released in the igloo will be collected in the carbon filtration system when all doors are closed.

~~A fume hood is attached along the side of the opening to the autoclave to provide engineering controls over any emissions that might be generated by transfer of wastes to the bins, placement of the thermocouples in the drums, or placement of the drums in the bins. The hood is set up to draw air from the worker's side, across the drums, and into the hood.~~

The autoclave is equipped with a powered lift to move the bins onto a chain drive that moves the bins on the inside of the autoclave. The side-hinged door on the autoclave can be closed and an air-tight seal established to allow the autoclave to be a pressure vessel.

Temperatures in the autoclave are controlled using thermocouples placed in the headspace region of the autoclave and within the wastes to record the temperatures experienced by the wastes. The headspace temperature prevents overheating/over pressurization of the autoclave. The thermocouples within the waste ensure temperatures in the wastes have reached the treatment temperature by the PLC controlling the system. Steam is added to the autoclave until all the thermocouples reach the minimum temperature. The temperature is maintained at the setpoint by the addition of steam to the autoclave until the minimum time at temperature is reached for the waste load.

Any moisture that condenses on the inside of the autoclave is collected in drains in the floor of the autoclave, and the condensate is drained, sent to the steam eductor, condensers, and to a holding tank before it is pumped to the SDS tanks. The steam vent on the autoclave is directed to the steam eductor followed by a two-stage cooler to condense the water vapor and any organic compounds exiting the system.

2.2 BOILER DESCRIPTION

The boiler was manufactured by Sellers Engineering Company of Danville, Kentucky, and is a horizontal, single pass, firetube boiler designed to burn natural gas. The boiler is rated at 5.2-million British thermal units per hour (Btu/hr), which is capable of operating to 125 psig. This maximum operating pressure is well below the autoclave vessel pressure rating and would not be capable of over pressurizing the autoclave vessel. A water treatment system is also included to provide treated water to the boiler. A water softener is used to treat water in the boiler to minimize fouling of the boiler. The water treatment will also remove oxygen from the water to reduce boiler corrosion. The boiler provides steam to the autoclave for heating the waste and

steam to operate the steam eductor which provides the vacuum to lower the pressure in the autoclave. The boiler is fired by natural gas.

2.3 VACUUM SYSTEM DESCRIPTION

The steam eductor was designed to evacuate the autoclave to a pressure of approximately 5.0 inHg in four minutes. The evacuation time may be influenced by the amount of water or organic compounds that off-gas during the evacuation period. The steam that operates the eductor will be condensed in the cooling system and collected in the SDS tanks. Use of a steam eductor saturates the air stream that is removed from the autoclave with water before it enters the condensers.

2.4 MOISTURE CONDENSING SYSTEM DESCRIPTION

The cooling system is a two-stage chiller. The first stage is a propylene glycol-chilled condenser with a cooling tower. The air exits the autoclave through the steam vent on the autoclave and is directed to a two-stage condenser to condense the water vapor and any organic compounds exiting the system. The gases removed from the autoclave are initially cooled in the heat exchanger after going through the steam eductor. The autoclave gases are cooled to ambient temperatures with this first stage of cooling.

The second stage of cooling is a refrigerant-cooled condenser used to further cool the gases removed from the autoclave. Both condensers are used to remove the moisture in the gases exiting the autoclave during evacuation. The condensate from the cooling step is drained to the condensate holding tank prior to being pumped to the SDS tanks.

2.5 AIR BLOWER SYSTEM

An air blower system was added to the autoclave system to provide air to cool and dry the wastes prior to opening the autoclave door to remove the wastes. The blower is a 30 horsepower CycloBlower Industrial blower manufactured by Gardner Denver of Quincy, Illinois. The blower was designed to flow approximately 300 scfm room air across the load. Once the moisture is removed by chilling the gases, the chilled and dried air stream is directed to an existing activated carbon filter system, which is used to remove any agent vapors prior to the air being released to the environment. The carbon filter system services both the autoclave operations in Igloo 1631 and the DVS/DVSSR operations in Igloo 1632.

2.6 COMPUTER CONTROL SYSTEM

The autoclave system is controlled with a PLC that automates the autoclave treatment process, evaluates the status, and records selected process parameters during treatment. Temperatures in the wastes will be monitored by the PLC until the minimum temperature is reached by each thermocouple. Once the temperature set point is reached, the PLC will start a timer for the minimum time for waste treatment. Temperatures and pressures will be recorded with a time line to allow reconstruction of the processing of each batch in the autoclave. The PLC will have the capability to down load its stored information to a computer for archiving data and preparation of the daily report.

2.7 SDS TANK STORAGE DESCRIPTION

The water condensed from the autoclave is collected and placed in two 1,000-gal storage tanks located inside the igloo. These tanks have secondary containment and are vented to the carbon filter system to prevent any emissions into the igloo. These tanks will be operated as ≤90-day accumulation tanks to hold the collected autoclave condensate.

Condensate will be collected from the cooling system, pumped to the SDS tanks by the condensate pumps, and stored in the tanks until the contents can be analyzed and transferred to a Subtitle C TSDF. The liquid collected in the SDS tanks will be sampled and analyzed for Agent VX, EA 2192 and other applicable characterization parameters ~~per WAP~~. prior to disposal. If agent concentrations are above the WCL, sodium hypochlorite will be added to the tank and then the tank contents will be circulated to mix the contents. The liquids will then be sampled and analyzed again to ensure the agent concentration is below the WCL. The SDS tank design made provisions for the addition of decon to the tanks and mixing the tank contents after the decon ~~had~~has been added.

2.8 AWFCO DESCRIPTION

There are no Automatic Waste Feed Cutoffs (AWFCOs) associated with the autoclave. The operation of the autoclave will be controlled by the operations SOPs, which will be used to control the start of the autoclave cycle to ensure the SDS tanks are not overfilled or the door is not opened unless the ACAMS readings are < ~~1.~~0.5 VSL.

2.9 AGENT MONITORING SYSTEMS

Operations of the agent monitoring systems are discussed in Attachment 22 to the TOCDF RCRA Permit (~~12~~13) and in Appendix A of this document. Agent concentrations in the autoclave headspace gases are monitored using ACAMS and DAAMS. The gases exiting the autoclave during the cooling/drying cycle will be monitored with DAAMS. The Executive Secretary may waive this requirement after review of the monitoring data collected during ~~Agent~~shakedown. Agent monitoring during the ADT will be for Agent VX. These systems have undergone extensive testing and evaluation under both simulated and actual field conditions.

Operations of the ACAMS and DAAMS are controlled by Laboratory Operating Procedures. These systems use a Gas Chromatograph with a Flame Photometric Detector (GC/FPD) for the detection of Agent VX. Agent VX is not volatile enough to be easily analyzed by GC, so a silver fluoride impregnated conversion pad is needed to convert Agent VX to its more volatile G-Analog. The G-Analog can be easily analyzed by GC. The silver fluoride pad will be located at the distil end of the sample probes for both the ACAMS and DAAMS. These pads will be changed on a per batch~~daily~~ basis. ~~or as directed by Attachment 22 (1213).~~

The precision and accuracy of each monitoring system is determined through actual on-site testing after installation of the equipment and then checked at periodic intervals. These data are used to establish quality control bounds, calibration and challenge frequencies, and procedures. These challenge frequencies and procedures are then delineated in a quality control plan for each system.

The ACAMS will monitor the autoclave headspace after completion of the autoclave cycle and will run for a minimum of one complete ACAMS ~~cycles~~ cycle on the headspace gas~~ and if~~. If the agent concentration is < ~~1.~~0.5 VSL, then the ~~wastes will~~autoclave can be ~~released to be shipped off-site.~~safely opened. If the agent concentration is ≥ ~~1.~~0.5 VSL, then the DAAMS tubes will be analyzed to confirm the ACAMS ~~reading~~concentration or the contents will be treated through another cycle in the autoclave.

The DAAMS tubes will collect sample over the same time period as the ACAMS if co-located or during the cooling/drying cycle if primary. The DAAMS tubes will include a QP sample to verify that the sampling would not affect the retention of the G-Analog of Agent VX on the DAAMS tubes.

3.0 SAMPLING AND ANALYSES PROCEDURES

The sampling and analysis objectives for the TOCDF ADT are to:

- Demonstrate control of agent emissions by showing that the agent concentrations ~~after treatment remain below the detection limits~~ in the autoclave headspace ~~of the autoclave~~. after treatment is~~are~~ < 0.5 VSL.

- Demonstrate removal of agent by analyzing spiked samples after treatment.

- Determine whether other organic compounds are off-gassed during autoclave treatment by analyzing the condensate samples for VOCs, SVOCs, metals and PCDDs/PCDFs.

~~Determine if metals are being removed by analyses of the condensate samples for 20 different metals.~~

3.1 SAMPLING LOCATIONS

Three types of samples will be collected for the ADT: ~~exhaust~~ autoclave headspace gas samples, condensate samples and spiked samples. Upon completion of the final evacuation process step, the TOCDF shall monitor the gases exiting the autoclave to the HVAC for VX (0.5 VSL), with DAAMS tubes, for the cooling/drying cycle. The Executive Secretary may waive this requirement after review of the monitoring data collected during shakedown. The ~~exhaust~~autoclave headspace gas samples will be collected ~~in the autoclave headspace~~ through a sampling port on the side of the autoclave to ensure there is no remaining agent before opening the autoclave. ~~Condensate samples will be collected from the discharge side of the condensate transfer pump between the condensate holding tank and the SDS tanks.~~ The condensate or a portion of the condensate will be collected in a condensate collection container. ~~during the time periods the condensate samples will be collected~~. The individual sample bottles will be filled from the condensate collection container. The spiked samples will be recovered from the wastes in the bins after they have been removed from the autoclave.

3.2 SAMPLING METHODS

The autoclave headspace gases will be monitored using the ACAMS and DAAMS. As a safety precaution, autoclave headspace gases will be monitored for Agent VX with an ACAMS using TE-LOP-524 and additional requirements specified in the QAPP, Appendix A to ensure that the

Agent VX concentration is < ~~1.~~0.5 VSL. The DAAMS tubes will sample the headspace gases during the same time period that the ACAMS is sampling the headspace gases using TE-LOP-526 and additional requirement specified in the QAPP, Appendix A. If the ACAMS determined agent concentration is ~~> 1.~~
~~>>~~ 0.5 VSL, then the DAAMS tubes will be analyzed, otherwise the DAAMS tubes will not be analyzed. These sampling methods are discussed in Appendix A (QAPP).

Condensate from the autoclave will be sampled to determine the concentration of Agent VX, Agent VX hydrolysis products, metals, VOCs, SVOCs, and PCDDs/PCDFs. The condensate from the condensers or a portion of the condensate will be collected each time the autoclave is evacuated. A set of sample bottles will be filled from the collected condensate. The samples will be collected as directed in Appendix A (QAPP).

3.3 ANALYSES METHODS

The DAAMS and condensate samples ~~are~~will be analyzed for agent and agent hydrolysis products by the CAL and the subcontracted laboratory will analyze the ~~liquid effluent~~condensate samples ~~are~~will be for the other parameters listed above in Section 3.2. ~~analyzed by the CAL and the subcontract laboratory~~.

3.3.1 Gas Sample Analyses Methods

The ACAMS and DAAMS methods are discussed in Appendix A (QAPP). The ACAMS analyses method is part of TE-LOP-524 because the analysis module is part of the ACAMS instrument. The gas sample is collected on the absorbent and then the absorbent is thermally desorbed into a field GC/FPD that conducts the actual analysis. The GC separates the agent from the other compounds and the FPD detects the phosphorus when the agent burns.

The DAAMS tubes are analyzed according to TE-LOP-562 The tubes are thermally desorbed into a GC/FPD where the organic compounds are separated from the agent by the GC and the agent is detected by the light emitted from the phosphorus in the agent when it burns in the FPD. The concentration is calculated by comparison to external standards. A QP sample will be analyzed with the field samples as a QC step and must be within 60 to 140 % recovery.

3.3.2 ~~Liquid~~Condensate Samples Analyses Methods

The ~~liquid~~condensate samples are analyzed for agent and agent decomposition products in an effort to better understand the decontamination process for wastes in the autoclave. The organic compounds will be extracted from the water matrix using chloroform and then analyzed by GC/FPD to detect the agent present in the samples.

The TOCDF CAL will analyze the agent decomposition products in the condensate samples. The compounds will be extracted using TE-LOP-572. The compounds will then be analyzed using TE-LOP-572.

The condensate samples will also be analyzed by the subcontract laboratory for VOCs by Gas Chromatograph/Mass Spectrometer (GC/MS) using SW-846, Method 8260B; for SVOCs by GC/MS using SW-846, Method 8270D~~C~~; for PCDDs/PCDFs using SW-846, Method 8290A, for mercury using SW-846, Method 7470A, and for the other 19 metals by Inductively Coupled Plasma/Mass Spectrometer (ICP/MS) using SW-846, Method 6020A.

3.3.3 Agent Spiked Samples

The spiked samples were sized to allow the entire sample to be extracted for analyses. A 10-gram (or smaller) sample matrix was used in all cases to allow the agent to be spiked on the matrix, treated, recovered from the waste, extracted, and the extract analyzed. Method TE-LOP-572 will be used for the extraction and analyses of the samples. The analytes will include Agent VX, EA-2192, EMPA, and MPA. ~~Each 10-gram sample matrix of DPE, LSS and wood will be spiked with 1ul of neat agent. This sample will then be placed in a extraction timble and sealed……~~ Prior to starting the Compliance Performance Test, all spiking procedures must be approved by the Executive Secretary. Spiking procedure may be developed during shakedown.

4.0 AUTOCLAVE DEMONSTRATION TEST SCHEDULE

The ADT is scheduled for the second quarter of 2009. The DSHW will be notified at least 30 days in advance of the actual ADT date. The ADT will begin after TOCDF has: received approval of the ADT Plan; Method approval, -successfully completed autoclave installation and startup; and successfully completed the autoclave shakedown. The ADT should span about 5 days: 1 day for setup, 3 days of testing, and 1 day for cleanup. Typical test runs will be one complete cycle of the autoclave.

The ADT will consist of one test condition with three replicate sampling runs. One run per day is planned. Actual sampling time during each sampling run will last about 8 hours. The autoclave will be charged with the wastes to be decontaminated and the process started. Once the autoclave is vented after the final segment of steam treatment, the autoclave will be filled with ambient air, which will flow through the autoclave for a minimum of 30 minutes. The flow will then be stopped to allow the agent concentration in the headspace over the wastes to stabilize, which will be a minimum of 15 minutes. The headspace will then be analyzed for agent using the ACAMS and DAAMS. This time period will be set based on the test results from the shakedown period.

5.0 AUTOCLAVE DEMONSTRATION TEST PROTOCOLS

The ADT will consist of three replicate runs performed with a mixture of wastes. The wastes used for this test will be spiked with Agent VX to demonstrate that the autoclave is capable of destroying the hardest agent. The following subsections will discuss the waste to be treated, the test operating conditions, ~~waste feed rates,~~ and total waste to be processed.

5.1 WASTE CHARACTERIZATION

The State of Utah has defined chemical agents as acutely hazardous and identified them as a P999 waste. The same identification is applied to any waste that has been contaminated by chemical agents. Once the wastes have undergone successful treatment, the waste code is changed to F999. In ~~speciaal~~ cases where it is not possible to analyze the treated residues to the waste control limit 20ppb GB/VX and 200ppb for mustard, the wastes will carry a ~~special~~ dual waste code of P999/F999. After treatment in the autoclave, the wastes can be shipped off-site to a Subtitle C TSDF.

~~Four different agent combinations will be processed in the autoclave and the various wastes to be processed are shown in Tables 5-1 to 5-3. In addition to the wastes listed in the tables, a set of wastes will be processed that could contain both Agent GB and Agent VX and this combination is limited to carbon from the agent filtration system (215,040 lb) and prefilters for the carbon filters (9,879 lb) that were used during the plant change over from Agent GB to Agent VX. Table 5-1 shows the secondary waste inventory for Agent GB and Table 5-2 shows the Agent VX secondary waste inventory summary. Mustard wastes to be processed are listed in Table 5-3. These tables demonstrate that the major items are directly covered by wastes treated in the ADT.~~ Tables 5-1 through 5-3 ~~These tables~~ list the wastes that are in storage currently and identify those wastes thought to be the best candidates for treatment in the autoclave. The three wastes streams demonstrated in the ADT may~~will~~ be approved for processing after successful demonstration, ~~the ADT with the~~ additional wastes listed in these tables may be approved ~~to be approved for processing~~ after approval ~~they have a~~ function testing has been ~~performed to~~ demonstrated and approved by the Executive Secretary. ~~their treatment in the autoclave.~~ These tables show that the total wastes to processed are over 1,079,744 lb plus the Agents GB/VX wastes for a total of about 1,305,000 lb.

Several waste streams are proposed for treatment in the autoclave, but only three will be demonstrated by the ADT: DPE suits, LSS hoses, and wood. These wastes will be contained in polyethylene/ polypropylene drums. Wastes designated as DPE suits will be DPE suits and the plastic bags the suits were stored in with possibly some DPE tape. Wastes designated as wood may also contain items such as metal banding, plastic, paper, and tape. The wastes designated as LSS air hoses are anticipated to be just hoses, but may contain a small fraction of other items

such as hose fittings. The materials will not be sorted to more closely resemble the actual wastes that will be treated on a daily basis. ~~The segregation of the wastes into separate bins is not necessary and the fourth bin will have a drum of each of the three waste types.~~

~~TABLE 5-1. Agent GB Secondary Waste Inventory~~
~~1 page~~

TABLE 5-1. AGENT GB SECONDARY WASTE INVENTORY

Profile	lb	Percent of Total	Planned Treatment	Autoclave Treatment Covered by
Carbon	109,394	29.8	Autoclave	Separate Carbon Function Test
Wood Dunnage	105,226	28.7	Autoclave	ADT Demo - Wood
Agent Contaminated Debris	73,798	20.1	Autoclave	ADT Demo - Function Test
Trash & Plastic	54,908	15.0	Autoclave	ADT Demo - Function Test
DPE Suits	7,267	1.98	Autoclave	ADT Demo - DPE
Carbon Filters/Plastic Holder	6,884	1.88	Autoclave	Separate Carbon Function Test
Paint Wastes	3,519	0.96	TBD	Not Applicable
Tap Gear	1,272	0.35	Autoclave	ADT Demo - Function Test
Sludges and Liners	2,486	0.68	TBD	Not Applicable
LSS Hoses	960	0.26	Autoclave	ADT Demo - LSS Hoses
Cotton Goods	526	0.14	Autoclave	ADT Demo - Function Test
Air Filters	284	0.08	Autoclave	ADT Demo - Function Test
Airlock Trash & V/G Pads	111	0.03	Autoclave	ADT Demo - Function Test
Agent Sampling Debris	119	0.03	Autoclave	ADT Demo - Function Test
Mortar Dry Mix	43	0.01	TBD	Not Applicable

Totals	366,797	100.0		

~~TABLE 5-2. Agent VX Secondary Waste Inventory~~

TABLE 5-2. AGENT VX SECONDARY WASTE INVENTORY

Profile	Weight (lb)	Percent of Total	Planned Disposition	Autoclave Treatment Covered by
DPE Suits	195,857	32.9	Autoclave	ADT Demo - DPE Suits
TAP Gear	133,522	22.5	Autoclave	ADT Demo - Function Test
*Airlock Trash, Booties	75,438	12.7	Autoclave	ADT Demo - Function Test
*Plastic	36,807	6.2	Autoclave	ADT Demo - Function Test
*Metal Maint. Equip	34,088	5.7	TBD	Not Applicable
LSS Air Hoses	22,925	3.9	Autoclave	ADT Demo - LSS hoses
Wood Dunnage	18,966	3.2	Autoclave	ADT Demo - Wood
Houghto 620	15,666	2.6	TBD	Not Applicable
*Non-Burnable Maint. Items	14,539	2.4	Autoclave	ADT Demo - Function Test
*Mine Debris	12,429	2.1	Autoclave	ADT Demo - Function Test
Paint Waste	7,112	1.2	TBD	Not Applicable
Charcoal Filters	6,679	1.1	Autoclave	Separate Carbon Function Test
Cardboard	6,505	1.1	Autoclave	ADT Demo - Function Test
*Absorbent		< 1	TBD	Not Applicable
*Electronic Equipment		< 1	Autoclave	ADT Demo - Function Test
V/G Pads	3,104	0.52	Autoclave	ADT Demo - Function Test
TYVEK, SARANEX	2,795	0.47	Autoclave	ADT Demo - Function Test
SDS Tank Liners	2,949	0.50	TBD	Not Applicable
SDS Sludge	642	0.11	TBD	Not Applicable
TOX Sump Sludge	1,806	0.30	TBD	Not Applicable
SDS Strainers/Debris	1,528	0.26	TBD	Not Applicable
Cotton Goods	575	0.10	Autoclave	ADT Demo - Function Test

Spent Sodium Lamps	376	0.06	Autoclave	ADT Demo - Function Test
SCBA Assembly	153	0.03	TBD	Not Applicable
Totals	594,461	100.0	-	-

* Complete description of waste will be determined during function testing.~~1 page~~

~~TABLE 5-3. Mustard Secondary Waste Inventory~~

TABLE 5-3. MUSTARD SECONDARY WASTE INVENTORY

Profile	Weight (lb)	Percent of Total	Planned Disposition	Autoclave Treatment Covered by
Tap Gear	28,733	24.1	Autoclave	ADT Demo - Function Test
*Airlock Trash, Booties	24,763	20.7	Autoclave	ADT Demo - Function Test
*Misc. Plastic	19,323	16.2	Autoclave	ADT Demo - Function Test
Poly Drums	10,928	9.1	Autoclave	ADT Demo - Function Test
*Non-Burnable	10,589	8.9	Autoclave	ADT Demo - Function Test
V/G Pads (HD)	7,154	6.0	Autoclave	ADT Demo - Function Test
Tyvek, OSHA A	6,907	5.8	Autoclave	ADT Demo - Function Test
Glovebox Gloves	1,697	1.4	Autoclave	ADT Demo - Function Test
*Metal Maint. Equip.(VX/HD)	1,494	1.3	Autoclave	ADT Demo - Function Test
Sampling Igloo HEPA Filter	1,490	1.2	Autoclave	ADT Demo - Function Test
DPE Suits	787	0.66	Autoclave	ADT Demo - DPE Suits
Charcoal Filters	693	0.58	Autoclave	Separate Carbon Function Test
Sampling Igloo Prefilters	672	0.56	Autoclave	ADT Demo - Function Test
SDS Strainers	606	0.51	TBD	Not Applicable
ACAMS, ONC Charcoal Filters	601	0.50	Autoclave	Separate Carbon Demo Test
*Maintenance Waste	584	0.49	Autoclave	ADT Demo - Function Test
Paint Waste	549	0.46	TBD	Not Applicable
*Metal Maintenance Equipment	472	0.40	Autoclave	ADT Demo - Function Test

Sand From HD Leakers	443	0.37	Autoclave	Separate Soil Function Test
LSS Hoses	430	0.36	Autoclave	ADT Demo - LSS hoses
*ECR Debris	393	0.33	TBD	Not Applicable
*HD Lab Impurity Stds/Residue	94	0.08	TBD	Not Applicable
Spent Sodium Lamps	38	0.03	Autoclave	ADT Demo - Function Test
*HD Solid Waste	6	0.01	TBD	Not Applicable
Totals	119,446	100.0	-	-

* Complete description of waste will be determined during function testing. ~~1 page~~

TABLE 5-4. AIRLOCK TRASH CHARACTERIZTION

Parameter	Drum 1 Contents		Drum 2 Contents	
	(lb)	(Wt%)	(lb)	(Wt%)
Total Contents Weight	111	-	76	-
DPE Booties	57	51.4	22	28.9
Butyl Gloves	25	22.5	22	28.9
DPE Tape	17	15.3	14	18.4
Plastic bags	12	10.8	18	23.7
-	-	100.0	-	100.0

Activated carbon treatment will be demonstrated in a separate ~~demonstration~~function test once the analytical methods are developed to show that the treatment of carbon hydrolyzes the agent present even if it is absorbed on activated carbon. The treatment of wastes in metal drums will be demonstrated in a separate function test to show that the contents of metal drums can be treated when the drum lids have been removed.

One mixed waste common to all the agents is airlock trash, which is shown in Table 5-4~~1~~ as trash and plastic. To better understand that waste stream, two drums of airlock trash were opened and the contents sorted; the summary is shown in Table 5-4. There were four items found in the drums: DPE booties, butyl gloves, DPE tape, and plastic bags. ~~Therefore,~~ The airlock trash could~~can~~ be treated in the autoclave ~~based on the major items demonstrated as ADT wastes. The drums of DPE suits treated in the ADT will contain DPE material, DPE tape, and plastic bags; while the LSS hoses are butyl rubber, thus covering the butyl rubber gloves found in the airlock trash.~~after an approved~~a~~ function test has determined the maximum individual drum weight that can be processed in the autoclave.

The wastes will not be characterized in detail for this test, but the agent concentration in the ~~headspace will be monitored after treatment as a demonstration that chemical agents are not present in the autoclave and~~ spiked samples will demonstrate that any agent present was treated and the headspace agent concentration will demonstrate that it is safe to remove the wastes from the autoclave. ~~The analyses of the spiked materials will demonstrate that the agent present in the secondary wastes has been destroyed.~~ The diversity of the matrices spiked will show that the agent destruction will take place regardless of the surface contaminated with agent.

5.2 TREATMENT STRATEGY FOR NON-ADT WASTE MATRICES

Other secondary waste matrices not demonstrated during the ADT will be processed ~~by limiting their feed based on their similarity to wastes demonstrated in the ADT.~~in the autoclave after completion of a function test for the waste type. Tables 5-1, 5-2, and 5-3 list the different secondary wastes currently in storage and ~~their justification~~whether they are candidates for treatment in the autoclave ~~without demonstrating every specific waste matrix. The treatment of DPE suits will demonstrate that the autoclave can decontaminate plastics at the autoclave operating conditions. The other plastics that would be similar to the DPE suits are the Level A suits, Kaplar suits, TYVEK suits, SARANEX suits, and general plastics listed for each of the waste streams. Other waste streams covered by the processing of DPE suits would be agent contaminated debris, trash and plastic~~Other waste streams must~~would~~ have a function test performed before the waste stream would be processed in the autoclave.

~~LSS hoses will demonstrate the treatment of rubber products, which would cover the processing of other rubber products such as rubber gloves and TAP Gear. The treatment of DPE suits and LSS air hoses will demonstrate the treatment of airlock trash.~~ Waste streams listed in Tables 5-1 to 5-3 that are not well defined such as agent contaminated debris, agent sampling debris, air filters, maintenance wastes, and trash will be characterized during the function test preparations

for each waste stream as discussed in the ~~revised~~ Module VIII. In preparation of function test for specific waste types, TOCDF will be able to open drums selected at random to determine the range of contents for waste types described as debris. Wastes encountered in drums that do not meet the definitions cannot be treated in the autoclave.

~~Wood will demonstrate that the agent can be hydrolyzed when it is absorbed into a porous material such as wood. Other cellulose materials such as cotton goods and the packing~~Another group of wastes are those with surface contamination where the surface cannot be penetrated and the contamination is limited to the surface area. These waste streams include agent sampling debris, metal maintenance equipment, non-burnable maintenance materials, electronic equipment, and spent sodium lamps. Treatment of these materials ~~used with the mine drums~~ would be demonstrated ~~covered~~ by a ~~the wood~~function test demonstration. ~~Other porous materials that could be covered by the processing of wood would include air filters, V/G pads, cardboard, and absorbent packages.~~ These varied surfaces can be decontaminated by steam, and then the non-porous surfaces of these items will be decontaminated as well.

~~TABLE 5-4. AIRLOCK TRASH CHARACTERIZATION~~
~~1 page~~

~~Another group of wastes are those with surface contamination where the surface cannot be penetrated and the contamination is limited to the surface area. These waste streams include agent sampling debris, metal maintenance equipment, non-burnable maintenance materials, electronic equipment, and spent sodium lamps. These materials treatment would be covered by the combination of the DPE, LSS hoses, and wood demonstrations. These varied surfaces can be decontaminated by steam, and then the non-porous surfaces of these items will be decontaminated as well.~~

~~Absorbent packages soaked in chemical agents will not be processed in the autoclave, but only in the MPF since their agent concentrations are high.~~

5.3 AGENT DESTRUCTION DEMONSTRATION

Materials designated as secondary wastes are mainly commercial items contaminated by contact with agent vapors or by surface exposure to liquid agents. These items are generally surface decontaminated with bleach or caustic before being placed in storage, which would further break down the agent concentration while in storage.

TOCDF will demonstrate the removal of Agent VX from a series of spiked samples as a demonstration that the wastes treated in the autoclave are safe to ship to a Subtitle C TSDF. The spiked samples will be placed in a minimum of three drums of each waste type. The spiking assemblies will be placed in the bottom third of the drum and wastes will be placed on and around the spiking assemblies. Additional spiking material may be required as determined during shake-down testing. The wastes will be hand packed onto the spiking assemblies to maximize the packing density to establish the worst case demonstration for agent treatment. After treatment, the spiked samples will be recovered from the wastes and analyzed for Agent VX. ~~TOCDF will show that the Agent VX is not a vapor hazard by monitoring the autoclave headspace and show that the Agent VX concentration is < 1.0 VSL.~~ The analysis of the spiked samples will show that the minimum amount of Agent VX removed is 99 %. ~~and therefore, the waste is not a contact hazard because the agent~~Agent VX concentration will be ~~≤~~ < 1 mg/kg or < 20ppb for ~~based~~~~VX based~~VX based on the spiked~~10-gram~~ samples. If TOCDF cannot obtain a waste control limit of 20 ug/kg~~ppb~~ for VX during the demonstration tests, then dual~~additional~~ waste code of P999/F999 will apply after treatment for the analytical detection of 1 mg/kg. TOCDF will also show that the Agent VX is not a vapor hazard by monitoring the autoclave headspace and show that the Agent VX concentration is < 0.5 VSL.

5.4 PROPOSED ADT OPERATING CONDITIONS

The ADT will be conducted under the normal operating conditions for the autoclave with the exception that the wastes will be spiked with Agent VX on 10-gram (or smaller) pieces of the sample matrices.

5.4.1 Autoclave Operating Conditions

The optimization of feed rates is based on the ability to demonstrate a maximum individual drum weight/density and the treatment time at the treatment temperature match the charge volumes and charge ~~intervals to the temperature and steam supplied to~~ in the autoclave. Waste feed rate limits for the ADT are proposed at 259 ft^3/charge with the demonstrated maximum individual drum weight/density. These feed rate limits are based on the capacity of the autoclave~~. Exact charge intervals~~ and ~~charge volumes~~the ability to have steam access the wastes. Drum weight/density~~s~~ and treatment times will be finalized during the shakedown period. The charge volume will not exceed 259 ft^3 and the total heat treatment time (i.e. time at temperature) will not be less than 3 hours at a minimum temperature of 275 °F. The DSHW will be notified if these

~~charge intervals and charge volumes~~times and temperatures change during the shakedown period, but the charge volume and heat treatment time will not exceed the values listed in this plan and the minimum temperature will not be less than 275 °F.

The ADT will include triplicate sampling runs using three different waste matrices in each charge to the autoclave. These runs will be conducted to demonstrate removal of the agent from spiked samples to a level that has an agent concentration that is less than 1 % of the original agent mass spiked onto the sample matrix and an agent ~~headspace~~ concentration in the autoclave headspace that is < ~~1.~~0.5 VSL. The ADT operating conditions will be discussed below.

~~The bins will be prepared such that air is drawn from the loading side to the hood at the mouth of the autoclave.~~ The feed material will be drums of DPE suits in one bin, drums of wood wastes in the second bin, drums of LSS air hoses in the third bin, and the fourth bin will be filled with drums of the three waste types. The bins for each run will be prepared before the run begins in the DVS/DVSSR. The shakedown will determine the optimum arrangement of the wastes for treatment.

Condensate samples will be collected for each run. The condensate or a portion of the condensate will be collected in a condensate collection container as it drains from the condensers. Sample bottles will be filled from the condensate collection container. Each time the autoclave is evacuated, the condensate samples will be collected. The final condensate sample will be collected into the cool down and drying cycle. It is anticipated that four condensate samples will be collected for each run.

The autoclave will operate with four bins at a time. The Test Director will authorize the run to begin when the bins have been placed in the autoclave and the door secured. The autoclave will then be evacuated using the steam eductor to develop a vacuum on the system. Once the vacuum goal is reached in the autoclave, the evacuation will stop and the autoclave will have steam added and the heating of the wastes will begin. A minimum of two additional vacuum/steam cycles will be used during the heating process to help the wastes reach the minimum treatment temperature. Once the waste temperature, as measured by the four thermocouples in the waste, reaches the minimum treatment temperature, a timer will be started that will maintain that temperature for a minimum of ~~120~~180 minutes. Adjustments to the time may be necessary based on system performance during shakedown. At the end of the heating cycle, a vacuum will again be drawn on the autoclave and the autoclave will be filled with ambient air. A blower will be used to add ambient air to the autoclave for a minimum of 30 minutes to cool and dry the wastes.

After cooling, the air flow will be stopped to allow the agent concentration in the autoclave headspace to be determined. The ~~autoclave will be allowed to reach a steady state~~ agent concentration will develop over a minimum 15-minute period based on the Battelle report on headspace monitoring (11). The time will be no less than 15 minutes, but it may be more than 15 minutes based on testing results during the shakedown period. The ACAMS and DAAMS will be used to determine the agent concentration for one complete ACAMS cycle. If the agent concentration is ~~greater than 1~~>~~.>~~ 0.5 VSL, then the DAAMS tubes will be analyzed, otherwise

the DAAMS tubes will not be analyzed. If the headspace agent concentration is ~~below 1.~~< 0.5 VSL, then the waste will be removed and placed in a roll-off bin ~~or in a DOT shipping container~~ until shipped to a Subtitle C TSDF. If the agent concentration is ≥ ~~1.~~0.5 VSL, the DAAMS tubes will be analyzed and if the agent concentration is confirmed, the waste will be treated in an additional cycle. A confirmed agent concentration ~~above 1.~~ ~~>>~~ 0.5 VSL will result in the run being aborted and require the waste to be treated by an additional cycle to remove the agent contamination. The aborted run and the operating conditions will be evaluated with possible changes proposed before another run is conducted. Another run will be made to replace the failed run.

The ADT will consist of three successful runs. There are two items that would invalidate a run; one is if one of the thermocouples indicated that the waste was not being adequately heated and the second is an ACAMS reading that is ~~greater than 1.~~≥ 0.5 VSL. ~~There are four thermocouples used and the test should be allowed to finish if one of the thermocouples fail, but if the thermocouple indicates that the waste is not being adequately heated, then the treatment time would never start and the run would have to be evaluated as to a solution to the problem.~~

5.4.2 Spiking Operations

Samples of DPE, LSS air hoses, and wood will be spiked with Agent VX to demonstrate the treatment of the wastes in the autoclave. After they are spiked, these samples will be placed in packages and sealed, placed in the wastes to be treated, then treated in the autoclave, recovered, and finally analyzed for Agent VX. One spiked sample from each matrix will be taken to the Igloo 1631, Autoclave for the same time period the other sample are treated in the Autoclave, but these QC samples will not be opened in the field, they will be transferred back to the CAL and ~~retained at the CAL as a control and~~ analyzed with the returned samples as a QC step.

A 10-gram (or smaller) sample of the matrix will be prepared for spiking. The DPE sample will be a 10 gram (or smaller) piece cut from DPE suit material that may or may not have been used. Then, 1 µL of neat Agent VX will be placed in the center of the DPE sample. The LSS air hoses will have a 10-gram (or smaller) section cut from a length of hose and 1 µL of neat Agent VX placed on the interior portion of the hose. The wood spiking matrix will be a section of a wood dowel with a hole drilled in the center of the dowel. The 1 µL aliquot of neat Agent VX will be pipetted into the hole in the wood dowel and the dowel replaced into the wood.

Once the samples have been spiked, they will be placed in various devices discussed below to allow the recovery of the samples for analyses. The DPE sample will be placed in an extraction thimble and the thimble will be placed inside a section of pipe with holes drilled in it to allow access of steam to the interior of the pipe. The pipe will be placed in a plastic bag and the bag will be placed in a vapor-tight container to prevent agent evaporation. The spiking assembly will then be transported to the staging area (DVS/DVSSR) where the vapor tight container will be opened, a wire cable attached to the pipe and the pipe placed in a drum with one package of DPE suits already in the drum. Additional DPE suits will be placed on top of the spiking assembly and a lid placed on the drum. The wire cable will be placed along the drum wall to assist in the

retrieval of the spiking assembly. The drum will then be placed in a bin and loaded into the autoclave. After autoclave treatment, the spiking assembly will be placed in a vapor tight container and returned to the CAL for analyses.

The spiked wood sample will be placed inside a section of pipe with holes drilled in it to allow steam access to the wood. The pipe will then be placed in a bag and the bag placed in a vapor-tight container to minimize the evaporation of agent. The spiking assemblies will be transported to the staging area where the vapor-tight container will be opened, a wire cable attached to the pipe, and the pipe placed in the center of the wood in the drum. The wood in the drum will be hand packed to maximize the weight of wood in the drum. The wire cable will be placed to assist in the recovery of the spiking assembly for analyses. The drum will then be placed in a bin and loaded into the autoclave. After autoclave treatment, the spiking assembly will be placed in a vapor tight container and returned to the CAL for analyses.

The spiked LSS hose sample will be placed in a plastic bag and the bag placed in a vapor-tight container to minimize the evaporation of agent. The spiking assemblies will be transported to the staging area where the vapor-tight container will be opened, and the spiked sample placed inside a hose that has been cut in the middle. The hose sections will be rejoined and placed in a drum with other LSS air hoses. The drum will then be placed in a bin and loaded into the autoclave. After autoclave treatment, the spiking assembly will be placed in a vapor tight container and returned to the CAL for analyses.

~~Three~~A minimum of three drums of each waste type will contain spiked samples. The number and placement of the spiked samples will be evaluated during the shakedown period to determine if more spiked samples are needed and where they should be placed within the drum. The spiked samples will be placed in areas least likely to receive adequate treatment based on the evaluation of treated wastes during the shakedown period; thereby providing a worst case situation to demonstrate that the worst locations still receive adequate treatment. Provisions will be made to locate the spiking assemblies so they can be recovered for analyses.

The autoclave will be carefully unloaded to allow the spiking assemblies to be recovered. Once the spiking assemblies are recovered, they will be placed in a vapor-tight container to protect the sample and minimize the evaporation of the agent or other compounds present. The container label will contain sample identification and identify the matrix and the sample location. The samples will be transferred to the CAL for Agent VX analyses.

The spiking methodologies will be finalized during shakedown. TOCDF will submit a final spiking protocol for each matrix to the Executive Secretary for approval prior to the start of the ~~Compliance Performance test~~ADT.

Drums will be weighed prior to moving into the autoclave waste bins using a calibrated scale to an accuracy of 0.5 pounds.

5.5 AUTOCLAVE TEMPERATURE RANGES

The anticipated temperature limits for the autoclave are between 275 °F and 310 °F. The anticipated temperatures will vary within this range. Initial heating of the loaded bins will continue until all four thermocouples reach the minimum temperature of 275 °F when the treatment timer will start. This temperature may be increased during shakedown depending on the autoclave performance, but the minimum temperature for the treatment timer to begin will not be less than 275 °F. The autoclave timer will continue the steam addition to maintain temperature for 180 minutes above 275 °F, but this time may be extended based on system performance during shakedown. The bins will then cool down until they are removed from the autoclave.

5.6 ADT WASTE QUANTITIES

The autoclave has the capacity to hold four waste bins, which have a volume of 64.7 ft^3 each for a total volume of 258.8 ft^3. For three runs, the total volume would be 776 ft^3. The waste drums range in size from ~~2~~ 1 gallon to 110 gallons, so the number of drums in the waste bin will vary based on the size of the drums. The volume of the waste load and the maximum drum weight and drum density of the individual drums by waste type are proposed as OPLs. The weight of the individual drums relates to the packing density of the waste in the drums. If the packing density is too high, the access of steam to the interior of the wastes is restricted. The weight of the waste in the drums do not affect the treatment time at the treatment temperature, but it can affect the amount of time required to heat the wastes to the treatment temperature. The time it takes loads of waste to reach the minimum temperature will vary, with the heavier loads experiencing a longer "ramp-to-temperature" time than the lighter loads. The "ramp-to-temperature" time is not part of the treatment time and should not be an OPL because the measure of success of the process is the amount of time at the treatment temperature. The process timer and thermocouples will ensure that these loads of various weights receive the same treatment time at the minimum temperature because the temperature of each thermocouple must reach the minimum temperature before the process timer begins to count down.

Table 5-5 shows some statistics on the weight of the drums to be treated in the autoclave. These statistics do not cover every drum, but they illustrate the range of weights of the drums and allow decisions to be made on the wastes to be used for the ADT. The number of drums is listed to indicate the basis for the statistics. The average weights listed are for the drums and their contents. The heavier weights for wood dunnage were usually for drums that were larger than 55 gallons. The total weight of the drum by waste type will be the OPL that is limited based on the

drum weight/density demonstrated during the ADT. The standard deviation is a measure of the variation from the average. The range of the weights is also shown. This data was used to set maximum weights for the demonstrated wastes in the ADT. The ADT will be conducted with 55-gal plastic drums and the maximum weights for the three waste types will be determined during the shakedown period, but they will not exceed 225 lb for DPE suits, 200 lb for LSS hoses, and 300 lb for wood dunnage in a 55-gal drum. The demonstrated weights may be less than these limits, but they will not exceed them.
Drums will be weighed prior to moving into the autoclave waste bins using a calibrated scale to an accuracy of 0.5 pounds.

5.7 AUXILLARY FUEL

Natural gas will be used to fire the boiler used to generate steam for the autoclave heating and the steam eductor. The natural gas used at TOCDF has an average heat content of 1,046 Btu/ft^3, and is 94.5 volume % methane, 3.88 volume % ethane, 0.46 volume % propane, 0.37 volume % nitrogen, and 0.61 volume % carbon dioxide based on data from December 2008.

TABLE 5-5. STATISTICS ON THE SECONDARY WASTE DRUMS

Waste Description	Number of Drums	Average Weight (lb)	Standard Deviation	Maximum Weight (lb)	Minimum Weight (lb)
VX DPE Suits	1567	127.7	22.7	222	54
VX Tap Gear	1118	122.1	19.2	201	58
Airlock Trash, Booties	591	129.6	34.4	259	35
VX Plastic	540	69.4	31.7	245	22
VX LSS Hoses	198	116.9	21.4	192	78
VX Wood Dunnage	148	127.3	54.3	293	38
GB DPE Suits	64	113.5	35.7	315	49
GB Wood Dunnage	512	204.4	58.4	410	44
GB Trash & Plastic	609	89.9	36.4	280	33
GB Agent Contaminated Debris	440	127.5	50.5	382	39
GB LSS Hoses	9	106.7	36.0	165	42
HD Tap Gear	127	109.1	24.4	185	41
HD Plastic	173	54.0	17.0	140	5

HD LSS Hoses	63	101.9	24.3	149	46
HD Airlock Trash, Booties	187	103.7	28.7	197	37

Notes:

These wastes represent 81.4 % of the VX Wastes.

These wastes represent 66.0 % of the GB Wastes.

These wastes represent 61.4 % of the Mustard Wastes.

~~Table 5-5. Statistics on the Secondary Waste Drums~~.

5.8 ADT REPORT

The final report will be a summary of the operating conditions recorded by the PLC, Agent VX concentrations in the autoclave headspace and spiked samples, condensate sample analyses, and copies of the final analytical data packages. The final report will be submitted within 90 days after the completion of the ADT to comply with the requirements for reports as stated in Title 40, Code of Federal Regulations, Part 63.1207(j) [40 CFR 63.1207 (j)].

5.9 AUTOCLAVE PERFORMANCE

The autoclave performance is discussed in this section as required by 40 CFR 264.601. The TOCDF believes that the conditions specified in Section 5.4 for the ADT will be adequate to meet the performance standards of 40 CFR 264.602 as incorporated into the TOCDF RCRA Permit while processing secondary wastes because:

- Testing conducted on a bench scale and full scale indicates that the autoclave will be successful in the treatment of agent contaminated secondary waste (9, 10).
- The range of operating conditions planned for the ADT is within the design envelope.
- The individual drum weights will be controlled to weights that are less than the maximum demonstrated during the ADT.
- The autoclave is controlled by a PLC and whenever hazardous waste is being treated in the autoclave, the autoclave will not be opened until the headspace gas has been tested and determined to be safe.
- Each batch of waste treated will be monitored with an ACAMS to ensure it is safe to open the autoclave.
- One condition with three runs was selected to demonstrate the autoclave operation with the specified secondary wastes.

6.0 SHAKEDOWN PERIOD PROCEDURES

Shakedown testing will proceed in accordance with the TOCDF ADT Shakedown Plan (see Appendix B). This shakedown plan defines all activities, methodologies, shakedown criteria, and compliance actions associated with the testing of the system. As stated in the shakedown plan, operating conditions will be maintained within the envelope of anticipated final operating limits throughout the shakedown period. These limits on operating conditions are based on good engineering practice, the bench-scale testing conducted at Southwest Research Institute (9), and the full-scale testing conducted at Bondtech's facility in North Carolina (10). These conditions will comply with the requirements of 40 CFR 264.601. Proposed operating conditions are preliminary, and final values will be confirmed or modified as shakedown progresses. Agent-contaminated secondary wastes will not be treated in the system at any time unless the conditions discussed above are satisfied.

This plan provides DSHW with a 60-day notice of the intent to conduct the ADT Shakedown and the anticipated start date. The shakedown will consist of up to 720 hours of secondary waste processing. The DSHW will be notified of the start date of the ADT two weeks before the test begins.

Once the approval of this plan is received from the DSHW, shakedown will commence as described in the ADT Shakedown Plan found in Appendix B. The entire system will be thoroughly tested during the shakedown period to verify that it performs in a safe, consistent, and predictable manner when processing secondary wastes.

6.1 ADT SHAKEDOWN

The objectives of the ADT shakedown are to:

- Demonstrate the ability of the autoclave to treat ~~a variety of~~ secondary wastes to agent concentrations that allow the safe handling of the wastes until they can be shipped to a Subtitle C TSDF based on demonstrated treatment of spiked samples of DPE suits, LSS hoses, and wood.

- Familiarize the operators and support personnel with the autoclave for decontaminating secondary waste.

- Determine the optimum charge volume, maximum individual drum weights/densities, and ~~charge intervals~~treatment time at the treatment temperature for secondary wastes to be processed during the ADT.

- Establish operating conditions governing the treatment of secondary wastes in the autoclave that establish an operating envelope allowing the treatment of the secondary wastes based on waste temperatures and treatment times. This will include establishment of the optimum locations and numbers of thermocouples in waste loads.

- Establish the number and location of spiked samples to ensure the agent is treated in every drum.

- Characterize the condensate samples to establish the final treatment for the condensate waste stream.

- Establish the process to monitor agent inside the autoclave to ensure satisfactory treatment of secondary waste.

- Validate the agent spiking process.

- Demonstrate that the autoclave can safely and efficiently treat secondary wastes at the ADT feed rates.

- Collect monitoring data for the gases exiting the autoclave during the cooling/drying cycle for review by the Executive Secretary.

The TOCDF will track ADT shakedown processing time as determined by the time the autoclave door seals to the time the door opens to remove the treated secondary wastes. Shakedown time will be counted only when hazardous waste~~when contaminated wastes~~ are treated. ~~Treatment of wastes that were monitored and determined to have an agent concentration that would allow it to be shipped off-site without treatment will not count against the shakedown time.~~

The shakedown will involve a series of tests as described in the ADT Shakedown Plan (see Appendix B). During this time, increasing numbers of drums and increasing weights of individual drums will be charged to the autoclave. The values of the regulated operating parameters will be recorded before the charge volumes or weights are increased or the charge interval adjusted. The charge volumes, individual drum weights/densities, and charge intervals to be used during the demonstration test will be determined during the shakedown period. The TOCDF may request final modifications to the ADT Plan based on data obtained during the shakedown period. If changes to the ADT plan are necessary, TOCDF will coordinate them with the DSHW.

6.2 POST ADT OPERATION

Treatment of secondary wastes in the autoclave will continue after completion of the ADT, but the treated wastes will be held on-site until the preliminary data from the testing can be submitted to DSHW and approved. The preliminary data submitted will include the operational data from the autoclave, agent concentration data from the autoclave headspace, the analyses results from the spiked samples, and the agent results from the condensate samples. Upon approval of the preliminary data submittal, the wastes treated during the ADT and the post-test wastes treated will be sent to a Subtitle C TSDF. The headspace in the autoclave at the end of the treatment cycle will continue to be monitored during this time period to ensure the agent concentrations are ~~less than 1.~~< 0.5 VSL.

6.3 AUTOCLAVE PERFORMANCE

TOCDF believes that the conditions specified in Section 6.0 for the startup, shakedown, demonstration test, and post-test operation will be adequate to meet the performance standards of 40 CFR 264.602 while processing secondary waste because:

- Test results from the Southwest Research Institute Report (9) indicate the agent is destroyed in the time frame used in processing secondary wastes in the autoclave.

- The headspace in the autoclave will be monitored for agent before the door is opened. If agent remains, the treatment time will be increased until the agent is destroyed.

- The autoclave operation during the shakedown and post-test periods will be controlled by the PLC and the SOPs directing the operation of the autoclave.

7.0 FINAL OPERATING LIMITS

The demonstration that agent is destroyed by treatment in the autoclave will be used to establish the operating permit limits for the autoclave. The successful completion of this ADT will establish the operating permit. The anticipated final operating conditions resulting from this ADT will be summarized in the ADT Report.

Agent destruction in the autoclave takes place by a hydrolysis reaction, which requires the water and temperature the steam introduces into the autoclave to go to completion. The temperatures measured in the wastes demonstrate operating conditions that ensure the destruction of agent. The waste feed rates demonstrated during this ADT and Agent VX will present the maximum challenge for the autoclave.

The following ~~Operating Parameter Limits~~OPLs will be established by the ADT:

- Maximum Secondary Waste Feed Rates – The ADT will be performed as close to the maximum feed rates as possible. The final approved permit limit for waste feed will be the demonstrated ADT feed rates. The demonstrated feed rate will include the volume of waste processed in the four bins and the maximum individual drum weights and drum densities by waste type.

- Minimum Autoclave Temperature – The minimum autoclave temperature will be 275 °F as the temperature to activate the treatment timer demonstrated during the ADT, provided that the agent is destroyed.

- Minimum Autoclave Time-The minimum autoclave time will be 180 minutes at the specified processing temperature needed to destroy agent.

- Agent Concentrations – The agent concentration in the spiked samples will determine the successful treatment of the wastes~~ and the~~. The agent concentration in the autoclave headspace ~~below 1.0~~will be < 0.5 VSL ~~will demonstrated~~to demonstrate that it is safe to open the autoclave to remove the wastes. This demonstration will allow TOCDF to place the treated wastes in a roll-off and ship the treated secondary wastes contained in the bins to a Subtitle C TSDF.

8.0 REFERENCES

(1) ***Test Methods for Evaluating Solid Waste, Physical/Chemical Methods***, 3rd Edition, including Update III, USEPA, SW-846, December 1996.

(2) ***Chemistry of VX***, Noblis website, www.noblis.org/ChemistryOfVX.htm

(3) Muro, N.B., S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, V. Hauschild, "The Sources, Fate, and Toxicity of Chemical Warfare Agent Degradation Products," ***Environmental Health Perspectives***, 1999, *107*, No. 12, December, 933-974.

(4) Yang, Y.C., J.A. Baker, J.R. Ward, "Decontamination of Chemical Warfare Agents," ***Chem. Rev.,*** 1992, *92*, 1729-1743.

(5) ***Chemical Agent Data Sheets***, EO-SR-74001, December 1974.

(6) Zamejc, E.R., E.J. Mezey, T.L. Hayes, D.K. Wetzel, B.C. Garrett, ***Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaiminated Facilities***, "Phase II – Laboratory Evaluation of Novel Agent Decontamination Concepts," **AD-B093 506**, Battelle Columbus Laboratory, Columbus, Ohio, June 1985.

(7) ***Assessment of the Treatability of Caustic VX Hydrolysate at the Du Pont Secure Environmental Treatment Facility***, Attachment #4, Carmagen Engineering, Inc., November 3, 2004.

(**8**) ***Autoclave Evaluation Test Report***, Continental Research and Engineering. LLC, Englewood, CO, Revision 0, April 21, 2008.

(**9**) J. Scott, R. Martinez, ***Autoclave Secondary Waste VX on DPE, Wood and Charcoal***, Final Report, Southwest Research Institute, San Antonio, TX, December 12, 2008.

(10) ***Autoclave Processing Test Report***, EG&G Defense Materials, Inc., Stockton, UT, November 25, 2008.

(11) E. Burckle, K. Siddoway, ***Testing of Headspace Monitoring for Waste Characterization***, Battelle, Columbus, OH, November 18, 2008.

(12) A. Shaffer, C. Mecham, K. McCarthy, ***TOCDF Drum Headspace Monitoring Testing***, Headspace Monitoring Phase II Testing, EG&G Defense Materials, Inc., Stockton, UT, February 6, 2009.

(~~12~~13) **Attachment 22 to the TOCDF Permit,** ***Agent Monitoring Plan***, EG&G Defense Materials, Inc., TOCDF CDRL 23.

TOOELE CHEMICAL AGENT DISPOSAL FACILITY (TOCDF)

DEMONSTRATION TEST PLAN FOR THE

AUTOCLAVE SYSTEM

APPENDIX A

ADT QUALITY ASSURANCE PROJECT PLAN

Revision ~~0~~1

~~October 21, 2008~~

March, 2009

APPENDIX A

QUALITY ASSURANCE PROJECT PLAN

TOOELE CHEMICAL AGENT DISPOSAL FACILITY

Facility EPA Identification Number: UT5210090002

Prepared for:

EG&G Defense Materials, Inc.
11600 Stark Road
Stockton, UT 84071

Prepared by:

EG&G Defense Materials, Inc.
11600 Stark Road
Stockton, UT 84071

Revision No.: **~~0~~**
1

Date: **~~October 21, 2008~~March, 2009**

1.0 TITLE PAGE

PROJECT TITLE:

**QUALITY ASSURANCE PROJECT PLAN
FOR THE TOCDF
AUTOCLAVE DEMONSTRATION TEST**

1.2 EXPECTED DEMONSTRATION TEST DATES: April 2009

1.3 PROJECT APPROVALS:

Thaddeus A. Ryba, Jr. **Site Project Manager**	**Date**
Gary Mc Closkey **EG&G DMI General Manager**	**Date**
Craig M. Young, Ph.D. **EG&G DMI Project Specialist**	**Date**
Subcontractor Quality Assurance Director	**Date**

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LIST OF ACRONYMNS AND ABBREVIATIONS

ACAMS	Automatic Continuous Air Monitoring System
~~ADAFC~~	~~ACAMS Dilution Air Flow Controller~~
ADT	Autoclave Demonstration Test
ASTM	American Society for Testing Materials
CAL	Chemical Assessment Laboratory
CAR	Contract Administrative Representative
CC	Correlation Coefficient
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
COC	Chain-of-Custody
~~CPSM~~	~~Column Performance Standard Mixture~~
CS	CAL Continuing Calibration Standard
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
%D	Percent Difference
DAAMS	Depot Area Air Monitoring System
DAQ	Department of Environmental Quality (State of Utah),

	Division of Air Quality
DCD	Deseret Chemical Depot
DCS	Duplicate Control Sample
~~DDAFC~~	~~DAAMS Dilution Air Flow Controller~~
DFS	Deactivation Furnace System
DPE	Demilitarization Protective Ensemble
DQO	Data Quality Objectives
DRE	Destruction and Removal Efficiency
DSHW	Department of Environmental Quality (State of Utah), Division of Solid and Hazardous Waste
ECL	Engineering Control Level
EG&G	EG&G Defense Materials, Inc.
EPA	U.S. Environmental Protection Agency
~~GC/FID~~	~~Gas Chromatograph/Flame Ionization Detector~~
GC/FPD	Gas Chromatograph/Flame Photometric Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
ICAL	Initial Calibration
ICP/MS	Inductively Coupled Plasma/Mass Spectrometer
ICV	Initial Calibration Verification
LC/MS	Liquid Chromatography/Mass Spectroscopy
LCS	Laboratory Control Sample
LIC	Liquid Incinerator
LOQ	Limit of Quantitation
LSS	Life Support System

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

MDL	Method Detection Limit
MPF	Metal Parts Furnace
MS	Matrix Spike
MSD	Matrix Spike Duplicate
PPE	Personal Protective Equipment
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QL	CAL Laboratory Control Sample

QP	CAL Field Surrogate Sample
%R	Percent Recovery
~~RATA~~	~~Relative Accuracy Test Audit~~
RCRA	Resource Conservation and Recovery Act
RF	Response Factor
RPD	Relative Percent Difference
RRF	Relative Response Factor
RRT	Relative Retention Time
RSD	Relative Standard Deviation
SEL	Source Emission Limit
SOP	Standard Operating Procedure
~~SPCC~~	~~System Performance Check Compounds~~
STEL	Short Term Exposure Limit
SVOC	Semi-Volatile Organic Compound
SW-846	Test Methods for Evaluating Solid Waste, 3rd Edition including Update III, USEPA, SW-846, December 1996.
TAP Gear	Butyl Rubber coated garments
TE-LOP	Tooele Laboratory Operating Procedure
TOCDF	Tooele Chemical Agent Disposal Facility
TSDF	Treatment Storage and Disposal Facility
VOA	Volatile Organic Analysis
VOCs	Volatile Organic Compounds
VSL	Vapor Screening Limit
WDM	Window Defining Mix
U.S.	United States

LIST OF UNITS AND MEASUREMENTS

acfm	actual cubic feet per minute
amu	atomic mass units
atm	atmospheres
cP	centipoise
cfm	cubic feet per minute
°C	degree centigrade

°F	degree Fahrenheit
D	Dalton
dscf	dry standard cubic feet
dscfm	dry standard cubic feet per minute
dscm	dry standard cubic meter
ft	foot
g	gram
g/sec	grams per second
gal	gallon
gpm	gallons per minute
gr/dscf	grains per dry standard cubic foot (1 atm, 68 ºF)
inHg	inches of mercury
inWC	inches of water column
Kg	kilogram
L	liter
L/min	liters per minute
µg	microgram
m^3	cubic meter
mg	milligram
mL	milliliters
mm	millimeter
N	Normal
ng	nanograms
ppb	parts per billion
ppm	parts per million
ppmdv	parts per million on a dry volume basis
lb/hr	pounds per hour
psig	pounds per square inch gauge
ΔP	pitot velocity pressure

LIST OF CHEMICAL SYMBOLS AND FORMULAS

Agent GB	Sarin or methylphosphonofluoridic acid 1-methylethyl ester
Agent VX	O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate
Al	aluminum

Ag	silver
As	arsenic
B	boron
Ba	barium
Be	beryllium
Cd	cadmium
Cl^-	chloride
Cl_2	chlorine
CO_2	carbon dioxide
CO	carbon monoxide
Co	cobalt
Cr	chromium
Cu	copper
DFTPP	decafluorotriphenylphosphine
HNO_3	nitric acid
Hg	mercury
HCl	hydrogen chloride
HF	hydrogen fluoride
H_2O_2	hydrogen peroxide
HpCDD	heptachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofuran
HxCDD	hexachlorodibenzo-p-dioxin
HxCDF	hexachlorodibenzofuran
$KMnO_4$	potassium permanganate
Mn	manganese
Mustard	*bis*(2-chloroethyl) sulfide
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
H_2SO_4	sulfuric acid
Ni	nickel
NO_x	oxides of nitrogen
O_2	oxygen
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofuran

LIST OF CHEMICAL SYMBOLS AND FORMULAS (Continued)

P	phosphorus
Pb	lead
PCBs	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofurans
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofuran
PFTBA	perfluorotributylamine
PFK	perfluorokerosene
Sb	antimony
Se	selenium
SO_2	sulfur dioxide
Sn	tin
TCDD	tetrachlorodibenzo-p-dioxins
TCDF	tetrachlorodibenzofurans
Tl	thallium
V	vanadium
Zn	zinc

3.0 PROJECT DESCRIPTION

The Tooele Chemical Agent Disposal Facility (TOCDF) was designed and built for the United States (U.S.) Army as a hazardous waste incinerator facility for the destruction of the chemical munitions stockpile at the Deseret Chemical Depot (DCD), 20 miles south of Tooele, Utah. The TOCDF is designed to dispose of chemical agents GB, VX, and mustard (H-series); drained munitions; contaminated refuse; bulk containers; liquid wastes; and explosive and propellant components. The TOCDF operates under a Resource Conservation and Recovery Act (RCRA) Permit issued pursuant to delegation by the State of Utah, Department of Environmental Quality, Division of Solid and Hazardous Waste (DSHW) under the Utah Administrative Code, Section 315. The TOCDF also operates under a Title V Air Permit from the State of Utah, Department of Environmental Quality, Division of Air Quality (DAQ). Emissions from the TOCDF incinerators are regulated under the joint authority of the Clean Air Act and RCRA. The U.S. Environmental Protection Agency (EPA) identification number for the TOCDF is UT5210090002.

The TOCDF facility has four incinerator systems designed to meet the RCRA performance requirements: two Liquid Incinerators (LIC1 and LIC2), the Metal Parts Furnace (MPF), and the

Deactivation Furnace System (DFS). Under the requirements of the TOCDF RCRA Permit, ~~the incinerator~~these systems must demonstrate an ability to effectively treat any hazardous wastes such that human health and the environment are protected.

Wastes are also generated from the demilitarization of the DCD chemical stockpile and are referred to as secondary wastes. Secondary wastes contaminated with chemical agent need to be treated on-site to prevent agent exposure at off-site facilities. Secondary wastes include Personal Protective Equipment (PPE) such as Demilitarization Protective Ensemble (DPE) suits and butyl-rubber-coated garments (TAP Gear), packaging material (dunnage), plastic sheeting, spill absorbent, Life Support System (LSS) air hoses, spent activated carbon, and other miscellaneous wastes. Large amounts of wastes are currently being placed in storage, so the quantity of secondary wastes in permitted storage continues to grow.

The current estimate of secondary wastes generated during the remainder of TOCDF operations is 1,000 tons. The mustard campaign requires most of the munitions to be treated in the MPF; therefore, there will be limited time available for the processing of secondary wastes in the MPF. This will result in significantly extended the duration of TOCDF closure by processing both the chemical munitions and the secondary wastes in the MPF.

The TOCDF intends to install and operate an autoclave for the purpose of treating the secondary waste inventory currently in storage in DCD Area 10. An autoclave is a pressure vessel into which steam is injected. The elevated pressure at which the autoclave is operated allows the steam to reach temperatures greater than the 212 ºF limit associated with atmospheric pressure steam. This increased temperatures and steam from the autoclave will hydrolyze any chemical agents to non-toxic compounds to provide an alternate treatment to incineration of secondary wastes. The decontaminated wastes can be shipped off-site to a licensed Subtitle C Treatment, Storage and Disposal Facility (TSDF) as hazardous waste.

A demonstration test, rather than a trial burn, is proposed to demonstrate the decontamination capability of the autoclave. This test will be referred to as the Autoclave Demonstration Test (ADT). A set of samples will be collected to characterize the autoclave effluent streams, and a set of process data will also be collected to document autoclave performance under test conditions. ~~Agent emissions will be monitored~~The agent concentration remaining in the spiked matrices will be determined and the agent in the headspace will be verified.~~determined, but an agent Destruction and Removal Efficiency (DRE) will not be determined~~.

EG&G Defense Materials, Inc. (EG&G), is responsible for operating the TOCDF, and conducting the ADT. EG&G is the principal data user and decision-maker for the ADT, but will subcontract some ADT analyses support. This support will include some analyses of the condensate samples and the Quality Assurance/Quality Control (QA/QC) associated with these samples. The subcontractor will provide in-process approvals with final acceptance and approval by EG&G. EG&G will be responsible for the collection of certain monitoring

information, system operating data, collection of the samples; and preparation of the final report.

This Quality Assurance Project Plan (QAPP) describes the sampling and analytical activities that will be performed by the TOCDF Chemical Assessment Laboratory (CAL) and the subcontract laboratory during the ADT. The QAPP was developed using methods from SW-846 (1) and EPA Region 6 guidance (2). The ~~gases leaving the autoclave will be analyzed for Agent VX using Depot Area Air Monitoring System (DAAMS) tubes, while the~~ autoclave headspace will be analyzed for Agent VX using an Automatic Continuous Air Monitoring System (ACAMS~~). Samples of the~~) and a Depot Area Air Monitoring System (DAAMS). The condensate samples will be analyzed for Agent VX~~,~~ (O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate), Agent VX hydrolysis products [S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA-2192), ethyl methylphosphonic acid (EMPA), and methylphosphonic acid (MPA)], Volatile Organic Compounds (VOCs), Semi-Volatile Organic Compounds (SVOCs), ~~and~~ metals, and polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDDs/PCDFs).

The ADT plan is designed to demonstrate that treatment of secondary wastes in the autoclave results in the destruction and removal of Agent VX ~~to~~ based on the analyses of the spiked samples showing a minimum of 99 % removal and that the autoclave headspace agent concentration is less than ~~1.~~0.5 Vapor Screening Limit (VSL) ~~in the headspace~~ above the treated wastes. ~~and that it is not a contact hazard based on the analyses of the spiked samples [1 milligram per kilogram (mg/kg)].~~ Scheduling for the project is found in the ADT Plan and will be updated as necessary. An example of a daily sample run schedule is found in Section 6.0. Individual project and quality records are identified in this QAPP. Data Quality Objectives (DQOs) for each method are found in Annex A to this QAPP, and Annex B contains resumes of the key individuals for this project. The DSHW will be updated if any changes occur.

4.0 PROJECT ORGANIZATION

The ADT organization is summarized in Figure A-4-1. This organization has three groups working together for the successful completion of the ADT. One group is the EG&G organization, the second is the Battelle group, and the third is the laboratory subcontractor. This project management structure anticipates the direct personal responsibility for each task and provides the mechanism for review and corrective action. The direct supervisory line of responsibility also provides flexibility and allows timely action to correct problems.

The EG&G Test Director has the overall responsibility for the ADT, and as such, is the point of contact between EG&G Operations and the ADT organization. The EG&G Contract Administrative Representative (CAR) will be the Test Director and will interface with the subcontractor organizations and the CAL. Annex B contains copies of the resumes of the

subcontractor key individuals involved in the ADT.

4.1 TEST DIRECTOR AND CONTRACT ADMINISTRATIVE REPRESENTATIVE

The Test Director is an employee of EG&G and has the overall responsibility for the conduct of the ADT. The Test Director will also serve as the CAR and has the responsibility of oversight of the subcontractors to ensure that they perform as directed by the QAPP and their contract. The CAR coordinates the activities of EG&G, Monitoring personnel, CAL personnel, and the laboratory subcontractor. In addition, the Test Director will coordinate the information to be provided in the final ADT Report. The duties of the Test Director include:

Ensuring that the feed is prepared for the ADT.

Establishing the system operating parameters as described in the ADT Plan.

Determining when Operations is ready to begin the performance run.

Notifying Monitoring personnel to begin sampling.

Determining whether the performance run is acceptable from an EG&G perspective.

Figure A-4-1. ADT Project Organization Chart

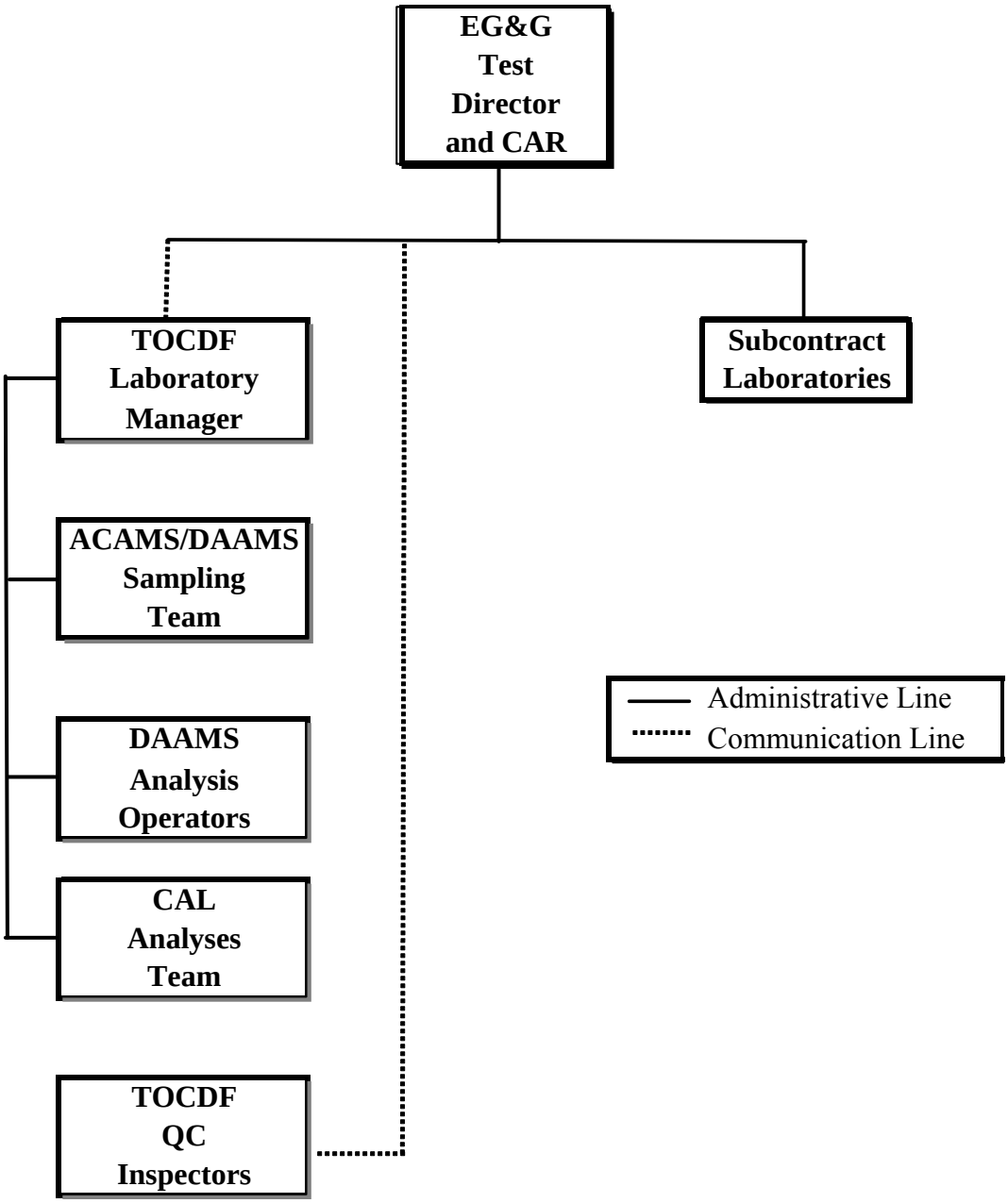

FIGURE A-4-1. ADT ORGANIZATION CHART

4.2 TOCDF LABORATORY MANAGER

The TOCDF Laboratory Manager is a Battelle employee who manages both the Monitoring group and the CAL. The Monitoring group has the responsibility for the ACAMS Sampling Team and the DAAMS Sampling Team. The CAL has the responsibility for the agent analyses, including agent ~~screening~~ analyses and the DAAMS analyses. The TOCDF Laboratory Manager is responsible for the tracking of samples through the CAL, archiving analytical data generated by the CAL, and the DAAMS analyses QC and verifying all laboratory procedures have been validated per R315 for each matrix.

4.3 SUBCONTRACT LABORATORY

The subcontracted laboratory will verify and document that the incoming field samples match the Chain-of-Custody (COC) and analyses request forms. They will be responsible for tracking the samples through the laboratory and performing the appropriate tasks to meet the QC requirements outlined in the QAPP. The laboratory subcontractor is responsible to ensure the samples are analyzed for the correct parameters and the development of the final data package submitted to EG&G. Additionally, the laboratories will be responsible for archiving the laboratory data that they generate. Subcontracted laboratories must be Utah certified for all methods/parameters reported or follow the procedures found in R315.

5.0 QUALITY ASSURANCE AND QUALITY CONTROL OBJECTIVES

The overall objective of the ADT is to demonstrate that chemical agents are treated in secondary wastes in the autoclave so that agent ~~emissions~~spiked samples will contain less than 1 % of the spiked agent. Also, the agent concentrations in the headspace are less than ~~1.~~0.5 VSL~~ and the wastes are not a contact hazard~~. To assess the quality of the data, a series of QC objectives have been established for each method used for the analysis of samples collected during the ADT. Summaries of the DQOs for the analytical data are presented in Annex A, and they will be used to evaluate the data generated during the ADT. The data quality indicators produced to meet the Annex A DQOs will be evaluated against the data to assess the data quality. Annex A was developed using the criteria in the Region 6 EPA Guidance (2), in EPA QA/G-5 (3), and SW-846 (1).

The field and analytical data will be reviewed for the ADT, and a complete assessment of the data quality indicators will be included in the ADT report. The data quality will be discussed

with regard to the planned data acceptance criteria and the overall project objectives. Data that are determined to be outside the QC limits will be evaluated relative to the overall project objectives to determine their impact on defining system performance. A discussion of this evaluation will be included in the ADT report.

Several procedures will be used for monitoring the precision and accuracy objectives of the analytical program. The sampling and analytical activities will follow standard referenced procedures whenever possible. Calibration standards, internal standards, Laboratory Control Samples (LCS), and surrogate compounds will be high-purity materials that are commercially available, when available. Prior to sample analysis, the analytical instruments will be calibrated per the reference method requirements to demonstrate that accurate performance levels are being met. Data precision and accuracy will be assessed by evaluating the results from the analysis of internal standards, surrogate compounds, laboratory blanks, calibration check standards, reagent blanks, method blanks, field and trip blanks, duplicate samples, and matrix or surrogate spiked samples. Sections 6.0 and 10.0 describe the project-specific QC sample types that will be analyzed and list the sampling and analytical methods to which they apply.

If analytical QC procedures reveal that a DQO has exceeded the target criterion, the source of the deviation will be identified, and corrective action will be taken, as described in Annex A. If data fall outside the acceptable range of precision and accuracy, even after the corrective action has been taken, those data points will be flagged and discussed specifically in the data validation report. Alternative procedures (either sampling or analytical) will be considered and recommended to the analytical project manager when necessary. Any changes or additions will be submitted to the DSHW for approval as soon as the need is identified.

5.1 EVALUATION OF PRECISION

Calculation of the precision for each analysis will be based on different criteria taken from the analytical methods. Estimates of precision are different for each method. Estimates of variability levels for replicate measurements of the same parameters are expressed in terms of Relative Percent Difference (RPD) for duplicate samples and as Relative Standard Deviation (RSD) when three or more data points are being compared. Section 13.1 discusses how the estimates of method precision will be calculated, and method-specific DQOs are listed by method in Annex A.~~.~~

Some analyses require the evaluation of a larger data set; in these cases, precision will be reported as RSD. When the analytical results approach the detection limit, precision often is affected adversely because of the enhanced uncertainty of determinations at the lower end of the method applicability. For those determinations near the method detection limit, the precision estimates that are outside the target DQOs will be flagged as estimated measurements. In cases

where duplicates are analyzed and one result is less than the Practical Quantitation Limit (PQL), the average will be calculated using the PQL, and the reported result will be flagged to explain that the precision was not calculated. Precision data will be calculated and presented in the data validation report.

5.2 EVALUATION OF ACCURACY

Accuracy will be expressed as a percent recovery for each method. The standard used to measure the percent recovery is method dependent and is identified in Annex A. Analysis of an LCS will be assessed as a measure of accuracy. Matrix effects on accuracy will be assessed using a Matrix Spike/Matrix Spike Duplicate (MS/MSD). A combination of LCS and MS/MSD analyses will be used to evaluate the accuracy of most analysis methods. Section 13.0 provides the accuracy calculations, and accuracy data will be presented in the data validation report.

Calculation of the accuracy for each analysis will be based on different criteria taken from the analytical methods. Accuracy measurements for the PCDD/PCDF analyses will be taken from the LCS data.

5.3 EVALUATION OF COMPLETENESS

Data completeness represents the percentage of valid data collected from a measurement system as compared to the total amount expected to be obtained under optimal or normal conditions. The completeness objective for the ADT will be to obtain representative results for all analytical parameters while operating the autoclave at the desired test conditions for a total of three test runs. The completeness DQO (100 % completeness) will be met if valid tests runs are obtained. Results for all samples collected and analyzed for valid runs will be reported. However, samples resulting from runs that are judged to be invalid based on field indicators of system performance will not be submitted to the laboratory for analysis and are not considered part of the sample completeness objective. Three complete runs will be completed. The impact of any sample loss will be assessed against the objective to obtain valid runs and will be discussed in the ADT report.

5.4 DETECTION AND REPORTING LIMITS

The laboratories will prepare Method Detection Limit (MDL) and PQLs for parameters to be analyzed for the ADT using the laboratory's Standard Operating Procedures and the analytical methods referenced in this document. Method Validation must be approved per R315. These limits will be compared to the actual analytical results in the final report. Analytes not detected in the analyses will be reported as less than (<) the PQL; analytes detected with a concentration

between the MDL and the PQL will be qualified as an estimate and reported. The laboratory conducting the analysis will determine the MDLs and PQLs. The PQLs for the ADT parameters are included in Annex A.

5.5 REPRESENTATIVENESS AND COMPARABILITY

Representativeness is defined as "the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, process condition, or an environmental condition." Comparability is defined as "expressing the confidence with which one data set can be compared to another" as discussed in EPA QA/G-5 (3).

The usefulness of the data is also contingent upon meeting the criteria for representativeness and comparability. Wherever possible, reference methods and standard sampling procedures will be used. The representativeness QA objective is that all measurements be representative of the media and operation being evaluated. Therefore, the detailed requirements for each parameter, given in their respective methods, will be followed to ensure representative sampling.

The comparability QA objective is that all data resulting from sampling and analysis be comparable with other representative measurements made by the sampling contractor or another organization on this or similar processes operating under similar conditions. The use of published sampling and analytical methods and standard reporting units will aid in ensuring the comparability of the data.

6.0 SAMPLING AND MONITORING PROCEDURES

The autoclave must demonstrate the ability to effectively treat the TOCDF secondary wastes such that human health and the environment are protected. The ADT will demonstrate that the autoclave operating parameters meet the required performance standards, and the data obtained will demonstrate compliance with these regulations. The ADT will be considered successful if analyses results fall within parameters stated in this QAPP.

This section describes the process and ~~exhaust~~headspace gas sampling procedures to be performed, and the equipment to be used, during the ADT, including sample types, sampling locations, and sample collection procedures. Any proposed modifications to approved methods or procedures will be presented to the DSHW for approval prior to implementation and will be documented in the final report. Figure A-6-1 shows the typical daily schedule for the ADT with the sampling times for the collection of the various samples.

6.1 PRE-SAMPLING ACTIVITIES

Pre-sampling activities include equipment calibration and glassware preparation. Calibration of the process control instruments is required on a regular basis. The calibration status of the autoclave ~~process control instruments~~thermocouple transmitters, pressure transmitters, and the ACAMS at the time of the ADT will be included in the ADT report.

The consumables used in the sampling for the ADT will be the sample bottles~~,~~ and extraction thimbles~~, and sachets~~. Sample containers require specialized cleaning to avoid contamination of the sample from the collection containers or sampling equipment. The sample containers will be purchased pre-cleaned, according to EPA criteria for clean containers per the specific container type and purpose. A certificate will be provided with the containers to document compliance with the specifications. The extraction thimbles ~~and sachets~~ will be one time use items used as received from the vendors, because agent contamination is not a possibility.

6.2 FIELD QUALITY CONTROL ACTIVITIES

The QC checks for the process data collection and sampling aspects of the ADT will include:

Use of standardized forms and field notebooks to ensure completeness, traceability, and comparability of the process information and samples collected.

Field checks of standardized forms to ensure accuracy and completeness.

~~Strict adherence to the~~The sample traceability procedures (i.e. COC) outlined in Section 7.2.1 will be followed.

Figure A-6-1. TYPICAL SAMPLING SCHEDULE FOR ADT_

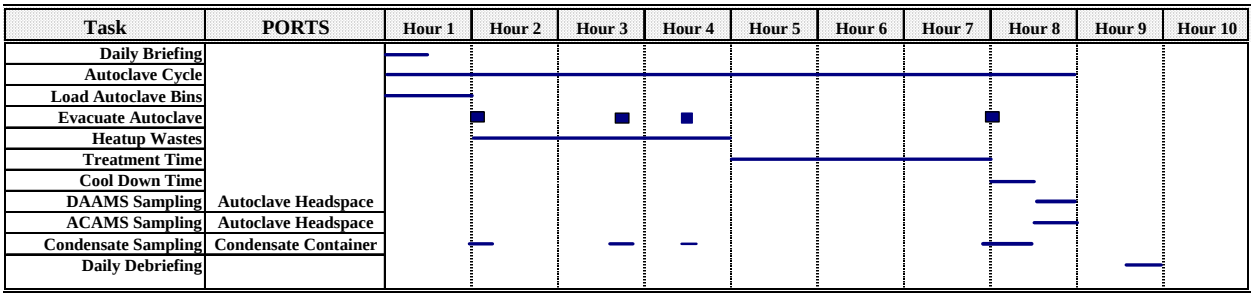

FIGURE A-6-1. DAILY SAMPLING SCHEDULE EXAMPLE FOR THE AUTOCLAVE DEMONSTRATION TEST

The QC field samples used for the ADT include blanks and field duplicates. Field blanks will be collected during the ADT for the DAAMS tubes~~ according to the sampling method. Samples from the field blanks are analyzed by the same methods as the samples~~. Trip blanks will be used to check for contamination resulting from the shipping and transport of the DAAMS samples and condensate volatile samples. These DAAMS tubes are transported from the analytical laboratory to the field site and returned to the laboratory for storage and analysis along with the field test samples. -The trip blank data are used to demonstrate that the samples are not exposed to fugitive contamination during storage and transport to their final laboratory destination. Field Spike will be a spike matrix that goes to the field, opened for the time the spikes, but never processed through the autoclave, and then transported back to the laboratory for analysis. ~~Trip blanks are analyzed for the same analytical parameters as the actual test samples.~~ A Field Duplicate sample of the condensate will be collected during one run and analyzed for the same analytes as the other condensate samples.

6.3 AGENT MONITORING METHODS

Agent VX monitoring will be conducted by TOCDF Monitoring Personnel during the ADT. The two agent monitoring techniques are the ACAMS and DAAMS. The ACAMS and DAAMS will monitor the headspace of the autoclave at the completion of ~~the~~each run~~ and the DAAMS will monitor the gas between the condensers and the carbon filters~~. The Test Director or a designated representative will authorize the sampling team to begin sampling. Operation of the agent monitoring system and detailed descriptions are provided in Attachment 22 to the TOCDF RCRA Permit (4).

Operations of the ACAMS and DAAMS are controlled by Tooele Laboratory Operating Procedures (TE-LOPs). These two monitoring systems use gas chromatographs with flame photometric detectors (GC/FPD) to detect the G-Analog of Agent VX. Analysis of Agent VX differs from the analysis of Agent GB due to the difference in volatility between the two compounds. Agent VX is not volatile enough to be easily analyzed by GC. Therefore, a silver-fluoride-impregnated conversion pad (V/G pad) is needed to convert Agent VX to its more volatile G-Analog, which can then be easily analyzed by GC. The silver fluoride pad will be located at the distil end of the sample probes for both the ACAMS and DAAMS. These pads will be changed ~~as directed by RCRA Permit Attachment 22 (4)~~each run~~on a daily basis~~.

~~A DAAMS station will sample the gas in the duct between the autoclave condensers and the carbon filter bank. The DAAMS sampling will begin just before the first vacuum~~
Upon completion of the final evacuation process step, the interior of the autoclave is ~~drawn on the chamber and end 30 minutes after the steam~~backfilled with ambient air at atmospheric pressure. Ambient air is ~~added to~~ passed through the autoclave~~. A second DAAMS sample will be collected from just before the second vacuum~~ using an external blower introducing about 300 cubic feet/minute (cfm) to dry and cool the wastes for a minimum of 30 minutes. The duration

of this cooling/drying cycle ~~begins and continue to 30 minutes after the steam is readmitted to the autoclave. These two DAAMS samples will~~ will be optimized during shakedown. After the drying/cooling cycle, the autoclave will be ~~collected to identify whether~~sealed and allow any agent ~~vapor is escaping~~present in the wastes to off-gas and develop a headspace agent concentration. After a minimum of 15 minutes, the ACAMS and DAAMS will be used to determine the headspace agent concentration. The 15 minute time period was based on the Battelle study on headspace monitoring (5) that determined that 15 minutes was the optimum time period for the agent concentration to stabilize, but the time will be set by testing during the shakedown period. The ACAMS will determine the agent concentration in the head space using a minimum of one complete ACAMS cycle to determine the agent concentration. If the ACAMS agent concentration is indicated to be greater than or equal to~~in excess of~~ 0.5 VSL, the DAAMS tubes will be analyzed. The DAAMS result will be the confirmation of the agent concentration. If the DAAMS tubes are analyzed, their result will be the agent concentration used to determine the handling of the wastes. If the ACAMS results show that the agent concentration is < 0.5 VSL, the treatment of the secondary waste to remove agent contamination is complete, and the treated wastes are removed from the autoclave~~.~~, and shipped to a Subtitle C TSDF. If the confirmed agent concentration is ≥ 0.5 VSL, then the waste is treated by another autoclave cycle.

Each run~~day~~ the V/G pad will be changed and systems leak checked. Then the ACAMS will be challenged to ensure the system is ready to monitor the agent concentration. The headspace samples will then be collected at the ~~appropriate~~ after the minimum time has elapsed to monitoring.~~time during the run~~. The ACAMS will monitor the agent concentration for a minimum of one complete ACAMS cycle, actual ACAMS~~sample~~ cycless~~times~~ will be determined during the shakedown period. The DAAMS tubes will sample the headspace gases from the time the ACAMS monitoring begins until the ACAMS monitoring is completed. This will be a minimum of one ACAMS cycle, but if additional ACAMS cycles are required, then the DAAMS will continue to sample until the ACAMS monitoring is completed. At the completion of the agent monitoring, the sample line will be challenged and the final leak checks will be made. If the ACAMS results indicate that the DAAMS tubes need to be analyzed, the tubes will be sent to the CAL for analysis. If the DAAMS tubes are not required to be analyzed, then the tubes will be returned to the CAL to be cleaned and reused.

6.3.1 Automatic Continuous Air Monitoring System

The ACAMS provides quantitative agent data and is capable of detecting Agent VX at the Engineering Control Level (ECL) (high-level), the VSL limits (low-level) in ambient air set by the U.S. Surgeon General for unmasked workers, and at the exhaust stack at the Source Emission Limit (SEL). Operation of the ACAMS is covered in TE-LOP-524 and the ADT Plan.

The ACAMS represents state-of-the-art instrumentation for the detection and quantification of chemical agents in workplace environments and the autoclave headspace gas. Some gases are difficult to sample because of their high temperature and high moisture content. The ACAMS

will monitor the autoclave headspace after the blower has cooled and dried the wastes in the autoclave.

The evaluation and testing program for these units in the field is rigorous. -Precision and ~~accuracy~~Accuracy data are generated while sampling actual exhaust gases during non-agent operations. The ~~Limit of Quantification (LOQ) of the~~ ACAMS agent concentration at the 1.0 VSL level is 0.~~00006~~00005 mg/m^3 VX with a Response Level of 0.000025 mg/m^3 VX. Testing and evaluation in all agent modes have been completed. All monitors met the 95-% confidence level for ± 25-% accuracy. Baselines studies on all monitors in Area 10 including the Autoclave monitors will be performed prior to implementation.

The ACAMS cycle time in the VX mode will be six minutes based on testing results. The ACAMS cycle time is divided into a sample collection period and a purging and analysis period. The ACAMS consists of a sampling pump, a sample collection module, a GC/FPD, a monitor with strip chart recorder, and a computer interface module for automated data acquisition. The ACAMS uses the GC column to separate other compounds from agent and the selectivity of its FPD to improve the specificity of the response to chemical agents. The ACAMS provides quantitative agent data.

6.3.2 Depot Area Air Monitoring System

The DAAMS is a sampling and analysis technique capable of detecting agents GB, VX, and mustard in ambient air at the VSL limits ~~and at the exhaust stack at the SEL~~ established by the U.S. Surgeon General for unmasked workers. The TE-LOP-522, ~~and~~ TE-LOP-562, QAPP and Attachment 22 cover collection and analysis of samples on the DAAMS tubes. A DAAMS sampling station will be located ~~in~~with the ACAMS and the samples will be withdrawn from a port on the ~~duct between~~side of the ~~condensers and the carbon filters~~autoclave vessel. The DAAMS sampling period for the ADT will be ~~about 40 minutes~~the same time as the ACAMS.

A Quality Plant (QP) sample is a field surrogate sample. A QP sample will be run with each DAAMS set during the ADT to verify that agent is not lost from the DAAMS tubes during sample collection. The QP sample is a DAAMS tube spiked with Agent VX before sample collection. It is a QC step to ensure agent will be detected if it is present.

6.4 PROCESS SAMPLING

Process samples will include condensate samples ~~collected from the discharge of the condensate pump~~ and spiked samples placed in the loaded bins as a test for destruction and removal of Agent VX. ~~Liquid samples will be collected from taps on the discharge side of pumps.~~

6.4.1 Liquid Sampling Method

~~Liquid process samples~~ Samples of the condensate will be collected during times when the autoclave is being evacuated using the ~~method described by the American Society of Testing and Materials (ASTM) Method 3370 (5)~~steam eductor. The ~~sample~~ condensate from the condensers will be ~~collected by attaching~~diverted or a portion of the condensate diverted to a sample ~~line to the tap and flushing~~collection container. Sample bottles will be filled from the sample ~~line~~collection container. The flush and any remaining sample will be managed in accordance with applicable EPA and DSHW regulations. ~~The sample line is inserted into the sample container, and the tap is opened to collect the sample. This method ensures that the actual material collected is representative of the stream.~~

Separate sub-sample bottles are used for each sample. The condensate samples will be analyzed by the CAL for pH, Agent VX, EA-2192, ~~ethyl methylphosphonic acid~~EMPA, and ~~methylphosphonic acid~~MPA. The subcontract laboratory will analyze the condensate samples for metals, SVOCs, ~~and~~ VOCs and PCDDs/PCDFs. To accommodate these analyses, the condensate samples will be placed in three Volatile Organic Analysis (VOA) vials, one 500-mL plastic bottle (metals), one 250-mL amber glass bottle (agent screen), one 500-mL amber glass bottle (SVOCs), and two 1-liter amber glass bottles (PCDDs/PCDFs).

6.4.2 Post-Test Sampling

Spiking samples will be recovered from the waste materials after the test has been completed to determine the amount of agent remaining on the spiking matrix. The spiked samples will be attached to a ~~string and the string~~wire cable placed along the outside of the waste materials to allow the spiked samples to be recovered ~~easily~~. The samples will be recovered and placed in an appropriately-sized amber glass bottle and sealed.

6.5 PROCESS MONITORING EQUIPMENT

Process electronic data output will be monitored carefully by operators in order to maintain steady-state operating conditions during the ADT. Process monitoring equipment will be inspected and calibrated ~~periodically~~every six months except for agent monitoring. Where duplicate monitors or methods of determination exist, the data generated will be compared for consistency. EG&G will be responsible for collecting operations data, the Permit-required monitoring information, and system operating data in accordance with Standard Operating Procedures (SOPs). Process data to be collected includes: autoclave atmosphere temperature, minimum of four thermocouple ~~lance~~ temperatures, feed volume and weight/weight density, autoclave pressure, and thermal treatment time.

