U.S. Army
Program Manager for Chemical Demilitarization

Laboratory Test Report for Chemical Neutralization of Mustard Agent

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U.S. Army Program Manager for Chemical Demilitarization
Alternative Technology Program

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SECTION 1
EXECUTIVE SUMMARY

1. BACKGROUND

This document reports the results of testing performed according to the Laboratory Test Plan for Chemical Neutralization of Mustard Agent (reference 6). The tests were conducted at the U.S. Army's Edgewood Research, Development, and Engineering Center (ERDEC) in Edgewood, Maryland. The data developed for this report support larger scale testing and the design of a pilot-scale facility for chemical demilitarization of mustard agent (HD) stored in bulk containers at Aberdeen Proving Ground (APG), Maryland. Complete experimental details were reported in August 1996 (references 1 and 2).

1.1 Introduction

In 1994, the U.S. Army chose to begin research and development (R&D) of a process to achieve chemical neutralization of HD at low temperatures, less than 212°F (100°C), and at low pressures.

1.2 Objectives

The objective of laboratory testing was to evaluate HD/sodium hydroxide (NaOH) and HD/water reaction chemistries. The data derived from the experiments were used to select the best reaction conditions for the destruction of HD, confirm results of the concurrent bench-scale tests, and support design of the pilot-scale facility.

1.3 Summary of Tests

Seven subtests were conducted, using either the HD/NaOH process or the HD/water process. These tests determined:

- the effect of agent loading on product composition,
- the effect of impurities on the reaction process,
- the effect of chlorinated hydrocarbons (CHC) on the reaction, and
- the fate of CHC during the reaction.

1.4 Conclusions and Recommendations

HD/NaOH hydrolysis at a 16.7 weight percent (wt %) HD loading is a feasible process that affords a product for subsequent stabilization, where the low thiodiglycol (TDG) content is not a concern.

HD/water hydrolysis at a 1.3 wt % HD loading, with pH adjustment after the hydrolysis, is a feasible process that affords a product suitable for subsequent biotreatment, where the high conversion to TDG is needed.

The HD/NaOH process destroys HD to a level below 0.02 milligrams per liter (mg/L) within 30 minutes after the end of the agent addition. Likewise, the HD/Water process destroys HD to a level below 0.02 mg/L. The time for agent destruction in the HD/Water process appears to be delayed at higher loadings because of the impact of sulfonium ions on the low level analytical method for HD. The sulfonium ions present during the first half hour after agent addition either alter the extraction efficiency of HD or they are converted to HD upon heating in the gas chromatograph (references 16 and 17). Spike recovery data showed no trends in extraction efficiency versus reaction time. Forty five minutes after agent addition the sulfonium ions are significantly reduced and the analysis is no longer affected. At lower agent loadings in HD/Water and in the HD/NaOH process sulfonium ion concentrations are not significant, so the analysis is not affected.

Lower HD loadings give higher conversions of HD to TDG. At the same HD loadings, the HD/water process gives a higher conversion to TDG than the HD/NaOH process. The maximum conversions to TDG were obtained in the HD/water process at a 1.3 wt % HD loading, with adjustment to basic pH made after the hydrolysis. These conclusions support the earlier experiments by ERDEC (references 3 and 5) and the HD/bench 2-L Mettler tests.

In both the HD/NaOH and the HD/water processes, HD destruction and conversion to TDG were not adversely affected by use of lower purity HD. Similarly, hydrolysis of a heel from the ton container having a high residue level proceeded without difficulty.

The HD/water process at the higher HD loading (8.6 percent) resulted in sulfonium ions, which were converted to TDG upon pH adjustment with NaOH. At the lower HD loading (1.3 percent), no sulfonium ions were detected.

The five landbanned chlorinated hydrocarbons found in some HD ton containers are partially evolved in the offgas stream and partially retained in the hydrolysate. They do not appear to interfere with the HD hydrolysis. Distilling part of the hydrolysate (stripping) can be used to remove most of the remaining chlorinated hydrocarbons for their potential separate treatment.