6.6 POST-SAMPLING ACTIVITIES

Wastes generated during sample collection will be handled safely. Liquid wastes will be placed in appropriately-sized containers at ~~a hazardous waste collection point~~the sample recovery area and Waste Management will be notified to pick up the wastes as needed.

7.0 SAMPLE HANDLING, TRACEABILITY, AND HOLDING TIMES

This section describes the sample preservation methods, holding times, field documentation, and shipping requirements for the ADT. Condensate samples will be collected by the TOCDF Monitoring personnel. The DAAMS tubes will be collected by Battelle Monitoring personnel, who will be responsible for labeling and transporting the samples to the CAL for analysis.

7.1 SAMPLE PRESERVATION AND HOLDING TIMES

The requirements for preserving samples and holding times were taken from Table 3-1 in SW-846 (1~~)~~) and are shown in Table A-7-1. Condensate samples will be cooled to ≤ 4 °C until prepared and analyzed. DAAMS tubes will be analyzed within 72 hours of their collection. Holding times will be monitored by keeping track of the time elapsed since the samples were collected. Samples will be delivered or shipped to the laboratory as necessary to meet the holding times for the sample analyses.

TABLE A-7-1. SAMPLE PRESERVATION AND HOLDING TIMES

Autoclave Demonstration Test

Parameter	Preservation	Holding Time
Process Streams ~~(Residue)~~		
Metals	Cool (≤ 4 °C) pH < 2 Unpreserved	6 months (28 day for Hg) 28 days (14 days for Hg)
VOCs	Cool (≤ 4 °C)	~~1~~47 days
SVOCs	Cool (≤ 4 °C)	Extract 5~~1~~4 days, analyze 40 days
PCDDs/PCDFs	Cool (≤ 4 °C) pH adjusted 7-9 with 0.008% $Na_2S_2O_3$/liter if residual chlorine is present	Extract 30 days, analyze 45 days
Exhaust Gas		
DAAMS Tubes	None Required	72 hours

7.2 DOCUMENTATION

The following subsections present the requirements for labeling, maintaining the COC, and handling environmental samples. Recording information necessary for reconstruction of the sampling event will be discussed. Entries made on documents will use the error correction protocol, which requires one line drawn through the error and the correction initialed and dated. Documentation will be available to regulators upon request.

7.2.1 Sample Labels

Sample labels are necessary to prevent misidentification of samples. Condensate samples collected will be labeled using ~~a designated code system, developed for this project, similar to prior testing~~the assigned TOCDF sample number. Samples will be sealed, and the volume of the sample marked. Data for each sample run will be recorded on a run sheet during each performance run. After each run, the data will be checked for completeness. The sampler will complete the appropriate COC forms when the samples are collected, and these forms will be sent to the laboratory. The sampler will sign the appropriate forms relinquishing custody, and the laboratory representative will sign the form indicating that they have taken custody of the samples.

The DAAMS tubes are marked with a unique number by the CAL to avoid misidentification. Tamper-resistant gummed-paper labels or tags will be used to identify the other samples.

The labels will include at least the following information:

Sample number~~, including a sample code that distinguishes field samples, duplicates, or blanks where appropriate~~.

Signature or initials of sample collector.

Date and time of collection.

ADT run number.

Type of preservative used, or "None," as applicable.

Labels will be affixed to sample containers prior to, or at the time of, sampling. The labels will be filled out at the time of sample collection.

7.2.2 Sample Collection Logbook

Information pertinent to sampling will be recorded in a sampling logbook. The logbook shall be bound, with pages consecutively numbered. All entries will be made in indelible ink, and all corrections will follow the error correction protocol described in Section 7.2. Sampling personnel also will record all information on the appropriate sampling forms.

At a minimum, entries in a logbook for the samples shall include:

- Purpose of the sampling event;
- Location and description of the sampling points for the process samples;
- Identification of sampling crew members;
- Type of samples collected;
- Sampling methodology;
- Date and times of sampling events;
- General observations; and
- Deviations from the sampling methods.

7.2.3 Chain-of-Custody Forms

The purpose of COC procedures is to document the identity of the sample from its inception through all transfers of custody. To establish the documentation necessary to trace sample possession from the time of collection, a COC record must be filled out and accompany every sample or group of individually identified samples. When a sample arrives at a laboratory, an individual with the COC authority, trained in the laboratory sample receiving and control methods, will take custody of the samples. The sample coolers will be opened by the sample custodian (or their designee) and logged into the master sample log. A laboratory internal COC form will be completed, and the sample will be placed in storage. Laboratory analysts will sign out samples prior to analysis. The sample custodian will use a standard form to record the location of the sample and any transfers of the sample to analytical personnel. The laboratory sample custodian will keep the form until the project is complete. The forms will then be transferred to the TOCDF Document Control Center with the project file.

The COC for the process samples will be filled out at the end of each performance run. Before that point, the samples will remain in the possession of the person collecting the samples. The samples may be secured in a cooler with COC tape until the performance run is completed. The samples will be secure because the sample collection area is within in a high-security area. Only authorized personnel are allowed into the areas where the samples are held until shipment to the laboratory. These personnel must have a security clearance or be escorted by a security-cleared person before they are allowed within the double-fenced area.

Each person who has custody of the samples must sign the COC form, which must contain:

- Sample identification number;
- Date and time of sample collection;
- Signature or initials of sample collector;
- Matrix type;
- Number of containers;
- Signatures of persons in the COC; and
- Date and time of each change in custody.

~~-~~8.0 SPECIFIC CALIBRATION PROCEDURES AND FREQUENCY

This section contains information pertaining to the calibration of process monitoring systems. Process control instruments are calibrated ~~on a regular basis as directed in the Instrument Calibration Plan (6)~~every six months except for the ACAMS. The calibration status of the autoclave process control instruments at the time of the ADT will be summarized in the final report. The calibrations will be conducted in accordance with the manufacturer's instructions. The process instruments calibrated include the ~~thermocouples~~thermocouple transmitters, the pressure transmitters, and the ACAMS. Temperature transmitter ~~calibration frequencies vary. The ACAMS~~calibrations will be ~~calibrated~~conducted every six months as are other thermocouple systems at TOCDF. The ACAMS will be challenged before the run at the distal end (75-125%) and checked after the run. The ACAMS will be ~~challenged before and after each run~~ calibrated as ~~directed in TE-LOP-524~~needed based on the challenge results. Detailed information on the calibration of the ACAMS is available in Attachment 22 (4).

9.0 ANALYTICAL OBJECTIVES AND PROCEDURES

This section describes the procedures used to analyze the samples collected during the ADT. The methods used include GC/FPD, gas chromatograph/mass spectrometer (GC/MS), liquid chromatograph/mass spectrometer (LC/MS), inductively coupled plasma/mass spectrometer (ICP/MS) and cold vapor atomic absorption spectroscopy (CVAAS). Should a failure in the analytical system occur, the laboratory will notify the EG&G Test Director immediately. Corrective action will be as directed by Annex A and EG&G. The QA procedures for the ADT will follow the basic guidelines given in the methods. Table A-9-1 summarizes the samples collected, sample matrix, preparation methods, and analyses methods.

~~The sample number will include a sample code that distinguishes field samples, duplicates, or blanks where appropriate.~~ The DAAMS samples will consist of ~~sets with one set of~~ four tubes (1 QP) collected during the ~~two DAAMS collection periods~~agent monitoring. The ACAMS monitoring of the autoclave headspace ~~and~~ will be analyzed for Agent VX. Condensate samples will be collected during the ADT ~~every time~~when the ~~condensate holding tank~~autoclave is ~~pumped to the SDS tanks~~evacuated. Each condensate sample will be analyzed, no composite samples will be taken. One duplicate set of condensate samples will be collected during one run. Condensate samples will be analyzed by the CAL for pH, Agent VX~~ (O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate), S-(2-diisopropylaminoethyl) methylphosphonothioic acid (~~, EA-2192~~), ethyl methylphosphonic acid (~~, EMPA~~)~~, and ~~methylphosphonic acid (~~MPA~~)~~. Condensate samples will be analyzed by the subcontract laboratory for metals, SVOCs, ~~and~~ VOCs, and PCDDs/PCDFs. The recovered spiking samples will be analyzed for Agent VX, EA-2192, EMPA, and MPA.

The CAL will prepare the DAAMS tubes, prepare the QC samples, and analyze the samples. Laboratory QC samples will include method blanks, blank spikes (calibration checks and LCSs), matrix spikes, and replicates. These will be performed as required by the methods, or at least one round of samples per batch and one round every 20 samples.

TABLE A-9-1. ANALYTICAL METHODS
Autoclave Demonstration Test

PARAMETER	NUMBER OF SAMPLES	MATRIX	PREPARATION METHOD	ANALYSIS METHOD
Agent	6	DAAMS Tubes	TE-LOP-562	TE-LOP-562
Agent	~~9~~12	Condensate	TE-LOP-572	TE-LOP-572
Metals	~~9~~12	Condensate	Method 3010A	Method 6020A
VOCs	~~9~~12	Condensate	Method 5030B	Method 8260B

SVOCs	~~9~~12	Condensate	Method 3510C	Method 8270D~~C~~
pH	12	Condensate	TE-LOP-574	TE-LOP-574
Dioxins/Furans	12	Condensate	Method 3510C	Method 8290A
Hydrolysis Products	Minimum 27	Spiking Samples	*TE-LOP-572	*TE-LOP-572
Agent VX	Minimum 27	Spiking Samples	*TE-LOP-572	*TE-LOP-572

* Must be approved in accordance with R315 prior to shakedown.

9.1 ANALYSIS METHODS FOR PROCESS STREAM SAMPLES

Process samples collected include condensate samples and spiked samples.

9.1.1 Agent Analysis Method

Condensate samples must be analyzed~~screened~~ for Agent VX before the samples can leave the facility. The method used for this analysis is TE-LOP-572. This method uses 0.5 % 2-(diisopropylamino) ethanol in chloroform to extract Agent VX. An aliquot of the extract is injected into a GC/FPD, where the agent is separated from any other compounds and the phosphorus in the agents detected.

9.1.2 pH Analysis

The pH of condensate samples will be determined with a pH probe and pH meter using TE-LOP-574. The pH probe and meter are calibrated using standards. The pH probe is then rinsed, dried, and placed in the solution to be analyzed. The pH reading recorded will be the average of two readings, and the pH probe is removed from the solution, rinsed, and dried. The probe is then ready for the next measurement.

9.1.3 CAL Analyses Methods for Organic Compounds

Condensate samples will be analyzed for EA-2192, EMPA, and MPA by the CAL using LC/MS. A sample aliquot is injected into an LC/MS to analyze for EA 2192. The organic compounds are separated by the HPLC and detected by MS. Quantitation is achieved by comparison to internal standards. -

9.1.4 Analyses Methods for Spiked Samples

Three types of spiking samples will be used for the ADT: DPE material samples, LSS air hose samples, and wood samples. The DPE material samples will be a 10-gram (or smaller) sample of material that will be spiked with Agent VX, treated in the autoclave, and then extracted and analyzed for Agent VX. The LSS air hose samples will be 10-gram (or smaller) samples of hose sections that are spiked with Agent VX, spiked, treated in the autoclave, and then extracted and analyzed for Agent VX. The wood samples are 10-gram (or smaller) ~~blocks~~sections of ~~particle board~~ wood dowels that are spiked with Agent VX, treated in the autoclave, and then extracted and analyzed for Agent VX. These samples are extracted and analyzed using Method TE-LOP-572. The analytes will include Agent VX, EA-2192, EMPA, and MPA. The MDL study and analysis methods need to be approved by SHW board before the ADT.

9.1.5 Subcontract Laboratory Analyses Methods for Organic Compounds

Condensate samples will be analyzed for VOCs, SVOCs, and ~~SVOCs~~PCDDs/PCDFs using the specified~~most recent~~ method versions~~ of Methods 8260B and 8270C, respectively~~. Their performance will be evaluated using the criteria listed in the QA/QC tables found in Annex A.

SW-846 Method 8260B - Volatile Organic Compounds by Gas Chromatograph/ Mass Spectrometer. A representative portion of the liquid samples is introduced into a purge device using SW-846, Method 5030B (1). The liquid is purged with an inert gas, and the volatile compounds are collected on a sorbent trap. Next, the trap is heated and backflushed to desorb the compounds into the GC/MS. The sample is then analyzed for the Target Analyte List shown in Table A-9-2 using SW-846, Method 8260B (1). Quantitation is achieved by comparison of sample component responses to the responses of internal standards.

SW-846 Method 8270D~~C~~ - Semi-Volatile Organic Compounds by Gas Chromatograph/ Mass Spectrometer. Representative aliquot samples of the condensate samples are extracted by SW-846, Method 3510C (1), using methylene chloride; then, these aliquots are concentrated to a known volume. The aliquots of the extracts are analyzed by SW-846, Method 8270C (1), using GC/MS. Quantitation is achieved by comparison of sample component responses to the responses of internal standards. Table A-9-3 lists the target analytes for the total SVOC analyses.

SW-846 Method 8290A – PCDDs/PCDFs by HRGC/HRMS. A representative sample is extracted with toluene, the extract is then concentrated to a known volume, and the extract is subjected to a series of cleanup steps. The sample is then evaporated to a small volume and diluted to a known volume. An aliquot of the cleaned extract is then injected into a HRGC/HRMS and the compounds quantitated against internal standards.

TABLE A-9-2. TOTAL VOC TARGET ANALYTE LIST FOR CONDENSATE SAMPLES

Autoclave Demonstration Test

TABLE A-9-2. TOTAL VOC TARGET ANALYTE LIST FOR CONDENSATE SAMPLES

1	Acetone	29	1,2-Dichloropropane
2	Benzene	30	1,3-Dichloropropane
3	Bromobenzene	31	2,2-Dichloropropane
4	Bromochloromethane	32	1,1-Dichloropropene
5	Bromodichloromethane	33	*cis* -1,3-Dichloropropylene
6	Bromomethane	34	*trans* -1,3-Dichloropropylene
7	2-Butanone	35	1,4-Dioxane
8	Carbon Disulfide	36	Ethylbenzene
9	Carbon tetrachloride	37	n-Hexane
10	Chlorobenzene	38	2-Hexanone
11	2-Chloro-1,3-butadiene	39	Iodomethane
12	Chlorodibromomethane	40	Methylene chloride
13	Chloroethane	41	Methyl isobutyl ketone
14	Chloroform	42	n-Propylbenzene
15	2-Chloroethyl vinyl ether	43	Styrene
16	Chloromethane	44	1,1,1,2-Tetrachloroethane
17	2-Chlorotoluene	45	1,1,2,2-Tetrachloroethane
18	4-Chlorotoluene	46	Tetrachloroethylene
19	Cumene (isopropylbenzene)	47	Toluene
20	1,2-Dibromoethane	48	Tribromomethane (Bromoform)
21	Dibromomethane	49	1,1,1-Trichloroethane
22	*trans* -1,4-Dichloro-2-butene	50	1,1,2-Trichloroethane
23	Dichlorodifluoromethane	51	Trichloroethylene
24	1,1-Dichloroethane	52	Trichlorofluoromethane
25	1,2-Dichloroethane	53	1,2,3-Trichloropropane
26	1,1-Dichloroethylene	54	1,1,2-Trichloro-1,2,2-trifluoroethane
27	*cis* -1,2-Dichloroethylene	55	Vinyl chloride
28	*trans* -1,2-Dichloroethylene	56	Xylenes(o-, m-, p-)

TABLE A-9-3. TOTAL SVOC TARGET ANALYTE LIST FOR CONDENSATE SAMPLES

1	Acenaphthylene	35	1,4-Dinitrobenzene
2	Acenaphthene	36	4,6-Dinitro-o-cresol
3	Acetophenone	37	2,4-Dinitrophenol
4	Aniline	38	2,4-Dinitrotoluene
5	Anthracene	39	2,6- Dinitrotoluene
6	Benz(a)anthracene	40	Di-n-octyl phthalate
7	Benzo(b)fluoranthene	41	Diphenylamine
8	Benzo(k)fluoranthene	42	Fluoranthene
9	Benzo(g,h,i)perylene	43	Fluorene
10	Benzo(a)pyrene	44	Hexachlorobenzene
11	4-Bromophenyl phenyl ether	45	Hexachlorobutadiene
12	Butyl benzyl phthalate	46	Hexachlorocyclopentadiene
13	p-Chloroaniline	47	Hexachloroethane
14	Chlorobenzilate	48	Indeno(1,2,3-c,d) pyrene
15	*Bis* (2-Chloroethoxy)methane	49	Naphthalene
16	*Bis* (2-Chloroethyl)ether	50	2-Naphthylamine
17	*Bis* (2-Chloroisopropyl) ether	51	2-Nitroaniline
18	4-Chloro-3-methylphenol	52	4-Nitroaniline
19	2-Chloronaphthalene	53	Nitrobenzene
20	2-Chlorophenol	54	2-Nitrophenol
21	Chrysene	55	4-Nitrophenol
22	o-Cresol	56	Pentachlorobenzene
23	m-Cresol	57	Pentachloroethane
24	p-Cresol	58	Pentachloronitrobenzene
25	Dibenz(a,h)anthracene	59	Pentachlorophenol
26	m-Dichlorobenzene	60	Phenanthrene
27	o-Dichlorobenzene	61	Phenol
28	p-Dichlorobenzene	62	Pyrene
29	2,4-Dichlorophenol	63	1,2,4,5-Tetrachlorobenzene
30	2,6-Dichlorophenol	64	2,3,4,6-Tetrachlorophenol
31	Diethyl phthalate	65	1,2,4-Trichlorobenzene
32	2,4-Dimethyl phenol	66	2,4,5-Trichlorophenol
33	Dimethyl phthalate	67	2,4,6-Trichlorophenol
34	Di-n-butyl phthalate		

9.1.6 Inorganic Analysis Methods

The condensate samples will be analyzed for metals. Mercury will be analyzed by SW-846, Methods 7470A (1), which uses CVAAS. The other metals analyzed by ICP/MS are aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, tin, vanadium, and zinc. The methods are described below.

SW-846 Method ~~6020~~ 6020A- ICP/MS. Selected metals concentrations in the condensate samples will be determined by ICP/MS. (The most recent version of the method will be used.) A representative portion of the sample is digested with HNO_3, and the sample digest is aspirated into the nebulizer of the ICP/MS. The sample mist enters the plasma, the plasma converts the sample to an atomic vapor, and the mass spectrometer separates the elements by mass. The masses detected are used to quantitate the elements present. Quantitation is achieved by comparison of sample responses to the responses of internal standards. The response of the internal standards for each sample are compared to the internal standards from the initial calibration standard and if they do not agree within the limits in Annex A, then the samples will need to be reanalyzed. When the internal standard recovery is less than 70 %,- follow requirements of Section 9.6 of method 6020A.~~the sample can be diluted and reanalyzed~~.

SW-846 Method 7470A - Manual Cold-Vapor Technique. A representative portion of the sample is digested with acids, potassium permanganate, and potassium persulfate. Mercury ions are reduced to metallic mercury and stripped from the solution with a gas stream. The mercury vapors are then directed into the path of an atomic absorption spectrometer. Quantitation is achieved by comparison of sample component responses to the responses of external standards.

~~**TABLE A-9-2. TOTAL VOC TARGET ANALYTE LIST FOR CONDENSATE SAMPLES**~~

~~**Autoclave Demonstration Test**~~

~~1 page~~

~~**TABLE A-9-3. TOTAL SVOC TARGET ANALYTE LIST FOR CONDENSATE SAMPLES**~~
~~**Autoclave Demonstration Test**~~

~~1 page~~

9.2 DAAMS TUBES ANALYSIS METHOD

The DAAMS tubes are analyzed using TE-LOP-562. This method uses the thermal desorption of the organic compounds into a GC/FPD. The other organic compounds are separated from the agents by the GC analytical column. The agent compounds are detected as they elute from the column and are burned in a flame. A photomultiplier tube detects light emitted by the phosphorus in the agents. The detector response is compared to external standards for quantitation. Performance of the method will be evaluated using the criteria listed in the QA/QC tables found in Annex A.

Four DAAMS tubes are collected in each set, and each set will run for ~~one hour~~the same time period that the ACAMS monitored the headspace gas. The DAAMS tubes on the midbed and stack of the Carbon filter system will be reported. One tube will be spiked with agent prior to being sent to the field as a field surrogate (QP) for the sampling method.

The other three tubes will be analyzed as directed below:

The A tube will be analyzed. If ~~no~~ the agent ~~is found~~concentration in the A tube is less than 0.5 VSL~~below the PQL~~, no further analyses will be conducted on this set of DAAMS tubes. ~~, and the PQL will be used in the calculation of a concentration. (The PQL is estimated to be 0.0180 ng for Agent VX).~~

If the agent ~~is found~~concentration in the A tube at or above 0.5 VSL~~is above the PQL~~, then the B tube will be analyzed. If ~~no~~the agent ~~is found~~concentration in the B tube is less than 0.5 VSL and the associated QP concentration is within 75-125% ~~is below the PQL~~, then no further analyses will be conducted.~~, and the PQL will be used to calculate the concentration~~.

If the agent ~~is found~~concentration in the B tube at or above 0.5 VSL~~is above the PQL~~, then the autoclave run will be aborted and the batch reprocessed. ~~the B tube value will be used to calculate the concentration.~~

The C tube will be reserved for GC/MS analysis or used if either the A or B tubes are lost. The C tube may also be used if additional analyses are required.

10.0 SPECIFIC LABORATORY QUALITY CONTROL CHECKS

The QC checks are performed to ensure the collection of representative samples and the generation of valid analytical results. The project participants will perform QC checks throughout the program. TOCDF ~~Standard Army~~ methods will be used for the agent-related analyses. The QC samples analyzed will include blanks, duplicate samples, LCS, and MS/MSD.

Reagents used in the laboratory are normally of analytical reagent grade or higher purity; each lot of acid or solvent used by the subcontract laboratory is checked for acceptability prior to laboratory use. All reagents are labeled with the date received and the date opened. The quality of the laboratory-deionized water is routinely checked. Standard laboratory practices for laboratory cleanliness, personnel training, and other general requirements will be in effect. The results of these QC procedures will be included in the final report.

10.1 METHOD BLANKS

Method blanks contain all the reagents used in the preparation and analysis of samples and are processed through the entire analytical scheme to assess any spurious contamination arising from reagents, glassware, and other sources. The QC Criteria for method blanks are shown in Annex A by individual method.

10.2 LABORATORY CONTROL SAMPLES

The LCSs are samples generated from analyte spikes into a control matrix prepared independently from the calibration concentrates and are used to establish that an instrument or procedure is in control. An LCS is carried through the entire sample preparation and analysis procedure. The QC Criteria for the LCSs are listed in Annex A by analysis method.

10.3 DUPLICATE ANALYSES

Duplicate sample analysis will be used to evaluate the variance in a particular applied analytical method. Field duplicate samples will be collected for one condensate sample during one performance run.

10.4 MATRIX SPIKE SAMPLES

Matrix Spikes are samples spiked with the analyte of interest and then analyzed to determine a percent recovery. These analyses will assess the behavior of actual analyses in individual program samples during the entire preparative and analysis scheme. Matrix spike analysis will be conducted to evaluate accuracy and general matrix recovery. An MS/MSD will be prepared from the condensate samples. The QC Criteria for percent recoveries and RPD are shown in Annex A for each method.

10.5 ANALYTICAL INSTRUMENT CALIBRATION

The analytical instrumentation used in the laboratory for analysis of ADT samples will undergo several performance checks. An initial calibration curve will be analyzed before any samples are analyzed to compare linearity of response to concentration of known amounts of the analytes of interest. ~~The initial calibration for some methods will use a calculated Correlation Coefficient (CC) to demonstrate acceptability of the calibration.~~ On a daily basis, a continuing calibration check will be performed before any samples are run for that day. If acceptance criteria (as specified in the appropriate analytical methods for initial or continuing calibrations) are not met, sample analysis will not proceed until the analytical problem has been rectified and the criteria have been met. Linearity checks will be used to verify that response has not shifted significantly from the most recent calibration. Some methods will use an Initial Calibration Verification (ICV) sample to demonstrate that the calibration was accurate. Continuing Calibration Verification (CCV) samples will be used to ensure that the calibration remains within limits throughout the analysis run. The instrument initial calibration procedures and acceptance criteria will be those established in the analytical method and listed in Annex A. Internal standards will be analyzed to evaluate instrument and method performance. A summary of the calibration procedures and frequency for the laboratory instruments to be used for this project is provided in Table A-10-1. The QC Criteria for the internal standards are listed in Annex A by analysis method.

TABLE A-10-1. CALIBRATION PROCEDURES FOR ANALYTICAL METHODS

METHOD	ANALYTICAL EQUIPMENT	CALIBRATION CURVE	CALIBRATION CHECKS	TARGET CRITERIA
7470A	CVAAS	Calibration blank and five standards to give CC = 0.995	CCV every 10 samples and at the end of the run sequence	CCV ± 10 % of known value

6020A	ICP/MS	Calibration blank and one standard	CCV every 10 samples and at the end of the run sequence	CCV ± 10 % of known value
8260B	GC/MS	Five-point calibration	Calibration Check Compound every 12-hour tune period	Drift ≤ 20 % ~~for condensate, = 25 % for SMVOC tubes~~
8270D~~C~~	GC/MS	Five-point calibration	Verified every 12-hour tune period	Variability of average Relative Response Factor (RRF) of 30 % RSD
8290A	HRGC/HRMS	Five-point calibration	Verified every 12-hour tune period	Variability of average RRF of 30% RSD
DAAMS	GC	Three-point calibration	Verified every 12 operating hours	Mid-range standard ± 15 % known value
ACAMS	GC	Three-point calibration	Verified every batch	Mid-range standard ± 25 % known value

11.0 DATA REPORTING, DATA REVIEW, AND DATA REDUCTION

Reporting data generated during the ADT is an important part of the overall project. The ADT report will summarize all the work required to conduct a successful test.

11.1 DATA REPORTING

The data reporting process will discuss the analytical data packages, review of the ADT data generated, and review the final ADT report. The use of significant figures in reporting the data will follow the guidelines published by the ASTM (~~9~~8).

11.1.1 Analytical Data Packages

The data reported from commercial laboratories is required to be similar in format to that used by the EPA Contract Laboratory Program (CLP). This format will include a case narrative section, Analytical Data Summary Sheets, QC Sample Results, the COC forms, and raw data organized by analytical method. Complete data packages are included so that an independent verification of the final analytical results can be conducted. These data packages are stand-alone deliverables that include the instrument raw data, parameter-specific QC documentation, calibration and calibration check performance, and instrumentation performance information.

The case narrative will describe the data package and identify project-specific information. It will discuss any pertinent information concerning data quality and any difficulties or analytical anomalies encountered in the analyses. In addition, the case narrative will provide a cross-referenced listing of the field sample and laboratory sample identities, and discuss information on achieving DQOs or project-specific objectives.

The Analytical Data Summary Sheets will contain a summary of the analytical results and the key QC data. A separate sheet will be provided that reports the results for each sample; the data on this sheet will include the results, recovery of any surrogate materials, date sampled, and analysis date. This information will confirm both the QC and holding time requirements were met. Summary sheets for the analysis of the QC samples will follow the sample results sheets.

Copies of the COC forms are also a part of the data package. These include copies of the COC forms submitted with the samples and copies of any internal COC forms used to track the samples through the different analyses in the laboratory.

Raw data will be included in the Analytical Data Packages. This raw data will include chromatograms for those methods generating them, blank data, sample preparation sheets, copies of sequence files, and calibration data. The raw data will be organized by analysis method. Enough data will be supplied to allow recreation of the sample analysis event.

11.1.2 Analytical Data Format

Any data reported as "not detected" will use the PQL for the lower reporting limit. The PQL is the same as the reporting limit used by some commercial laboratories and the LOQ used by the CAL. The PQL is the quantitation level at the lowest level that the entire analytical system gives reliable signals and an acceptable calibration point or low-level matrix spike. Each compound or element is assigned a PQL that is contingent upon the behavior of the compound or element during analysis. Changes to extraction protocol, amount of sample prepared, or dilution applied to the sample can raise or lower the PQL. PQL must meet the regulatory or Permit limits.

Sample analysis results will be reported by the laboratory in matrix-specific units. These results will be reported for all samples and parameters required for the ADT. The laboratory will assign qualifiers to the results, when necessary, based on guidelines found in the analytical method, CLP, or in this QAPP. Qualifiers appearing on the analytical summary sheets are defined on that specific sheet. The data presented in the ADT Report will carry any data qualifiers, and the blank corrected results will show the uncorrected results.

11.1.3 ADT Report

An ADT Report will be prepared and submitted to the DSHW. The ADT Report will contain:

- Daily run summaries.
- A summary of operating parameter data and associated limits.
- A summary of sampling and analytical methods used and any deviations from referenced methods.
- Analyses results, protocols, and quantitative gas analyses.
- A compilation and evaluation of analytical calibration data and QA/QC data and identification of problems encountered and the solutions implemented.
- Copies of log books, laboratory notebooks, calibration data, chromatograms, and other raw data.
- Examples of calculations, concentrations, and emission rates for DAAMS samples.

A QA/QC Report will be submitted to the Test Director and included in the ADT Report as an appendix. Additionally, each formal data deliverable will contain a summary of QA/QC activities. This summary will include:

Estimates of precision, accuracy, and completeness of reported data.

Reports of performance and system audits.

Any quality problems found.

Corrective actions taken for any quality issues found.

11.2 DATA REVIEW

The DAAMS sampling data will be reviewed to determine that the LOP/QAPP was followed in the collection of the samples and was recorded on prepared forms and reviewed at the end of each run by Monitoring personnel to ensure that each sheet is properly completed.

The analyst generating the data will review the laboratory data, and then the analyst's supervisor will review the data. The laboratory QC personnel will review the data per the laboratory procedure before the project report is prepared by the subcontract laboratory project manager. When the analytical data are submitted to EG&G, the data will again be reviewed before it is used to prepare the ADT Report. This review process will confirm that the data are usable for an assessment of the autoclave's performance.

11.2.1 Data Validation

Data validation is the process of accepting or rejecting data on the basis of established criteria. Analytical and sampling data will be validated by QC personnel using criteria outlined in this QAPP. The ADT subcontractor QC personnel will use validation methods and criteria appropriate to the type of data, even those judged to be "outlying" or spurious values. The persons validating the data will have sufficient knowledge (i.e., at least one year of experience in data validation) of the sampling and analytical methods to identify questionable values and deviations from criteria specified in the methods and the QAPP.

The results from the laboratory method blanks, replicate samples, and internal QC samples will be used to further validate analytical results. Analytical results on the replicate samples also are valuable for validation of sample collection. The QA/QC personnel will review all laboratory and sampling raw data to verify: calculated results presented, consistency, duplicate sample analysis, spike recoveries, tests for outliers, and transmittal errors.

The criteria listed below will be used to evaluate analytical data:

Use of approved analytical procedures.

Use of properly operating and calibrated instrumentation.

Precision and accuracy comparable to that achieved in previous analytical programs and consistent with the objectives listed in Annex A.

See Section 10.0 for the anticipated minimum number of QC samples. The percent recovery of each matrix will be calculated as shown in Section 13.0. Inorganic data will be evaluated using the general methods outlined in the EPA CLP guidelines for inorganic data (~~7~~6) using the criteria from Annex A. The organic data will be evaluated using the general methods outlined in the

EPA CLP guidelines for low-level organic data (~~8~~7). These evaluations will be included in the QA report, which will be an appendix to the ADT Report.

11.2.2 Identification and Treatment of Outliers

Any point that deviates from others in its set of measurements will be investigated, and the suspected outlier will be recorded and retained in the data while it is investigated. One or both of the following tests will be used to identify outliers:

Dixon's test for extreme observations, which is a computed procedure for determining whether a single, very large or very small value is consistent with the data set.

The one-tailed t-test for differences.

If more than one outlier is suspected in the same data set, other statistical sources will be consulted, and the most appropriate test of the hypothesis will be used and documented.

If a data outlier is suspected, those persons involved in the analysis and data reduction will be consulted for additional insight about the evaluation of the suspect data. This evaluation may provide an experimental basis for the outlier to be rejected or included in the data set. Two data sets may be reported: one including the outlier, and the other excluding the outlier.

11.3 DATA REDUCTION

Specific QC measures will be used to ensure the generation of reliable data from sampling and analysis activities. Proper collection and organization of accurate information followed by clear and concise reporting of the data are primary goals for all projects.

11.3.1 DAAMS Data Reduction

DAAMS sampling data will be reduced on a daily basis and will be reviewed by the Battelle QC personnel. The Test Director will be apprised of all deviations from the standard protocol or of QP results that do not meet the DQOs.

11.3.2 Laboratory Analyses Data Reduction

Analytical results will be reduced to concentration units specified by the analytical procedures, using the equations given therein. Results will be reported on an as-received basis. If the units are not specified, data from the analysis of liquid samples will be reported in units of milligrams per liter (mg/L). ~~Solid samples will be reported on a dry weight basis in milligrams per kilogram (mg/kg).~~ Agent exhaust gas concentrations will be reported in micrograms/cubic meter ($\mu g/m^3$)

and VSL level. Carbon filter results will be reported per Attachment 22.

12.0 ROUTINE MAINTENANCE PROCEDURES AND SCHEDULES

The DAAMS sampling equipment will be calibrated and maintained in accordance with Attachment 22 of the TOCDF Permit (4).

The subcontract laboratory will maintain their instrumentation in accordance with the instrument manufacturer specifications and appropriate methods. The laboratory will maintain a stock of replacement parts to minimize downtime resulting from foreseeable breakage or typical consumption.

13.0 ASSESSMENT PROCEDURES FOR ACCURACY, PRECISION, AND COMPLETENESS

The QA/QC Criteria for the analyses of samples for this project are presented in Annex A, which contains criteria for method calibrations, data accuracy, and precision of data. Each method has a set of criteria to meet. Methods of calculating the evaluation criteria are discussed in this section.

13.1 PRECISION

Precision is defined as the degree of mutual agreement among individual measurements made under prescribed conditions. Criteria for precision of each method have been included in Annex A. Precision will use two different measurements depending on the number of data points being considered. Two data points will have the RPD calculated. Three or more data points will use the RSD as a measure of the precision. Precision will be calculated for laboratory duplicate analysis using the following equations:

$$RPD = \{(X_1 - X_2) / [(X_1 + X_2)/2]\} \times 100$$

Where: RPD = Relative Percent Difference
X_1 = Highest Analytical Result

X_2 = Lowest Analytical Result

RSD = (standard deviation/average value) x 100

Calculation of the precision for each analysis will be based on different criteria as discussed in the analytical methods. The precision of the VOCs and SVOCs analyses will be based on the RPD from the MS/MSD samples because of the historically-low concentrations found in condensate samples. The precision of metals in the condensate samples will be based on analyses of MS/MSD samples because of the anticipated low concentrations in the samples.

13.2 ACCURACY

Accuracy is the degree of agreement between a measurement and an accepted reference or true value. The accuracy of the ADT data will be determined from analyses of samples spiked with a known concentration. The number of spiked samples and the spiking levels will be taken from the respective methods. Accuracy objectives for each method are presented in Annex A.

The formula used to assess the accuracy of the LCS is:

$$\%R = (Q_{LCS} / Q_{KC}) \times 100$$

Where: %R = Percent Recovery
Q_{LCS} = Quantity of Analyte Found in the LCS
Q_{KC} = Known Concentration of the LCS

The formula used to assess the accuracy of the MS/MSD samples is:

$$\%R = ((Q_{ss} - Q_{us})/Q_s) \times 100$$

Where: %R = Percent Recovery
Q_{ss} = Quantity of Analyte Found in the Spike Sample
Q_{us} = Quantity of Analyte Found in the Unspiked Sample
Q_s = Quantity of Added Spike

Calculation of the accuracy for each analysis will be based on different criteria as discussed in the analytical methods. The accuracy for the VOCs, SVOCs, and metals analyses will be determined by the %R calculated from the analysis of the LCS and MS/MSD samples.

13.3 COMPLETENESS

Completeness is defined as the amount of valid data for the ADT compared to the amount that was expected to be obtained under optimal conditions. The completeness objective is to have 100 % of the data valid for three performance runs for the ADT. Acceptable results must be obtained for three performance runs. The completeness objective for the entire monitoring project is to obtain the necessary data needed to complete the statistical design.

Completeness will be reported as the percentage of all measurements judged to be valid, and every attempt will be made to ensure the data generated will be valid. If data appears questionable based on circumstances observed during the field sampling, additional runs will be completed (as soon as the system can be reset) to ensure that three successful performance runs are completed. In reality, some samples may be lost in laboratory accidents, and some results may be qualified based on laboratory QC procedures. The following formula will be used to calculate a percent completeness:

$$C = (V/T) \times 100\ \%$$

Where: C = Percent Completeness
V = Number of Measurements Judged Valid
T = Total Number of Planned Measurements

AUDIT PROCEDURES, CORRECTIVE ACTION, AND QUALITY ASSURANCE REPORTING

The ADT QA program will comply with EPA and State requirements for audits. These include both performance and system audits as independent checks on the quality of data obtained from sampling, analysis, and data-gathering activities. The procedures and techniques in place will ensure that the audits are representative of the measurement process in normal operation. Either type audit may show the need for corrective action.

14.1 PERFORMANCE AUDITS

A performance audit checks the performance or accuracy of measurements. The sampling and analysis segments of the project are also checked during a performance audit. The sampling performance audits will be accomplished through observation of the sampling operations by the regulatory agency representative and the Battelle QC Monitoring Inspectors. If a spiked audit sample is supplied by the DSHW, it will be extracted and analyzed according to the same methods used for the field samples.

14.2 SYSTEM AUDITS

A system audit involves observations by a subcontractor or a regulatory agency to ascertain that the work is being performed in accordance with the methods specified in this QAPP.

14.2.1 Field Audit

An EG&G Environmental observer will ensure that the QAPP is being followed and that sample COCs are accurate before sample shipment. The observer will report any discrepancies to the Test Director, and maintain a log of discrepancies for the Test Director. Any findings will be documented in the final report.

Representatives from the DSHW are expected to be on-site to observe all sampling activities. The point of contact for Federal and State environmental regulatory agencies staff during the ADT will be the Test Director or his designee.

During each performance run, the Battelle QC Monitoring Inspectors will perform a system audit, which consists of an inspection and review of the ACAMS and DAAMS sampling system.

The inspection will consist of:

A pretest leak check of the ACAMS and DAAMS.

Final leak checks of the ACAMS and DAAMS.

Sample recovery for the DAAMS tubes.

DAAMS tubes sample analyses.

Results of the leak checks are noted on the field data sheets while the remaining item checks are documented on the audit checklist.

14.2.2 Laboratory Audit

The Test Director will direct that an audit of each laboratory be conducted to ascertain that work is performed in accordance with the methods specified in the QAPP. The audits will include observations of the sample analyses by the CAL and the condensate analyses by the subcontract laboratory. Auditors will be selected from the EG&G Environmental Department or Battelle QC Inspectors.

14.3 CORRECTIVE ACTION AND QA REPORTING

The need for corrective action will occur when a circumstance arises that adversely affects the quality of the data output. In most instances, the personnel conducting the field work and the laboratory analyses will be in the best position to recognize problems that will affect data quality. Awareness on their part can detect minor instrument changes, drifts, or malfunctions that can then be corrected, thus preventing a major breakdown of the system. These personnel will be in the best position to decide upon the proper corrective action and will be responsible to initiate it immediately, thus minimizing data loss. Therefore, the field sampling and laboratory analyses personnel will have the prime responsibility for recognizing the need for a nonconformance report.

The personnel identifying or originating a nonconformance report will document each nonconformance. For this purpose, a variance log, a testing procedure record, a notice of equipment calibration failure, results of laboratory analysis QC tests, an audit report, an internal memorandum, or a letter will be used, as appropriate. These reports will be included in the data package for the samples, and the EG&G Test Director will be notified.

15.0 REFERENCES

(1) ***Test Methods for Evaluating Solid Waste, Physical/Chemical Methods***, 3rd Edition including Update III, USEPA, SW-846, December 1996.

(2) ***Hazardous Waste Combustion Unit Permitting Manual***, **Component 2**, "How to Review A Quality Assurance Project Plan," U.S. EPA, Region 6, Center for Combustion Science and Engineering, January 1998.

(3) ***EPA Guidance for Quality Assurance Project Plans***, EPA QA/G-5, December 2002.

(4) **Attachment 22 to the TOCDF Permit,** AGENT MONITORING PLAN, EG&G Defense Materials, Inc., TOCDF, ***CDRL 23***.

(5) ~~American Society for Testing and Materials (ASTM) Method D3370, "Standard Practices for Sampling Water from Closed Conduits."~~E. Burckle, K. Siddoway, ***Testing of Headspace Monitoring for Waste Characterization***, Battelle, Columbus, OH, November 18, 2008.

~~(6) **Attachment 6 to the TOCDF Permit,** INSTRUMENT CALIBRATION PLAN, EG&G Defense Materials, Inc., TOCDF~~(6) ***USEPA Contract Laboratory Program National***

Functional Guidelines for Inorganic Review, EPA-540-R-04-004, October 2004.

(7) ***USEPA Contract Laboratory Program National Functional Guidelines for ~~Inorganic Review~~***, ~~EPA-540-R-04-004, October 2004.~~

~~(8) USEPA Contract Laboratory Program National Functional Guidelines for~~ ***Low Concentration Organic Data Review***, EPA-540-R-00-006, June 2001.

(~~9~~8) American Society for Testing and Materials, ASTM DI-10, "International System of Units."

AUTOCLAVE DEMONSTRATION TEST PLAN

FOR SECONDARY WASTE TREATMENT

APPENDIX A

ANNEX A

QA/QC OBJECTIVES FOR ANALYTICAL METHODS

REVISION 1

~~**February 10, 2009**~~

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1.0 INTRODUCTION

QA/QC OBJECTIVES FOR ANALYTICAL METHODS

These Quality Assurance/Quality Control (QA/QC) objectives are prepared based on the input from the laboratories performing the analyses for the Autoclave Demonstration Test (ADT). The objectives were developed from the guidance provided in the EPA reference methods (1, 2, 3), EPA Guidance for Quality Assurance Project Plans (4), each laboratory QA program, and guidance in the EPA QA/QC Handbook (5). The DSHW will be notified of any changes to these tables when they occur.

2.0 METHOD 6020A ICP/MS

2.1 Summary QA/QC Criteria

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
Instrument Tune	Daily, prior to calibration and sample analysis	Mass resolution < 1.0 amu @ 10% peak height. Mass calib. ± 0.1 amu	Retune instrument. Repeat tune solution and analysis.
Initial Calibration	Blank and at least one standard.	ICV ± 10% of expected value	Evaluate and reanalyze ICV Recalibrate.
Calibration Blank	After ICV and CCV	< PQL	Clean system. Rerun. Reanalyze affected samples.
CCV	Every 10 samples and end of run sequence	± 10% of expected value	Reanalyze CCV. Recalibrate. Reanalyze samples.
Method Blank	1 per analytical batch	< PQL	Reanalyze. Recalibrate as necessary.
Internal Standard	Each sample	70 to 130 %R	Dilute, reanalyze, and/or narrate.
Duplicate Control Sample (DCS) *	1 per analytical batch	75% to 125% Recovery, RPD ≤ 25%	Check calculations. Assess impact on data. Re-extract and reanalyze as necessary. Narrate.
Duplicate Analyses	1 per analytical batch	RPD ≤ 20%	Check calculations. Reanalyze. Assess impact on data
MS/MSD*	1 per analytical batch (20 samples).	75-125% Recovery	Check calculations. Evaluate LCS. Assess impact on data.
Holding Time		Unpreserved – 28 days pH < 2 - 180 days	

Note: amu = atomic mass unit
ICV = Initial Calibration Verification
CCV = Continuing Calibration Verification
* The MS/MSD will be measured for aqueous samples.

2.2 Method 6020A PQLs

ELEMENT	AQUEOUS SAMPLES, PQL (MG/L)
Aluminum	0.050
Antimony	0.020
Arsenic	0.020
Barium	0.010
Beryllium	0.0010
Boron	0.050
Cadmium	0.0010
Chromium	0.0020
Cobalt	0.0010
Copper	0.0020
Lead	0.0010
Manganese	0.0010
Nickel	0.0020
Selenium	0.0020
Silver	0.0010
Thallium	0.0010
Tin	0.010
Vanadium	0.010
Zinc	0.0050

3.0 MERCURY ANALYSES METHOD (7470A)

Summary QA/QC Criteria
SW 846 Methods 7470A, Mercury by Cold Vapor AAS

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
Initial Calibration	Blank and five standards. Daily before analysis	Corr. Coefficient ≥ 0.995	Evaluate system. Recalibrate.
Calibration Blank	After ICV and each CCV	< PQL	Rerun. Clean system. Reanalyze affected samples.
ICV	After calibration	80-120%	Reanalyze ICV. Recalibrate.
CCV	Every 10 samples and end of run sequence	80-120%	Reanalyze. Recalibrate. Reanalyze affected samples.
Method Blank	1 per analytical batch	< PQL	Reanalyze. Recalibrate as necessary. Reanalyze.
LCS	1 per analytical batch	80-120%	Check calculations. Reanalyze as necessary. Assess impact on data. Narrate.
MS/MSD	1 per analytical batch (20 samples).	75-125%	Check calculations. Evaluate LCS. Assess impact on data.
Practical Quantitation Limit	Aqueous Samples	0.0002 mg/L	
Holding Time		Unpreserved - 14 days pH < 2 – 28 days	

Note: The term PQL refers to the laboratory's standard Reporting Limit.

4.0 VOLATILE ORGANIC COMPOUNDS IN PROCESS SAMPLES (8260B)

4.1 Summary of QC and Calibration Criterion for Method 8260B (Aqueous)

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	1 per analytical batch	< PQL [1]	Reanalyze. Assess impact on data. Narrate.
Instrument Tune	Every 12 hours	Refer to method.	Retune instrument. Repeat BFB analysis.
Initial Calibration, Five point	SPCC RRF	> 0.10 Chloromethane > 0.10 1,1-DCA > 0.10 Bromoform > 0.30 Chlorobenzene > 0.30 1,1,2,2-TCA	Evaluate system. Recalibrate.
	CCC	RSD ≤ 30%	
	Compounds < 15% RSD	Average RF if 80% of the compounds meet the criteria	
Continuing Calibration	SPCC RRF	Same as initial	Evaluate system. Repeat calibration check.
	CCC	< 20% drift	Recalibrate. Reanalyze affected samples.
	Every 12 hours	RSD ≤ 50% for non-CCCs [2]	Evaluate system. Repeat calibration check.
Internal Standards	RRT	≤ 0.50 or 30 seconds	Check sensitivity of system. Reanalyze standard.
	Recovery	50 – 200%	
Precision/ Accuracy	LCS per batch	Historical lab data (See Table 4.2)	Check calculations. Reanalyze. Assess impact on data. Narrate.
	MS/MSD per batch	Historical lab data (See Table 4.2)	Check calculations. Analyze LCS. Assess impact on data.
	Surrogates	Historical lab data (See Table 4.2)	Check calculations. Reanalyze. Assess impact on data. Narrate.
Holding Time		14 days	

TOCDF

Note: The term PQL refers to the laboratory's standard Reporting Limit.

[1] Except for common lab contaminants: methylene chloride, acetone, and 2-butanone may be reported with qualifiers if the concentration of the analyte is less than five times the PQL. Such action must be addressed in the case narrative.

[2] Allowance for up to 6 target analytes ≥ 50%.

4.2 Control Limits for Process Samples by Method 8260B

	COMPOUND	ACCURACY (% RECOVERY)	PRECISION RPD
LCS			
	1,1-Dichloroethene	66 to 130	NA
	Benzene	77 to 121	NA
	Trichloroethene	75 to 116	NA
	Toluene	78 to 120	NA
	Chlorobenzene	80 to 120	NA
MS/MSD			
	1,1-Dichloroethene	66 to 130	32
	Benzene	77 to 121	21
	Trichloroethene	75 to 116	24
	Toluene	78 to 120	25
	Chlorobenzene	80 to 120	20
Surrogates			
	4-Bromofluorobenzene	66 to 121	NA
	1,2-Dichoroethane-d_4	64 to 139	NA
	Toluene-d_8	72 to 128	NA
	Dibromofluoromethane	71 to 135	NA

Notes: Historical limits for the method are reported here. Current established limits will be used for the evaluation of the data as required by SW-846 (1) and will be provided to DSHW prior to ADT~~.~~
NA = Not Applicable

5.0 SEMI-VOLATILE ORGANIC COMPOUNDS IN PROCESS SAMPLES

5.1 Summary of SVOC QC and Calibration Criterion for Method 8270~~C~~D

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	1 per analytical batch	< PQL *	Reanalyze. Assess data, Narrate.
Instrument Tune	Every 12 hours, initially and as required	As per 8270C	Retune instrument. Repeat DFTPP analysis.
Initial Calibration, Five point	SPCC RRF	≥ 0.050	Evaluate system. Recalibrate.
	CCC	RSD ≤ 30%	
	Compounds < 15% RSD	Average RF if 80% of the compounds meet the criteria	
Continuing Calibration	SPCC RRF	Same as initial	Evaluate system. Repeat calibration check.
	CCC	RSD < 20%	Recalibrate. Reanalyze affected samples.
Internal Standards	RRT	± 30 seconds	Check sensitivity of system. Reanalyze standard.
	Accuracy	50 – 200%	
Precision/ Accuracy	LCS per batch	Historical lab data (See Table 5.2)	Check calculations. Reanalyze. Assess data, Narrate.
	MS/MSD per batch.	Historical lab data (See Table 5.2)	Check calculations. Analyze LCS. Assess impact on data.
	Surrogates	Historical lab data (See Table 5.2)	Check calculations. Reanalyze. Assess data, Narrate.
PQL		0.050 mg/L to 0.25 mg/L	
Holding Time		Extraction – 14 days Analysis – 40 days	

Note: The term PQL refers to the laboratory's standard Reporting Limit.

* Except for common lab contaminants: Phthalate esters may be reported with qualifiers if the concentration of the analyte is less than five times the PQL. Such action must be addressed in the case narrative.

5.2 Historical Control Limits for Method 8270D~~C~~
(for Semi-Volatile Organic Compounds in Aqueous Samples)

	COMPOUND	%R
LCS	Acenaphthene	62 to 103
	4-Chloro-3-methylphenol	60 to 100
	2-Chlorophenol	48 to 102
	1,4-Dichlorobenzene	51 to 91
	2,4-Dinitrotoluene	60 to 113
	4-Nitrophenol	18 to 63
	Pentachlorophenol	35 to 118
	Phenol	16 to 56
	Pyrene	47 to 126
	1,2,4-Trichlorobenzene	57 to 97

	COMPOUND	%R	RPD
MS/MSD	Acenaphthene	62 to 103	15
	4-Chloro-3-methylphenol	60 to 100	26
	2-Chlorophenol	48 to 102	34
	1,4-Dichlorobenzene	51 to 91	29
	2,4-Dinitrotoluene	60 to 113	26
	4-Nitrophenol	18 to 63	67
	Pentachlorophenol	35 to 118	39
	Phenol	16 to 56	71
	Pyrene	47 to 126	36
	1,2,4-Trichlorobenzene	57 to 97	27
Surrogates	2-Chlorophenol-d_4	25 to 101	NA
	1,2-Dichlorobenzene-d_4	49 to 99	NA
	2-Fluorobiphenyl	47 to 106	NA
	2-Fluorophenol	10 to 70	NA
	Nitrobenzene-d_5	50 to 102	NA
	Phenol-d_5	10 to 47	NA
	Terphenyl-d_{14}	40 to 125	NA
	2,4,6-Tribromophenol	21 to 127	NA

Note: Historical limits for the method are reported here. Current established limits will be used for the evaluation

of the data as required by SW-846 (1)~~.~~ and will be provided to DSHW prior to ADT

6.0 PCDD/PCDF ANALYSES METHOD

6.1 Summary QA/QC Criteria for Dioxins by Method 8290A

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
ICAL	Five point calibration Initially and as required.	Int Std RSD ≤ 30% Natives RSD ≤ 20%	Evaluate system. Recalibrate.
CCAL	Midpoint Standard at Start of Each 12 hour sequence	%D of IS ≤ 30% from avg RRF (ICAL); %D of natives ≤ 20% from avg RRF (ICAL).	Evaluate system. Reanalyze CCAL. Recalibrate as necessary.
WDM CPSM	Once per 12 hours prior to sample analysis.	Used to set retention times CPSM must have ≤ 25% valley resolution for 2,3,7,8-TCDD	Readjust windows. Evaluate system. Perform maintenance. Reanalyze WDM/CPSM.
Method Blanks	1 per analytical batch	< PQL, except for OCDD @ < 5 X PQL	Reanalyze. Assess impact on data.
LCS	1 per analytical batch	60 - 140% for target analytes	Review internal standards. Assess impact on data. Reextract and/or reanalyze as necessary.
MS/MSD	1 per ATB	60 - 140% recovery for target analytes; RPD ≤ 20%	Review LCS. Assess impact on data. Narrate.
Internal Standards	Every sample	40 – 135% for tetra through hexa isomers 25 – 150% for hepta and octa isomers	Check chromatogram for interference. Check instrument and reanalyze. Check signal-to-noise, if < 10:1, reextract. Assess impact on data and

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
			narrate.
Holding Time		30 Days Extraction 45 Days Analysis	

Note: The term PQL refers to the laboratory's standard Reporting Limit.

6.2 Practical Quantitation Limits for PCDDs/PCDFs

COMPOUND	METHOD 8290 (µg/L)
2,3,7,8-TCDF	0.0005
1,2,3,7,8-PeCDF	0.0025
2,3,4,7,8-PeCDF	0.0025
1,2,3,4,7,8-HxCDF	0.0025
1,2,3,6,7,8-HxCDF	0.0025
1,2,3,7,8,9-HxCDF	0.0025
2,3,4,6,7,8-HxCDF	0.0025
1,2,3,4,6,7,8-HpCDF	0.0025
1,2,3,4,7,8,9-HpCDF	0.0025
OCDF	0.0050
2,3,7,8-TCDD	0.0005
1,2,3,7,8-PeCDD	0.0025
1,2,3,4,7,8-HxCDD	0.0025
1,2,3,6,7,8-HxCDD	0.0025
1,2,3,7,8,9-HxCDD	0.0025
1,2,3,4,6,7,8-HpCDD	0.0025
OCDD	0.0050
TOCDF	

7.0 DAAMS TUBE ANALYSIS (TE-LOP-562)

Summary QA/QC Criteria for DAAMS Tube Analyses

QUALITY PARAMETER	METHOD/ FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Analyzed with calibration standards	< PQL	Reanalyze. Assess impact on data. Narrate.
Initial Calibration		Correlation Coeffnt ≥ 0.995	Recalibrate.
Accuracy (QL)	2 per sample batch	± 15% %R for > 0.3 ng; ±35% %R for ≤ 0.3 ng	Check calculations. Reanalyze QL. Reanalyze CS and recalibrate if necessary. Reanalyze QL. Assess impact on data.
Field Surrogate (QP Sample)	1 per DAAMS set	± 40% Recovery	Analyze a QL to verify instrument operation.
PQL	Agent VX	0.0180 ng	
Holding Time		72 hours	Contact Environmental Office

Note: The term PQL refers to the laboratory's standard Limit of Quantitation.

8.0 REFERENCES

(1) ***Test Methods for Evaluating Solid Waste, Physical/Chemical Methods***, 3rd Edition including Update III, USEPA, SW-846, December 1996.

(2) Title 40, ***Code of Federal Regulations***, Part 60, Appendix A, "Test Methods."

(3) Title 40, ***Code of Federal Regulations***, Part 136, Appendix A, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

(4) EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5, November 1999.

(5) ***Handbook: Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration***, EPA/625/6-89/023, January 1990.

(6) ***Guidance for Total Organics***, Final Report, EPA/600/R-96-036, March 1996.

TOOELE CHEMICAL AGENT DISPOSAL FACILITY (TOCDF)

DEMONSTRATION TEST PLAN FOR THE AUTOCLAVE SYSTEM

APPENDIX B

AUTOCLAVE SYSTEM SHAKEDOWN PLAN

Revision 1

February 10, 2009

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AUTOCLAVE SHAKEDOWN PLAN

1.0 INTRODUCTION

The Tooele Chemical Agent Disposal Facility (TOCDF) was designed and built on the Deseret Chemical Depot (DCD) as a hazardous waste disposal facility for the United States (U.S.) Army. The TOCDF is designed to dispose of the chemical agents GB, VX, and mustard (H-series), drained munitions, contaminated refuse, bulk containers, liquid wastes, explosives, and propellant components, which are all a part of the chemical agent stockpile at DCD. The DCD is located 20 miles south of Tooele, Utah. EG&G Defense Materials, Inc., (EG&G) operates the TOCDF under contract to the U.S. Army through the Chemical Materials Agency (CMA).

The TOCDF has purchased a 6-foot diameter x 20-foot-long direct steam autoclave, which was designed for medical waste sterilization. However, this autoclave technology has also been tested to decontaminate agent-contaminated waste. The TOCDF is required to perform testing to demonstrate compliance with its Resource Conservation and Recovery Act (RCRA) Permit for handling secondary waste. This testing will be the Autoclave Demonstration Test (ADT) and will include a demonstration that the system can meet the decontamination goals of the project. A pre-demonstration shakedown period is necessary for TOCDF to ensure that the appropriate processes are in place, the workers understand how to perform the tasks involved in the

secondary waste decontamination process, and the equipment is functioning properly.

The Autoclave System Shakedown process will commence when approval for the demonstration test plan is received from the State of Utah Department of Environmental Quality (DEQ), Division of Solid and Hazardous Waste (DSHW) and all associated approvals have be granted. During shakedown, the autoclave will be thoroughly tested to verify that it performs in a safe, consistent, and predictable manner when processing agent-contaminated secondary waste.

The Autoclave System includes a 6-foot diameter x 20-foot-long Bondtech autoclave with a steam vacuum eductor, high volume steam condensers, and a conveyor. The exhaust vent from the autoclave is routed to the building ventilation system, followed by a carbon filter system. Condensate is collected in a 175-gallon transfer~~holding~~ tank, and then pumped to one of two 1,000-gallon Spent Decontamination System (SDS) tanks for decontamination prior to being shipped off-site for disposal.

The secondary waste operation conditions for the TOCDF autoclave will be developed during the shakedown period.

For the autoclave, the objectives of the shakedown are to:

- Demonstrate the ability of the autoclave to treat a ~~variety of~~ secondary wastes to agent concentrations that allow the safe handling of the wastes until they can be shipped to a Treatment, Storage, and Disposal Facility (TSDF) based on feeding Demilitarization Protective Ensemble (DPE) suits, Life Support System (LSS) hoses, and wood.

- Familiarize the operators and support personnel with the Autoclave System for decontaminating secondary waste.

- Establish operating conditions governing the treatment of secondary wastes in the autoclave that establish an operating envelope allowing the treatment of the secondary wastes based on waste temperatures, pressure and treatment times.

- Characterize the condensate samples to establish the final treatment for the condensate waste stream.

- Establish the process to monitor agent inside the autoclave to ensure satisfactory treatment of secondary waste.

- Validate the spiking process
  - Determine number of spikes per autoclave treatment batch.
  - Determine procedure for spiking.
- Determine number of thermocouples per autoclave treatment batch.
- Validate equilibration time for monitoring.

- Demonstrate that the autoclave can safely and efficiently treat secondary wastes at ADT feed rates
- Determine the optimum charge volume, maximum bin weight, maximum individual drum weights/densities, and charge intervals for secondary wastes to be processed during the ADT
- Collect monitoring data for the gases exiting the autoclave during the cooling/drying cycle for review by the Executive Secretary.

2.0 PREPARATORY ACTIVITIES

Several administrative activities to prepare for agent-contaminated waste processing will take place simultaneous to plant activities. The status of all operator, maintenance, and shift risk management personnel training and certification will be audited, including signoff sheets for procedure (and other pertinent) changes specific to the agent-contaminated secondary waste handling process. Any remaining entries in logs such as the Temporary Change Log, the Lock Out/Tag Out Log, and the log of open Maintenance Work Orders will be evaluated for any impact on the agent secondary waste handling process. Finally, the plan for Environmental and Quality Assurance audits and surveillances will be reviewed to ensure proper coverage.

Formal briefings of key shift personnel will begin two days prior to the start of Autoclave System Shakedown processing, as required by the TOCDF Operations Project Regulatory Procedure (PRP-OP)-044, *Critical Activities Manual*. Preparations for a new agent decontamination process are governed by Critical Activity # CA-01, which provides for the briefing of key management and shift personnel for two days before the agent secondary waste handling process begins. The briefings are repeated on each of the first three days of the new campaign. These briefings ensure that the processing team is prepared prior to commencing the campaign; they also help personnel evaluate the adequacy of the preparations once the secondary waste handling process has begun.

Environmental personnel will conduct a review of permit requirements and issues. In addition, they will confirm that all modifications have been incorporated into the appropriate permits and will review laboratory and monitoring procedures to ensure that the provisions of the Waste Analysis Plan (WAP) have been satisfied. Certain types of plant modifications require that an independent Professional Engineer certify the proper completion of construction through a Facility Construction Certification (FCC); therefore, the completion of any FCC activities will be confirmed.

Environmental will verify receipt of State approval of the demonstration test plan and that all permit conditions for agent-contaminated secondary waste handling and autoclave processing have been met, including approval of methods. In addition, they will notify the Autoclave Manager when the plant has met the environmental requirements for startup, and then inform the DSHW of the same before processing agent-contaminated secondary waste in the Autoclave System.

3.0 GENERAL SHAKEDOWN ACTIVITIES

The DSHW will be provided with two weeks notice before contaminated secondary waste is introduced into the Autoclave System. ~~Non-agent-contaminated secondary waste material or agent contaminated secondary waste (i.e., DPE material, wood, LSS air hoses) that has been monitored with a headspace agent concentration of < 1.0 VSL will be used to establish the function of the Autoclave System and test for any potential Automatic Continuous Air Monitoring System (ACAMS) interferents.~~ VX-contaminated waste will be introduced into the Autoclave System to bring the unit to a point of operational readiness by establishing the optimal time and temperature, and maximum load capacity. Agent spiking operation will be systemized during this shakedown period. This phase will take four-to-six weeks and consist of up to 720 hours of agent-contaminated secondary waste processing. If events dictate that more time is needed to ensure operational readiness before the demonstration test, TOCDF will request an extension of up to 720 additional hours of operating time. Extreme caution will be exercised as shakedown operations begin to ensure that all systems are functioning properly for the new Autoclave System.

The TOCDF will conduct the shakedown as pre-testing at the proposed demonstration test conditions during the 720-hour shakedown to verify autoclave performance. Pre-testing will be conducted using the ACAMS to verify that no agent levels are greater than or equal to (=) 0.5 VSL ~~exist~~exists in the autoclave following the completion of the autoclave cycle. DAAMS sampling will be used to monitor for Agent in the gases exiting the autoclave during the cooling/drying cycle. The TOCDF may request final modifications to the demonstration test plan based on the pretest results; any such changes will be coordinated with DSHW.

The collection and analysis of samples during shakedown will follow the provisions in the WAP.

A dry run for the autoclave will be performed once it demonstrates the ability to process agent-contaminated secondary waste at design parameters. The test will be run using the autoclave and the ACAMS to monitor for agent as proposed in the demonstration test plan. The dry run will consist of one run at proposed test conditions for each type of waste to be demonstrated. The objectives of this dry run are to:

Operate the autoclave at full demonstration test conditions for an established period of time at maximum temperatures.

Demonstrate performance capabilities of the complete system and its individual components.

Finalize preliminary operating conditions for the demonstration test.

Confirm that the process data collection can meet the needs for the ADT. This includes

verification that the ACAMS will produce the data needed for a successful test.

Finalize the spiking process for the demonstration test.

Characterize the condensate samples to include Agent VX, agent hydrolysis compounds, Volatile Organic Compounds (VOCs), Semi-Volatile Organic Compounds (SVOCs) and metals, to establish the final treatment for the condensate waste stream.

The dry run results will be evaluated, and the test conditions for the demonstration test results will be finalized.

4.0 AUTOCLAVE SYSTEM SHAKEDOWN ACTIVITIES

The following outlines the steps that will be taken during shakedown. The activities begin after the specified number of processing bins of secondary waste are established. Transitions between steps will be at the discretion of the EG&G Autoclave Manager and Test Director.

4.1 Initial Ramping of Feed

The shakedown period will involve a series of tests to verify that the objectives can be met. Bins loaded with barrels of secondary waste will be processed through the autoclave and agent spikes will be added to some barrels. The series of tests to be conducted, in order, are Autoclave Agent Monitoring, Drum Weight Verification, Agent Spiking Verification and equilibration verification.

Autoclave Agent Monitoring

This section of the shakedown will consist of processing bins of either non-agent-contaminated or < 0.5~~1~~ VSL agent contaminated secondary waste material to verify that the autoclave can monitor for agent without interferents affecting the effectiveness of the ACAMS or DAAMS. TOCDF will also be collecting data on temperature profiling in the drums of waste. Each waste bin~~drum~~ will have a minimum of 4 thermocouples (one per drum)~~thermal couples~~ ~~located in each drum~~ for a total of 16 thermal couples per autoclave batch until data can determine the optimal location for the controlling ~~thermal couples~~ thermocouples. Then each drum per waste bin will have a thermocouple at the predetermined location from above to determine variation in location per drum. If that is successful, then ~~At this poin~~t each bin will have 4 drums with one controlling thermal couple placed inside one of the drums of secondary waste.

Drum Weight Verification

This section of the shakedown will consist of processing bins of either non-agent-contaminated or < 0.5~~1~~ VSL agent contaminated secondary waste material to verify the maximum ~~weight drum~~ drum weight/drum density that the autoclave can process for each of the three types of waste to be processed in the autoclave.

Agent Spiking Verification

This section of the shakedown will consist of placing agent spiking packages inside agent contaminated secondary waste < 0.5~~1.0~~ VSL to verify ≥ 99% removal efficiency of the agent from the spiking media and the agent

concentration is < 1.0 mg/kg or less. The first step is to place a spiking package in each drum of the waste bin of the DPE, LSS, wood and combination waste bin to determine if variation occurs and to determine the packaging mechanism for the agent spiking package.

Equilibration Verification

This section of shakedown will determine if monitoring within 15 minutes is the most conservative approach.

4.2 Sustained Autoclave Operations

After establishing maximum load size/weight, optimal temperature, and appropriate time intervals, the autoclave operating parameters will undergo additional optimization. During this portion of the shakedown, Operators will verify that:

The system is within operating parameters.

During these operations the ~~maxium~~maximum vapor stabilization time will be established.

The autoclave containing secondary waste will be monitored for any signs of agent contamination at the end of the cycle. If ACAMS indicates that agent is present with any load, that load will be processed with additional time as necessary.

The autoclave condensate samples will be analyzed during the ADT for agent, pH, metals, SVOC, VOC, and Dioxins and Furans ~~and agent levels~~ to ensure compliance with the permit.~~that all levels are below the Waste Control Limit~~.

The autoclave gases exiting the during the cooling/drying cycle will be monitored for agent with DAAMS.

Following optimization, a performance run will be conducted to confirm that the autoclave is ready for the demonstration test. These performance runs will consist of processing the three types of secondary waste using the same conditions under which the demonstration test will be conducted.

5.0 POST-DEMONSTRATION-TEST ACTIVITIES

Treatment of secondary wastes in the autoclave will continue after completion of the ADT and the wastes will be held on-site until the preliminary data from the testing can be submitted to DSHW and approved. The preliminary data submitted will include the operational data from the autoclave, DAAMS data from monitoring during the cooling/drying cycle, ACAMS data from the autoclave headspace, the analyses results from the spiked samples, and the agent results from the condensate samples. Upon approval of the preliminary data submittal, the wastes treated during the ADT and the post-test wastes treated will be sent to a Subtitle C TSDF. Monitoring the headspace in the autoclave at the end of the treatment cycle will continue during this time period to ensure that the wastes have met their treatment conditions.

TOOELE CHEMICAL AGENT DISPOSAL FACILITY (TOCDF)

DEMONSTRATION TEST PLAN FOR THE

AUTOCLAVE SYSTEM

APPENDIX C

ADDITIONAL SUPPORTING DATA

Revision 1

February 10, 2009

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APPENDIX C

Section 1.0

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DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES FOR CHEMICAL AGENTS (GB, VX, HD) CONTAMINATED FACILITIES

Phase II - Laboratory Evaluation of Novel Agent Decontamination Concepts

E. R. Zamejc, E. J. Mezey, T. L. Hayes,
D. K. Wetzel, B. C. Garrett

BATTELLE COLUMBUS LABORATORIES
505 KING AVENUE
COLUMBUS, OHIO 43201-2693

JUNE 21, 1985

TASK FINAL REPORT FOR THE PERIOD AUGUST 1983
TO MARCH 1985

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Prepared for:

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MARYLAND 21010

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DISCLAIMER

The views, opinions and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documents.

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EXECUTIVE SUMMARY

As part of their responsibilities in DOD real property disposal, USATHAMA must identify, contain and eliminate toxic and hazardous materials where facilities, potentially available for alternate government or private use, have been declared excess or are candidates for excessing. With this mandate USATHAMA must provide not only the technical basis to implement decontamination but also the standards to insure decontamination has been effective. Battelle's Novel Processing Technology Program supported USATHAMA through identification, development, and recommendation of decontamination methods for Army facilities which have been contaminated with chemical warfare agents.

In a first phase study about 65 decontamination concepts were generated, described in detail, and rank/ordered. The most promising concepts were recommended for further evaluation - hot gases, FREON® vapor circulation, flashblast, monoethanolamine, steam, ammonia, ammonia/steam, and an aqueous solution of n-octylpyridinium 4-aldoxime bromide (OPAB).

In this second phase study, the selected concepts were experimentally evaluated for their effectiveness in decontaminating HD, GB and VX. Emphasis was placed on the concepts ability to decontaminate these agents spiked onto painted and unpainted mild and stainless steels and unpainted porous materials. The experimental data demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated. Each of the other techniques (i.e., flashblast, ammonia, etc.) was effective to some extent, but either the effectiveness was limited to specific agent/material combinations or the concept appeared less promising.

An engineering/economic analysis suggested that either hot gas or steam decontamination of field structures contaminated throughout with agent is feasible. In terms of cost, the hot gas concept is preferred over the steam concept. As such, the hot gas concept was recommended as the primary decontamination concept for field evaluations in Phase 3 of the program. The steam and OPAB concepts were also recommended for Phase 3 evaluations. That is, OPAB is recommended for use as a protective coating

and as a non-corrosive decontaminant for inside of pipes, sumps, and other equipment; steam should be retained as a back-up to the hot gas concept.

Analytical method development activities indicated that HD, GB and VX interact with concrete. The interaction, possibly a chemical reaction, (i.e., hydrolysis) may obviate the need to decontaminate unpainted concrete in the field, especially in the case of the nerve agents GB and VX. The need for agent impermeable paint on concrete in future agent demilitarization facilities should also be reconsidered because of this apparent reaction (i.e., paint may not be necessary).

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TASK 3

on

DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES
FOR CHEMICAL AGENT (GB, VX, HD),
CONTAMINATED FACILITIES - PHASE 2

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

from

BATTELLE
Columbus Laboratories

June 21, 1985

1.0 INTRODUCTION

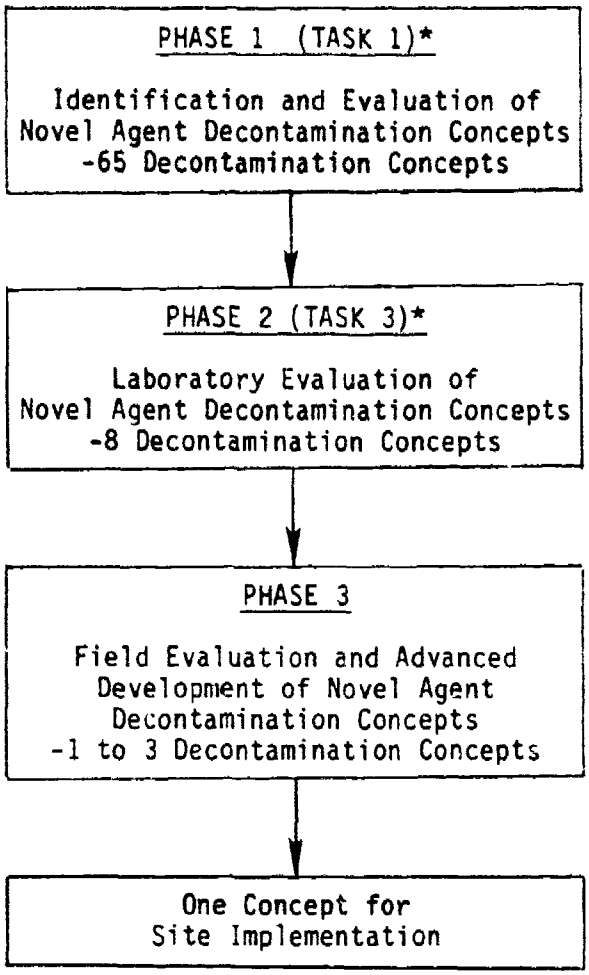
As part of their responsibilities in DOD real property disposal, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) must identify, contain, and eliminate toxic and hazardous materials and related contamination where lands and facilities, potentially available for alternate government or private use, have been declared excess or are candidates for excessing. With this mandate USATHAMA is to provide the technical basis to implement the decontamination and also provide the standards to insure decontamination has been effective. Facilities which might require such decontamination are located at Tooele Army Depot, Rocky Mountain Arsenal, and Edgewood Area of Aberdeen Proving Ground. Of concern are contaminated building structures, underground and above ground storage tanks, reaction vessels, sumps, waste stream conduits, and pipes. Both the exposed surfaces of the materials as well as the interior areas into which chemical warfare agents have penetrated (i.e., through cracks, pores, or other openings) may require decontamination.

USATHAMA envisions that new, improved procedures for the decontamination of facilities previously utilized for chemical agent manufacture or testing will be required. The only currently approved method of decontaminating materials involves incineration at a temperature of 1000 F for a period of 15 minutes. Materials exposed to such conditions are described as having attained the 5X status and are defined as suitable for unrestricted use. Unfortunately, the time and expense required to accomplish such decontamination is immense. Successful development of an alternative decontamination technique which would not require the dismantling of a facility and which would result in a 5X decontamination status rating (or its equivalent) without incineration represents a potentially large cost savings to the Government.

USATHAMA tasked Battelle Columbus Laboratories in the Novel Processing Technology Program to identify and develop treatment methods and to recommend plans for carrying out the decontamination. The ideal concept would be a single method that is both universally applicable and most cost effective. Decontamination of structures and equipment contaminated with chemical agents to a level that does not pose a hazard during unrestricted use, represents an extremely difficult problem in any excessing action. This document details the efforts of Phase 2 of USATHAMAs three phase research and development program for the restoration of chemical warfare agent installations. A description of the program which leads to site implementation of one decontamination concept is given in Figure 1.

1.1 Phase 1 Results

In the first phase study, about 65 concepts (See Table 1) were generated and described in sufficient detail to permit their evaluation against the criteria of mass transfer, destruction efficiency, safety, damage to structures, penetration depth, applicability to complex structures, operating costs, capital costs, and waste treatment costs.[1] This evaluation was the basis for the selection of the most promising concepts for experimental evaluation in the second



* Task 2 and 4 were parallel efforts focusing on explosive decontamination concepts.

FIGURE 1. DESCRIPTION OF RESEARCH AND DEVELOPMENT PROGRAM FOR AGENT INSTALLATION RESTORATION

TABLE 1. AGENT DECONTAMINATION CONCEPTS EVALUATED DURING PHASE I

CHEMICAL

OCTYL PYRIDINIUM 4-ALDOXIME BROMIDE (OPAB)
DS2 (A)
CD-1 (B)
SUPERTROPICAL BLEACH (STB)
ALL PURPOSE DECONTAMINANT (APD) (C)
MONOETHANOLAMINE
GAMMA RADIATION
NITRIC ACID
AMMONIUM HYDROXIDE
HYPOCHLORITES
DANC
GASEOUS AMINES
CHLORINE
STEAM
AMMONIA/STEAM
PERCHLORYL FLUORIDE
GERMAN EMULSION
HYDROXAMIC ACIDS
SODIUM HYDROXIDE SOLUTION
DIMETHYLSULFOXIDE
MACROCYCLIC ETHERS
PROPIONYL FLUORIDE
PHENOLS/CATECHOLS
CARBONATE/BICARBONATE SOLUTIONS
CHLORITE SOLUTIONS
CHLORINE DIOXIDE
NITROGEN TETROXIDE
BORON TRIFLUORIDE
OZONE
SULFUR DICHLORIDE
UV/OZONE
ULTRASONIC DECOMPOSITION
COPPER LIGANDS
VANADIUM CATALYZED HYDROLYSIS
ANTHRANILIC ACID-SILVER COMPLEXATION
MAGNESIUM HYDROXIDE IMPREGNATED ALUMINA
COMPLEXATION WITH MOLYBDENUM LIGAND
PERBORATES
MICROBIAL DEGRADATION
PERMANGANATE SOLUTIONS
ENZYME PROTEINS
SODIUM SULFIDE

PHYSICAL/EXTRACTION

SURFACTANTS
STRIPPABLE COATING
VAPOR CIRCULATION
SOLVENT CIRCULATION
SUPERCRITICAL FLUIDS
ULTRASONIC EXTRACTION

PHYSICAL/ABRASIVE

HYDROBLASTING
ACID ETCH
SANDBLASTING
DEMOLITION
VACU-BLASTING
CRYOGENICS
SCARIFICATION
ELECTROPOLISHING
DRILL AND SPALL

THERMAL

FLASHBLASTING
HOT PLASMA
MICROWAVE HEATING
FLAMING
HOT GASES
SOLVENT SOAK/BURN
INFRARED HEATING
CARBON DIOXIDE LASER
ELECTRICAL RESISTANCE CONTACT HEATING

A) Mixture of 70 weight percent diethylenetriamine, 28 weight percent methyl cellosolve and 2 weight percent sodium hydroxide.

B) Mixture of 55 volume percent monoethanolamine, 45 volume percent propylene glycol and 2.5 weight percent lithium hydroxide.

C) Mixture of 54 weight percent monoethanolamine, 44 weight percent isopropanolamine and 2.5 weight percent lithium hydroxide.

phase laboratory studies. The most promising concepts recommended for further evaluation in Phase 2 were the use of:

- Hot gases
- Steam
- N-Octyl-pyridinium 4-aldoxime bromide (OPAB)
- Monoethanolamine (MEA)
- FREON 113® Vapor Circulation
- Ammonia Gas or Ammonia/Steam
- Flashblast

These suggested decontamination methods are briefly described as follows.

Hot Gases. The interior of a building is heated by hot exhaust gases from a combustion device located outside the building. As the material temperature increases, agents will decompose by pyrolysis and/or volatilize from the surface. The interior of the building will be heated by conduction. If agent volatilization occurs, provision to treat the building exhaust gas to remove/destroy the intact agent would be required.

Steam. A boiler is provided outside the building and steam is piped into the structure, decontaminating the entire building at once. The elevated temperature will promote agent hydrolysis reactions and cause volatilization of agents from subsurfaces. The steam itself should penetrate concrete, perhaps more readily than might be expected for liquid reactants. The condensate must be considered hazardous until proven otherwise.

OPAB. OPAB is a dilute aqueous solution of 1-octylpyridinium 4-aldoxime bromide. The reaction of oximes with the nerve agents is well documented, but this reagent appears to be especially effective with VX. Its safety has been validated and, in fact, it is closely related in structure to the nerve agent antidotes, PAM and toxogonin. The products produced with OPAB and nerve agents are the same as those produced on hydrolysis, but this reagent is especially appealing because of its speed and safety.

MEA. MEA is known to be a very active reagent for HD. It is good solvent for HD and is rapidly alkylated by HD. Unlike HD, the products of HD decomposition by this reagent are all water soluble (as is MEA), thus facilitating removal of products via a water wash. Once reaction with HD has taken place, it should not be reversible.

FREON 113 Vapor Circulation. FREON 113 is heated to its boiling point and the vapors allowed to circulate in a building. The vapors permeate porous building materials where they condense, solubilize the agent, and aid diffusion. The condensed FREON, laden with contaminant, is collected in a sump and treated to permit recycle.

Ammonia Gas. The appeal of gaseous decomposition systems is their ability to permeate throughout a building including subsurfaces. Ammonia should react with HD to produce thiomorpholines. Ammonia alone is not expected to effectively decontaminate nerve agents, but, in the presence of water (perhaps as steam), will raise the pH and promote hydrolytic decomposition. Because ammonia is moderately toxic, it can be introduced into a sealed building and exhausted through an absorber. This approach is thus similar to steam treatment, but provides a reagent specific for HD which will at the same time promote base catalyzed GB and VX hydrolysis in the presence of moisture.

Flashblast. The flashblast device consists of a high intensity Xenon-quartz strobe light which can be focused onto a contaminated surface. The high energy light pulse produces enough heat to remove paint and rust films and to thermally decompose surface contaminants.

1.2 Background of Phase 2 - Laboratory Evaluation

The second phase effort was designed to experimentally evaluate the concepts selected from Phase 1 and to recommend one to three of the most promising concepts for field evaluation in Phase 3. The ideal case was development of a single decontamination method which is both cost effective

and universally applicable to all types of agent-contaminated materials. However, the development of a single decontamination method specific to one agent would also be considered in the event that a "universal" concept was infeasible. Materials of concern identified from Phase 1 site surveys for which decontamination methods were to be developed in Phase 2 included:

- Stainless steel - painted and unpainted
- Mild steel - painted and unpainted
- Concrete - painted and unpainted

The approach used to develop the decontamination concepts through experimental evaluation focused on subjecting the concepts to conditions/ materials progressively more difficult to decontaminate. At each stage of the process, attempts were made to make the concept work by either altering process parameters or the use of additives. A logic plan detailing the stages of the concept development process is illustrated in Figure 2 and discussed as follows.

In the first stage of the evaluation, the decontamination effectiveness of each chemical concept (i.e., MEA, OPAB, Steam, and Ammonia) against HD, GB, and VX was determined in laboratory glassware (i.e., no matrix present). Based on these experiments the most promising concepts were selected for further evaluations. If in these tests, conditions could not be found in which an agent(s) was effectively decomposed by any one chemical concept, then an alternative replacement concept would be selected from the Phase 1 concept list and its effectiveness determined in the same manner.

In the second stage of the evaluation process, the selected chemical concepts as well as the hot gas, flashblast and vapor circulation concepts were evaluated in a test chamber. Unpainted stainless steel spiked with HD, GB, or VX was selected as the substrate for the second screening of the concepts. Unpainted stainless steel allowed the highest recovery of agent and therefore yielded the most accurate measure of decontamination effectiveness. Based on the experimental data, the three most promising concepts were then selected.

The third stage of the evaluations focused on the decontamination of painted and unpainted mild steel, painted stainless steel and concrete

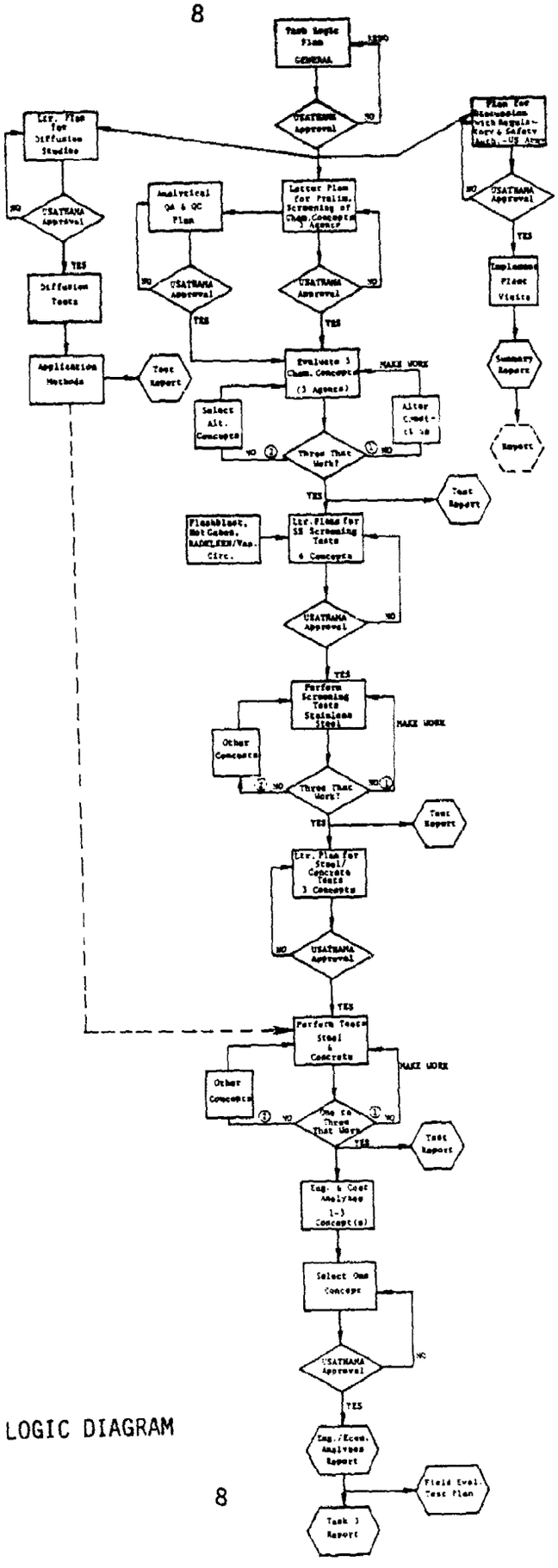


FIGURE 2. TASK 3 LOGIC DIAGRAM

in the test chamber. The materials provided places into which agent can be absorbed (i.e., paint and concrete pores). Two concepts were then selected for evaluation in the engineering/economic analyses from which a concept applicable to all three agents was recommended.

2.0 OBJECTIVES

The purpose of Phase 2 was to validate novel cost effective decontamination concepts selected in Phase 1 for the decontamination of agent contaminated facilities. The objective was to demonstrate the applicability of the selected concepts for decontamination of building materials to concentrations below the detection limit using samples that have been contaminated in a controlled manner in a laboratory environment. Data on their effectiveness, reliability, waste product characteristics, possible hazards and approximate cost were used to make a selection of the most cost-effective method for pilot testing in the subsequent phase and for detailed concept design for field trials.

3.0 SYNOPSIS OF PHASE 2 RESULTS

The Phase 2 experimental program was divided into subtasks as follows (See the Design Plan in Appendix I).

Subtask 1. Regulatory/Agency Visits
Subtask 2. Test Preparations
Subtask 3. Chemical Concept Prescreening
Subtask 4. Diffusion Studies
Subtask 5. Stainless Steel Surface Screening
Subtask 6. Steel/Concrete Tests
Subtask 7. Engineering/Economic Analysis
Subtask 8. Preparation of Final Report and Field Test Plan
Subtask 9. Fate of Agent in Concrete*
Subtask 10. JACADS Decontaminations Evaluation*
-- Analytical Summary Report*

* Additional efforts requested by USATHAMA in contract modifications.

The subtasks are summarized as follows. Detailed descriptions of the experimental and engineering efforts are given in the appendices.

3.1 Regulatory/Agency Visits

Program overviews were given and issues (e.g., 5X decontamination versus decontamination to below the detectable limit) were raised at presentations to various safety and regulatory groups. The presentations served to acquaint the DOD safety community of near-term future plans for facility decontamination methods. An initial safety agency presentation was conducted at U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) on November 2, 1983, to brief the USATHAMA Safety Group. Other briefings were given at the U.S. Army Pollution Abatement Symposium (November 6-8, 1984) held at Blacksburg, Virginia and the 21st DOD Explosives Safety Seminar (August 28-30, 1984) held at Houston, Texas.[2]

3.2 Test Preparations

A test chamber was designed and constructed such that application of a decontamination concept could be performed in a controlled environment. Design criteria for the test chamber include

- access ports to allow introduction of coupons and removal of effluents,
- allow decontamination of coupons by liquid decontaminants/solvents, by gaseous decontaminants/solvents, and by thermal methods,
- be sized to fit within a toxic materials laboratory hood.

A detailed description of the test chamber is given in the Subtask 5 test report (See Appendix IV).

3.3 Chemical Decontamination Concept Prescreening

A preliminary evaluation of the five chemical decontamination concepts identified in Phase 1 of the Novel Processing Program was performed

in Subtask 3. The concepts which were evaluated in laboratory scale glassware included monoethanolamine (neat and 50 percent aqueous solution), aqueous solution of 1-octylpyridinium 4-aldoxime bromide (OPAB), anhydrous ammonia, steam, and steam/ammonia.

The results indicated that all of the chemical decontaminants were effective on specific chemical agents. The most promising concepts, involving the use of either steam or OPAB, achieved high destruction efficiencies (i.e. 99.5 to the detection limit of 99.8 percent destruction) for all three agents (HD, GB, and VX). Product identification results indicated that both OPAB and steam caused hydrolysis of the agent molecule whereby key bonds on the molecule (e.g., P-F on GB, P-S on VX, and C-Cl on HD) were broken. As such, Battelle and USATHAMA selected the steam and the OPAB concepts for further evaluation in subsequent subtasks involving decontamination of steel and concrete matrices. Because of the effectiveness of the other chemical decontaminants, no concept was eliminated but rather, all remaining concepts were retained in the event that an alternative decontaminant would be required in the subsequent efforts.

Detailed experimental results and mass spectra obtained from the chemical concept prescreening studies are given in Appendix II.

3.4 Diffusion Studies

Because facility decontamination includes decontamination of trace quantitites of agents which have penetrated into porous materials such as concrete, an evaluation criterion was incorporated in Phase 1 evaluations which focused on the anticipated depth of penetration of the decontaminant into porous materials. It was assumed that the depth of penetration of chemical decontaminants would be less than 1/8 inch for liquids and more than 1/8 inch (but less than complete penetration) for gases. It was recognized that an experimental effort would be required to substantiate these assumed penetration depths.

The ability for liquid and gaseous decontaminants to penetrate mortar was investigated in Subtask 4. Aqueous solutions and FREON® 113 were applied to mortar coupons by spraying and by a constant contact method.

The diffusion rate of gaseous ammonia (a candidate agent decontaminant) through mortar was determined.

Experimental results indicated spraying is the preferred method for application of aqueous based decontaminants to concrete. However, application of FREON® 113 to concrete does not appear feasible. Penetration depths of 1/4 to 1 inch were achieved by aqueous solutions applied with the spraying method. Operating parameters were determined for further evaluation of the spraying method in subsequent subtasks (5, 6 and 7) of both Task 3 (agents) and in a related effort focusing on explosive decontamination.

Gaseous ammonia was demonstrated to readily penetrate one inch thick mortar coupons. Detailed experimental results from the diffusion studies are given in Appendix III.

3.5 Stainless Steel Surface Decontamination Screening

Five decontamination concepts (steam, OPAB, hot gases, vapor, circulation, and flashblasting) were evaluated for their decontamination effectiveness of agent contaminated unpainted stainless steel surfaces. The results indicated that steam, hot gases, and OPAB are the most promising concepts. The steam and hot gases concepts decontaminated the stainless steel contaminated with HD, GB, or VX to below the detectable limit. The detectable limit for the stainless steel decontamination tests was equivalent to a 99.9 percent agent decontamination efficiency for an initial spike level of 1.2 mg agent/m^2 of surface area. Mass spectral analyses confirmed that neither agents nor agent decomposition products remained on the stainless steel surfaces following application of the hot gas decontamination concept.

The OPAB concept decontaminated stainless steel to below the detectable limit when GB was the contaminant. Results suggested that a similar decontamination effectiveness could be achieved with OPAB when either HD or VX is the contaminant. As such, Battelle and USATHAMA selected the steam, OPAB, and hot gases concepts for further evaluations in Subtask 6. Detailed experimental results from the stainless steel screening tests are given in Appendix IV.

3.6 Steel/Concrete Decontamination Tests

The steam, hot gas, and OPAB decontamination concepts were evaluated for their effectiveness in decontaminating painted mild steel, unpainted mild steel, painted stainless steel, concrete, and unglazed porcelain* coupons contaminated with HD, GB, or VX. The detectable limit for the Subtask 6 steel tests was equivalent to a 99.9 to 99.999 percent agent decontamination efficiency for an initial dose level of 1.2 mg agent/m^2. A similar decontamination efficiency was observable in the concrete and unglazed porcelain tests for an initial dose level of 1.8 mg agent/g of material.

Results of the hot gas experiments indicated that painted and unpainted mild and stainless steels, unpainted concrete and unglazed porcelain can be decontaminated to below the detectable limit by maintaining the material at a temperature of 150 C for 60 minutes when either HD, GB, or VX are the contaminant. Because undecomposed agent was volatilized from the coupons during the process, a method to remove or to decompose agent contained in the exhausted gas from a building must be defined.

Results of the steam experiments indicated that painted and unpainted mild and stainless steels, unpainted concrete and unglazed porcelain can be decontaminated to below the detectable limit by maintaining the material at a temperature near the boiling point of water for either 60 minutes when either HD or GB are the contaminants or for 240 minutes when VX is the contaminant. Because undecomposed agent was volatilized from the coupons during the process, a method to remove or to decompose agent contained in the exhausted steam and condensate from a building must be defined. One such method is to recycle the condensate through the steam generator. Experimental data indicated that boiling of contaminated condensate from the process resulted in the destruction of the residual agent.

Results of the OPAB experiments indicated that painted and unpainted mild and stainless steel can be decontaminated by applying about 15 to 30 liters/m^2 OPAB solution when HD is the contaminant and about 25 to 45 liters/

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* Unglazed porcelain was selected as an inert alternative to concrete for GB and VX tests (See Appendix V and VII).

m^2 of OPAB solution when either GB or VX is the contaminant. Results of the concrete and unglazed porcelain tests indicated that VX contaminated unglazed porcelain can be decontaminated to below the detectable limit by spraying with OPAB solution. Decontamination of either HD contaminated concrete or GB contaminated unglazed porcelain to near the detectable limit by spraying with OPAB solution was also achieved. The data from these decontamination tests and the diffusion studies (See Section 3.4) indicate that the effectiveness of OPAB for decontamination of porous materials such as concrete is limited to a penetration depth of about 1/8 to 1/4 inch.

Based on the experimental evaluations, Battelle and USATHAMA selected the steam and the hot gas concepts for further evaluations in the subsequent engineering/economic analysis subtask (Subtask 7). OPAB was not selected for the engineering analyses because of its limited ability to penetrate porous materials. However, specific applications for OPAB were identified including use as a decontaminant for pipes, pumps, tanks, and other equipment and as a protective coating for external building surfaces during either hot gas or steam decontamination.

In conjunction with the decontamination tests, an air sampling method employing heated air for extraction (i.e., volatilization) of residual agent from decontaminated coupons was evaluated. Results from the heated air extractions were compared with results obtained using a solvent (e.g., hexane or methylene chloride) extraction method on similar samples. The results indicated that the solvent extraction method is more reliable in terms of specificity to the agents and more effective at extracting agent than the air sampling method.

Detailed experimental results from the steel/concrete tests are given in Appendix V.

3.7 Engineering/Economic Analyses

An engineering/economic analysis was performed on the hot gas and steam decontamination concepts selected from the experimental evaluations in Subtask 6. Equipment was specified and costs were estimated for application of the concepts to a model facility representative of structures observed

during the Phase 1 site surveys. Results of the analyses suggest that it is feasible to apply the hot gas and steam contamination concepts for decontamination of field structures. In terms of cost, the hot gas concept is slightly preferred over the steam concept for the assumption that the entire building is contaminated throughout. In the hot gas concept, flue gases from the combustion of oil or natural gas are directed into a sealed and insulated building. Gas exhausted from the building is treated in an afterburner to destroy traces of volatilized agent, cooled by quenching with water, directed through an induced draft fan, and exhausted to the outside from a stack. The induced draft fan maintains both a flow through the system and a slight negative pressure within the building to minimize leakage of air potentially contaminated with agent to the outside. A detailed discussuion of the results of the analyses is given in Appendix VI.

3.8 Fate of Agent in Concrete

Suitable analytical methods for the agent decontamination studies were unavailable when laboratory experiments were being initiated. Consequently, analytical method development was undertaken for the agents GB, HD, and VX on selected building materials. Building materials examined included painted and unpainted mild steel, stainless steel, and concrete. Attempts to recover agents by solvent extraction from the painted and unpainted steels were successful and produced no unanticipated results. Use of the solvent extraction method proved significantly less successful for agents added to concrete than was observed for agents on metal. Assorted modifications to this basic method were tried but the results were disappointing, in that GB could not be extracted by any technique attempted at levels significantly above the method detection limit. Although HD and VX could be partially recoved from unpainted concrete, the precision (repeatability) observed was extremely poor. These results suggested that all or part of the agent applied to the concrete specimen was not available to be extracted due to interaction with the concrete. Results of the analyses suggest that the interaction of the nerve agents with concrete is a chemical

reaction which causes agent hydrolysis. The interaction of concrete with HD appears to be incomplete or reversible in that substantial amounts of HD are extractable even after a 24 hour exposure period.

A detailed discussion of the results on the fate of agent in concrete studies is given in Appendix VII.

3.9 JACADS Decontaminants Evaluation

In support of routine decontamination anticipated during operations at the JACADS facility, the JACADS experimental study evaluated the ability of three candidate chemical decontaminants to decontaminate specific unpainted and painted steel surfaces representative of construction materials selected for the JACADS design. Solutions of 10 percent Na_2CO_3 and 1 percent NaOH were separately tested to decontaminate steel coupons spiked with GB. A 5 percent commercial NaOCl solution was tested to decontaminate VX and HD. Following decontamination, the coupons, spent decontamination solution and chamber rinses were analyzed for residual agent. Results suggested that the JACADS decontaminants are effective in that the coupons were decontaminated to either below the detectable limit or to low levels of residual agent.

A detailed discussion of the results on the JACADS study is given in Appendix VIII.

3.10 Summary of Analytical Methodology in Support of Task 3

At the request of USATHAMA, a summary report detailing the analytical methodology used in support of Task 3 was prepared and is given in Appendix IX. The analytical method developments indicate the utility of the extraction/GC-FPD method of analysis for determining residual HD, GB, or VX in or on matrices found in agent contaminated structures. It has been used instead of the air sampling-impinger method accepted by the Army. The extraction procedure proved to be rapid and was reliable enough to demonstrate the effectiveness of various substrate decontamination concepts.

4.0 CONCLUSIONS/RECOMMENDATIONS

The concept selection results from the Phase 2 experimental and engineering subtasks are illustrated in Figure 3. The experimental evaluations (Subtasks 3, 4, 5 and 6) demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated. Each of the other decontaminants (e.g., flashblast, ammonia, etc.) was effective to some extent, but either the effectiveness was limited to specific agent/material combinations or the concept appeared less promising.

The engineering evaluations indicated that it is feasible to apply either the hot gases or the steam decontamination concept to structures representative of Army installations. Because of the limited depth of penetration into porous materials, the use of OPAB as a general decontaminant is not feasible. However, OPAB is recommended for use as a protective coating during application of the hot gas or steam concept and as a non-corrosive decontaminant for specific applications such as decontamination of the inside of pipes, sumps, and other equipment.

Results of the economic analyses indicated that the hot gas concept is preferred over the steam concept. As such, the hot gas concept is recommended as the primary decontamination concept for field evaluation in Phase 3 of the program. Steam should be retained as a back-up concept to the hot gas concept.

Analytical method development activities demonstrated the utility of the solvent extraction/gas chromatography technique for the quantification of agent on building materials such as painted and unpainted steels. Attempts to quantitatively recover HD, GB or VX when spiked onto concrete were unsuccessful. Investigations as to the fate of agent on concrete indicated that an agent/concrete interaction, possibly a chemical reaction such as hydrolysis, is responsible for the inability to recover the spiked agents.

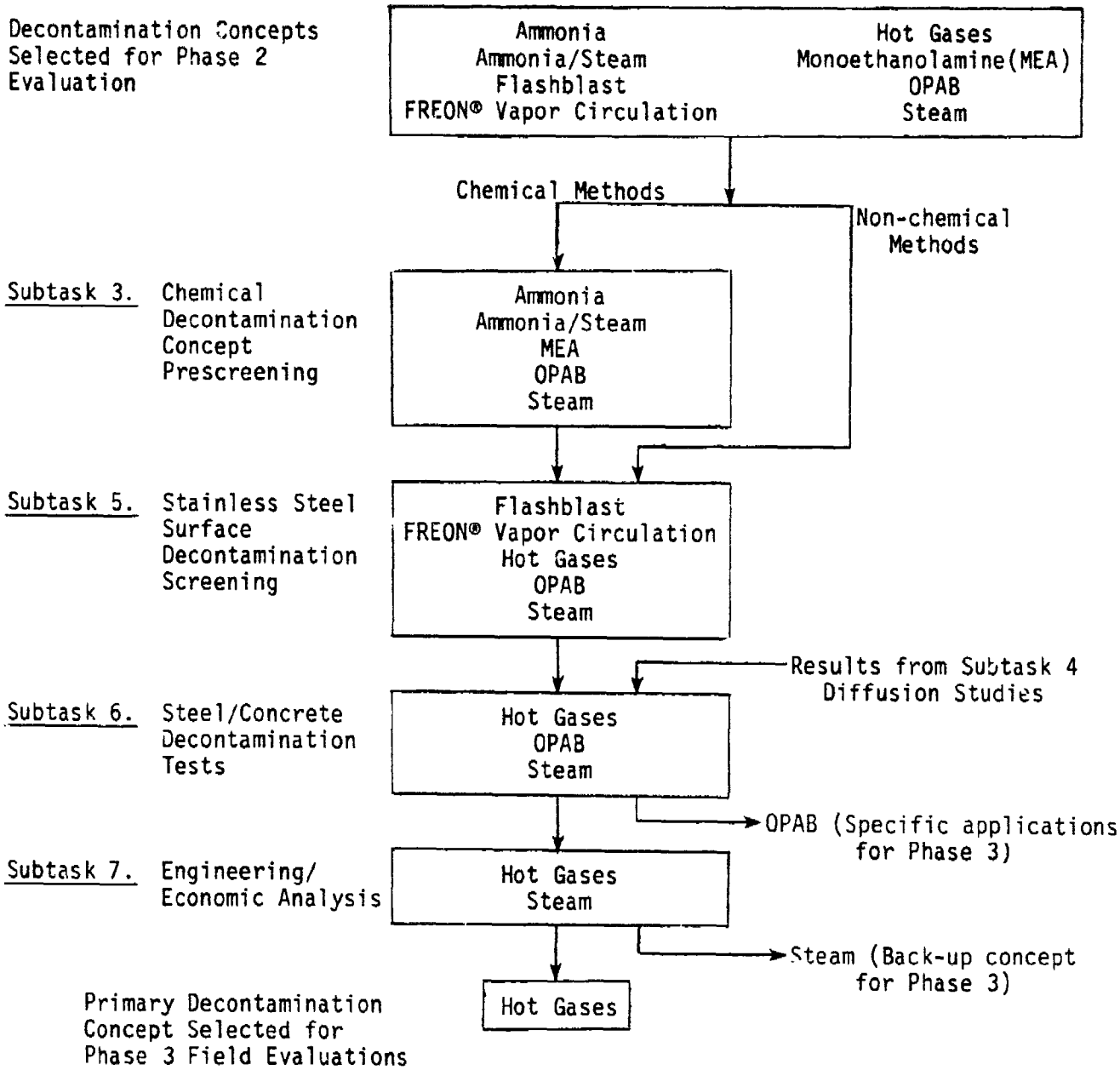

FIGURE 3. CONCEPT SELECTION RESULTS FROM THE PHASE 2 EXPERIMENTAL AND ENGINEERING EVALUATIONS

APPENDIX I

DESIGN PLAN

DESIGN PLAN

for

TASK 3

DEVELOPMENT OF NOVEL DECONTAMINATION
TECHNIQUES FOR AGENT-CONTAMINATED FACILITIES

Contract DAAK11-81-C-0101

by

Edward R. Zamejc

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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APPENDICES

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TASK 3

DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES FOR AGENT-CONTAMINATED FACILITIES

1.0 SUMMARY

The development of novel concepts for the decontamination of chemical agent-contaminated buildings is being carried out by Battelle Columbus Laboratories (Battelle) for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAK11-81-C-0101. In the previous phase (Task 1), ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Also, knowledge gaps relating to application of the concepts were selected for laboratory evaluation in Task 3 including five chemical concepts (OPAB, MEA, Steam, NH_3, NH_3/Steam), two thermal concepts (hot gases, flashblast) and one physical concept (RADKLEEN®/vapor circulation). Task 3 has the objectives of resolving the technical uncertainties identified in Task 1 through bench-scale experiments and refining the technical/economic analyses of the most promising concepts.

Task 3 is broken into eight technical subtasks covering (1) a resource/work plan, (2) test preparations, (3) chemical concept prescreening, (4) diffusion studies, (5) surface decontamination, (6) surface/subsurface decontamination, (7) engineering/economic analyses, and (8) report/field test plan.

2.0 BACKGROUND

Decontamination of previously utilized chemical agent manufacturing and testing facilities is necessary to allow the Department of the Army to restore the facilities for alternate use or to dispose of them in excessing actions. Included in the facilities are the building structures, sumps, processing equipment, underground and above-ground storage tanks, and associated transfer systems. Facility decontamination involves not only the decontamination of exposed surfaces but also the decontamination of trace quantities of

agents which may have penetrated into the material through pores, cracks, or other openings.

Materials of concern identified from Task 1 site surveys for which decontamination methods are to be developed in Task 3 include:

- stainless steel - painted and unpainted
- mild steel - painted and unpainted
- concrete - painted and unpainted

3.0 OBJECTIVES

The objectives of this task are to:

- experimentally evaluate the concepts selected in Task 1 for decontamination effectiveness on various materials,
- perform an engineering/economic analysis on the most promising concepts selected from the experimental effort,
- identify remaining knowledge gaps associated with the most viable concept(s) and prepare a test plan to resolve the knowledge gaps through implementation of the concept at a field site.

4.0 TECHNICAL APPROACH

Task 3 efforts are divided into eight technical subtasks as shown in the work breakdown structure (WBS) illustrated in Figure 1. The objectives and technical approaches to be used in each subtask are described below.

4.1 Subtask 1. Resource/Work Plan

The objectives of this subtask are to (1) provide an overall plan for the task (this document) and to (2) review government regulatory and safety requirements relating to agents and agent decontamination.

TASK 3

LABORATORY EVALUATION OF

AGENT DECONTAMINATION CONCEPTS

- 1.0 Resource/Work Plan
  - 1.1 Design Plan
    - 1.1.1 USATHAMA Approval
  - 1.2 Regulatory/Safety Agency Review Plan
    - 1.2.1 USATHAMA Approval
  - 1.3 Agency Visits
  - 1.4 Regulatory/Safety Findings Report
- 2.0 Test Preparations
  - 2.1 Chamber Design
  - 2.2 Chamber Operation Test Plan
    - 2.2.1 USATHAMA Approval
  - 2.3 Chamber Construction/ Performance Tests
  - 2.4 Analytical QA & QC Plan
    - 2.4.1 USATHAMA Approval
  - 2.5 Coupon Preparation
- 3.0 Chemical Concept Prescreening
  - 3.1 Test Plan
    - 3.1.1 USATHAMA Approval
  - 3.2 Chemical Prescreening Tests
  - 3.3 Test Report (Select 1-3 concepts)
    - 3.3.1 USATHAMA Approval
- 4.0 Diffusion Studies
  - 4.1 Test Plan
    - 4.1.1 USATHAMA Approval
  - 4.2 Diffusion Calculations
  - 4.3 Diffusion Tests
  - 4.4 Diffusion Test Report
    - 4.4.1 USATHAMA Approval

FIGURE 1. WORK BREAKDOWN STRUCTURE TASK 3

TASK 3, CONTINUED

5.0 Stainless Steel Surface Screening

- 5.1 Flashblast/Hot Gases/ Vapor Circ. - RADKLEEN Test Plan
  - 5.1.1 USATHAMA Approval
- 5.2 Flashblast/Hot Gases/ Vapor Circ. - RADKLEEN Tests
- 5.3 Chemical Concept(s) Test Plan
  - 5.3.1 USATHAMA Approval
- 5.4 Chemical Concept(s) Tests
- 5.5 Test Report
  - 5.5.1 USATHAMA Approval

6.0 Steel/Concrete Tests

- 6.1 Test Plan
  - 6.1.1 USATHAMA Approval
- 6.2 Testing S.S./C.S./ Concrete - with and without paint
- 6.3 Test Report (Select 1-3 concepts)
  - 6.3.1 USATHAMA Approval

7.0 Engineering/Economic Analysis

- 7.1 Engineering Analysis
- 7.2 Economic Analysis
- 7.3 Knowledge Gap Identification
- 7.4 Analysis Report (Recommend one concept)
  - 7.4.1 USATHAMA Approval

8.0 Field Test Plan/ Task 3 Report

- 8.1 Task 3 Report (Draft)
  - 8.1.1 USATHAMA Approval
- 8.2 Field Test Plan
  - 8.2.1 USATHAMA Approval

FIGURE 1, continued

Safety regulations which will be reviewed include DARCOM Safety Regulation 385-31 (HD) and DARCOM-R 385-102 (GB and VX). Information from these and other pertinent documents will be used to prepare a regulatory/safety agency review plan which consists of a letter recommending the agencies to be visited and the topics to be discussed. Tentatively scheduled for visits are agencies such as Department of Defense Explosion Safety Board and safety offices at agent manufacturing/demilitarization sites such as Rocky Mountain Arsenal and Tooele Army Depot. Included in the discussion topics will be the question of "5X" decontamination, defined as thermal treatment at 1000 F for 15 minutes, versus decontamination to below the detectable limit by chemical, physical, or milder thermal methods.

4.2 Subtask 2. Test Preparations

The objectives of this subtask are to (1) design, construct, and evaluate a test chamber, (2) develop a Quality Assurance and Quality Control (QA/QC) Plan, and (3) prepare coupons of the materials used in the chamber tests.

The test chamber will be designed and constructed such that application of a decontamination concept may be performed in a controlled environment. A chamber operation test plan which will include design drawings of the chamber and operating scenarios will be submitted for USATHAMA approval. Design criteria for the test chamber will include:

- access ports to allow introduction of coupons and removal of effluents,
- allow decontamination of coupons by liquid decontaminants/solvents, by gaseous decontaminants/solvents, and by thermal methods,
- be sized to fit within a toxic materials laboratory hood.

A QA/QC plan will be prepared based on guidance to be received from USATHAMA. The plan will be submitted for USATHAMA approval.

Painted and unpainted coupons of stainless steel, concrete, and carbon steel will be prepared in this subtask for subsequent use in diffusion and chamber decontamination experiments. The coupons will be uniformly sized to allow direct comparison of results obtained from the experiments.

4.3 Subtask 3. Chemical Concept Prescreening

The objective of this subtask is to experimentally evaluate the five chemical concepts in terms of reaction kinetics and decontamination effectiveness. The five chemical concepts include:

- OPAB (1-Octylpyridinium-4-aldoxime bromide) in an aqueous solution containing a surfactant
- MEA (monoethanolamine) in an aqueous solution or undiluted
- Steam
- NH_3 (anhydrous)
- Steam/NH_3

Each concept will be evaluated under a variety of conditions in an attempt to determine the optimum operating conditions that will sufficiently decompose each of the three agents (GB, HD, and VX). A letter test plan detailing the methodology, parameters to be investigated (e.g., time, temperature, decontaminant concentration), and analytical techniques will be submitted for USATHAMA approval.

The experiments will be performed in laboratory glassware in which known quantities of neat agent will be contacted with an excess of decontaminant. The mixture will then be periodically sampled and analyzed for residual agent. Analytical techniques will be refined, as required, to permit quantitative detection of agent in the presence of the decontaminants and the decomposition products. If conditions cannot be found in which an agent(s) is effectively decomposed by any one chemical concept, then an alternative replacement concept will be selected with USATHAMA approval and its effectiveness determined in the same manner.

Based on the experimental results, a maximum of three chemical concepts will be selected for further evaluation in Subtask 5. A test report detailing the test results and the selected concepts will be submitted for USATHAMA approval.

4.4 Subtask 4. Diffusion Studies

The overall effectiveness of a chemical or solvent decontamination concept is dependent upon the ability of the decontaminant to penetrate into (and in the case of a solvent, out of) porous materials into which agents may have penetrated. The objective of Subtask 4 is to determine the conditions which will allow optimum penetration of chemical or solvent decontaminant into a porous material, i.e., concrete.

The decontaminants to be investigated in this subtask include:

- Aqueous solutions containing surfactants
- MEA
- Gaseous NH_3 (anhydrous)
- Freon® solvent

Since these decontaminants/solvents are representative of the chemical and physical decontamination concepts for both agents and explosives, the results of this subtask will be utilized in both Task 3 (agents) and Task 4 (explosives).

Aqueous solutions, MEA, Freon®, and similar liquids will be applied to concrete coupons by spraying. Spray pressure, the time the spray is maintained on the coupon, and the number of spray applications will be varied to determine optimum application times to be used for subsequent chamber tests. Surfactants (e.g., Triton X-100®) will also be added, if necessary, to enhance the penetration of aqueous solutions into concrete.

The diffusion rate of gaseous NH_3 through concrete coupons will be determined experimentally by exposing one side of a concrete coupon to NH_3 and measuring the concentration of NH_3 with time on the opposite side of the coupon.

A letter test plan detailing the planned liquid and gas diffusion experiments will be submitted to USATHAMA for approval. During the two- to three-week period required for approval, calculations will be performed to estimate the depths the various decontaminants will penetrate into concrete. A literature search will also be performed to determine a range of values for various physical properties of concrete, i.e., porosity, pore sizes, etc., which will be used in these calculations. The calculations will be used to determine initial operating parameters for the diffusion experiments and may allow correlations to be developed indicating the effective penetration of decontaminants in various types of concrete.

A test report summarizing the diffusion test results, calculations, and proposed operating conditions for decontaminant application to concrete will be submitted for USATHAMA approval.

4.5 Subtask 5. Stainless Steel Surface Screening

In this subtask, the most promising chemical concepts from Subtask 3 (maximum of three concepts), as well as hot gases, flashblast, and vapor circulation/RADKLEEN^R concepts will be evaluated in a test chamber. Unpainted stainless steel (S.S.) coupons spiked with HD, GB, or VX will be used as the test substrate. S.S. coupons were selected as the first test substrate since it is the substrate from which analytical techniques achieve the highest recoveries of agent and therefore yield the most accurate measure of decontamination effectiveness. Also in this subtask, waste products from the treatment will be characterized, reaction kinetics determined, and analytical performance verified.

Two test plans covering this subtask will be submitted for USATHAMA approval. One test plan covering the hot gases, flashblast, and vapor/circulation concepts which will not be prescreened will be submitted. Following selection of the most promising chemical concepts from Subtask 3, a second test plan (chemical concepts) will be submitted. By submitting two test plans, work may proceed while the Subtask 3 test results are being evaluated.

The experimental data will be analyzed and the three (maximum) most promising concepts selected for further evaluation in Subtask 6. If, however, the data indicate that none of the concepts effectively decontaminates stainless steel coupons spiked with a particular agent(s), a replacement concept will be selected with the concurrence of USATHAMA and its effectiveness determined in the same manner. A test report summarizing the results of Subtask 5 will be submitted for USATHAMA approval.

4.6 Subtask 6. Steel/Concrete Tests

Subtask 6 represents the final test series in Task 3. In this subtask, the three most promising concepts from Subtask 5 will be thoroughly evaluated based on decontamination effectiveness, reaction kinetics, analytical performance, and waste product formation. Substrates to be investigated will include coupons of stainless steel (painted and unpainted), carbon steel (painted and unpainted), and concrete (painted and unpainted) spiked with HD, GB, or VX. Results from the diffusion studies (Subtask 4) will be used to specify initial conditions for application of liquid and/or gaseous decontaminants to the concrete coupons. Decontamination versus depth of penetration into this porous substrate will be investigated. A letter test plan detailing this experimental effort will be submitted for USATHAMA approval.

Experimental results will be analyzed and the best one to three concepts will be selected for evaluation in Subtask 7. A Subtask 6 test report will be submitted for USATHAMA approval.

4.7 Subtask 7. Engineering/Economic Analysis

A detailed engineering/economic analysis will be performed on the concepts selected in Subtask 6. The engineering analysis will utilize experimental data obtained in the previous subtasks to specify a decontamination process. The process will then be costed based on decontamination of the model facility defined in Task 1.

The experimental data which will serve as the basis for the analyses includes:

- Reaction kinetics
- Heat requirements
- Solvent/decontaminant requirements
- Waste product characterization
- Application methods, e.g., spraying times, number of applications, etc.

From these data, the following will be specified:

- Process flowsheets
- Process equipment
- Waste disposal requirements
- Building preparation/clean-up requirements
- Operation schedule (set-up, application, and equipment tear-down times)
- Safety requirements (potential hazards and protective methods)

Knowledge gaps that remain following the above analysis will then be identified.

Next, an economic analysis will be performed. The process(es) identified above will be costed based on building damage/repair costs, material/utility costs, equipment cost and manpower cost. Following this analysis, decontamination procedures which are applicable to all three agents will be recommended. USATHAMA will participate in the selection of the final concept(s). Results of the analyses will then be summarized in a final subtask report which will be submitted for USATHAMA approval.

4.8 Subtask 8. Field Test Plan/Task 3 Report

A field test plan will be prepared in Subtask 8 for (1) applying the decontamination procedure(s) identified in Subtask 7 to decontaminate Army concrete/steel structures, (2) sampling the structures for residual agent, i.e., sampling methods and types of samples, and (3) resolving the knowledge gaps identified in Subtask 7. The field test plan will be submitted for USATHAMA approval.

Included in Subtask 8 will be the submission of the Task 3 report which will summarize test results, agency discussions, and technical analyses performed in Task 3. The report will be submitted for USATHAMA approval.

4.9 Contingency Plans

As indicated in the Task 3 logic diagram illustrated in Figure 2, it may be necessary to select alternative replacement concepts during the course of the Task 3 experimental effort. Alternatives will be selected if the concept(s) remaining following the selection procedures are not applicable to all three agents and if attempts to make the concept(s) work have failed. In this case, concepts from previous subtasks will be re-examined and, if necessary, alternative concepts identified in the Task 1 efforts may be utilized. The selection of a replacement concept will be performed with USATHAMA participation.

5.0 DEVIATIONS/ADDITIONS

This design plan generally follows the government tasking document and all 32 work units have been incorporated into the eight subtasks. Deviations from the tasking document include:

- The chemical concepts will be prescreened in laboratory glassware rather than in the test chamber.
- Diffusion studies will focus on the penetration of decontaminants (not agents or simulants) into concrete.

6.0 INTERFACING

Task 3 will interface with the Task 4 efforts involving explosive decontamination. Parallel efforts in both tasks will provide in economies in chamber design, construction, and performance tests; coupon preparation; and

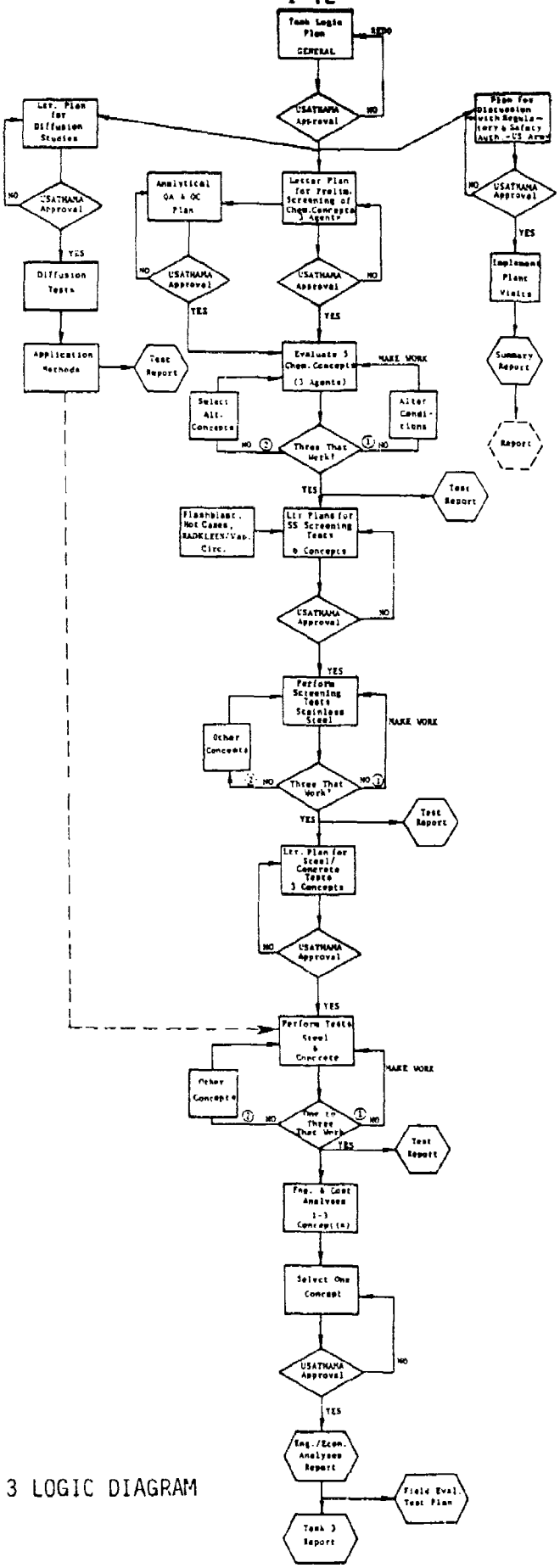


FIGURE 2. TASK 3 LOGIC DIAGRAM

engineering/economic analyses. Also, the results from the diffusion studies (Subtask 4) will be utilized by both Tasks 3 and 4 for designation of liquid/solvent application methods.

7.0 FACILITIES

Experiments involving surety levels of agent will be performed in the Hazardous Materials Laboratory. Experiments with non-surety levels of agent will be performed in the Toxic Substances Laboratory. A brief description of these laboratories is given in Appendix B. A more complete description of the Hazardous Materials Laboratory is in the Facility Security Plan provided to USATHAMA during Task 1 efforts.

8.0 GOVERNMENT-FURNISHED PROPERTY/ASSISTANCE

The following supply of agents, in storage at the Hazardous Materials Laboratory, is currently available for Task 3 use:

HD - 13.9 ml (includes 5 ml of SARM)
GB - 13.6 ml (includes 5 ml of SARM)
VX - 18.9 ml (includes 10 ml of SARM)

It is anticipated that the above supply is sufficient to complete Task 3 experimental work.

The government will make arrangements for meetings with government regulatory/safety agencies (Subtask 1).

APPENDIX A

GOVERNMENT TASKING DOCUMENT

A. Task Order Number: 3

B. Task Order Title: Development of Novel Decontamination Techniques for Chemical Agent (GB, VX, HD) Contaminated Facilities - Phase II

C. Contract Number: DAAK11-81-C-0101

D. Background:

1. Decontamination of facilities previously utilized for chemical agent manufacture or testing is anticipated to permit the Department of the Army to restore such facilities for alternate use or to dispose of them in excessing actions. Included are not only the structures themselves but also underground and above surface storage tanks, processing equipment, sumps and associated transfer systems. Required decontamination involves exposed surfaces of the materials as well as the decontamination of trace quantities of agents which have penetrated into the materials, cracks, or other openings.

2. Materials of concern which shall require decontamination and which shall be included in this study are:

a. Stainless steel - painted and unpainted.

b. Mild steel - painted and unpainted.

c. Concrete - painted and unpainted.

3. This study follows Task 1 of this contract wherein the contractor identified potential decontamination technologies, applied selected economic and technical evaluation criteria to those technologies, rank ordered the candidates, and in conjunction with USATHAMA recommended those worthy of further laboratory evaluation in Phase II (this task). It is anticipated that at the completion of this task order effort, decontamination concepts will have been evaluated sufficiently such that recommendations can be made for pilot testing the selected concept(s).

E. Phase II Purpose and Objectives: The purpose of this task order is to validate new cost effective decontamination concepts selected in Phase I for decontamination of agent contaminated facilities. The objective is to develop sufficient information so that the final selected concept(s) can be recommended for subsequent pilot testing.

F. Statement of Work:

1. Figure 1 outlines the various work units for this task and the schedule for their implementation. This SOW is keyed to work units on Figure 1. The work to be performed on this task is based on the Task 1 effort and generally follows the recommendation of the preliminary Phase II test plan submitted under Item F.7 of that task order.

2. The first work unit after task initiation shall be preparation of the overall work plan/resource plan. This plan shall include a detailed schedule, a detailed work breakdown structure (WBS) and a resource utilization plan keyed to the WBS.

3. Work units 3 and 4 entail a review of regulatory and safety requirements and shall be performed to determine the most recent developments in these areas in order to better define decontamination levels. Germane organizations such as EPA, Department of Defense Explosives Safety Board, Department of Transportation and the DARCOM Field Safety Office shall be included. A report summarizing the findings of this study shall be prepared and submitted.

4. Also early (work unit 5) in this task order, a chamber for conducting agent testing of various concepts shall be designed, constructed and evaluated. This chamber shall be small enough to fit into a conventional fume hood, fitted with entry/exit ports for introduction and removal of samples and exhaust ports to permit sampling of out-gassed products.

5. Work units 6-10 are the preliminary screening tests of chemical concept candidates determined in Task 1. These concepts include: MEA, OPAB, NH_3, steam NH_3/steam and flashblast. A letter test plan shall be submitted for USATHAMA's written concurrence before testing is begun and a letter test report shall be submitted detailing test results when concluded. Chamber tests of each concept shall be conducted and waste products and analytical performance shall be characterized. From these tests, a maximum of three concepts shall be recommended for further evaluation.

6. Work units 11-15 are for diffusion studies to evaluate penetration of agents into concrete (worst case). Agents and/or simulants shall be allowed to penetrate concreted samples which shall subsequently be sectioned, pulverized, extracted, and analyzed. These data shall be used to obtain diffusion data which shall allow assessment of penetration of agents and decontaminants into concrete over a period of time and the effects of variables such as temperature, concentration and exposure duration. These studies shall indicate appropriate application times for decontaminants. A diffusion letter test report shall be submitted detailing results of these tests.

7. Work units 16-20 are for stainless steel surface screening tests, including a letter test plan and letter test report. This test series shall include chamber tests of the three chemical concepts (from the preliminary screening) plus hot gas, vapor circulation and Rad-Kleen concepts; on stainless steel coupons. Waste product shall be evaluated as well as analytical performance. These tests shall provide data to select the best three concepts for evaluation in the next phase. The test report shall detail test results and the logic for selection of the three recommended concepts.

8. Work Units 21-25 detail the final evaluation testing. Each of the three concepts selected from the stainless steel surface screening tests shall be thoroughly evaluated with each of the designated materials of concern - mild steel (painted and unpainted), stainless steel (painted and unpainted), concrete (painted and unpainted). Decontamination effectiveness, waste product verification and analytical performance shall be determined. These data shall

be analyzed and shall form the basis for selection of the one (minimum) to three (maximum) final recommended decontamination methods. Details of this recommendation shall be included in the letter test report.

9. Work units 26-28 include an engineering/economic analysis of the final 1-3 concepts chosen above. Auxiliary considerations (to technical performance) shall be considered such as building repair costs, development costs, utility and fuel costs, equipment costs, material costs and labor costs. The economic analysis shall be utilized as the basis for making the selection of the final single best concept (if more than one was considered) to be field/pilot tested. USATHAMA shall participate in and approve the selection in writing.

10. Work units 29-31 are for preparation of a comprehensive final report (Contract Data Item A002). All pertinent information developed during efforts on this task order shall be compiled into a draft final report and submitted for review and approval. The final report shall be submitted within 30 days after Government approval of the draft.

11. Work unit 32 is the preparation of a recommended test plan for field evaluation of the decontamination concept selected in this task order.

12. Technical reviews shall be held as delineated in work unit 33. Four of these reviews shall be held at the contractor's facility and four shall be held at USATHAMA. Additional meetings shall be scheduled on an as required basis.

13. Analytical method development/refinement/certification shall be performed as required to support this task.

G. Testing Requirements: Analytical methods certified in accordance with the USATHAMA QC Plan shall be utilized if available. However, the actual QA/QC level shall be specified by the COR.

H. Items/Data to be Delivered:

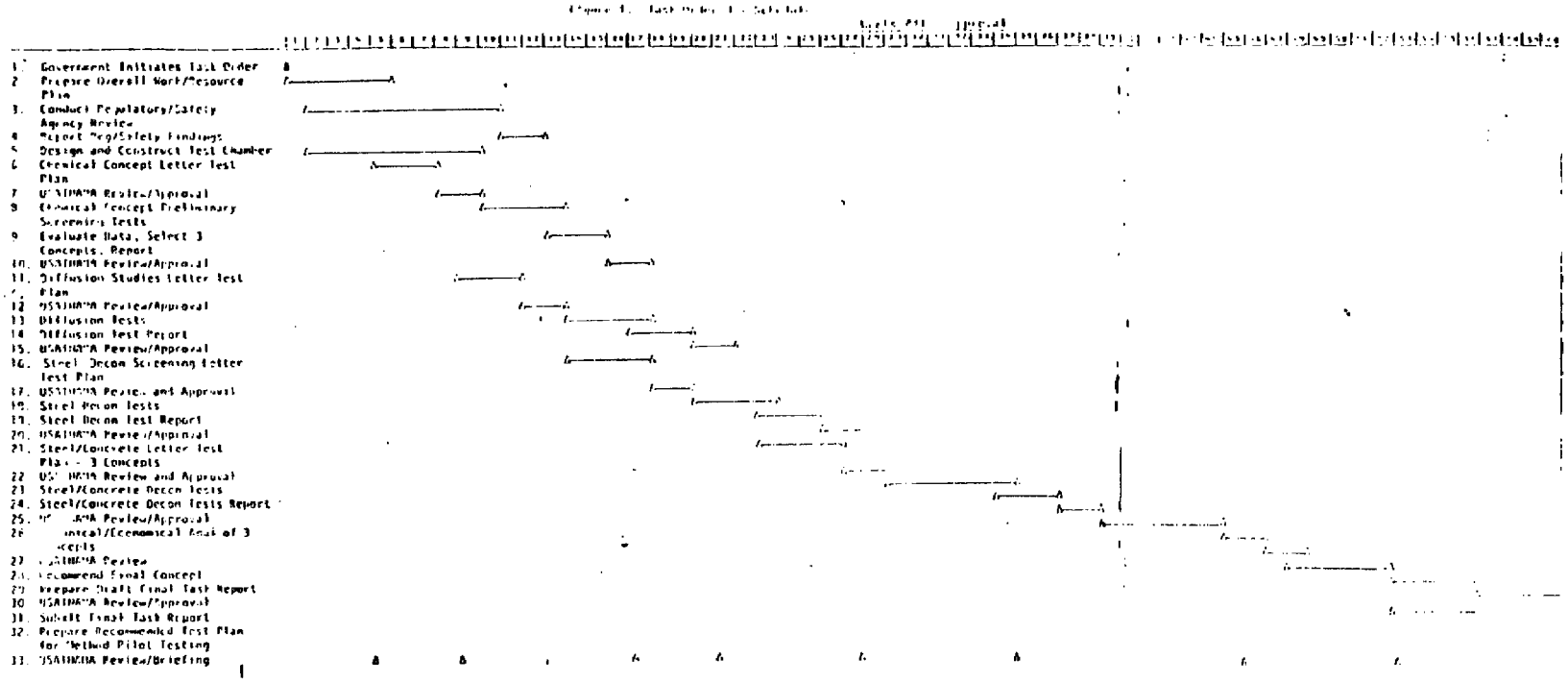
1. Letter test plans and letter test reports shall be submitted for each of the four test sequences outlined in Chart 1. (Work units 3, 6, 9, 11, 14, 16, 19, 21 and 24). Ten copies of each shall be submitted.

2. A draft technical report (10 copies) documenting the findings and recommendations of this study shall be provided to the Government 52 weeks after task initiation. The final technical report (Sequence A002 CDRL, DD Form 1423), shall be provided to the Government within 30 days after approval of the draft.

I. Government Furnished Property and/or Assistance: The Government shall make arrangements for meetings with Regulatory/Safety Government Agencies for the purpose of conducting the Regulatory/Safety Review (work unit 3).

J. Hazard Information: Information regarding safety materials used on this task order are contained in the contract.

K. Desired Period of Performance or Completion Date: Refer to Figure 1. The overall period of performance is 30 weeks.


1. Government Initiates Task Order
2. Prepare Overall Work/Resource Plan
3. Conduct Regulatory/Safety Agency Review
4. Report Reg/Safety Findings
5. Design and Construct Test Chamber
6. Chemical Concept Letter Test Plan
7. USATHAMA Review/Approval
8. Chemical Concept Preliminary Screening Tests
9. Evaluate Data, Select 3 Concepts, Report
10. USATHAMA Review/Approval
11. Diffusion Studies Letter Test Plan
12. USATHAMA Review/Approval
13. Diffusion Tests
14. Diffusion Test Report
15. USATHAMA Review/Approval
16. Steel Decon Screening Letter Test Plan
17. USATHAMA Review and Approval
18. Steel Decon Tests
19. Steel Decon Test Report
20. USATHAMA Review/Approval
21. Steel/Concrete Letter Test Plan - 3 Concepts
22. USATHAMA Review and Approval
23. Steel/Concrete Decon Tests
24. Steel/Concrete Decon Tests Report
25. USATHAMA Review/Approval
26. Chemical/Economical Anal of 3 Concepts
27. USATHAMA Review
28. Recommend Final Concept
29. Prepare Draft Final Task Report
30. USATHAMA Review/Approval
31. Submit Final Task Report
32. Prepare Recommended Test Plan for Method Pilot Testing
33. USATHAMA Review/Briefing

APPENDIX B

FACILITY DESCRIPTION

Hazardous Materials Laboratory (HML)

Battelle has available a remote site hazardous materials laboratory at its West Jefferson facility. The laboratory is designed to provide all of Battelle's sponsors with a facility in which to conduct research projects using toxic and hazardous materials in a controlled, acceptable manner. A more detailed description of HML can be found in the Facility Security Plan submitted under Task 1.

The laboratory functions as both a research laboratory and as a technology development laboratory. Scientists in this laboratory are experienced in the specific needs of hazardous materials handling including decontamination, detection, alarms technology, general analysis, and evaluation of new materials. Newer technologies such as improved processes, improved analytical methods, test methods development, etc., also fall under this laboratory's activities. It is a 1,250-square foot facility, located within an existing laboratory building.

The hazardous materials laboratory has the following characteristics. The walls are 8-inch cement block; the floor and ceiling are reinforced concrete. All surfaces are painted with two coats of epoxy to create an impermeable, easy-to-wash surface.

The perimeter doors are heavy-duty hollow metal units with locks and hardware as required by security regulations with all doors except the controlled access door security-sealed. All perimeter doors are equipped with crash hardware. Door glass, windows, and perimeter openings greater than 92 square inches are security-screened with No. 9 expanded metal. A Honeywell security system, including door alarm switches and an area motion detection device, gives alarm annunciation at the site guardhouse, as does the area fire alarm system.

Stainless steel-lined fume hoods with dished work surfaces are used to keep any spills contained and to simplify clean-up. The hoods have been modified with the addition of interconnecting passthroughs. One hood has a pair of lockable storage cylinders that offers secure containment of materials in the event of a tornado.

Airflow through the laboratory comes from a separate mechanical system which supplies ventilation. The work areas are kept at negative pressure with respect to the clean areas by a pneumatic control system. All laboratory air exhausts through the hoods at 150 fpm average face velocity. A modulating damper in the exhaust ductwork compensates for changes in system static pressure and maintains constant flow. Each hood is equipped with a velocity alarm that gives an audible and visual alarm.

All exhaust air passes through a filter system consisting of a prefilter, a primary absolute, a primary charcoal, a redundant charcoal, and a final absolute filter. The filters are installed in a welded steel, bagout-type housing with sampling ports, static pressure ports, and isolation dampers to allow filter changes without system shutdown.

Primary and redundant blowers are installed on each filter system with automatic changeover controls. Exhaust stacks rise about 10 meters above-ground. Both the blowers and the filters are outside the laboratory.

All laboratory drains connect to a pair of 6,000-gallon underground fiberglass tanks. There the liquid waste is sampled, treated as necessary, and disposed. The tanks are equipped with a remote level indicator with high and low alarm points.

An emergency generator provides backup power to the blowers, security, and system alarms to allow the laboratory to make an orderly shutdown if required.

The HML is surrounded by approximately 1,000 acres of Battelle-owned property. The area is also available for outdoor testing and research programs.

Toxic Substance Laboratory (TSL)

All activities involving the storage or handling of toxic substances at the Columbus site are conducted in the Toxic Substances Laboratory. This facility is separated from adjacent Battelle facilities by concrete block walls. There are three doors to this facility located on the same corridor. Two access doors provide entry into the laboratory. A third door is an emergency exit door with no access. All three doors are metal and the two access doors are locked to prevent unauthorized access.

Four laboratory hoods have been provided with face velocities of 150 ± 30 fpm. An alarm has been incorporated into the ventilation system in case of failure. A glovebox has been provided for use in weighing toxic substances. The exhausts from both the hoods and the glovebox have been equipped with HEPA filtering systems to prevent discharge of toxic agents into the atmosphere. The filter system is checked each time a filter is changed. Three doors providing exits from all areas of the laboratory have been installed.

The HEPA filters on the hood exhausts are changed periodically as required. The hoods are equipped with automatic monitoring devices which indicate reduced air flow due to filter clogging. Protective clothing is worn when the filters are changed and the used filters, assumed to be contaminated with toxic substances, are stored for future decontamination and disposal.

The laboratory has also been equipped with shower facilities and eyewash fountains. In addition, all laboratory benches have been equipped with stainless steel pans to contain spills for each of cleanup and detoxification.

Personnel protective gear is provided including disposal laboratory overalls, safety glasses and goggles, and gloves.

APPENDIX II

SUBTASK 3. CHEMICAL CONCEPTS PRELIMINARY SCREENING

TEST REPORT

for

TASK 3 SUBTASK 3
CHEMICAL CONCEPTS PRELIMINARY SCREENING
CONTRACT DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

S. M. Tauschek
B. C. Garrett
T. L. Hayes
H. M. Grotta
E. R. Zamejc

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, OH 43201

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EXECUTIVE SUMMARY

A Preliminary evaluation of the five chemical decontamination concepts identified in Phase 1 of the Novel Processing Program was performed. The concepts which were evaluated in laboratory scale glassware included monoethanolamine (neat and 50 percent aqueous solution), aqueous solution of 1-octylpyridinium 4-aldoxime bromide (OPAB), anhydrous ammonia, steam and steam/ammonia.

The results indicate that all of the chemical decontaminants were effective on specific chemical agents. The most promising concepts, involving the use of either steam or OPAB, achieved high destruction efficiencies for all three agents (HD, GB and VX). As such the steam and the OPAB concepts were selected for further evaluation in subsequent subtasks involving decontamination of steel and concrete matrices. Because of the effectiveness of the other chemical decontaminants, no concept will be eliminated at this time. Rather, all remaining concepts will be retained in the event that an alternative decontaminant is required in the subsequent efforts.

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APPENDIX II
TASK 3 SUBTASK 3
CHEMICAL CONCEPTS PRELIMINARY SCREENING
CONTRACT DAAK11-81-C-0101
to
UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

In the previous phase (Task 1), ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Knowledge gaps relating to application of the concepts were selected for laboratory evaluation in Task 3 including five concepts utilizing chemical reactions as the decontamination technique (OPAB, MEA, Steam, NH_3, NH_3/Steam). This report details the results of the preliminary laboratory evaluation of these five chemical decontamination concepts using neat agents.

2.0 OBJECTIVES

The objective of this study was to provide preliminary evaluation of the five proposed chemical decontamination concepts so that the list of promising candidates is narrowed to three or less with the minimum experimental effort. The chemical concepts evaluated were:

- Monoethanolamine (MEA) - neat and 50% aqueous solution
- Aqueous solution containing a surfactant and 1-octyl pyridinium 4-aldoxime bromide (OPAB)
- Anhydrous NH_3
- Steam
- Steam/NH_3

The primary criterion for evaluation was destruction of agent so that the minimum amount of agent remained unaltered following the chemical treatment. Secondarily, rate of agent destruction was considered. Toxicity of by-products was also taken into account by attempts at by-product identification through GC-MS.

3.0 FACILITIES AND EQUIPMENT

Since neat munition grade agents (HD, GB, VX) were used in the tests, the experiments were performed in hoods located at Battelle's Hazardous Materials Laboratory (HML).

Analyses were done by gas chromatography (GC) or gas chromatography coupled with a mass spectrometer (GC-MS). A Varian Model 3700 GC equipped with a Varian Flame Photometric Detector (FPD) was used. This detector has two modes of use, the P mode (phosphorus), and the S mode (sulfur). The P mode was used when analyzing for the phosphorus-containing agents, GB and VX. The S mode was used when analyzing for one of the sulfur-containing agents, HD. The column used in the GC was a 3 percent SP 2100-DBon 100/120 Supelcoport (6 feet long, 0.25 inches O.D., 4 mm I.D.).

The GC-MS used for analysis was a Finnagan Model A 1020 using electron impact as the mode of ionization. The scan range and cycle time was 40-450 amu/second. A fused silica capillary column coated with DB5 (30 meters x 0.025 mm) was used for GC separation.

Each of the five proposed chemical decontaminants has its own characteristics and therefore was treated individually. For the gaseous systems (steam, ammonia, and steam and ammonia combined), the gaseous reactant apparatus illustrated in Figure 1 was designed. The apparatus allowed only vapor, not condensed liquid, to contact the agent.

The reagent (water, anhydrous ammonia, or aqueous ammonia) was contained in a boiling flask. Connected to the neck of the flask was an extension tube into which an inert Teflon® plug was inserted for the purpose

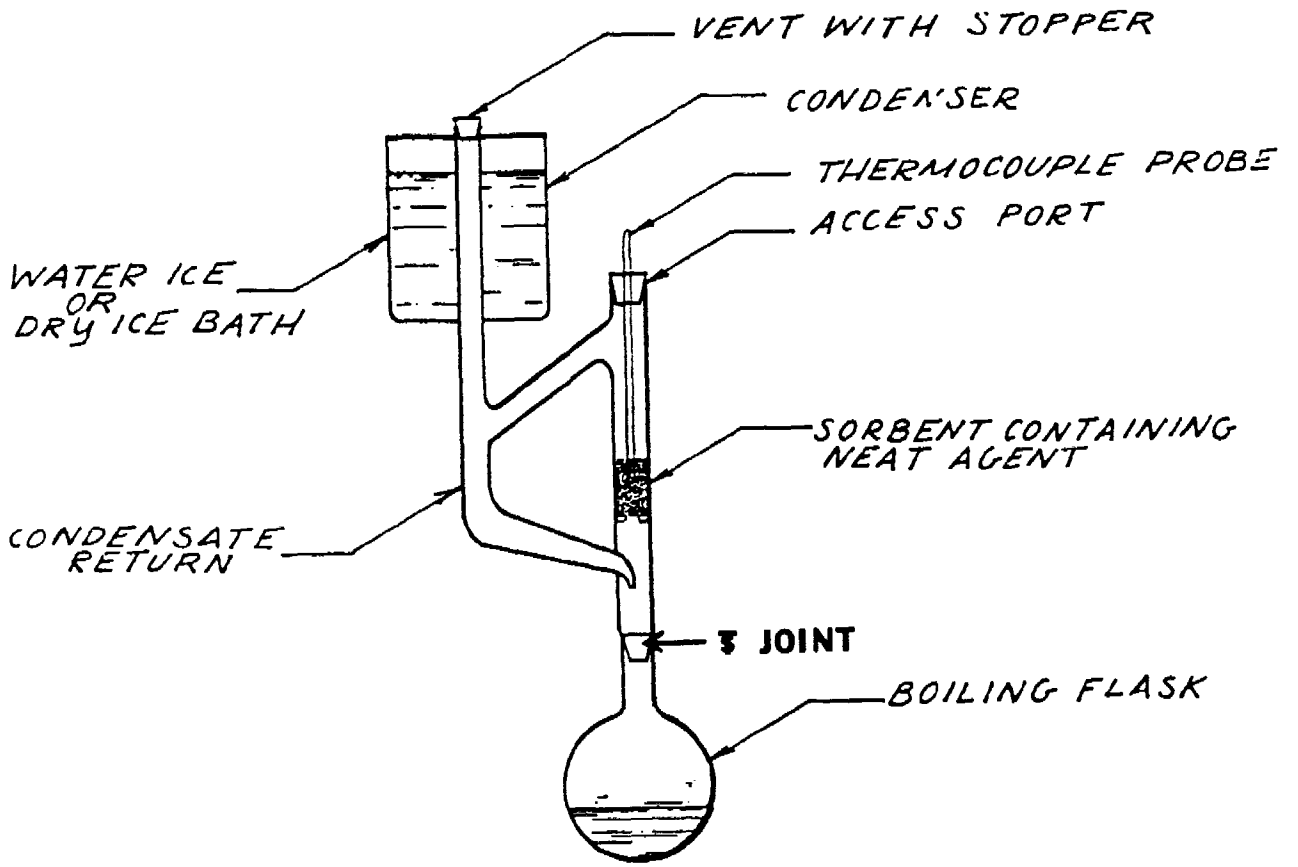


FIGURE 1. GASEOUS REACTANT APPLICATION APPARATUS

of retaining the agent under examination. A reflux condenser, located above the extension tube, served to return decontaminant to the boiling flask. Water ice was used in the condenser when operating with either steam or NH_3/steam, while dry ice (mp = -78.5 C) was used when operating with NH_3. When operating with liquid ammonia (boiling point = -33 C), the sorbent plug was maintained at room temperature.

More flexibility was available for the two liquid systems. Undiluted (neat) agent was placed in a 100 ml beaker containing a magnetic stirrer. Liquid reactant (OPAB solution or MEA) was added and the mixture stirred. Reaction kinetics in terms of residual agent were observed by withdrawing aliquots at specified intervals.

4.0 EXPERIMENTAL PROCEDURES

A USATHAMA approved test plan was used as the basis for conducting the experiments. Actual laboratory and analytical data are given in Battelle Laboratory Record Book No. 39064 and 39108.

For each of the five chemical concepts, a baseline experiment was performed to determine recovery efficiency. For OPAB and 50 percent MEA and neat MEA, this involved spiking the decontaminating solution with each agent, stirring a few seconds, and removing an aliquot for GC analysis. For steam and ammonium hydroxide (NH_3/steam), this involved spiking water or ammonium hydroxide with each agent, stirring a few seconds, and removing an aliquot for GC analysis. A similar experiment was not done for anhydrous ammonia since there was no liquid remaining in the pot to be extracted. Instead, the recovery data from the baseline experiment with VX and the gaseous application apparatus described above were used.

Recovery efficiencies of agent from solution of decontaminant are given in Table 1. The baseline experiments indicated that extraction of either HD or GB from MEA required acidification to pH 3 with acetic acid in order to achieve desirable recovery efficiencies. However, in the case of VX,

TABLE 1. RECOVERY EFFICIENCIES OF AGENT FROM DECONTAMINANTS

Agent	Decontaminant	Amount of Agent Spiked, mg	Amount of Agent Recovered,[a] mg	Recovery Efficiency,[b] %
HD	50% MEA	317	297.5	93.8
GB	50% MEA	287	39.9	13.9
VX	50% NEA	323	219.4[c]	68.5
VX	100% MEA	324	214.3[c]	66.1
HD	5% OPAB	279	371.3[c]	133.1
HD	5% OPAB	279	387.4[c]	138.9
GB	5% OPAB	283	(d)	(d)
VX	5% OPAB	282	88.3[c]	31.3
VX	5% OPAB	282	91.3[c]	32.4
GB	H_2O	10	5.24[c]	52.4
GB	NH_4OH	10	7.80[c]	78.0

a) The decontaminant solution was spiked with agent while stirring. A sample was immediately withdrawn and extracted with hexane or methylene chloride. The extract was then analyzed for agent using a gas chromatograph equipped with a flame photometric detector (GC/FPD).

b) Recovery efficiency (%) = 100 x (Agent recovered (mg) ÷ Agent spiked (mg))

c) Average of two analyses.

d) Interferences prevented the use of the GC/FPD. The samples were analyzed by a GC/mass spectrometer.

extraction from MEA was performed without acidification. The recovery efficiency of VX from a 50 percent solution of MEA using methylene chloride was 109 percent without acidification while only 5.3 percent of the VX spiked was recovered upon acidification.

In addition to the decontaminant extraction experiments, several baseline tests were performed with the gaseous reactant apparatus. A hexane wash of the apparatus containing the Teflon® wool plug (no agent) was performed to determine if interferences were present. Analysis of the hexane by gas chromatography indicated the sample was clean (i.e., no observable peaks). The apparatus was reassembled and 10 mg of neat VX was applied to the Teflon® wool plug. The apparatus, including the plug, was then extracted with 30 ml of hexane. Analysis of the hexane indicated that 10.8 mg of VX was extracted (108 percent recovery efficiency). A second extraction of the apparatus with 30 ml of hexane indicated that 0.042 mg (0.42 percent of original spike) was extracted. The Teflon® wool was then removed from the apparatus and separately extracted. No agent was detectable in this extract.

Munition grade agents used in these experiments were compared to SARMs (PA796, PA1126, and PA1128) by GC to determine if adjustments were needed in amounts of agent delivered to the reaction vessels. Munition grade rather than high purity agent was selected for use in these studies because buildings used to manufacture and handle agent will most likely be contaminated with munition grade rather than high purity agent. Also, munition grade agent may be considered as being the worst case since it may contain stabilizers which either inhibit decomposition reactions or lead to agent reformation. Agents were delivered with Eppendorf pipettes; and the density of each was taken into account in calculations.

Table 2 outlines the experimental procedures and analysis conditions for the evaluation of the chemical decontamination concepts. Sections 4.1 to 4.6 describe these procedures in more detail. All experiments were run in duplicate and each experiment had two aliquots withdrawn at each interval for GC analysis.

GC-FPD analyses were all performed on the same column (SP2100 - see Section 3.0) using different temperature programs. For all HD analyses, the program was 135 C isothermal. For all VX analyses, the program

TABLE 2. SUMMARY OF EXPERIMENTAL PROCEDURES

Decontamination Concepts	GB	HD	VX
50% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2CL_2 Analyze by GC-FPD[a]
100% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]
Steam	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[a]	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[b]	Extract pot with CH_2Cl_2 Extract apparatus with hexare Extract wool with CH_2Cl_2 Analyze by GC-FPD[c]
Anhy. Ammonia	Same as steam	Same as steam	Same as steam
Ammonium Hydroxide	Same as steam[f]	Same as steam	Same as steam
OPAB	Extract with CH_2Cl_2 Analyze by GC-MS[d]	Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]

(a) Column: SP 2100; Program: 100 C (hold 1 minute) to 240 C at 90 C/minute; FPD detector; in P mode

(b) Column: SP 2100; Program: 135 C isothermal; FPD detector: in S mode

(c) Column: SP 2100; Program; 190 C (hold 4 minutes) to 240 C at 35 C/minute (hold 4 minutes); Detector in P mode

(d) Column: DB 5; Program: 35 C (1 minute hold) to 250 C at 12 C/minute (hold 2 minutes); Mass spectrometer: splitless, EI, range 40-450 amu/sec.

(e) To pH 3 using dilute acetic acid

(f) GC/MS analysis required because of analytical interferences with the GC-FPD approach

was 190 C (with 4-minute hold) to 240 C at 35 C/minute (with 4-minute hold). For all GB analyses run on GC-FPD, the program was 100 C (with 1-minute hold) to 240 C at 90 C/minute. For all GB analyses run on GC-MS, the program (on a DB5 column) was 35 C (with 1-minute hold) to 250 C at 12 C/minute (with 2-minute hold).

The detection limit of the standard curve for each of the agents (GB, VX, and HD) was 2 μg/ml. Quantification of the peaks was possible at a concentration of 5 μg/ml. These detection limits apply to agent in the final solution being analyzed.

4.1 Experiments with 50 Percent Monoethanolamine (MEA)

4.1.1 50 Percent MEA/VX

Eighty ml of a 50 percent solution of monoethanolamine and distilled water (by weight) were placed in a 150-ml beaker and stirred at room temperature for five minutes. VX, in the amount of 322.7 mg, was then added and stirring continued. At intervals of 10, 20, 40, 60, 120, 240, 1440 minutes, 5-ml aliquots of the mixture were removed and extracted once with 5 ml of methylene chloride. The extract was then analyzed by GC-FPD for VX.

4.1.2 50 Percent MEA/GB

These experiments were performed as above with VX except that 287.0 mg of GB were spiked into the beaker and each 5-ml aliquot removed was brought to pH 3 by addition of 40 ml of 63 percent acetic acid prior to extraction with methylene chloride. GC analyses showed no change in the amount of GB present over time. Since literature reports noted fast reaction of MEA and GB, the experiment was repeated using GC-MS as the detector for GB. The second experiment was similar to the first except for the intervals at which aliquots were drawn, 1 and 20 minutes. GC-MS analyses showed that GB was reacting with MEA to form a decomposition product that had an identical retention time on GC as GB, thus no change in the GB peak on GC was observed in the first experiment.

4.1.3 50 Percent MEA/HD

These experiments were performed in a manner similar to 50 percent MEA and VX. HD, in the amount of 317.0 mg, was spiked. The intervals for removing aliquots were the same except no 1440-minute aliquot was taken. Again, each aliquot removed was brought to pH 3 by addition of 40 ml of 63 percent acetic acid prior to extraction and analysis by GC-FPD.

The reaction mixture in the beaker in this case, however, was not always a single phase. Yellow beads of HD were initially observed, but as the reaction approached completion, the reaction mixture became homogeneous, indicating the decontamination product(s) are more soluble in 50 percent MEA than HD.

4.2 Steam

4.2.1 Steam/HD

This experiment was performed using the gaseous-reactant application apparatus described in Section 3.0. HD, in the amount of 101.5 mg, was spiked on the Teflon wool plug. Distilled water, in the amount of 50 ml, was placed in a 100-ml round bottom flask and refluxed for 5, 20, or 60 minutes. The apparatus was allowed to cool after each reflux period, the flask was removed, and a 5 ml aliquot from the flask was extracted with 5 ml of methylene chloride. Hexane, in the amount of 30 ml, was then placed in a new 100-ml round bottom flask and placed under the apparatus. The condenser was moved to the access port (see Figure 1), and the hexane left to reflux for one hour. The Teflon plug was then removed and extracted in 5 ml of methylene chloride. The extracts from the condensate, the hexane rinse, and the plug rinse were all analyzed by GC-FPD.

4.2.2 Steam/GB

This experiment was performed in a manner similar to Steam/HD except 97.9 mg of GB were spiked onto the Teflon wool. The boiling water

was refluxed for periods of 20, 60, or 120 minutes. Each of the three extracts were analyzed by GC-FPD.

4.2.3 Steam/VX

This experiment was performed in a manner similar to Steam/GB except 100.9 mg of VX were spiked onto the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.3 Experiments with Anhydrous Ammonia

4.3.1 Anhydrous Ammonia/GB

This experiment was performed in a manner similar to the Steam GB experiment except a dry ice condenser was used in place of the water condenser. GB, in the amount of 59.9 mg, was spiked on the Teflon wool plug. After refluxing for 20, 60 or 120 minutes, the dry ice condenser was removed and the ammonia evaporated. The 100-ml round bottom flask contained some water condensed from the air, but no ammonia. The flask was extracted with methylene chloride as in the steam experiments. The three extracts were analyzed by GC-FPD.

4.3.2 Anhydrous Ammonia/HD

This experiment was performed in a manner similar to the Anhydrous Ammonia/GB experiment, except 63.4 mg of HD were spiked on the Teflon wool plug. Only a 60-minute reflux experiment was performed. Each of the three extracts from this experiment were analyzed by GC-FPD.

4.3.3 Anhydrous Ammonia/VX

This experiment was performed in a manner similar to the Anhydrous Ammonia/GB experiment except 60.5 mg of VX were spiked on the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.4 Experiments with Ammonium Hydroxide (NH_3/Steam)

4.4.1 Ammonium Hydroxide/GB

This experiment was performed in a manner similar to Steam/GB except 98.0 mg of GB were spiked on the Teflon wool plug and only a single 60-minute reflux experiment was performed. Each of the three extracts were analyzed by GC-FPD.

4.4.2 Ammonium Hydroxide/HD

This experiment was performed in a manner similar to Ammonium Hydroxide/GB except 101.5 mg of HD were spiked on the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.4.3 Ammonium Hydroxide/VX

This experiment was performed in a manner similar to Ammonium Hydroxide/GB except 55.5 mg of VX were spike on the Teflon wool plug. Each of the three extracts were analyzed by GC-FPD.

4.5 Experiments with OPAB

Two OPAB formulations were evaluated. The BF-OPAB formulation furnished by Battelle-Frankfurt, was composed of 5 weight percent 1-octylpyridimium 4-aldoxime bromide sodium salt, 1 percent foam stabilizers, 5 percent polyethyleneglycol and 89 percent water. The BCL-OPAB formulation, synthesized in-house*, was composed of 5 weight percent 1-octylpyridinium 4-aldoxime bromide and 95 percent water. The experimental procedures, which were identical for each OPAB formulation, are described as follows.

---

* Synthesized under ARO-STAS TCN-84-273.

4.5.1 OPAB/GB

GB, in the amount of 283.1 mg, was spiked into 140 ml of OPAB in a 150-ml beaker. While the solution was being stirred at room temperature, 10-ml aliquots were removed at intervals of 0, 20, and 40 minutes. The aliquots were extracted once with 10 ml of methylene chloride. These extracts were analyzed by GC-MS and GC-FPD.

4.5.2 OPAB/HD

This experiment was performed in a manner similar to OPAB/GB except 279.0 mg of HD were spiked into the OPAB solution. The aliquots were removed at 20, 40, 60, 180, 240, and 360 minutes. The methylene chloride extracts of these aliquots were analyzed by GC-FPD.

4.5.3 OPAB/VX

This experiment was performed in a manner similar to OPAB/GB except 283.0 mg VX were spiked into the OPAB solution. The aliquots were removed at 20, 40, 60, 180, 240, 360, and 1440 minutes. The methylene chloride extracts were analyzed by GC-FPD.

4.6 Experiments with 100 Percent MEA

4.6.1 MEA/GB

This experiment was performed in a manner similar to 50 percent MEA/GB. The 5-ml aliquots were removed from the spiked mixture at intervals of 0 and 20 minutes. Acidification of those aliquots was accomplished with 40 ml of 63 percent acetic acid. The aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-MS.

4.6.2 MEA/HD

This experiment was performed in a manner similar to MEA/GB except 317 mg of HD were spiked into the MEA. The 5-ml aliquots were removed at

intervals of 1, 30, and 60 minutes. After acidification as in the case of MEA/GB, the aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-FPD.

This experiment was performed in a manner similar to MEA/GB except 317 mg of HD were spiked into the MEA. The 5-ml aliquots were removed at intervals of 1, 30, and 60 minutes. After acidification as in the case of MEA/GB, the aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-FPD.

4.6.3 MEA/VX

This experiment was performed in a manner similar to the other MEA experiments except 322.7 mg of VX were spiked into the MEA. The CH_2Cl_2 extracts were analyzed by GC-FPD.

5.0 ANALYTICAL RESULTS

Tables 3 and 4 summarize the analytical results of the text experiments. (See Appendix A for the detailed results of all experiments.)* Table 3 lists the time in each reaction that no detectable agent is present if that point occurred. If not, the highest destruction efficiency observed is described. "Time" indicates reaction time, "Resid" indicates milligram amount of agent still present, and "% D" indicates percentage destruction efficiency, which was calculated by the following equation:

$$\% \text{ Decon Effectiveness} = \left[\frac{[\text{agent}]_{\text{initial}} - [\text{agent}]_{\text{time x}}}{[\text{agent}]_{\text{initial}}}\right] \times 100$$

It can be seen from Table 3 that the decontaminants selected in Task 1 are effective decontaminants for each agent and that, as anticipated, VX is the most resistant to destruction. Displaying an unexpected efficiency in destroying HD as well the expected GB and VX destruction,

* Sample chromatograms are given in Appendix B and sample mass spectra and given in Appendix C.

TABLE 3. SUMMARY OF ANALYTICAL RESULTS

Decontamination Concepts	GB Time (min)	GB Resid (mg)	GB % D	HD Time (min)	HD Resid (mg)	HD % D	VX Time (min)	VX Resid (mg)	VX % D
50% MEA	1	BDL[a]	99.8	240	BDL	99.9	1440	52.8	83.6
Steam	120	BDL	99.8	20	BDL	99.8	120	0.5	99.5
Anhydrous Ammonia	60	0.8	98.6	60	57.3	9.7	60	8.6	85.8
NH_3/Steam	60	BDL	(c)	60	BDL	99.8	60	19.5[b]	80.7[b]
BF-OPAB	1	BDL	99.8	360	BDL	99.8	240	BDL	99.8
100% MEA	1	BDL	99.8	240	BDL	99.9	1440	173.0	46.0

(a) BDL = Below Detection Limit (<2 μg/ml)

(b) Average of duplicate experiments: Resid = 31.0 and 7.9; % D = 69.3 and 92.1, respectively.

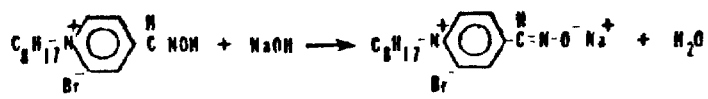
(c) Analyzed by GC/MS

TABLE 4. SUMMARY OF RESULTS FROM OPAB BEAKER TESTS

Agent	Sample Time(c), min.	BCL-OPAB(a) Residual Agent, mg	BCL-OPAB(a) Decon. Efficiency, percent(d)	BF-OPAB(b) Residual Agent, mg	BF-OPAB(b) Decon. Efficiency, percent(d)
GB	1	35.8	87.3 (f)	<0.2(e)	>99.9
GB	20	33.5	88.2 (f)	--	--
HD	40	<0.21	>99.9	105.8	62.1
HD	360	<0.21	>99.9	<0.1	>99.9
VX	20	0.53	99.8	41.9	85.2
VX	240	0.31	99.9	<0.2	>99.9

(a) BCL-OPAB = 5 weight percent OPAB (synthesized at Battelle-Columbus) dissolved in water.

(b) BF-OPAB = 5 weight percent OPAB as the sodium salt, 1 weight percent foam stabilizer and 5 weight percent polyethyleneglycol (anti-freezing agent) dissolved in water. Note: the sodium salt of OPAB is prepared by the following reaction:



(c) Sample time = Time after OPAB solution was spiked with agent.

(d) Decon. efficiency = 100 x [1 - Residual agent (mg)/Agent spiked (mg)].

(e) Analyzed by GC/MS because of agent interferences.

(f) The apparently low decon efficiency was probably caused by decomposition product(s) which interfered with GC/FPD analysis.

OPAB appears to be the single reagent of greatest promise. Steam is also seen to show excellent results in decontaminating all three agents.

A comparison of the results from the OPAB beaker experiments utilizing the two different OPAB formulations are shown in Table 4. The results suggest that the BCL-OPAB formulation (neat OPAB dissolved in water) was more effective in destroying HD and VX and less effective in destroying GB than the BF-OPAB formulation (sodium salt of OPAB and additives dissolved in water). It is important to note that the residual GB detected in the experiments using the BCL-OPAB formulation may be a decomposition product(s) which interferes with the GC/FPD analyses for GB. Previous work in Subtask 3 involving the BF-OPAB formulation required the use of GC/MS to quantitatively analyze for GB because of interferences which resulted when GC/FPD was used.

The activity of OPAB for destruction of HD appears to be related to the solution formulation. The BCL-OPAB formulation (neat OPAB dissolved in water) is slightly acidic (pH 4 to 5) whereas the BF-OPAB formulation (sodium salt of OPAB and additives dissolved in water) is basic (pH 9 to 10). The slightly acidic OPAB formulation appears to be more reactive with HD than the basic OPAB formulation. However, the basic OPAB formulation may still be preferred for nerve agent decontamination.

Although not specifically investigated, information on the degree of agent reformation in reaction solution was obtained from the kinetic data. In most experiments where kinetic data was obtained, the destruction of agent increased with time thereby indicating that agent reformation did not occur. One exception is for anhydrous ammonia and VX. Results (see Appendix A) indicate a lower destruction for the 120 minute experiments than for the 60 minute experiments. The lower destruction may be due to either reformation of VX or ice formation on the neck of the reaction vessel which occurred during the 120-minute experiments but not the 60 minute experiments (the ice may have lowered the reaction temperature at the Teflon plug).

Mass spectral data was obtained on several selected reactions, namely Steam/HD, GB, VX; OPAB/HD, GB, VX; 50% MEA/GB; 100% MEA; NH_3-Steam/GB, VX and VX/NH_3. Table 5 summarizes the interpretation of the mass spectral data. The table includes comments pertaining to the confidence of the

TABLE 5. MASS SPECTRAL DATA OF AGENT DEGRADATION PRODUCTS

Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
VX/NH_3; 60 minutes; hexane rinse	$CH_3\overset{O}{P}(OCH_2CH_3)_2$	P-S bond broken; OCH_2CH_3 ligand may come from cleavage of a phosphate polymer by displaced OCH_2CH_3 as below.	x	
		$CH_3\overset{O}{P}(OCH_2CH_3)-O-\overset{O}{P}(CH_3)-O-\overset{O}{P}(CH_3)-$		
	$CH_3\overset{O}{P}(OCH_2CH_3)-X$	P-S bond broken; unknown donor X=?	x	
	$HS-CH_2CH_2N-(CH(CH_3)_2)_2$ - - - - - - - - - -	P-S bond broken; thiol left; dotted line indicates probable identification of fragment	x	
VX/NH3; 60 minutes; Teflon plug extract	trichloromethane	Good fit; stabilizer		x
	cyclohexane	Solvent artifact or from stabilizer ($C_6H_{11}N=C=NC_6H_{11}$)		x
VX/NH_3; 60 minutes; pot extract	$X-SCH_2CH_2N-C(CH_3)_2-CH(CH_3)_2$	P-S bond broken; then sulfur react with X; X=? unknown donor, possibly oxidation of thiol to $-\overset{O}{\overset{\|\|}{S}}-OH$.	x	
	Trichloromethane	Good fit; stabilizer		x
VX/Steam;	$CH_3\overset{O}{P}(OCH_2CH_3)_2$	P-S bond broken; OCH_2CH_3 ligand may be from cleavage of phosphate polymer as shown for VX/NH_3	x	
	cyclohexane	Stabilizer or solvent artifact		x

TABLE 5. (Continued)

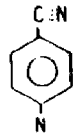
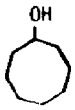
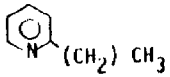
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
GB/OPAB		OPAB fragment or impurity		x
	1-(2-Propenyloxy)-2-propanol	Good fit; unknown origin; possibly solvent artifact		x
		Possibly solvent artifact		x
	$CH_3P(=O)(OCHCH_3)(OCH(CH_3)CH_3)$	P-F bond broken; similar to VX/NH_3, the ligand $OCH(CH_3)CH_3$ attacks after being displaced by formation of phosphate polymer	x	
	$C_8H_{17}Br$	Good fit; OPAB fragment or impurity		x
	$H-C(=O)NHC_8H_{17}$	Weak spectrum; OPAB fragment or impurity		x
		Possibly an OPAB fragment or impurity		x
GB/50% MEA	$CH_3CH_2C(=O)OCH(CH_3)CH_3$	Good fit; solvent impurity or stabilizer		x
	$CH_3CH_2CH_2C(=O)OCH_2CH_3$	Good fit; solvent impurity or stabilizer		x

TABLE 5. (Continued)

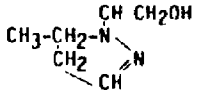
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
	$CH_3COCH_2CH_2CH_2CH_3$	Good fit; solvent impurity or stabilizer reaction		
	$CH_3CH_2CH_2\overset{O}{C}OCH(CH_3)_2$	Good fit; solvent impurity or stabilizer reaction		x
		Good fit, solvent impurity or stabilizer reaction		x
(also at 15 seconds)	$CH_3\overset{O}{P}(CH_3)-O-CH(CH_3)-O-CH(CH_3)_2$	Good fit; P-F bond broken; same as found in OPAB/GB fragment	x	
(also at 15 seconds)	$CH_3\overset{O}{C}OCH_2CH_2O\overset{O}{C}CH_3$	Good fit; solvent impurity or stabilizer reaction		x
		Good fit; solvent impurity		x
	$CH_3\overset{O}{P}(OH)-O-CH(CH_3)-CH_3$	Probable fragment; P-F bond broken	x	
VX/100% MEA	$X-SCH_2CH_2N(CH(CH_3)_2)_2$	P-S bond broken; good fit	x	

TABLE 5. (Continued)

Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
GB/Steam	Butanoic acid, 1-methyl ethyl ester	Solvent impurity		x
	Acetic acid, butyl ester	Solvent impurity		x
	Ethylene glycol diacetate	Solvent impurity		x
	$CH_3P(=O)(OCH(CH_3)_2)OCH(CH_3)_2$	P-F bond broken	x	
	1-Butanamine, N, N-Dibutyl	Stabilizer?		x
GB/NH_3 - Steam	$CH_3P(=O)(OCH(CH_3)_2)OCH(CH_3)_2$	P-F bond broken	x	
	CH_2Cl_2	Solvent impurity		x
HD/OPAB	$\overline{SCH_2CH_2SCH_2CH_2}$	C-Cl bond broken	x	
	Dibromo - ?	OPAB impurity or fragment		x

TABLE 5. (Continued)

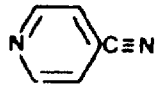
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
HD/Steam	$\overline{SCH_2CH_2SCH_2CH_2}$	C-Cl bond broken	x	
	Toluene	Solvent impurity		x
	$CH_3CH_2\overset{O}{\overset{\|\|}{S}}CH{=}CH_2$	C-Cl bond broken, sulfur oxidized	x	
	Ethylene glycol diacetate	Solvent impurity		x
VX/NH_3 - Steam	$((CH_3)_2CH)_2N(CH_2)_2NH_2$	Stabilizer?		x
	$((CH_3)_2CH)_2N(CH_2)_2OH$	Stabilizer?		x
	$CH_3\overset{O}{\overset{\|\|}{P}}(OCH_2CH_3)SCH_2CH_3$	C-N bond broken	x	
	$H_2N\overset{S}{\overset{\|\|}{C}}N(CH(CH_3)_2)_2$	P-S bond broken	x	
	VX	--		
	N, N-bis-isopropylbutane amine	Stabilizer?		x
	Butyl isopropylamine	Stabilizer?		x
	N-alkyl urea	Stabilizer?		x
VX/OPAB		OPAB reaction product	x	
	Octanol	OPAB impurity or fragment		x

TABLE 5. (Continued)

Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
VX/OPAB, Cont.	1- Bromooctane	OPAB impurity or fragment		x
	$CH_3\overset{O}{\overset{\|\|}{P}}(OCH_2CH_3)SCH_2CH_3$	C-N bond broken	x	
	Octylpyridine	OPAB impurity or fragment		x
	Octane, 1,1' - oxybis-	OPAB impurity or fragment		x
	Octylpyridyl ketone	OPAB impurity or fragment		x

identification indicated, as well as the implication of the presence of the compound identified. Where possible the table also lists the source of an identified compound. The compounds derive from either chemical reaction of the decontaminant, agent with the reaction of impurities such as solvents and stabilizers added to the agents prior to use, or the presence of other impurities. The stabilizers include diisopropylcarbodiimide and dicyclohexylcarbodiimide found in all the agents and dibutylamine found in GB only.

In addition to product identification attempts, GC/MS data was generated to confirm decontamination on selected experiments. For example, the mass spectra for the NH_3-steam decontamination of GB and VX were obtained to verify that the apparently low decontamination effectiveness observed in initial tests was caused by interferences. GC/MS results from the GB/NH_3-steam experiments indicate that the compound with the largest peak area in the chromatogram of the extract (see Appendix B) is diisopropylmethylphosphonate, a transesterification product of GB hydrolysis. GB was not detected by GC/MS in the extract. With an estimated detection limit of 25 µg GB/ml x 30 ml = 0.75 µg GB, approximately 98 percent of the GB was destroyed by the NH_3-steam treatment in 60 minutes. This is comparable to the destruction efficiency achieved using either anhydrous ammonia alone or steam alone. Therefore, the initially reported low GB destruction efficiency by NH_3-steam was due to an interference in the GC/FPD analysis method. GC/MS analysis of the VX/NH_3-steam extract did, however, indicate residual VX remained following 60 minutes of the NH_3-steam treatment (See Figure C17 in Appendix C). Although the VX peak size was not quantified, it is likely that sufficient VX was present to account for the relatively low destruction efficiency previously observed (i.e., 80.7 percent of VX was decontaminated after being in contact with NH_3-steam for 60 minutes).

6.0 COMPARISON OF RESULTS WITH SOME LITERATURE REPORTS

It is interesting to observe the correlation (or contrast) between results obtained in this subtask and some of those reported in the literature.

Rossmann[1] reports a halflife of 8.6 minutes at 20 C for VX in OPAB (OPAB, foam stabilizer, polyethylene glycol and water) and 1.8 minutes for DFP (diisopropyl fluorophosphonate) under the same conditions. The results from the current experiments indicate destruction of VX to be below the detection limit (99.8 percent destruction) between 60 and 180 minutes (intermediate intervals were not explored) which is in good agreement with the 78 minutes (9 halflives) required by Rossmann's value for 99.8 percent destruction. There appears to be no literature data for the destruction of GB and HD by OPAB.

Monoethanolamine (MEA) is reported to destroy HD. At 25 C HD was observed[2] to have a halflife of 321 minutes in neat MEA. More rapid results were observed in the current experiments where 50 percent aqueous MEA achieved 99.9 percent destruction of HD in 240 minutes. It has been rationalized[3] that GB and MEA (aqueous or anhydrous) should react rapidly and this was observed to be the case (see Appendix A). Additional information is available concerning MEA in combination with other components (e.g. solvents, caustic) but direct comparison with the current results is not applicable.

Attempts to decontaminate HD contaminated clothing with 10 percent anhydrous NH_3 were reported to be unsuccessful[4]. This confirms the low decontamination efficiency of 9.7 percent obtained from our experiments. No unclassified reports were located which report tests on the decontamination efficiency of GB or VX with anhydrous NH_3.

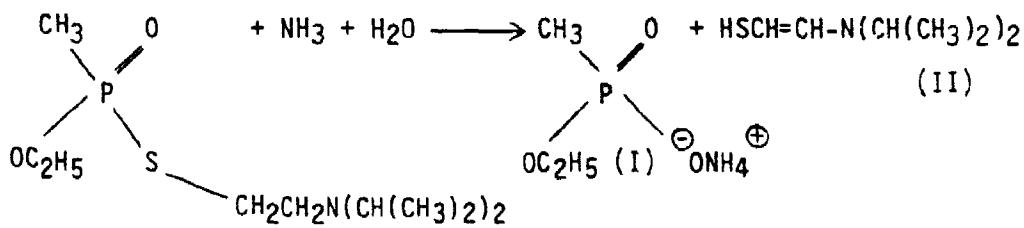
While good results were observed with aqueous ammonia in the vapor phase (i.e. NH_3/steam) against HD, results with the VX were less favorable. It has been reported that ammonium hydroxide at 100 C hydrolyzes VX rather slowly[5] and this appears to confirm the current observations.

Steam alone has been reported to decontaminate HD to very low residue (99.95 percent removal) levels in as little as 10 minutes if the contaminated surface, in this case painted steel, is not preheated.[6] Current experimental results indicate the disappearance of 99.8 percent HD in 20 minutes under somewhat different conditions.

In general, then, where the literature contains data obtained under conditions close enough to those employed in this subtask to permit at least rough comparisons to be made, there are no major discrepancies between this work and that of others.

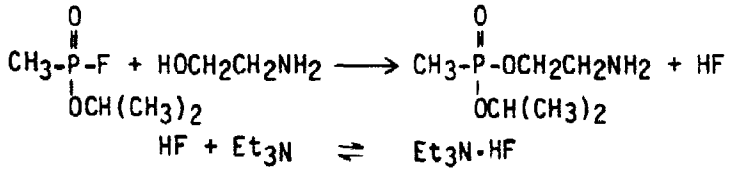
In terms of the results obtained by MS analysis of selected reactions, some correspondence with literature was found. Rossmann(1) predicted that the reaction between OPAB and GB would be a nucleophilic displacement of the fluorine to produce HF and the phosphoric acid of GB. While the phosphoric acid was not directly observed, the P-F bond was broken. It has been reported(7) that phosphorus-containing agents form polymers called "pyro" agents upon reaction at the phosphorus-fluorine or phosphorus-sulfur bond. MS data reveal a product which could result from hydrolysis of this polymer followed by attack by the displaced ligand, $^{-}OCHCH_3$. Reaction of steam with VX show a reaction similar to the OPAB/GB reaction except that the attacking ligand is $^{-}OCH(CH_3)_2$.

Domjan(4) shows the mechanism for the reaction of VX+NH_3 as follows.



The thiol (II) was observed in the reaction product analysis by MS, but not the ammonium phosphinate (I). It is unlikely that such a phosphinate would form a polymer, hydrolyze, and be attacked by a displaced ligand, as discussed above for OPAB/GB and Steam/VX. However, "pyro-VX" was observed by MS, indicating that perhaps the phosphinate does not form or that the "pyro-VX" observed by MS was generated by a different mechanism.

The reaction of MEA and GB in chloroform with triethylamine as proton acceptor is thought(3) to occur as follows:



The author warns, however, that these results may not be used to forecast the reactivity of aqueous MEA with GB, since MEA and water have high dielectric constants which would favor reaction between these materials as opposed to the poor, low dielectric of chloroform. On the basis of the MS results from this study it is difficult to determine whether the phosphate moiety has reacted to form a phosphate amide alcohol or a phosphate ester amine or something else.

7.0 EVALUATION AND RECOMMENDATION

The results of this subtask indicate that all of the decontaminants investigated (50% MEA, Steam, NH_3, NH_3/Steam, OPAB and 100% MEA) were effective to some extent. As such, no concept will be eliminated although a selection of the most promising concepts will still be performed. The less promising concepts will be retained for consideration in the event that an alternative concept(s) is required in subsequent efforts.

Although it is not a requirement of this program that a decontamination system be developed which is applicable to all three agents under consideration, there is a certain logistical advantage to identifying such a universal reagent. With this in mind, the candidate reagents can be summarized as follows.

- MEA - Although MEA (50 percent aqueous and undiluted) is rapidly effective against GB and reacts slowly yet completely (i.e. below detection limit) with HD, it is less effective in decontaminating VX. As such, the performance of MEA is less promising as compared with other systems evaluated.

- NH_3 - Anhydrous ammonia was evaluated in spite of its potential hazards (relatively toxic, gas with explosion limits) because of the advantages arising from the ability of a gaseous reagent to distribute itself throughout a structure and to penetrate inaccessible spaces and surfaces. It was found to have less effective decontaminating properties especially for HD as compared with other decontaminants.

- NH_3/Steam - A mixture of ammonia and steam, i.e. boiling aqueous ammonia, produced somewhat ambiguous results. Because there is no direct evidence that this system is superior to steam alone, the NH_3/steam concept merits no further study at this time.

- Steam - Steam has many obvious advantages for use as a decontaminant. It is inexpensive, non-toxic and easily applied to complex configurations. The principal hazard expected to be associated with its use is the possible risks for burns to operating personnel. Steam is an effective decontaminant: nerve agents are reduced to 1 percent or less residue within two hours and mustard is decomposed in even less time. In field application longer exposure times can be achieved if required. The degradation products of Steam/VX seem innocuous. Steam is an obvious candidate for more extensive evaluation.

- OPAB - The OPAB formulation was specifically developed for and evaluated against VX. The very effective results reported by the Battelle-Frankfurt research group were confirmed in this subtask. In addition, OPAB was demonstrated to be effective against GB as anticipated and against HD which was not expected.

OPAB is a safe material to apply since it is not toxic and can be applied at ambient temperature. OPAB is a relatively low viscosity liquid and the presence of a surface active chemical should enhance spreading. The surface active chemical may be removed to enhance penetration of concrete, if necessary. The degradation products of OPAB/GB seem innocuous. The OPAB system is one of the most effective decontaminants for all three agents examined. One apparent negative attribute of OPAB is the cost, although commercial production of OPAB might reduce its cost significantly.

We recommend that further evaluations be made of the steam and OPAB decontamination methods.

REFERENCES

1. Klaus, Rossmann, Personal Communication, October 19, 1983.

2. Brankowitz, William R., "Demilitarization of Mustard Agent (HD) At Fort McClellan, Alabama", AD-A054 740, Chemical Systems Laboratory, Aberdeen Proving Grounds, MD, April, 1978.

3. Davis, George T., et al., "Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components", AD-B017 249L, Edgewood Arsenal, Aberdeen Proving Ground, MD, March, 1977.

4. Albizo, Johnnie M., "Evaluation Gases as Potential Decontaminants for Building Decontamination", AD-A028 951, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July, 1982.

5. Domjan, Viktor, "Physico-Chemical Characteristics of V-Agents and Their Decontamination", AD-B012 260L, U.S. Army Foreign Science and Technology Center, Charlottesville, VA, September 15, 1975.

6. Davis, Harry R., et al., "Laboratory Studies of Mustard Decontamination by Steam", AD-493 566, Naval Research Laboratory, Washington, D.C., January 4, 1950.

7. Cox, J. R., Jr. and Ramsay, O. B., Chem Rev, 64, (1964), 317.

APPENDIX A

DETAILED ANALYTICAL RESULTS

TABLE A-1. DETAILED ANALYTICAL RESULTS

Decontamination Concepts	GB Time (min)	GB Resid (mg)	GB % D	HD Time (min)	HD Resid (mg)	HD % D	VX Time (min)	VX Resid (mg)	VX % D
50% MEA	1	BDL[a]	99.8	1	213.2	32.7	10	186.4	42.2
	20	BDL	99.8	1	218.8	31.0	10	198.4	38.5
				3	1149.5	>0	20	187.2	42.0
				3	1264.1	>0	20	194.4	39.8
				20	618.0	0	40	189.6	41.3
				20	352.0	0	40	199.2	38.3
				40	183.8	42.0	60	180.8	44.0
				40	257.4	18.8	60	193.6	40.0
				60	133.4	57.9	120	201.6	37.5
				60	no data	--	120	205.6	36.3
				60	741.0	>0	240	182.4	43.5
				60	1.6	99.5	240	262.3	18.7
				120	1.9	99.4	1440	29.6	90.8
				120	107.0	66.2	1440	52.8	83.6
				120	2.4	99.2			
				120	99.7	68.6			
				240	BDL	99.9			
				240	BDL	99.9			
				360	BDL	99.9			
				360	BDL	99.9			
Steam	20	12.8	87.0	5	12.0	88.2	20	5.2	94.8
	20	1.3	(98.7)	5	15.6	84.6	20	5.0	95.0
	60	1213.2μg	(98.3)	20	1.5	98.5	60	3.4	96.6
	60	762.3μg	(99.2)	20	0.9	99.1	60	2.8	97.2
	120	BDL	97.0	20	BDL	99.8	120	0.7	99.4
	120	BDL	97.0	20	BDL	99.8	120	0.5	99.5
				60	BDL	99.8			
				60	BDL	99.8			
				60	0.2	99.8			
				60	BDL	99.8			

TABLE A-1. (Continued)

Decontamination Concepts	GB Time (min)	GB Resid (mg)	GB % D	HD Time (min)	HD Resid (mg)	HD % D	VX Time (min)	VX Resid (mg)	VX % D
Anhyd. Ammonia	20	4.6	92.3	60	59.8	5.7	20	4.7	22.0
	20	3.5	94.1	60	57.3	9.7	20	69.0	0
	60	1642.0µg	97.3				60	8.6	85.8
	60	847.0µg	98.6				60	9.4	84.4
	120	2.4	96.0				120	37.1	38.6
	120	2.9	95.2				120	46.9	22.4
NH_3/Steam	60	44.8	54.3 (b)	60	BDL	99.8	60	31.0	69.3 (b)
	60	44.8	54.3 (b)	60	BDL	99.8	60	7.9	92.1 (b)
BF-OPAB	1	BDL	99.8	20	293.4	>0	20	40.6	85.6
				20	291.0	>0	20	43.1	84.7
				40	90.7	67.5	40	19.8	93.0
				40	120.9	56.7	40	23.4	91.7
				60	23.5	91.6	60	10.8	96.2
				60	52.3	81.3	60	12.8	95.5
				180	3.7	98.7	180	0.2	99.8
				180	5.3	98.1	180	BDL	99.8
				240	0.1	99.8	240	BDL	99.8
				240	0.2	99.8	240	BDL	99.8
				360	BDL	99.8	360	BDL	99.8
				360	BDL	99.8	360	BDL	99.8
							1440	BDL	99.8
							1440	BDL	99.8
100% MEA	1	BDL	99.8				1	201.0	38.0
	1	BDL	99.8				1	227.0	30.0
	20	BDL	99.8				20	172.0	46.6
	20	BDL	99.8				20	177.0	45.0

(a) BDL = Below Detection Limit

(b) As determined by GC/FPD, the experiments were subsequently repeated and the samples were analyzed by GC/MS. No residual GB was detected in the repeat experiment. However, intact VX was detected by GC/MS.