SECTION 2
BACKGROUND AND SUMMARY OF TESTING PERFORMED

2. BACKGROUND

In October 1994, the U.S. Army Program Manager for Chemical Demilitarization (PMCD) established the ATP to test and evaluate chemical neutralization as a method for demilitarizing two chemical warfare agents, distilled mustard agent, 2,2'-dichlorodiethyl sulfide (HD) and nerve agent, O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (VX). These agents are stored in bulk (ton) containers at two storage sites, HD at Aberdeen, Maryland, and VX at Newport, Indiana. After the start of the ATP, the program was given additional responsibility tor evaluating other nonincineration technologies and was renamed Product Manager for Alternative Technologies and Approaches (PMAT&A). The objective of PMAT&A is to obtain the data on which to base a decision as to whether or not a technology should be demonstrated in pilot scale. An Overarching Integrated Product Team will make this final decision in December 1996.

2.1 Introduction

HD/NaOH Process. Although HD is insoluble in water, it can be hydrolyzed by a hot aqueous base, such as NaOH in a heterogeneous reaction (reference 10). Major advantages of this reaction include low reagent cost and process similarities with the basic hydrolysis of VX. A major concern about this reaction is that the product is a complex mixture of TDG and its various ether/thioether derivatives. The simplified chemical equation for the hydrolysis reaction in base is as follows.

$$ClCH_2CH_2SCH_2CH_2Cl + 2NaOH \rightarrow \underset{(TDG)}{HOCH_2CH_2SCH_2CH_2OH} + 2NaCl$$

The reaction occurs in two steps with the chlorohydrin $ClCH_2CH_2SCH_2CH_2OH$ formed as an intermediate. Sulfonium ions are also formed as intermediates, but they rapidly decompose in the presence of base. In the simplified equation, TDG is shown as the only organic product. However, in addition to TDG, the product contains significant amounts of other organic compounds (reference 3). They result because TDG reacts with the hydroxide ion to form the intermediate thiodiglycolate anion.

$$HOCH_2CH_2SCH_2CH_2OH + OH^- \rightarrow {}^-OCH_2CH_2SCH_2CH_2OH + H_2O$$

This thiodiglycolate anion then undergoes further reactions. If it reacts with chlorohydrin, ether/thioether oligomeric derivatives are formed.

$$\begin{aligned}&HOCH_2CH_2SCH_2CH_2Cl + {}^-OCH_2CH_2SCH_2CH_2OH \rightarrow \\ &\qquad HOCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH + H_2O\end{aligned}$$

The general formula of these oligomers is $HO(CH_2CH_2SCH_2CH_2O)_nH$ where n = 2, 3, or higher. The thiodiglycolate anion may also form cyclic products, such as oxathiane ($-CH_2CH_2SCH_2CH_2O-$). Additionally, in the presence of base, TDG or its oligomeric derivatives may undergo elimination of water, producing unsaturated olefinic compounds.

$$HOCH_2CH_2SCH_2CH_2OH \rightarrow CH_2{=}CHSCH_2CH_2OH + H_2O$$

Work at ERDEC (reference 3) has demonstrated that neutralization by NaOH can be successfully conducted with HD loadings (concentration of HD in the total reaction mass or volume) of up to 38 wt % using only a 10 percent excess of NaOH over the stoichiometric amount. However, at HD loadings of 21 wt % and higher, the product contains a separate organic phase, which complicates the analytical methodology and presents problems both in scale-up and downstream treatment. In feasibility tests, a loading of 16.7 wt % HD produced a single-phase solution; therefore, HD loadings of 16.7 wt % were investigated in the work of this report.

HD/Water Process. Recent experiments have shown that HD can be rapidly and completely neutralized by adding it to water held at or near the boiling point (reference 4). Because these conditions lead to a higher yield of TDG than the HD/NaOH reaction, there is significant potential that the HD/water reaction products would be more suitable for subsequent biotreatment.

The main hydrolysis reaction in water is as follows:

$$ClCH_2CH_2SCH_2CH_2Cl + 2H_2O \rightarrow \underset{\text{(TDG)}}{HOCH_2CH_2SCH_2CH_2OH} + 2HCl$$

Loadings of 1.3 wt % (1 volume percent) have produced a product that is primarily TDG and HCl. Loadings of up to 12 wt % (10 volume percent) destroyed agent and produced a single-phase product but resulted in higher levels of sulfonium ions (reference 11). A reaction scheme showing the reversible formation of these sulfonium ions is presented in figure 2-1 (reference 10).

A major objective of the HD/water tests was to determine the highest HD concentration that can be run and achieve an agent destruction efficiency (ADE) of at least 0.9999 without producing a high concentration of sulfonium ions. Different methods of adjusting pH to basic were tested to determine the effect on product composition.