APPENDIX B

GAS CHROMATOGRAMS

APPENDIX B

GAS CHROMATOGRAMS

The following sample chromatograms of extracts (i.e. CH_2Cl_2, hexane) obtained after decontamination are given in Appendix B.

Agent	Decontaminant	Figure No.
HD	Steam	B1
HD	OPAB	B2
GB	Steam	B3
GB	NH_3/Steam	B4
VX	NH_3/Steam	B5
VX	100 percent MEA	B6
VX	OPAB	B7

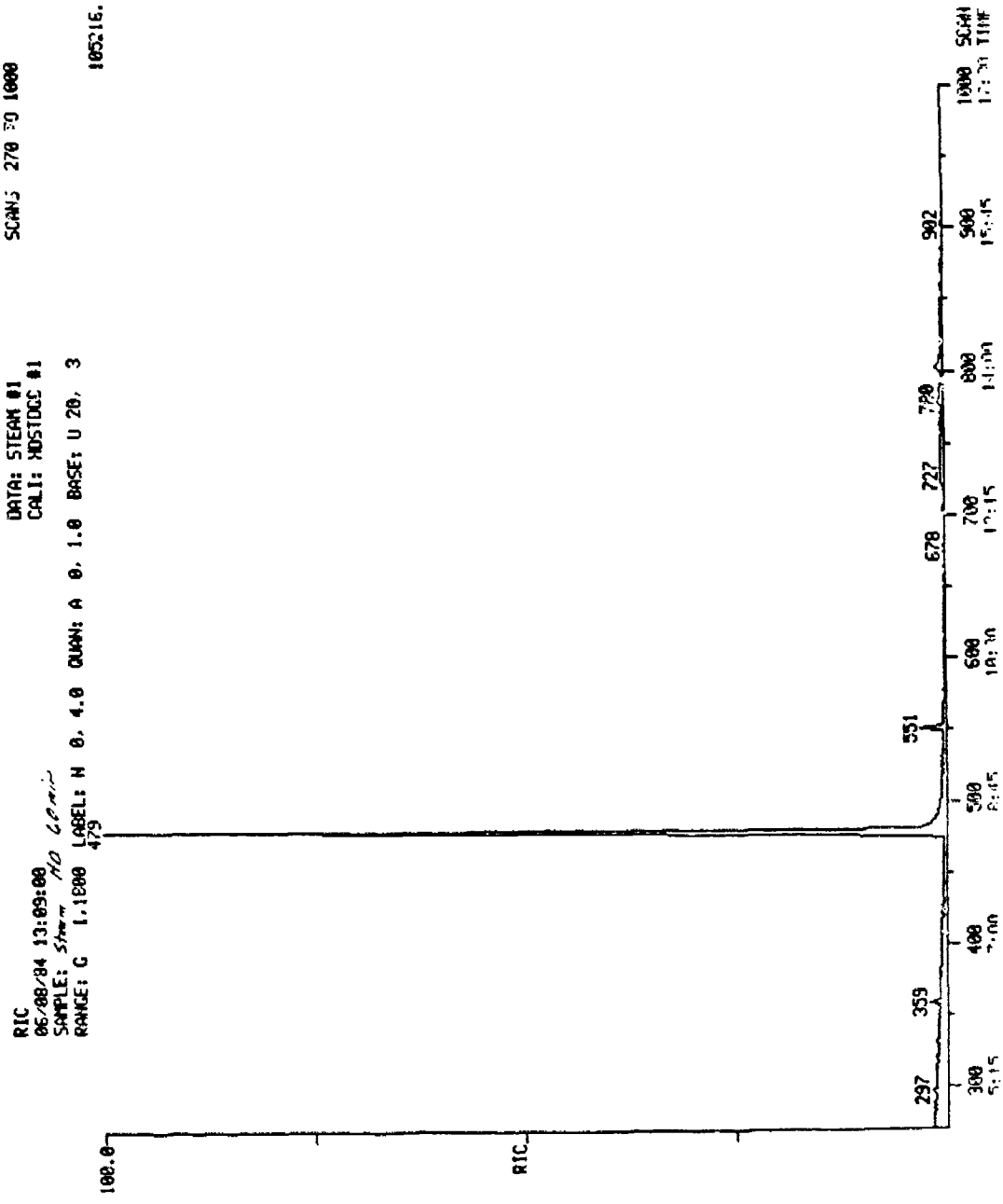


FIGURE B1. GAS CHROMATOGRAM OF EXTRACT FROM STEAM DECONTAMINATION OF HD

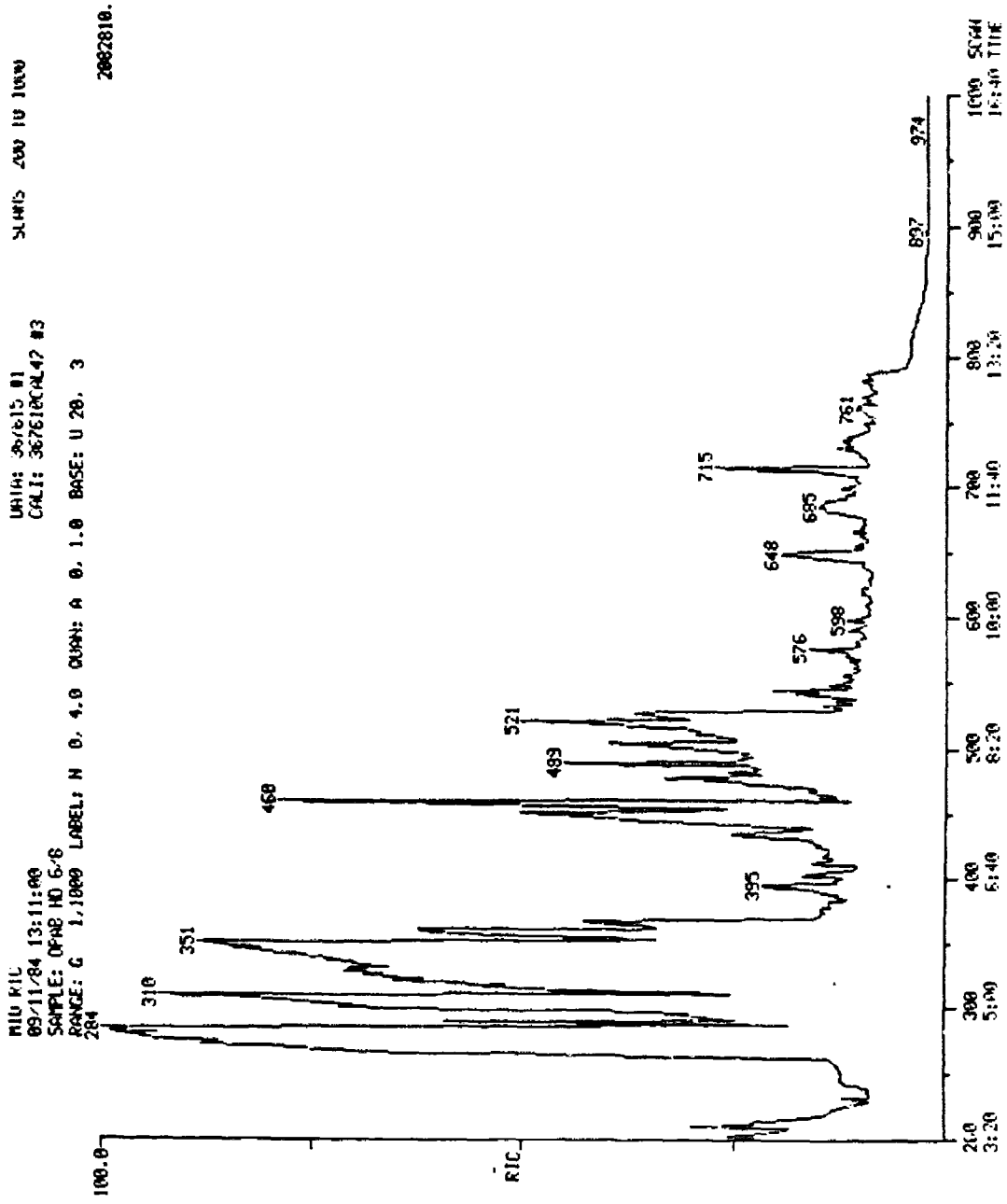


FIGURE B2. GAS CHROMATOGRAM OF EXTRACT FROM OPAB DECONTAMINATION OF HD

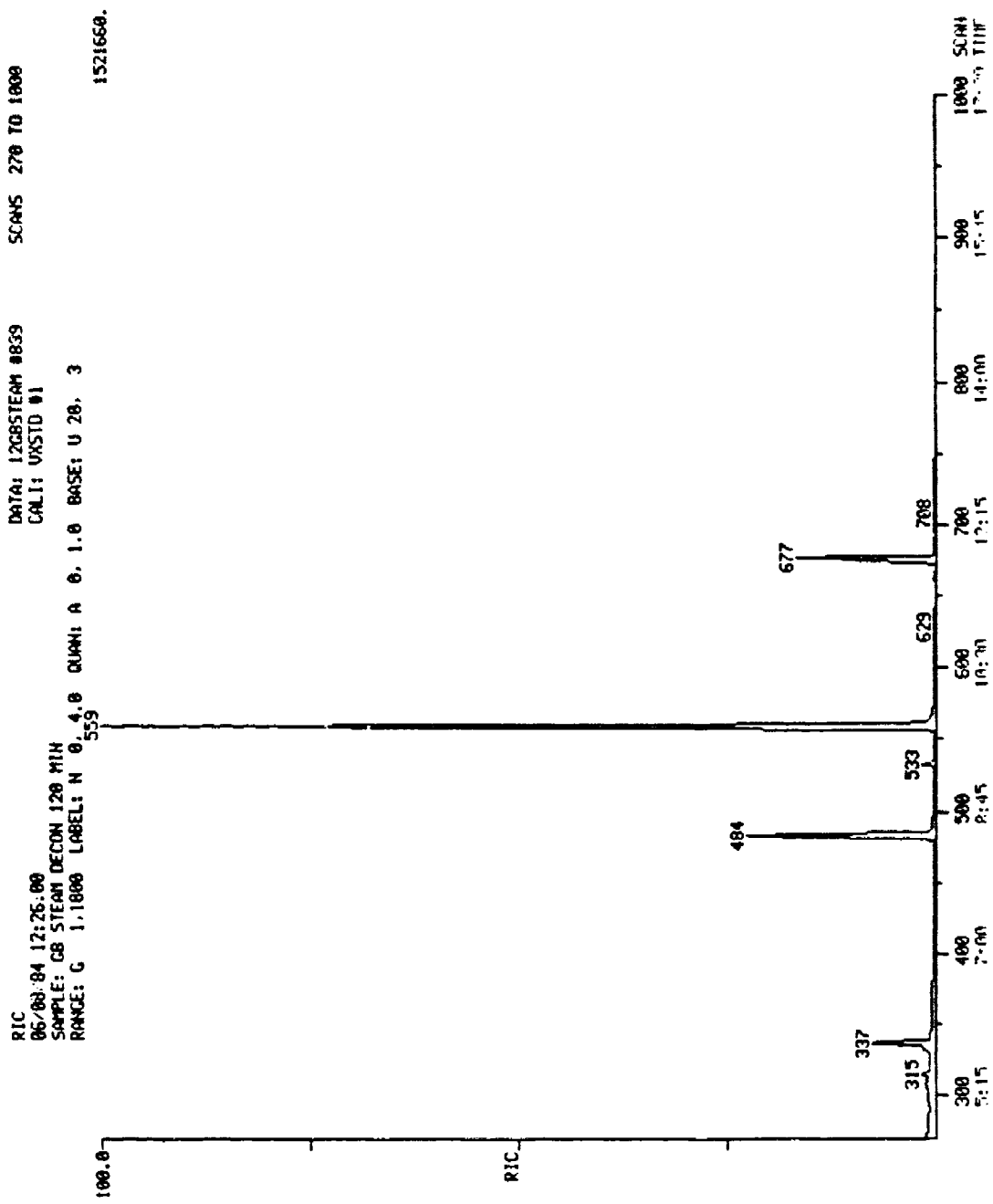


FIGURE B4. GAS CHROMATOGRAM OF EXTRACT FROM STEAM DECONTAMINATION OF GB

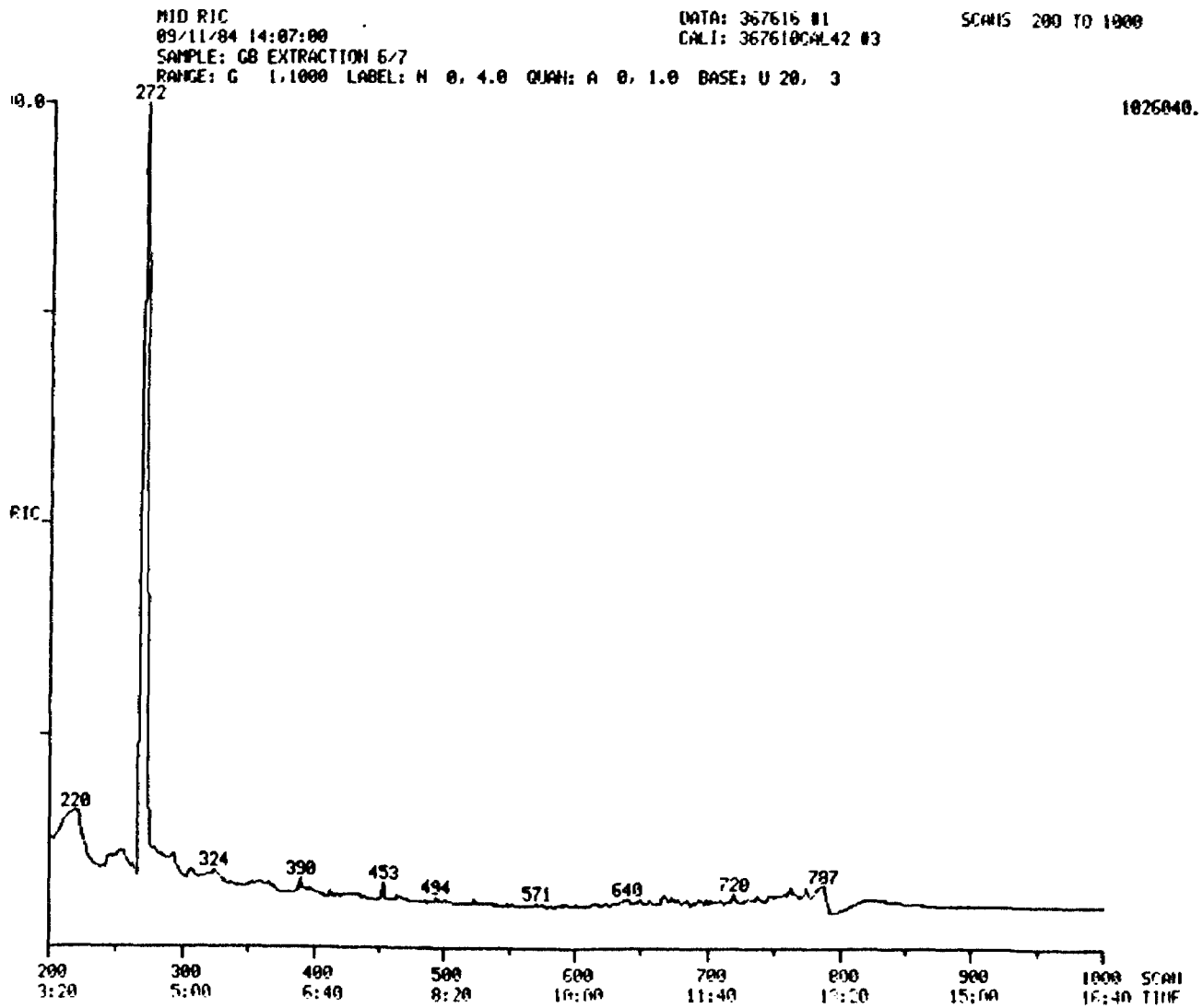


FIGURE B4. GAS CHROMATOGRAM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF GB

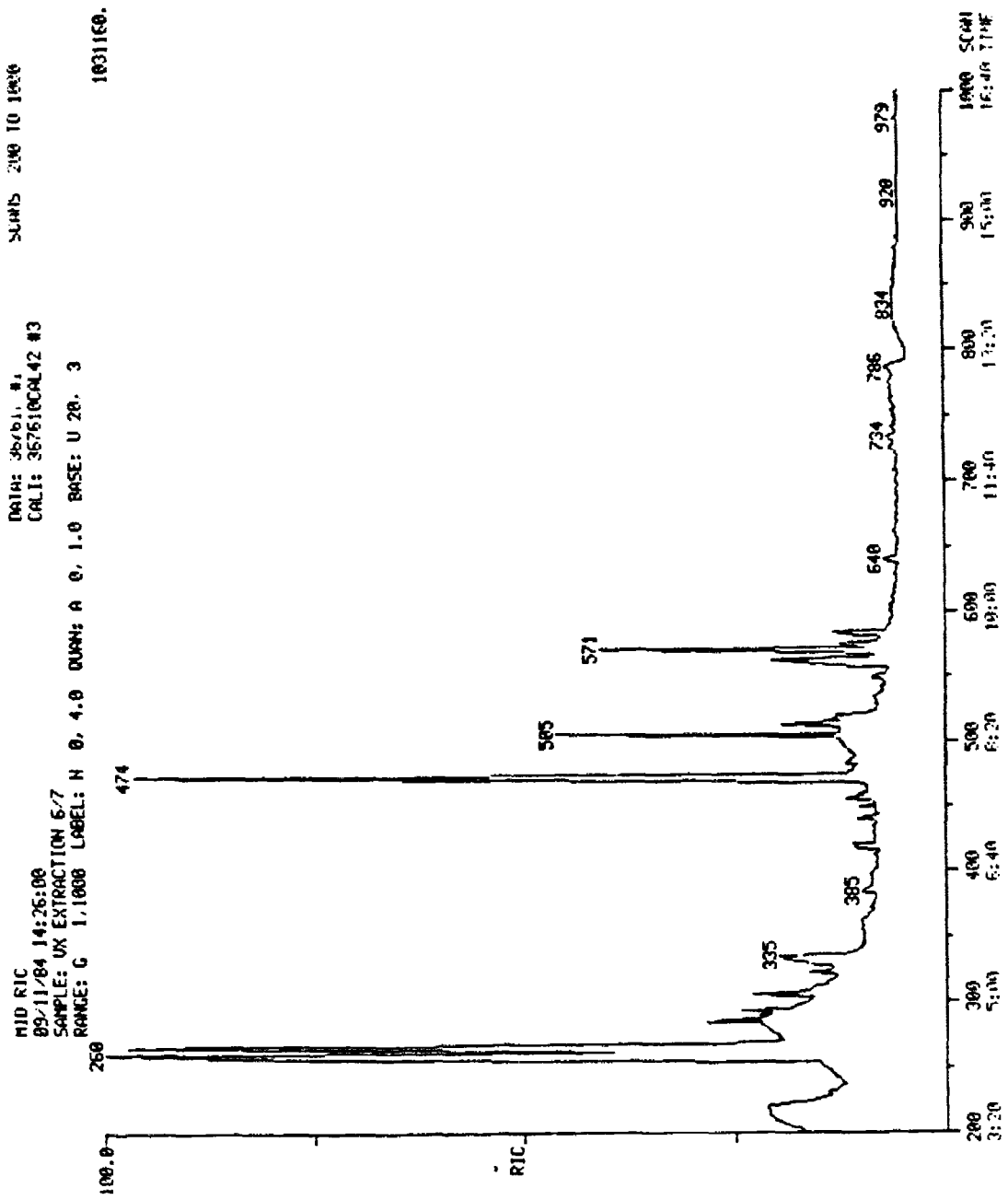


FIGURE B5. GAS CHROMATOGRAM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX

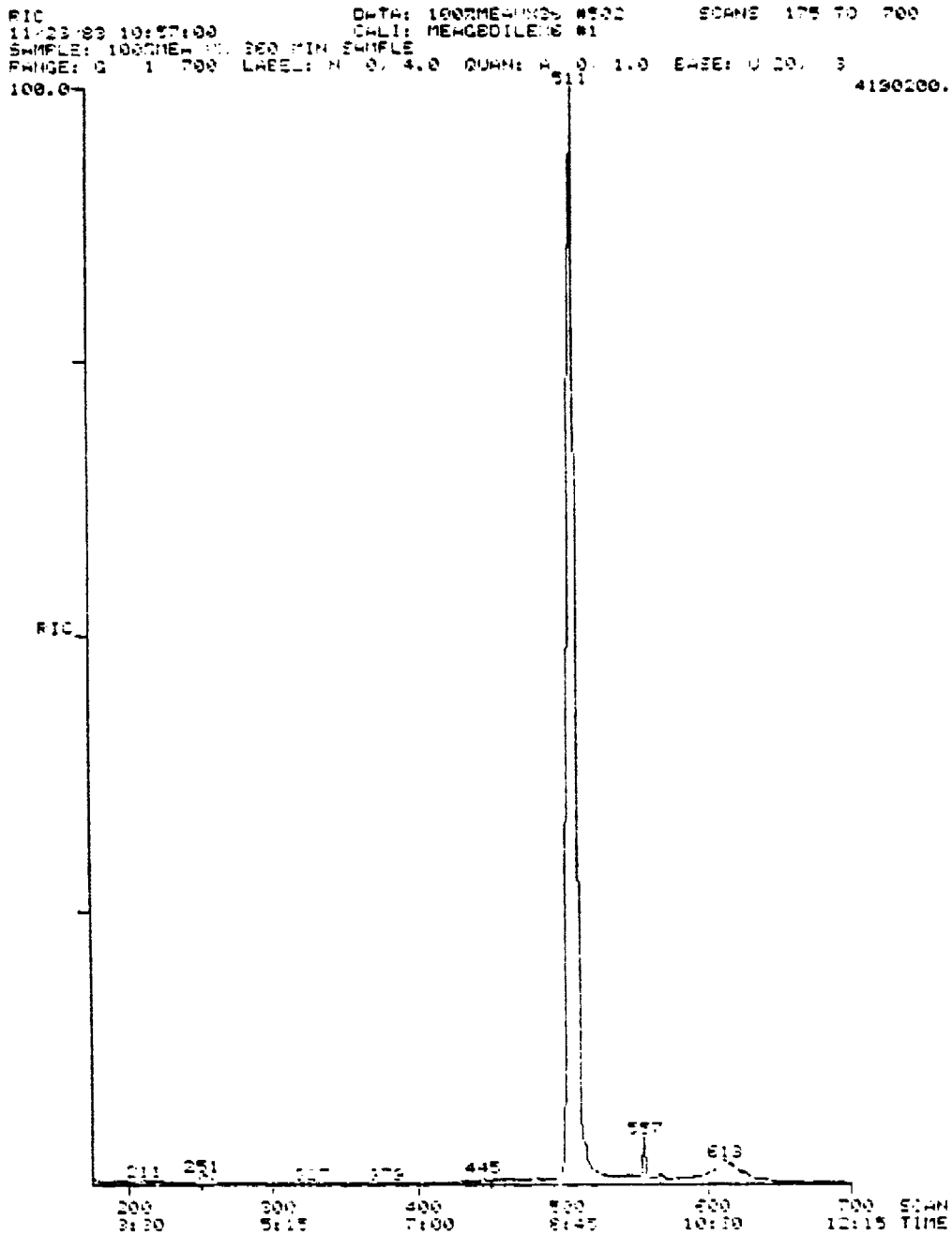


FIGURE B6. GAS CHROMATOGRAM OF EXTRACT FROM MEA (100 PERCENT) DECONTAMINATION OF VX

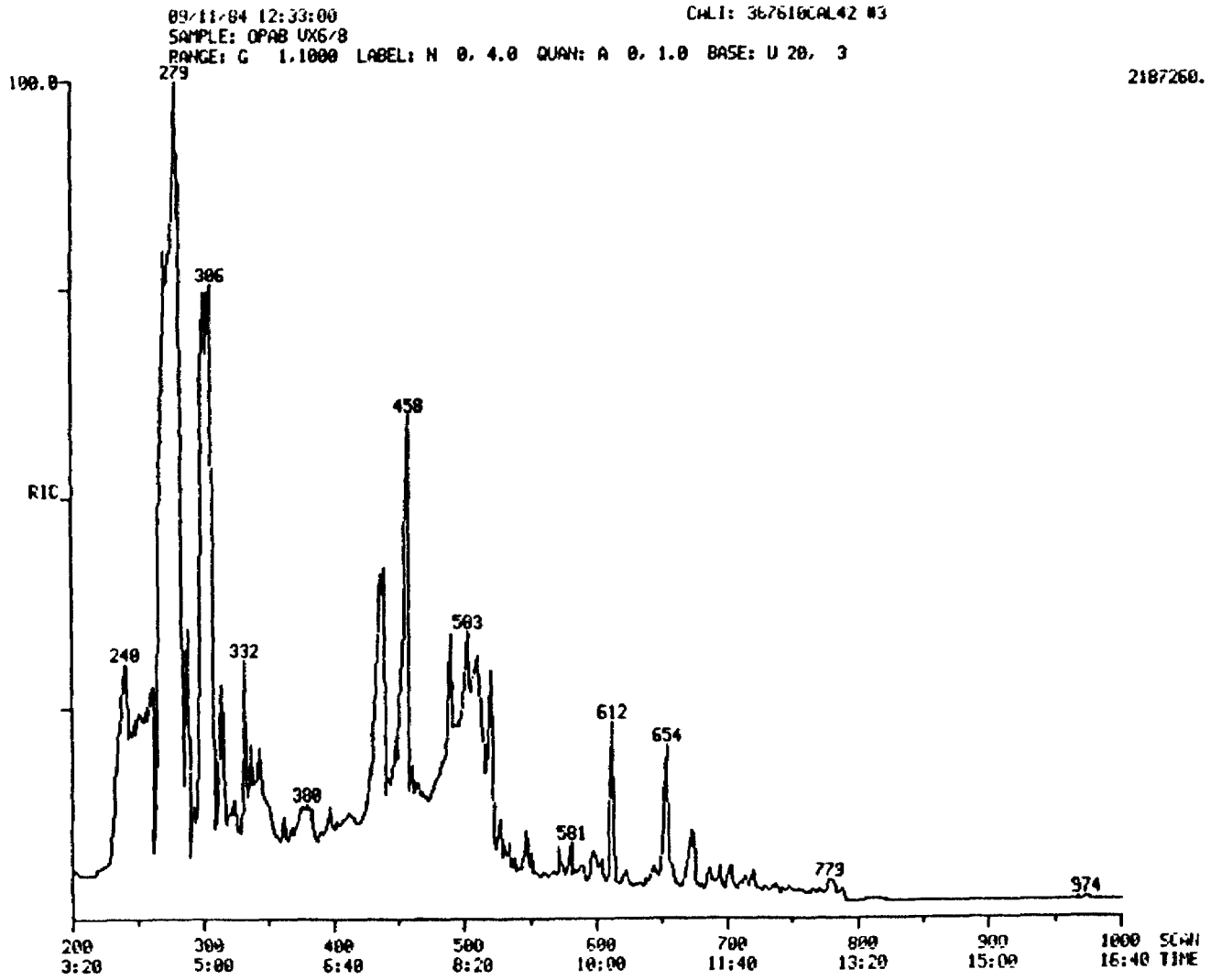


FIGURE B7. GAS CHROMATOGRAM OF EXTRACT FROM OPAB DECONTAMINATION OF VX

APPENDIX C

MASS SPECTRA

APPENDIX C

MASS SPECTRA

The following mass spectra were used in either identification of agent decomposition products or confirmation for the presence of intact agent.

Agent	Decontaminant	Figure No.
HD	Steam	C1-C3
GB	Steam	C4
VX	Steam	C5
HD	OPAB*	C6
GB	OPAB**	C7-8
VX	OPAB*	C9-C10
GB	50% MEA	C11-C12
VX	100% MEA	C13
GB	NH_3/Steam	C14
VX	NH_3/Steam	C15-C17
VX	NH_3	C18-C21

* BCL-OPAB (neat OPAB dissolved in water)

** BF-OPAB (sodium salt of OPAB and additives dissolved in water)

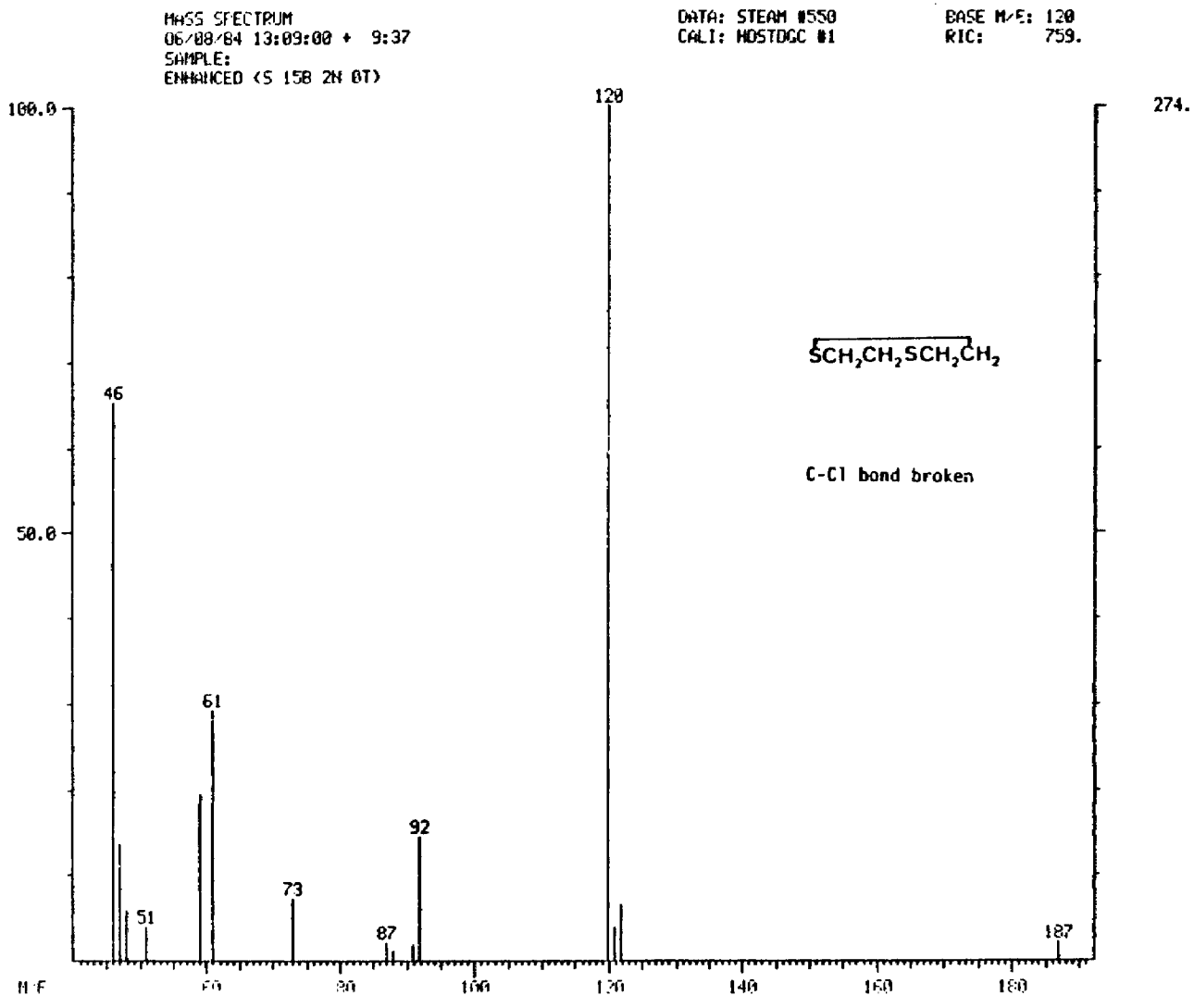


FIGURE C1. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#1)

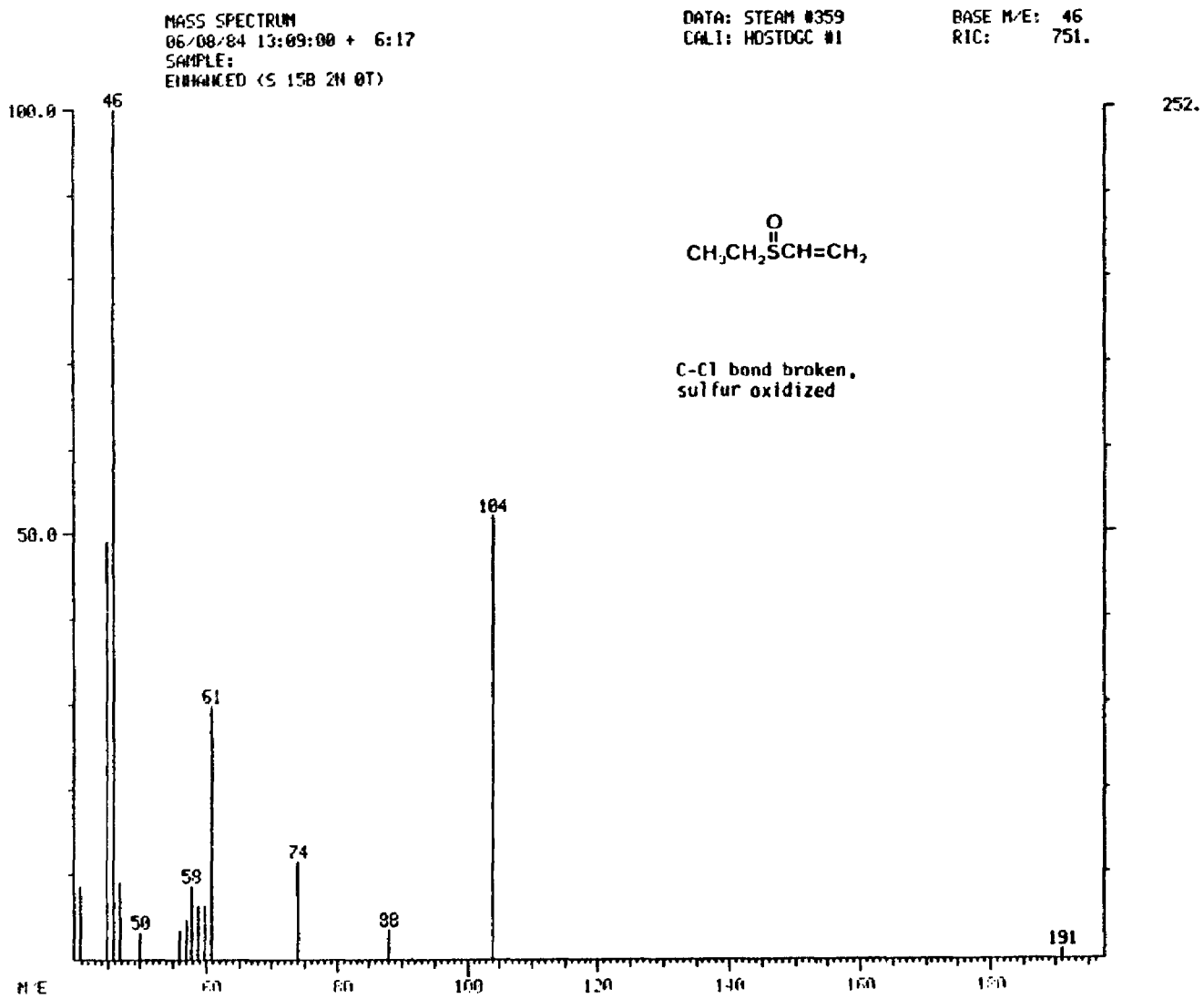


FIGURE C2. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#2)

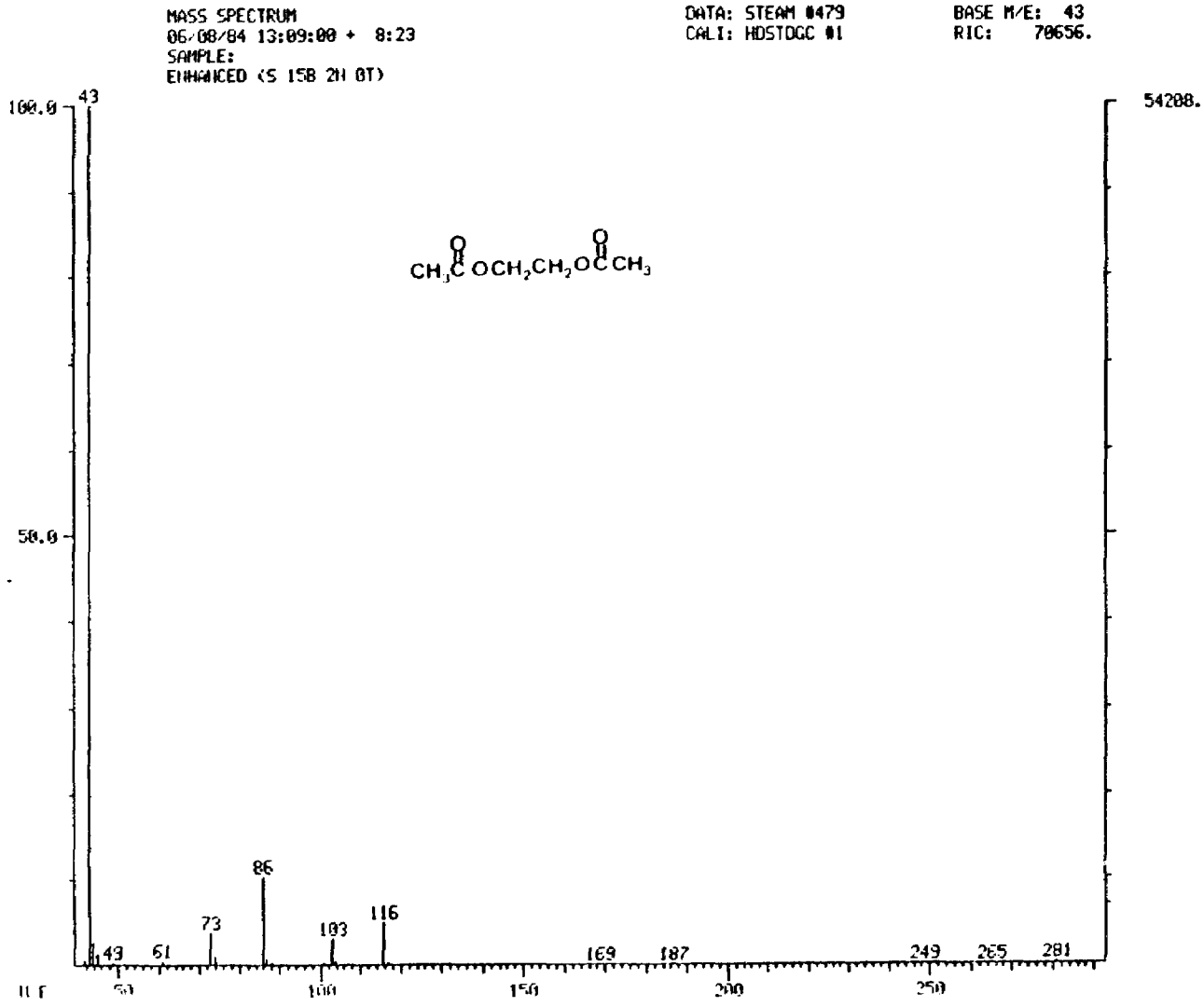


FIGURE C3. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#3)

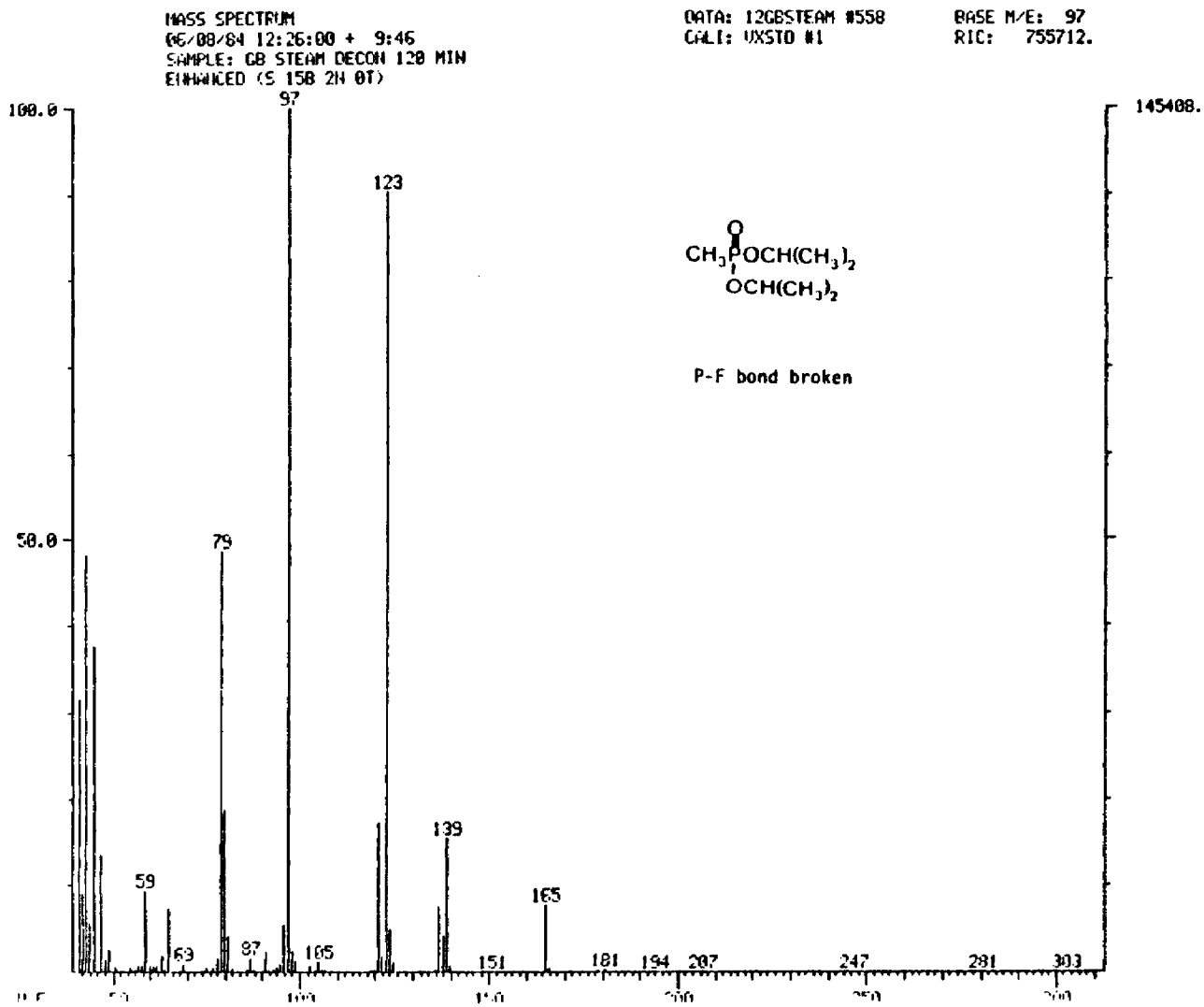


FIGURE C4. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF GB

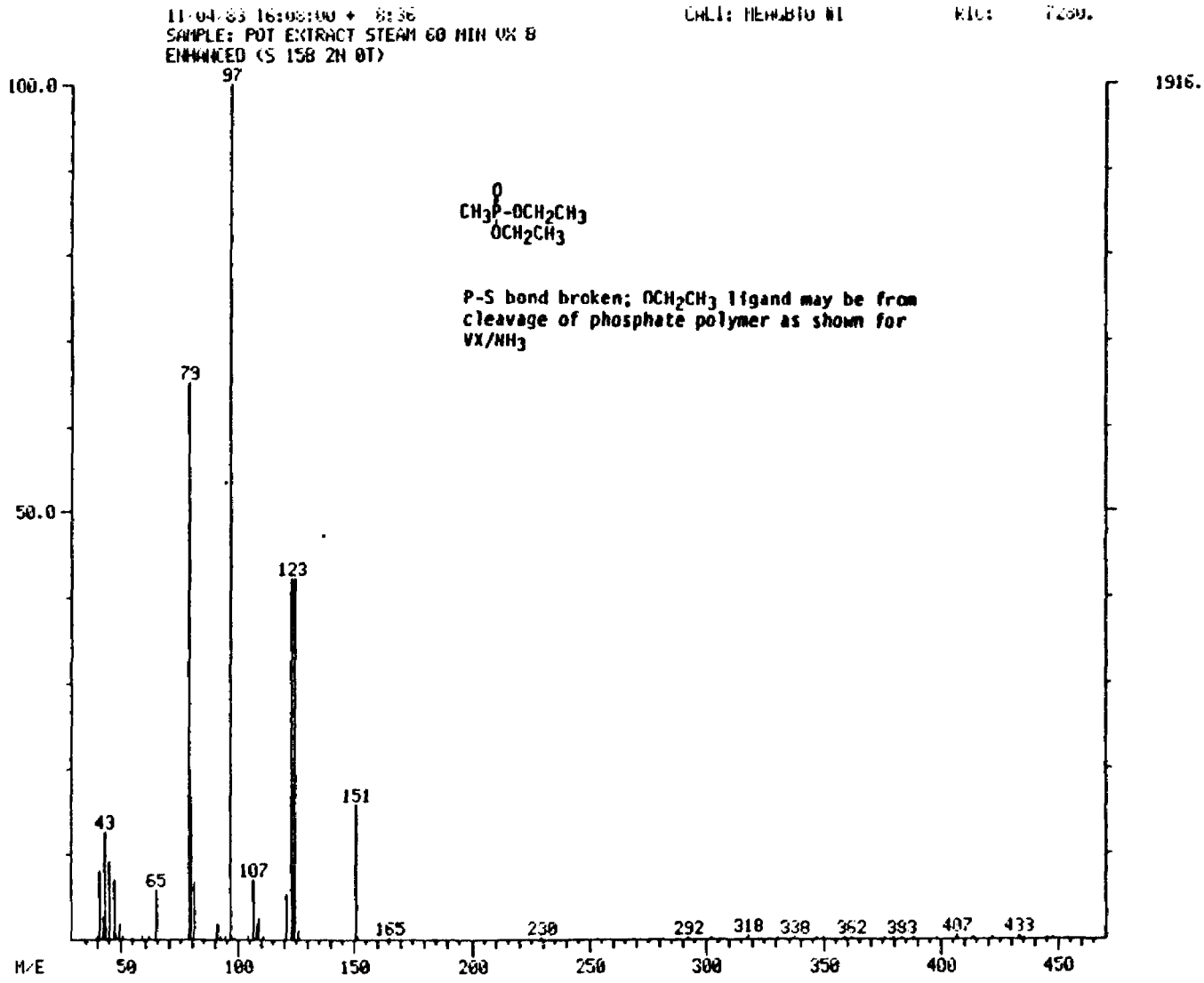


FIGURE C5. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF VX

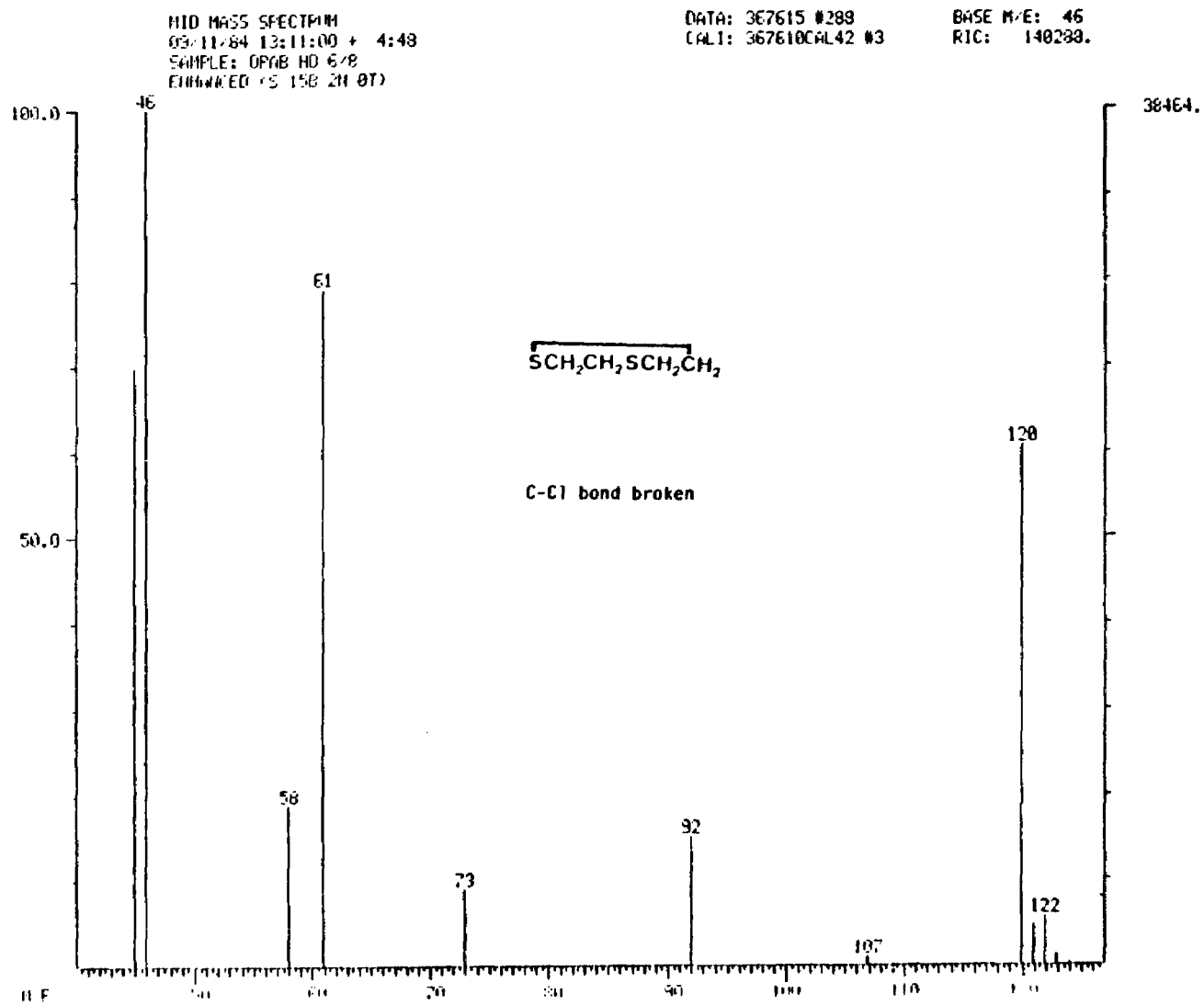


FIGURE C6. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF HD

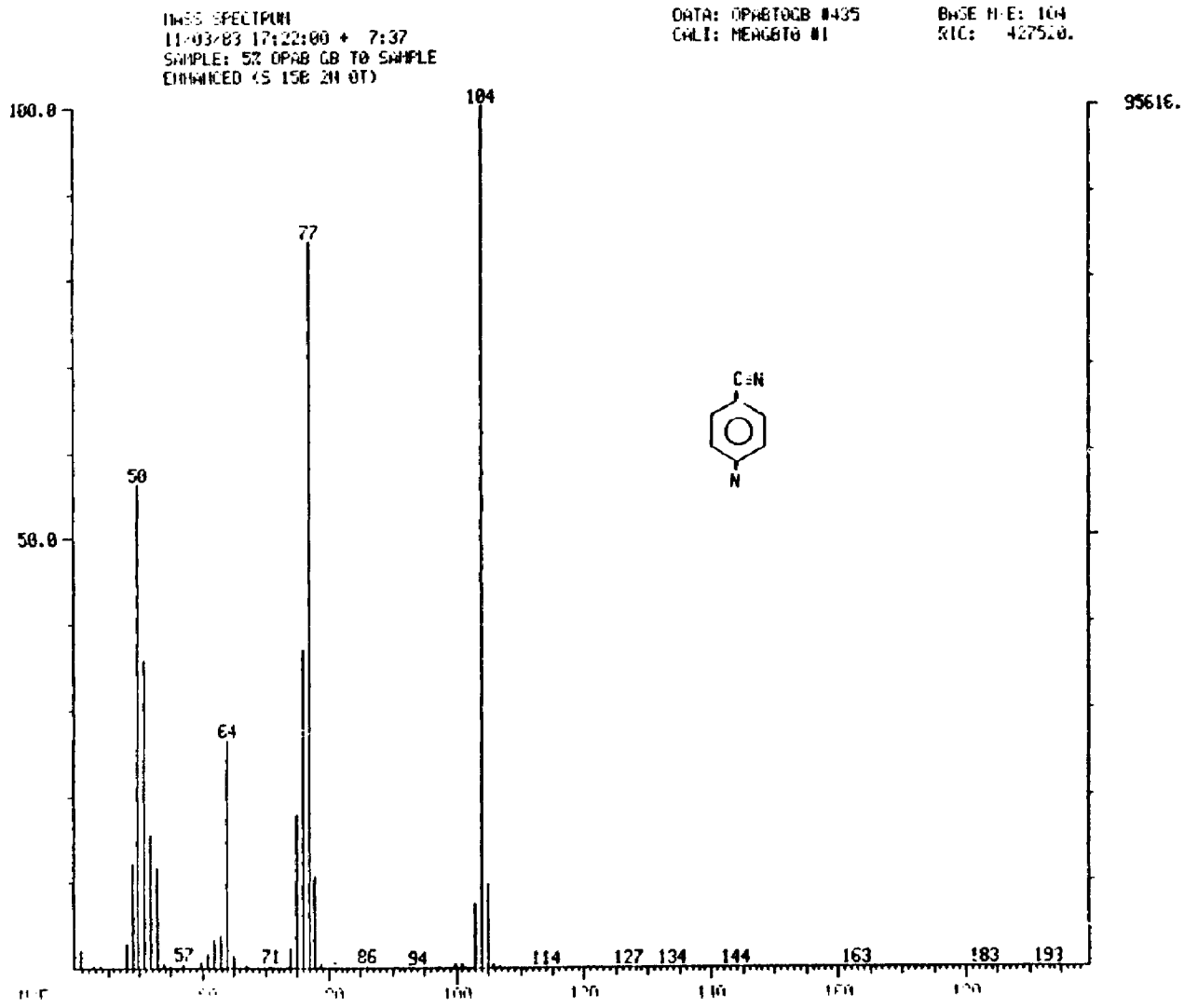


FIGURE C7. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF GB (#1)

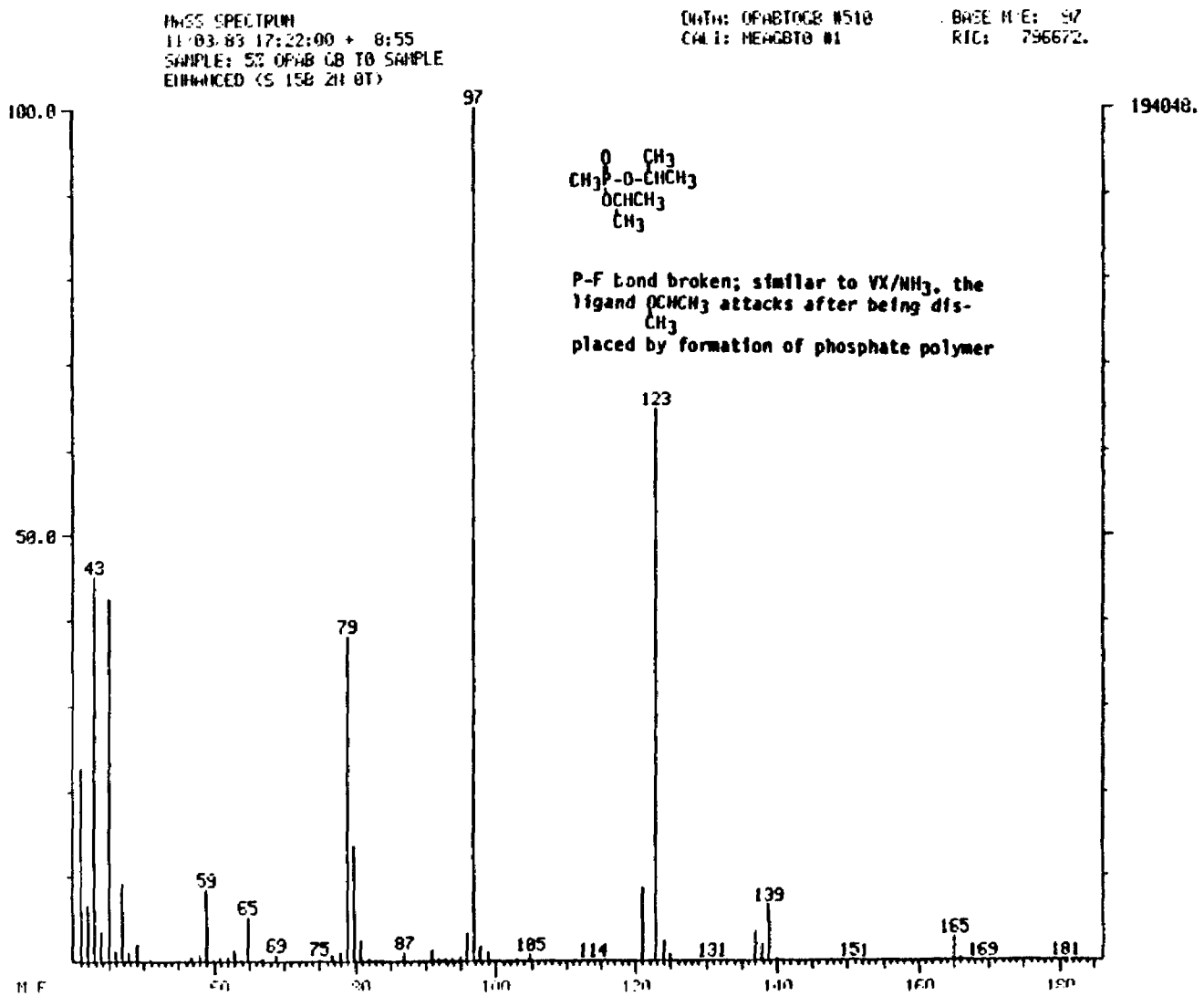


FIGURE C8. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF GB (#2)

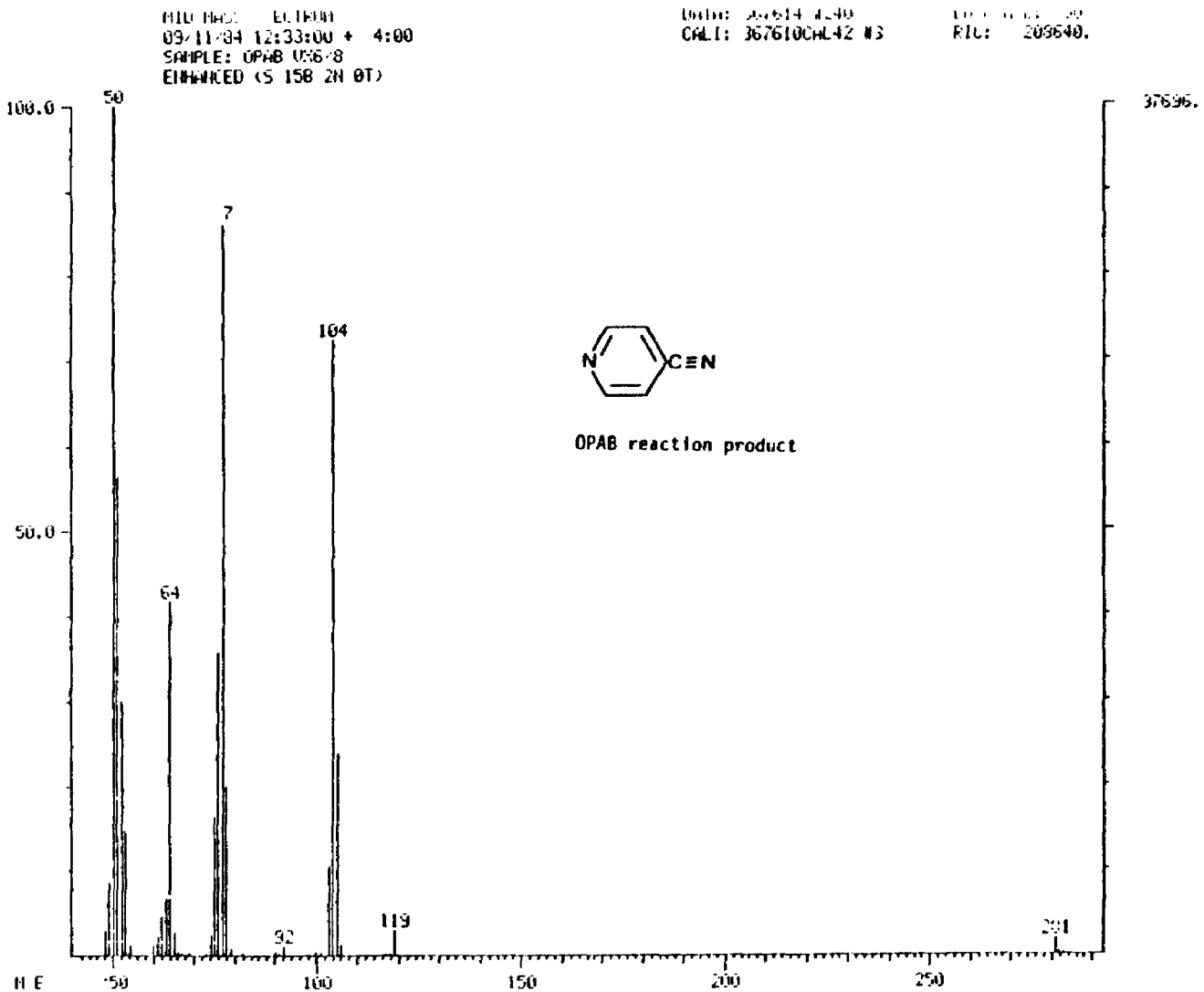


FIGURE C9. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF VX (#1)

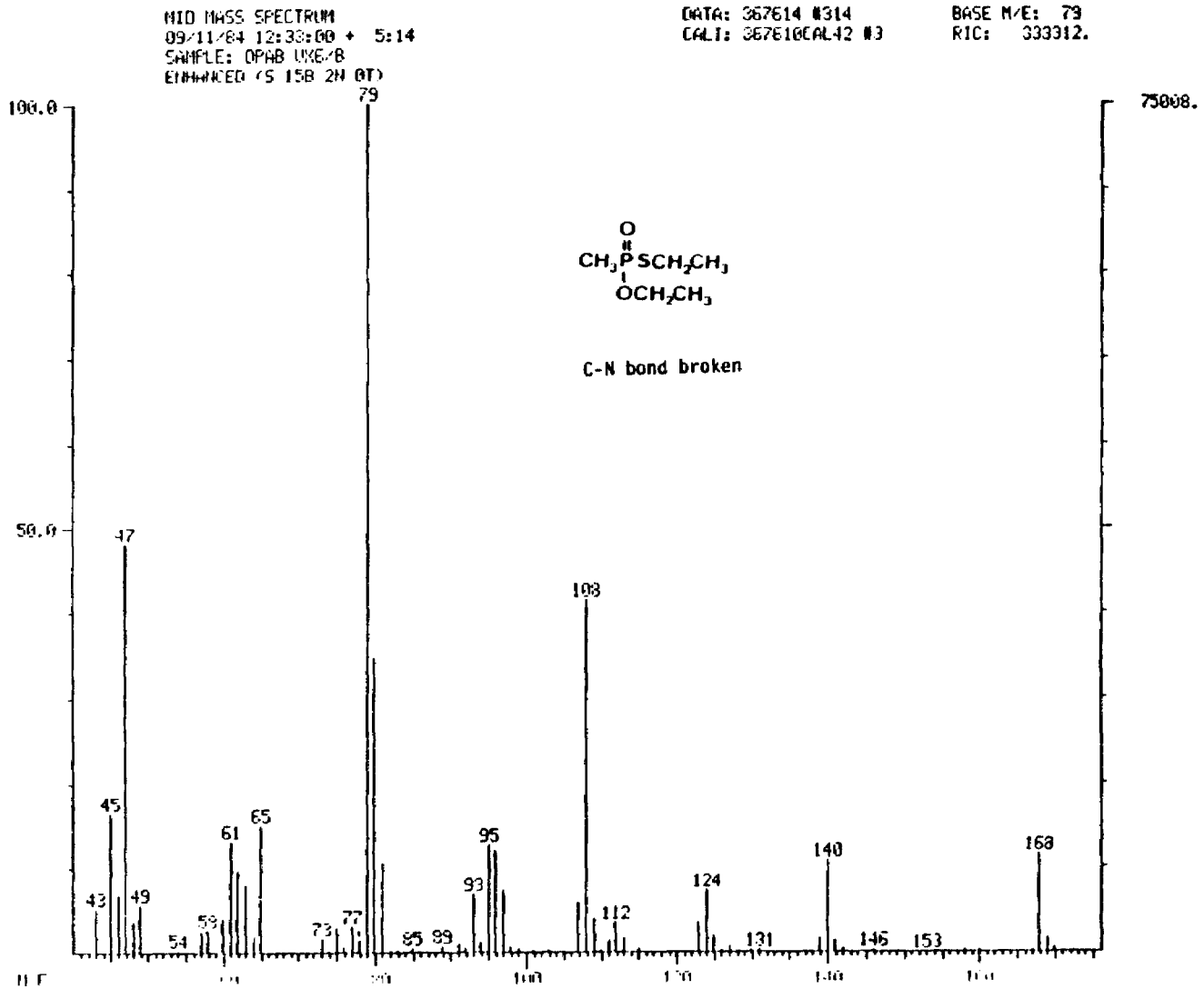


FIGURE C10. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF VX (#2)

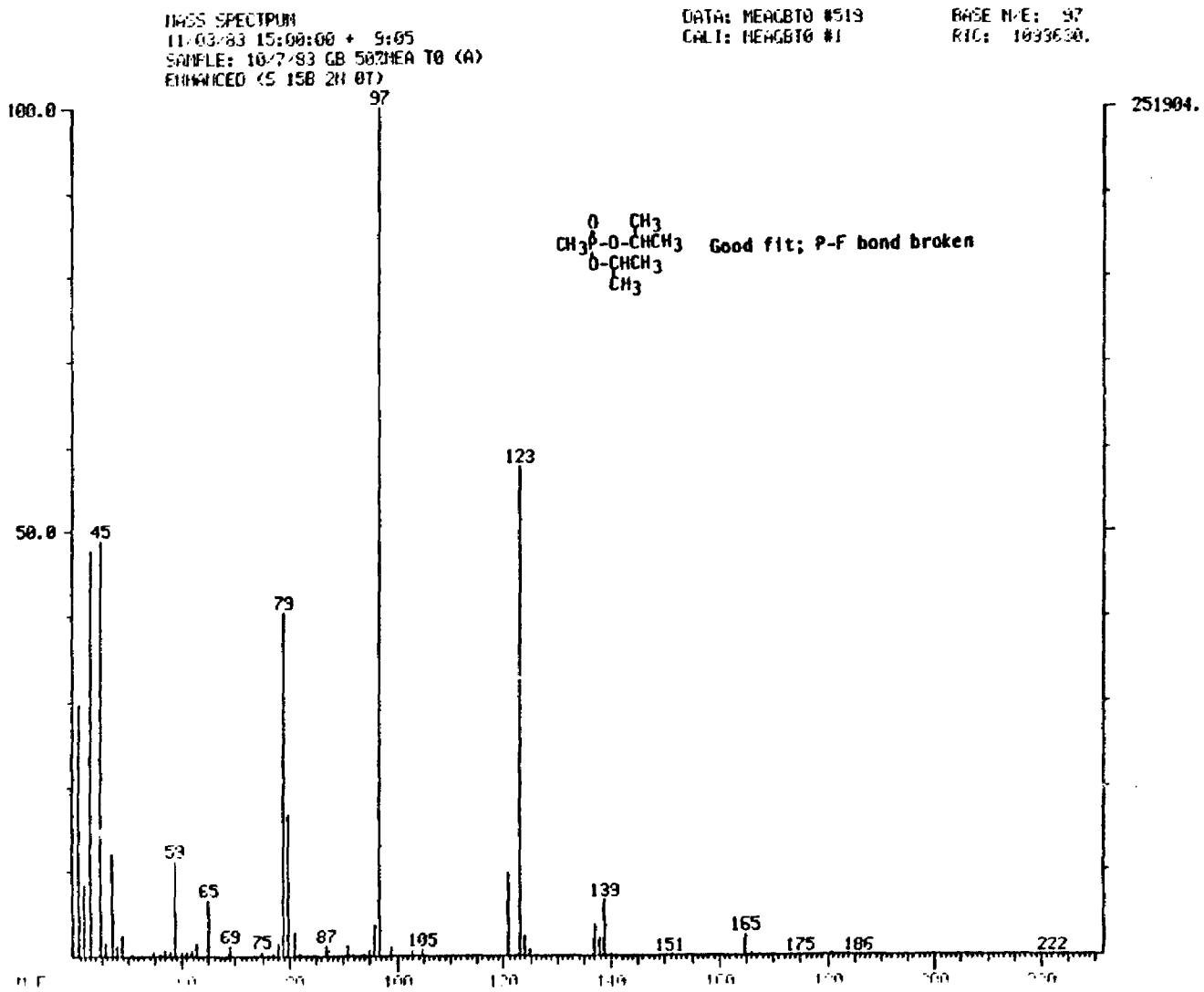


FIGURE C11. MASS SPECTRUM OF EXTRACT FROM MEA (50 PERCENT) DECONTAMINATION OF GB (#1)

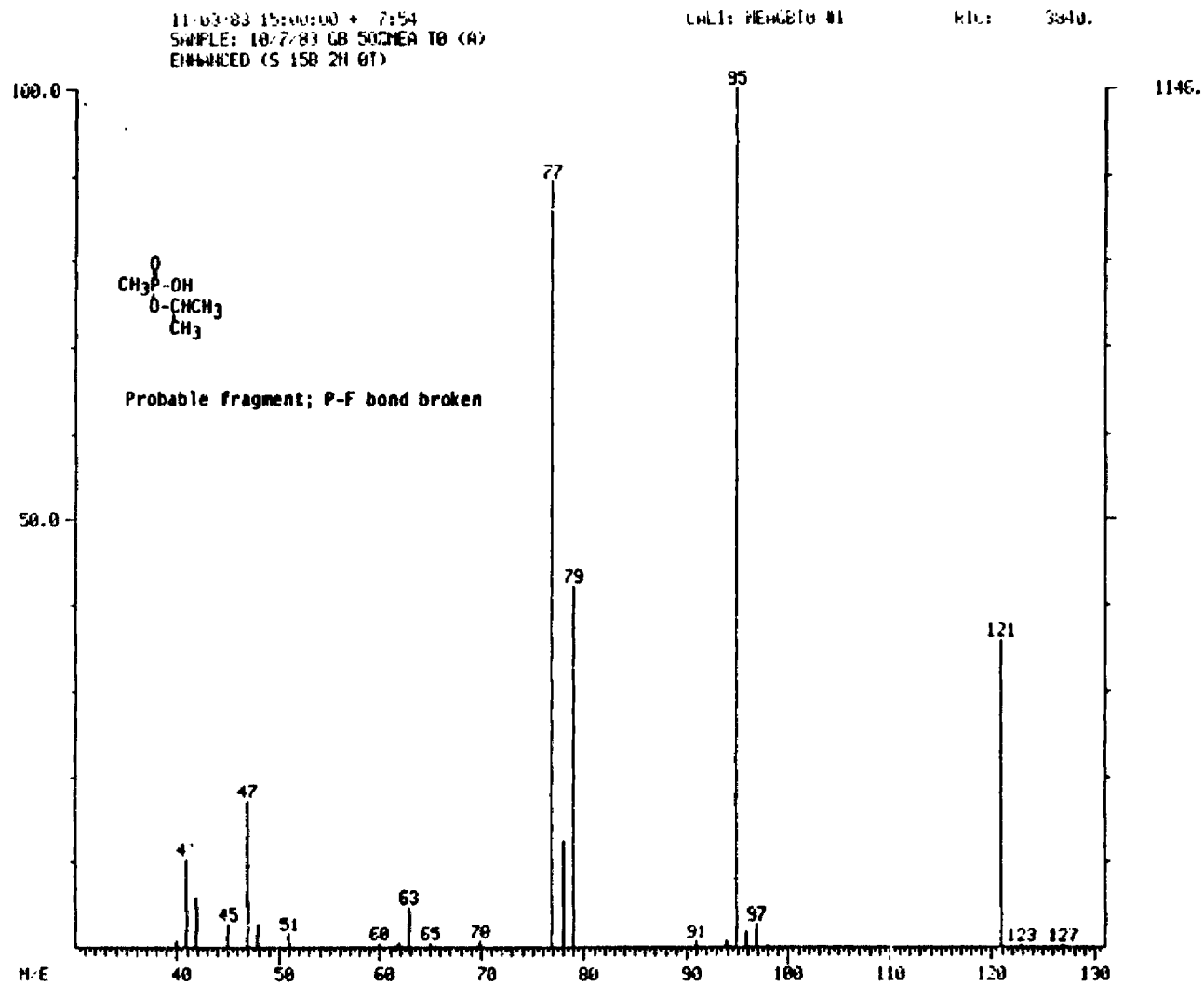


FIGURE C12. MASS SPECTRUM OF EXTRACT FROM MEA (50 PERCENT) DECONTAMINATION OF GB (#2)

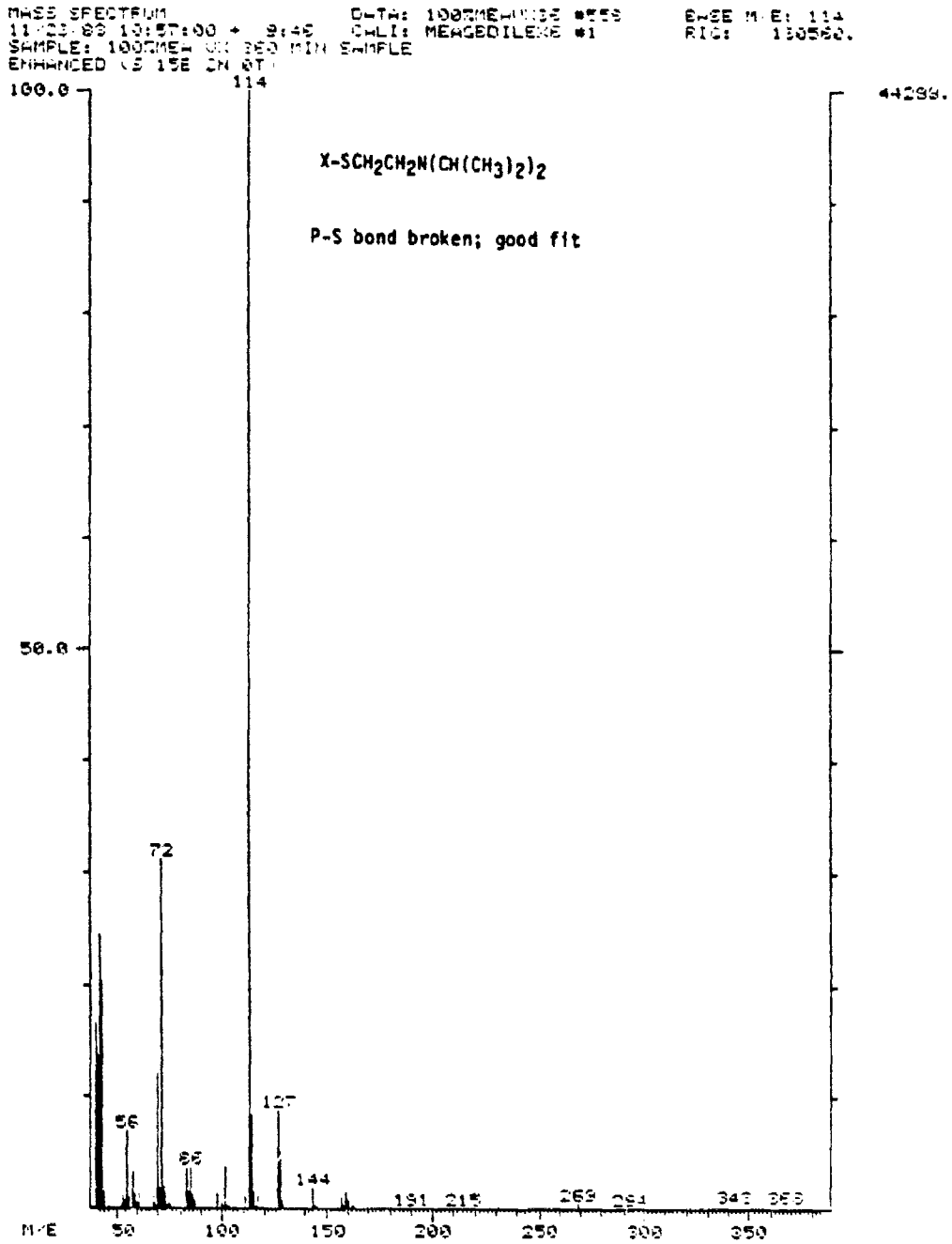


FIGURE C13. MASS SPECTRUM OF EXTRACT FROM MEA (100 PERCENT) DECONTAMINATION OF VX

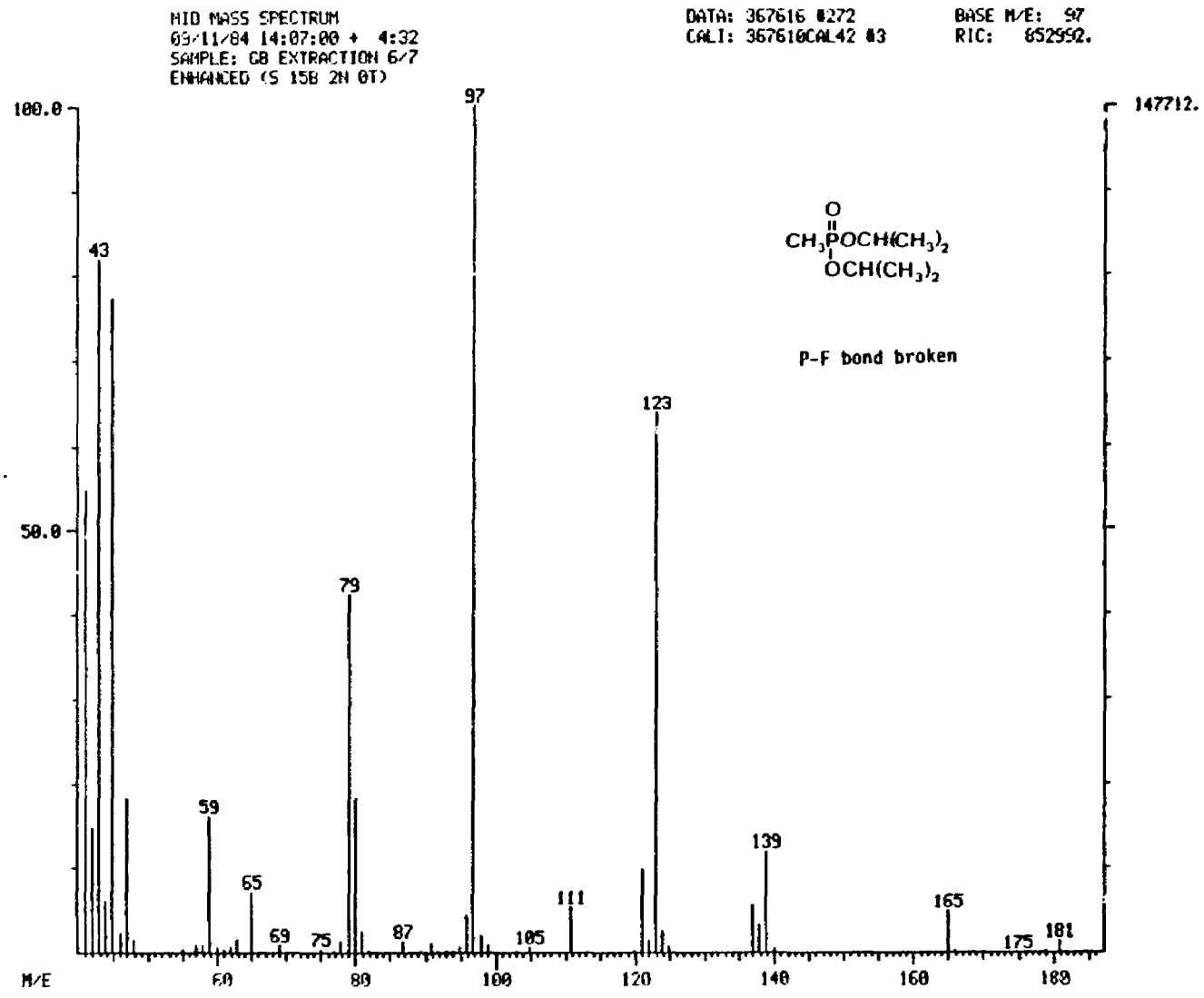


FIGURE C14. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF GB

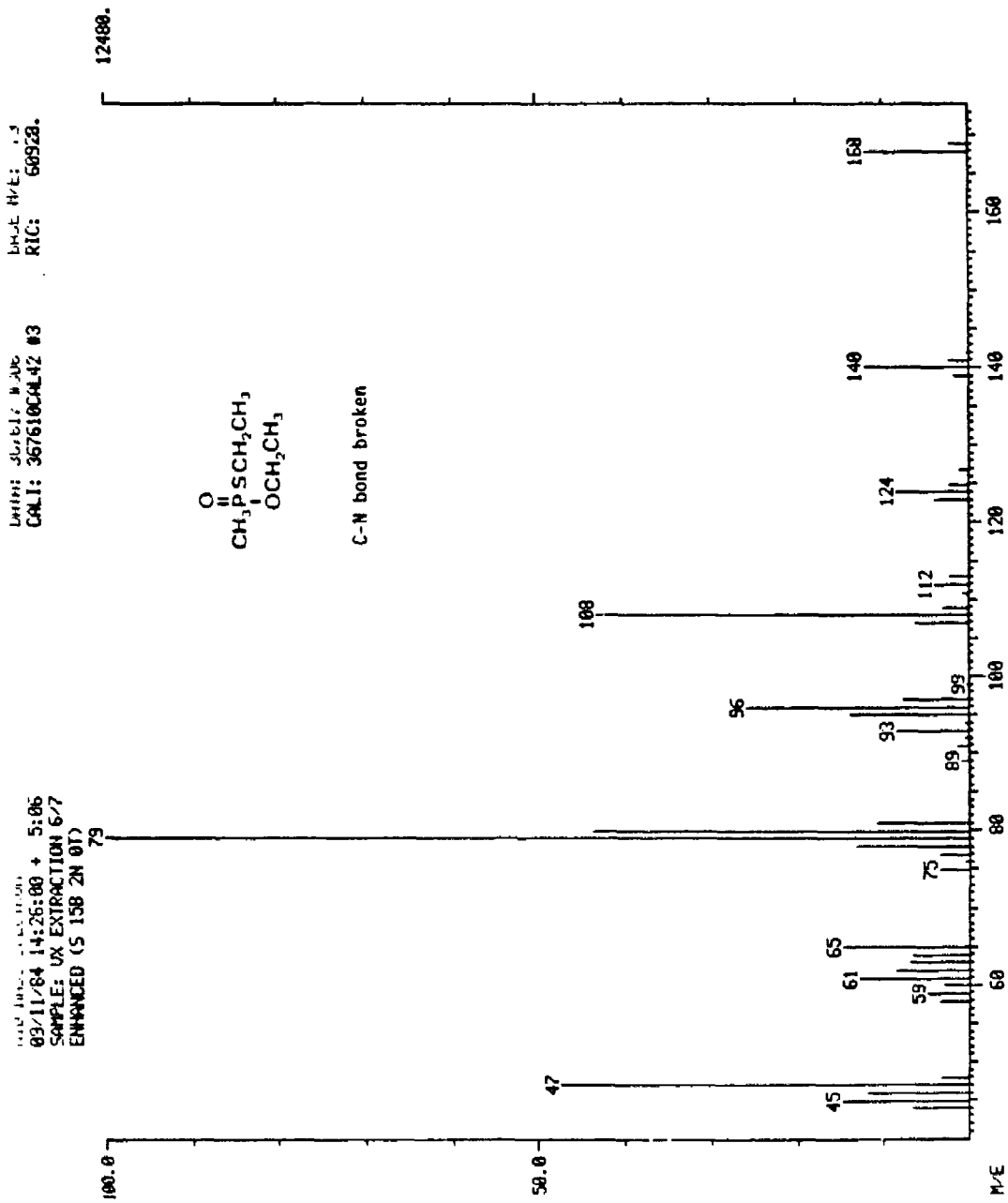


FIGURE C15. MASS SPECTRUM OF EXTRACT FROM H_3/STEAM DECONTAMINATION OF VX (#1)

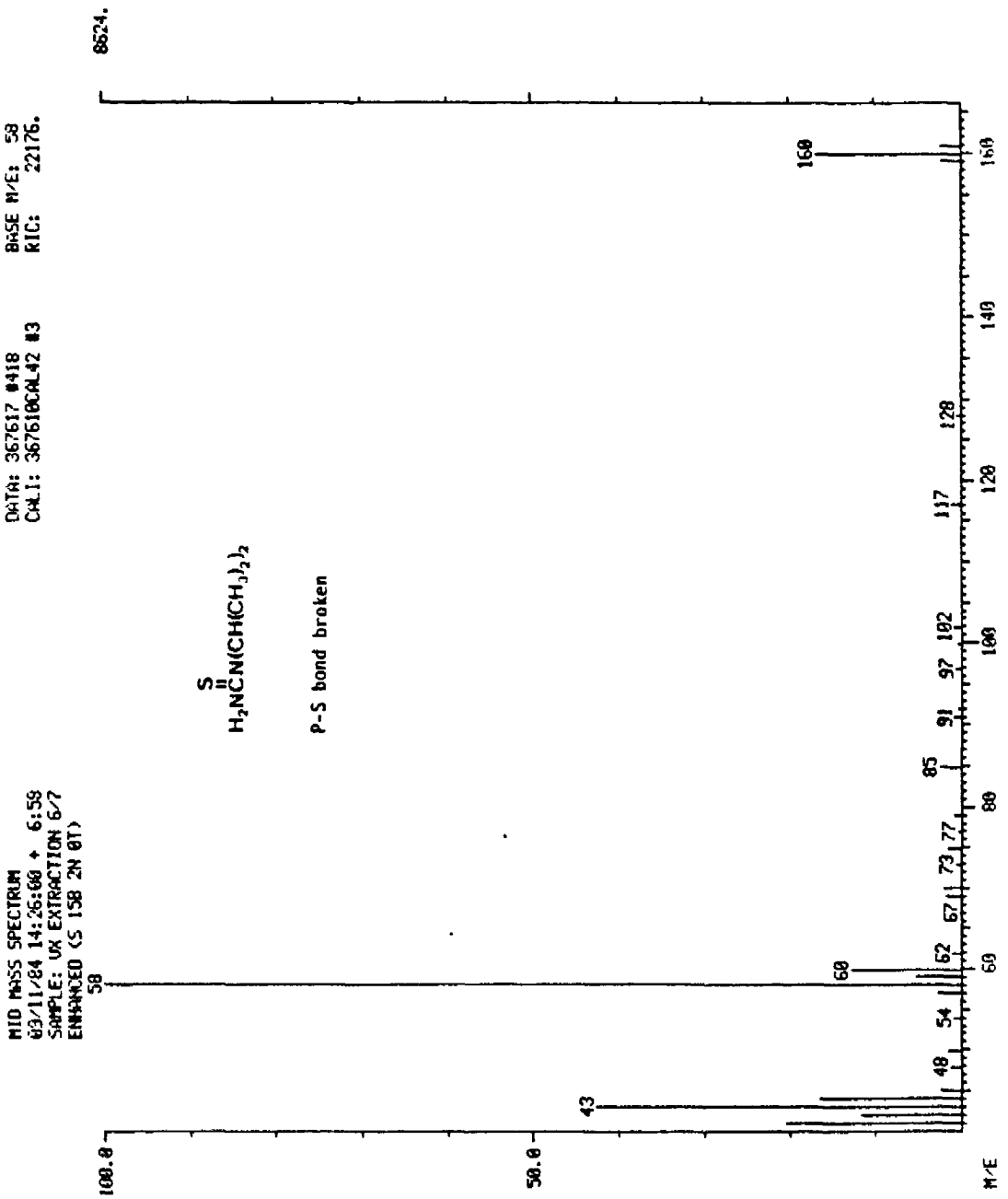


FIGURE C16. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX (#2)

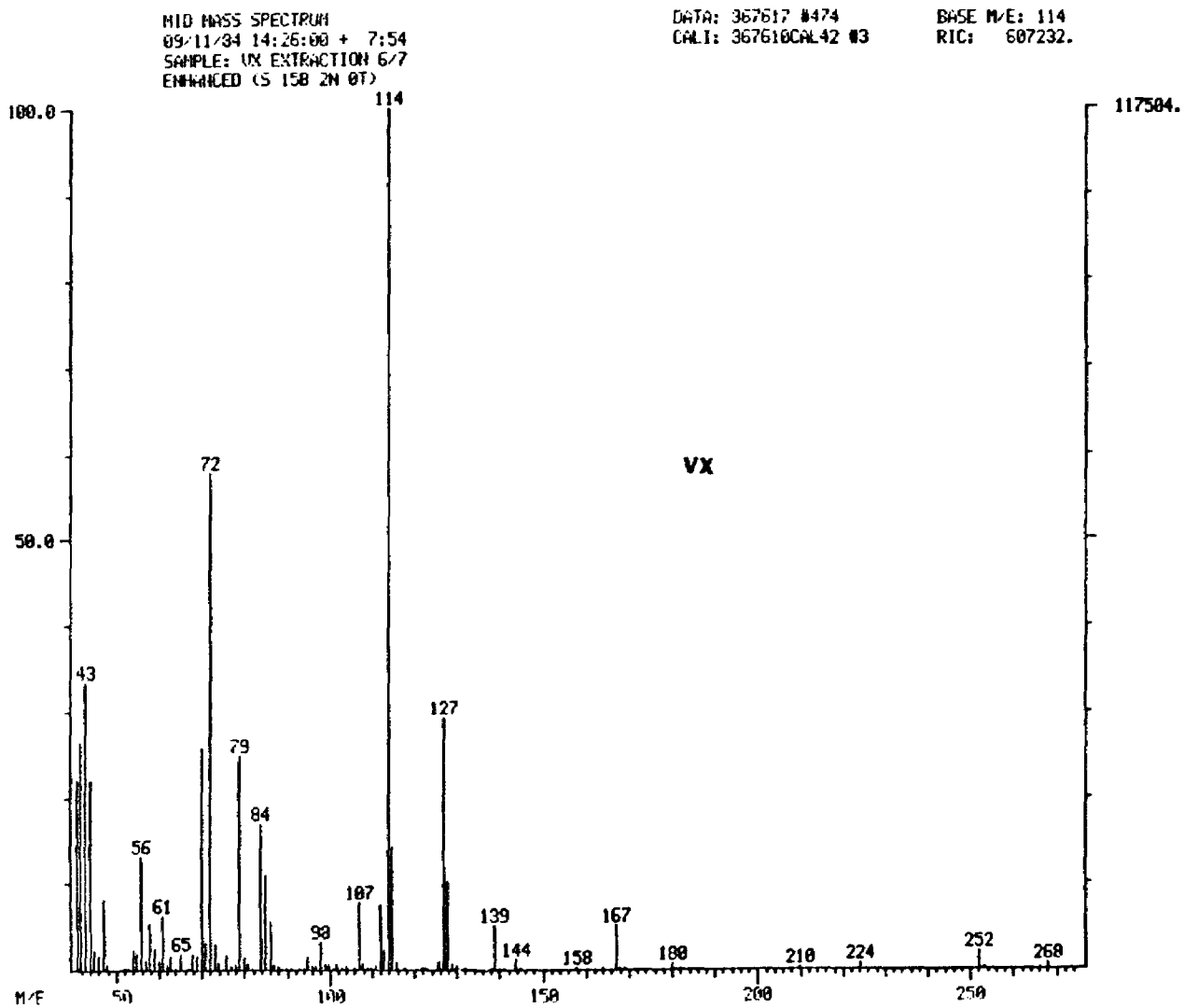


FIGURE C17. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX (#3)

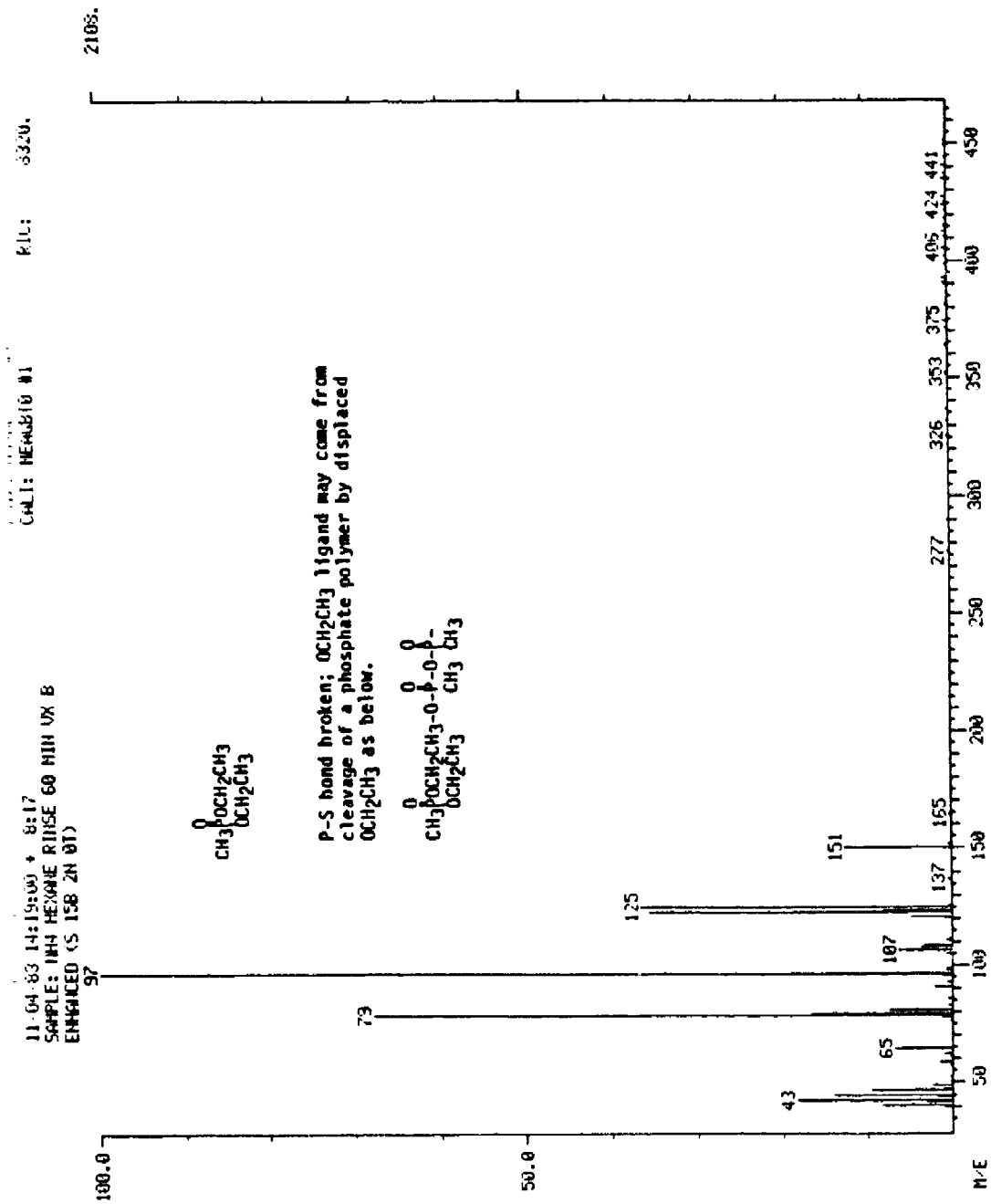


FIGURE C18. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#1)

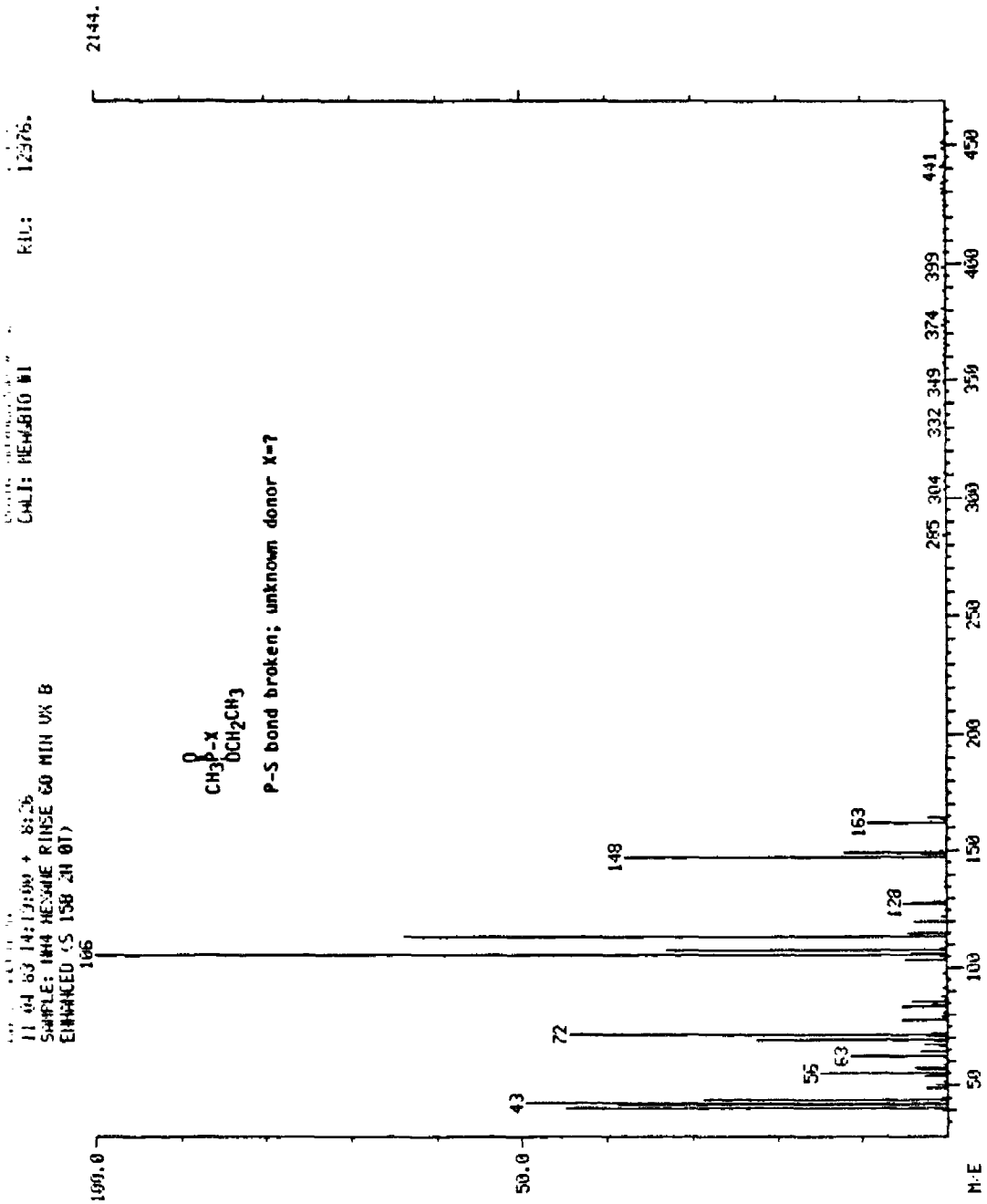


FIGURE C19. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#2)

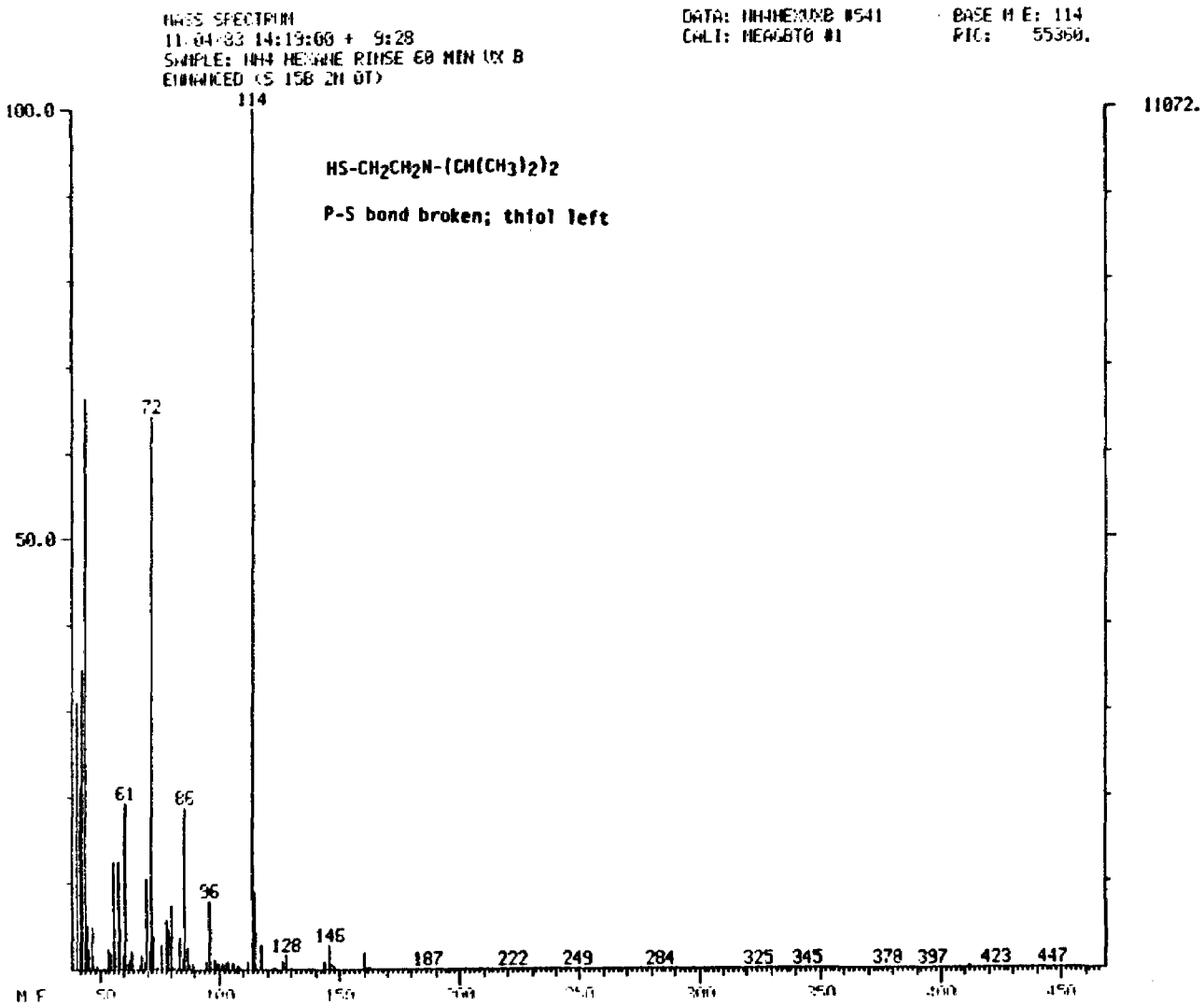


FIGURE C20. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#3)

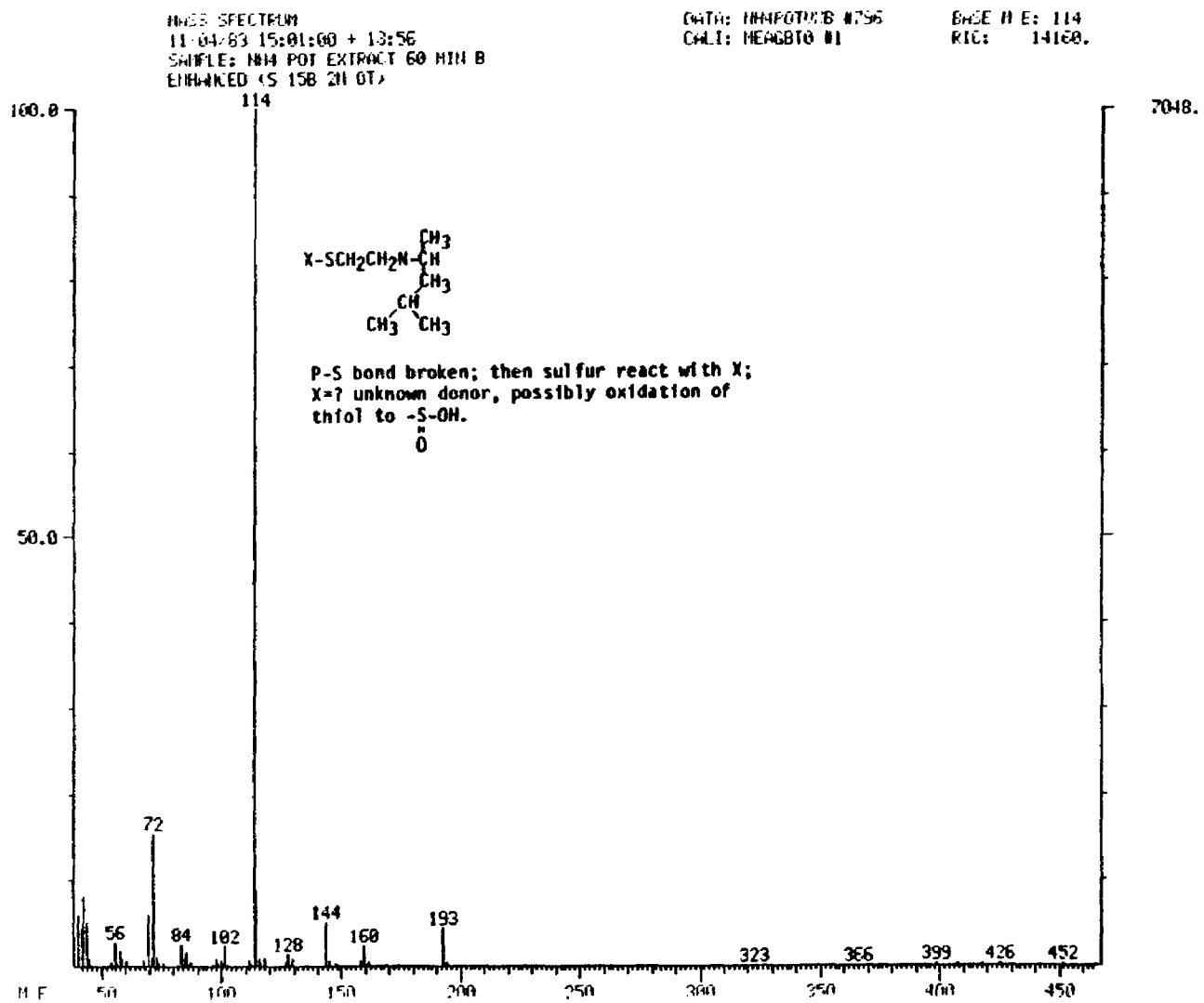


FIGURE C21. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#4)

APPENDIX C

Section 2.0

Assessment of the Treatability of Caustic VX Hydrolysate at the Du Pont Secure Environmental Treatment Facility, Attachment #4,
Carmagen Engineering, Inc.,
November 3, 2004.

Attachment #4

Assessment of the Treatability of Caustic VX Hydrolysate at the DuPont Secure Environmental Treatment Facility

By

Carmagen Engineering, Inc.
in consultation with the
Centers for Disease Control and Prevention

November 3, 2004

SUMMARY

To completely ascertain the capability and effectiveness of the DuPont Secure Environmental Treatment (SET) facility to treat caustic VX hydrolysate (CVXH), the Centers for Disease Control and Prevention (CDC) and Carmagen Engineering, Inc. (Carmagen), recognized that, in addition to reviewing the DuPont treatability test results, the Newport Chemical Agent Disposal Facility (NECDF) destruction process and the analytical methodologies for CVXH clearance also had to be assessed to ensure that the hydrolysate being shipped to the SET facility will be adequately characterized and that VX and EA 2192 levels in the CVXH will meet Army clearance specifications. Please note that in this report, the more technically accurate term *CVXH* generally is used in place of *Newport caustic hydrolysate* or *NCH*. These assessments were considered essential elements to ensure safe SET facility operations. Therefore, the Carmagen Team (Team) focused its review in three areas consisting of (1) process issues at NECDF, (2) analytical methods, and (3) CVXH treatment at DuPont. The review comprised several meetings with people from the Army, Chemical Materials Agency, Parsons, and DuPont at which presentations were made, followed by in-depth discussions. These meetings were followed up by written questions and requests for additional documentation. Documentation received in response to the Team's questions and requests for additional information was substantial.

The major findings from the three areas examined by the Team are shown below. *These findings are valid only for an 8% diisopropylcarbodiimide (DIC)-stabilized VX hydrolysate. The current database is insufficient to allow extrapolation to other VX loadings or stabilizers.*

Process Issues (Chapter 2)

Only laboratory/bench-scale runs have been completed for the process, and scale-up to the integrated full-size facility is based on anticipated processing conditions. Recently, several safety studies were completed that recommended changes in the design and operation of the NECDF. The impact of the responses to these recommendations and possible facility changes on the final process is unknown.

Finding 2.1. The database supports the efficacy of neutralizing DIC-stabilized VX using sodium hydroxide at the 8% VX-loading rate. Scale-up of the process from laboratory/bench scale to pilot scale should be operationally feasible. However, because the NECDF will be a pilot facility, changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

Finding 2.2. VX loading (weight percent) and the specific stabilizer (DIC; dicyclohexyldicarbodiimide [DCC]) employed significantly impact the process, hydrolysate composition, analytical methods validation, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes from 16% to 33% VX-loading batches), the potentially high VX concentration in the resulting organic layer, and the analytical problems identified with 33% VX loading.

Finding 2.3. The impact is unknown of solids formation during hydrolysis on operations (potential for blockage of the in-line static mixer, control valves, and sampling system), VX analytic methods, and off-site hydrolysate treatment. The transition from 8% to 16% VX loading, as well as stabilizer change, is of concern and requires additional detailed studies.

Analytical Methods (Chapter 3)

The purpose of the review and evaluation of the analytical methods was to define the adequacy of the proposed NECDF analytical methods to meet current programmatic requirements for detecting and quantifying VX and EA 2192 in the CVXH.

Finding 3.1. The methods for analyzing VX and EA 2192 in 8% VX-loaded, DIC-stabilized CVXH are adequate to detect and quantify at the established clearance levels for VX and EA 2192 (non-detected with a U.S. Environmental Protection Agency (EPA) method detection limit (MDL) of ≤20 parts per billion [ppb] for VX and ≤1 part per million [ppm] for EA 2192).

Finding 3.2. The use of the EPA's method detection limit (MDL) for clearance levels does not preclude analytical instrument detection of low levels of VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the MDL clearance criteria indicate absence of analytically detectable VX and EA 2192 could be misleading. While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

Finding 3.3. The overall quality assurance (QA) and quality control (QC) plan and procedures for the NECDF laboratory are well designed and documented. However, NECDF laboratory personnel must continue to implement the QA/QC plan by developing day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup.

Caustic VX Hydrolysate Treatment (Chapter 4)

Once transported to the SET facility, CVXH will be further treated to adjust the pH and remove the organic by-products by a series of physicochemical and biologic processes. The DuPont treatability studies were designed and executed to obtain scale-up parameters for engineering design and regulatory compliance, rather than (except for a few specific species) to assess fate, transport, and biodegradability of environmental contaminates. The treatability studies also investigated the capability of the SET facility to treat alternating hydrolysate feeds from Aberdeen (sulfur mustard [HD]) and Newport (VX).

Finding 4.1 The SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer (i.e., pH adjustment, thiolamine destruction, conversion of ethyl methylphosphonic acid to methyl phosphonic acid [MPA]), except for MPA, for which only minimal reduction is demonstrated.

Finding 4.2. The SET facility treatment performance should be unaffected when treatment of hydrolysate feeds from Aberdeen (HD) and Newport (VX) is alternated.

Finding 4.3. The DuPont treatability studies have not yet demonstrated the effective treatment of 16% VX-loaded CVXH, nor of 8% VX-loaded CVXH with DCC or a mixture of DIC and DCC stabilizers.

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1. Introduction

1.1 Background

The Newport Chemical Depot, Newport, Indiana, stockpile comprises the chemical nerve agent O-ethyl S-[2- (diisopropylamino) ethyl] methyl phosphonothiolate (VX) stored in bulk quantities (1269 tons in 1690 containers). VX contains phosphorus double-bonded to an oxygen atom and single-bonded to a carbon atom. VX is stabilized with several percent of either diisopropylcarbodiimide (DIC) or dicyclohexyldicarbodiimide (DCC) to protect against decomposition. Forty-six percent of the stockpile at Newport consists of VX stabilized with DIC (potentially with small amounts of DCC stabilizer as a contaminant), 16% stabilized with DCC, and 38% stabilized with both DIC and DCC. VX is highly toxic and lethal in both liquid and vapor forms. Because munitions containing agent and energetics are not present at Newport, the process requirements for disposing of only ton containers of agent are less demanding than the processing requirements for the more complex stockpiles at most sites.

The Newport Chemical Agent Disposal Facility (NECDF) was designed and is to be operated as a pilot-plant facility because the process has been demonstrated only at a laboratory/bench scale. Production operation will begin only after pilot-scale operations have been completed, the data reviewed and assessed, and approval granted by the State of Indiana and the federal government. Because pilot-plant operations generally uncover unknown elements, the probability is high of process modifications and change—including possible changes in the analytical methods and procedures used to support plant operations and hydrolysate clearance—during this piloting period.

The NECDF was designed to destroy VX using caustic hydrolysis in a hot (194 degrees Fahrenheit [°F]) solution of sodium hydroxide. Initially the plan was to further treat the resulting hydrolysate on-site by Supercritical Water Oxidation (SCWO) and to ship the final SCWO effluent (brine) to a Treatment, Storage, and Disposal Facility (TSDF). Mechanical problems encountered in the SCWO engineering-scale test, conducted in Corpus Christi, Texas, in 2000, led to initiation of studies to directly ship the NECDF hydrolysate to an off-site treatment facility as an alternative to on-site SCWO treatment. The terrorist attacks of September 11, 2001, and continuing questions about the feasibility of implementing SCWO on-site in any reasonable timeframe supported the decision to adopt "Project Speedy Neutralization." This involves shipment of the neutralized product (i.e., caustic hydrolysate) off-site for further treatment.

Detailed testing of the caustic hydrolysis process began with the Alternative Technologies and Approaches program in the 1990s. The "recipe" for NECDF agent destruction using sodium hydroxide was tested on a laboratory scale, and an agent loading of 33% was chosen for the program.

Confirmation of the efficiency of destruction of VX depends on the analytical methods available to monitor for residual VX and EA 2192 levels in the resultant hydrolysate. During the past ten years changes in analytical techniques and instrumentation, coupled

with increased personnel experience with these analyses, have lowered the detectable concentration of VX to the low parts per billion (ppb) levels and the detectable concentration of EA 2192 to the low tenths of parts per million (ppm) levels for 8% VX loading hydrolysate. However, the complexity and variability of the 33% VX loading hydrolysate continued to complicate the VX analysis.

By October 2003, the Project Manager for Alternative Technologies and Approaches had begun to investigate the use of reduced VX loading to preserve resources and obviate the need to resolve differences in data and data interpretation for the 33% VX-loading hydrolysate. The program plans to begin operations at 8% VX loading of DIC-stabilized agent and then, through a carefully monitored ramping-up process, move to 16% VX-loading, DIC-stabilized agent.

1.2 Nature of the Caustic VX Hydrolysate

The hydrolysate that will result from the caustic hydrolysis of VX at the NECDF comprises an aqueous phase and an organic phase. The organic phase exists both as an emulsion with droplets distributed throughout the continuous aqueous phase and as a visible organic layer that floats on top of the continuous aqueous phase. The extent to which a separate organic phase floats on the lower aqueous layer depends on the VX loading. As the VX loading increases, the quantity of organic phase available to form an organic layer (above that which forms a stable [or metastable] emulsion) increases.

At 33% agent loading (weight percent), the organic layer was significant (3%–5% by volume). The VX concentration in this organic layer was approximately 20 times the concentration in the bulk hydrolysate (>20 ppb), although disagreement exists within the program about the validity of the measurements (Wojciechowski, 2003). For 16% agent loading, the organic layer was 2–3 volume percent; for 8% agent loading, the separate "organic layer" was only a sheen at the surface of the hydrolysate. The "organic layer" has not been analyzed at 8% and 16% agent loadings; only mixed (homogenized) samples were analyzed. Obtaining samples of this organic layer for 8% agent loading poses significant technical difficulties. Centrifugation of a 550-milliliter (mL) sample of 8% CVXH showed that the maximum organic layer that could be "separated" was 0.45%–0.5%. These differences demonstrate the significant impact of agent loading on hydrolysate characteristics.

1.3 Clearance

Since its inception, a key tenet of the Army Chemical Demilitarization program has been safety of the workers and public. Department of the Army (DA) Pamphlet (PAM) 385-61, entitled "Toxic Chemical Agent Safety Standards," defines the approach for verifying the thoroughness of the neutralization process as using laboratory analyses to ensure that the chemical agent is ≤20 ppb. This concentration is measurable and is a quantifiable upper limit concentration in drinking water (20 ppb criterion is for soldiers). However, the procedure and methodology to verify the 20 ppb criterion in CVXH have been a

challenge (see Section 3). As stated in the Low Level VX (LLVX) panel report (Science Applications International Corporation [SAIC], 2003):

> The panel is not aware of any document that clearly states the exact criteria for offsite shipment of VX hydrolysate from NECDF or any document that codifies the Army's commitment to the public for offsite shipment.

The report, *Generation and Clearance of Hydrolysate for Treatability Studies in Support of Newport Operations*, states:

> To clear the hydrolysate, the analytical results must be non-detect for VX with a method detection limit (MDL) of less than or equal to 20 parts per billion (ppb). Non-detect is defined as the absence of a signal in the VX retention time window for ion 128, or a signal with a signal-to-noise (S/N) ratio of less than or equal to 3, or a concentration below the calculated MDL.

These criteria are incompatible in that an analytical response for VX could be classified as "analytically detected" by implementation of the "analyte retention time/signal-to-noise (S/N) ratio equal to or greater than 3" detection criteria, but reported as "non-detect" by the "less than the established MDL" criterion (see Section 3).

.

1.4 Analytical Methods

Significant resources were expended for almost a decade to develop an analytical method that could reliably and accurately measure VX concentration in CVXH at lower and lower levels for a 33% VX agent loading without success. The newer analytical methods demonstrated the presence of detectable levels of VX in 33% DIC-stabilized CVXH and the inability to demonstrate an MDL of ≤20 ppb. This unexpected result led to an aggressive investigation of the causes and possible solutions for addressing the issue to bring the plant into operation.

An independent assessment panel was convened in October 2003 to evaluate the significance of the observation of "persistent" LLVX in caustic hydrolysate at the 33% agent loading level and to determine whether data were sufficient to confirm whether VX forms in CVXH (SAIC, 2003). Two conclusions of the panel were:

> There are significant uncertainties in the Solid Phase Extraction (SPE)/gas chromatography-ion trap mass spectrometry (GC-ITMS) method that make it difficult or impossible to quantify LLVX.
>
> It is not possible to determine the origin of the "persistent" LLVX in VX hydrolysate from the currently available data. The panel could not rule out formation of VX in VX hydrolysate or the hypothesis that has been advanced that there is a quasi steady state concentration of VX in VX hydrolysate due to a competition between agent destruction and formation. The current data from the analytical method did not enable the panel to determine if detectable VX was

originating from VX hydrolysate (that is, either residual untreated VX or formation within the VX hydrolysate matrix) or was formed during the analytical procedure.

Consequently, efforts during the past year have been devoted to evaluating the effect of reduced VX loading on

- VX caustic hydrolysis destruction,
- VX reformation during long-term storage, and
- VX formation after a reduction in pH accompanied by a concomitant formation of an organic layer.

This evaluation has paralleled the development, evaluation, and validation of analytical methodologies for measuring VX and EA 2192 in the 8% DIC-stabilized CVXH. At the time of this writing, methods for analyzing VX and EA 2192 in 8% DIC-stabilized CVXH and VX in 16% DIC-stabilized CVXH had been established in the NECDF laboratory, and the performance of these methods had been validated through various precision and accuracy studies. Implementation and validation of methods for ethyl methylphosphonic acid (EMPA), methyl phosphonic acid (MPA), and thiolamine in 8% DIC-stabilized hydrolysate are expected to be completed shortly. Similar work on other methods required for 16% DIC-stabilized hydrolysate and 8% DCC-stabilized hydrolysate were scheduled for completion later in 2004. Validated methods for anticipated processing conditions are essential to ensure that hydrolysate shipped off-site to a TSDF meets Army criteria.

1.5 Carmagen Engineering, Inc.

The Centers for Disease Control and Prevention (CDC) engaged Carmagen Engineering, Inc. (Carmagen) to assemble a group of knowledgeable experts (Team) to help evaluate the DuPont Technical Assessment on U.S. Army Newport (Indiana) Project (March 2004). The Team consisted of a former chairman of the National Research Council Stockpile Committee, a retired assistant director for the CDC/NCEH Division of Laboratory Sciences, a retired Program Manager for Chemical Demilitarization, a professor at Stevens Institute of Technology, a retired regional laboratory director for EPA, and a former environmental health and safety manager/process design manager for ARCO Chemical. Specifically, Carmagen was asked to evaluate the "Treatability of Newport (Indiana) Caustic Hydrolysate" portion of the DuPont report.

To ascertain the capability and effectiveness of the DuPont Secure Environmental Treatment (SET) facility at Chambers Works (Deepwater, New Jersey) to treat CVXH, the Team recognized that an assessment of the NECDF destruction process and an examination of the analytical methodologies to be used for CVXH clearance were required to ensure that the hydrolysate being shipped to the SET facility will be adequately characterized and that VX and EA 2192 levels in the CVXH will meet Army clearance specifications. These assessments were considered essential elements to ensure safe SET facility operations. Therefore the Carmagen Team focused on three areas:

- Process Issues (NECDF),
- Analytical Methods, and
- Caustic VX Hydrolysate Treatment (DuPont).

The review comprised several meetings with people from the Army, Chemical Materials Agency, Parsons, and DuPont at which presentations were made and discussed in depth. These meetings were followed up by written questions and requests for additional documentation. Documentation received in response to the Team's questions and requests for additional information was substantial.

1.6 Report Outline

The report contains five chapters.

- Introduction—Discusses the historical evolution of the NECDF project and the charge to and approach taken by the Carmagen Team.
- Process Issues—Discusses the impact of VX loading on the process, i.e., nature and extent of the two-phase CVXH, VX partitioning to the organic layer, clearance quality assurance (QA) and quality control (QC), scale-up, and storage.
- Analytical Methods—Reviews and evaluates the use and data quality objectives of VX and EA 2192 measurements, sampling procedures, validation of methods, and QC of the analytical processes.
- Caustic VX Hydrolysate Treatment—Describes pH adjustment, oxidative pretreatment, PACT® biotreatment, and VX and EA 2192 destruction.
- Major Findings—Presents major findings.

2. Process Issues

2.1 Introduction

Although the primary purpose of this report is to examine issues associated with the treatability of the hydrolysate produced by the Newport facility, as noted in the Introduction, a discussion of processing issues is important. The composition of hydrolysate sent for treatment depends on the nature of the VX being hydrolyzed (i.e., agent loading, stabilizer), neutralization process, process operating conditions, process effectiveness, and consistent process operation. Confirmation of the composition of the hydrolysate (efficacy of treatment) is related to the accuracy of the analytical methodologies (see Chapter 3) and whether the sample(s) used for the analysis represent the batch being processed. The satisfactory treatment of each batch is determined on the basis of analysis of the hydrolysate samples.

Only laboratory/bench-scale runs have been completed for the process, and scale-up to the integrated full-size facility is based on the anticipated processing conditions. At startup, NECDF intends to operate the reactor at a VX loading of 8%, rather than the 33%

originally planned. This has process and operational consequences that are discussed later in this chapter. The Army proposes that VX loading will be increased to 16% as experience is gained with the process and equipment, and when analytical methodologies and successful off-site treatment capability demonstrated at the higher loading are validated. The change from the proposed 33% VX loading to 8% VX loading will increase substantially the total quantity of hydrolysate to be treated and the length of time the Newport facility will operate.

2.2 Process Description

The process for VX neutralization at Newport uses batch processing (Figure 2-1). Each batch consists of the following sequential steps:

1. The reactor is charged with caustic.
2. The reactor is heated to approximately 194ºF.
3. The reactor circulation loop is activated, and the agitator in the reactor is started.
4. Agent is added to the reactor using a feed line in the recirculation piping. The amount of agent added is determined by the VX loading target for a given batch. Two phases are present in the reaction mixture—an aqueous phase and an organic phase. The relative volumes of the two phases are determined by the VX loading.
5. VX and caustic are mixed by the agitator in the reactor and by the static mixer in the recirculation piping. The static mixer is designed to achieve an organic droplet size of approximately 10–30 microns (µm).
6. After the reaction has been circulated at temperature (194ºF) for a period of time sufficient to complete the hydrolysis reaction, the mixture is cooled and a sample taken from the recirculation line. If the sample meets the criteria for VX and EA 2192 destruction, the resulting mixture (the hydrolysate) is pumped from the reactor to storage. If the VX and EA 2192 destruction criteria are not met, then the mixture is reheated, and processing continues. This is repeated until the batch is successfully processed.
7. After the batch is processed, it will be transferred to intermediate storage, and then shipped off-site for final treatment.

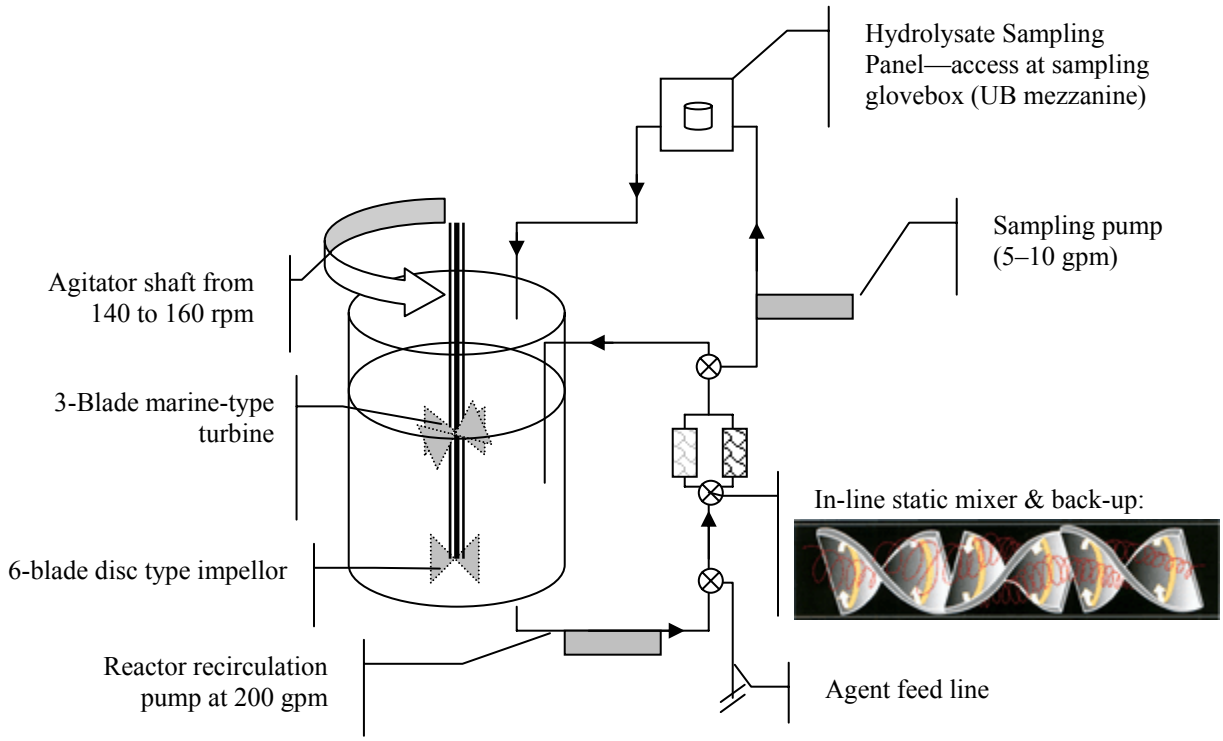

Figure 2-1. Hydrolysate reactor

Texas A&M performed a safety study of the Newport facility using fault-tree techniques. One scenario examined was "Offsite Transfer of Hydrolysate Containing Excess VX Concentration."

The Executive Summary of this report stated:

> *Fault tree analysis techniques were applied to the VX project speedy neutralization (PSN) process and related process support systems in order to estimate the frequency that the cited hazard scenario can be expected to occur.*
>
> *The study results indicate that the best estimate for an annual frequency of this undesired event is 5 x 10^{-5}.*

The annual frequency is estimated at 1 in 20,000 chance for CVXH being outside of specification for VX (>20 ppb). The existing design does not detect contamination of acceptable hydrolysate after the batch sampling procedures have been completed. The amount of potential contamination is minor and not thought to present a public health risk. This issue could be corrected by good engineering practices such as physical isolation using piping blinds, spool pieces or a double block and bleed valve configuration or by development of a sampling method at the storage tank. CDC has alerted Army representatives regarding this design issue as part of the normal oversight activity. Any potential design changes to the facility and schedule impacts need to be balanced by the national security risk associated with extended storage of the VX.

At the time of this report, the recommendations in Safety Study Reports by Texas A&M and other safety studies relating to the design and operation of the Newport facility were still being evaluated for implementation.

2.3 Process Chemistry

The process chemistry involved with VX neutralization is complex when an extremely high destruction of VX is required. At the time this report was written, investigations into the process chemistry are still under way, and not all of the details of the main and side reactions involved (e.g. solids formation) were fully understood. The major variables that affect the chemistry include the agent loading (i.e., the relative amount of agent per unit volume of caustic in the reactor at the start of the batch) and the type of stabilizer present in the agent being processed. (The stabilizers used to minimize the decomposition of the VX during storage were DIC or DCC or DIC + DCC).

The main reaction by which VX is neutralized by caustic is well understood and is pseudo-first order with respect to VX concentration. However, the presence of two phases (organic and aqueous), the presence of VX in the organic phase, the creation of EA 2192, and the presence of stabilizers complicate the physical and chemical process. If all other system parameters and the composition of initial caustic solution remain constant, then the size, composition, and partitioning of the reaction products between the aqueous and organic layers depend on the VX loading. Mass transfer limitations become more pronounced as the droplet size increases and the organic layer is formed. This will affect the rate, as well as the pathways of the reactions, and may produce different final products. In addition, some of the ton containers are now known to contain gelled/solid material. How much of this material will be removed with the VX and how much will remain in the ton container is uncertain. The effect of any gelled/solid material on the chemistry or operation of the neutralization reactor mixing process and sampling system also is unknown.

The purpose of the agitator and the static mixer are to mix the phases and to transform the organic phase into tiny droplets. The smaller the droplet size, the faster the diffusion processes in leaching and neutralizing the VX in the organic droplets. Therefore, VX is rapidly destroyed at the start of the batch operation; then a slower, diffusion-limited process follows as the VX in the organic phase droplets is neutralized. Moreover, the size

and chemical compositions of the dispersed droplets and the organic layer will differ for the various VX loadings and stabilizer types.

In a response to questions from CDC, the Army and its contractor (Parsons) summarized these issues:

> *Because of the highly reactive nature of hot caustic, less than 0.1% of the VX added to the reactor during the FILL period accumulates in the reactor with virtually all of this residual VX removed during the first minute of REACT. Additional REACT time is needed to destroy residual VX that partitions into the organic phase during FILL, and to ensure that EA2192 is non-detect. ……. It is expected that the NECDF's full-scale pilot reactor will provide the necessary mixing and droplet size to produce non-detectable levels of both VX and EA2192. This conclusion is based on laboratory-scale results and full-scale pilot plant calculation results provided herein. The actual reaction time required to obtain non-detectable levels of both VX and EA2192 will be determined during Controlled Start-up testing of the full-scale NECDF pilot plant. If the reaction time required to obtain non-detectable levels of both VX and EA2192 determined during Controlled Start-up differs from that which was predicted during laboratory-scale testing, the types and configuration of the elements within the static mixer and the volumetric flow rate through the recirculation line can be changed, as needed.*

This response accurately describes the process, neglecting the effect of any gelled/solid materials in the feed to the reactor or generated within the reactor.

As previously noted, the reaction originally was designed to have used a 33% agent loading in each batch. However, studies demonstrated that, at 33% agent loading, a significant organic phase (3%–5% by volume) formed during the reaction, and this organic layer separated from the aqueous phase during storage and floated on top. Remaining (un-neutralized) VX partitioned into this organic phase, and the VX concentration in this organic phase was approximately 20 times the VX concentration in the bulk hydrolysate (nominally <20 ppb). Therefore, operation with 33% agent loading could have resulted in a "significant" volume of organic phase with a "high" VX concentration in storage tanks and during transportation. This was considered unacceptable, and modifications to the process were proposed and implemented.

Additional investigation showed that operation at 16% agent loading reduced the organic layer to approximately 2–3 volume percent. At 8% agent loading, the organic layer was only a sheen on the surface of the hydrolysate (approximately 0.5% by volume determined by centrifuging the sample). The VX concentrations in the organic phase for 8% and 16% agent loadings had not been determined at the time this report was written.

Significant changes in organic liquid loading occur between 8% VX loading and 16% VX loading (approximately a 1:5 volume ratio at a minimum) and between the 16% and 33% VX loading (approximately 1:1.5 ratio). The physical and/or chemical processes involved and the reason(s) for such a significant increase in organic loading between 8% and 16% VX loading have been the subject of some investigation, but no conclusion has been reached.

Laboratory studies have demonstrated that the reaction times required to complete neutralization vary with agent loading and stabilizer. With DIC-stabilized agent (approximately 46% of the Newport stockpile), the reaction times are 2.5–4 hours for 8% loading and 4–6 hours for 16% loading. With DCC-stabilized agent, the reaction time is 10–14 hours for 8% loading. The reason(s) for the apparent additional processing time required by DCC-stabilized agent is (are) not fully understood. The amount of stabilizer in each ton container also can vary significantly. Therefore, what is valid for 8% VX loading stabilized with DIC may not be valid for 16% VX loading case and other stabilizers. The data do not warrant generalizations that apply to all VX loadings and stabilizers.

In addition, laboratory studies have determined that solids are generated during the neutralization process. These solids have been variously described as a sticky gel and as a more coherent material. The amount of solids, their composition, and the amount of VX, (if any) these solids contain have not been determined.

The presence of solids in the hydrolysate within the reactor may be problematic in the full-scale unit and impact plant operations. Concern has been expressed that the solids may precipitate onto the surfaces of the agitator in the reactor and result in an imbalance that could cause mechanical failure of this item. A more likely source of concern may be the potential blockage of the in-line static mixer or deterioration of the performance of control valves, particularly the three-port valve that controls the introduction of chemical agent to the reactor and the transfer of the hydrolysate to the storage tanks. The in-line mixer is constructed deliberately with small flow paths (10–30 μm) to break up the organic phase into small droplets. Any solids formation could result in blockage, with the potential for reduced production rates and the need to remove the in-line mixer for cleaning. Solids also can also be deposited on the surfaces of the internal parts of the three-port valve, impacting valve closure and enabling leakage of agent, thereby contaminating previously sampled and acceptable hydrolysate batches as they are transferred from the reactor to the storage tanks. Another possibility is that modification of the process equipment to incorporate an upstream filter may be required. Furthermore, the solids may negatively impact the sampling system and the analytic measurements and treatment of the hydrolysate.

Appendix K of the documentation, provided in response to CDC Question 1, discusses solids formation. The “Conclusions” section of this document states

a. Formation of solids in 8 weight % hydrolysate have (SIC) the potential to impact process throughput due to reactor hardware

plugging in the pumps or static mixer. Preventative maintenance needs to be scheduled as experience determines.

b. Difficulties have been encountered clearing the hydrolysate with gelatinous material. When hydrolysate fails to clear, more processing is required. Detailed analysis of the gelatinous material may lead to procedures that could expedite clearance.

c. Further testing is underway to characterize the observed solids and identify whether stabilizer type (DCC vs. DIC) or VX loading causes changes in solid volume or content.

d. At [the Chemical Agent Munitions Disposal System (CAMDS)], twenty five batches of DCC hydrolysate and one batch containing DIC hydrolysate were processed without process failure due to these solids. (Note—Whether a static mixer with very small passages [such as at Newport] was installed at CAMDS) is not known)

In the subsystem hazard analysis of the process, the following finding (Failure Mode and Effects Analysis [FMEA] Item 01-04-134) was noted:

> *Over-or Under-Reaction Creates Gelatinous Matrix in Neutralization Reactor Containing VX*
>
> *Several mis-operations and reaction inconsistencies can result in the creation of a gelatinous matrix in the neutralization reactor (1- and 2-L401). It might not be possible to completely prevent this occurrence. A study is being performed to identify ways to dissolve or solubilize any gelatinous matrix that might form. Additional information or data from the study could determine methods to prevent the polymer formation and ways to mitigate such a formation if it occurs. This evaluation addresses FMEA Item 01-04-134.*

Whether this finding in the safety studies documenting issues associated with solid/gel formation in the reaction system has been addressed at the time this report was completed is not known.

Except for solids formation and its possible effects, the scale-up of the reactor from laboratory to full-scale operation should succeed. Adequate heating and cooling have been provided for the reactor system, the equipment is simple in design and the batch will be run until the analytic methods demonstrate that VX and EA 2192 have been adequately destroyed. However, the effect of gelled/solid material in the ton containers passed into the reactor does not appear to have been examined in detail. Therefore, no conclusion can be reached about the effects of such material on the neutralization reaction, the destruction efficiency, and the operation of the reaction system.

2.4 Findings

1. Scale-up of the process for 8% VX loading from laboratory-scale data should be operationally feasible. The database supports the efficacy of neutralizing 8% VX (stabilized with DIC) using sodium hydroxide. However, the Newport facility will be a pilot operation when it starts operation, and changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

2. VX loading and the specific stabilizer employed significantly impacts the process, hydrolysate composition, analytical methodology, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes between 16% and 33% VX loading batches) and the analytical problems identified with 33% VX loading.

3. The effects of solids formed during the hydrolysis reaction in the process on the hydrolysate and on the efficacy of treatment at a TSDF are unknown. The solids may contain VX. The impact of solids formation on the operation of the reaction system and, in particular, the potential for blockage of the in-line static mixer and other components (including the sampling system) is unknown. In addition, the presence of solids may impact the VX analytics, as well as the off-site hydrolysate treatment process.

4. At the time this report was written, all the findings from safety studies had not been fully addressed. In particular, findings relating to possible solids formation in the reactor and the required process modifications to provide additional assurance that no off-specification CVXH is shipped from the Newport facility may affect the CVXH composition shipped off-site.

3. Analytical Methods

3.1 Introduction

The purpose of this review and evaluation is to define the adequacy of the proposed methods for the analysis of VX and EA 2192 in the CVXH to meet the programmatic requirements of the NECDF. The scope of this review is limited to laboratory analyses of hydrolysate from the neutralization of DIC-stabilized VX at the 8% VX-loading level. Adequate analytical data were not available to evaluate analyses of hydrolysate related to other VX-loading levels or stabilizers.

3.2 Sampling Representativeness

We recognize that the validity of the clearance process depends on the sample taken and delivered to the laboratory for analysis; the sample must truly represent the total hydrolysate process batch. To evaluate the sample procurement process, all available documents describing the design and operation of the equipment and the sampling procedures were reviewed. We also had detailed discussions with NECDF personnel.

NECDF personnel believe the sampling will be highly representative on the basis of the mixing capability of the reactor, the design and operation of the sampling equipment, and the detailed protocols that have been established. On the basis of our understanding of reviewed information, we agree—as long as solids formation does not block the sampling points. The planned sampling program should provide representative samples for CVXH batches to the laboratory for analyses.

QA/QC procedures are in place to ensure and document adequate training of personnel, performance of sampling equipment, availability and quality of supplies, proper and complete recordkeeping, establishment and maintenance of chain of custody, and the safety of plant and laboratory personnel.

Maintaining representativeness of the analytical sample during transfer of the 5-mL analytical portion from the plant batch sample will be challenging because of the potential for separation of an organic layer. The laboratory method for VX analysis in CVXH calls for the analyst to "verify hydrolysate is as homogeneous as possible" during the subsampling process. This process can be highly subject to analyst technique error and will require careful QC.

3.3 Analysis of VX in Caustic VX Hydrolysate

3.3.1 Data Evaluation/Interpretation Criteria

Instrument or qualitative detection as defined in Laboratory Field Instruction (LAFI)-A-30-053:

Consider VX present in the sample if the following criteria are met:

1. Retention time of analyte peak within +/- 0.1 minute of average standard VX retention time.
2. The m/z 128 ion, the m/z 139 ion, and the m/z 167 ion maximize within 0.05 minute of each other.
3. The m/z 139 and 167 ions may not be present at concentrations <1 microgram per milliliter (µg/mL) in the sample.
4. The m/z 128 ion response must be at least three times the background noise level, i.e., S/N ratio 3 or greater.

Quantitative criterion as defined by the Army is as follows:

MDL, calculated according to U.S. Environmental Protection Agency (EPA) procedure published in the Code of Federal Regulations (40 CFR, Part 136, Appendix B) ≤20 ppb.

3.3.2 Method Description and Documentation

LAFI-A-30-053 provides a comprehensive, step-by-step description of the method for analyzing VX in CVXH. The method is based on multiple hexane extractions of the hydrolysate, followed with solid-phase extraction techniques for initial fractionation of the extract, then final separation and detection of the VX using gas chromatography (GC) coupled with ion-trap (IT) mass-spectrometry/mass-spectrometry (MS/MS) techniques. The use of high-resolution capillary GC coupled with the dual-phased MS/MS IT techniques gives this method extremely high selectivity and sensitivity for VX in the hydrolysate. Stated in layman's terms, the method can detect and quantify VX in the highly complex CVXH mixture at ≤20 ppb with a high level of confidence against both false positives and false negatives.

The laboratory QC procedures defined in LAFI-A-30-053 and in Section 11.2 of the NECDF Laboratory Quality Control Plan, Revision 2, are consistent with procedures and requirements published in EPA SW-846. Implementation of these procedures should provide the QC data needed to define the overall validity of the analytical results.

Evaluation of MDL data for 8%VX-loaded, DIC-stabilized hydrolysate shows that, with this type of hydrolysate, the NECDF laboratory can consistently generate MDL values below the 20-ppb criterion. In a study to characterize batch-to-batch variation, the NECDF laboratory generated three MDL values for each of two batches of hydrolysate. The six MDL values ranged from 6 to 17 ppb, with a mean of 11 ppb, with no appreciable differences between the two hydrolysates.

In summary, the current method for analyzing VX in CVXH is adequate to detect and quantify VX well below the established clearance level of 20 ppb. The GC/IT/MS/MS technique provide a method with extremely high analyte selectivity and sensitivity. The method consistently shows an instrument detection limit below the 5–10 ppb range.

3.4 Analysis of EA 2192 in Caustic VX Hydrolysate

3.4.1 Data Evaluation/Interpretation Criteria

Instrument or qualitative detection as defined in LAFI-A-30-030:

Consider EA 2192 present in the sample if the following criteria are met:

1. Retention time of analyte peak is within +/- 1.0 minute of the average retention time of the standard EA 2192 during instrument calibration.
2. The m/z 162 ion is present with a 128/162 ion ratio of 0.3.
3. At EA 2192 concentrations <1 mg/mL the 128/162 ion ratio may not equal 0.3, but m/z 162 ion must be present.
4. The m/z 128 ion response must have a minimum S/N ratio of 3.

Quantitative criterion as defined by the Army:

MDL, calculated according to EPA procedure published in 40 CRF, Part 136, Appendix B, ≤1 ppm.

3.4.2 Method Description and Documentation

LAFI-A-30-030 provides a comprehensive, step-by-step description of the method for analyzing EA 2192 in CVXH. The method consists of a simple 1:25 dilution of the CVXH sample, followed by analyte separation using liquid chromatography (LC) techniques, with final detection and quantification using dual-phase IT/MS/MS. The use of LC/IT/MS/MS techniques results in a highly sensitive, extremely selective analysis of EA 2192 in the CVXH.

Laboratory QA/QC procedures defined in LAFI-A-30-030 and the NECDF Laboratory Quality Control Plan are consistent with those published in EPA SW-846. Analytical data characterizing the performance of this method are limited. MDL data show values of 0.23 ppm and 0.09 ppm; both well below the clearance level of 1 ppm. Precision and accuracy data show overall very good precision of the method with analyte recoveries ranging from 82% to 95%.

In summary, the current method for analyzing EA 2192 in CVXH is adequate to detect and quantify EA 2192 in laboratory-generated hydrolysate well below the established clearance level of 1 ppm. Data also indicate that the qualitative (analytical presence) instrument detection limit of the method is consistently <0.1 ppm.

3.5 Use of Analytical Data for Clearance

The Army has stated its intended use of VX and EA 2192 analytical data in the clearance of CVXH for off-site shipment, as follows:

> Since its inception, a key tenet of the Army Chemical Militarization program has been the safety of the workers and the public. Department of the Army (DA) Pamphlet (PAM) 385-61, entitled "Toxic Chemical Agent Safety Standards," defines the approach for verifying the thoroughness of the neutralization process as using laboratory analysis to assure that the chemical agent is at a level less than or equal to 20 ppb. This level has been deemed protective of soldiers and Department of Defense personnel. The Project Manager for Alternative Technologies and Approaches (PMATA) elected to use the standard EPA method detection limit (MDL) as the means for determining whether the detection limit specified in the DA PAM has been met. Thus, the requirement for successful neutralization of VX is that the hydrolysate must be non-detect for VX with an MDL of 20 ppb or less.

The Army also has stated that EA 2192 must be "non-detect with an MDL of 1 ppm or less."

As discussed in Sections 3.3 and 3.4, we believe that NECDF methods LAFI-A-30-053 for VX in CVXH and LAFI-A-30-030 for EA 2192 in CVXH can provide valid qualitative and quantitative data for detecting and quantifying VX and EA 2192, respectively, in the concentration ranges needed for programmatic clearance of the hydrolysate material for off-site shipment. NECDF's intended practice for measuring and reporting "non-detects" is potentially misleading. Specifically, we are concerned with the Army's plan to classify and report analytical results above the instrument detection level, but below the established MDL, as "non-detects." While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

The Army's clearance criteria of "non-detect with an MDL less than an established concentration level" combines two related, but different, analytical chemistry concepts. First, "instrument or analytical detection" is a qualitative-based "yes or no" criterion. Second, MDL is a statistically calculated, quantitative criterion.

The first criterion, "detection," addresses two questions: (a) Was an instrument response observed at the expected retention time of the analyte? and (b) If so, was the level of that response greater than three times the background noise (S/N ratio $\geq$3)? If the answers to both of these questions are "yes," then according to instructions in LAFI-A-30-053 and LAFI-A-30-030, the analyte (either VX or EA 2192) is considered "present" or "detected." If the answer to either question is "no," then the result of the analysis is a "non-detect."

The second criterion, MDL, addresses the level of confidence in the quantitative value calculated from the observed instrument response using an established calibration curve for the instrument. EPA's definition of an MDL, calculated according to the published procedures in 40 CFR, Part 136, Appendix B, is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a highly conservative criterion designed to all but completely eliminate false-positive results. Failure to meet the quantitative-based MDL criterion does not negate the analytical "presence" established by the "detection" criterion.

Our issue is that the Army, through its current use of the EPA MDL concept, could improperly classify analytical data as "non-detects" when, in fact, the data have been determined analytically as "detects." Although EPA-prescribed uses of the MDL concept may be appropriate for many applications in regulatory monitoring, in this public health-driven application, it is open to criticism when low-level instrument detects are discarded.

We are not suggesting that using the MDL concept and reporting "analytical detects" as "non-detects" will compromise the process of clearing the CVXH concentration at 20 ppb for VX and 1 ppm for EA 2192. Rather the issue is improper classification of analytical

results. Usually no issue would involve MDL, if the MDL was used only to help determine a quantitation level at which a reliable number can be provided to help make an action decision. In this case, the Army used "detection," not a quantitative level, as its primary clearance criterion. We stated in sections 3.3 and 3.4 that the current NECDF methods can support a clearance process on the basis of quantifiable measurements. The Army could report analytical results as "less then," rather than as "detects" and "non-detects," which would more accurately represent the analytical data.

3.6 Quality Assurance and Quality Control Procedures

The Laboratory Quality Control Plan clearly defines the comprehensive laboratory QA/QC procedures and techniques. This document defines the procedures for: preparation and verification of analytical standards; the certification, maintenance, and calibration of analytical instruments; the certification of methods and personnel; and the QC procedures, techniques, and samples used to define the operational status of the analytical processes and the basic validity of the analytical data. The overall QA/QC plan and procedures are well designed and documented.

3.7 Findings

1. The planned sampling program should provide representative samples for CVXH batches.

2. The current method for analyzing VX in CVXH (LAFI-A-30-053) is adequate to detect and quantify VX in laboratory-generated, 8% VX-loaded, DIC-stabilized hydrolysate well below the established clearance level of 20 ppb.

3. The current method for analyzing EA 2192 in CVXH (LAFI-A-30-030) is adequate to detect and quantify EA 2192 in laboratory-generated, 8% VX-loaded, DIC-stabilized hydrolysate well below the established clearance level of 1 ppm.

4. The use of EPA's MDL for clearance levels does not preclude analytical instrument detection of low levels of VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the clearance criteria (defined as "non-detected" with a MDL of ≤20 ppb VX or ≤1 ppm EA 2192) indicate absence of analytically detectable VX and/or EA 2192 could be misleading. While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

5. The overall QA/QC plan and procedures are well designed, and documented. NECDF laboratory personnel must generate day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup according to written plans and procedures.

4. Caustic VX Hydrolysate Treatment

4.1 Introduction

The CVXH is the liquor obtained from the alkaline hydrolysis of the chemical agent VX at elevated temperatures. The details of the processes that generate the CVXH at the Newport facility are described earlier in this report. Once transported to the DuPont SET facility, CVXH will be further treated to remove the organic by-products by a series of physicochemical and biologic processes. The exact composition and phase characteristics of the CVXH received at the SET plant will depend on the stabilizer type and VX loading used in the NECDF process batch. The major parameters and characteristics of 8% VX–loaded, DIC-stabilized hydrolysate (which is the main focus of this report), as received by DuPont, are given in the Table 4.1 for two separate CVXH samples.

pH	TOC, mg/L	COD mg/L	TN mg/L	EMPA mg/L	MPA mg/L	Thiolamine mg/L
>13	33,852	61,000	6,739	39,135	2,789	11,200
13.1	44,147		4,334	35,937	2,826	42,900

total organic carbon (TOC), total nitrogen (TN), milligrams per liter (mg/L)

Table 4.1 Characteristics of caustic VX hydrolysate generated from 8% VX loading with DIC stabilizer

The DuPont treatability studies were designed and executed to obtain scale-up parameters for engineering design and regulatory compliance. Because of their relatively high concentrations in the CVXH, only thiolamine, EMPA, and MPA were analyzed or monitored within the treatment train or in the process effluent. Trace contaminates, such as VX and EA 2192, were not monitored during the studies. (Note: Because of the high 1500- to 2000-fold dilution factor in the DuPont SET process, monitoring of these compounds may not be analytically possible.)

The pH adjustment and neutralization of the CVXH is the first step of the pretreatment process before introduction of the waste to the biologic treatment system. CVXH neutralization is followed by peroxide treatment to destroy odorous substances. The most recent biotreatability studies, the final step in the treatment train, use two-stage PACT®-activated sludge systems that are operated under conditions emulating the actual plant flow rate and hydraulic retention time. In addition to CVXH, the reactors received mustard (HD) hydrolysate from the Aberdeen operations because an alternating treatment scheme may be implemented at the DuPont SET facility.

The studies described in the two DuPont treatability reports (March 3, 2004, and July 19, 2004) were performed with different types of hydrolysates. The inconsistencies in the samples used to conduct the treatability studies make evaluation of the entire treatment process on the same basis and extrapolation of the treatability studies to pilot-plant performance challenging. For example, the pH adjustment and neutralization experiments reported in the Basic Data Summary Report (July 19, 2004) were conducted using 16% VX–loaded, DIC-stabilized CVXH (actual), but the biotreatability studies were

performed with 8% VX-loaded, DIC-stabilized CVXH (actual). Although 20% sulfuric acid was used in the pH-treatment experiments, DuPont proposes to use 5% acid in the full-scale process. The heat of reaction for acidification was measured for 8% and 16% VX-loaded CVXH (reformulated)[1] with DCC stabilizer, not DIC, which is the focus of our investigation. In summary, the studies reported in the Technical Assessment and the Basic Data Summary Report suffer from inconsistencies with respect to the type of CVXH used in each test. The experimental findings do not support the assumption that the CVXH has identical physical and chemical properties regardless of the VX loading and stabilizer type. The volume of the organic layer formed, which differs for 16% VX-loaded CVXH and 8% VX-loaded CVXH, clearly indicates that the system chemistry differs depending on how much VX is added to the caustic solution. Moreover, the volume of the organic layer formed during hydrolysis is not directly proportional to the VX loading. Therefore, linear extrapolations of the experimental results obtained in the preliminary treatment studies should not be used to predict performance at higher agent loadings, and equating the 8% VX-loaded 7000-gallons per day (gpd) CVXH with 16% VX-loaded 3500-gpd CVXH (Table 5, Basic Data Summary Report) for design and modeling purposes should be avoided.

Because the Army's stated objective is to begin operations with 8% VX-loaded, DIC-stabilized CVXH, the assessment of the DuPont treatability studies focused mainly on treatment of the CVXH at this condition. Occasionally, however, other data and material reported by Parsons on the VX alkaline hydrolysis treatment are cited to support the main findings of this assessment. Data are insufficient to assess treatment of CVXH at other VX loadings and for other stabilizers. In the following sections, the hydrolysate acidification process, the peroxide oxidation, and the biologic treatment studies are evaluated and the major findings presented.

4.2 Extent of Treatment

4.2.1 pH Adjustment

The CVXH acidification experiments were conducted with actual CVXH (16% VX-loaded, DIC-stabilized) titrated with 20% sulfuric acid to a final pH of 4–6. The titration curve obtained from the actual CVXH was compared with the aqueous layer from a centrifuged sample after separation of the organic layer. The heat of reaction also was computed, but for 8% and 16% VX-loaded, DCC-stabilized (reformulated) CVXH. The results of these experiments demonstrated that

- The organic layer is destroyed. pH adjustment produces a homogeneous amber yellow clear solution.
- The process generates 3.07 calories per gram (cal/g) during the titration of 8% VX-loaded, DCC-stabilized (reformulated) CVXH, producing a temperature increase of 6.4 ºC. This energy is expected to dissipate through heat losses during plant operation, and cooling and heat exchanger installation will be unnecessary.

[1] Reformulated VX hydrolysate was prepared by diluting 33% VX loaded hydrolysate to achieve the desired VX loading.

- Removal of the organic layer lowers the buffering capacity of the mixture (hydronium ions appear to be consumed during destruction of the organic layers).
- The process increases the volume of the CVXH waste by about 30%. If 5% sulfuric acid is used, as DuPont proposes to avoid cooling the reaction mixture, the volume increase will be close to 100%, further diluting the sample by a factor of 2. The effect of the 5% sulfuric acid on the organic treatment is unknown; the available reports did not present data using 5% sulfuric acid.

In response to the May 25, 2004, clarification questions (Responses to CDC Clarification Questions, Final, 17 June, 2004), Parsons indicates that pH adjustment does not destroy the organic layer. DuPont's 3 March 2004 report, "Treatability of Newport (Indiana) Caustic Hydrolysate" (Reich et al), confirmed that the adjustment of pH without additional treatment measures aggravates the odor of hydrolysate. Furthermore, the uncharged form of thiolamine is poorly-soluble and results in the formation of a large organic layer, on the order of 10% by volume. This organic layer is presumed to have a low flashpoint, which would add risk to the shipping process.

However, DuPont and its treatability study as presented in the Basic Data Summary Report, states

> *The sample was observed to change from a yellowish cloudy color to a slightly amber clear color once a single phase was formed which occurred around pH 6.0. Once a single phase formed, there was no longer any organic material coating the glass.*

Addition of a strong acid to the CVXH profoundly affects the physical and chemical stability of the organic droplets dispersed in the hydrolysis liquor and the dissipation of the organic layer. Attachment 1, "Characterization of Droplets Resulting from NECDF Static Mixers," of the Parsons report (July 22, 2004) states that the average size of the colloidal droplets ranges from 5 to 10 µm, with specific gravity of about 0.87 and strong negative charges. This charge most likely keeps the droplets suspended, preventing efficient collisions and subsequent aggregation. The electrophoresis experiments to determine the particle surface charge were performed with 16% VX- loaded, DIC-stabilized CVXH (actual). No experimental data are presented in the Parsons white paper on the properties of the droplets formed in the hydrolysate from the 8% VX-loaded, DIC-stabilized CVXH. The Parsons reports documented, and experimental observations by DuPont verified, that the volume of the organic layer and the size distribution and dispersion of the droplets in the final CVXH depends on the VX loading. The higher the loading rate the larger the resulting organic layer volume. However a direct proportional relation does not appear to exist (i.e., doubling the VX loading does not increase the volume of the organic layer by a factor of two). Visual observations by Parsons personnel of the formation of the organic layer estimated that the layer thickness remains unchanged for up to 4 months. However, no kinetic information is provided about the rate of formation of the organic layer.

Given that the organic droplets carry an overall negative charge, addition of hydronium ions should compress the electrical double layer that typically exists in the boundary of the organic-aqueous interface and allow the attraction forces to take over. Because this is not observed, i.e., addition of sulfuric acid does not appear to enhance flocculation or layer formation and separation, we can conclude that either the solubility of the organic phase is higher or its components become chemically unstable and decompose at lower pH or both. The disappearance of the organic phase during pH adjustment supports this.

The exact composition of the organic layer is not known, but the response of the whole (as received) CVXH to the addition of sulfuric acid suggests that it imparts alkalinity to the sample, probably because of weak organophosphorous acids and carbonates in the process water. More sulfuric acid (about 30 grams [g]) is required to reduce the pH of the whole CVXH sample than the aqueous layer to a pH of 8 (Figure 1 of the Basic Data Summary Report). However, the two titration curves intersect at a pH of 7 indicating that the same amount of acid is needed to bring the solutions to this endpoint. From that point, further addition of small amounts of acid brings about a steep pH drop in the aqueous layer but has little effect on the whole CVXH (as received), until about 380 g acid (x-axis of Figure 4-1), where pH drops substantially. This behavior is consistent with a chemically reactive solution. The organics exert a hydronium ion demand in excess of the amount required to neutralize the base. The organic layer appears to react with the hydronium ions participating in a chemical reaction rather than to be simple acid-base equilibrium chemistry. Moreover, the observation that this step modifies the odorous intensity of the mixture provides additional evidence that the organic components undergo significant chemical changes during pH adjustment.

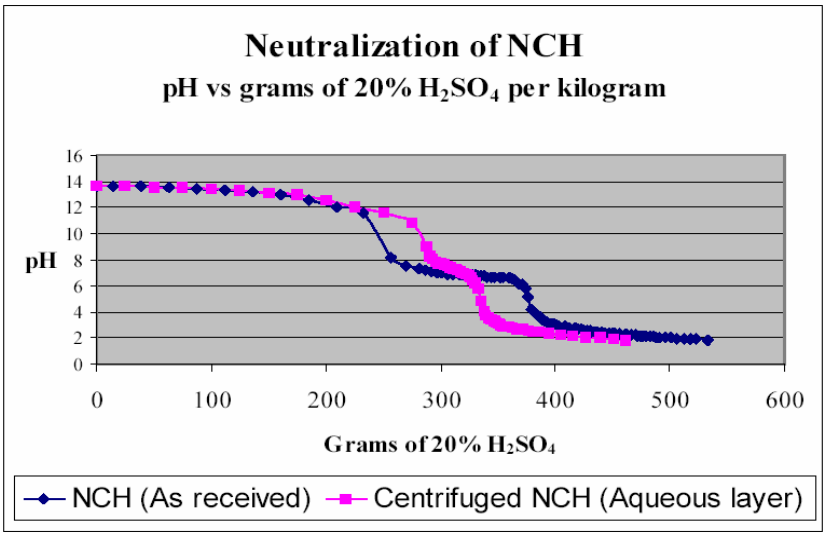

Figure 4-1 Caustic CVXH titration curves provided by DuPont in the Basic Data Summary Report.

4.2.2 Hydrogen Peroxide Oxidation

Once the pH of the hydrolysate is adjusted to a pH of 4–6, the mixture is treated with 10% peroxide to control objectionable odors emanating from the CVXH caused mainly by the volatilization of thiolamine. Peroxide and the free radicals formed by its addition to the reaction mixture attack the organics present in the hydrolysis liquor and initiate thiolamine destruction. Again, these studies were conducted with 16% VX- loaded, DCC-stabilized CVXH (actual or reformulated). Thiolamine is destroyed quickly by the peroxide, with most of the compound depleted within the first minute of reaction (Figure 4-2). After 20 minutes, the concentration drops below the detection limit of 5 ppm. The degradation products of thiolamine are presented in the Technical Assessment Report (March 3, 2004). Four compounds were identified as possible thiolamine degradation products: acetic acid, diisopropyl amine, urea, and 2-diisopropylaminoethyl ethyl disulfide. Acetic acid and urea are readily biodegradable compounds and are expected to break down in the two-stage PACT® bioreactors. However, the biodegradability of isopropyl amine and the 2-diisopropylaminoethyl ethyl disulfide is not documented in the Technical Assessment Report or the Basic Data Summary Report; only qualitative references (page 49 of the Technical Assessment Report) state that samples analyzed from the effluent of one of the bioreactors had no detectable amounts of thiolamine or any of its oxidation products. No other information is provided that confirms the biodegradation of these two by-products. EMPA and MPA remain unaffected by the peroxide process.

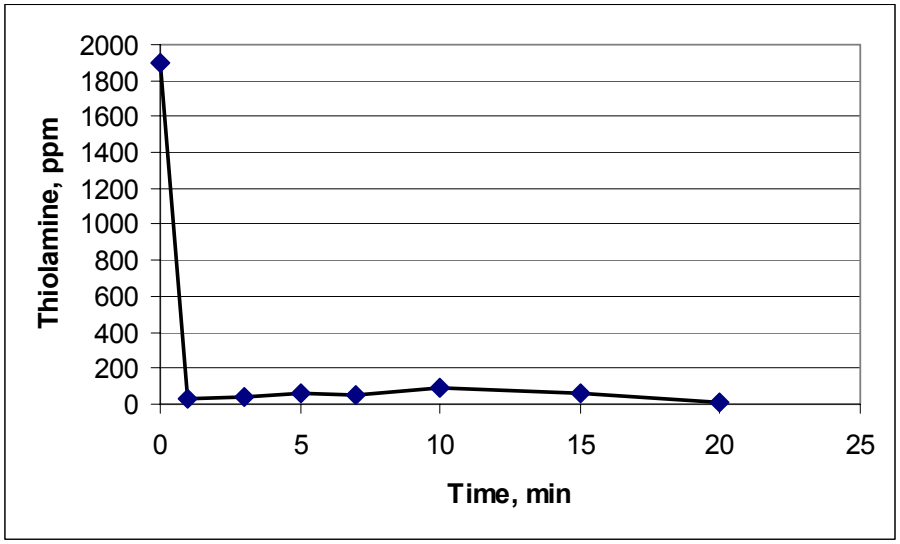

Figure 4-2 Destruction of thiolamine by hydrogen peroxide oxidation.

The oxidation step is an exothermic process releasing approximately 14 cal/g of heat. This value was obtained from a reformulated 16% VX–loaded, DCC-stabilized, CVXH that was first treated with 20% sulfuric acid to a pH of 6.4, then subjected to 20% weight equivalent of 10% hydrogen peroxide solution. Gas-generation measurements conducted in 2-liter flasks showed that the amount of gas generated during the peroxide oxidation is

negligible. The lack of gas evolution suggests that the degradation of thiolamine is incomplete; in other words, the compound is not mineralized to the simple innocuous carbon dioxide and water.

4.2.3 PACT® Biotreatment

Two sets of biodegradation experiments were conducted using one- and two-stage PACT® bioreactors. The first treatability study was performed with CVXH; in the second, both CVXH and HD hydrolysate from Aberdeen were tested to determine the effect of alternating the bioreactor feeds on the performance of the biologic system. Co-processing will be necessary when both types of hydrolysates will be sent for treatment to DuPont's SET facility. The objectives and the criteria of both studies were stated in the Basic Data Summary Report:

1. To confirm that the anticipated rates of CVXH can be processed successfully through the SET [wastewater treatment plant (WWTP)], enhancing the database provided by the original treatability study;
2. To assure that the CVXH can be processed at appropriate rates while HD hydrolysate from Aberdeen is being managed at the WWTP using a plan to either alternately campaign each hydrolysate or process the pretreated hydrolysates simultaneously;
3. To ascertain the degree of improvement in treatment that can be anticipated with a two stage PACT® system.

As for the earlier Treatability Study there were three general criteria for judging the treatment of CVXH to be successful:

1. Ability to maintain satisfactory control of wastewater and sludge odors.
2. Ability to maintain control of SET WWTP operations (e.g., effective dissolved organic carbon [DOC] removal, manageable foaming, pH control, solids management, etc.)
3. Ability to assure permit compliance (e.g., effluent BOD5 [5-day biochemical oxygen demand], BOD5 percent removal, effluent TSS, effluent NH3-N and WET). In addition the fate of EMPA, MPA and thiolamine were monitored.

As mentioned before, the studies were designed to provide information about system performance in terms of regulatory compliance and to obtain design parameters for scale-up.

To ensure adequate treatment, two PACT® bioreactors were operated in series. This biologic system, in addition to the microbial degradation, was dosed with activated carbon, which in general enhances the treatment capacity by removing recalcitrant compounds that are resistant to biodegradation. Six reactors were set up to evaluate various treatment scenarios using 8% VX-loaded, DIC-stabilized CVXH and the HD hydrolysate. The flow rate and retention time in the bioreactors were set to simulate actual plant conditions treating 7000-gpd CVXH and 15,000- and 25,000-gpd HD

hydrolysate. A large dilution of the hydrolysate, to the order of approximately 2000 times, occurred at introduction of the pretreated CVXH to the biologic PACT® system. Appropriate controls were used throughout the study, and all pertinent system parameters were monitored to assess system performance. However, the fate of individual compounds as they pass through the bioreactors is not as well documented. Only EMPA and MPA were monitored in the pilot-plant effluent.

The data presented in figures 7, 8, 9, and 10 and tables 8 and 9 of the Basic Data Summary Report indicate that, after a short acclimation period, the removal efficiency, as measured by DOC and BOD reduction, stabilizes to an average of about 85%–90% in all reactors. Even during the acclimation period, the removal does not drop below 75%. This high-removal efficiency also is observed in the alternating Aberdeen/DIC CVXH influents, indicating that the biologic system is not affected by these input changes. The 7000–gpd, 8% VX-loaded CVXH is equated to 3500–gpd, 16% VX-loaded CVXH (Table 5). However no evidence suggests that this is a valid approach. See Section 4.3 for a discussion of the potential differences on the composition and general chemistry of the 8% and 16% VX-loaded CVXH.

The Technical Assessment and Basic Data Summary reports clearly document the conversion of EMPA to MPA. Both compounds remain unaffected by the pH reduction, and conversion during peroxide treatment appears to be limited. Biologic treatment by the two-stage PACT® process converts essentially all of the EMPA to MPA but appears not to affect the MPA decomposition. Data are sufficient to support this conclusion. The slight decrease in MPA effluent concentration most likely results from partitioning in the organic sludge.

DuPont's Technical Assessment and Basic Data Summary reports contain no information about the fate of VX or EA 2192 during treatment of the CVXH in the DuPont SET facility. The presence of these two compounds in the plant effluent in trace amounts cannot be excluded.

4.3 Environmental Persistence and Agent Loading Effects

The major hydrolysis products of VX are well characterized, and the reaction rate and pathways depend strongly on solution pH and temperature (Figures 4-3 and 4-4). With solubility of approximately 30 grams per liter (g/L), VX is considered to be highly mobile in the environment and can persist for days or even weeks in slightly acidic waters. Other VX hydrolysis products in the CVXH include EMPA, which has a half life in soils of about 8 days, with MPA being the major transformation product.

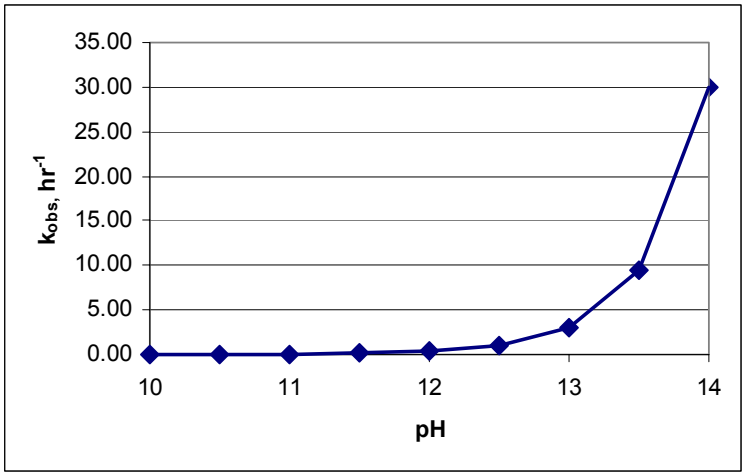

Figure 4-3 pH dependence of apparent rate constant for VX hydrolysis

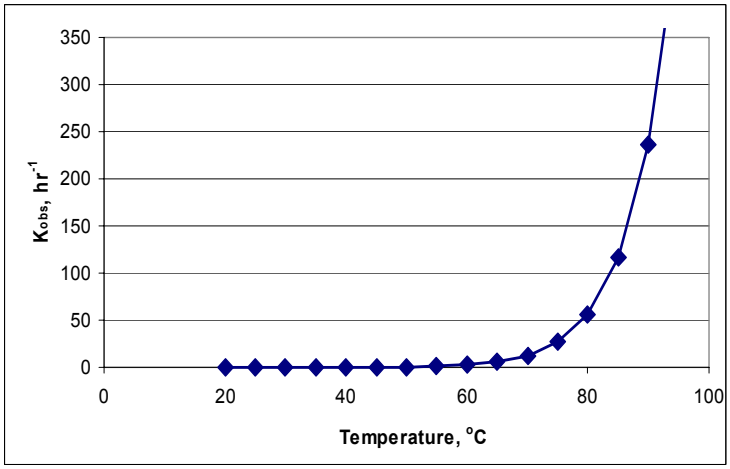

Figure 4-4 Temperature dependence of apparent rate constant for VX hydrolysis at a pH of 7.7.

As discussed in Section 4.2.3, the treatability studies with the 8% VX-loaded CVXH demonstrates conversion of EMPA to MPA in the activated sludge bioreactors. MPA is stable in the environment because it is resistant to hydrolysis, photolysis, and thermal decomposition. It is also soluble in water and has a low coefficient for sorption onto soil particles. Therefore, it can migrate easily in the soil and groundwater (Munro et al., 1999). Another major by-product of the hydrolysis of VX at neutral and high pH values, is EA 2192 (S-(2-diisopropylaminoethyl)methyl phosphonothioic acid), an environmentally persistent highly toxic compound with infinite water solubility.

Some of the hydrolysis products, namely EA 2192, EMPA and MPA, are stable at neutral pH; whether these, or other byproducts that are not identified or exist at low concentrations, can react and form stable VX molecules is questionable. This is a concern because the CVXH is adjusted to a pH below 6 in preparation for the oxidation and

biologic treatment. Parsons attempted to partially address this concern by studying the CVXH over a 5-hour period at a pH of 10 or 71 days at a pH of 14. These conditions, however, do not represent the low (<6) pH range in the system after pH adjustment. Neutral pH is a worst-case scenario because of the stability of the by-products at those conditions and the possibility of recombining to reform VX. Thermodynamic analyses also should have been performed to assess the tendency of the pH-adjusted CVXH to move toward VX reformation. Because experimental data are not presented, the questions regarding possible VX reformation remain unanswered.

4.4 Findings

1. The 8% VX-loaded, DIC-stabilized CVXH is treated by pH adjustment to a pH <6 to eliminate the two-phase mixture, followed by hydrogen peroxide oxidation to destroy the odor-causing thiolamine, and finally biologic treatment to convert most of the EMPA to MPA.
2. The DuPont SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer, except for MPA, for which only minimal reduction is demonstrated.
3. Alternating feeds from Aberdeen HD hydrolysate and CVXH did not affect the performance of the DuPont bench-scale reactor.
4. The effects of the SET facility on the destruction of any trace quantities of VX and EA 2192 in the CVXH are unknown. In addition, the fate of diisopropyl amine and 2-diisopropylaminoethyl ethyl disulfide through the SET plant is not well documented.
5. The possibility of VX reformulation at acidic (<6) pH conditions (after pH adjustment) in the Dupont SET treatment process has not been adequately investigated and remains unresolved.
6. Effective treatment of 16% VX-loaded CVXH and 8% VX-loaded CVXH with DCC or DIC/DCC stabilizers were not demonstrated in the DuPont studies.

5. Major Findings

NECDF was designed to destroy VX using caustic hydrolysis in a hot solution of sodium hydroxide. Initially the plan was to further treat the resulting waste on-site by SCWO and to ship the SCWO effluent to a TSDF. After the terrorist attacks of September 11, 2001, the plan was modified to eliminate on-site SCWO treatment and ship the resulting hydrolysate directly off-site for treatment at a TSDF. Critical to this modified plan was the development and validation of analytical methods to clear the hydrolysate for shipment. The stringent Army clearance levels for VX and EA 2192 proved challenging to the analysts. The original plan to operate at 33% VX loading was abandoned, and the program plans to begin operations at 8% VX loading and move to 16% VX loading.

This programmatic change has necessitated an intensive effort to develop the analytical methods needed to assess process performance and suitability of the hydrolysate for off-

site shipping, process modification to ensure adequate mixing and VX droplet size, and search for a TSDF capable of treating the hydrolysate. The current plans are for NECDF to ship the CVXH to the DuPont SET facility in Deepwater, New Jersey.

CDC engaged Carmagen Engineering, Inc., to assemble a team of experts (Team) to assist in the evaluation of the DuPont SET facility's treatment of the CVXH. The Team recognized that an assessment of the NECDF destruction process and an examination of the analytical methods to be used for CVXH clearance were required to ensure that the hydrolysate being shipped to SET will be adequately characterized and that VX and EA 2192 levels in the CVXH meets Army specifications.

The Team addresses its findings in chapters 2–4 of the report. The reader is encouraged to review all of the findings, as well as the supporting documentation in each chapter. The major findings follow.

Process Issues (Chapter 2)

Finding 2.1. The database supports the efficacy of neutralizing DIC-stabilized VX using sodium hydroxide at the 8% VX-loading rate. Scale-up of the process from laboratory/bench scale to pilot scale should be operationally feasible. However, because the NECDF will be a pilot facility, changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

Finding 2.2. VX loading (weight percent) and the specific stabilizer (DIC, DCC) employed significantly impact the process, hydrolysate composition, analytical methods validation, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes from 16% to 33% VX-loading batches), the potentially high VX concentration in the resulting organic layer, and the analytical problems identified with 33% VX loading.

Finding 2.3. The impact is unknown of solids formation during the hydrolysis process on operations (potential for blockage of the in-line static mixer, control valves, and sampling system), VX analytic methods, and off-site hydrolysate treatment. The transition from 8% to 16% VX loading, as well as stabilizer change, is of concern and requires additional detailed studies.

Analytical Methods (Chapter 3)

Finding 3.1. The methods for analyzing VX and EA 2192 in 8% VX-loaded, DIC-stabilized CVXH are adequate to detect and quantify at the established clearance levels for VX (20 ppb) and EA 2192 (1 ppm).

Finding 3.2. The use of EPA's MDL for clearance levels does not preclude analytical instrument detection of low-level VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the MDL clearance criteria indicate absence of analytically detectable VX and EA 2192 could be misleading. While CDC believes

that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

Finding 3.2. The overall QA/QC plan and procedures for the NECDF laboratory are well designed and documented. However, NECDF laboratory personnel should continue implementing the QA/QC plan by developing day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup.

Caustic VX Hydrolysate Treatment (Chapter 4)

Finding 4.1. The SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer (i.e., pH adjustment, thiolamine destruction, conversion of EMPA to MPA), except for MPA, for which only minimal reduction is demonstrated.

Finding 4.2. The SET facility treatment performance should be unaffected when treatment of hydrolysate feeds from Aberdeen (HD) and Newport (VX) are alternated.

Finding 4.3. The DuPont treatability studies have not yet demonstrated the effective treatment of 16% VX-loaded CVXH, nor of 8% VX-loaded CVXH with DCC or DIC + DCC stabilizers.

6. References

DuPont. DuPont Technical Assessment on U.S. Army Newport (Indiana) Project. 3 March, 2004.

DuPont. Basic Data Summary Report for Newport Caustic Hydrolysate. 19 July, 2004.

Munro, N.B., Talmage, S.S., Griffin, G.D., Waters, L.C., Watson, A.P., King, J.F., and Hauschild, V. The sources, fate, and toxicity of chemical warfare agent degradation products. Environ Health Perspect. 1999;107(12):933–974.

Parsons. CVXH Analytical Testing Results (Response to CDC Request for Information: Item No. 1). 15 May 2004.

Parsons. Sampling Protocols (Response to CDC Request for Information: Item No. 2). 14 May 2004.

Parsons. Analytical Methods for VX in Hydrolysate (Response to CDC Request for Information: Item No. 4). 14 May 2004.

Parsons. Newport, Indiana Process Variability Impact on Secondary Treatment (Response to CDC Request for Information: Item No. 6). 14 May 2004.

Parsons. Responses to EPA Questions to DuPont [16 questions]. 14 June 2004.

Parsons. Responses to Additional CDC and EPA Questions [9 EPA questions, 19 CDC questions]. 17 June 2004.

Parsons. Responses to CDC 29 June, 2004 Questions [11 requests and 5 questions]. 22 July 2004.

SAIC. Assessment of Low-Level VX in CVXH LLVX Independent Assessment Panel. October 2003.

Texas A&M University System. Quantitative Subsystem Hazard Analysis of Potential for Off-Site Transfer of Hydrolysate Containing VX Above the 20 ppb Method Detection Limit. Draft Report. August 2004.

Wojciechowski P, Mokos J. Analysis for VX in Hydrolysate at NECDF. Presentation to CDC, 27 March 2003.

APPENDIX C

Section 3.0

Autoclave Evaluation Test Report,
Continental Research and Engineering. LLC,
Englewood, CO, Revision 0,
April 21, 2008.

CONTINENTAL RESEARCH AND ENGINEERING, LLC

Autoclave Evaluation Test report

07017

Revision 0

April 21, 2008

Prepared for
EG&G Defense Materials, Inc.

By

Continental Research and Engineering, LLC
9785 S. Maroon Circle Suite 100 • Englewood, Colorado 80112
Tel (303) 758-7373 Fax: (303) 758-1072 www.cre-denver.com

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I. Executive Summary

An autoclave test was developed and executed[1] to determine the effectiveness of an autoclave to neutralize an agent surrogate applied to various secondary waste materials. This report documents and presents the results of the completed Autoclave Evaluation Test Plan. The test results demonstrate the ability of an autoclave to decontaminate secondary wastes from chemical warfare weapons demilitarization facilities.

The testing was conducted to evaluate autoclave technology as an alternate technology for decontamination of secondary wastes at TOCDF. The tests were conducted utilizing five waste materials: Charcoal, DPE suits, Soil, wood and Tap Gear. The wastes were contaminated with the agent surrogate material chloromethylnaphthalene. The surrogate contaminated wastes were treated in an autoclave at various temperatures to determine destruction removal efficiency of the surrogate material. Minicams measurement of surrogate levels was conducted on the autoclave headspace after each test. Extraction analysis was conducted on contaminated samples (sachets) spiked at both a high and low levels contained in each of the processed loads. Extraction analysis of all samples (sachets) spiked at a low level did not detect any surrogate material remaining. Because of this, only the samples (sachets) spiked at a high level were used in calculating DREs.

Decontamination tests on charcoal in both bulk and contained in a HVAC filter tray were successful. Minicams readings on the head space were very low and extraction analysis indicated a DRE of 99.99 to 99.999 %. Tests were conducted at 190°F for a period of 1 hour.

Decontamination tests on soil were successful. Minicams readings on the head space indicated that the surrogate was present in the vapor state at completion of the test. Extraction analysis indicated a DRE of 99.999% or better. Tests were conducted at 190°F for a period of 1 hour.

Decontamination tests on wood were successful. Minicams readings on the head space indicated that the surrogate was present in the vapor state at completion of the test. Extraction analysis indicated a DRE of 99. 9% on one sachet and the rest indicating 99.99% or better. The wood test was conducted with a full bin approximately 120 lbs. The test was conducted at 250°F for a period of 2 hrs and 30 minutes. There is the potential to increase the DRE by increasing processing temperature.

Decontamination tests on DPE suits and TAP gear were successful. Extraction analysis indicated a DRE in the range of 99% or above in most cases, with one test run at below the 99% DRE. The DPE suit tests were run at varying temperatures and times in an attempt to increase the DRE. The test temperature for DPE suits was increased to 280°F without degradation of the suits. It may be possible to treat the DPE suits at 290°F or higher without melting the suits.

It became apparent during the testing that the surrogate was not fully hydrolyzing before vaporizing and was not being hydrolized in the gas phase. This may be due to the surrogate selection or the selection of the carrier fluid (toluene). The testing demonstrates that secondary waste can be decontaminated in an autoclave. It is recommended that additional laboratory testing be completed using chemical agents and chloromethylnaphthalene without a carrier fluid. These tests should be used to further clarify the results of the surrogate tests and to identify the differences in reactions between the surrogate and chemical agents.