2.2 Test Objectives and Criteria

The subtests of the HD/NaOH series were directed to a process in which the reaction products were to be stabilized and landfilled. The HD loading was fixed at 16.7 wt %, which is optimal for balancing throughput and a single liquid phase product (reference 3).

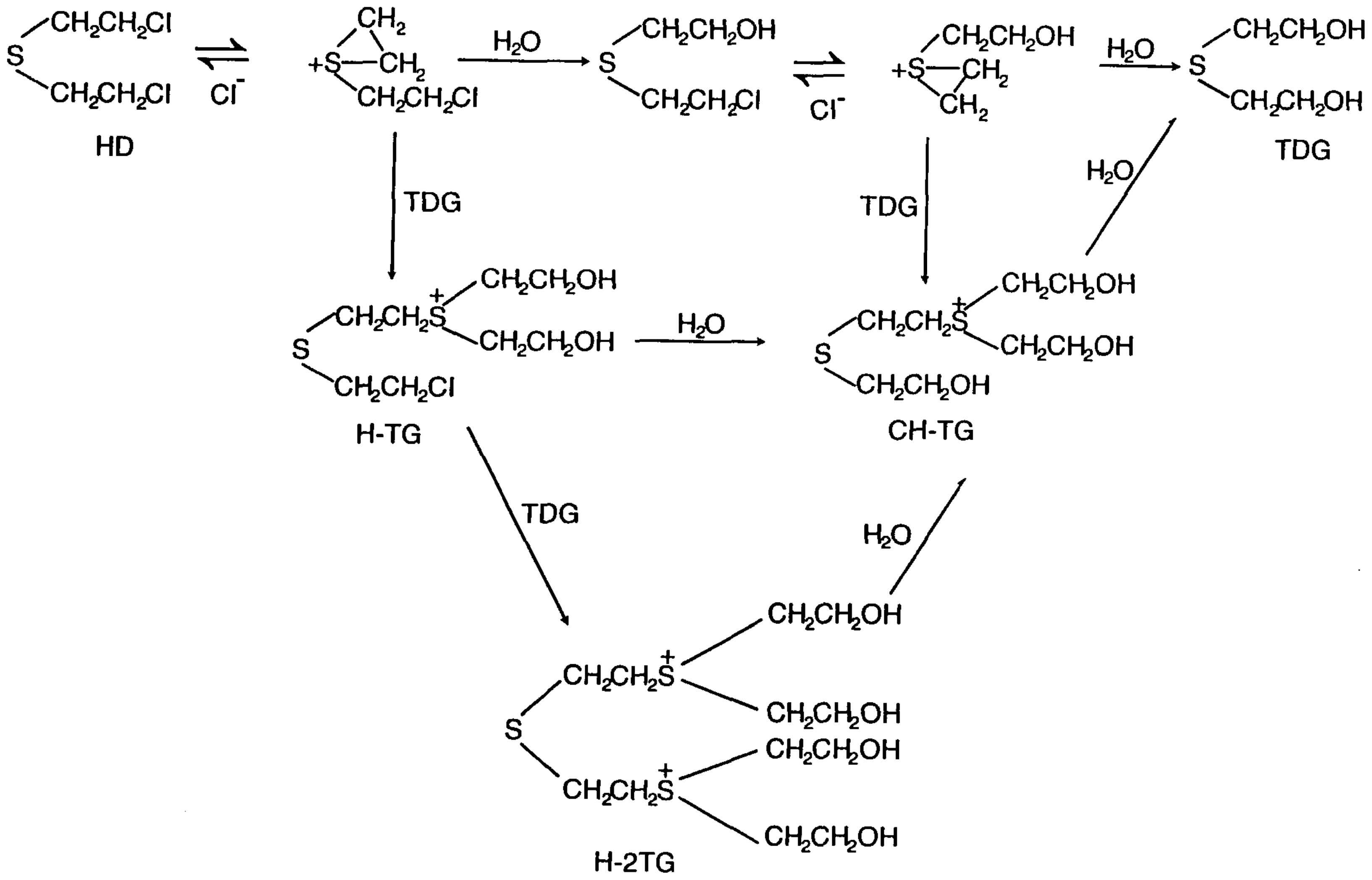

Figure 2-1. Reversible Formation of the Sulfonium Ion Aggregates in HD Hydrolysis

The objectives of the HD/NaOH tests were as follows:

- to analyze products from agent addition (at 16.7 wt % HD loading) to NaOH solution
- to determine the effect of impurities in HD on the HD/NaOH hydrolysis (at 16.7 wt % HD loading)
- to determine the effect of certain chlorinated hydrocarbon impurities on the HD/NaOH hydrolysis and their fate.