[1] Autoclave Evaluation Test Plan, Revision 3, CRE Project No. 07017 dated February 29, 2008

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II. Introduction

The Tooele Chemical Agent Disposal Facility (TOCDF) is currently planning for processing of secondary and closure wastes. The site has sufficient time to implement changes that will avoid schedule impacts created by processing secondary wastes. The additional time allows the review and consideration of alternate technologies and addition of equipment to improve secondary waste processing. Installation of a system specifically for processing of secondary and closure wastes would allow parallel processing of secondary wastes, increase the availability of the Metal Parts Furnace (MPF) to process munitions, and shorten the facility's overall schedule. There is significant risk to the facility's schedule if alternate techniques (i.e., utilizing processing systems dedicated to secondary wastes) are not utilized for processing secondary waste.

Continental Research & Engineering (CR&E) completed an investigation of processing alternatives to reduce the schedule impact resulting from processing secondary waste through the existing demilitarization furnaces. Treatment of waste through an autoclave is an attractive processing alternative due to its relative low cost and short implementation schedule. Autoclaves have been successfully used for decontamination of BDO suits contaminated with chemical agents GB, VX and HD[2].

An autoclave test was developed and executed[3] to determine the effectiveness of an autoclave to neutralize an agent surrogate applied to various secondary waste materials. This report documents and presents the results of the completed Autoclave Evaluation Test Plan. The test results demonstrate the ability of an autoclave to decontaminate chemical warfare weapons demilitarization facilities secondary wastes.

III. Process Description

Autoclaves are designed to decontaminate materials by subjecting them to steam at high temperature and pressure. The contact of steam at high temperature and pressure with an agent surrogate is intended to neutralize the surrogate through hydrolysis in the same manner that chemical agents would decompose. All waste is fed to the autoclave through an autoclave inlet door. Waste is either bulk loaded into waste processing carts or loaded into processing trays and placed within the autoclave. Size of the autoclave and cart design determines the loaded autoclave capacity. The test autoclave had a capacity of one cart approximately 24"x 36"x 18" deep or three trays approximately 24" x 24" x 2" deep. A drawing and specifications for the autoclave and cart / tray system are contained in the Test Plan.

[2] Battle Dress Overgarment (BDO) Decontamination Test, U.S. Army Dugway Proving Ground, Dugway, UT Dec. 1992 and Battledress Overgarment (BDO) Decontamination Test - Follow-On Testing, U.S. Army Dugway Proving Ground, Dugway, UT July 1993.

[3] Autoclave Evaluation Test Plan, Revision 3, CRE Project No. 07017 dated February 29, 2008

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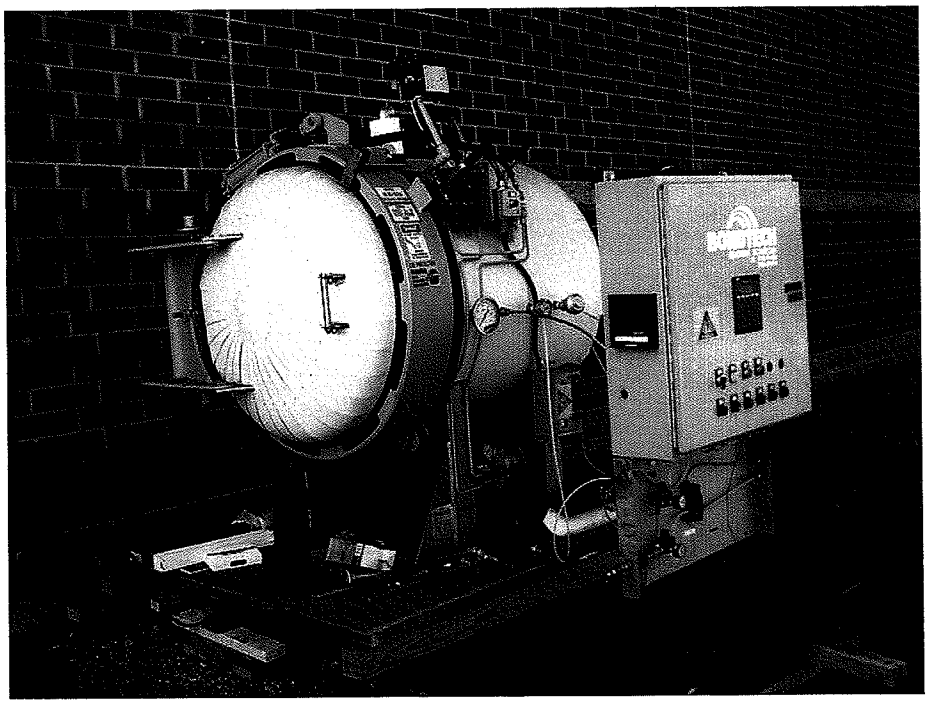

Test Autoclave

The decontamination process is started following loading of the autoclave and securing of the inlet door by creating a vacuum within the autoclave vessel. The vacuum removes residual air from the autoclave vessel and aids in the permeation of steam throughout the waste.

The autoclave vessel is pressurized with saturated steam. The steam from the autoclave vessel is vented through a condenser at the end of the processing cycle.

A vacuum is again applied to the autoclave vessel following venting of the unit. The post vacuum cycle removes remaining moisture from the vessel and waste. This completes the processing cycle.

The inlet door is opened and the waste carts are removed from the autoclave following completion of the-processing cycle. The sterilized waste is allowed to cool and is then removed from the processing carts for disposal with the normal shop waste.

IV. Test Description

The Autoclave evaluation test equipment was set up on March 3, 2008. This included the Autoclave, Minicam, materials check, procurement of required test materials, thermocouple setup, steam line connection, and a pretest meeting.

The test runs started the morning of March 4, 2008.

Test Run 1 - DPE Suits, Whole

Feed Set-Up

The autoclave bin was set inside the autoclave and a high temperature plastic bin liner placed in the bin. The 6 mil bags had not arrived from TOCDF (The 6 mil polyethylene bags were coming via

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FedEx from TOCDF). A standard 30 gallon Polyethylene garbage bag and a heavy duty 20 gallon zip lock bag were used to contain the DPE suits. Two bags were used instead of one as stated in the test procedure because of the small size of the bags. The bags were loaded with 2 ½ DPE suits each and two suits were placed around the bags in the bin for a total of 7 suits, approximately 75 lbs. The sachets were placed randomly in the bags to cover the bottom, middle and top areas. 1400 mg of surrogate material was then poured in the bottom, middle and top portions of the bags and on the loose suits in the bin.

Four thermocouples were randomly place around the bags for temperature monitoring.

Test Description

The autoclave temperature was set at 235°F. The autoclave steam cycle was set at 60 minutes. The autoclave steam jet air ejector was designed for 125 psig steam. The vacuum cycle set point was increased from -27"hg to approximately -18"hg because the shop steam supply only provided approximately 80 psig steam pressure.

The temperature and pressure were recorded manually during this test because the autoclave Temperature recorder was not functioning.

The bin was loaded at 0816 on 3/4/08 and the door closed.

The autoclave cycle was started at 0818 on 3/4/08. The initial autoclave temperature at the start of the test was 63°F. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The steam heat cycle was started at 0822.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
0825	231	7.6
0835	235	9.0
0845	235	8.5
0855	235	8.6
0905	235	8.0
0915	235	8.2
0920	235	8.1

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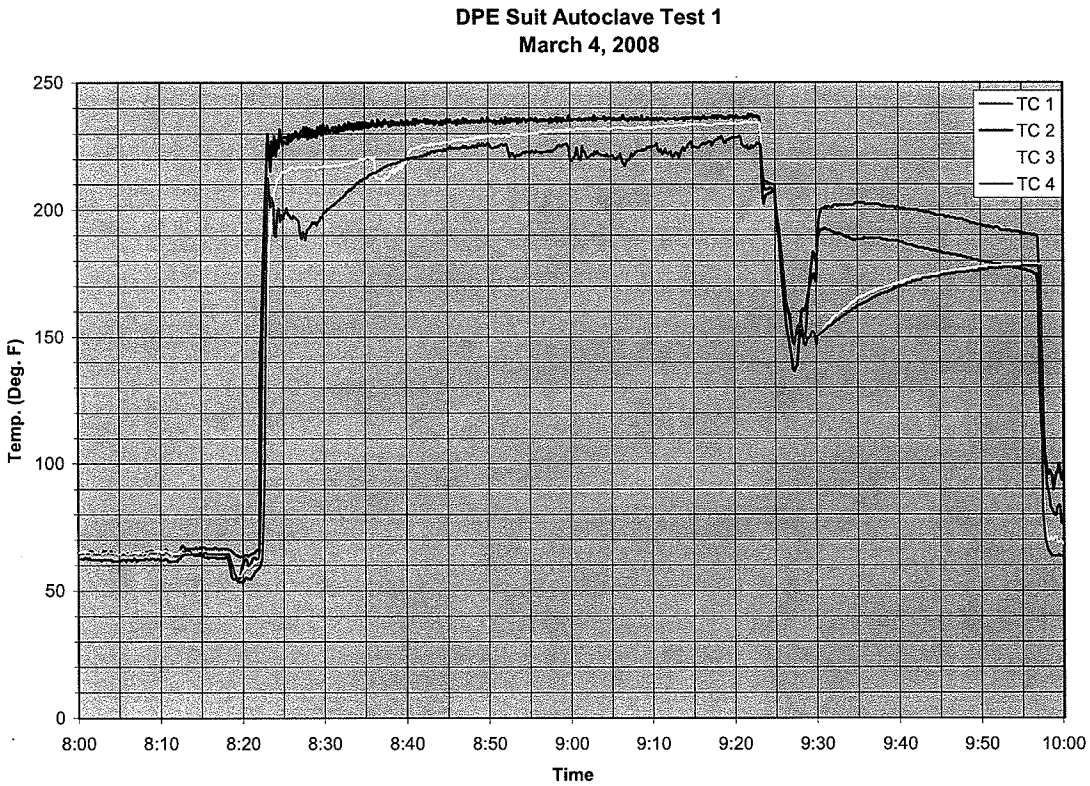
The following chart indicates the temperatures of the test thermocouples distributed around the suits.



The autoclave steam heat cycle was completed at 0922 on 3/4/08

The vent and the post vacuum cycle were completed at 0945 on 3/4/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/4/2008	0954 hrs	Test 1 Sample Concentration	= 1.95 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.020313 mg/M^3

The autoclave was open to inspect the load.

No deterioration or discoloration of the DPE suits was noted. The Polyethylene garbage bag and the heavy duty ziplok bags were intact and did not allow the steam from the autoclave to contact the DPE suits. The test was stopped and sachets collected based on these observations. The cycle time was not extended as the test temperature was not enough to allow the steam to contact the suits for decontamination. It was decided to increase the autoclave temperature to 250°F for the next DPE suit test due to the excellent condition of the DPE suits.

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Extraction analysis

The sachets recovered from this test will not be subjected to laboratory analysis as they have not been exposed to steam during the processing cycle.

Test Run 2 - DPE Suits, Whole

Feed Set-Up

The autoclave bin was set inside the autoclave and a high temperature plastic bin liner placed in the bin. The 6 mil bags had not arrived from TOCDF (The 6 mil polyethylene bags were coming via FedEx from TOCDF). A standard 30 gallon Polyethylene garbage bag and a heavy duty 20 gallon zip lock bag were used to contain the DPE suits. Two bags were used instead of one as stated in the test procedure because of the small size of the bags. The bags were loaded with 2 ½ DPE suits each and two suits were placed around the bags in the bin for a total of 7 suits, approximately 75 lbs. The sachets were placed randomly in the bags to cover the bottom, middle and top areas. 1400 mg of surrogate material was then poured in the bottom, middle and top portions of the bags and on the loose suits in the bin.

Four thermocouples were randomly place around the bags for temperature monitoring.

Test Description

The autoclave temperature was set at 250°F. The autoclave steam cycle was set at 60 minutes. The autoclave steam jet air ejector was designed for 125 psig steam. The vacuum cycle set point was increased from -27"hg to approximately -18"hg because the shop steam supply only provided approximately 80 psig steam pressure.

The temperature and pressure were recorded manually during this test because the autoclave Temperature recorder was not functioning.

The bin was loaded at 1020 on 3/4/08 and the door closed.

The autoclave cycle was started at 1024 on 3/4/08. The vacuum achieved during the pre-vacuum was -9 psi or -18.3"hg.

The steam heat cycle started at 1029.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1030	249	14.0
1040	250	14.8
1050	250	14.9
1060	250	14.9
1110	250	15.1
1120	250	14.6
1130	250	14.8

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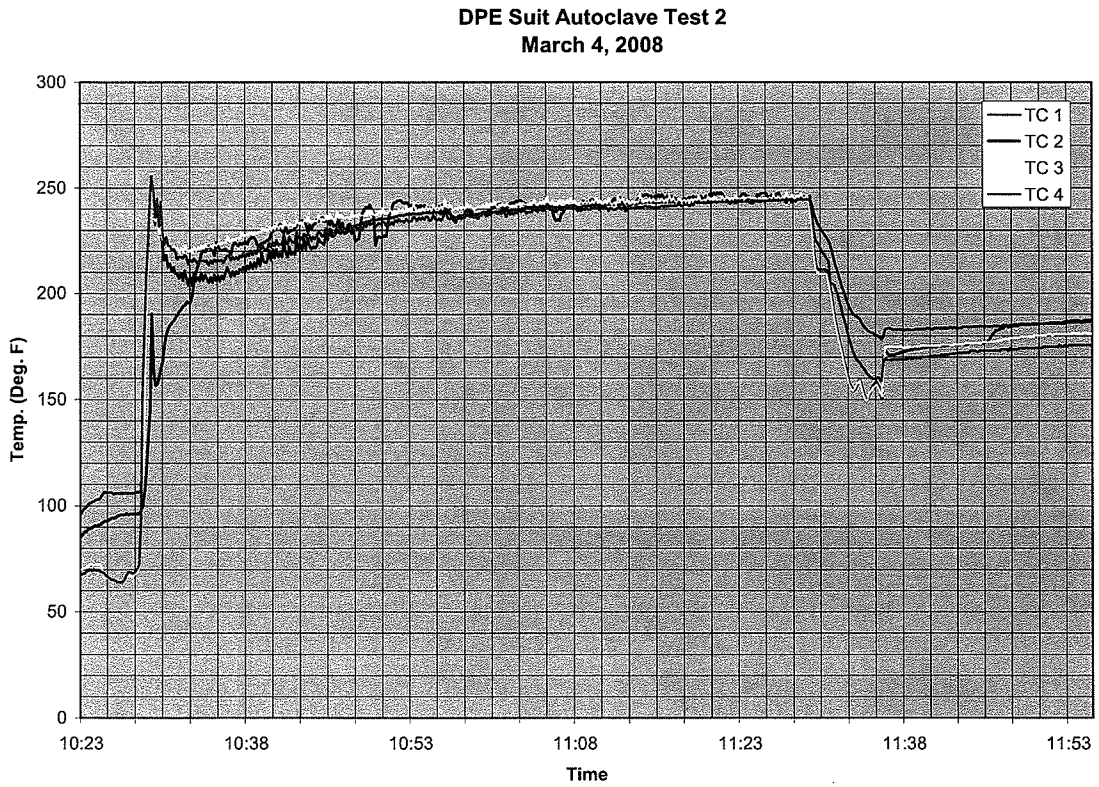
The following chart indicates the temperatures of the test thermocouples distributed around the suits.



The autoclave steam heat cycle completed at 1130 on 3/4/08

The vent and the post vacuum cycle was completed at 1137 on 3/4/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/4/2008	1159 hrs	Test 2 Sample Concentration	= 2.07 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.02156 mg/M^3

The autoclave was open to inspect the load.

No deterioration or discoloration of the DPE suits was noted. The Polyethylene garbage bag and the heavy duty ziplok bags were intact and did not allow the steam from the autoclave to contact the DPE suits. The test was stopped and sachets collected based on these observations. The cycle time was not extended as the test temperature was not high enough to allow the steam to contact the suits for decontamination. It was decided to cut the bags containing the DPE suits in order to allow the steam to contact the suits for the next test (Shredded DPE suits).

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Extraction analysis

The sachets recovered from this test will not be subjected to laboratory analysis as they have not been exposed to steam during the processing cycle.

Test Run 3 - DPE Suits, Shredded

Feed set up

The autoclave bin was set inside the autoclave and a high temperature plastic bin liner placed in the bin. The 6 mil bags had not arrived from TOCDF (The 6 mil polyethylene bags were coming via FedEx from TOCDF). A standard 30 gallon Polyethylene garbage bag and a heavy duty 20 gallon zip lock bag were used to contain the DPE suits. Two bags were used instead of one as stated in the test procedure because of the small size of the bags. The bags were loaded with approximately 2 ½ DPE suits each (5 total), approximately 53 lbs. The DPE suit material varied in size, but the pieces were each approximately 6" X 6". The sachets were placed in the bags to cover the bottom, middle and top areas. 1400 mg of surrogate material was then poured in the bottom, middle and top portions of the bags. The bags were split to allow steam exposure to the suit material without the need to melt the bags.

Four thermocouples were randomly place between the pieces of suit material for temperature monitoring.

Test Description

The autoclave temperature was set at 250°F. The autoclave steam cycle was set at 60 minutes. The autoclave steam jet air ejector was designed for 125 psig steam. The vacuum cycle set point was increased from -27"hg to approximately -18"hg because the shop steam supply only provided approximately 80 psig steam pressure.

The temperature and pressure were recorded manually during this test because the autoclave Temperature recorder was not functioning.

The bin was loaded at 1234 on 3/4/08 and the door closed.

The autoclave cycle was started at 1238 on 3/4/08. The vacuum achieved during the pre-vacuum was -9 psi or -18.3"hg.

The steam heat cycle was started at 1242.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1243	235	12.7
1250	249	13.6
1300	250	14.3
1310	250	14.8
1320	250	14.9
1330	250	14.9
1340	250	14.9

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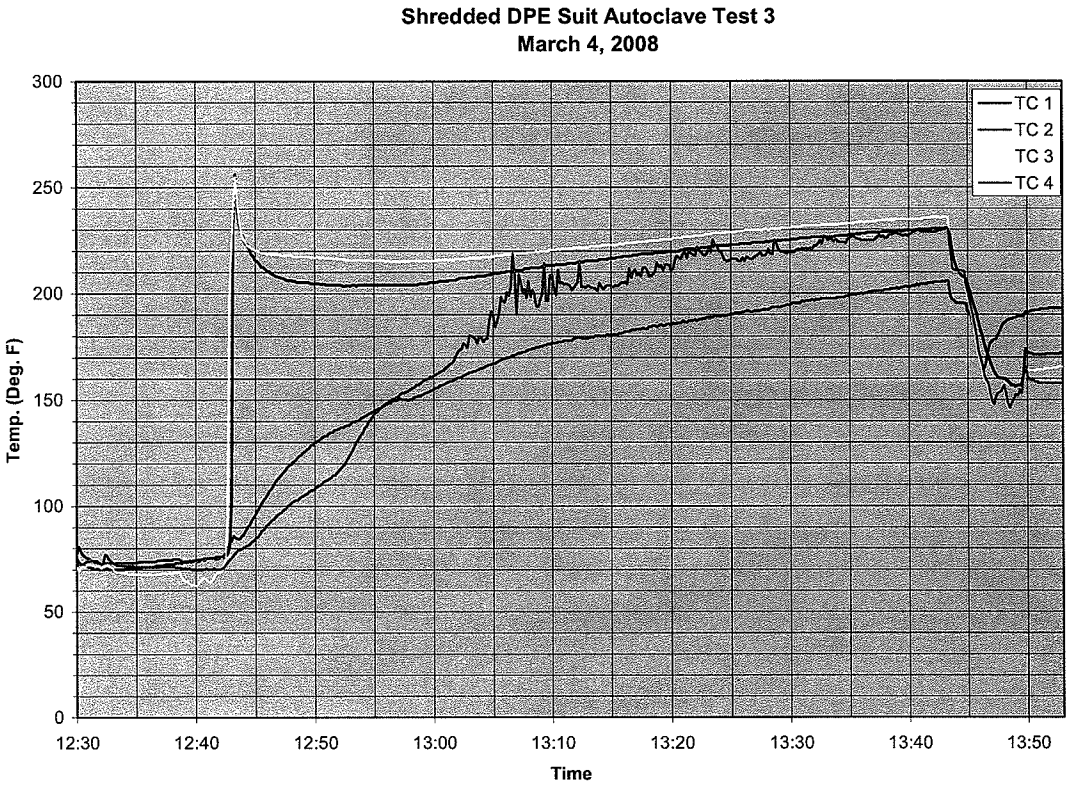
The following chart indicates the temperatures of the test thermocouples distributed around the suits.



The autoclave steam heat cycle was completed at 1342 on 3/4/08

The vent and the post vacuum cycle were completed at 1350 on 3/4/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/4/2008	1424 hrs	Test 3 Sample Concentration	= 2.32 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.02417 mg/M^3

The autoclave was open to inspect the load.

No deterioration or discoloration of the DPE suits was noted. The Polyethylene garbage bag and the heavy duty ziplok bag were intact and open (Cut at start of test), which allowed the steam from the autoclave to contact the DPE suits. The test cycle was not continued. Additional DPE suit runs will be completed at the end of the scheduled test runs after further evaluation of the test time and temperature based on minicams results.

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The test sequence was changed to run wood next, in place of the tap gear, as it was anticipated that a similar problem will exist with TAP gear. It was also decided to operate the minicams throughout the steam cycle in close proximity to the steam trap vent. This will allow detection of the surrogate material while processing.

Extraction analysis

The sachets recovered from this test were not subjected to laboratory analysis, based on results from additional testing completed after the scheduled test runs.

Test Run 4 (Test 5 in Test Plan) - Wood

Feed set-up

The autoclave bin was set inside the autoclave and a high temperature plastic bin liner placed in the bin. Wood 2X4's were cut in random lengths (8 to 18 inches) and placed randomly in the in the lined bin.

Four thermocouples were placed between the pieces of wood. Some of the sachets with DPE suit material were inadvertently placed in this load. The 10 wood sachets were placed in the load.

Test Description

The autoclave temperature set point was 250°F. The initial autoclave steam cycle was set at 60 minutes. The cycle was extended due to low temperature readings of the thermocouples and detection of surrogate by the minicams at the steam trap vent.

The bin was loaded at 1438 on 3/4/08 and the door closed.

The autoclave operation was started at 1442 on 3/4/08. The vacuum achieved during the pre-vacuum was -9 psi or -18.3"hg.

The steam heat cycle started at 1447.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1450	249	13.0
1505	250	13.9
1515	250	13.9
1525	250	14.3
1535	250	14.1
1545	250	14.3
1555	250	14.9
1610	250	14.2
1625	250	14.1
1635	250	14.0
1655	250	13.9
1705	250	14.1
1715	250	14.0

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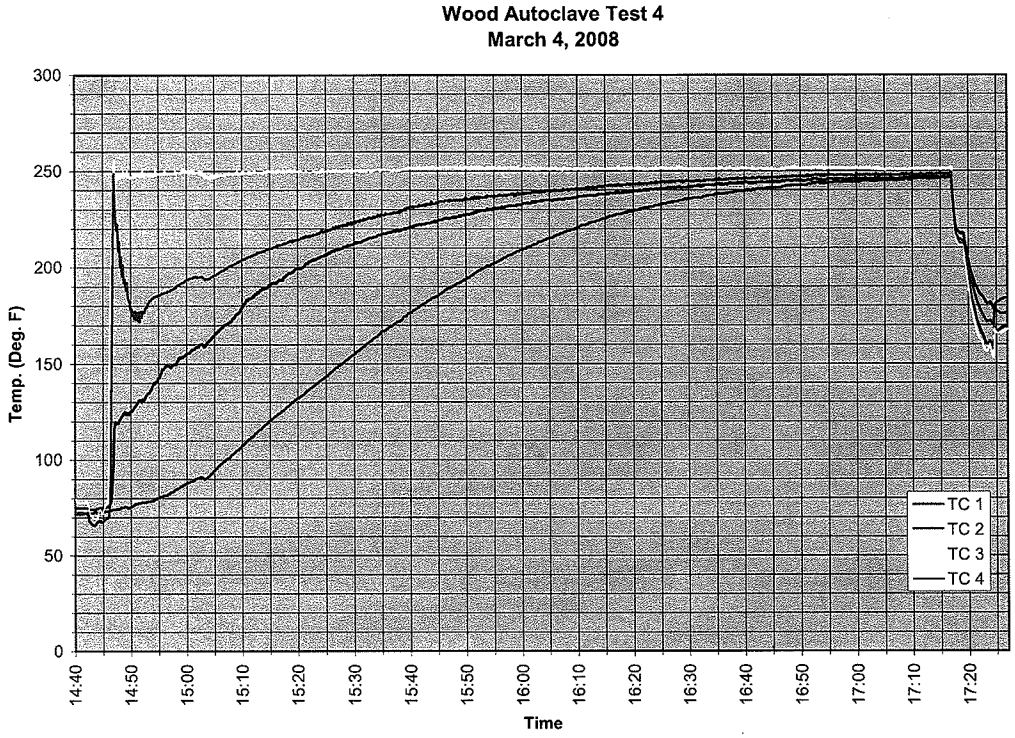
The following chart indicates the temperatures of the test thermocouples distributed around the suits.



The autoclave steam heat cycle was completed at 1718 on 3/4/08.

The vent and the post vacuum cycles were completed at 1725 on 3/4/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/4/2008	1749 hrs	Test 4 Sample Concentration	= 1.13 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.01177 mg/M^3

The autoclave was open to inspect the load.

The wood appeared dry with very little moisture, no discoloration.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
Wood-H-1	0.013	99.9993
Wood-H-2	0.506	99.9747
Wood-H-3	0.182	99.9909
Wood-H-4	0.086	99.9957
Wood-H-5	0.058	99.9971
	Average DRE % for Wood:	**99.9916**

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Test Run 5 (Test 6 in Test Plan) - Charcoal

Feed set up

This test used three trays as identified in the test plan. The trays are each 24" square with 2" separation between them. Each tray contained approximately 14 lbs of charcoal for a total of 42 lbs of charcoal per load. Sachets were placed in each tray at the middle and corners using a total of 10 sachets.

Test Description

The autoclave temperature set point was changed from the test plan to be 290°F. The autoclave steam cycle was set at 60 minutes. Four thermocouples were place in the trays, two in the top tray, and one in the center of the middle and bottom tray.

The bin was loaded at 0745 on 3/5/08 and the door closed.

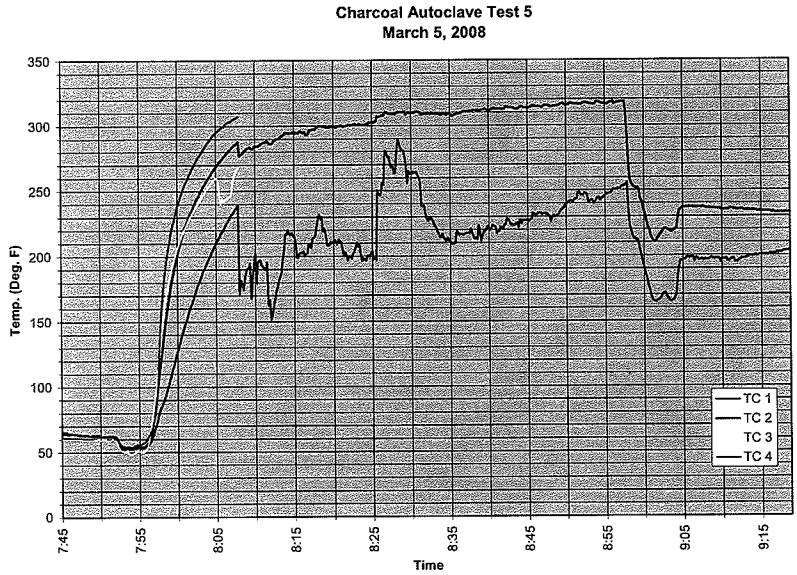
The autoclave operation was started at 0752 on 3/4/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The steam heat cycle started at 0757.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
0757	286	35.6
0805	289	41.1
0815	290	42.6
0830	291	42.7
0840	290	39.7
0850	290	39.1
0857	290	39.2

The following chart indicates the temperatures of the test thermocouples distributed in the trays.



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The autoclave steam heat cycle completed at 0857 on 3/5/08.

The vent and the post vacuum cycle were completed at 0905 on 3/5/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams did not indicate a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/5/2008	0930 hrs	Test 5 Sample Concentration	= 0.26 VSL	X	0.010417 mg/M^3 / 1 VSL	=	0.00271 mg/M^3

The autoclave was open to inspect the load.

The top tray of charcoal had pock marks that may indicate boiling water out of the charcoal during the post vacuum cycle. The top tray did appear to be moist. The middle and the bottom trays appeared dry and had pock marks around the edges but not in the center. There was charcoal in the bottom of the autoclave that had been blown out of the tray during the process cycle.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
Carbon-H-1-1	0.0800	99.996
Carbon-H-1-2	0.0800	99.996
Carbon-H-1-3	0.0329	99.998
Carbon-H-1-4	0.0634	99.997
Carbon-H-1-5	0.0755	99.996
Average DRE % for Bulk Carbon Test 1:		**99.997**

Test Run 6 (Not Identified in test plan) - Blank DPE test

Feed set up

The 6 mil bags arrived from TOCDF. This test was conducted to determine if an autoclave processing temperature of 250°F will melt the bags that are used at TOCDF. Two clean uncontaminated DPE suits were place in a 6 mil polyethylene bag and closed with duct tape as is practice at TOCDF. No sachets were placed in the autoclave for this run.

Test Description

The autoclave temperature was set at 250°F. The autoclave steam cycle was set at 60 minutes. Three thermocouples were randomly placed around the bag and one was placed inside the bag.

The bin was loaded at 0948 on 3/5/08 and the door closed.

The autoclave operation was started at 0951 on 3/5/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The steam heat cycle was started at 0959.

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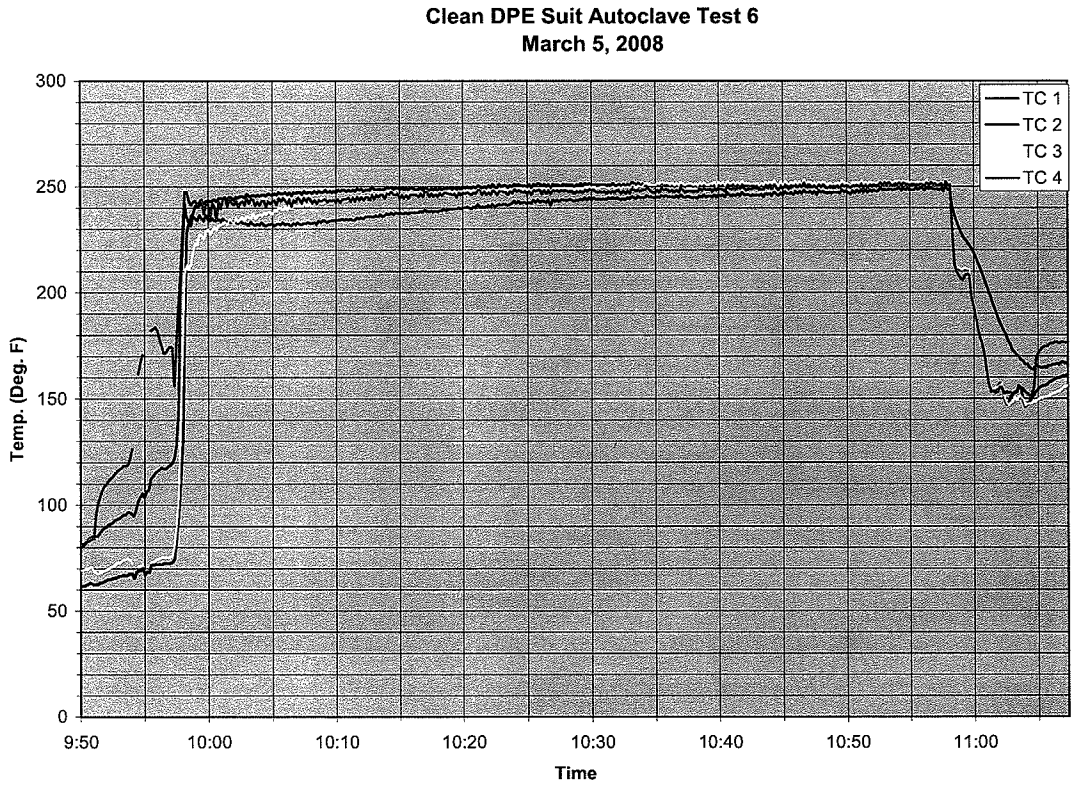
Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
0959	246	12.2
1008	250	13.2
1015	249	13.4
1025	250	14.1
1035	250	14.2
1045	250	14.2
1055	250	14.1

The following chart indicates the temperatures of the test thermocouples.



The autoclave steam heat cycle was completed at 1058 on 3/5/08.

The vent and the post vacuum cycles were completed at 1106 on 3/5/08 and the 15 minute hold time for the mini-cams test was started.

The autoclave was open to inspect the load.

The bag had significantly degraded but only a very small hole could be found that may allow steam to penetrate the bag. There was some moisture in the bag, indicating that some steam penetration had occurred.

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Test Run 7 - Charcoal

Feed set up

This test used three trays as identified in the test plan. The trays are each 24" square with 2" separation between them. Each tray contained approximately 14 lbs of charcoal for a total of 42 lbs of charcoal per load. Sachets were placed in each tray at the middle and corners using a total of 10 sachets.

Test Description

The autoclave temperature set point was changed from the test plan to 290°F. The autoclave steam cycle was set at 60 minutes. Four thermocouples were place in the trays, two in the top tray and one in the center of the middle and bottom tray.

The bin was loaded at 1305 on 3/5/08 and the door closed.

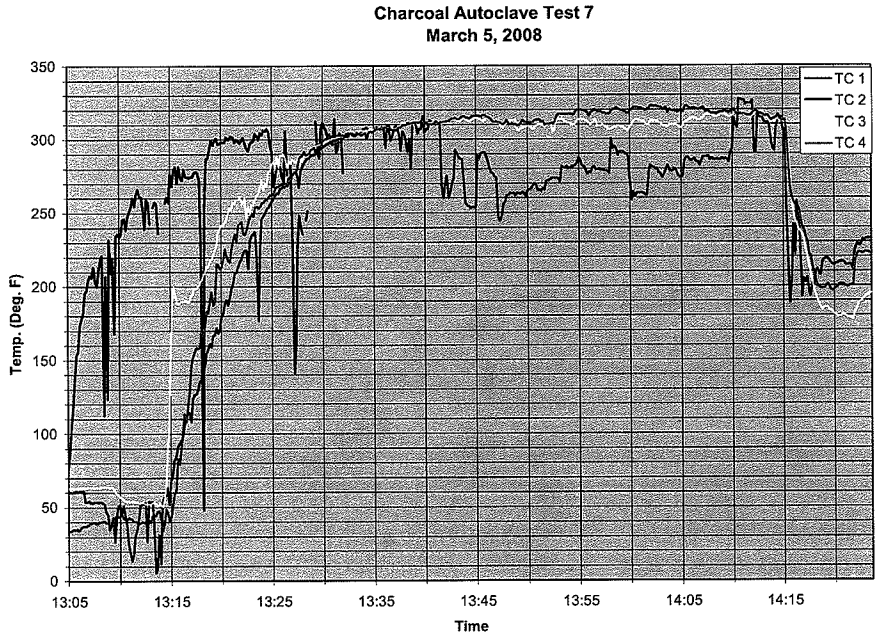
The autoclave operation was started at 1309 on 3/5/08. The vacuum achieved during the pre-vacuum was -9 psi or -18.3"hg.

The steam heat cycle was started at 1315.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1315	290	38.9
1330	290	39.4
1340	290	37.7
1350	290	37.5
1405	290	37.2

The following chart indicates the temperatures of the test thermocouples distributed on the trays,



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The autoclave steam heat cycle was completed at 1415 on 3/5/08.

The vent and the post vacuum cycle was completed at 1422 on 3/5/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams did not indicate a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/5/2008	1445 hrs	Test 6 Sample Concentration	= 0.33 VSL	X	0.010417 mg/M^3 / 1 VSL	=	0.00344 mg/M^3

The autoclave was open to inspect the load.

The results were similar to those obtained in test run 6. The top tray of charcoal had pock marks that may indicate water boiling out of the charcoal during the post vacuum cycle. The top tray did appear to be moist. The middle and the bottom trays appeared dry and had pock marks around the edges, but not in the middle. There was charcoal in the bottom of the autoclave that had been blown out of the trays during the cycle.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
Carbon-H-2-1	0.0389	99.998
Carbon-H-2-2	0.0182	99.999
Carbon-H-2-3	0.0508	99.997
Carbon-H-2-4	0.0276	99.999
Carbon-H-2-5	0.0515	99.997
Average DRE % for Bulk Carbon Test 2:		**99.998**

Test Run 8 - Charcoal Filter

Feed set up

This test used one processing tray as identified in the test plan. The charcoal filter was placed on top of the processing tray. This allowed an air space around the entire filter. The filter was filled with charcoal directly in front of the autoclave. The sachets were placed at varying levels as the charcoal was added. Wires were placed on the sachets to allow removal without empting the charcoal filter. The filter was loaded with 46 lbs. of charcoal.

Test Description

The autoclave temperature set point was changed from the test plan to 290°F. The autoclave steam cycle was set at 60 minutes. Four thermocouples were place in the filter.

The tray was loaded at 1505 on 3/5/08 and the door closed.

The autoclave operation was started at 1510 on 3/5/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The steam heat cycle was started at 1515.

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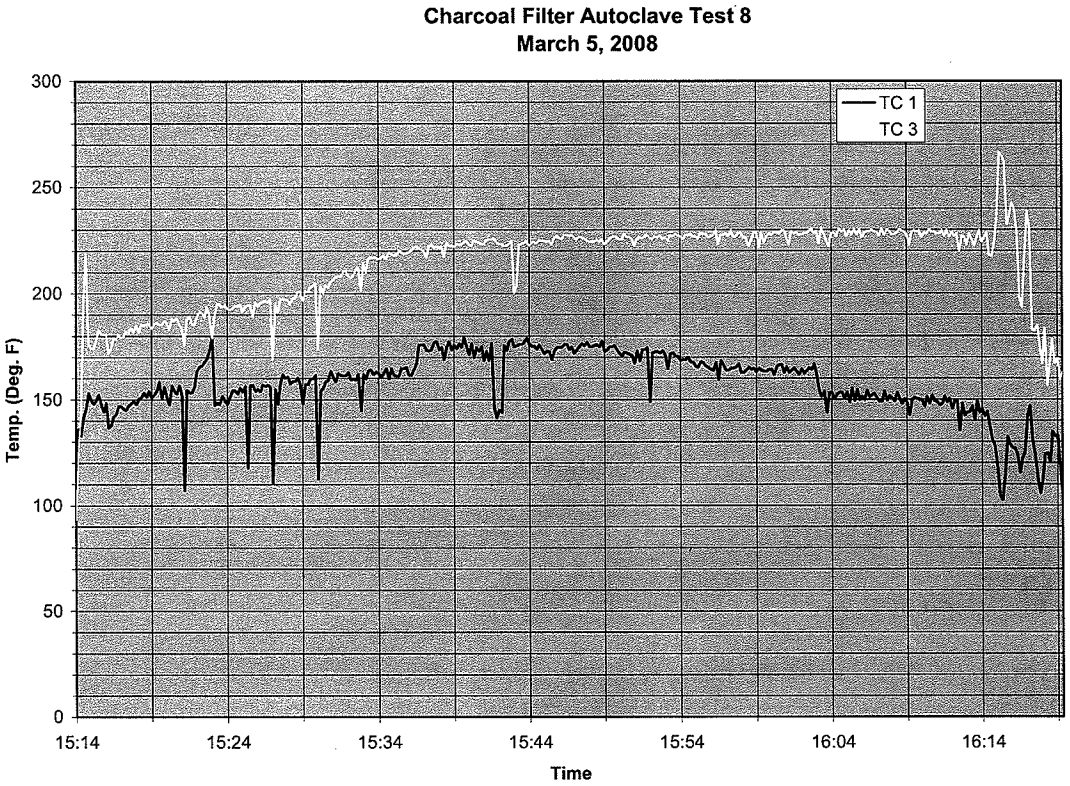
Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1515	290	40.7
1530	290	40.6
1540	290	40.9
1555	290	40.5
1609	290	40.4

The following chart indicates the temperatures of the test thermocouples distributed in the filter:

Note: TE's appear to be grounded through the autoclave on this test and do not indicate properly.



Note: TE's appear to be grounded through the autoclave on this test and do not indicate properly.

The autoclave steam heat cycle completed at 1615 on 3/5/08.

The vent and the post vacuum cycles were completed at 1642 on 3/5/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams did not indicate a significant amount of surrogate present as vapor in the autoclave head space.

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Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/5/2008	1645 hrs	Test 7 Sample Concentration	= 0.23 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.002396 mg/M^3

The autoclave was open to inspect the load.

The charcoal filter cover was removed. The charcoal appeared dry and the sachets were removed without dumping out the charcoal.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
Carbon-H-3-1	0.0373	99.998
Carbon-H-3-2	0.0098	99.9995
Carbon-H-3-3	0.0253	99.999
Carbon-H-3-4	0.0508	99.997
Carbon-H-3-5	0.0298	99.999
Average DRE % for Carbon (Filter):		**99.998**

Test Run 9 (4 in Test Plan) - Tap gear

Feed set up

One 6 mil. Polyethylene bag was utilized to contain the tap gear. The bag was cut to allow steam penetration in case it did not deteriorate. The bag contained approximately 60 lbs of TAP gear (boots only).

Test Description

The autoclave temperature set point was changed from the test plan to be 290°F. The autoclave steam cycle was set at 60 minutes. Four thermocouples were placed at various points within the bagged material.

The bin was loaded at 0734 on 3/6/08 and the door closed.

The autoclave operation was started at 0735 on 3/6/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The pre-steam heat cycle started at 0740. A steam leak was noticed around the autoclave door and the process stopped to correct the problem. The o-ring around the door had come out of its groove and was pinched between the door and the autoclave vessel. The o-ring was placed back in the groove and the seal area cleaned.

The autoclave operation was restarted at 0749 on 3/6/08.

The autoclave heat cycle was started at 0754 on 3/6/08.

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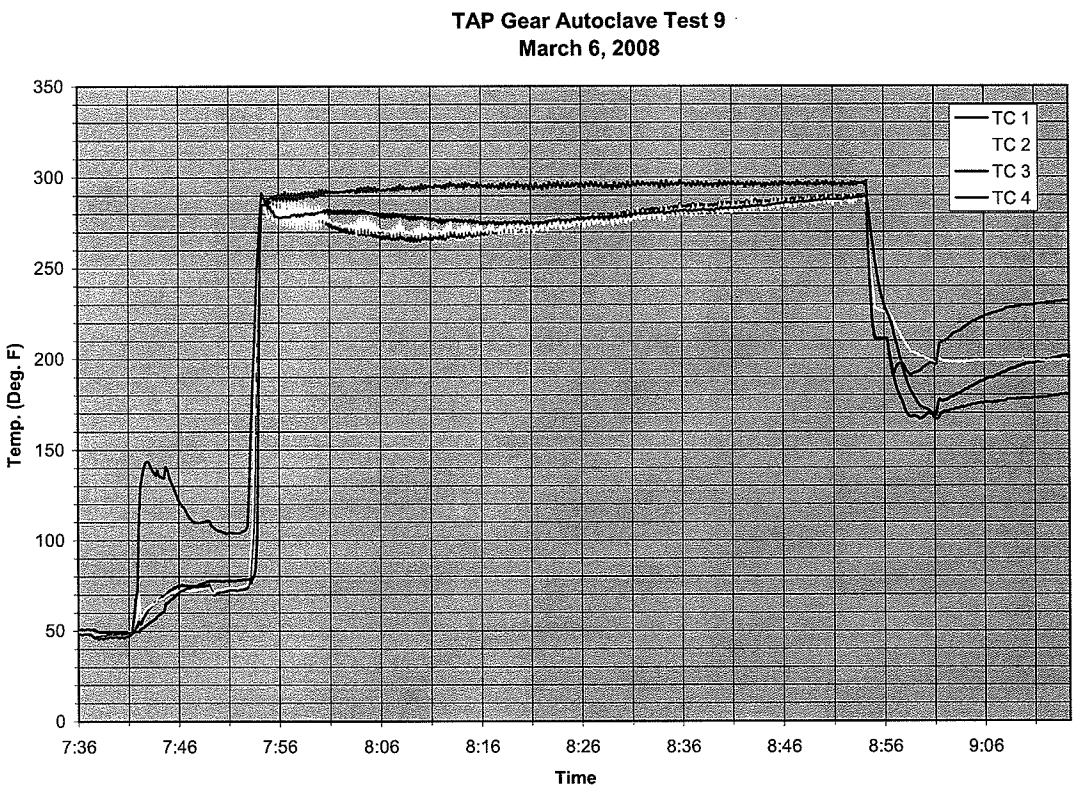
Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
0800	288	36.3
0812	291	40.1
0827	290	41.9
0845	290	41.0
0855	290	41.0

The following chart indicates the temperatures of the test thermocouples distributed around the boots:



The autoclave steam heat cycle was completed at 0901 on 3/6/08.

The vent and the post vacuum cycles were completed at 0910 on 3/5/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams did not indicate a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/6/2008	0930 hrs	Test 8 Sample Concentration	= 2.95 VSL	X	0.010417 mg/M^3 / 1 VSL	=	0.030729 mg/M^3

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The autoclave was open to inspect the load.

The polyethylene bag was significantly melted. The TAP boots were still in excellent condition.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
TAP-H-1	2.96	99.85
TAP-H-2	2.19	99.89
TAP-H-3	1.65	99.92
TAP-H-4	5.72	99.71
TAP-H-5	8.17	99.59
	Average DRE % for TAP Gear:	**99.79**

Test Run 10 (9 in Test Plan) - Dirt

Feed set up

This test used three trays as identified in the test plan. The trays are each 24" square with 2" separation between them. Each tray contained approximately 28 lbs of Dirt (Home Depot potting soil) for a total of 76 lbs of dirt per load. Sachets were placed in each tray at the middle and corners using a total of 10 sachets.

Test Description

The autoclave temperature set point was changed from the test plan to be 290°F. The autoclave steam cycle was set at 60 minutes. Four thermocouples were place in the trays, two in the top tray, and one in the center of the middle and bottom trays.

The autoclave operation was started at 0952 on 3/6/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The autoclave heat cycle was started at 0957 on 3/6/08.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1000	289	40.5
1010	290	41.9
1020	290	41.6
1030	290	41.7
1045	290	41.3

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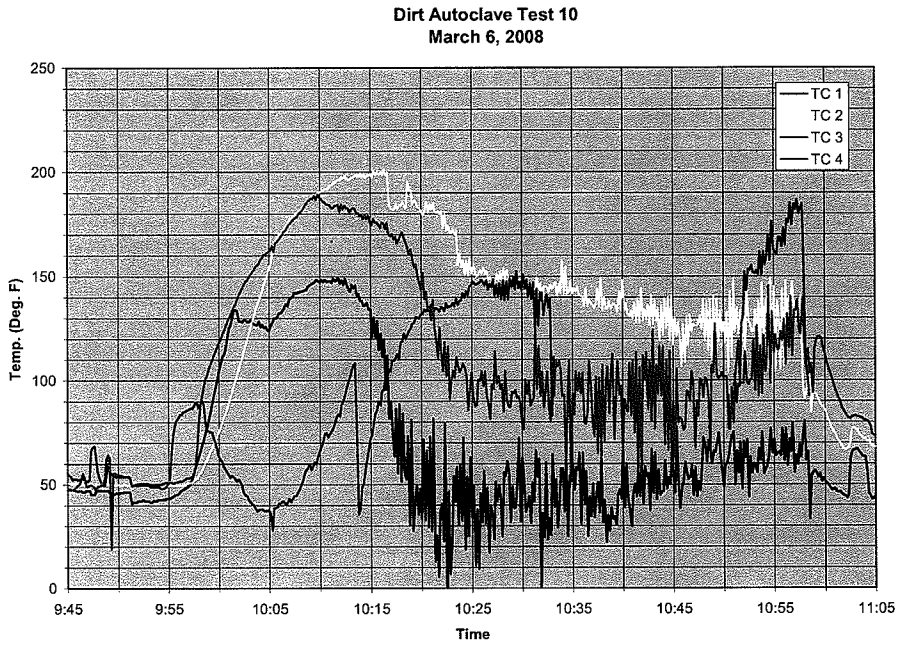
The following chart indicates the temperatures of the test thermocouples distributed around the soil:
Note: TE's appear to be grounded through the autoclave on this test and do not indicate properly



The autoclave steam heat cycle was completed at 1057 on 3/6/08.

The vent and the post vacuum cycles were completed at 1104 on 3/6/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams did indicate a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/6/2008	1130 hrs	Test 9 Sample Concentration	= 1.71 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.01781 mg/M^3

The autoclave was open to inspect the load.

The dirt appeared moist and pock marks were noted in the upper tray and around the edges of the middle and lower trays. Indications were similar to those noted in the bulk charcoal tests.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
Soil-H-1	0.00308	99.99985
Soil-H-2	Not Detected (<0.001)	>99.99995
Soil-H-3	0.00328	99.99984
Soil-H-4	0.0046	99.99977
Soil-H-5	Not Detected (<0.001)	>99.99995
	Average DRE % for Soil:	**>99.99987**

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Test Run 11 (duplicate of test 2 in Test Plan with some modifications) - DPE Suits

Feed set up

The autoclave bin was set inside the autoclave and a high temperature plastic bin liner placed in the bin. A polyethylene bag was loaded with approximately 10 lbs of DPE suit pieces. Sachets were placed in the bagged material and surrogate solution sprinkled as evenly as possible throughout the load. The polyethylene bag was cut to make sure the suits and the surrogate materials were exposed to the process steam. This test is intended to demonstrate if mass makes a difference in decontamination of the material.

Four thermocouples were randomly placed around the bag for temperature monitoring.

Test Description

The autoclave temperature set point was 250°F. The autoclave steam cycle was set at 60 minutes.

The bin was loaded at 1152 on 3/6/08 and the door closed.

The autoclave operation was started at 1155 on 3/6/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

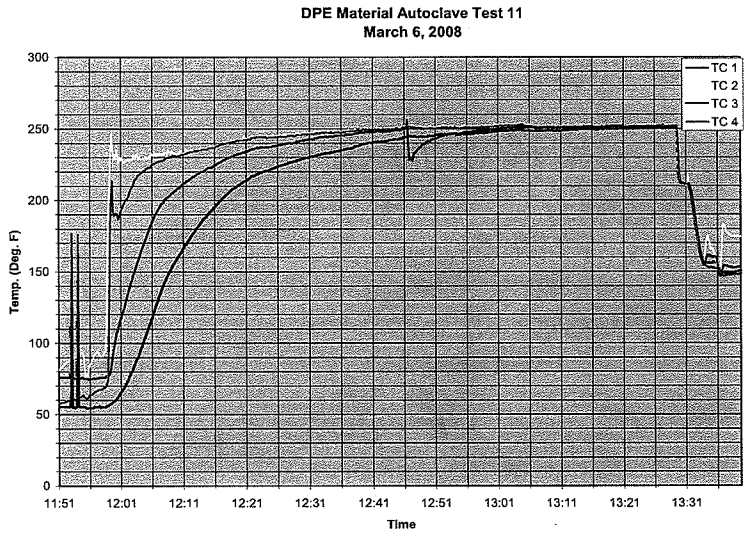
The steam heat cycle was started at 1200.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1210	249	15.0
1220	250	17.0
1230	250	14.7
1240	250	15.1
1250	250	14.6

At 1224 the TE's in the suits reached 220°F.

The following chart indicates the temperatures of the test thermocouples distributed in the suit material.



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The autoclave steam heat cycle was completed at 1310 on 3/6/08.

The vent and the post vacuum cycles were completed at 1337 on 3/6/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/6/2008	1400 hrs	Test 10 Sample Concentration	= 2.73 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.028438 mg/M^3

Preparations were made to restart cycle in an attempt to decontaminate suits.

The autoclave operation was re-started at 1402 on 3/6/08.

Started the autoclave heat soak at 1414 on 3/6/08.

Autoclave temperature was set at 250°F. Pressure was set at 14 to 15 psig.

Autoclave cycle was completed at 1515 on 3/6/08.

Final vent was completed at 1520 on 3/6/08.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/6/2008	1545 hrs	Test 11 Sample Concentration	= 1.66 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.017292 mg/M^3

Made preparations to restart cycle in an attempt to decontaminate suits.

Re-started the autoclave operation at 1547 on 3/6/08.

Started the autoclave heat soak at 1551 on 3/6/08.

Autoclave temperature was set at 250°F. Pressure was set at 14 to 15 PSIG

Autoclave cycle was completed at 1651 on 3/6/08.

Final vent was complete at 1658 on 3/6/08.

The mini-cams indicated surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/6/2008	1720 hrs	Test 12 Sample Concentration	= 1.32 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.01375 mg/M^3

Completed testing for the day.

It is apparent that the surrogate vapor may not be hydrolyzing very quickly in the vapor phase based on the above testing. The autoclave chamber is vented and placed under a post vacuum but is not purged. Tomorrow morning we will try some quick tests to see if opening the autoclave door between cycles makes a difference.

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Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
DPE-H-4-1	3.52	99.82
DPE-H-4-2	4.05	99.80
DPE-H-4-3	14.4	99.28
DPE-H-4-4	Not Detected (<0.6)	>99.97
DPE-H-4-5	4.50	99.78
Average DRE % for Shredded DPE:		**>99.73**

Test Run 12 (not in test plan) - Surrogate only in tray

Feed set up

This test used two trays as identified in the test plan. The trays are each 24" square with 2" separation between them. No waste medium was placed in the trays. Surrogate sachets and solution only were placed in a sample jar in the middle of the tray.

Test Description

The autoclave temperature set point was changed from the test plan to be 250°F. The autoclave steam cycle was set at 60 minutes. No thermocouples were used in this test.

The autoclave cycle was started at 0729 on 3/7/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The autoclave heat cycle started at 0735 on 3/7/08.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
0740	248	16.8
0800	250	16.0
0815	250	15.6
0830	250	15.2

The autoclave steam heat cycle was completed at 0835 on 3/6/08.

The vent and the post vacuum cycles were completed at 0841 on 3/6/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/7/2008	0905 hrs	Test 13-A Sample Concentration	= 2.54 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.026458 mg/M^3

The autoclave was open in an attempt to purge the vapor space. The door was opened for approximately 60 seconds and closed to allow another minicams sample. It was noted when the door was open that there was very little liquid left in the sample jar. The liquid may be condensate.

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The following Minicams sample indicated a significant quantity of surrogate, although lower than the first measurement.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/7/2008	0910 hrs	Test 13-B Sample Concentration	= 1.46 VSL	X	$\frac{0.010417 \text{ mg/M}^3}{1 \text{ VSL}}$	=	0.015208 mg/M^3

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
DPE-H-5-1	60.3	96.98
DPE-H-5-2	23.8	98.81
DPE-H-5-3	118	94.09
DPE-H-5-4	130	93.49
DPE-H-5-5	112	94.39
Average DRE % for DPE Sachet:		**95.55**

Test Run 13 (not in test plan) - Uncontaminated DPE suit in Polyethylene bag

This test was conducted to determine if the DPE suits will hold up at a processing temperature of 270°F and if the 6 mil polyethylene bags will melt at this temperature.

Feed set up

Two uncontaminated DPE suits were loaded into one 6 mil polyethylene bag. The bag was tightly closed using duct tape similar to the closing method used at TOCDF. The autoclave bin was lined with the autoclave bin liner and the bag containing the DPE suits was place in the bin.

Test Description

The autoclave temperature set point was 270°F. The autoclave steam cycle was set at 60 minutes. No thermocouples were used in this test.

The autoclave cycle was started at 0932 on 3/7/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The autoclave heat cycle was started at 0937 on 3/7/08.

Autoclave conditions recorded during the processing cycle:

Time	Temperature, °F	Pressure, Psig
1000	270	26.1
1010	270	26.4
1025	270	26.5

The autoclave steam heat cycle was completed at 1037 on 3/7/08.

The vent and the post vacuum cycles were completed at 1042 on 3/7/08 and the 15 minute hold time for the mini-cams test started.

The autoclave was open to inspect the load.

The bag had melted and the DPE suits were still intact.

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Test Run 14 (duplicate of test 2 in Test Plan with some modifications) - DPE Suits

Feed set up

Two DPE suits were loaded into one 6 mil polyethylene bag. The bag was tightly closed using duct tape similar to the closing method used at TOCDF. The suits were contaminated with the surrogate naphthalene solution and the 10 sachets were placed throughout the bag. The autoclave bin was lined with an autoclave bin liner and the bag containing the DPE suits was place in the bin.

Test Description

The autoclave temperature set point was 280°F. The autoclave steam cycle was set at 60 minutes. No thermocouples were used in this test.

The autoclave cycle was started at 1106 on 3/7/08. The vacuum achieved during the pre-vacuum was -9 Psi or -18.3"hg.

The autoclave heat cycle was started at 1110 on 3/7/08.

The autoclave operated at 280°F and 32 to 33 Psig throughout the processing cycle.

The autoclave steam heat cycle was completed at 1210 on 3/7/08.

The vent and the post vacuum cycles were completed at 1217 on 3/7/08 and the 15 minute hold time for the mini-cams test was started.

The mini-cams indicated a significant amount of surrogate present as vapor in the autoclave head space.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/7/2008	1240 hrs	Test 14-A Sample Concentration	= 2.64 VSL	X	0.010417 mg/M^3 / 1 VSL	=	0.0275 mg/M^3

The autoclave door was opened for one minute and closed for re-sampling.

Date	≈Time		MINICAMS Result		1 VSL		Concentration
3/7/2008	1310 hrs	Test 14-B Sample Concentration	= 1.58 VSL	X	0.010417 mg/M^3 / 1 VSL	=	0.01646 mg/M^3

The autoclave was open to inspect the load.

Inspection showed that the bag containing the DPE suits had melted, allowing the steam to access the suits. The DPE suits were still intact.

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DPE suit following autoclave processing at 280°F.

Extraction analysis

Sample I.D.	Chloromethylnaphthalene µg/sample	Chloromethylnaphthalene DRE, percent
DPE-H-6-1	90.2	95.49
DPE-H-6-2	873	56.34
DPE-H-6-3	71.3	96.43
DPE-H-6-4	901	54.94
DPE-H-6-5	24.6	98.77
Average DRE % for Bulk DPE:		**80.39**

V. Sampling and Analysis

Samples from nine (9) tests conducted during the week of 3-7 March 2008 were analyzed by GC/MS/SIM for the agent surrogate chloromethylnaphthalene. Two sets of five sachets containing a small mass (1 to 4 grams) of the waste matrix were distributed among the bulk waste articles being autoclaved in each test. One set of five sachets was spiked at a "High" loading value of 2 milligrams of chloromethylnaphthalene per sachet. The second set of five sachets was spiked at a "Low" loading value of 1 microgram of chloromethylnaphthalene per sachet. A draft report summarizing the analytical results obtained by Southwest Research Institute® (SwRI®) from the samples collected during the series of autoclave tests is contained in appendix A.

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A valid Destruction and Removal Efficiency (DRE) was not able to be calculated from the Low spike samples. The residual mass found on the majority of the sachets was either below the instrument detection limit or at a level comparable to the field blanks. The bulk waste in each test was also spiked with 1.4 grams of chloromethylnaphthalene mixed into 25 milliliters of toluene. The spiked toluene solution was sprinkled throughout the bulk waste items. The presence of this large quantity of chloromethylnaphthalene inside the autoclave further confounded interpretation of the "Low" spike sachet sample results. Some sachets yielded a residual mass greater than their theoretical spike values.

Only the analytical results from the High spike samples are felt to be representative of the DRE achieved by the autoclave relative to the different waste matrices. The analytical data from the High spike samples summarizing the residual masses of chloromethylnaphthalene recovered from the samples and the subsequent DRE values are presented for each test.

VI. Conclusions and Recommendations

The autoclave surrogate testing demonstrates the ability to decontaminate chemical weapons demilitarization secondary wastes in an autoclave. Based on these tests, there is a relatively wide range of decontamination levels that may be achieved, depending on the waste being processed. This may be due to the surrogate and / or carrier fluid selection. In order to eliminate results biased by the surrogate and / or carrier fluid selection, it is recommended that testing be conducted in an chemical agent certified laboratory using the chemical agents GB, VX and HD to determine the exact reaction of these chemicals. The surrogate chloromethylnaphthalene should also be tested without a carrier fluid under the same conditions as the chemical agents to identify the reaction differences between the surrogate and the chemical agents.

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APPENDIX C

Section 4.0

J. Scott, R. Martinez,
Autoclave Secondary Waste VX on DPE, Wood, and Charcoal,
Final Report,
Southwest Research Institute,
San Antonio, TX,
February, 2009.

AUTOCLAVE SECONDARY WASTE
VX ON DPE, WOOD AND CHARCOAL

Final Report

Prime Contract DACA87-89-C-0076
Subcontract G51972
SwRI® Project 01.14121

Prepared by:

Jim Scott
Robert Martinez

Prepared for:

EG&G Defense Materials, Inc.
11600 Stark Road
Stockton, UT 84071

December 12, 2008

SOUTHWEST RESEARCH INSTITUTE®
6220 Culebra Road • P.O. Drawer 28510
San Antonio, Texas 78228-0510

SOUTHWEST RESEARCH INSTITUTE®
6220 CULEBRA ROAD • P.O. DRAWER 28510
SAN ANTONIO, TEXAS 78228-0510

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Stockton, UT 84071

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APPROVED:

Brewer for

Michael G. MacNaughton, Ph.D., P.E.
Vice President
Chemistry and Chemical Engineering Division

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1. INTRODUCTION

The Tooele Chemical Agent Disposal Facility (TOCDF) is currently planning for processing of secondary and closure wastes. Installation of a system specifically for processing of secondary wastes would allow parallel processing of secondary wastes, increase the availability of the Metal Parts Furnace (MPF) to process munitions, and shorten the facility's overall schedule. In an earlier study, Continental Research & Engineering (CR&E) conducted an investigation of processing alternatives and found that the treatment of secondary waste through an autoclave is an attractive processing alternative due to its relative low cost and short implementation schedule. In addition, autoclaves have been used successfully by the Army for decontamination of BDO suits contaminated with chemical agents GB and VX, and Battelle has evaluated HD destruction in an autoclave environment for the Pueblo Chemical Agent-Destruction Pilot Plant Project (PCAPP).

In this project, Southwest Research Institute® (SwRI®) was tasked to conduct decontamination experiments using a commercial-off-the-shelf (COTS) bench model autoclave. The objectives of the test program were to: (1) obtain analytical results documenting the capability of an autoclave system to decontaminate secondary wastes contaminated with chemical agents (i.e., 'proof-of-concept' tests); and (2) document the operating/processing parameters (temperature, time, pressure, and vacuum) needed by the bench model autoclave to achieve a given level of decontamination performance.

SwRI® performed autoclave tests to treat three solid matrices contaminated with neat VX agent – DPE, wood, and charcoal. The tests were performed in triplicate. The test results are summarized in this report.

2. EXPERIMENTAL APPROACH

2.1 Test Procedure

The experimental approach for the test program is detailed in "Test Plan for Barnstead – Harvey Autoclave Agent Testing," Draft – E, Revision 2, dated July 7, 2008. The Test Plan presents a detailed description of the operational and test procedures employed during the experiments, and it is referenced here for additional information.

A couple of modifications to the original test plan had to be adopted as the capabilities of the autoclave became apparent and impediments to the original vapor monitoring technique were discovered during early tests. These are discussed in Section 3.1. The modifications were necessary to yield reproducible test results indicative of the autoclave performance. A synopsis of the modified test procedure follows:

- A 10-gram sample of the secondary waste matrix (DPE, wood, or charcoal) is spiked with 900 micrograms (µg) of neat chemical agent VX.
- The spiked sample is placed on a tray inside the autoclave, positioned so that the sample is near the rear of the chamber, and the door is closed.
- After approximately 45 minutes, the agent vapor concentration inside the headspace of the autoclave is monitored using a near-real time monitor (MINICAMS).

- Since the autoclave is limited to a maximum exposure time of 99 minutes for a single cycle, the autoclave is operated at 275 °F for two, 90-minute exposure cycles using the "Unwrapped" program cycle (i.e., a total exposure time of 180 minutes at 275 °F). Each exposure cycle is followed by a 30-minute drying cycle before venting.

- A 10 to 12 minute period of time elapses between the two exposure cycles to permit recovery of the water and vapor condensate discharges collected from the first cycle.

- At the conclusion of the second 90-minute exposure cycle, the agent vapor concentration inside the headspace of the autoclave is monitored using a near-real time monitor (MINICAMS).

- The spiked sample is recovered from the autoclave and assayed for residual agent content along with the liquid and vapor condensate discharges from both exposure cycles utilizing the analytical protocols referenced in the Test Plan.

- The CycleStor data files detailing the operating conditions for each of the two cycles are downloaded for documentation.

- Following a test, with the autoclave empty, the autoclave is operated for a 90-minute exposure cycle at 275 °F followed by a 30-minute drying cycle to purge any residual VX from the autoclave chamber headspace and the discharge lines prior to the next test. This purge cycle typically occurs at the end of the day and the autoclave door remains latched in the closed position, but unsealed, overnight. Headspace monitoring of the autoclave chamber prior to a test yields VX concentrations at baseline levels (typically 0.02 to 0.06 VSL).

Testing of charcoal contaminated with VX chemical agent followed the DPE and wood tests. As will be described in Section 3.4 of this report, the performance of the autoclave became unpredictable when attempting to operate it at 275 °F for two, back-to-back, 90-minute exposure cycles. Whether this situation was caused by deterioration of components within the autoclave, or issues related to the waste matrix (i.e., minute particles of charcoal dust clogging fill/purge lines) is uncertain. Regardless of the cause, the treatment process for the charcoal tests had to be altered with the objective of trying to expose the contaminated charcoal to 275 °F for 180 minutes in sequential cycles as it was for the DPE and wood tests.

2.2 Waste Discharges

Again, the Test Plan presents a detailed description of the procedures employed to collect the waste discharges from the autoclave for subsequent agent analyses. To reiterate, there are two waste discharges from the autoclave:

- Water – In the "Unwrapped" cycle, 400 mLs of deionized water is automatically added into the autoclave chamber during the pre-vacuum stage. The loading inside the chamber is very small (10 grams of waste) compared to the 12-pound maximum loading limit for the "Unwrapped" cycle (according to the manufacturer's Operation Manual). Thus, only a small percentage of this water volume can be adsorbed into the waste matrix (this water is recovered from the waste matrix during the drying stage). Consequently, at the end of the exposure cycle, approximately 250 mLs of water remains inside the chamber. This excess water is expelled from the chamber by the pressure (~ 31 to 32 psig) present inside the chamber.

- Vapor Condensate – During the pre-vacuum and drying stages, the autoclave vacuum pump is used to attain a negative pressure (~ -10 to -13 psig) inside the chamber. As the vapor is pulled from the chamber it passes through a heat exchanger upstream of the pump. The discharge from the vacuum pump consists of condensate and vapors.

The original plumbing of the autoclave directed both of the waste discharges into a polymeric waste tank. Since the intent was to analyze each waste discharge separately, the plumbing was modified to accomplish this task. Figure 1 presents a schematic of the waste discharge collection system. The water discharge is routed to two, 500-mL traps in series immersed in ice. The vapor condensate discharge is routed to an identical 500-mL trap, followed by a 500-mL impinger filled with 150 mL of triacetin; again both vessels are immersed in ice. Please note that Figure 1 does not show the plumbing configuration that enabled the MINICAMS to directly monitor the headspace of the autoclave chamber. As discussed in the next section, this approach for the headspace monitoring had to be abandoned, and the plumbing was removed at the end of the initial test series. Hence, Figure 1 illustrates the system, as it existed for the 'official' performance tests.

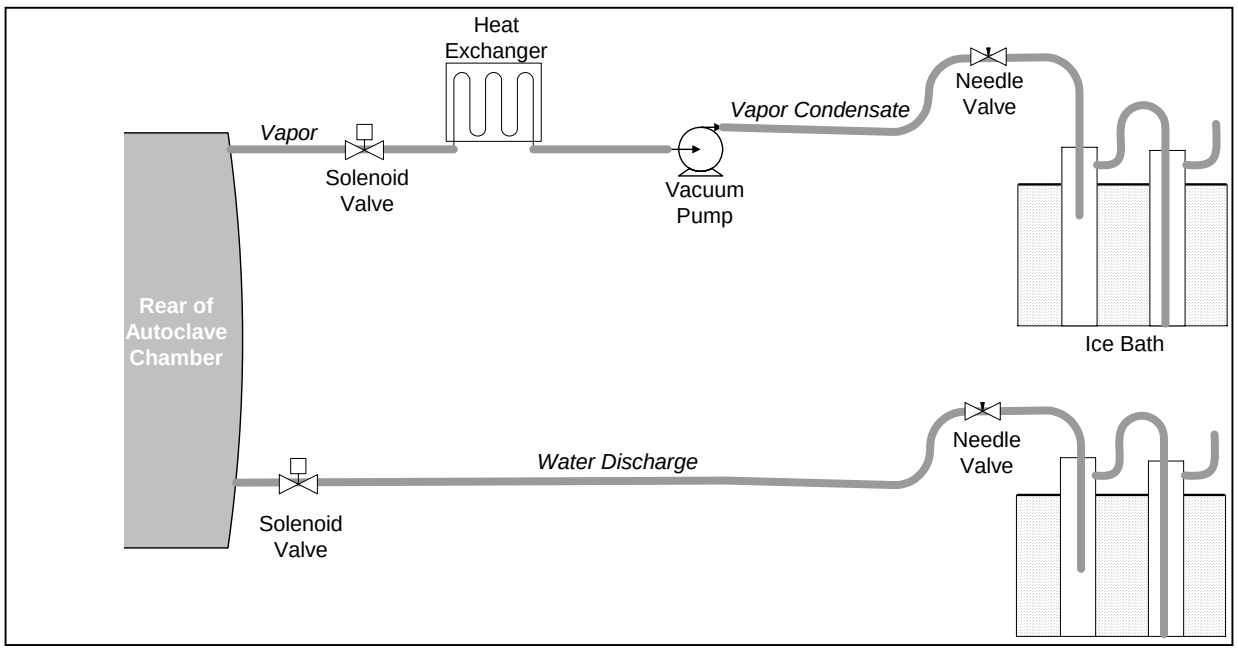

Figure 1. Waste discharge collection system.

3. FINDINGS

3.1 Initial VX Tests

A series of six (6) tests with VX agent were performed during which 'lessons learned' were discovered concerning the autoclave performance and the VX vapor monitoring technique. Subsequent modifications to the Test Plan were adopted to alleviate the discovered deficiencies. These initial tests are described below solely to document the rationale for the Test Plan modifications. The results for the remaining tests, as presented in the next section, represent the 'official' performance results obtained by the autoclave using the operating procedures as summarized above.

It is stressed that during the first five tests, the pre- and post-exposure vapor monitoring technique for the autoclave chamber headspace was implemented exactly as described in the Test Plan. That is, the chamber headspace was monitored directly by the MINICAMS using a port located in the rear of the chamber (see Figure 2). A series of two, 3-way valves were utilized to a vacuum pump to pull the chamber headspace sample into the MINICAMS during the pre- and post-exposure monitoring periods. During the autoclave cycle, the valves were switched to route the vapor discharge to the heat exchanger while the MINICAMS monitored the air inside the glove box.

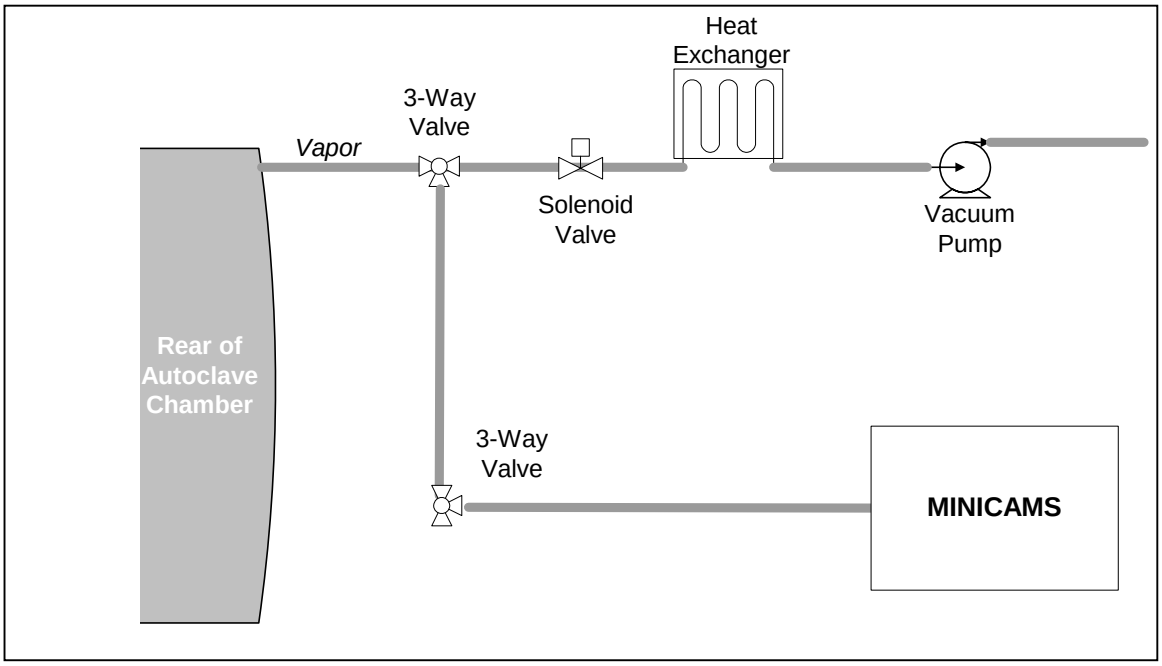

Figure 2. Direct headspace monitoring of autoclave chamber using MINICAMS.

For the pre-exposure monitoring, the autoclave door remained sealed (i.e., the chamber remained completely closed from the time the spiked sample was loaded into chamber until the monitoring began). For the post-exposure monitoring, the automatic program sequence for the autoclave unseals the door at the conclusion of the drying period. However, the door remains latched in the closed position, and the MINCAMS pulled the headspace sample from the rear of the chamber.

3.1.1 VX – DPE Test #1

Preliminary tests performed by SwRI spiking onto wood with VX had indicated that a loading of approximately 400 µg of neat agent should yield a desirable vapor concentration within the 20-Liter chamber headspace (targeting a concentration of ~ 10 VSL). However, using this dosage mass in the first test with a 10-gram swatch of DPE (20-mil) only yielded a pre-exposure VX vapor concentration of 5.0 VSL. The autoclave cycle for this test was performed as detailed in the Test Plan: an "Unwrapped" cycle with a 60-minute exposure period at 275 °F followed by a 30-minute drying period. Following the conclusion of the drying period, the post-exposure VX vapor concentration inside the headspace was 0.48 VSL. Although the post-exposure vapor concentration was acceptable (i.e., < 1.0 VSL), the lower-than-anticipated vapor concentration obtained prior to initiation of the autoclave cycle caused us to seek a higher spiking level for the subsequent tests.

3.1.2 VX – DPE Tests #2 & #3

In these two tests, the autoclave operating conditions remained unchanged, but the spike level was increased to 900 µg of neat VX. Despite the increase, the pre-exposure VX headspace concentrations remained low (0.76 and 3.3 VSL for tests #2 and #3, respectively). The post-exposure vapor concentrations (0.32 and 0.57 VSL for tests #2 and #3, respectively) continued to show that the 60-minute exposure period and 30-minute drying period was yielding satisfactory results. The decision was made to keep the dosage at 900 µg for the upcoming tests of VX on wood.

3.1.3 VX – Wood Tests #1 & #2

Short segments of wooden dowels (untreated, 3/8-inch diameter) totaling 10 grams were used for the wood tests. A shallow depression was punched into the side of one of the dowel segments as a 'receptacle' for the VX spike. The spike loading remained at 900 µg and the autoclave operating conditions remained unchanged from the DPE tests. The pre-exposure VX vapor concentrations inside the chamber were comparable to the levels seen in the DPE tests (3.0 and 1.2 VSL for tests #1 and #2, respectively).

The post-exposure VX vapor concentration in Test #1 was 0.46 VSL, however, numerous interferences were observed in the MINICAMS chromatogram that may have affected measurement of the true agent concentration. Following the test, the heat-trace sampling line for the MINICAMS was cleaned and droplets of water were observed near the AgF conversion pad. The AgF conversion pad was replaced and additional heat tape was wrapped around the vapor sampling line at the rear of the autoclave chamber.

The post-exposure VX vapor concentration in Test #2 was 3.49 VSL, however, the validity of this measurement was uncertain, as the interferences were even worse than observed in the previous test despite the additional heat tape and line cleaning. Further investigation of the sampling line revealed that the AgF conversion was soaked by condensed water. Flushing the sampling line with solvent revealed traces of residue. It was apparent that moisture from the autoclave chamber was capable of entering the MINICAMS sample line, and that this moisture was gradually fouling the line and the AgF pad over successive cycles.

Therefore, to obtain reliable vapor concentration measurements, the monitoring approach given in the Test Plan (and illustrated in Figure 2) had to be abandoned. The pre- and post-exposure vapor monitoring of the chamber headspace is currently accomplished by inserting the MINICAMS sample line directly into the chamber via the door. A short length of ¼-inch stainless steel tubing is placed on the end of the MINICAMS heat-trace line, with an AgF conversion pad positioned on the distal end of the steel tubing. The length of the steel tubing is just long enough to place the AgF conversion pad in the middle of the autoclave chamber. To obtain the pre-and post-exposure vapor concentrations, the autoclave door is cracked open just wide enough to slip the ¼-inch stainless steel tubing past the door, and then the door is pressed tightly against the tubing.

3.1.4 VX – DPE Test #4

With the change to the vapor monitoring protocol, an additional test was performed using spiked DPE. The purpose of the test was to ascertain whether the changed protocol affected the promising results that were observed during the first three tests. This test did show that the vapor readings obtained by the MINICAMS utilizing the sampling line connected into the earlier tests were misleading:

- Spiking 900 µg of VX onto the DPE sample yielded a pre-exposure VX vapor concentration in the chamber headspace of 12.5 VSL, more than double the level seen in any of the prior measurements.

- After the completion of the 60-minute exposure period and 30-minute drying period, the post-exposure VX vapor concentration inside the chamber was 13.2 VSL. A second measurement collected 35 minutes later yielded a VX vapor concentration of 3.0 VSL.

- The autoclave cycle was repeated (60-minute exposure period and 30-minute drying period) on this same sample. The post-exposure VX vapor concentration inside the chamber following the second cycle was initially 3.3 VSL, with a second reading of 1.30 VSL obtained 14 minutes later.

The conclusions derived from these early tests were:

- The plumbing arrangement devised to enable the MINICAMS to directly sample the autoclave chamber obviously caused erroneously low VX vapor concentration measurements at both the pre- and the post-exposure time periods.

- Although cracking the door slightly ajar to insert the sample line into the autoclave chamber is less than ideal, it afforded more reliable vapor concentration measurements than the protocol originally specified in the Test Plan.

- The time required to achieve acceptable VX vapor concentrations (<1.0 VSL) inside the chamber was greater than could be achieved by a single cycle (limited by the autoclave program to 99 minutes). The decision was made to operate two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period, for each test.

- The water and vapor condensate discharges for each of the two cycles in a test are collected at the completion of their respective cycle and analyzed separately (Tables 3 and 6).

3.2 Triplicate VX Test Results for DPE

Table 1 presents the headspace vapor measurements obtained for the 'official' triplicate autoclave tests performed with 900 µg of neat VX agent spiked onto 10-gram swatches of 20-mil DPE. To re-iterate, each test consists of two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period. The post-exposure vapor concentration is obtained immediately after the completion of the drying period in the second cycle. In addition, a second post-exposure vapor concentration measurement is collected 28 minutes after the initial measurement (the MINICAMS sample/purge cycle for VX is 7 minutes; collecting a sample after 4 cycles was a somewhat arbitrary selection, but it approximated a 30-minute 'hold' period at the conclusion of a cycle that possibly might be imposed upon an operational autoclave before the door was opened).

Table 2 summarizes: (1) the residual VX agent found in the spiked DPE sample after undergoing the two successive autoclave cycles in a test, and (2) the DRE percentage calculated by comparing the residual VX mass to the spike mass of 900 µg.

A discussion of these results is given in Section 4 following the presentation of the remaining VX test data.

Table 1. VX Vapor Headspace Concentrations inside Autoclave Chamber for DPE Spiked with 900 Micrograms of VX

Test	Pre-Exposure Concentration, VSL	Initial Post-Exposure Concentration, VSL	Post-Exposure + 28 Minutes Concentration, VSL
1	11.0	1.49	0.68
2	15.9	1.01	0.31
3	16.9	0.44	< 0.06

Table 2. VX DRE for DPE Spiked with 900 Micrograms of VX

Test	Residual VX in DPE, micrograms	DRE, percent
1	0.055	99.994
2	0.100	99.989
3	0.249	99.972

Table 3 summarizes: (1) the volumes of water and vapor condensate collected at the conclusion of the two individual autoclave cycles in each test, (2) the concentration of VX agent found in the water and vapor condensate samples, and (3) the total mass of VX agent in the water and vapor condensate samples.

Table 3. VX in Discharges for DPE Spiked with 900 Micrograms of VX

Test	Cycle	Discharge	Volume, mL	VX concentration, nanograms/mL	Mass of VX, micrograms
1	1	Water	265	6.94	1.84
		Condensate	160	22.3	3.57
	2	Water	290	2.43	0.71
		Condensate	155	3.44	0.53
2	1	Water	265	7.48	1.98
		Condensate	160	21.2	3.40
	2	Water	270	3.22	0.87
		Condensate	155	3.81	0.59
3	1	Water	260	8.25	2.15
		Condensate	155	26.0	4.03
	2	Water	280	3.69	1.03
		Condensate	160	5.91	0.94

3.3 Triplicate VX Test Results for Wood

Table 4 presents the headspace vapor measurements obtained for the 'official' triplicate autoclave tests performed with 900 µg of neat VX agent spiked onto 10-grams of wooden dowel segments. To re-iterate, each test consists of two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period. The post-exposure vapor concentration is obtained immediately after the completion of the drying period in the second cycle. In addition, a second post-exposure vapor concentration measurement is collected 28 minutes after the initial measurement.

Table 4. VX Vapor Headspace Concentrations inside Autoclave Chamber for Wood Spiked with 900 Micrograms of VX

Test	Pre-Exposure Concentration, VSL	Initial Post-Exposure Concentration, VSL	Post-Exposure + 28 Minutes Concentration, VSL
1	39.3	0.63	0.16
2	37.0	0.73	< 0.06
3	46.6	0.55	0.07

Table 5 summarizes: (1) the residual VX agent found in the spiked DPE sample after undergoing the two successive autoclave cycles in a test, and (2) the DRE percentage calculated by comparing the residual VX mass to the spike mass of 900 µg.

Table 5. VX DRE for Wood Spiked with 900 Micrograms of VX

Test	Residual VX in Wood, micrograms	DRE, percent
1	6.42	99.29
2	1.21	99.87
3	4.58	99.49

Table 6 summarizes: (1) the volumes of water and vapor condensate collected at the conclusion of the two individual autoclave cycles in each test, (2) the concentration of VX agent found in the water and vapor condensate samples, and (3) the total mass of VX agent in the water and vapor condensate samples.

3.4 Triplicate VX Test Results for Charcoal

Towards the conclusion of the wood tests, the autoclave began to experience difficulties maintaining the requisite 275 °F temperature for the 90-minute exposure period. Based upon recommendations obtained from the autoclave vendor, several components of the autoclave were replaced (Main Logic PC Board, chamber temperature sensor), and the autoclave temperature control system was re-calibrated. These corrective actions enabled completion of the wood tests and the special tests performed to evaluate the possible formation of EA2192 in DPE and wood contaminated with VX (Section 3.5).

Table 6. VX in Discharges for Wood Spiked with 900 Micrograms of VX

Test	Cycle	Discharge	Volume, mL	VX concentration, nanograms/mL	Mass of VX, micrograms
1	1	Water	270	6.05	1.63
		Condensate	157	12.5	1.97
	2	Water	280	5.26	1.47
		Condensate	160	2.93	0.47
2	1	Water	262	9.50	2.49
		Condensate	158	11.2	1.77
	2	Water	250	6.88	1.72
		Condensate	162	3.05	0.49
3	1	Water	260	8.15	2.12
		Condensate	155	16.5	2.56
	2	Water	280	6.68	1.87
		Condensate	160	3.97	0.64

However, these actions failed to solve the problem when testing re-commenced on charcoal contaminated with VX. The chamber temperature failed to stay at 275 °F during the 90-minute exposure period, which automatically triggered the programmed cycle to abort. In a couple of tests, the chamber pressure increased above the pre-set maximum pressure limit (38 psig) causing the cycle to abort. Again, components of the autoclave were replaced (Main Logic PC Board, chamber temperature sensor, heating element, heating element temperature sensor, heater over-temperature protection sensor, and pressure sensor), and an authorized service representative performed preventive maintenance cleaning on the solenoid valves controlling the water fill and discharge venting systems. Some traces of charcoal dust were observed in the liquid discharge solenoid and charcoal dust particles were occasionally observed in the vapor condensate discharge collections.

Following this extensive overhaul, the autoclave (empty) was operated at 275 °F for two consecutive 90-minute exposure cycles back-to-back, on 2 consecutive days without any aborted cycles occurring. However, during the very next operation of the autoclave, with 10 grams of spiked charcoal inside the chamber, the first 90-minute exposure cycle aborted due to low temperature. With the replacement of the primary operational components of the autoclave and its successful performance with an empty chamber, there does appear to be at least some circumstantial evidence that the erratic performance of the bench-scale autoclave may have been partially attributable to the charcoal.

Consequently, the triplicate autoclave tests of VX on charcoal were performed with the objective of attempting to attain a total exposure time at 275 °F that approximated the 180-minute period achieved in the DPE and wood tests. The exposure conditions for the triplicate tests are summarized below:

- Test 1: 75-minute exposure cycle at 275 °F (90-minute program aborted by low temperature), followed by a 60-minute exposure cycle at 275 °F with a 30-minute drying stage;

- Test 2: Three consecutive 60-minute exposure cycles at 275 °F, each with a 30-minute drying stage; and

- Test 3: Two consecutive 60-minute exposure cycles at 275 °F, each with a 30-minute drying stage, followed by a 48-minute exposure cycle at 275 °F (60-minute program aborted due to high pressure).

It should be noted that due to the pre-programmed settings in the software for the bench-scale autoclave, a chamber temperature that was only a few tenths of a degree (F) below the set point (275 °F) for a period of less than a minute was sufficient to trigger the cycle abortion. The autoclave vendor was contacted about the possibility of modifying the program software to allow more leeway in the conditions before the cycle would be aborted. The vendor's response was that they purchased the program from another supplier, and that they did not have the capability to re-program the software.

The activated charcoal was provided to SwRI by EG&G (clean, uncontaminated coconut shell charcoal). Per the Test Plan, the 10-grams of charcoal granules were loaded into a polymeric mesh 'sachet' that was placed onto the autoclave tray. The sachet enabled complete access of the steam to the individual particles while minimizing solid surfaces that could retain condensate. It also provided a means for retrieving all of the loose granules from the autoclave following the test for assaying. The mesh size of the sachet is such that the syringe needle could easily penetrate into the bag for direct application of the liquid agent onto the individual granules.

Table 7 presents the headspace vapor measurements obtained for triplicate autoclave tests performed with 900 µg of neat VX agent spiked onto 10-grams of charcoal. The post-exposure vapor concentration was obtained immediately after the completion of the drying period in the last exposure cycle (for Test 3, the post-exposure measurements were obtained after the chamber door opened following the conclusion of the aborted exposure cycle). As in the prior tests, a second post-exposure vapor concentration measurement was collected 28 minutes after the initial measurement.

Table 7. VX Vapor Headspace Concentrations inside Autoclave Chamber for Charcoal Spiked with 900 Micrograms of VX

Test	Pre-Exposure Concentration, VSL	Initial Post-Exposure Concentration, VSL	Post-Exposure + 28 Minutes Concentration, VSL
1	0.35	< 0.06	< 0.06
2	0.15	< 0.06	< 0.06
3	15.1	< 0.06	< 0.06

The pre-exposure headspace concentrations inside the chamber were expected to be low to the adsorption characteristics of activated charcoal. Hence, the low vapor concentrations obtained in Test 1 and 2 were not unexpected. The cause for the elevated pre-exposure headspace concentration in Test 3 is unknown.

Table 8 summarizes: (1) the residual VX agent found in the spiked charcoal sample after undergoing the autoclave cycles in the test, and (2) the DRE percentage calculated by comparing the residual VX mass to the spike mass of 900 µg.

Table 8. VX DRE for Charcoal Spiked with 900 Micrograms of VX

Test	Number of Autoclave Cycles	Total Exposure Time at 275 °F, minutes	Residual VX in Charcoal, micrograms	DRE, percent
1	2	165	4.16	99.54
2	3	180	1.03	99.89
3	3	168	3.66	99.59

Table 9 summarizes: (1) the volumes of water and vapor condensate collected at the conclusion of the individual autoclave cycles in each test, (2) the concentration of VX agent found in the water and vapor condensate samples, and (3) the total mass of VX agent in the water and vapor condensate samples.

Table 9. VX in Discharges for Charcoal Spiked with 900 Micrograms of VX

Test	Cycle	Discharge	Volume, mL	VX concentration, nanograms/mL	Mass of VX, micrograms
1	1	Water	285	0.53	0.150
		Condensate	60	7.17	0.430
	2	Water	325	0.57	0.185
		Condensate	150	1.51	0.227
2	1	Water	290	< 0.05	< 0.015
		Condensate	125	0.14	0.018
	2	Water	295	< 0.05	< 0.015
		Condensate	147	0.07	0.010
	3	Water	280	< 0.05	< 0.014
		Condensate	143	< 0.05	< 0.007
3	1	Water	275	1.06	0.291
		Condensate	145	0.67	0.097
	2	Water	282	0.61	0.171
		Condensate	146	0.70	0.102
	3	Water	294	0.92	0.269
		Condensate	100	0.40	0.040

3.5 EA2192 Tests

During the DPE and wood tests, SwRI was tasked to evaluate whether the VX degradation product EA2192 was present either in the autoclaved waste matrix or in the waste discharges. To detect and quantify EA2192, SwRI utilized a high performance liquid chromatography/mass spectrometry (HPLC-MS) analytical procedure previously developed to quantify agent decomposition products (ADPs) for the JACADS closure. Since this procedure requires extraction of solid matrices using HPLC-grade water, the EA2192 analysis could not be accomplished on the same waste sample analyzed for residual VX (i.e., the latter requires extraction with IPA/DCM solvent). Thus, separate autoclave tests had to be performed for the EA2192 analyses.

Two tests were performed for the EA2192 evaluations – one with DPE and one with wood dowels. The autoclave operational parameters were identical to the prior VX tests (two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period) and the VX spiking mass remained unchanged (900 micrograms). The EA2192 results are presented in Table 10. No detectable concentrations of EA2192 were measured in any of the spiked waste samples or in the discharges.

Table 10. EA2192 Results for DPE & Wood Spiked with 900 Micrograms of VX

Sample I.D.	Volume, mL	EA 2192ppb (ng/mL)	EA2192, micrograms
10-grams DPE spiked w/900 ug VX	-	< 2	< 0.10
DPE, Water Cycle 1	260	< 2	< 0.52
DPE, Water Cycle 2	259	< 2	< 0.52
DPE, Condensate Cycle 1	165	< 2	< 0.33
DPE, Condensate Cycle 2	160	< 2	< 0.32
10-grams wood spiked w/900 ug VX	-	< 2	< 0.10
Wood, Water Cycle 1	260	< 2	< 0.52
Wood, Water Cycle 2	275	< 2	< 0.55
Wood, Condensate Cycle 1	162	< 2	< 0.32
Wood, Condensate Cycle 2	159	< 2	< 0.32

Comparable tests were not performed with charcoal spiked with VX agent since no verified analytical method was found for EA2192 on this solid matrix.

4. DISCUSSION

Some general observations concerning the tests:

- The collection traps, immersed in ice, used to collect the water and vapor condensate discharges yielded remarkably comparable volumes among the 12-autoclave cycles that comprised the triplicate series of DPE and wood tests.

- Two traps in series are used to collect the water discharge from the chamber that occurs at the conclusion of the exposure period. Despite being a single discharge event under pressure (~ 31 to 32 psig) and at temperature (275 ºF), all but 5 to 10 mLs of the water is collected in the first trap. The installation of a needle valve to limit the flow rate of the water discharge from the autoclave chamber is largely responsible for the efficient collection by the first trap.

- In contrast to the water discharge, the vapor condensate discharge consists of a slow, trickle that occurs intermittently during the pre-vacuum and the drying stages. It was apparent that the heat exchanger on the autoclave efficiently condenses the water vapor to enable effective collection by the discharge trap.

- In the charcoal tests, the volume of liquid collected in the water and vapor condensate discharge traps was influenced by the length of the exposure cycle, and whether the cycle was aborted due to low temperature or high pressure. A complete 60-minute exposure cycle yielded slightly higher water discharges and slightly lower vapor condensate volumes compared to the 90-minute exposure cycles, a logical result of the shorter exposure time.

- The operational data collected by the CycleStor data system showed, for the DPE and wood tests, that the autoclave operated in a fairly repeatable manner. Chamber temperatures during the exposure stages were typically in the range of 276 to 277 ºF at pressures of 31 to 32 psig. Subsequent to these tests, a lag thermometer was inserted into the chamber to confirm chamber temperatures. This calibrated instrument showed that the actual chamber temperature was nominally a couple of degrees higher than indicated by the CycleStor data.

- As previously discussed, the bench-scale autoclave was not capable of consistently operating at 275 °F for a full 90-minute exposure cycle in the charcoal tests. Whether this was a result of diminished performance capability that incrementally accrued over the course of the experimental program, possible aggravated in some manner by the charcoal matrix, or due to some other unknown phenomenon is not clear. The rigid programming features inherent to the autoclave software prohibited modifications that might have averted some of the anomalous test cycles. A full-scale autoclave should have a much more robust operational system that would preclude the problems experienced during this study.

Regarding the analytical results for the tests:

- The average post-exposure VX vapor headspace concentration immediately following the conclusion of the drying stage for the triplicate DPE tests was close to the 1.0 VSL target (0.98 VSL average). Within 28 minutes, the VX vapor concentration inside the chamber was comfortably below the 1.0 VSL criteria.

- In the wood tests, the post-exposure VX vapor headspace concentration immediately following the conclusion of the drying stage was below the 1.0 VSL limit in all 3 tests.

- In the charcoal tests, the post-exposure VX vapor headspace was below the detection limit (0.06 VSL) in all 3 tests

- The DRE for the DPE tests exceeded 99.9 percent, while the wood and charcoal tests yielded a DRE of greater than 99.0 percent.

- The VX agent trends for the water and condensate discharges differed among the test substrates.
    - In the DPE tests:
        - The cumulative mass of VX found in the two discharges during the first cycle was consistently greater (by a factor of at least 3) than the total mass collected from both discharges in the second cycle. This would indicate that most of the VX emissions occurred during the first cycle, which is a reasonable expectation.
        - Furthermore, in the first cycle of the DPE tests, the mass of VX in the condensate was approximately double the mass detected in the water discharge.
        - In the second cycle of the DPE tests, the masses of VX in the condensate and water discharges were very similar to one another.
    - In the wood tests, however:
        - While the mass of VX discharged during the first cycle was greater than the second cycle, the difference was not as significant as seen in the DPE tests. This would indicate that the VX release during the second cycle was still prominent and possibly the impetus for a lower DRE compared to DPE.
        - There was little disparity between the masses of VX detected in the condensate compared to that observed in the water discharges during the first cycle of the wood tests.
        - Finally, while the mass of VX in the condensate dropped significantly during the second cycle of the woods tests, there was only a small decrease in the mass of VX found in the water discharged in the second cycle compared to the first cycle.
    - In the charcoal tests, the occurrence of aborted exposure cycles in two of the three tests confounds data interpretation to any great extent. There was one very notable observation:
        - The total mass of VX found in the vapor condensate and the water discharge in each of the charcoal tests was dramatically lower than the masses found in the combined discharges during the DPE and wood tests as shown below in Table 11. Again, the slight difference in the VX discharges between DPE and wood may be indicative of the comparable difference in their respective DRE values (i.e., wood with a lower DRE would retain more VX and yield less VX in the condensate and water discharges compared to DPE). However, charcoal and wood exhibited nearly identical DRE values – the average DRE of the triplicate wood tests was 99.55% while the average DRE of the triplicate charcoal tests was 99.67%. These DRE values do not explain the order of magnitude disparity in the mass of VX found in the discharges from these two substrates.

Table 11. Comparison of VX Masses in Autoclave Discharges

Test	Total Mass of VX Found in Condensate and Water Discharges Combined, micrograms		
	DPE Average DRE = 99.985%	Wood Average DRE = 99.55%	Charcoal Average DRE = 99.67%
1	6.65	5.54	0.99
2	6.84	6.47	0.08
3	8.15	7.19	0.97
Average of 3 Tests	7.21	6.40	0.68

- One possible explanation for the disparity is that a chemical reaction occurred with the VX on the activated charcoal at the elevated temperature within the autoclave chamber. The occurrence of an unexplained sudden surge in the chamber pressure in two tests causing the cycles to be aborted due to excessive pressure could be consistent with such a phenomenon.

5. CONCLUSION

The initial tests yielded information regarding the length of the exposure cycles to achieve VX vapor headspace concentrations near the 1.0 VSL targeted criteria. These tests also showed that some modification to the originally envisioned headspace monitoring approach was needed to obtain reliable VX vapor concentrations.

Once the cycle lengths and headspace monitoring methodology were refined, the subsequent experiments yielded insight into the performance results associated with autoclaving DPE, wood, and charcoal contaminated with neat VX agent under the defined test conditions. The extrapolation of these results to a full-scale, operational system is beyond the scope of this 'proof-of-concept' experimental program.

One cautionary note is made regarding the interpretation of the residual VX mass present in the 10-gram waste samples following the autoclave cycles (Tables 2, 5, and 8). Using the 10-gram weight of the spiked sample to calculate a residual VX concentration (e.g., ppb of VX in the 'treated' waste) could be misconstrued or deceptive regarding the autoclave performance capability. The 900 micrograms of neat VX occupied a minute portion of the surface area represented by the 10-gram sample. If the waste samples had been even larger (i.e., up to the maximum load limit of 12 pounds for this autoclave model), the identical spike loading likely would have yielded about the same residual mass of VX after treatment, but it would equate to a much lower VX residual on a concentration (ppb) basis.

APPENDIX C

Section 5.0

Autoclave Processing Test Report,
EG&G Defense Materials, Inc.,
Stockton, UT,
November 25, 2008.

Autoclave Processing Test Report

Final

November 25, 2008

EG&G Defense Materials, Inc.
TOOELE CHEMICAL AGENT DISPOSAL FACILITY
(TOCDF)

Prepared by the TOCDF Secondary Waste Team

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1 Introduction

The Tooele Chemical Agent Disposal Facility (TOCDF) has selected autoclave technology to treat secondary waste that is agent contaminated at >1.0 vapor screening level (VSL). Several tests have been completed that demonstrate the suitability of this technology for secondary waste treatment. These tests include live agent destruction tests that were completed in a laboratory scale autoclave at Southwest Research Institute (SwRI).

The results of these tests prove that over 99 percent of agent VX on secondary waste can be destroyed when the secondary waste is exposed to a 275 degree F steam atmosphere for three hours. Based on this information EG&G has selected and purchased an autoclave system that will be installed in Igloo 1631 in Area-10.

2 Purpose of Test

To increase the potential for successfully treating agent contaminated secondary wastes, a decision was made to conduct additional full scale autoclave tests. The intent of these tests was to:

- Determine optimum waste processing temperature
- Evaluate the impact of various waste loading configurations on processing time and handling requirements. This objective included evaluating if secondary wastes could be successfully processed without removing them from the storage drums.
- Determine overall cycle time
- Measure condensate production rates
- Evaluate thermocouple installation options
- Provide samples of “treated” substrates to the CAL for method development

The primary treatment criteria for agent destruction is time at temperature. For the full scale tests it was assumed that success was to drive the thermocouples that were imbedded in the waste to temperatures above 275 degrees F for three hours.

Our intent with these tests was to be as transparent as possible. To this end representatives from both the field office and the State of Utah were asked to witness the tests. Kris Snow from the field office witnessed the testing. Unfortunately the State representatives were unable to attend.

3 Test Setup

Arrangements were made with the company that is providing the autoclave system to EG&G (Bondtech Corporation) to conduct these tests at their manufacturing facility in Salisbury North Carolina. The tests began on November 10, 2008.

The equipment available for this test included:

- A 6’ by 30’ steam heated autoclave.
- A 50 boiler horsepower saturated steam boiler
- Waste processing bins
- High temperature polypropylene liners for the waste processing bins

- Thermocouples for determining waste material temperature measurement
- Data logging equipment to record thermocouple data every 10 seconds during operation
- Metal 55 gallon drums for collection of autoclave condensate
- Moisture indicating desiccant

It should be noted that the autoclave and boiler combination that was used for this test was slightly different in size and capacity than the autoclave system that will be installed in Area-10. The TOCDF autoclave is 6' by 20' and our boiler is rated at 125 boiler horsepower. However, the processing conditions in the test unit are consistent with our system.

The tests were conducted using uncontaminated DPE suits that were double bagged to the same configuration as waste DPE suits from the plant. Note: the bags of the DPE suits were left "in-tact" (they were not cut). The suits were placed in standard blue poly drums (with no drum liner) or placed in the bottom of autoclave waste processing bins. Thermocouples were installed to monitor the internal temperature of the waste. The thermocouples were located in the coldest portion of the waste based on the results of previous autoclave tests.

Figure 1 – Bagged DPE suits in poly drums

Figure 2 – Thermocouple being installed in drum

The test was organized into three major sections:

1. Determine the maximum practical operating temperature for waste processing

2. Determine if processing without removing the waste from the poly drums was a practical option

3. If processing in the drums was practical, evaluate this configuration versus processing "loose" waste that was not in drums

3.1 Processing Cycle

The processing cycle is as follows:

1. Steam from the boiler is passed through a steam ejector (venturi) to create a vacuum in the autoclave. The vacuum generated by the test unit is about negative 9 psi. The boiler that will be installed with the TOCDF autoclave is more powerful and will generate an estimated negative 12 psi. This part of the cycle lasts approximately 4 minutes

2. Steam is added to the autoclave at a predetermined ramp rate until the unit is at operating temperature. This autoclave is controlled by temperature, not pressure. Steam pressure is added or removed to achieve a desired autoclave temperature. Normal operating pressure ranges from 40 to 50 psi.

   To facilitate good steam penetration additional vacuum cycles are conducted after the waste has heated for approximately 2 hours. When all waste thermocouples are at or above 275 degrees F vacuum/pressure cycles stop and the waste is allowed to maintain temperature to decontaminate for three hours. These times and temperatures are based on live agent decontamination tests conducted at Southwest Research Institute.

3. At the conclusion of the decontamination time venturi created suction will again be used to create a vacuum in the autoclave. Because water at reduced pressure boils, the vacuum generated "boils off" most of the water remaining in the autoclave. This part of the cycle is estimated at 4 minutes.

4 Results

4.1 Operating Temperature

The criteria for selecting the optimum operating temperature was the ability to melt the drums and polyethylene bags without causing significant degradation to the waste materials. Avoiding melting or fusing the waste materials is important to allow recovery of the agent spiking that will be used during the performance test.

The starting point for these tests was 300 degrees F. This temperature was selected based on previous full scale autoclave tests that were conducted at 290 degrees F. The 290 degree F tests showed that polyethylene was melting but it was believed that operation at higher temperatures was possible. After two tests at increasing temperature it was determined that 305 degrees was an optimum processing temperature for DPE type wastes.

After processing at 305 degrees F the polyethylene bags and drums were significantly degraded allowing steam to contact the waste. At the same time it was still possible to pull the treated DPE suits apart (they were not fused or melted). When the waste was examined all areas were hot, all plastic was heat affected, and moisture was evident.

Figure 3 – DPE suits after processing at 305 degrees F

The Department of Homeland Security has conducted tests using autoclaves for decontamination of anthrax contaminated materials. During these tests it was determined that multiple vacuum/pressure cycles were beneficial in achieving efficient decontamination. Our testing confirmed that internal waste heating rates were best achieved by use of multiple vacuum cycles.

Wastes were allowed to preheat in the autoclave for approximately two hours. This time allowed the polyethylene bags and drums to soften. At the end of the preheating cycle two vacuum/pressure cycles were conducted. These cycles ruptured the bags and allowed the steam to penetrate the waste resulting in significant gains in temperature.

Figure 4 – Impact of pressure cycles on heating rates

4.2 Processing in Polyethylene Drums

Most of the TOCDF waste is stored in polyethylene drums. Polyethylene has a melting point of approximately 260 degrees F. The concept of processing waste materials inside the poly drums is that at autoclave temperatures the poly drums and the bags inside the drums will melt exposing the waste to the steam and heat required to decontaminate chemical agents. If processing waste in drums could be demonstrated it would be a significant benefit to the safety of the employees who are required to handle the waste.

Three tests were conducted to determine if melting the drums to expose the waste was a practical treatment option. The tests were conducted using poly drums containing "in-tact" bagged DPE suits. The drums were fitted with thermocouples located in the most difficult to area to heat, between the two bottom bags in the drum. This was determined by previous testing. In several of the tests packages of indicating desiccant were placed inside the waste load. This was done to provide an indication of steam penetration into the waste load.

After refinement of technique, two tests were conducted at 305 degrees F with two vacuum cycles starting approximately two hours after the beginning of the cycle. These tests produced excellent results. Decontamination temperate was achieved after approximately 3 hours (see figure 3). At the conclusion of the tests the indicating desiccant that was recovered indicated the presence of water (steam) in the center of the waste.

Additional testing determined that it is possible to process wastes in poly drums with the lids and "drum rings" installed.

Figure 5 – Desiccant before (blue = dry) and after (white = wet) processing

4.3 Loading Configuration

Two different loading configurations were evaluated during the test. These configurations were:

- Loose bags of DPE suits placed on the bottom of the waste processing bins
- Polyethylene drums containing bags of DPE suits

These tests were conducted to directly compare processing waste in drums versus emptying the waste into autoclave processing bins. Figures 6 and 7 shows the loading configurations before and after processing at 305 degrees F.

Figure 6 – Loose waste before and after processing

Figure 7 – Drummed waste before and after processing

The results of the loading configuration tests were that the loose bags placed in a processing bin heated faster than drummed waste. However, both configurations achieved decontamination temperature within three hours. The data from the test indicates that both loading configurations will achieve the desired decontamination temperature as shown by the imbedded thermocouples.

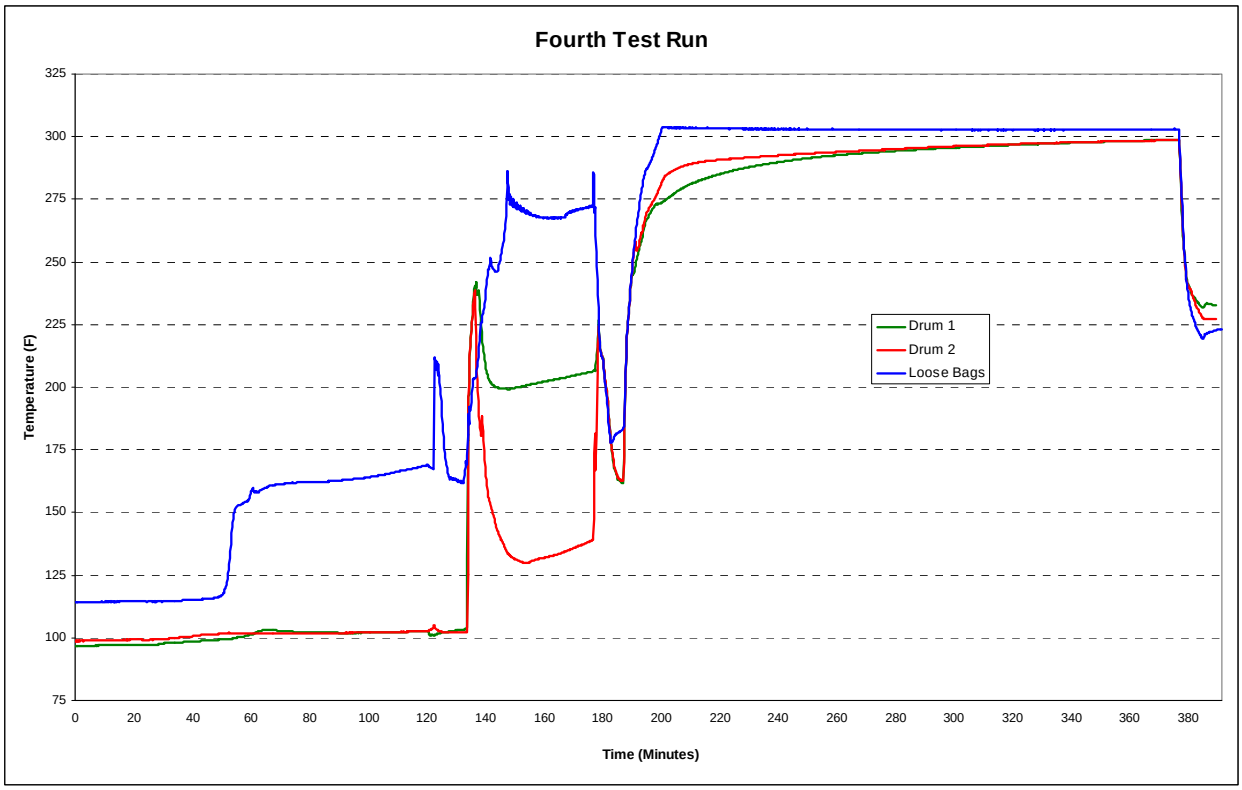

Figure 8 – Heating rate difference between different loading configurations.

4.4 Water Volume Generated

Condensate from the autoclave operation was collected in drums and measure during the test. The intent was to provide an estimate of the condensate produced to verify handling system capacity. The estimated amount of condensate that was produced during one autoclave cycle was:

Liquid collected in drums		223 gallons
Autoclave steam volume (calculated)		36 gallons
Steam from vacuum ejector (calculated)		24 gallons
	Total	**283 gallons**

The measured/calculated volume is well within the capacities of the condensate collection system

4.5 Treated Substrates for Method Development

Samples of DPE suits, LSS hoses, and wood were collected and returned to the CAL. These materials will be used for method development.

Figure 9 – LSS hoses and Wood after processing

5 Test Conclusions

- 305 degrees F appears to be the optimum temperature for processing secondary wastes. At this temperature polyethylene bags and drums melt exposing waste to autoclave conditions. Achieving the necessary time at temperature to destroy VX is achievable in practical periods of time. (Time at temperature required to destroy agent is based on live agent test conducted at Southwest Research Institute).

- Autoclave cycle time appears to be as follows:

Preheat	3 hours
Decontamination	3 hours
Cooling/Drying (estimated – not tested)	4 hours

Total cycle time is estimated at 10 hours

- It appears practical to process wastes in the poly drums without empting the contents and while leaving the lids in place. Using this configuration a small pressure equalization hole would need to be drilled in the drum or lid to avoid autoclave vacuum cycle from rupturing the drums.

- The volume of condensate produced during an autoclave cycle is well within system capacities.

6 Discussion

Using the information from the test series and our autoclave design, TOCDF will have the ability to process 16 – 55 gallon poly drums of waste per autoclave cycle. The cycle time should be approximately 10 hours not including loading, unloading, and monitoring. Assuming two hours for these activities the total cycle time is estimated at 12 hours.

TOCDF does have secondary waste in metal drums. Processing waste in metal drums may be possible. However because the drum will stay in place it is possible that processing times may be different. Additional testing will be required to verify times and temperatures required to process waste in metal drums.

The TOCDF autoclave been fitted with a drying/cooling air blower. This system will circulate room air through the autoclave at the conclusion of the cycle before the autoclave is opened. This should remove any remaining water from the autoclave and waste.

Information gathered (cycle time, drying time, condensate production, etc.) during the autoclave shakedown period will be incorporated appropriately to optimize operations.

APPENDIX C

Section 6.0

E. Burckle, K. Siddoway,
Testing of Headspace Monitoring for Waste Characterization,
Final Report,
Battelle Hazardous Materials Research Center,
Columbus, OH,
November 18, 2008.

Test Report

for

Testing of Headspace Monitoring for Waste Characterization

Prepared for

Tooele Chemical Demilitarization Facility (TOCDF)

18 November 2008

By

Eric Burckle
Kemla Siddoway
Battelle
Hazardous Material Research Center

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EXECUTIVE SUMMARY

The Tooele Chemical Agent Disposal Facility (TOCDF) generates secondary waste as a result of the demilitarization of nerve (GB and VX) and blister agents (H, HD, and HT). TOCDF currently uses a solvent extraction technique to determine the level of agent contamination of secondary waste material as specified in the Waste Analysis Plan (WAP), Attachment 2 of the TOCDF Resource Conservation and Recovery Act (RCRA) Hazardous Waste Permit. EG&G is currently exploring headspace monitoring as an equally representative characterization of the secondary wastes' level of contamination as compared to the solvent extraction technique for three chemical agents (GB, HD, VX) on four matrices (wood, charcoal, demilitarization protective ensemble [DPE] suits and butyl rubber aprons). Successful demonstration of headspace monitoring would eliminate sample collection, reduce the analytical and reporting time, and reduce generation of other additional waste from laboratory analyses. Plant efficiency in waste handling could increase by 30% to 480% per bag (the first increase in efficiency is based on a 4-hour headspace sample versus a 12-hour sample collection, extraction, and reporting interval; the second increase in efficiency is based on a 15-minute headspace sample versus the 12-hour sample collection, extraction and reporting interval), ultimately shortening the schedule and decreasing the cost of eliminating the secondary waste generated in the facility.

The objective of this test was to determine if headspace monitoring is as representative a method for waste contamination characterization at the Waste Control Limit (WCL) as compared with sample extraction techniques currently used or planned for use on three chemical agents (GB, HD, VX) on four matrices (wood, charcoal, DPE suits and butyl rubber aprons). The criteria for determining success was if the headspace monitoring resulted in detection of agent at the 95% confidence level for the agent alarm setpoint determined by the Precision and Accuracy (P&A) evaluation, then it was concluded that headspace monitoring is as representative for the detection of agent contamination at the WCL as sample extraction under the conditions of the test.

The ability of the Automatic Continuous Air Monitoring System (ACAMS) to detect VX at a suitable dermal contact hazard level was also investigated for the DPE suit and Butyl Rubber Apron material. These materials are routinely handled in the TOCDF and it is important to establish that a contact hazard would be identified using the headspace monitoring approach.

The contact hazard level (CHL) that was selected is the Negligible Severity (low-level) Effect Level for Percutaneous Liquid Exposure (reference 1).

Seven replicate simulated waste material samples were prepared in each trial and contaminated with agent at the WCL. The samples were sealed in containers with a known volume of air and allowed to sit for pre-determined time periods (holding times) before the headspace in the containers was monitored with an ACAMS. An eighth sample for each waste material/agent combination was prepared, contained, and monitored as described for the seven samples, except that the initial and successive holding times were accelerated. The results are summarized below:

- DPE Suit Samples
  - HD was detected above the alarm setpoint in 6 of 7 DPE samples (HD was detected in the outlier above the Limit of Quantification [LOQ] at 0.33 Vapor Screening Limit [VSL])
  - HD was detected at 15 min in the accelerated sampling interval (ASI) sample
  - GB was detected above the alarm setpoint in 7 of 7 DPE samples
  - GB was detected at 15 min in the ASI sample
  - VX was NOT detected above the alarm setpoint in 7 of 7 DPE samples (VX was detected above the LOQ between 0.15 VSL and 0.37 VSL)
  - VX was NOT detected above the alarm setpoint in the ASI sample (VX was detected above the LOQ at 0.20 VSL)
- Butyl Rubber Apron Samples
  - HD was detected above the alarm setpoint in 7 of 7 butyl rubber samples
  - HD was detected at 15 min in the ASI sample
  - GB was detected above the alarm setpoint in 7 of 7 butyl rubber samples
  - GB was detected at 15 min in the ASI sample
  - VX was NOT detected above the alarm setpoint in 7 of 7 butyl rubber samples (VX was detected above the LOQ between 0.14 VSL and 0.31 VSL). The positive control sample did not alarm above the alarm setpoint; the spike mass was not large enough to generate a vapor headspace concentration greater than

the alarm setpoint but was large enough to allow detection of VX above the background.

  - VX was NOT detected above the alarm setpoint in the ASI sample (VX was detected above the LOQ at 0.45 VSL). The positive control sample for the trial (measured at the same holding times as the seven replicate samples) did not alarm above the alarm setpoint; the spike mass was not large enough to generate a vapor headspace concentration greater than the alarm setpoint but was large enough to allow detection of VX above the background.

- Wood Samples
  - HD was detected above the alarm setpoint in 7 of 7 wood samples
  - HD was detected at 15 min in the ASI sample
  - GB was detected above the alarm setpoint in 7 of 7 wood samples
  - GB was detected at 15 min in the ASI sample
  - VX was detected above the alarm setpoint in 7 of 7 wood samples
  - VX was detected at 15 min in the ASI sample
- Charcoal Samples
  - No agent was detected above the alarm setpoint from the charcoal samples. HD was detected in all of the control samples above the LOQ suggesting that charcoal is a low-level positive interferent for HD. GB and VX were detected above the LOQ in the positive control sample; the spike mass was not large enough to generate a vapor headspace concentration greater than the alarm setpoint but was large enough to allow detection of GB and VX above the background.

The agent/matrix combinations that met the criteria specified for this program are listed below. It is concluded that headspace monitoring of these agent/matrix combinations is as representative for the detection of agent contamination at the WCL as sample extraction at the 4-hour containment period, under the conditions of this test:

- DPE suit material contaminated at the WCL with agents HD and GB
- Butyl Rubber Apron material contaminated at the WCL with agents HD and GB

- Wood material contaminated at the WCL with agents HD, GB, and VX

Moreover, the results from the ASI samples indicate that headspace monitoring of the agent/matrix combinations listed below may be as representative for the detection of agent contamination at the WCL as sample extraction at the 15-minute containment period, under the conditions of this test:

- DPE suit material contaminated at the WCL with agents HD and GB
- Butyl Rubber Apron material contaminated at the WCL with agents HD and GB
- Wood material contaminated at the WCL with agents HD, GB, and VX

The ACAMS was capable of detecting VX contamination at the CHL in the headspace from both DPE Suit material and Butyl Rubber Apron material. The monitoring results were orders of magnitude above the alarm setpoint value.

During all of the VX trials, an additional peak was observed on the ACAMS strip chart. The extraneous peak was in all of the samples, including the solvent/matrix interference control (SMIC), and the matrix interference control (MIC). The peak was present in all VX samples, but did not interfere with agent analysis unless carry-over allowed the interferent to accumulate to high levels in the ACAMS instrument. This peak resulted in a false positive from one sample in the WCL trials, and both false positives and false negatives in the CHL trials. Due to the high VX concentrations in the CHL trials, the VX peak shifted slightly which caused the ACAMS not to report the VX concentration in some samples. The agent gate was not enlarged for the VX CHL trials. The false negatives from the CHL trials were evaluated from the strip charts. VX concentrations were estimated by comparing the peak heights in the non-reported samples to the peak heights of the samples that were reported by the ACAMS.

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ACRONYMS and ABBREVIATIONS

ABCDF	Aberdeen Chemical Agent Disposal Facility
ACAMS	Automated Continuous Air Monitoring System
AEL	Airborne Exposure Limit
ASI	Accelerated Sampling Interval
CAS RN	Chemical Abstracts Services Registration Number
CCV	Continuing Calibration Verification
CDC	Centers for Disease Control
CEMO	Chemical, Environmental and Materials Operations
CHL	Contact Hazard Level
cm	Centimeter
CMA	Chemical Materials Agency
DPE	Demilitarization Protective Ensemble
FID	Flame Ionization Detector
FDWS	Field Drinking Water Standard
g	Gram
GB	Sarin, a nerve agent (o-isopropyl methylphosphonofluoridate)
GC	gas chromatography
H	Sulfur mustard (bis(2-chloroethyl) sulfide), a blister agent
HD	distilled sulfur mustard
hr	Hour
HT	mixture of H and agent T (Bis (2- chloroethylthioethyl) ether)
IAW	In accordance with
ID	Inner diameter
IPA	Isopropyl Alcohol
L	Liter
LDPE	Low-density polyethylene
LMQAP	Laboratory and Monitoring Quality Assurance Plan
LOQ	Limit of Quantification
lpm	liters per minute
m^3	cubic meter
mg	Milligram
min	Minute
MCP	Monitoring Concept Plan
MIC	Matrix Interference Control Sample
MSDS	Material Safety Data Sheet
µL	Microliter
mL	Milliliter
NEG	Negative
ng	Nanogram
NIOSH	National Institute for Occupational Safety and Health

OD	Outer diameter
P&A	Precision and Accuracy
PI	Principal Investigator
ppb	Parts Per Billion
PCT	Pre-concentrator Tube
POS	Positive
PPE	PI
QA	quality assurance
RCRA	Resource Conservation and Recovery Act
RDS	Research Dilute Solution
RH	Relative Humidity
SMIC	Solvent Spiked Matrix Interference Control Sample
STEL	Short Term Exposure Limit
TBD	To Be Determined
TOCDF	Tooele Chemical Agent Disposal Facility
TPCS	Test Parameter Control Sheet
USACHPPM	U.S. Army Center for Health Promotion and Preventive Medicine
VSL	Vapor Screening Limit
VX	A nerve agent, (O-ethyl S-2-diisopropyl aminoethyl methylphosphonothiolate)
WAP	Waste Analysis Plan
WCL	Waste Control Limit

1.0 INTRODUCTION

1.1 BACKGROUND

The Tooele Chemical Agent Disposal Facility (TOCDF) is mandated by the U.S. Government to destroy chemical weapons stored at Deseret Chemical Depot. TOCDF began demilitarization operations in 1996. The first agent treated at the facility was GB followed by VX; currently the facility is processing HD. Secondary wastes are generated as a result of the demilitarization process. Many of the wastes have been placed in temporary storage until an appropriate disposition plan is determined. The wastes of concern are: Personal Protective Equipment (PPE), specifically demilitarization protective ensemble (DPE) suits and butyl rubber gear; activated charcoal that has been exposed to agent vapor; and wood dunnage which is used in the storage and transport of munitions. TOCDF currently uses a solvent extraction technique to determine the agent contamination status of secondary waste material.

EG&G is currently exploring treatment/disposal methods for secondary waste generated during the demilitarization of nerve (GB and VX) and blister agents (H, HD, and HT) at the TOCDF. This test measures the efficacy of headspace monitoring for characterization of the secondary wastes' level of contamination for three chemical agents (GB, HD, VX) on four matrices (wood, charcoal, DPE suits and butyl rubber aprons).

1.2 OBJECTIVE

The primary objective of this test was to determine if headspace monitoring is as representative a method for characterizing waste contamination at the Waste Control Limit (WCL) as compared with sample extraction techniques currently used or planned for use on three chemical agents (GB, HD, VX) on four matrices (wood, charcoal, DPE suits and butyl rubber aprons).

The secondary objective of the test was to determine the ability of the Automatic Continuous Air Monitoring System (ACAMS) to detect VX at a suitable dermal contact hazard level for the DPE suit and Butyl Rubber Apron material. These materials are routinely handled

in the TOCDF and it is important to establish that a contact hazard would be identified using the headspace monitoring approach. The contact hazard level (CHL) that was selected is the Negligible Severity (low-level) Effect Level for Percutaneous Liquid Exposure (reference 1). The upper bound for VX is specified as 0.55 mg for a 70-kg man within the military population. This objective is specified in the Test Plan Addendum, dated 15 August 2008 (Appendix H).

1.3 STRATEGY

Table 1 shows the current WCLs listed in the TOCDF Waste Analysis Plan (WAP) Attachment 2 of the TOCDF Resource Conservation and Recovery Act (RCRA) Hazardous Waste Permit (reference 2) and the Vapor Screening Limit (VSL) listed in the TOCDF Agent Monitoring Plan, Attachment 22 of the TOCDF RCRA Hazardous Waste Permit (reference 3).

Field drinking water standards (FDWS) were developed to address the potential purposeful chemical agent contamination of drinking water supplies on the battlefield by US adversaries (reference 4). These water standards were developed assuming seven days of consumption of up to 15 liters of contaminated water a day by a battlefield soldier. For lack of an alternative, the 1986 FDWS (20 parts per billion [ppb] for nerve agents and 200 ppb for HD) have been used as acceptable levels (e.g., WCLs) for disposal of agent contaminated waste off-site.

The VSL is the same concentration value as the short term exposure limit (STEL), which is a time-weighted average agent vapor concentration protective of inhalation exposure pathways. The VSL is applied to items in enclosed containers, and also applied in point source monitoring such as clearing of DPE entrants in airlocks. The purpose of creating the VSL was to provide a screening method which would aid in the identification of potential risk to workers who would come in contact with the potentially contaminated item. A potential benefit of this vapor screening method is that it makes waste separation in the plant more efficient by allowing waste separation based on headspace contamination monitoring results. This concept was introduced in June 2004 in the U. S. Army Chemical Materials Agency (CMA) Monitoring Concept Plan (MCP) (reference 5).

Table 1. TOCDF WCL and VSL

	HD	GB	VX
WCL[a] (ng/g)	200	20	20
VSL[b] (mg/m^3)	0.003	0.0001	0.00001

[a] The WCLs listed in the table are specified in the TOCDF Waste Analysis Plan, an attachment in their RCRA permit.
[b] The VSL is equivalent to the STEL concentration value listed in the Implementation Guidance Policy for Revised Airborne Exposure Limits (AELs) for GB, GA, GD, GF, VX, H, HD, and HT, Department of the Army, Office of the Assistant Secretary of the Army Installations and Environment, 18 June, 2004 (reference 6).

The strategy of the test was to contaminate bagged, simulated, secondary waste with agent at the TOCDF WCL, and then measure the agent concentration in the headspace with an ACAMS at predefined time intervals (holding times). If the headspace monitoring resulted in detection of agent above the 95% confidence level at the agent alarm setpoint as determined by the Precision and Accuracy (P&A) evaluation, then it was concluded that headspace monitoring is as representative for the detection of contamination at the WCL as sample extraction under the conditions of the test. The simulated secondary waste consisted of unused, uncontaminated DPE suits; unused, uncontaminated butyl rubber aprons; unused, uncontaminated charcoal; and unused, uncontaminated wood. Headspace monitoring was conducted using a standard ACAMS.

1.4 LIMITATIONS

Headspace monitoring of the simulated waste material was performed in a controlled laboratory environment. Similar monitoring results may not be obtained when performed in the presence of interferents, or at significantly different temperature and humidity conditions.

The ACAMS monitoring during the test was performed with an appreciable and consistently applied headspace volume above one material type in the bag. The ACAMS output is a concentration (mass/volume); therefore, although headspaces with different volumes may contain the same mass of agent, the ACAMS will report a different value for each of those measurements.

Adding additional materials or moisture to the interior of the bag may result in headspace concentration measurements that are different than those obtained in this test. The amount of adsorption and/or absorption of the agent would be altered by addition of materials to the bag,

resulting in a different agent concentration in the headspace. Increased moisture content, resulting in hydrolysis of the agent, may also affect the results.

The agent vapor concentration in the bagged waste is dependent on the amount and type of waste, the amount of agent present in the waste, and the bag volume.

2.0 TEST DESIGN

This program tested the ability of the ACAMS to detect agent in the headspace above four simulated waste materials: DPE suits, butyl rubber aprons, wood, and charcoal. The agents that were tested were HD, GB, and VX. The DPE suit, butyl rubber apron, and wood materials were spiked using a liquid spiking methodology, where dilute agent in solution was applied to the material. Agent was spiked onto charcoal by a vapor generation method. The material was spiked with the quantity of agent that equates to one WCL.

In addition, five types of quality control samples were prepared and analyzed with each trial. These samples included a positive control, a negative control, spike controls, a matrix interference sample (matrix blank), and a solvent/matrix interference sample (preparation blank).

The materials were contaminated in doubled headspace bags, the inner bag of which was filled to 80 liters (L) with filtered, dry, house air. The dew point of the house air was controlled to -52ºF. The laboratory temperature and relative humidity were monitored throughout the trials, although the relative humidity (RH) of the room did not impact the test results. At the predetermined holding times, the headspace of the inner bag was monitored using a calibrated ACAMS for one cycle. One additional bag of simulated waste material, labeled as accelerated sampling interval (ASI), was spiked with agent in each trial and treated identically as described above, except that the initial and successive headspace monitoring holding times were shorter.

The initial holding time of 4-hours was chosen for the seven replicate samples because this is the holding time used at incineration demilitarization sites when monitoring laundry items. The initial holding time of 15-minutes for the ASI samples was chosen because it is the holding time used at the Aberdeen Chemical Agent Disposal Facility (ABCDF) when monitoring waste with a headspace less that 0.8 m^3 for HD.

The liquid agent application approach closely mimics the anticipated route for gross contamination for most waste materials during plant operations. Since the contamination route for the charcoal waste stream involves agent vapor, not liquid, a method of loading agent vapor onto the charcoal material was developed for the agents HD, VX, and GB. This vapor loading method was used to prepare the charcoal samples.

The ability of the ACAMS to detect VX at the specified CHL was also investigated for the DPE suit and butyl rubber apron material. These materials were spiked directly using the dilute agent in solution. The target mass of VX applied to the waste material sample was 0.55 mg. Unlike the WCL trials, the VX spike mass was not a function of the mass of the simulated waste material sample. Waste material sample sizes for the CHL trials were the same as those for the WCL trials.

2.1 TEST MATRIX

Fourteen trials were performed. The specific trials are listed in Table 2. Table 3 specifies the control sample types that were evaluated in each trial and Table 4 lists the parameters for the accelerated headspace evaluation sample that was tested concurrently with the primary samples.

Table 2. Sample Trial Matrix

Trial #	Agent/ Contamination Level	Simulated secondary waste material	Number of Replicates	Holding Times
1	HD/WCL	DPE suit	7	4 hr, 12 hr, 24 hr, 48 hr
2	HD/WCL	Butyl Rubber	7	4 hr, 12 hr, 24 hr*, 48 hr*
3	HD/WCL	Wood	7	4 hr, 12 hr, 24 hr*, 48 hr*
4	HD/WCL	Charcoal	7	4 hr, 12 hr, 24 hr, 48 hr
5	GB/WCL	DPE suit	7	4 hr, 12 hr, 24 hr*, 48 hr*
6	GB/WCL	Butyl Rubber	7	4 hr, 12 hr, 24 hr*, 48 hr*
7	GB/WCL	Wood	7	4 hr, 12 hr, 24 hr*, 48 hr*
8	GB/WCL	Charcoal	7	4 hr, 12 hr, 24 hr, 48 hr
9	VX/WCL	DPE suit	7	4 hr, 12 hr, 24 hr, 48 hr
10	VX/WCL	Butyl Rubber	7	4 hr, 12 hr, 24 hr, 48 hr, 122 hr[1], 125 hr[1]
11	VX/WCL	Wood	7	4 hr, 12 hr, 24 hr*, 48 hr*
12	VX/WCL	Charcoal	7	4 hr, 12 hr, 24 hr, 48 hr
13	VX/CHL	DPE suit	7	4 hr, 24 hr[1]
14	VX/CHL	Butyl Rubber	7	4 hr

*Planned but not performed based on results from the initial two readings.

[1] Additional holding times added for select samples during this trial.

Table 3. Control Sample Types per Trial

Type	Composition	Holding Times
Positive Control (POS)	Stainless Steel Disk*	4 hr, 12 hr, 24 hr, 48 hr
Negative Control (NEG)	Empty Bag (no spike)	4 hr, 12 hr, 24 hr, 48 hr
Matrix Interference Control (MIC)	Matrix (no spike)	4 hr, 12 hr, 24 hr, 48 hr
Solvent/Matrix Interference Control (SMIC)	Matrix + Solvent Spike	4 hr, 12 hr, 24 hr, 48 hr
Spike Control	Solvent Vials (3 replicates)	NA

*non-porous surface spiked with the same volume of agent solution as waste material samples.

Table 4. Accelerated Sampling Interval (ASI) Trial Matrix

Trial #	Agent/ Contamination Criteria	Simulated secondary waste	Number of Replicates	Holding times
1	HD/WCL	DPE suit	1	15 min, 45 min, 2 hr*, 4 hr*
2	HD/WCL	Butyl Rubber	1	15 min, 45 min, 2 hr*, 4 hr*
3	HD/WCL	Wood	1	15 min, 45 min, 2 hr*, 4 hr*
4	HD/WCL	Charcoal	1	15 min, 45 min, 2 hr, 4 hr
5	GB/WCL	DPE suit	1	15 min, 45 min, 2 hr*, 4 hr*
6	GB/WCL	Butyl Rubber	1	15 min, 45 min, 2 hr*, 4 hr*
7	GB/WCL	Wood	1	15 min, 45 min, 2 hr*, 4 hr*
8	GB/WCL	Charcoal	1	15 min, 45 min, 2 hr, 4 hr
9	VX/WCL	DPE suit	1	15 min, 45 min, 2 hr, 4 hr
10	VX/WCL	Butyl Rubber	1	15 min, 45 min, 2 hr, 4 hr, 122 hr[1], 125hr[1]
11	VX/WCL	Wood	1	15 min, 45 min, 2 hr*, 4 hr*
12	VX/WCL	Charcoal	1	15 min, 45 min, 2 hr, 4 hr
13	VX/CHL	DPE suit	1	15 min, 4 hr
14	VX/CHL	Butyl Rubber	1	15 min, 4 hr

*Planned but not performed based on results from the initial two readings.

[1] Additional holding times added for select samples during this trial.

3.0 PROCEDURE

3.1 TEST MATERIALS AND EQUIPMENT

3.1.1 Simulated Waste Materials

Simulated waste materials included unused, uncontaminated DPE Suits, butyl rubber aprons, virgin coconut shell charcoal, and wood. The DPE Suits, butyl rubber aprons, and charcoal were provided by TOCDF. Wood (Douglas fir, untreated, 2x4 dimensional lumber, kiln dried) was procured from a local vendor. No attempt was made to simulate the presence of decontamination solution in combination with the simulated waste materials. Detailed information regarding the sample swatches is included in Appendix C.

Swatch samples of the DPE suit material were prepared by first removing and discarding the charcoal filter and metal air-hose connection. Each suit was weighed; an average weight for each suit size was calculated. Seven or eight samples were cut from each suit. The samples were 1/8 the weight of the average for that suit size (±1 g). The samples were cut free-form so that each sample was as representative of the entire suit as possible; an attempt was made to include zippers, seams, etc. in each sample. The geometry and exact composition of each sample was dissimilar because of the heterogeneity of the original DPE suits. An attempt was made to prepare the swatch samples as one intact piece. However, in some cases additional pieces were required to ensure the total weight requirement was met. This procedure was repeated for the preparation of the butyl rubber apron samples with the exception that no items were removed (i.e., charcoal filters and metal air-hose connections were not present on the aprons).

The wood was purchased in the form of 2x4 dimensional lumber and was cut to 1-foot lengths (± ¼”). The wood was fir, and was not pressure treated. The samples were weighed and recorded. However, the wood samples were not modified if the weights were dissimilar. The difference between the weight of each sample in a trial and the average weight for the trial did not exceed 10%.

The charcoal samples were weighed to 10 g ± 1 g and placed into 3/8" outer diameter (OD), 5/16" inner diameter (ID) Teflon tubes. A small amount of glass wool was placed at the ends of the charcoal bed. The bed lengths were measured with an average value of 17.3 inches.

3.1.2 Chemical Agents

This test included the chemical agents GB (CAS RN 107-44-8), HD (CAS RN 505-60-2) and VX (CAS RN 50782-69-9). The chemical agent purity was measured prior to use by gas chromatography-flame ionization detection (GC/FID); only agent with purity in excess of 90% was used. The lot numbers of the chemical agents and the measured purity are included in Table 5. Chemical agent challenges were made as dilute solutions in solvents that do not degrade the performance of the materials being tested. Dilute agent solutions were prepared by adding known volumes of more concentrated agent stock solutions to known volumes of solvent. The measured agent purity was used to determine the volume of stock solution to add to the solvent. The final concentration of the solutions was verified by GC/FID as described in Section 4.0. Isopropyl Alcohol (IPA, CAS RN 67-63-0) was used as the solvent for GB and VX; hexane (CAS RN 110-54-3) was used as the solvent for HD. The solvents did not degrade the agent. Table 6 includes the vapor pressure of the solvents and the agents. The solvents have vapor pressures that are orders of magnitude higher than the agents, indicating the solvents volatilized much more quickly. Data from the individual trials are discussed in section 4. A detailed explanation of the negligible effect of the solvent on the agent volatility is provided in Appendix F.

Table 5. Purity of the Chemical Agents

Compound	Lot #	Purity [a]
HD	U-5032-CTF-N	96.9%
GB	U-5045-CTF-N	99.4%
VX	U-5251-CTF-N	93.0%

[a] Minimum purity measured during the program.

Table 6. Vapor Pressure Data for the Chemical Agents and Solvents

Compound	Vapor Pressure
HD	0.11 mm Hg @ 25°C [a]
GB	2.9 mm Hg @ 25°C [a]
VX	0.00063 mm Hg @ 25°C [a]
Hexane	130 mm Hg @ 20°C [b]
IPA	44 mm Hg @ 25°C [b]

[a] Data from Centers for Disease Control (CDC), National Institute for Occupational Safety and Health (NIOSH) Emergency Response Card (references 7-9)
[b] Data from Material Safety Data Sheets (MSDS) (references 10-11)

3.1.3 Headspace Bags

The headspace bags were similar to those used by TOCDF for waste packaging. Transparent, 6-mil thick, low density polyethylene (LDPE) bags (Associated Bag Company, item #64-8-01) were used in this study. The bags were inspected prior to use; bags containing rips or tears were rejected. The test items were double bagged to ensure containment of agent vapors during testing. Stainless steel bulkhead fittings were installed through both of the doubled bags to allow spiking of the test item (through a septum port). A second bulkhead fitting was installed to allow headspace sampling with the ACAMS (headspace sampling port). A representative headspace monitoring bag is shown in Figure 1. The locations of the fittings are highlighted. Each doubled bag was sealed by twisting the material at the opening of the bags, folding over the twisted section to form a "J," and then holding the section in place with a zip tie. During testing, the headspace sampling port was connected to an on/off valve using a 21" long, 1/8"OD, 1/16" ID Teflon tube (transfer line, 1.06 mL air volume). The ACAMS was connected to the on/off valve (using a heated sample line, Section 3.1.4) when the bag was sampled (see Figure 2). Only the inner headspace bag was monitored with the ACAMS during testing.

An in-line V-to-G conversion pad fitting was connected to the headspace sampling port when performing the VX trials. This in-line fitting consisted of two stainless steel unions coupled together (see Figure 3). Two V-to-G conversion pads and a back-up filter were placed in this coupling at the start of each trial. New pads were used for each trial. This in-line fitting was validated prior to use by performing a series of challenge injections at 1.0 VSL. The

challenge injections were made with the in-line fitting connected directly to the ACAMS sample inlet and with the in-line fitting connected to the heated sample line. Also, challenge injections were made using transfer line/valve/heated sample line test configuration: the injections were made with the in-line fitting disconnected from the headspace bag at the headspace sampling port (see Figure 3). ACAMS results for challenge injections (at 1.0 VSL) through the in-line conversion fitting at these three locations are listed in Table 7.

Table 7. Validation of In-Line V-G Conversion Fitting for VX Monitoring

Location of In-Line V-G Conversion Fitting	Average ACAMS Result (VSL)
Connected at ACAMS inlet [a]	0.88
Connected to Heated Sample Line [a]	1.02
Connected to end of transfer line, valve, and Heated Sample Line [b]	0.88

[a] Duplicate samples obtained.
[b] Triplicate samples obtained.

All challenge injections were within ±25% of the target value.

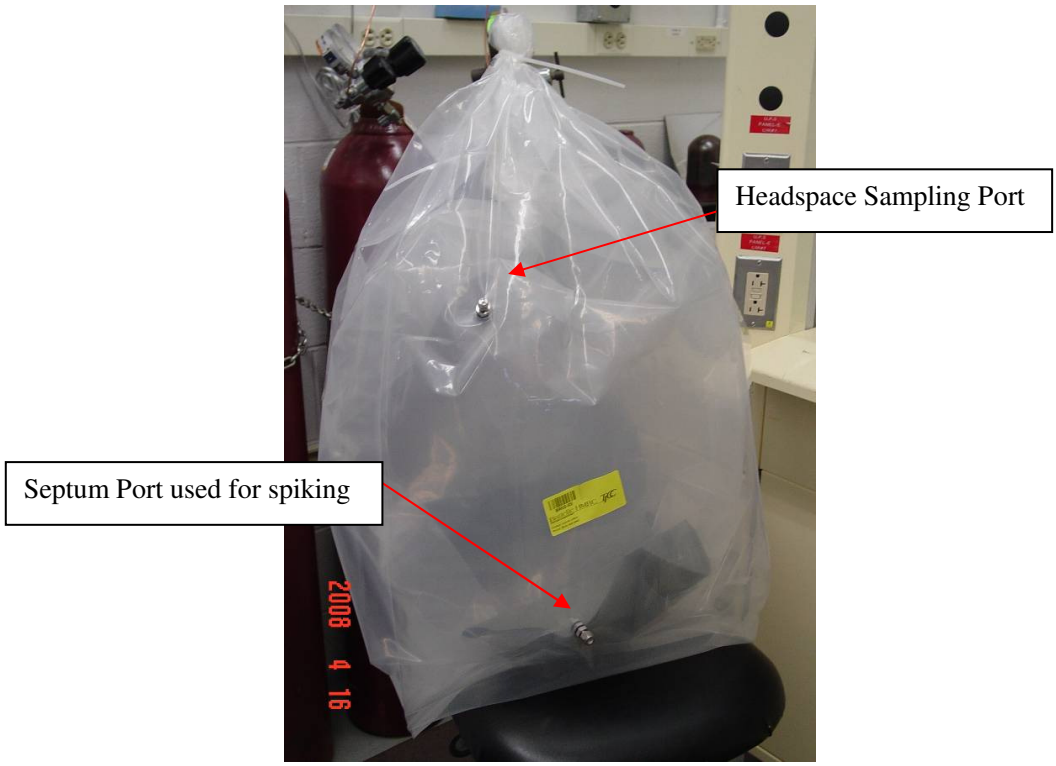

Figure 1. Representative Headspace Monitoring Bag

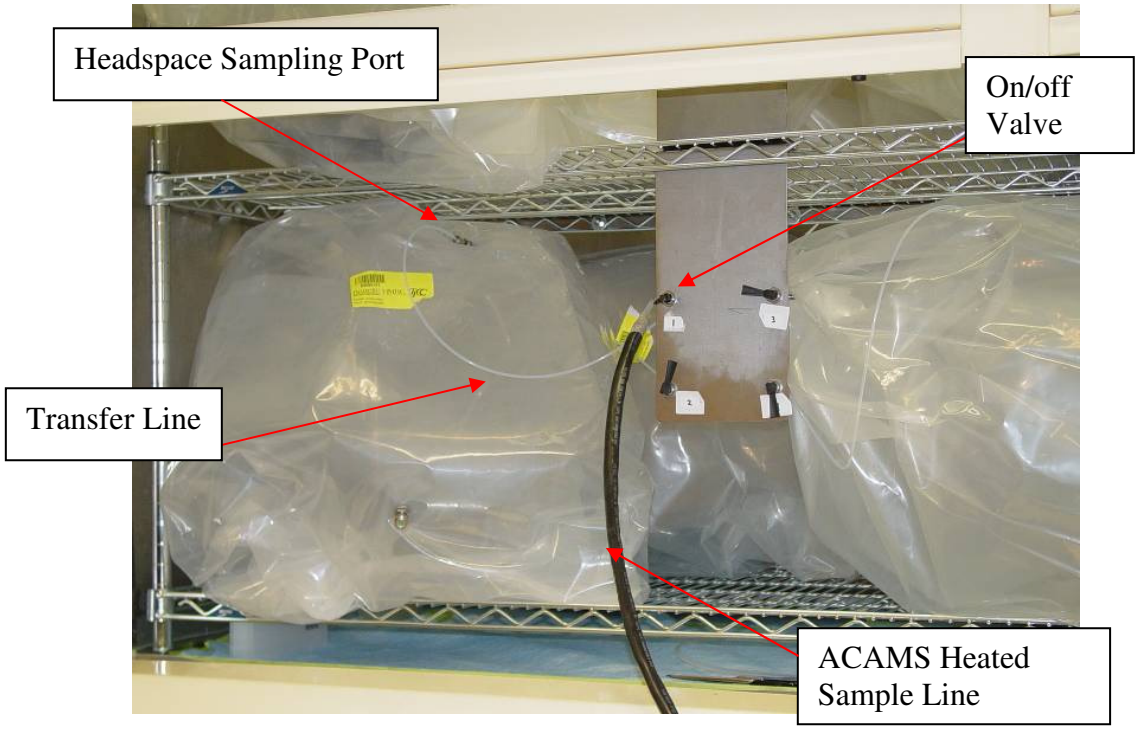

Figure 2. Headspace Monitoring by ACAMS

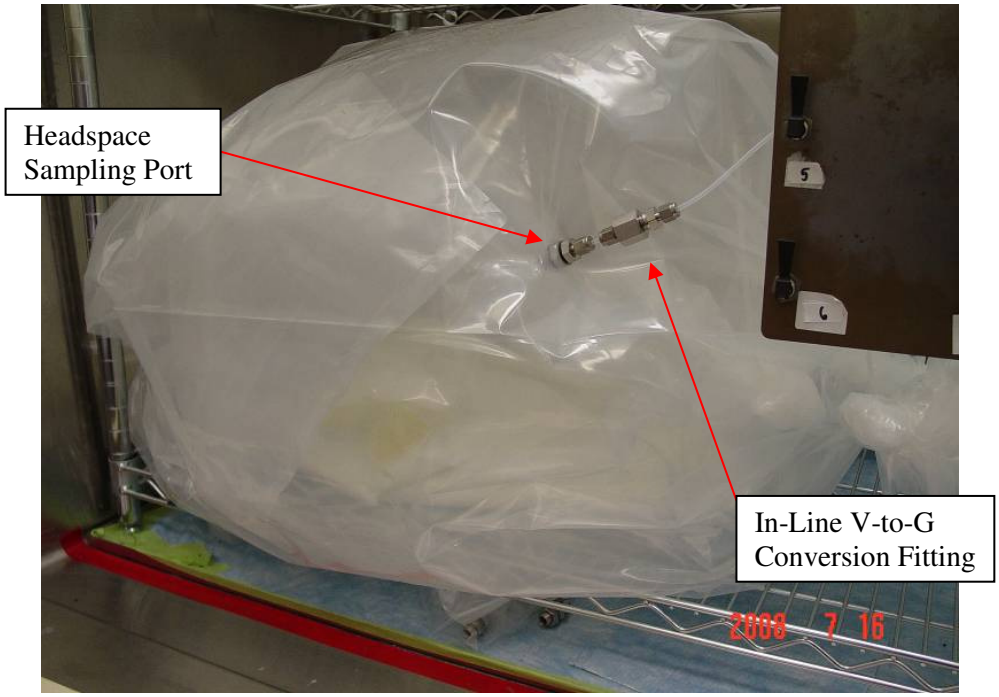

Figure 3. Headspace Bag with In-Line V-to-G Conversion Fitting

3.1.4 Automatic Continuous Air Monitoring Systems (ACAMS)

Three ACAMS were provided by TOCDF, along with all necessary consumable and ancillary equipment required for the duration of the test. One ACAMS was set up to monitor for each agent. A modified Class 1 P&A Study was performed on each ACAMS. This study is described in detail in Appendix A. The results from the P&A studies were evaluated using the CERTIFY 5.0 program to determine the alarm setting for 95% confidence of detecting agent at the monitoring level (1 VSL). The results are included in Appendix A. The alarm settings for the agents are included in Table 8.

Table 8. Alarm Settings and LOQ for the ACAMS

ACAMS Instrument #	Agent	Alarm Setting (VSL)	LOQ
28241	HD	0.90	0.05
14131	GB	0.95	0.05
14133	VX	0.91	0.06

The instruments (see Figure 4) were challenged and/or calibrated through the heated sample line for all agents. The heated sample line was approximately 6 feet in length with a 1/8" OD, 1/16" ID, and had an internal volume of approximately 3.6 mL. At a minimum, a sample line challenge was performed prior to the initiation of each trial. The calibration and challenge injections were performed as described in Appendix A. The sample line challenge result was required to be within ±25% of the target concentration. The calibration and challenge standards used on the ACAMS were prepared as described in Appendix A. All ACAMS standard solutions met the requirements described in Appendix A.

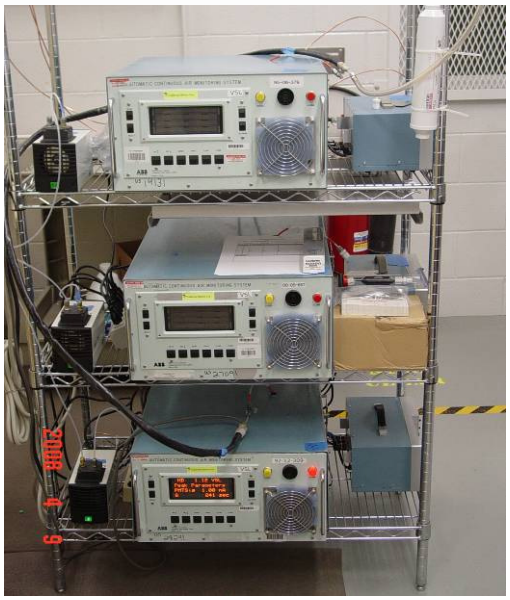

Figure 4. ACAMS Instruments

The ACAMS sampled a volume of approximately 3.06 liters during each cycle for HD, GB, and VX (sample flow rate of ~0.8 Lpm for 3.83 min). The volume of the headspace bags was 80 L; therefore, approximately 3.8% of the total headspace volume was removed during each sampling cycle. The maximum headspace volume change if four sampling events occurred was approximately 15.3%. The volume of air retained in the transfer line/valve/heated sampling line was less than 0.5% of the total volume of headspace air collected per sampling cycle.

3.2 TEST EXECUTION

3.2.1 Bagging and spiking

The DPE, butyl rubber apron, and wood simulated waste samples were contaminated with agent using a liquid spiking methodology, applying agent in dilute solution to the material. This method is described in Section 3.2.1.1. The charcoal samples were contaminated using a vapor loading method as described in Section 3.2.1.2. The trials performed at the CHL are described in Section 3.2.1.3.

The material was spiked with the quantity of agent that equates to one WCL or CHL. The mass of agent required in the CHL trials was 0.55 mg, and was not a function of material

mass. The spike mass for the WCL trials were determined by multiplying the average matrix mass by the WCL for each agent. An example of the calculation for the WCL trials is below (equation 1):

The TOCDF WCL for GB is 20 ng/g; average mass of matrix is 10 g

$$20 \text{ ng/g} * 10 \text{ g} = 200 \text{ ng of GB required} \quad (1)$$

The required spike mass and application volume (described in the sections below) were then used to determine the desired concentration of the spiking solution. An example calculation for both WCL (equation 2) and CHL (equation 3) trials is below:

200 ng GB required, 20.0 µL expected application volume:

$$200 \text{ ng GB} / 20.0 \ \mu\text{L} *(1 \ \mu\text{g}/1000 \text{ ng})*(1000 \ \mu\text{L/mL}) = 10.0 \ \mu\text{g/mL GB} \quad (2)$$

0.55 mg VX required, 600.0 µL expected application volume:

$$0.55 \text{ mg VX} / 600.0 \ \mu\text{L} *(1000 \ \mu\text{g/mg})*(1000 \ \mu\text{L/mL}) = 916.6 \ \mu\text{g/mL VX} \quad (3)$$

The concentrations of the spiking solutions were verified by GC analysis. The measured value was then used in equations above to solve for the required application volume. Therefore, the application volume was used to adjust for any error in the solution preparation; the required WCL or CHL was achieved.

3.2.1.1 DPE, Butyl Rubber, and Wood Test Items at the WCL

Each simulated secondary waste item was placed into a double LDPE bag. The bags were filled to 80 L with dry, filtered, compressed house air. The air was metered into the bags using a calibrated mass flow controller set to 10.0 Lpm for eight minutes (two samples during trial 1 were prepared at 20.0 lpm for four minutes). The agent was dispensed onto the test item using a 100-µL syringe inserted through a septum port in the side of the bag. The syringe was fitted with a Hamilton Repeating Dispenser that applies a reproducible volume with each drop (equal to 1/50th of the syringe size, 2 µL). The agent was applied to the material in ten different locations according to the pattern shown in Figure 5. The total volume (number of drops) was adjusted based on the actual concentration of the Research Dilute Solution (RDS), and the mass of the waste material sample; any adjustments are described in the appropriate area of Section 5.0. The diameter of the spike pattern did not exceed 4 inches. However, because of the specific

geometry of the material and folds, this pattern was approximated. Reference the log record book pages in Appendix G for documentation of the spiking pattern.

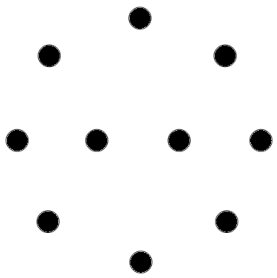

Figure 5. Spike Application Pattern.

The spike location on the DPE suit and butyl rubber apron was on the exterior of the material and, where accessible by the syringe needle, within folds of the material. The agent was applied to the 3 ½ -inch face of the wood sample. Figure 6 includes a representative photograph of the application method through the septum port. The CHL application method was the same as the WCL method, except that a larger syringe was used to apply the solution.

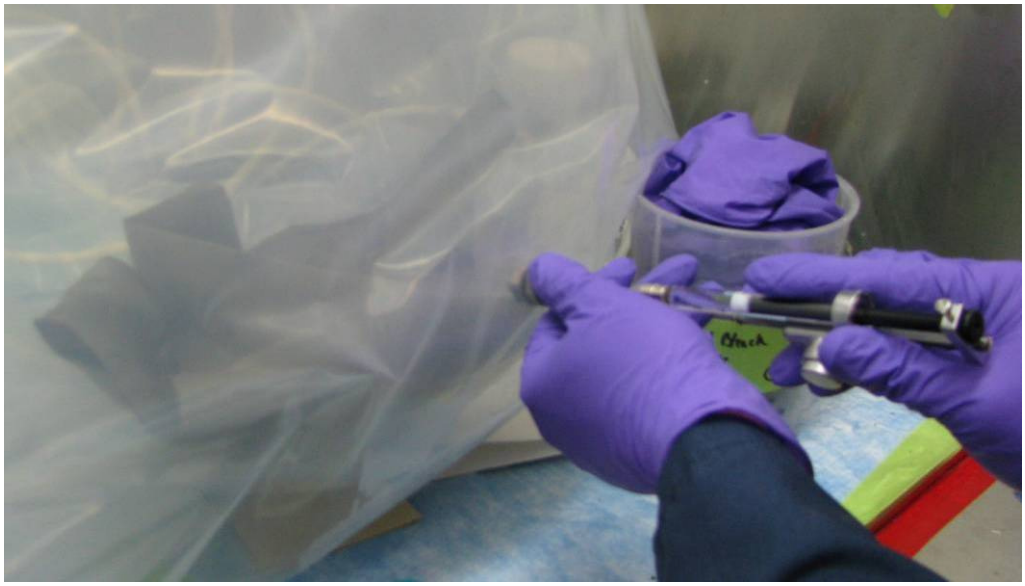

Figure 6. Agent Application through Septum Port.

The SMIC sample was prepared in the same manner, however only solvent (no agent) was applied to the material and at the same volume as the agent RDS that was applied to the test samples. The MIC sample was placed in the headspace bag and filled to 80 L as described above. No spike was applied to the MIC samples.

Time zero for the agent- and solvent-contaminated samples was taken as the time the samples were contaminated. Time zero for the MIC and the negative control sample was taken as the time the bag was sealed.

The POS control sample was a stainless steel disc (McMaster Carr part #2895T17, 4-inch diameter, 0.001-inch thick). The POS sample was prepared and spiked with the same volume of agent solution used to spike the waste material samples. The NEG control sample was an empty bag filled with 80 L of dry, filtered house air.

Spike controls were prepared in triplicate during each trial by adding the same volume of agent solution directly into a small vial containing a known amount of the appropriate solvent (Hexane for HD, and IPA for GB and VX) to verify the amount of agent applied to the samples. One spike control was prepared at the beginning of the spiking operation, one in the middle, and one at the end (except in trial 1; all spike controls were prepared at the end of the spiking operation).

3.2.1.2 Charcoal Test Items at the WCL

The charcoal packed beds were connected to the ACAMS sample line. At the start of the ACAMS sample cycle, the required amount of agent solution (6 µL) was applied to the glass wool using a 100-µL syringe with a stepper motor (three drops, each 2 µL in volume). The agent vapor was pulled through the charcoal bed at a flow rate of ~800 mL/min (the ACAMS sample flow rate) for the duration of the sample cycle (~3.83 min). The ACAMS verified that agent did not breakthrough or channel through the charcoal bed by reporting <0.2 VSL during the agent loading of each charcoal sample for each trial.

After the charcoal sample was loaded with agent, it was placed into the headspace bag by removing the glass wool at the end of the Teflon tubing and inverting the tube into the bag. The loose charcoal was sealed in the bag and the bag was filled to 80 L with dry, filtered, house air using the same compressed air and mass flow controller as described in Section 3.2.1.1. The

time required to place the loose charcoal into the headspace bag and seal the bag was less than 10 min. The time required to fill the bag with 80 L of air was 8 min. The glass wool and Teflon tubing was not placed in the headspace bags. Time zero was taken as the time the bag was sealed. This application method is depicted in Figure 7.

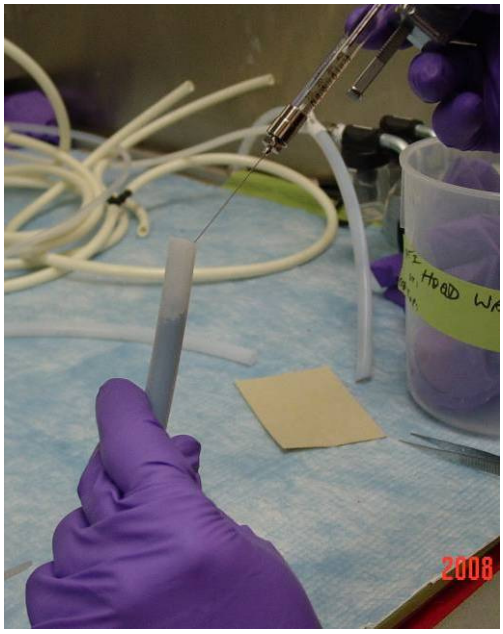

Figure 7. Agent Application for Vapor Loading Method

The SMIC was prepared in the same manner, however only solvent (no agent) was applied to the glass wool and at the same volume as the agent RDS that was applied to the test samples. The MIC was placed in the headspace bag and the bag was filled to 80 L as described above.

The POS was a stainless steel disc (McMaster Carr part #2895T17, 4-inch diameter, 0.001-inch thick). This sample was prepared and spiked with agent as described in Section 3.2.1.1; however agent was applied to only three locations. The NEG was an empty bag filled with 80 L of dry, filtered, house air.

Spike controls were prepared in triplicate during each trial by adding the same volume of agent solution directly into a small vial containing a known amount of the appropriate solvent (hexane for HD, and IPA for GB and VX). Also, the vapor loading method was validated by generating a reference sample at the start and end of each trial. These reference samples consisted of solid sorbent tubes (Orbo 90, Supelco product #20358, containing carboxen-564)

contaminated with agent using the same method as the charcoal samples described above. The agent RDS was spiked onto the glass wool in front of the solid sorbent bed. The solid sorbent tubes were extracted in chloroform. The glass wool was not extracted. The purpose of this sample was to verify the vapor loading process.

3.2.1.3 DPE and Butyl Rubber Test Items at the CHL

The DPE suit material and butyl rubber apron material were also tested at the CHL for VX. This value is equivalent to 0.55 mg of VX. Each simulated secondary waste item was placed into a double LDPE bag, and filled as described above for the WCL testing. A 2.5-mL syringe with a repeating dispenser was used to apply the VX solution (in IPA) to the material (50 µL of agent RDS per drop). The agent RDS was applied to the material according to the pattern shown in Figure 8. The diameter of the spike pattern did not exceed 4 inches. However, because of the specific geometry of the material and folds that were present, this pattern was approximated. Also, the total volume (number of drops) was adjusted based on the actual concentration of the RDS solution (as verified by GC) and the mass of waste material sample. The spike location on the DPE suit and butyl rubber apron was the exterior of the material and, where accessible by the syringe needle, within folds of the material.

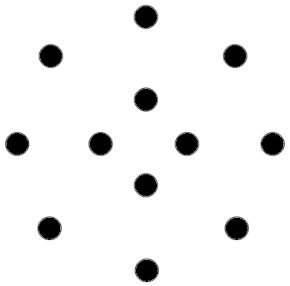

Figure 8. Spike Application Pattern.

The SMIC and POS were prepared using the same blank solvent and RDS volume, respectively, and using the same application pattern as described above. The spike controls were prepared in triplicate by adding the same volume of agent solution to a vial containing a known quantity of IPA. The MIC and NEG samples were prepared in the same manner as described for the tests at the WCL (section 3.2.1.1).

3.2.2 Headspace monitoring

Before each trial, the ACAMS was calibrated and a challenge check was performed (see Appendix A) by injecting through the heated sample line; all injections were made using the heated sample line. Calibrations were performed by making two 1.0-VSL injections into a heated sample line with a blank cycle in between. The minimum ACAMS response at 1 VSL was > 5 nA. The ACAMS was left running for the duration of the trial. The ACAMS was disconnected from the bags between sampling events. In order to maintain a clean sampling line between sampling events, a carbon filter was placed on the end of the ACAMS sample line between sampling events and overnight.

The inner bag was monitored at the specified holding time after the bag was sealed. The monitoring consisted of one full sample cycle from the inner bag. If any of the bags contained a headspace of 1.0 VSL or greater, one additional headspace sample was obtained, not to exceed the 48-hour sample period, and then no further monitoring of that bag was performed. For the purposes of the test, to determine whether additional headspace samples would be measured, the alarm setpoint was set to 1.0 VSL.

At the start and conclusion of each ACAMS monitoring interval, a 1.0-VSL challenge was performed through the heated sample line; if this challenge failed (exceeded ±25% of the target concentration), a second challenge was performed. If the second challenge failed, then corrective action was performed. Corrective action included performing a third challenge using another solution vial, performing a calibration, performing routine or preventive maintenance, or other activities. If the ACAMS failed all three challenge checks, then the results were flagged for further examination. At least one blank cycle was performed between calibration, challenge checks, and samples.

The ACAMS went out of control twice during the test. The first time was during the HD DPE suit 12-hour sampling event. The ACAMS ending challenge was 1.30 VSL. The results from the samples were high throughout the sampling event, however the previous blank cycle was clear (0.00 VSL) indicating that the high failure is likely not a result of carryover. The results from the sampling interval are valid since all of the samples were well above the reported

value of the 1 VSL challenge check (reported as 1.30 VSL). The ACAMS was recalibrated for the 24 hour sampling event.

The second time the ACAMS went out of control was during the VX CHL butyl rubber 4-hour sampling interval. There was significant carryover during the trial. The results of the samples are 20 – 290 times higher than the ACAMS challenge concentration. While VX carryover was significant, the results from the trial still show the headspace was above the VSL and are valid. The results were recorded on the test parameter control sheet (TPCS), included in Appendix B.

The monitoring of the agent-contaminated bags was performed in a chemical agent fume hood, as shown in Figure 2. Monitoring of the SMIC, the MIC, and NEG was performed on the laboratory bench.

4.0 ANALYSIS

The verification of the spiking solutions, the spike controls for each trial, and the vapor reference samples for the charcoal trials were performed by analysis on a GC/FID or a flame photometric detector (GC/FPD). The GC samples that were above the calibration range of the instrument were diluted and reanalyzed. Analytical requirements included:

- Calibration curve must have an $r^2 > 0.990$.
- Each point on the calibration curve must be within ±15% of the nominal value except for the lowest point on the curve which must be within ±25%.
- Continuing calibration verification (CCV) standards, at concentrations spanning the full range of the calibration curve, must be analyzed every five samples and at the end of an analytical sequence.
- CCVs must be within ±25% of the nominal value.

Each requirement was met during analysis of the GC samples.

The verification results (as measured by GC/FID) of the agent spiking solutions are included in Table 9. Also included in Table 9 are the spike volumes for the trials and the calculated average WCL value for the seven replicates in the trial.

Table 9. Agent Spiking Data

Trial #	Agent	Matrix	Concentration by GC (µg/mL)	Spike Volume (µL)	Agent Mass Applied (µg)	Average Matrix Mass (g)	Average WCL (ng/g)
1	HD	DPE	3797	22.0	83.5	428.3	195
2	HD	Butyl Rubber	2014	18.0	36.2	195.19	186
3	HD	Wood	4693	22.0	103	521.16	198
4	HD	Charcoal	306.9	6.0	1.84	10.01	184
5	GB	DPE	435.2	20.0	8.70	428.6	20
6	GB	Butyl Rubber	132.0	20.0	2.64	131.32	20
7	GB	Wood	445.0	20.0	8.90	481.31	18
8	GB	Charcoal	33.10	6.0	0.20	10.01	20
9	VX	DPE	464.8	18.0	8.37	428.6	20
10	VX	Butyl Rubber	125.3	20.0	2.51	131.34	19
11	VX	Wood	555.7	20.0	11.1	552.94	20
12	VX	Charcoal	36.52	6.0	0.22	10.00	22
13*	VX	DPE	869.8	600.0	522	428.44	na
14*	VX	Butyl Rubber	990.2	550.0	545	128.73	na

*VX/Contact Hazard Limit Trials

Spike control samples were analyzed by GC/FID or GC/FPD. The agent mass was calculated using the GC result, the volume of solvent in the spike control vial, and the volume of RDS applied; the calculation is shown in equation 4.

$$M = C * (V_{SC} + V_{RDS}) \quad (4)$$

Where: M = agent mass applied (µg)
C = Concentration by GC analysis (µg/mL)
V_{SC} = Volume in the spike control vial (typically 1 mL)
V_{RDS} = Volume of RDS spiking solution applied (typically 20.0 µL).

The average of the measured values of the triplicate spike controls in each trial met the requirement specified in the Test Plan (±20% of the target) during each trial. The target value was the agent mass listed in Table 9. The average values (based on 3 replicates) are reported in

Table 10 for each trial. The results for the replicate spike control samples prepared during each trial are reported in Appendix D.

Table 10. Spike Control Results

Trial #	Agent	Matrix	Found Average Agent Mass (µg)	% diff from Target	Found Average WCL (ng/g)
1	HD	DPE	85.3	2.2	199
2	HD	Butyl Rubber	37.0	2.2	190
3	HD	Wood	116	12	222
4	HD	Charcoal	1.95	5.8	195
5	GB	DPE	9.24	6.2	22
6	GB	Butyl Rubber	2.54	3.7	19
7	GB	Wood	9.68	8.7	20
8	GB	Charcoal	0.212	6.9	21
9	VX	DPE	7.26	13	17
10	VX	Butyl Rubber	2.45	2.3	19
11	VX	Wood	11.2	0.58	20
12	VX	Charcoal	0.193	12	19
13	VX	DPE	581	11	na
14	VX	Butyl Rubber	573	5.2	na

The agent vapor reference samples obtained during the charcoal tests are reported in Appendix D. The target value for these samples was the agent mass listed in Table 9. The measured values of the samples in each trial met the requirement specified in the Test Plan (±35% of the target value).

5.0 RESULTS

The results of each trial are discussed in the following sections. An evaluation of the results from the sampling intervals and the effect of the matrix on agent evaporation was performed.

5.1 TEMPERATURE AND HUMIDITY

The temperature and relative humidity of the laboratory were recorded during testing. The plot in Figure 9 includes the maximum, minimum, and average value for temperature and relative humidity for each trial. Detailed results of the temperature and humidity measurements are included in Appendix E. The temperature and relative humidity were measured at one minute intervals using a calibrated Oakton Microlog datalogger. The Oakton Microlog datalogger was calibrated by the Battelle Instrument Laboratory prior to testing.

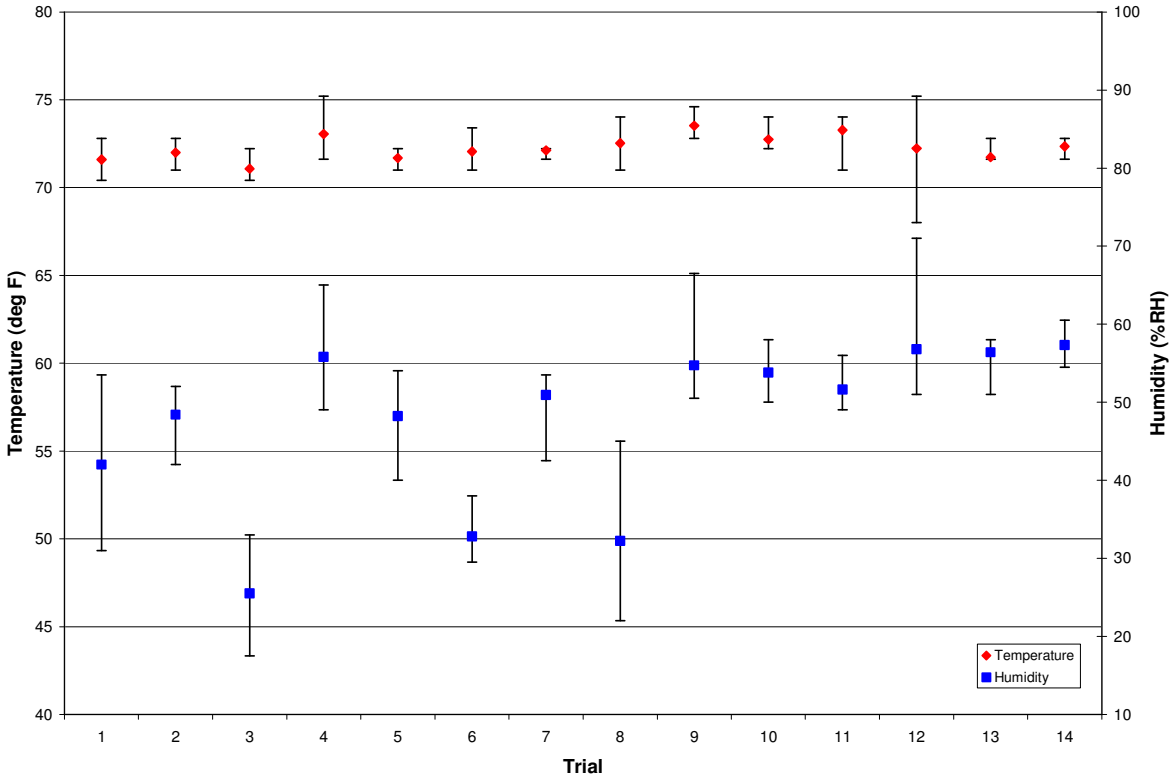

Figure 9. Laboratory Temperature and Relative Humidity

The laboratory temperature during the testing was 72±5°F as specified in the test plan. The average relative humidity in the laboratory during the program was 45% RH. However, the samples were sealed during testing and the relative humidity within the bags was much different since the waste bags were filled with filtered, dry, house air controlled to a dew point of -52°F.

5.2 AGENT HD

5.2.1 Trial 1- DPE Suit Contaminated with HD

The DPE material samples were sealed in LDPE bags, filled with air, and contaminated at the WCL. The first two headspace bag samples (DP01-01 and DP01-02) were filled to 80 L using an air flow rate of 20.0 Lpm for four minutes. The remaining bags were filled at 10.0 Lpm for eight minutes. The GC verification of the HD spiking solution for this trial resulted in a concentration of 3797 µg/mL. Therefore, a total of 22 µL of solution was applied at eleven locations to achieve the WCL, based on the weight of the DPE material samples. The spike controls were prepared in triplicate at the end of the spiking operation (for this trial only). After contamination with HD, sample bag DP01-04 was damaged when positioning it in the hood. The sample port bulkhead fitting was ripped from the inner headspace bag. The seal with the outer bag remained intact.

The ACAMS passed the challenge checks for all sampling intervals except the 12-hour period. The challenge checks at the end of the 12-hour monitoring period were high (1.30 VSL). Corrective action was taken by re-calibrating the ACAMS. The results of the 12-hour monitoring interval were flagged.

The ASI sample (DP01-08) was monitored at 15 minutes and 45 minutes with the ACAMS. The results were above the alarm setpoint as determined by the P&A study. Additional monitoring of DP01-08 was not performed.

The monitoring results for all samples are included in Table 11. Five of the seven replicate DPE samples were monitored above the alarm setpoint at the 4-hour interval. These samples were monitored at the 12-hour interval and at one additional time (the 24-hour period) because the ACAMS data at the 12-hour interval was flagged. The remaining two samples

(DP01-04 and DP01-07) were monitored through the 48-hour holding time because the monitoring results were below the 1 VSL threshold specified in the Test Plan (DP01-04 was monitored at 1.35 VSL at the 12-hour holding time, but the data was flagged).

Table 11. ACAMS Results for Trial 1- HD/DPE

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr[b]**	**24 hr**	**48 hr**
NA	ACAMS Check	1.09	1.25	0.98	1.03
1	DP01-01	4.11	3.62	1.98	NP
2	DP01-02	7.14	7.42	3.10	NP
3	DP01-03	4.91	3.70	2.06	NP
4	DP01-04[c]	0.77	1.35	0.95	0.46
5	DP01-05	6.12	4.48	2.59	NP
6	DP01-06	7.63	5.16	2.72	NP
7	DP01-07	0.33	0.21	0.12	0.06
MIC	DP01-09	<LOQ	<LOQ	<LOQ	<LOQ
SMIC	DP01-10	<LOQ	<LOQ	0.05	<LOQ
POS	DP01-11	10.1	6.76	3.52	1.66
NEG	DP01-12	<LOQ	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	1.12	1.30	1.00	1.08
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	1.00	NP[d]	NP	NP
ASI	DP01-08	14.0	10.8	NP	NP
NA	ACAMS Check	NP[d]	1.09	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Data has been flagged because the challenge check at the end of the sampling interval was outside of the allowed range (1.30 VSL).
c = The inner bag of DP01-04 was torn. The outer bag remained intact.
d = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL

The low result of sample DP01-04 was attributed to the tear in the bag. However, the low result of DP01-07 had no assignable cause. The sample DP01-07 was inspected at the end of the trial and no damage or tears in the bag were detected. The monitoring results of the SMIC, MIC, and NEG were at or below LOQ, indicating that HD was not present and these materials did not act as positive interferents.

The results from the 24-hr sampling interval are significantly lower that the 4- and 12-hr sampling intervals. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.2.2 Trial 2- Butyl Rubber Apron Contaminated with HD

During the first butyl rubber trial, a photomultiplier tube (PMT) voltage error was reported by the ACAMS. This error prevented monitoring of the headspace bags at the specified intervals. The ACAMS was repaired, and the trial was repeated with new butyl rubber samples and headspace bags. The new butyl rubber samples used in this trial were identified by adding an R to the sample identification (i.e. BR02**R**-01).

The butyl rubber material samples were placed into an LDPE bag and contaminated at an average WCL of 186 ng HD/g of butyl rubber. The GC verification of the HD spiking solution for this trial resulted in a concentration of 2014 µg/mL. Therefore, a total of 18 µL of solution was applied at nine locations to achieve the WCL, based on the weight of the butyl rubber material samples. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample (BR02R-08) was monitored at 15 minutes and 45 minutes with the ACAMS. The results were above the alarm setpoint as determined by the P&A study. Additional monitoring of BR02R-08 was not performed because the results were above the threshold value.

The monitoring results for all samples are included in Table 12. All seven replicate butyl rubber samples were monitored above the alarm setpoint at the 4-hour interval. These samples were also monitored at the 12-hour interval. The monitoring results of the SMIC, MIC, and NEG were all below the LOQ, indicating that HD was not present and these materials did not act as positive interferents.

Table 12. ACAMS Results for Trial 2R- HD/Butyl Rubber

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	0.89	1.06	NP	NP
1	BR02R-01	2.09	1.75	NP	NP
2	BR02R-02	2.47	2.27	NP	NP
3	BR02R-03	2.10	2.13	NP	NP
4	BR02R-04	2.14	1.88	NP	NP
5	BR02R-05	2.17	1.79	NP	NP
6	BR02R-06	2.31	1.78	NP	NP
7	BR02R-07	2.21	1.86	NP	NP
MIC	BR02R-09	<LOQ	<LOQ	NP	NP
SMIC	BR02R-10	<LOQ	<LOQ	NP	NP
POS	BR02R-11	3.81	2.61	NP	NP
NEG	BR02R-12	<LOQ	<LOQ	NP	NP
NA	ACAMS Check	0.99	1.06	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.93	NP[b]	NP	NP
ASI	BR02R-08	8.32	6.72	NP	NP
NA	ACAMS Check	NP[b]	0.90	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL

The results from the 12-hr sampling interval are lower than the 4-hr sampling interval for all samples with the exception of BR02R-03. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.2.3 Trial 3- Wood Contaminated with HD

The wood samples were placed in LDPE bags and contaminated at an average WCL of 198 ng HD/g wood. The GC verification of the HD spiking solution for this trial resulted in a concentration of 4693 µg/mL. Therefore, a total of 22.0 µL of solution was applied at eleven locations to achieve the WCL, based on the weight of the wood material samples. The spike

controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at 15 minutes and 45 minutes with the ACAMS. The results were above the alarm setpoint as determined by the P&A study. Additional monitoring was not performed.

The monitoring results for all samples are included in Table 13. All seven replicate wood samples were monitored above the alarm setpoint at the 4-hour interval. The monitoring results of the SMIC, MIC, and NEG were all below the LOQ, indicating that HD was not present and these materials did not act as positive interferents.

Table 13. ACAMS Results for Trial 3- HD/Wood

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	0.88	0.92	NP	NP
1	WD03-01	9.35	5.80	NP	NP
2	WD03-02	8.82	5.51	NP	NP
3	WD03-03	8.54	5.51	NP	NP
4	WD03-04	8.08	5.08	NP	NP
5	WD03-05	8.86	5.73	NP	NP
6	WD03-06	9.19	5.35	NP	NP
7	WD03-07	9.40	6.09	NP	NP
MIC	WD03-09	<LOQ	<LOQ	NP	NP
SMIC	WD03-10	<LOQ	<LOQ	NP	NP
POS	WD03-11	9.69	6.38	NP	NP
NEG	WD03-12	<LOQ	<LOQ	NP	NP
NA	ACAMS Check	0.89	0.99	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.99	NP[b]	NP	NP
ASI	WD03-08	19.5	14.6	NP	NP
NA	ACAMS Check	NP[b]	0.89	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL

The results from the 12-hr sampling interval are significantly lower that the 4-hr sampling intervals. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.2.4 Trial 4- Charcoal Contaminated with HD

The charcoal samples were contaminated using the vapor loading method described in Section 3.2.1.2. The charcoal was contaminated at an average WCL of 184 ng HD/g charcoal. The GC verification of the HD spiking solution for this trial resulted in a concentration of 306.9 µg/mL. Therefore a total of 6 µL was spiked into the charcoal. The spike controls were prepared at the beginning, middle, and end of the agent application operation.

When filling sample bag CH04-08 with air, it was observed that the "J" closure was not completely sealed. The bag was resealed and filled to 80 L. The vapor loading reference samples prepared at the start and end of the agent application procedure were both within the required ±35% of the target value. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at all intervals with the ACAMS. All results were below the alarm setpoint. The monitoring results for all samples are included in Table 14. All samples (including the POS) were monitored below the alarm setpoint at all intervals. The results of the POS indicate that the mass of agent added to the samples was not large enough to create a significant vapor concentration in the headspace. Therefore, the effect of the charcoal material on the HD vapor concentration (if any) cannot be determined.

Finally, the monitoring result for CH04-05 at the 48-hour interval is flagged because the sample port collapsed against the side of the bag during the ACAMS sample cycle, resulting in a low sample flow error.

Table 14. ACAMS Results for Trial 4- HD/Charcoal

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	1.05	1.04	0.95	0.95
1	CH04-01	0.12	0.10	0.05	0.05
2	CH04-02	0.11	<LOQ	<LOQ	0.05
3	CH04-03	0.11	<LOQ	0.05	0.05
4	CH04-04	0.08	<LOQ	<LOQ	0.05
5	CH04-05	0.05	<LOQ	0.05	0.13[b]
6	CH04-06	0.06	<LOQ	0.05	0.05
7	CH04-07	0.06	<LOQ	0.05	0.05
MIC	CH04-09	0.11	0.10	0.06	0.06
SMIC	CH04-10	0.10	0.09	<LOQ	0.06
POS*	CH04-11	0.08	0.05	0.06	0.05
NEG	CH04-12	0.11	<LOQ	0.06	0.05
NA	ACAMS Check	1.13	1.05	0.92	0.87
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	1.05	NP[c]	1.05	NP[c]
ASI	CH04-08	0.12	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	NP[c]	1.06	NP[c]	1.13

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Sample flow rate error during sampling. Bag collapsed against sample port during sampling.
c = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL
*Spike amount not significant enough to distinguish from matrix interferent

5.3 AGENT GB

5.3.1 Trial 5- DPE Suit Contaminated with GB

The DPE suit samples were contaminated at an average WCL of 20 ng GB/g DPE. The GC verification of the GB spiking solution for this trial resulted in a concentration of 435.2 µg/mL. Therefore, a total of 20 µL of solution was applied at ten locations to achieve the WCL, based on the weight of the DPE suit samples. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at 15 minutes with the ACAMS. The result of 484 VSL was above the alarm setpoint as determined by the P&A study. The second monitoring interval was late by 20 minutes because of the time required to clear down the previous sample.

The monitoring results for all samples are included in Table 15. All seven replicate DPE samples were monitored above the alarm setpoint at the 4- and 12-hour intervals. However, there was insufficient time to allow the ACAMS to clear down to <0.20 VSL between samples. Therefore, a residual value of ~10% of the original sample result remained when monitoring the contaminated samples.

Monitoring of the NEG, the SMIC, and the MIC samples was delayed because the ACAMS was required to clear down to <0.20 VSL. The MIC monitoring result (sample DP05-09) was lost for the 4-hour interval because of a pre-concentrator tube (PCT) heater error in the ACAMS. This error occurred during the analytical portion of the ACAMS cycle, after the bag was sampled. The ACAMS was restarted and a challenge check was performed prior to monitoring another headspace bag. The challenge check reported within tolerance and indicated the ACAMS remained in configuration control.

The monitoring results of the SMIC, MIC, and NEG were above the LOQ yet <0.20 VSL; this is due to the significant carryover from the high sample readings. Based on these results, low-level matrix interference cannot be assessed.

Table 15. ACAMS Results for Trial 5- GB/DPE

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr[b]**	**12 hr[b]**	**24 hr**	**48 hr**
NA	ACAMS Check	1.00	1.02	NP	NP
1	DP05-01	215	125	NP	NP
2	DP05-02	257	151	NP	NP
3	DP05-03	298	181	NP	NP
4	DP05-04	297	190	NP	NP
5	DP05-05	316	201	NP	NP
6	DP05-06	293	192	NP	NP
7	DP05-07	289	168	NP	NP
MIC	DP05-09	SL	0.14	NP	NP
SMIC	DP05-10	0.08	0.14	NP	NP
POS	DP05-11	691	619	NP	NP
NEG	DP05-12	0.14	0.12	NP	NP
NA	ACAMS Check	1.09	1.12	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.89	NP[c]	NP	NP
ASI	DP05-08	484	456	NP	NP
NA	ACAMS Check	NP[c]	1.00	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = GB contaminated samples were monitored without a complete clear down of the ACAMS. A residual reading of ~10% remained. Some samples were late because of the additional time required to clear down the ACAMS.
c = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
SL = Sample Lost because of ACAMS error (PCT Temp. error). Challenge check after corrective action was reported as 1.17 VSL.
NP = Sampling not performed.

The results from the 12-hr sampling interval are significantly lower than the 4-hr sampling interval. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.3.2 Trial 6- Butyl Rubber Apron Contaminated with GB

The butyl rubber samples were contaminated at an average WCL of 20 ng GB/g butyl rubber material. The GC verification of the GB spiking solution for this trial resulted in a concentration of 132 µg/mL. Therefore, a total of 20 µL of solution was applied at ten locations

to achieve the WCL, based on the weight of the butyl rubber material samples. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at 15 and 45 minutes with the ACAMS. The results were above the alarm setpoint. The ACAMS monitoring results are included in Table 16. All seven replicate butyl rubber samples were monitored above the alarm setpoint at the 4- and 12-hour intervals. Again, because of the high values of these samples, there was insufficient time to allow the ACAMS to clear down to <0.20 VSL between samples. Therefore, a residual value of ~10% of the original sample result remained when monitoring the contaminated samples.

Table 16. ACAMS Results for Trial 6- GB/Butyl Rubber

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr[b]**	**12 hr[b]**	**24 hr**	**48 hr**
NA	ACAMS Check	0.93	0.83	NP	NP
1	BR06-01	185	117	NP	NP
2	BR06-02	174	114	NP	NP
3	BR06-03	178	109	NP	NP
4	BR06-04	166	102	NP	NP
5	BR06-05	171	107	NP	NP
6	BR06-06	181	118	NP	NP
7	BR06-07	199	121	NP	NP
MIC	BR06-09	0.08	<LOQ	NP	NP
SMIC	BR06-10	0.07	<LOQ	NP	NP
POS	BR06-11	247	207	NP	NP
NEG	BR06-12	<LOQ	<LOQ	NP	NP
NA	ACAMS Check	0.98	0.97	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.89	NP[c]	NP	NP
ASI	BR06-08	272	255	NP	NP
NA	ACAMS Check	NP[c]	0.93	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = GB contaminated samples were monitored without a complete clear down of the ACAMS. A residual reading of ~10% remained.
c = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL

The monitoring results of the SMIC and MIC were above the LOQ yet < 0.20 VSL during the 4-hr sampling interval due to the significant carryover from the high sample readings. The SMIC and MIC were <LOQ at the 12-hr sampling interval. The NEG was <LOQ during both sampling events.

The results from the 12-hr sampling interval are significantly lower that the 4-hr sampling interval. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.3.3 Trial 7- Wood Contaminated with GB

The wood samples were contaminated at an average WCL for this trial at 18 ng GB/g wood. The GC verification of the GB spiking solution for this trial resulted in a concentration of 445 µg/mL. Therefore, a total of 20 µL of solution was applied at ten locations to achieve the WCL, based on the weight of the wood samples. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at 15 and 45 minutes with the ACAMS. The results were above the alarm setpoint. After the 45-minute sample was reported, a PCT heater error occurred at the ACAMS. The ACAMS was restarted and a challenge check was performed. The challenge check reported within tolerance and indicated the ACAMS remained in configuration control.

The ACAMS monitoring results are included in Table 17. The WD07-01 monitoring result was lost for the 4-hour interval because of a PCT heater error at the ACAMS. This error occurred during the analytical portion of the ACAMS cycle, after the bag was sampled. A challenge check was performed after corrective action was performed to correct the error (the PCT heater cable was adjusted) prior to monitoring another headspace bag. The challenge check reported within tolerance and indicated the ACAMS remained in configuration control. All other replicate wood samples were monitored above the alarm setpoint at the 4- and 12-hour intervals. Again, because of the high values of these samples, there was insufficient time to allow the

ACAMS to clear down to <0.20 VSL between samples. Therefore, a residual value of ~10% of the previous sample remained when monitoring the contaminated samples.

The monitoring results of the SMIC and MIC were above the LOQ yet < 0.20 VSL during the 4-hr sampling interval due to the significant carryover from the high sample readings. The SMIC and MIC were <LOQ at the 12-hr sampling interval. The NEG was <LOQ during both sampling events.

Table 17. ACAMS Results for Trial 7- GB/Wood

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr[b]**	**12 hr[b]**	**24 hr**	**48 hr**
NA	ACAMS Check	1.08	1.08	NP	NP
1	WD07-01	7.32[c]	370	NP	NP
2	WD07-02	496[c]	342	NP	NP
3	WD07-03	498[c]	339	NP	NP
4	WD07-04	483[c]	303	NP	NP
5	WD07-05	469[c]	307	NP	NP
6	WD07-07	450[c]	295	NP	NP
7	WD07-06	464[c]	323	NP	NP
MIC	WD07-09	0.06	<LOQ	NP	NP
SMIC	WD07-10	0.07	<LOQ	NP	NP
POS	WD07-11	700	585	NP	NP
NEG	WD07-12	<LOQ	<LOQ	NP	NP
NA	ACAMS Check	1.23	1.17	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	1.00	NP[d]	NP	NP
ASI	WD07-08	601	571	NP	NP
NA	ACAMS Check	NP[d]	1.08[e]	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = GB contaminated samples were monitored without a complete clear down of the ACAMS. A residual reading of ~10% remained.
c = PCT Temp. error occurred at the ACAMS while monitoring WD07-01 at the 4-hr interval. Challenge check after corrective action was reported as 1.09 VSL. The remaining samples were approximately one hour late because of the delay.
d = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
e = PCT Temp. error occurred at the ACAMS after monitoring WD07-08 at the 45-min interval. The challenge check reported in the table was performed after corrective action.
NP = Sampling not performed.
LOQ = 0.05 VSL

The results from the 12-hr sampling interval are significantly lower than the 4-hr sampling interval. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.3.4 Trial 8- Charcoal Contaminated with GB

The charcoal material samples were contaminated using the vapor loading method described in Section 3.2.1.2. The charcoal was contaminated at an average WCL of 18 ng GB/g charcoal. The GC verification of the GB spiking solution for this trial resulted in a concentration of 33.1 µg/mL. Therefore, a total of 6 µL of solution was applied to achieve the WCL, based on the weight of the charcoal. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The vapor loading reference samples prepared at the start and end of the agent application procedure were both within the required ±35% of the target value. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at all intervals with the ACAMS. All results were below the alarm setpoint. The monitoring results for all samples are included in Table 18. All samples except the POS were monitored below the alarm setpoint at all intervals. The ACAMS reported the POS above the alarm setpoint at all monitoring intervals.

Table 18. ACAMS Results for Trial 8- GB/Charcoal

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr[b]**
NA	ACAMS Check	1.10	0.98	1.22	1.20
1	CH08-01	<LOQ	<LOQ	<LOQ	<LOQ
2	CH08-02	<LOQ	<LOQ	<LOQ	<LOQ
3	CH08-03	<LOQ	<LOQ	<LOQ	<LOQ
4	CH08-04	<LOQ	<LOQ	<LOQ	<LOQ
5	CH08-05	<LOQ	<LOQ	<LOQ	<LOQ
6	CH08-06	<LOQ	<LOQ	<LOQ	<LOQ
7	CH08-07	<LOQ	<LOQ	<LOQ	<LOQ
MIC	CH08-09	<LOQ	<LOQ	<LOQ	<LOQ
SMIC	CH08-10	<LOQ	<LOQ	<LOQ	<LOQ
POS	CH08-11	18.5	11.4	7.03	1.74
NEG	CH08-12	<LOQ	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	1.07	1.03	1.16	1.20
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	1.17	NP[c]	1.07	NP[c]
ASI	CH08-08	0.08	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	NP[c]	1.12	1.10	1.07

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Initial calibration did not pass criteria. ACAMS was calibrated a second time. The monitoring was approximately one hour late because of the delay.
c = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.05 VSL

The POS results indicate that the mass of GB added to the headspace bags was sufficient to be detected by the ACAMS above the alarm setpoint. Therefore, the charcoal material prevented the GB vapor from accumulating to levels in the headspace that could be detected by the ACAMS.

The monitoring results for the SMIC, MIC, and NEG were all below LOQ, indicating that GB was not present and these materials did not act as interferents.

5.4 AGENT VX

During the VX trials a second peak was seen outside the agent window. The peak eluted after the agent window and grew larger over time which suggests that it was a result of carryover of some low-level interferent. This peak did not cause problems during the WCL trials (false positives were detected in one trial, Section 5.4.2). The agent gate was not widened prior to the CHL trials. Several times the ACAMS did not identify VX in the window. All of the data from the CHL trials were evaluated by examining the strip chart to verify the presence or absence of a VX peak in the VX window. For samples that were found to be false negatives, the VX concentration was calculated by comparing the peak height of the unreported peak to peak heights in samples where the ACAMS reported the VX concentration.

5.4.1 Trial 9- DPE Suit Contaminated with VX at the WCL

The DPE material samples were contaminated at an average WCL of 20 ng VX/g DPE. A total of 18.0 µL of a 464.8-µg/mL VX solution was applied at nine locations to each sample to achieve this WCL. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The monitoring results for the ASI sample and the seven replicate DPE samples were below the alarm setpoint for all monitoring periods. The monitoring results for all samples are included in Table 19. The monitoring results of the SMIC, MIC, and NEG were all below the LOQ, indicating that VX was not present and these materials did not act as interferents.

Table 19. ACAMS Results for Trial 9- VX/DPE

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	1.10	0.91	0.97	0.85
1	DP09-01	0.20	0.21	0.09	0.07
2	DP09-02	0.16	0.11	<LOQ	<LOQ
3	DP09-03	0.18	<LOQ	<LOQ	<LOQ
4	DP09-04	0.17	0.06	<LOQ	<LOQ
5	DP09-05	0.15	0.11	0.06	<LOQ
6	DP09-06	0.20	0.07	0.09	0.06
7	DP09-07	0.37	0.21	0.09	<LOQ
MIC	DP09-09	<LOQ	<LOQ	<LOQ	<LOQ
SMIC	DP09-10	<LOQ	<LOQ	<LOQ	<LOQ
POS	DP09-11	2.39	0.56	0.33	0.09
NEG	DP09-12	<LOQ	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	1.25	1.19	1.14	1.06
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.93	NP[b]	1.10	NP[b]
ASI	DP09-08	0.20	0.30	0.26	<LOQ
NA	ACAMS Check	NP[b]	1.22	NP[b]	1.25

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.06 VSL

The results of the 24-hr sampling interval are lower that the 4- and 12-hr sampling intervals. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.4.2 Trial 10- Butyl Rubber Apron Contaminated with VX at the WCL

The butyl rubber samples were contaminated at an average WCL of 19 ng VX/g butyl rubber. A total of 20.0 µL of a 125.3-µg/mL VX solution was applied at ten locations to each sample to achieve this WCL. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The monitoring results of the ASI sample and the seven replicate butyl rubber samples were below the alarm setpoint for all monitoring periods. Two additional monitoring periods were added at the request of EG&G; additional monitoring was performed on all samples at 122 hours, and on selected samples at 125 hours. The monitoring at 125 hours was performed after physically manipulating the sample bags in order to mix the headspace within the bag. The results at the 122- and 125-hour period were also below the alarm setpoint. The monitoring results for all samples are included in Table 20.

Table 20. ACAMS Results for Trial 10- VX/Butyl Rubber

		ACAMS Result (VSL)[a]					
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**	**122 hr**	**125 hr**
NA	ACAMS Check	1.04	0.93	0.90	0.84	0.91	0.85
1	BR10-01	0.24	0.14	0.10	0.08	<LOQ	<LOQ
2	BR10-02	0.16	0.10	0.09	0.06	<LOQ	NP
3	BR10-03	0.23	0.09	0.14	0.08	<LOQ	NP
4	BR10-04	0.31	0.11	0.11	0.10	<LOQ	<LOQ
5	BR10-05	0.14	0.09	0.06	0.06	<LOQ	<LOQ
6	BR10-06	0.19	0.10	0.38	0.11	<LOQ	NP
7	BR10-07	0.21	0.12	0.08	<LOQ	<LOQ	NP
MIC	BR10-09	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	NP
SMIC	BR10-10	<LOQ	<LOQ*	<LOQ	<LOQ*	<LOQ	NP
POS	BR10-11	0.62	0.25	0.17	0.13	<LOQ	<LOQ
NEG	BR10-12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	NP
NA	ACAMS Check	1.10	1.12	1.14	1.14	1.06	0.99
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**	**122 hr**	**125 hr**
NA	ACAMS Check	0.88	NP[b]	0.93	NP[b]	0.91	0.85
ASI	BR10-08	0.45	0.41	0.26	0.17	<LOQ	<LOQ
NA	ACAMS Check	NP[b]	1.01	1.04	1.10	1.06	0.99

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.06 VSL
*interferent peak caused a false reading. Strip chart was evaluated to confirm interferent peak.

The POS was > LOQ but less than the alarm setpoint. The monitoring results of the SMIC, MIC, and NEG were ≤ LOQ, indicating that VX was not present and these materials did not act as interferents. The interferent peak (discussed in Section 5.4) migrated into the agent

gate during the 12- and 48-hr sampling interval of the SMIC. The ACAMS strip chart was evaluated to verify the interference as a false positive.

The results from the 12-hr sampling interval (0.11 ± 0.02 VSL) are lower than the 4-hr sampling interval (0.21 ± 0.05 VSL). A t-test of the data showed significant difference at the 95% confidence level. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.4.3 Trial 11- Wood Contaminated with VX at the WCL

The wood samples were contaminated at an average WCL of 20 ng VX/g wood. A total of 20.0 µL of a 555.7-µg/mL VX solution was applied at ten locations to each sample to achieve this WCL. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The VX concentration in the headspace of the ASI sample was found to be above the alarm setpoint at the 15- and 45-minute periods. The seven replicate wood samples were found to be above the alarm setting at the 4 hour monitoring period. The monitoring results for all samples are included in Table 21. The results for sample WD11-04 were higher than those of the other samples. Although it appears that this sample may have been double spiked, the application procedure, performed by one staff member and observed by a second staff member, made this extremely improbable. The Hamilton repeating dispenser reproducibly delivers the same volume with each application. The gross error (i.e. malfunction of the dispenser) that would be required to deliver double the volume of agent solution would have also impacted the spike control sample prepared immediately after this sample. The spike controls were within the required range for this trial.

The monitoring results of the SMIC, MIC, and NEG were all below the LOQ, indicating that VX was not present and these materials did not act as interferents.

Table 21. ACAMS Results for Trial 11- VX/Wood

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr[b]**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	1.23	1.11	NP	NP
1	WD11-01	2.51	1.60	NP	NP
2	WD11-10	1.24	0.83	NP	NP
3	WD11-03	1.95	1.33	NP	NP
4	WD11-04	7.54	7.12	NP	NP
5	WD11-05	4.02	3.15	NP	NP
6	WD11-06	2.25	1.32	NP	NP
7	WD11-07	3.94	2.75	NP	NP
MIC	WD11-09	<LOQ	<LOQ	NP	NP
SMIC	WD11-02	<LOQ	<LOQ	NP	NP
POS	WD11-11	3.07	1.63	NP	NP
NEG	WD11-12	<LOQ	<LOQ	NP	NP
NA	ACAMS Check	1.23	1.18	NP	NP
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	1.22	NP[c]	NP	NP
ASI	WD11-08	4.89	2.49	NP	NP
NA	ACAMS Check	NP[c]	1.24	NP	NP

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Initial challenge check did not pass criteria. ACAMS was calibrated a second time. The monitoring was approximately one hour late because of the delay.
c = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.06 VSL

The results from the 12-hr sampling interval are lower than the 4-hr sampling interval. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.4.4 Trial 12- Charcoal Contaminated with VX at the WCL

The charcoal samples were contaminated using the vapor loading method described in Section 3.2.1.2. The charcoal was contaminated at an average WCL of 22 ng VX/g charcoal. A total of 6 µL of a 36.52-µg/mL VX solution was applied to each sample to achieve this WCL. The spike controls were prepared at the beginning, middle, and end of the agent application

operation. The vapor loading reference samples prepared at the start and end of the agent application procedure were both within the required ±35% of the target value. The ACAMS passed the challenge checks for all sampling intervals.

The ASI sample was monitored at all intervals with the ACAMS. All results were below the alarm setpoint. The monitoring results for all samples are included in Table 22. All samples (including the POS) were monitored below the alarm setpoint at all intervals; however, the POS was >LOQ indicating the presence of VX.

The monitoring results of the SMIC, MIC, and NEG were all below the LOQ, indicating that VX was not present and these materials did not act as interferents.

Table 22. ACAMS Results for Trial 12- VX/Charcoal

		ACAMS Result (VSL)[a]			
Simulated Waste Sample	**Sample ID**	**4 hr**	**12 hr**	**24 hr**	**48 hr**
NA	ACAMS Check	1.08	1.06	1.05	1.03
1	CH12-01	<LOQ	<LOQ	<LOQ	<LOQ
2	CH12-02	<LOQ	<LOQ	<LOQ	<LOQ
3	CH12-03	<LOQ	<LOQ	<LOQ	<LOQ
4	CH12-04	<LOQ	<LOQ	<LOQ	<LOQ
5	CH12-05	<LOQ	<LOQ	<LOQ	<LOQ
6	CH12-06	<LOQ	<LOQ	<LOQ	<LOQ
7	CH12-07	<LOQ	<LOQ	<LOQ	<LOQ
MIC	CH12-09	<LOQ	<LOQ	<LOQ	<LOQ
SMIC	CH12-10	<LOQ	<LOQ	<LOQ	<LOQ
POS	CH12-11	0.17	0.13	0.13	<LOQ
NEG	CH12-12	<LOQ	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	1.10	1.08	1.22	1.16
Simulated Waste Sample	**Sample ID**	**15 min**	**45 min**	**2 hr**	**4 hr**
NA	ACAMS Check	0.92	NP[b]	1.08	NP[b]
ASI	CH12-08	<LOQ	<LOQ	<LOQ	<LOQ
NA	ACAMS Check	NP[b]	1.19	NP[b]	1.10

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
NP = Sampling not performed.
LOQ = 0.06 VSL

5.4.5 Trial 13- DPE Suit Contaminated with VX at the CHL

In this trial, the DPE material samples were contaminated at the CHL as described in Section 3.2.1.3. A total of 600.0 µL of an 869.8-µg/mL VX solution was applied at twelve locations to each sample to achieve the CHL. The spike controls were prepared at the beginning, middle, and end of the agent application operation. The ACAMS passed the challenge checks for all sampling intervals.

The monitoring results for all samples are included in Table 23. The ASI sample was measured above the alarm setpoint at the 15-minute and 4-hour monitoring periods. All of the seven replicate DPE samples were found to be above the alarm setpoint at the 4-hour monitoring period. The ACAMS did not have sufficient time to clear down completely between samples. The agent window on the ACAMS was not adjusted to accommodate for the larger peak size from the samples.

Additionally, a second peak was present in all VX samples. It appeared to combine with the VX peak and impacted the capability of the ACAMS to report the VX peak. These peaks are illustrated in the sample chromatograms included in Figures 10-12. The dashed lines in these figures indicate the start and end of a sample cycle; the agent window is identified with tick marks below the chromatogram (with a corresponding set above the chromatogram). Figure 10 depicts a challenge check injection prior to headspace sampling; the secondary peak is not present. Figure 11 depicts the matrix interferent control sample (DP13-9) at valve position 9 (indicated in Figure 11 as POS 9). This Figure clearly shows the secondary peak just outside the agent window. The test samples DP13-5 and DP13-6 are shown in Figure 12 (DP13-5 located at position 5 and DP13-6 located at position 6 are indicated in the figure as POS 5 and POS 6, respectively). The interferent peak overlaps with the VX peak due to the large headspace concentration of the sample. The ACAMS was able to report the VX in sample DP13-5, but, with additional carryover in sample DP13-6, the ACAMS did not report agent. Therefore, the ACAMS strip chart was evaluated to determine the presence of VX in all of the samples in the trial; the concentration of the VX was evaluated by assessing the peak height and relating the peak height to the ACAMS readings from samples that were not impacted by the interferent.

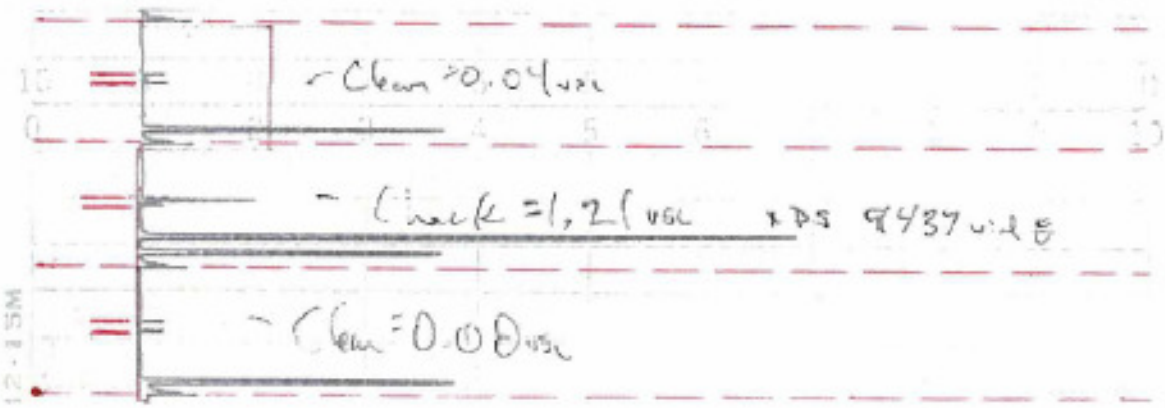

Figure 10. ACAMS Chromatogram of a Challenge Check at 1.0 VSL

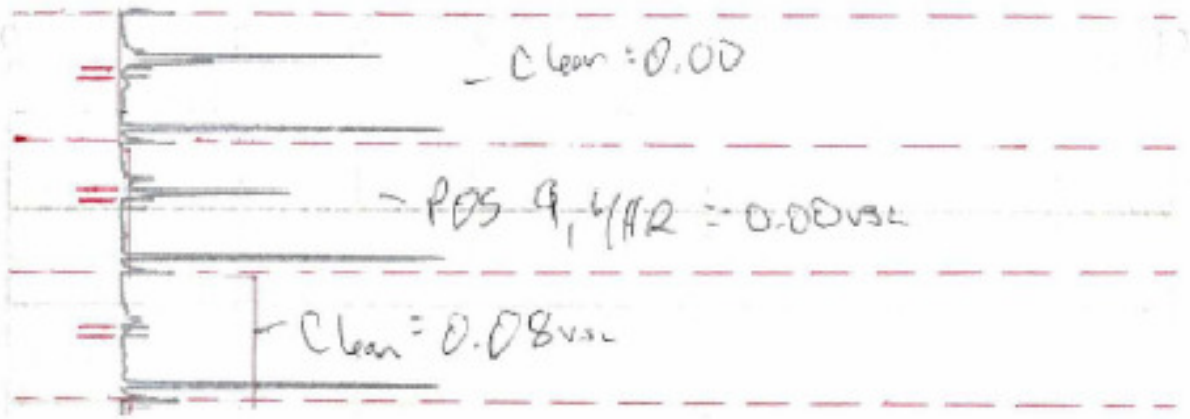

Figure 11. ACAMS Chromatogram of a Material Interference Control Sample

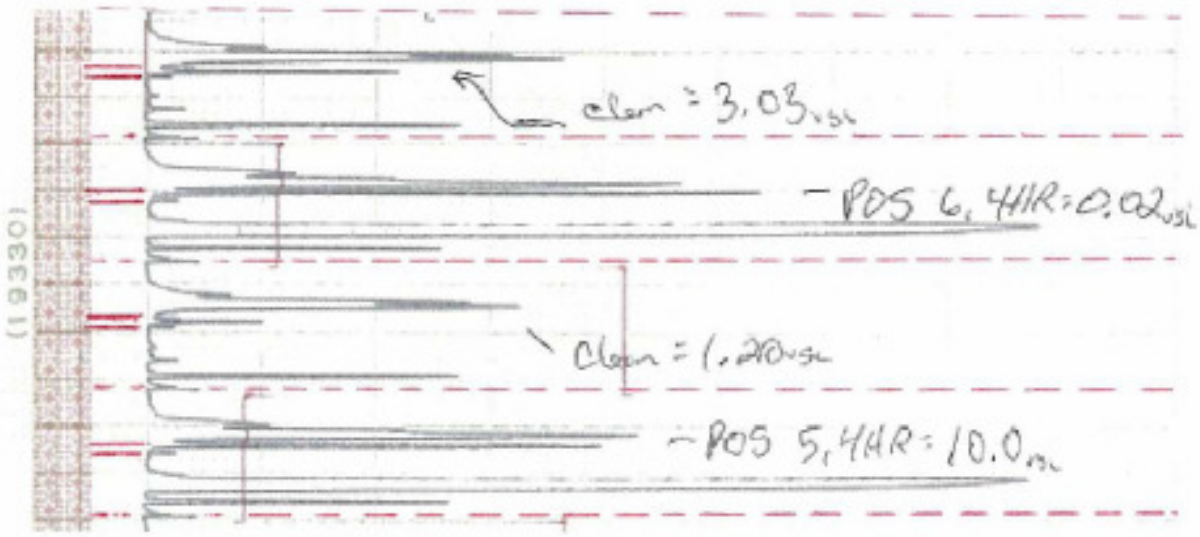

Figure 12. ACAMS Chromatogram of DPE Test Samples

An additional monitoring period was added at 23 hours to determine if clearing the secondary peak from the ACAMS would allow detection of VX from these three DPE samples. The ACAMS sampled filtered laboratory air overnight and a low background was observed prior to the 23-hour monitoring period. The DP13-3 and DP13-6 sample were measured well above the alarm setting. However, the ACAMS reported sample DP13-7 as <LOQ, although there was a peak present in the ACAMS agent window. Again the secondary peak did not clear down between samples and interfered with reporting of VX in sample DP13-7. Once this secondary peak decreased (approximately 45 minutes), DP13-7 was again monitored; the ACAMS reported 6.63 VSL.

The monitoring results of the SMIC responded above the LOQ. However, based on the ACAMS strip chart the secondary peak caused the false positive response. The data were corrected to SMIC < LOQ based on the strip chart evaluation. The MIC and NEG were <LOQ, indicating that VX was not present and these materials did not result in false positive results.

Table 23. ACAMS Results for Trial 13- VX/DPE at CHL

		ACAMS Result (VSL)[a]		
Simulated Waste Sample	**Sample ID**	**4 hr.**	**23 hr.**	**24 hr.**
NA	ACAMS Check	1.19	1.25	NP[b]
1	DP13-1	12.3	NP	NP
2	DP13-2	26.6	NP	NP
3	DP13-3	25.3[c]	11.2	NP
4	DP13-4	6.94	NP	NP
5	DP13-5	10.0	NP	NP
6	DP13-6	26.9[c]	14.3	NP
7	DP13-7	24.0[c]	9.98[c]	6.63
MIC	DP13-9	<LOQ	NP	NP
SMIC	DP13-10	<LOQ*	NP	NP
POS	DP13-11	1403	NP	NP
NEG	DP13-12	<LOQ	NP	NP
NA	ACAMS Check	1.20	NP[b]	1.07

Simulated Waste Sample	**Sample ID**	**15 min.**	**4 hr.**
NA	ACAMS Check	1.21	1.19
ASI	DP13-8	470	45.6
NA	ACAMS Check	NP[b]	1.20

a =ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = Challenge check not performed because of insufficient time before next sample. Configuration control of ACAMS validated with next challenge check.
c = VSL values calculated by comparing peak heights measured from strip chart to peak heights of samples with detections.
NP = Sampling not performed.
LOQ = 0.06 VSL
*interferent peak caused a false reading. Strip chart was evaluated to confirm interferent peak.

The results from the 23-hr sampling interval are lower that the 4-hr sampling interval. The drop in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

5.4.6 Trial 14- Butyl Rubber Apron Contaminated with VX at the CHL

The butyl rubber apron samples were contaminated at the CHL as described in Section 3.2.1.3. A total of 550.0 µL of a 990.2-µg/mL VX solution was applied at eleven locations to each sample to achieve the CHL. The spike controls were prepared at the beginning, middle, and

end of the agent application operation. Additional time was permitted between samples during the agent application procedure. This was done to allow additional clear down cycles of the ACAMS during monitoring.

As a result of the lengthy calibration, the ASI monitoring was performed at 45 minutes, not the intended 15 minutes. The ACAMS passed the initial challenge check for the ASI sampling interval. The ACAMS reported 92.0 VSL for the ASI sample at the 45-min period. The challenge at the end of this monitoring period was reported high (1.32 VSL). The secondary peak had not cleared from the ACAMS and appeared to interfere with the VX peak. This occurred again at the beginning (1.35 VSL) and end (1.38 VSL) of the 4-hour monitoring period. Although the challenge checks were reported high, it can be stated that the ACAMS successfully detected VX in the headspace samples above the alarm setpoint.

The monitoring results for all samples are included in Table 24. The ASI sample was measured above the alarm setting at the 45-minute and 4-hour monitoring periods. All seven replicate butyl rubber samples were found to be above the alarm setpoint at the 4-hour monitoring period. The ACAMS did not have sufficient time to clear down completely between all samples. At least one blank cycle was performed between each sample, with two blank cycles performed between every other agent-contaminated sample. Both the agent peak and the secondary peak were present in the ACAMS chromatograms between some samples. The additional blank cycles permitted the ACAMS to purge more of the interferent compound between samples. As a result, the ACAMS was able to properly identify and report VX in all agent-contaminated samples.

The monitoring results of the SMIC responded above the LOQ. However, based on the ACAMS strip chart the secondary peak caused the false positive response. The data were corrected to SMIC < LOQ, based on the strip chart evaluation. The MIC and NEG were <LOQ, indicating that VX was not present and these materials did not result in false positive results.

Table 24. ACAMS Results for Trial 14- VX/Butyl Rubber

		ACAMS Result (VSL)[a]	
Simulated Waste Sample	**Sample ID**	**4 hr**	
NA	ACAMS Check	1.35[c]	
1	BR14-1	82.2	
2	BR14-2	23.6	
3	BR14-3	63.4	
4	BR14-4	112	
5	BR14-5	139	
6	BR14-6	63.9	
7	BR14-7	67.1	
MIC	BR14-9	<LOQ	
SMIC	BR14-10	<LOQ*	
POS	BR14-11	291	
NEG	BR14-12	<LOQ	
NA	ACAMS Check	1.38[c]	
Simulated Waste Sample	**Sample ID**	**45 min[b]**	**4 hr**
NA	ACAMS Check	1.25	1.35[c]
ASI	BR14-08	92.0	88.2
NA	ACAMS Check	NP[d]	1.38[c]

a = ACAMS calibrated at 1.0 VSL. ACAMS measurements have been validated up to 2.0 VSL.
b = First calibration did not pass criteria. ACAMS was calibrated a second time. The first sample was performed at 45 min (not 15 min) because of the delay.
c = Challenge checks were high. Additional peaks in the chromatogram may have interfered with the agent peak.
d = Challenge check not performed because of insufficient time before next sample.
NP = Sampling not performed.
LOQ = 0.06 VSL
*interferent peak caused a false reading. Strip chart was evaluated to confirm interferent peak.

5.5 MATRIX EFFECT ON AGENT EVAPORATION

The agent vapor monitoring results from each matrix were compared to the results obtained when monitoring the POS (non-porous stainless steel coupon) at the 4-hr sampling interval. This allowed an estimation of the matrix effects on the evaporation of agent into the headspace. The graphs below show the ratio of the matrix results to the positive control. Ratios close to 1 show little matrix effects since the results are similar to the non-porous values. As the

ratio decreases, the tendency for the matrix to absorb and then slowly release agent vapor increases.

The HD/DPE results are depicted in Figure 13. Sample DP01-04 was excluded from this assessment due to the bag tear. DP01-07 was suspected as an outlier. However, evaluation of the data using a Q-test at 95% confidence indicated that the data for DP01-07 were not outliers and were included in the data set.

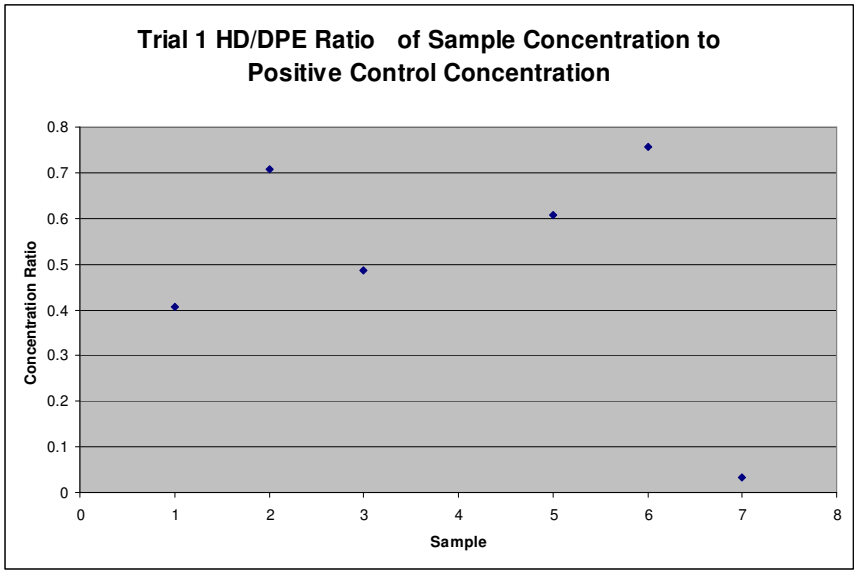

Figure 13. HD/DPE - Ratio of Sample Results to Positive Control Results

As seen in the graph there is variable matrix effect of the DPE suit on the HD evaporation rate.

The HD/butyl rubber results are depicted in Figure 14. All samples are included.

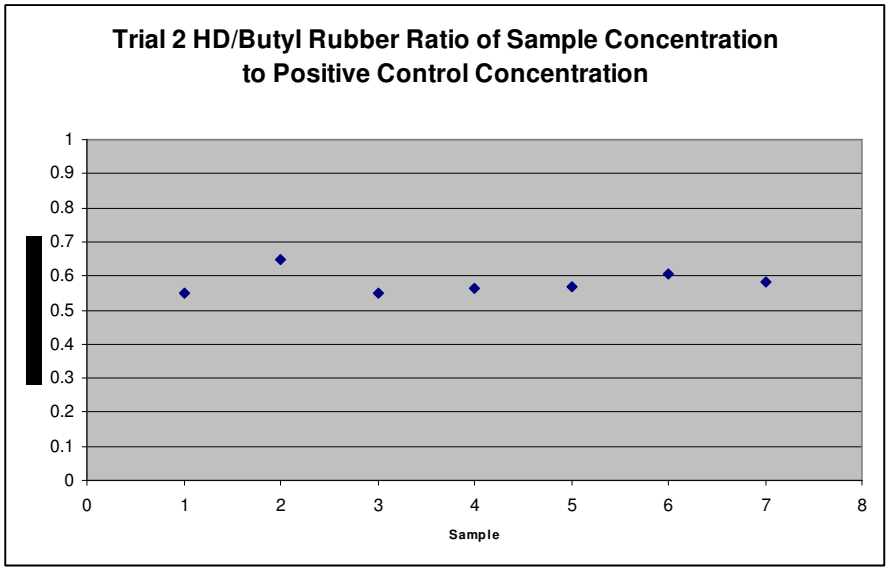

Figure 14. HD/Butyl Rubber - Ratio of Sample Results to Positive Control Results

As seen in the graph there is observable matrix effect of the butyl rubber on the HD evaporation rate.

The HD/wood results are depicted in Figure 15. All samples are included.

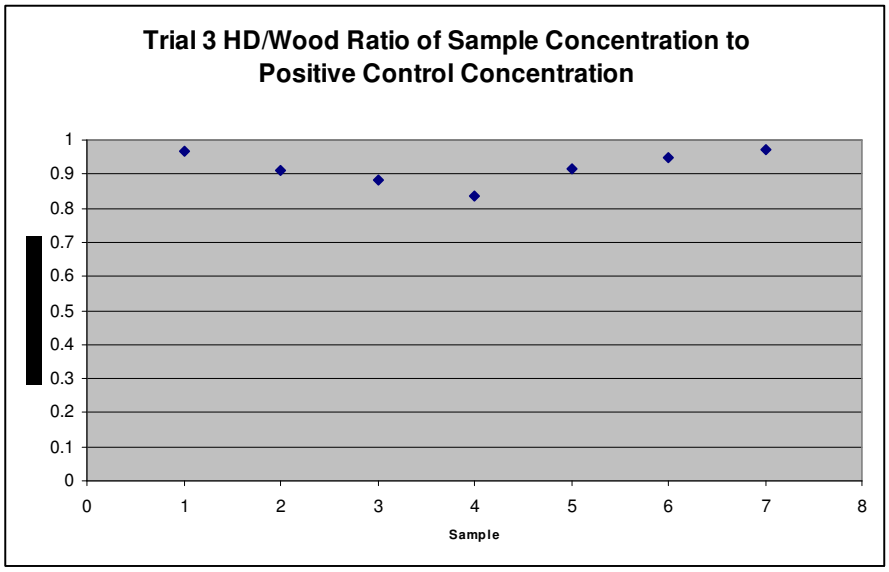

Figure 15. HD/Wood - Ratio of Sample Results to Positive Control Results

As seen in the graph, there is little matrix effect of the wood on the HD evaporation rate.

The HD/charcoal results are depicted in Figure 16. All samples are included.

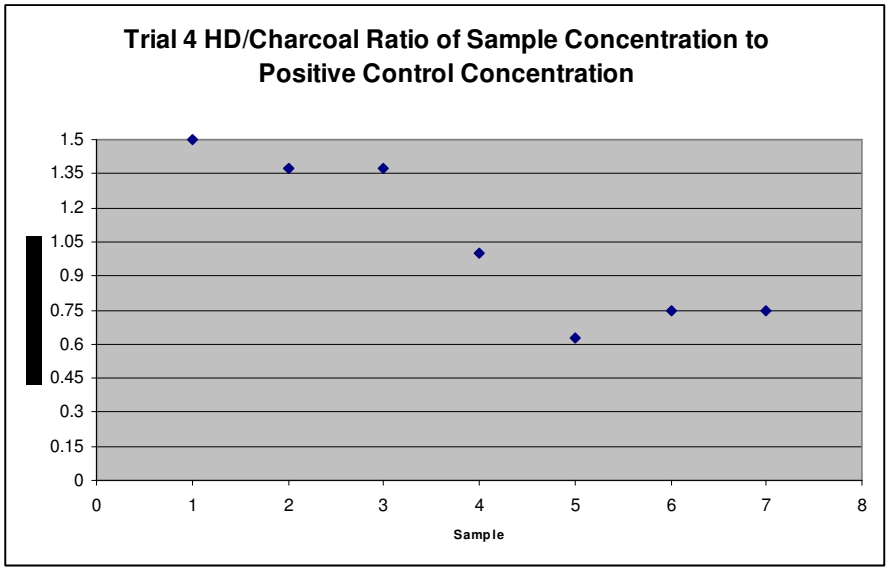

Figure 16. HD/Charcoal - Ratio of Sample Results to Positive Control Results

As seen in the graph, the behavior is not expected or uniform. The variability is due to the low spike concentration which did not produce a noticeable agent vapor response in the positive control and the background low-level interference found in all of the controls and samples. These factors prevent a determination of the effects of the charcoal material.

The GB/DPE results are depicted in Figure 17. All samples are included.

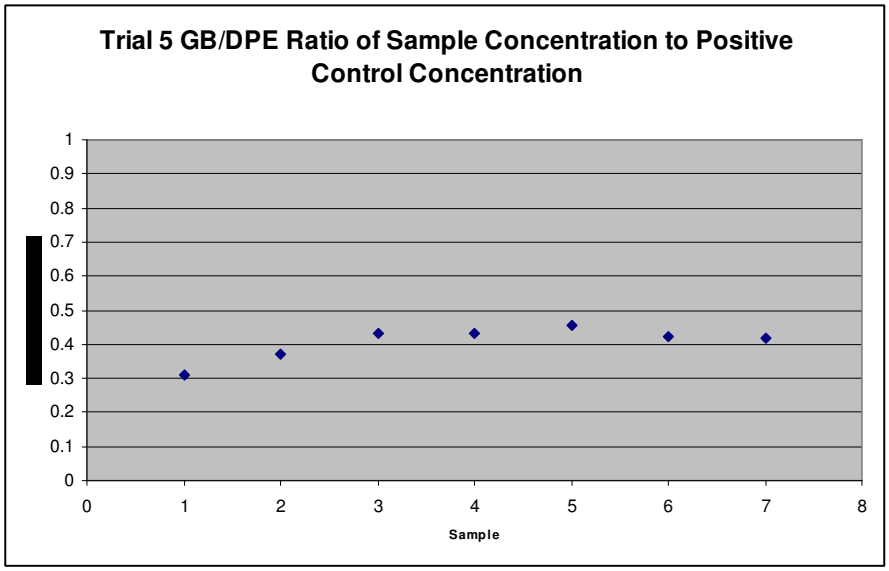

Figure 17. GB/DPE - Ratio of Sample Results to Positive Control Results

As seen in the graph, there is observable matrix effect of the DPE suit on the GB evaporation rate.

The GB/butyl rubber results are depicted in Figure 18. All samples are included.

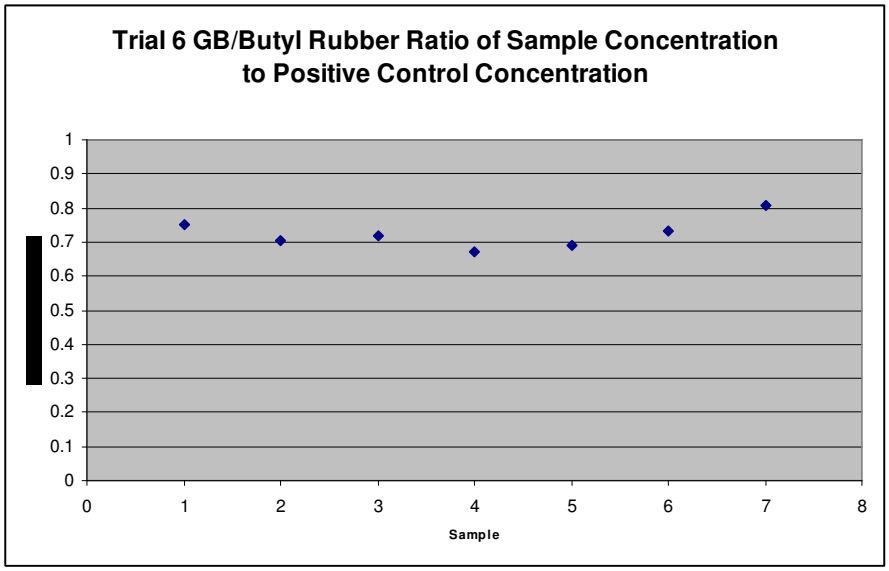

Figure 18. GB/Butyl Rubber - Ratio of Sample Results to Positive Control Results

As seen in the graph, there is some matrix effect of the butyl rubber on the GB evaporation rate.

The GB/Wood results are depicted in Figure 19. Sample WD07-01 was excluded from this assessment due to the ACAMS error during the 4-hr sampling period.

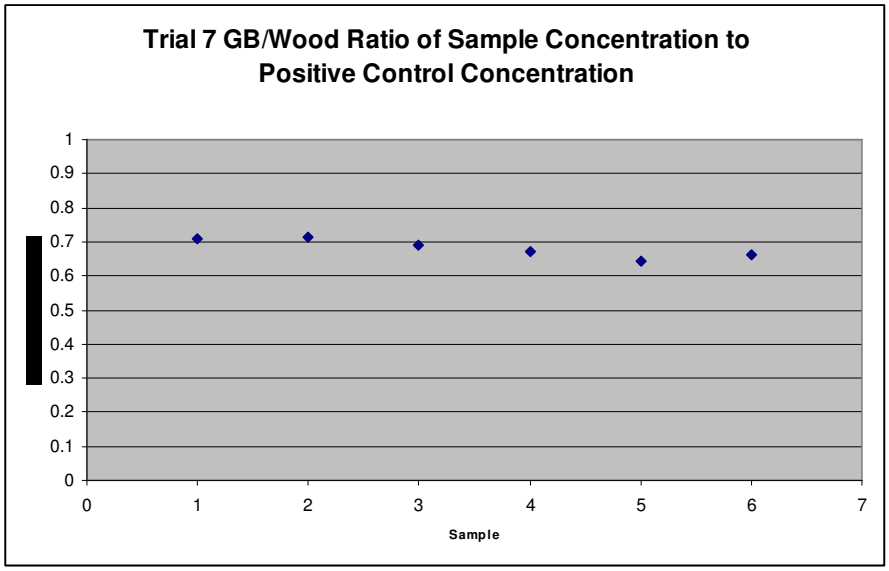

Figure 19. GB/Wood - Ratio of Sample Results to Positive Control Results

As seen in the graph, there is some matrix effect of the wood on the GB evaporation rate.

The GB/charcoal results are depicted in Figure 20. All samples are included.

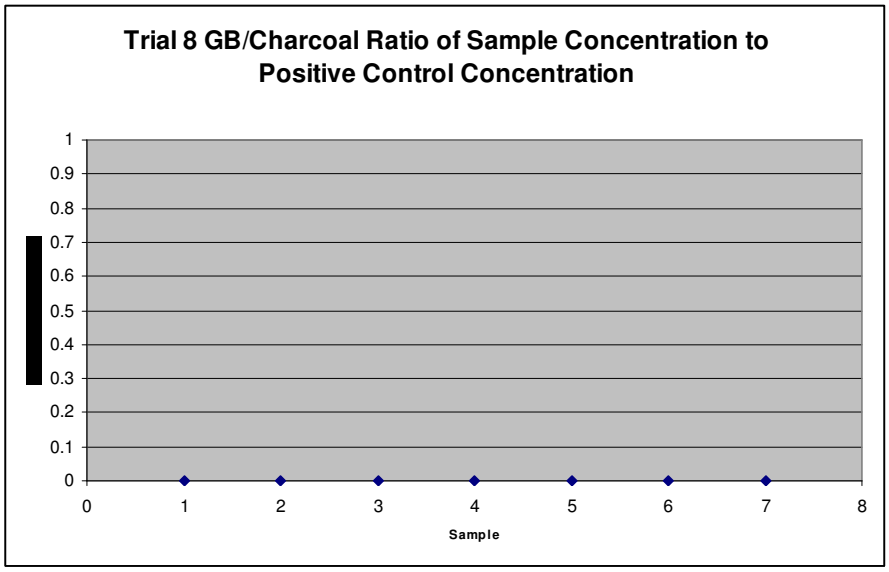

Figure 20. GB/Charcoal - Ratio of Sample Results to Positive Control Results

As seen in the graph, the charcoal absorbed the GB with no evidence of agent evaporation from the matrix.

The VX/DPE/WCL results are depicted in Figure 21. All samples are included.

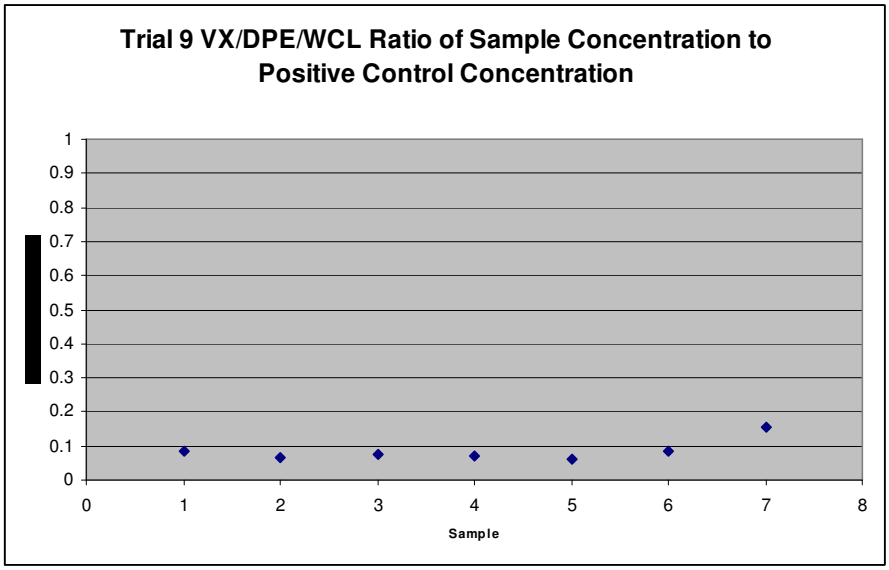

Figure 21. VX/DPE/WCL - Ratio of Sample Results to Positive Control Results

As seen in the graph, the DPE significantly impacted the VX evaporation.

The VX/Butyl Rubber/WCL results are depicted in Figure 22. All samples are included.

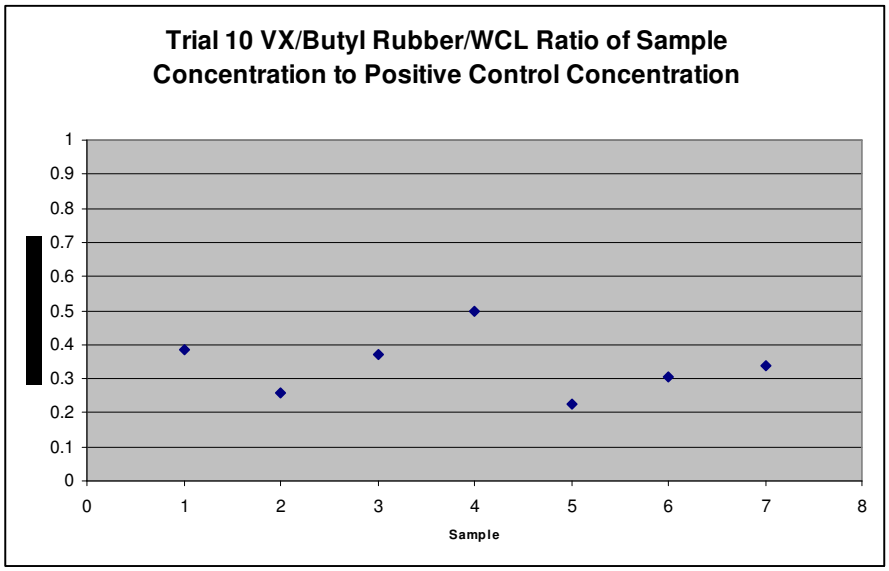

Figure 22. VX/Butyl Rubber/WCL - Ratio of Sample Results to Positive Control Results

As seen in the graph, the butyl rubber moderately impacted the VX evaporation.

The VX/Wood results are depicted in Figure 23. All samples are included.

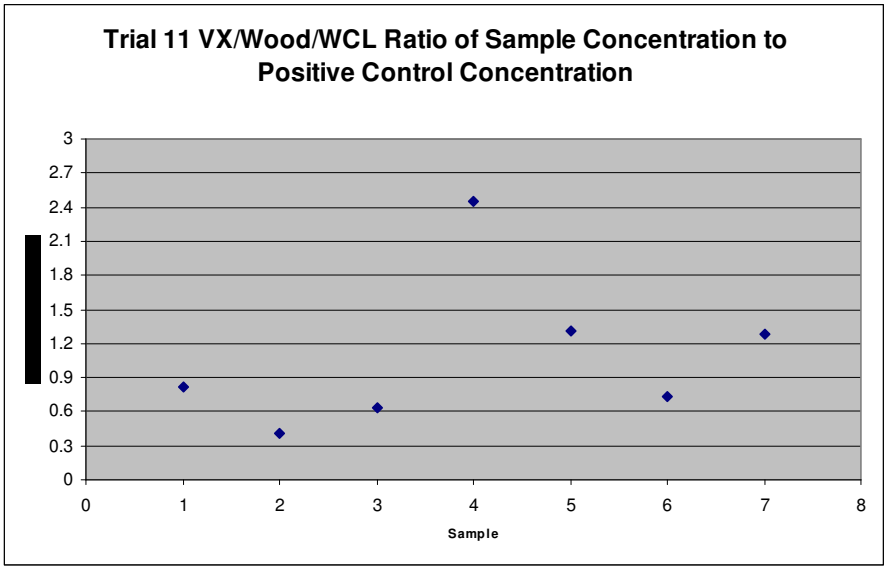

Figure 23. VX/Wood/WCL - Ratio of Sample Results to Positive Control Results

As seen in the graph the wood moderately impacted the VX evaporation. Sample #4 (WD11-04) was examined as a possible outlier. However, the data point could not be excluded because of error in the sample preparation and agent application. As discussed in Section 5.4.3, the application procedure utilized a Hamilton repeating dispenser that reproducibly delivers the same volume of liquid with each application; an error with this device would also have been measured in the spike control sample prepared immediately after WD11-04. An evaluation of the data using a Q-test at 95% confidence indicated that WD11-04 was not an outlier; therefore the sample was included in the data set.

The VX/Charcoal results are depicted in Figure 24. All samples are included.

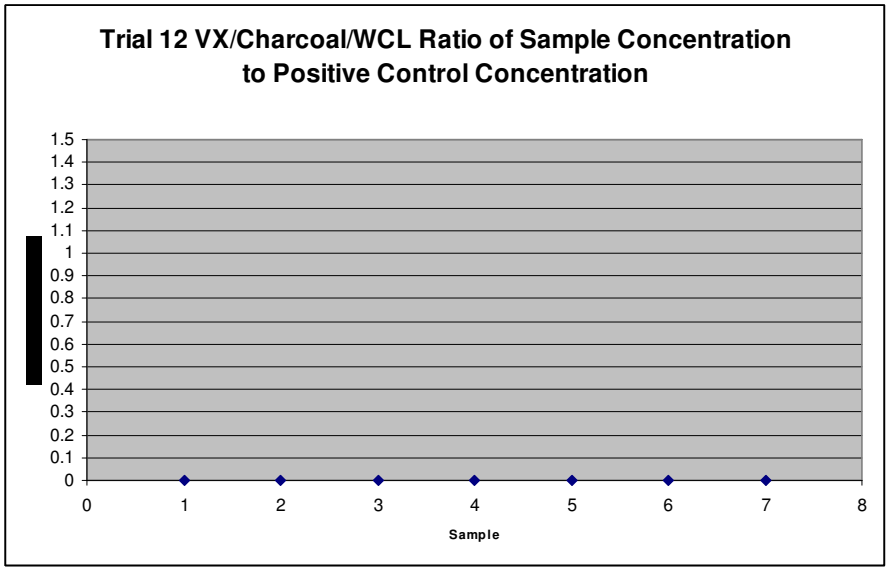

Figure 24. VX/Charcoal/WCL - Ratio of Sample Results to Positive Control Results

As seen in the graph, the charcoal absorbed the VX with no evidence of agent evaporation from the matrix.

6.0 QUALITY ASSURANCE

All aspects of this program were performed in accordance with the Quality Manual for Battelle's Chemical, Environmental and Materials Operations (CEMO) product line and ISO 9001 guidelines. The CEMO Quality Manual can be provided for review upon request. Other aspects of the Quality Assurance program included the Test Plan, a Program Plan and third party review of Plans and data.

7.0 CONCLUSIONS

7.1 AGENT CONTAMINATION AT THE WCL

The data from the seven replicate samples from each trial were reviewed to determine if headspace monitoring resulted in detection of agent above the 95% confidence level at the agent alarm setpoint as determined by the P&A evaluation. The following conclusions can be made:

- Contamination of DPE suit material at the WCL was detected by headspace monitoring with an ACAMS above the agent alarm setpoint for agents HD and GB. VX was detected, but below the agent alarm setpoint.
- Contamination of Butyl Rubber Apron material at the WCL was detected by headspace monitoring with an ACAMS above the agent alarm setpoint for agents HD and GB. VX was detected, but below the agent alarm setpoint.
- Contamination of Wood material at the WCL was detected by headspace monitoring with an ACAMS above the agent alarm setpoint for agents HD, GB, and VX.

These agent/matrix combinations met the criteria specified for this program. Therefore, headspace monitoring of these agent/matrix combinations is as representative for the detection of contamination at the WCL as sample extraction (for that agent/matrix combination listed above at the 4 hour period) under the conditions of this test. Also, monitoring of these agent/matrix combinations at the 15-minute period resulted in values above the alarm setpoint.

In each trial in which an agent concentration in the headspace was measured, the concentration reported by the ACAMS decreased with each additional monitoring interval. This decrease in headspace concentration is most likely attributable to permeation through the bag and/or absorption/adsorption into/onto the bag or the waste material.

Monitoring results of the positive control sample (non-porous stainless steel coupons) represented the maximum vapor concentration for each test. Varied matrix effects were observed during testing and discussed in Section 5.5. Although the ACAMS did not detect GB from charcoal above the alarm setpoint or VX from DPE material above the alarm setpoint, the positive control sample during these trials was above the alarm setpoint. This indicates that the

charcoal inhibits GB volatilization. Also, the DPE material prevented accumulation of the VX vapor in the headspace to levels above the alarm setpoint. Although the HD/charcoal, VX/charcoal, and VX/butyl rubber combinations did not meet the specified criteria, the positive control samples in the VX/charcoal and VX/butyl rubber did generate ACAMS readings >LOQ. The HD/charcoal trial was the only trial where there was not enough agent spiked to generate a headspace concentration above the LOQ for the POS control sample.

7.2 VX CONTAMINATION AT THE CHL

The monitoring results for the DPE and butyl rubber material contaminated with VX at the CHL indicated that the ACAMS was capable of detecting the agent at the Negligible Severity (low-level) Effect Level for Percutaneous Liquid Exposure, i.e., the ACAMS would respond above the alarm setpoint if there was a VX contact hazard on the DPE suit or butyl rubber material.

The ACAMS detected a second peak during VX testing; this peak interfered with agent analysis, resulting in both false negatives and a false positive. The data from the trials were verified by examining the ACAMS strip charts. The interference was alleviated by allowing additional clear-down cycles of the ACAMS to decrease the carryover of the interference peak (additional blank cycles between the agent-contaminated samples of trial 14 resulted in no false negatives). Therefore the interference peak appears to be an issue with carryover.

A VX vapor measurement at or below the VSL/STEL rules out ocular vapor exposure (0.0018 mg/m^3) or percutaneous vapor hazard (4 mg-min/m^3) (reference 1 and 12). Ingestion or intravenous are not likely routes of entry for TOCDF operations; this leaves direct dermal contact as the remaining route of exposure. In the testing, butyl rubber material was spiked with 2.51 µg of VX (in solution), which is 220 times less VX than is needed to reach the CHL of 0.55 mg/70 kg individual (reference 1). DPE was spiked with 8.37 µg of VX which is 66 times below the CHL. In a separate document, U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) published a dermal absorption factor of 2.2% per 8 hr, meaning that over 8 hours, only 2.2% of the agent present would be absorbed through the skin (reference 13). As a result, an individual placing his for her hand in a bag of butyl rubber gear containing 2.51 µg of VX or a bag of DPE material containing 8.37 µg (both masses of VX that were

detected by ACAMS in these experiments) would not be exposed to a hazardous amount of agent, whether it is absorbed at the published rate or even in the unlikely event that the entire mass of spiked agent was absorbed instantly.

8.0 REFERENCES

1 USACHPPM Report No. 47-EM-5863-04. Acute Toxicity Estimations and Operations Risk Management of Chemical Warfare Agent Exposures. May 2004.
2 TOCDF Waste Analysis Plan – October 2007.
3 TOCDF RCRA Hazardous Waste Permit – March 2005.
4 Field Drinking Water Standards (FDWS) for Liquid Media (DA Technical Bulletin – Medical (TB-Med) 577, Sanitation and Surveillance of Field Drinking Water, 2005, updated from Occupational and Environmental Health, Sanitary Control and Surveillance of Field Water Supplies, DA Technical Bulletin, March, 1986.
5 Programmatic Monitoring Concept Plan, U.S. Army Chemical Materials Agency, June 2004.
6 Implementation Guidance Policy for Revised Airborne Exposure Limits for GB, GA, GD, GF, VX, H, HD, and HT, Department of the Army, Office of the Assistant Secretary of the Army Installations and Environment, 18 June, 2004.
7 CDC, NIOSH Emergency Response Card, Mustard, Publication ERC: 505-60-2, June, 2004. http://www.bt.cdc.gov/agent/sulfurmustard/erc505-60-2.asp
8 CDC, NIOSH Emergency Response Card, Sarin, Publication ERC 107-44-8, May, 2004. http://www.bt.cdc.gov/agent/sarin/erc107-44-8.asp
9 CDC, NIOSH Emergency Response Card, VX, Publication ERC: 50782-69-9, April 2003. http://www.bt.cdc.gov/agent/vx/erc50782-69-9.asp
10 MSDS Number: H2381, JT Baker, http://www.jtbaker.com/msds/englishhtml/h2381.htm
11 MSDS Number: I8840, JT Baker, http://www.jtbaker.com/msds/englishhtml/I8840.htm
12 Watson, Annetta, D. Opresko, V. Hauschild. Evaluation of Chemical Warfare Agent Percutaneous Vapor Toxicity: Derivation of Toxicity Guidelines for Assessing Chemical Protective Ensembles. Oakridge National lab report ORNL/TM-2003/180 July 2003.
13 USACHPPM Report MCHB-TS-E. Management Criteria for Chemical Warfare Agent (CWA) Contaminated Waste and Media. October 2000.

Appendix A: ACAMS Precision and Accuracy Study and ACAMS Operation

Appendix B: Test Parameter Control Sheets

Appendix C: Simulated Waste Material

Appendix D: Results for Spike Control and Vapor Reference Samples

Appendix E: Temperature and Humidity Measurements

Appendix F: Agent Vapor Pressure in a Solvent

Appendix G: Logbook Record (LRB) Pages

Appendix H: Test Plan and Test Plan Addendums

APPENDIX C

Section 7.0

A. Shaffer, C. Mechan, K. McCarthy,
TOCDF Drum Headspace Monitoring Testing,
Headspace Monitoring Phase II Testing,
EG&G Defense Materials, Inc.,
Stockton, UT,
February 6, 2009.

Test Report
for

TOCDF Drum Headspace Monitoring Testing
Headspace Monitoring Phase II Testing

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By
Andrew Shaffer
Cory Mecham
Kelli McCarthy

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1 Introduction

The demilitarization of the Deseret Chemical Depot (DCD) chemical stockpile began in August of 1996 at the Tooele Chemical Agent Demilitarization Facility (TOCDF). The chemical agents destroyed at TOCDF are GB, VX, and Mustard (H-series). The hazardous wastes associated with each agent campaign consist of munitions, bulk containers, liquid wastes, explosives, propellants, and secondary wastes. Secondary waste can be described as items derived from the routine processing of chemical munitions, such as personal protective equipment (PPE), Demilitarization Protective Ensemble (DPE), plastics, clean-up materials and by-products from the treatment of chemical munitions. TOCDF is treating Mustard secondary waste items as they are being generated. During the course of operations at TOCDF, secondary waste items generated during the GB and VX campaigns (1996 to 2005) were placed into long-term storage. These items from the GB and VX campaign will be sorted, characterized, and further prepared for either shipping offsite for final disposition, or further treatment on-site at TOCDF.

In order to safely categorize this waste for treatment or disposal, a Drum Ventilation System (DVS) is being designed to monitor the headspace of the waste storage drums. The DVS strategy is based upon the premise that agent vapor levels will be consistent throughout the storage container after extended storage periods.

Prior testing[1] has determined that the Automatic Continuous Air Monitoring System (ACAMS) instruments utilized at TOCDF for process control and personnel protection can identify materials spiked with low levels of chemical agent by detecting the vapor which evolves into a contained headspace. This testing demonstrated that typical waste materials (DPE, Toxicological Agent Protective (TAP) gear, and wood) spiked at the waste control limits for GB and HD (20ppb and 200ppb respectively) generated a headspace agent vapor measurement of greater than 1.00 of the vapor screening level (VSL). These sample waste materials spiked at the waste control limit for VX (20ppb) generated consistently measureable levels of VX vapor, albeit at less than 1.00-VSL for DPE and TAP material. Further testing demonstrated that DPE and TAP spiked with a mass of VX equivalent to the negligible dermal contact hazard[2] generated headspace VX vapor measurements much greater than 1.00-VSL.

The headspace agent concentration measurement obtained by the DVS will be used to confirm that the contents of the waste container have been decontaminated through the processes in place at TOCDF. This headspace reading will be used in conjunction with generator knowledge to sort secondary waste for final disposition at an off-site treatment, storage, and disposal facility (TSDF) or for further treatment on site at TOCDF or Area-10. The intent of this headspace monitoring test was to demonstrate that the headspace agent concentration of the storage container (drum) is representative of the entire drum contents and is a suitable criterion for sorting this waste for final processing.

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[1] Battelle Report: Test Report for Headspace Monitoring Waste Characterization prepared for Tooele Chemical Agent Demilitarization Facility. K.Siddoway, E. Burckle. November 2008.
[2]USCHPPM Report No. 47-EM-5863-04. Acute Toxicity Estimations and Operations Risk Management of Chemical Warfare Agent Exposures. May 2004.

2 Test Objectives

The primary objective of this testing was to validate that the first sample of a drum headspace is representative of the agent vapor levels present within that drum. In conjunction with previous laboratory testing, this experiment was designed to establish the efficacy of drum headspace monitoring for safely identifying agent contamination within a drum. The test was designed to demonstrate whether this headspace reading, which will be used in conjunction with generator knowledge, is a safe and effective means of waste segregation. This test was performed under actual TOCDF plant conditions, using previously decontaminated agent contaminated waste generated during the VX campaign. Specifically, airlock trash (decontaminated DPE suits and plastic) was the waste stream selected for this testing.

3 Test Design and Planning

3.1 Waste Stream Selection

VX contaminated secondary waste was selected for the purpose of the test because:

- The physical properties of VX as compared to GB, especially the persistence of potential contamination on the material over time, make VX more likely than GB to still be present within the waste.
- VX Secondary Waste represents the largest portion of VX secondary waste in storage.
- The VX-airlock trash stream contains no neat VX based upon facility decontamination practices.

The material is the DPE waste stream as defined in the Waste Analysis Plan, paragraph 2.2.2.21. This includes DPE, Plastics generated during routine toxic operations, and Toxic Area Protective (TAP) Gear. DPE suits are the most appropriate material in this waste stream for the test purpose.

3.2 Sample (Drum) Selection Process

There are 1,566 drums of VX DPE waste in storage. These drums have been in long-term storage and were originally generated during routine toxic operations at TOCDF. As part of the exit process from toxic areas, these suits were decontaminated and/or monitored with an ACAMS prior to the entrants being removed from the DPE suit. The suits or other plastic materials were placed into plastic bags for transport and storage with the TOCDF toxic maintenance area (TMA) before being drummed for storage outside the TMA. The individual bags were split or intentionally cut to allow air to escape from the bag, facilitating the packaging process inside the 55 gallon drum.

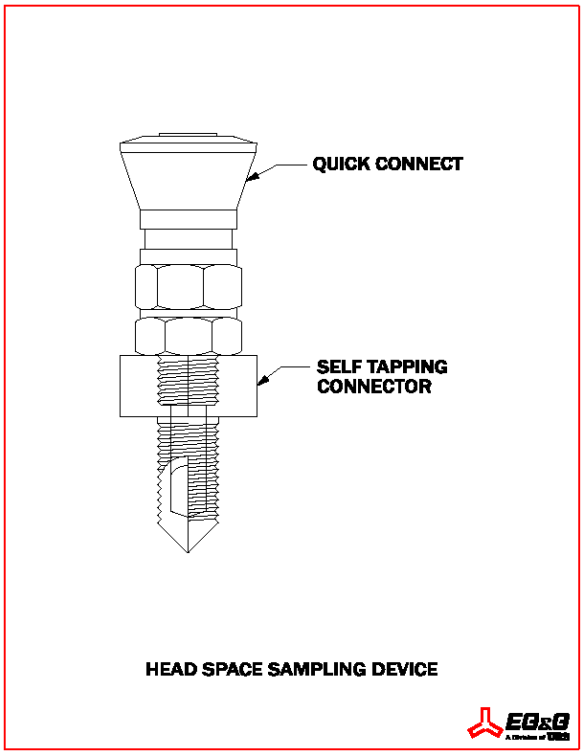
Using a Microsoft© Excel® spread sheet with all 1,566 VX DPE waste drums, the drums were sorted by date and by weight. Using the median date as the cut off, two groups were designated. Group 1 consists of drums filled before 6/25/2004 and Group 2 consists of those filled on or later than 6/25/2004. Fifteen drums were randomly selected from each group. It is assumed that the drum weights (which range from a low of 54 pounds to a high of 222 pounds) are distributed evenly through the span of the dates. A total sample size of 30 was chosen because it would ensure the statistical validity and acceptable confidence level for a paired t-test.

3.3 Drum Headspace Sample Collection

3.3.1 Sampling Device

In order to obtain a headspace sample from the sealed drum in the DVS a Headspace Sampling Device (HSD) will be used. This tool will allow TOCDF to rapidly drill into a closed container, extract a sample of the Headspace contents, and permanently re-seal the point of entry. The HSD uses a hollow, stainless steel self-tapping screw to drill and tap the container's lid. The hole diameter is approximately 7/16". During the drilling and tapping process, the exterior washer seals against the container lid and against the threads of the self-tapping screw to prevent escape of the container contents. The HSD will be inserted by an electric powered hand drill. These devices are commercially available and have been used by the United States Department of Energy. For the purposes of this test, HSDs have been fabricated at TOCDF. A schematic of the HSD is included as Figure 1.

Figure 1: TOCDF Headspace Monitoring Test – Headspace Sampling Device



3.3.2 Sample Collection Methodology

The secondary waste containers (drums) were moved from their storage site in the DCD Area 10 to the TOCDF Toxic Maintenance Area (TMA) A/B category area. The ACAMS verified to be in working configuration via a distal-end sample line challenge. The HSD was inserted into the lid of the secondary waste container (55-gallon drum) and. The ACAMS sample line was then attached to the HSD and allowed to monitor the interior of the drum for one cycle (5 minutes). If deemed necessary a Depot Area Air Monitoring System (DAAMS) sample was collected and analyzed.

The ACAMS was then disconnected so that the drum could be placed on a commercial drum roller. Rolling (mixing) was performed to mix vapor in the drum headspace and that

which may be contained within the folds of bags. The drum roller was operated for 1 minute (twenty revolutions) to agitate the contents of the drum. After mixing, the ACAMS was re-connected to the HSD and the drum headspace re-monitored for one cycle. If deemed necessary a Depot Area Air Monitoring System (DAAMS) sample was collected.

After sample collection was completed the drum lid was removed, and each bag of DPE waste in the container was removed and inspected. Initial plans dictated that if an interior bag was found to be intact (no obvious cuts or holes), then the interior contents of the bag would be monitored and recorded. However no un-cut bags were identified during the course of testing. Following inspection, bags were returned to their original 55-gallon drum container and a new lid was placed upon the drum. The HSD was removed from the old drum lid and re-used.

3.4 Data Quality Objectives

3.4.1 General Data Collection and Processing

Monitoring data was collected and recorded for this final report. All records referenced in the local procedures are maintained as part of this test report. A work order was generated with the specific sequence of operations and was used as the basis of this operation.

DAAMS tube collection and analysis were performed in accordance with TOCDF LOP 522 (Operations) and LOP 562 (Analysis of DAAMS Tubes). All results have been reviewed in accordance with Laboratory Quality Control Plan (LQCP) requirements by the Laboratory Quality Control (QC) group and validated prior to inclusion in this final report.

3.4.2 ACAMS Specific Data Quality Assurance and Control (QA/QC)

Prior TOCDF operational experience indicated that the measurement of VX in secondary waste streams was a difficult process. Both positive and negative interfering compounds can be present is VX secondary waste streams. Therefore, additional QA/QC measures were put in place for this test. Data collected for these additional QA/QC measures are captured in Appendix A.

3.4.2.1 Measures to Discount Positive Interference

Headspace measurements were taken using ACAMS station DEC 456V. This station utilizes the splitter-ACAMS instrumentation which has been designed to lower the incidence of false positive measurements for VX. ACAMS/Splitter ACAMS setup, operation, and challenges were in accordance with LOP 524 (ACAMS Operations).

Prior to taking beginning each day’s testing a new V/G conversion pad was installed on the distal-end of the sample line and a 1.00-VSL challenge was performed. This sample line and V/G pad were used for all samples pulled from a single drum. After pulling the post mixing samples from this drum, a second distal-end sample line challenge was performed to ensure that the V/G pad and sample line retained the ability to transmit VX within method parameters. For the second drum tested each day a new V/G pad was installed, and sample collection begun (the previous distal-end challenge confirmed sample line transmission). After the conclusion of gas sampling from a drum, a distal-end sample line challenge was performed.

3.4.2.2 Measures to Discount Negative Interference

To discount low readings as the result of negative interference from compounds in the drum headspace, a matrix spike was utilized. Immediately prior to beginning drum headspace monitoring, the ACAMS was spiked through an in-line fitting with the equivalent of 0.5-VSL of VX. This matrix spike was collected on the preconcentrator tube (PCT) of the ACAMS. The resulting ACAMS measurement is then the sum of the spike (0.5) and the actual concentration of VX in the drum headspace. For example, with a matrix spike of 0.5-VSL and final ACAMS measurement of 1.25-VSL, the actual concentration of VX in the sample is 0.75-VSL. It should be noted that matrix spiking was performed as an investigative measure to identify negative interference and is specific to this testing.

Prior to beginning each day's testing ACAMS station DEC 456V was spiked 10 times with the equivalent of 0.5-VSL VX. These 10 daily measurements were recorded and analyzed statistically to identify instrument variability within each day, and between days.

The distal-end sample line challenge procedure outlined in Section 3.4.2.1 also served to identify negative interferent issues.

4 Test Results

4.1 Instrument (ACAMS) Variability

Prior to each day's operations ACAMS station DEC 456V was challenged 10 times with the equivalent of 0.5-VSL VX. These challenges were performed to determine the variability of the ACAMS at the matrix spike level. The result of these challenges was used as the correction factor to adjust ACAMS readings as described in Section 3.4.2.2. The results of these challenges are provided in Table **4-1** below. Data collections sheets used during testing can be found in Appendix A.

Table 4-1: 0.5-VSL Instrument Challenge Results

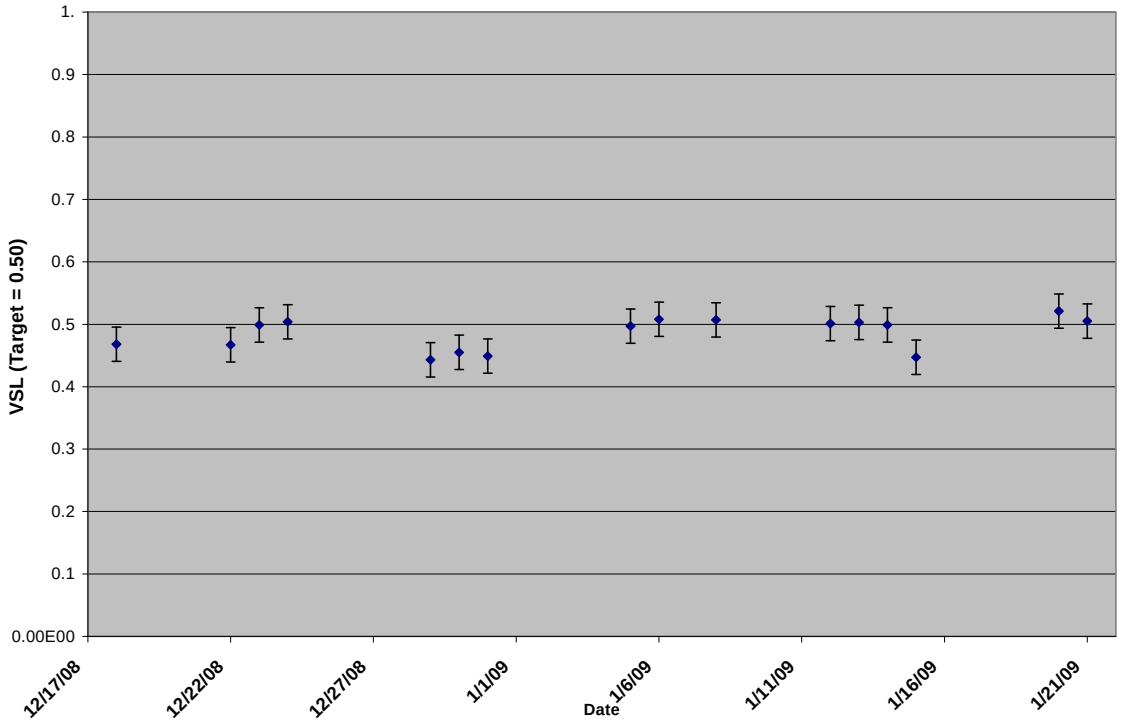
Shot#	12/18/2008	12/22/2008	12/23/2008	12/24/2008	12/29/2008	12/30/2008	12/31/2008	1/5/2009
1	0.48	0.45	0.45	0.45	0.45	0.46	0.44	0.51
2	0.51	0.45	0.51	0.44	0.48	0.46	0.47	0.51
3	0.28	0.48	0.51	0.52	0.48	0.42	0.44	0.47
4	0.47	0.49	0.47	0.54	0.43	0.46	0.46	0.47
5	0.48	0.5	0.51	0.49	0.47	0.43	0.45	0.49
6	0.52	0.49	0.57	0.53	0.46	0.46	0.46	0.49
7	0.45	0.5	0.54	0.54	0.44	0.45	0.43	0.48
8	0.47	0.47	0.51	0.53	0.47	0.48	0.43	0.51
9	0.5	0.33	0.41	0.45	0.47	0.46	0.46	0.51
10	0.52	0.51	0.51	0.55	0.28	0.47	0.45	0.53
group mean	0.47	0.47	0.50	0.50	0.44	0.46	0.45	0.50
Shot#	**1/6/2009**	**1/8/2009**	**1/12/2009**	**1/13/2009**	**1/14/2009**	**1/15/2009**	**1/20/2009**	**1/21/2009**
1	0.5	0.49	0.5	0.49	0.47	0.47	0.48	0.47
2	0.48	0.5	0.48	0.48	0.5	0.44	0.53	0.5
3	0.51	0.47	0.49	0.5	0.51	0.46	0.5	0.51
4	0.49	0.5	0.52	0.49	0.49	0.45	0.52	0.47
5	0.52	0.52	0.52	0.51	0.48	0.45	0.54	0.5
6	0.51	0.55	0.48	0.48	0.51	0.45	0.52	0.53
7	0.51	0.51	0.51	0.51	0.51	0.45	0.52	0.52
8	0.53	0.48	0.51	0.54	0.5	0.44	0.54	0.52
9	0.53	0.52	0.5	0.52	0.53	0.43	0.54	0.53
10	0.5	0.53	0.5	0.51	0.49	0.43	0.52	0.5
group mean	0.51	0.51	0.50	0.50	0.50	0.45	0.52	0.51

Total average	0.49
95% Confidence Limit	0.01
Spike adjustment	**0.48**

To determine the variance within these 0.50-VSL spikes within-day variance was first determined using Microsoft Excel. Then the variance between days was checked using Gabriel comparison intervals[3,4]. Measurements within and between days were deemed not independent of each other through this analysis. As such, the combined measurements were pooled and a mean measurement of 0.49-VSL was calculated. Using this same population, the 95% confidence interval (group variance multiplied by the t-statistic) was determined to be 0.01. A plot of the daily means with comparison intervals is shown in Figure 2 below.

[3] Biometry. 1995. RR Sokal, FJ Rohlf - Freeman New York
[4] McDonald, J.H. 2008. Handbook of Biological Statistics. Sparky House Publishing, Baltimore, Maryland.

Figure 2: Matrix Spike Precision Checks with Gabriel Comparison Intervals (95% Conf)

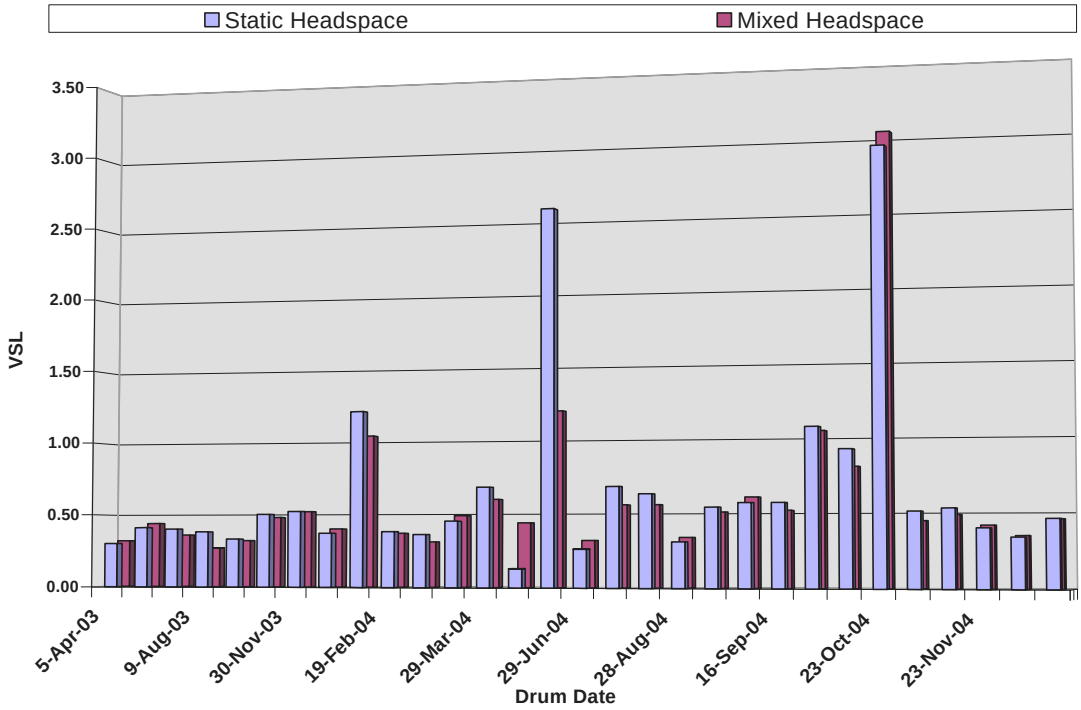


To apply a level of conservatism to the test results, the 95% confidence interval is subtracted from the mean to yield an ACAMS reading adjustment factor of 0.48-VSL. This approach is conservative because subtracting a value less than 0.50-VSL generates higher adjusted measurements (1.00-VSL – 0.48-VSL = .52-VSL).

4.2 Drum Headspace Monitoring Results

During the conduct of this testing, headspace VX vapor concentration along with additional drum characteristics and data fields were recorded. ACAMS results for pre and post drum mixing are presented in Figure 3 below. It should be noted that the results presented here have had the 0.48-VSL matrix spike subtracted. A summary table of all collected data, along with the operator data sheets, can be found in Appendix A.

Figure 3: VX Waste Drum Headspace Measurements



As seen in Figure 3 there is not a significant difference between the majority of pre (static) and post-mixing headspace results. The exception to this is for the drum dated 5/10/2004. DAAMS samples were collected and analyzed for this drum. Both A and B tubes collected confirmed the presence of VX, however chromatography for the A-tube samples (**Figure 4**, VX quantified at 1.88-VSL on a GC-FPD, DB-VRX column) was clean while the B-tube had a much higher reading of 12.28-VSL using GC-MSD (DB-1701 column). The B-tube presented a much different pattern in its chromatography (Figure 5 below). After review of the chromatography of the A and B-tube analyses, it is reasonable to attribute the higher B-tube reading (12.28-VSL) to positive interference. This variation in measurements of the same headspace indicates that there is variability in the measurements of this drum, which would also apply to the differences between static and mixed headspace measurements seen on the ACAMS.

Figure 4: Drum 5/10/04 DAAMS Analysis A-tube Chromatography (GC/FPD)

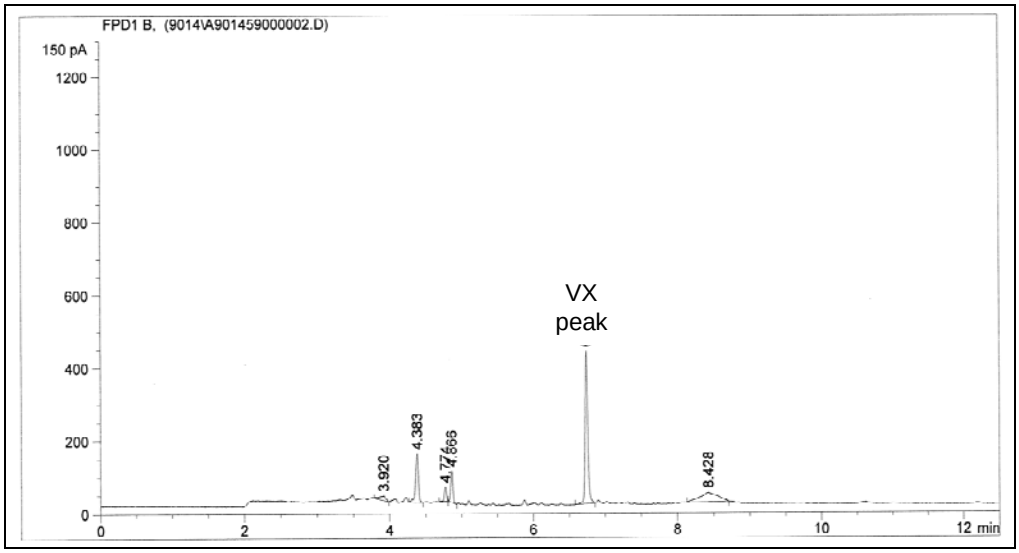
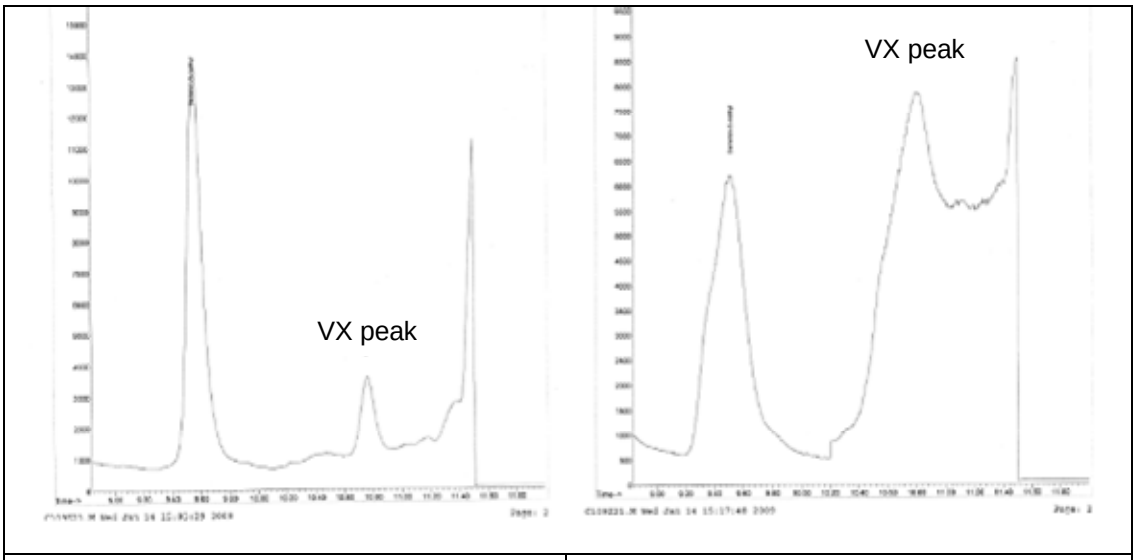


Figure 5: Drum 5/10/04 DAAMS Analysis B-tube Chromatography (GC/MS)



VX Calibration Standard – DB-1701	B-tube Analysis – DB-1701

Also, for the two drums which had measurements significantly greater than the mean (5/10/04 and 10/23/04) TOCDF monitoring records were examined (Records found in Appendix B). It was found that on both of these days there were VX related assisted cut-outs for DPE entries. Other drums which did not contain assisted cut-out generated suits did not generate high headspace vapor concentrations. This supports the TOCDF operation assumption that decontamination procedures in place during the VX campaign were protective, but that monitoring challenges (interferences in non-splitter ACAMS) prevented accurate screening of waste.

Within the 30 drums sampled, there were 146 individual bags. Each bag was removed from its respective drum and examined. All 146 bags contained DPE suits (items were

double bagged) and contained no residual liquids. All bags (both inner and outer) were cut, including those bags in the lightest and heaviest drums. The observation that all bags examined were cut is a strong indicator that bag cutting was part of the waste management process, and not a case by case act to permit additional waste to fit inside a drum. As such it is reasonable to conclude that all the bags in the 1566 VX DPE waste drums would have been cut before loading into the drums.

4.2.1 *t*-Test of Drum Headspace Monitoring Results

This experiment was designed to evaluate the relationship between static and mixed drum headspaces; a paired *t*-test was selected as the appropriate statistical test. The analysis was performed using Microsoft Excel and compared all of the adjusted static monitoring results with the adjusted mixed drum results using the null hypothesis that the two populations are the same. The *t*-test result is 0.263 (73.7% probability), which fails to meet the 95% confidence threshold. As such, the null hypothesis (that populations are similar) stands. Practically, this means that mixing the air within a drum does not change the resulting monitoring reading and that the first reading taken is representative of the total vapor within that drum.

4.2.2 Additional Data Analysis

Additional review of the data was conducted to determine if there were other relationships or patterns that might be identified in the test results.

Of the 30 drums sampled, the static measurement was the higher of the two readings 17 times, static and mixed readings were the same two times, and the mixed measurement was higher 11 times.

To examine the influence of drum weight on monitoring reading, the total drum population was split into heavy (>125lbs) and light (<125lbs) groups. Because each of these drums contained the same materials (DPE and plastic) density of the waste items was constant and differences in drum weight were the result of different amounts of waste (heavier drums had more material “packed” into them). A *t*-test was conducted on each weight groups to determine if drum weight, and by inference load density, made a difference between the static and mixed readings. The result for the light group was 0.212 (78.8%) and 0.385 (61.5%) for the heavy group. The conclusion from this analysis is that drum packing density does not limit the distribution of vapor within waste drums, as there is no difference between the static or mixed measurements for either weight group.

Excel was also used to determine if there is a correlation between the generation date of a drum and its headspace concentration. The *=correl()* function was used, and generated a correlation coefficient of 0.213. Using the standard significance 0.05 (equivalent to 95% confidence) there is not a correlation between drum generation date and headspace measurement. This suggests that TOCDF practices were generally consistent throughout the campaign that generated this waste source (VX).

5 Conclusions

The primary objective of this testing was to validate the assumption that the first sample of a drum headspace is representative of the agent vapor levels present within that drum. Measures taken to ensure the quality and integrity of the monitoring data (distal end challenges, inline matrix spikes) along with confirmatory DAAMS sampling and analysis verify the collected data as valid and representative of the headspaces sampled. This collected data indicates that there is not a statistically significant difference between static and mixed drum headspace measurements. Also, neither drum weight nor date of origin generates any significant relationship to drum headspace vapor concentration. Of the 30 drums monitored, 26 drums had headspace measurements of less than 1-VSL indicating that TOCDF decontamination procedures were sufficient.

It can be concluded that the first sample of a drum headspace is representative of the agent vapor levels present within that drum. Based on earlier laboratory testing, historical TOCDF waste management practices, and the results obtained in this testing, drum headspace monitoring in conjunction with generator knowledge is a safe and effective means for sorting waste for final disposition at an off-site TSDF or for further treatment on site at TOCDF or Area-10.