The subtests in the HD/water process are directed to provide a product for biological posttreatment. The HD loadings were 8.6 and 1.3 wt %. The 8.6 wt % loading (7 volume percent) was based on a preferred througput. The 1.3 wt % loading (1 volume percent) was based on ERDEC's early 1995 work (reference 4) and most of the biotreatment experimentation to date. The objectives of the HD/water tests were as follows:

- to determine the effect of the HD concentration (8.6 and 1.3 wt %) in the agent addition to water followed by pH adjustment with NaOH
- to determine the effect of impurities in HD on the HD/water hydrolysis (at 8.6 wt % HD loading)
- to determine the effect of using NaOH rather than water at the beginning of the hydrolysis (HD loadings of 8.6 and 1.3 wt %)
- to determine the effect of certain chlorinated hydrocarbon impurities on the HD/water hydrolysis and their fate.

The tests were designed to obtain data required by the Test and Evaluation Master Plan (TEMP) (reference 13). Table 2-1 shows which subtests address the TEMP requirements.

2.3 Summary of Tests

The experiments were performed at ERDEC by a Battelle team under contract to ERDEC from September 1995 to February 1996 (references 1 and 2). The experimental program was carried out in accordance with the Laboratory Test Plan for Chemical Neutralization of Mustard Agent (reference 6).

The reactions were run in a 1-liter (L) jacketed glass reactor fitted with a reflux condenser, as illustrated in appendix B. Nitrogen flow was provided from an ultrahigh-purity cylinder and its flow rate was monitored by a rotameter at the inlet line

Table 2-1. TEMP Requirements

Parameter	HD/NaOH Subtest No.	HD/Water Subtest No.
Reaction temperature	Note[a]	Note[a]
Reaction pressure	3	4
Reaction time	1,2,4	1,2,3,5
Agent destruction efficiency	1,2,4	1,2,3,5
Thermodynamics of reaction	3	4
Reaction products	1,2,4	1,2,3,5
Mixing		
Material		

NOTES:
[a] fixed at 194°F (90°C) based on feasibility studies

of the reactor. All materials and samples were weighed as they were added or removed from the reactor to provide a weight-in weight-out material balance. The reaction mixture was stirred continuously by a Lightnin Labmaster SI mixer and a Lightnin R-100 high shear radial flow stainless steel impeller. The HD was added via an Ismatec peristaltic pump. Samples were withdrawn from the reactor via a 30-milliliter (mL) polypropylene syringe connected to a leur lock fitting attached to a Teflon® tube submerged in the liquid above the stirrer impeller. Samples were transferred to precooled 40-mL bottles made of borosilicate glass with Teflon®-lined caps and were stored in a freezer maintained at 16°F (-9°C).

Samples to be analyzed were assigned numbers of the form L-abc-nn-Hp-wxyz, where:

L = denotes a laboratory scale test

a = section number of the test plan: 2 if HD/NaOH process, or 3 if HD/water process

b = subtest number within each process

c = reserved for run number (this digit was used incorrectly in some subtests, but the wxyz date code provided satisfactory unique sample identification)

nn = sample sequence number within each run

H = denotes HD agent

p = process designation: N for NaOH process, W for water process

wxyz = day of hydrolysis in Julian system, with z digit being 5 for 1995 and 6 for 1996.

Table 2-2 lists the analytical methods used. Most of them are detailed in the Onsite Sample Analysis Test Plan (reference 7) with variations as listed in appendix D of this report. HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results were reported as <0.02 mg/L.

Table 2-2. Analytical Methods

Sample Source	Analysis	Method	Reference
HD/NaOH hydrolysate	HD concentration	ATP HN-01	Reference 7
HD/NaOH hydrolysate, spiked with HD	HD recovery	ATP HN-01	Appendix D-2
HD/water hydrolysate	HD concentration	ATP HN-01 with hexane extraction	Appendix D-1
HD/water hydrolysate, spiked with HD	HD recovery	ATP HN-01 with hexane extraction	Appendixes D-1 and D-3
Hydrolysate	TDG	ATP HN-05A, BAT-01	Reference 7
Hydrolysate	Organosulfur compounds	ATP HN-04	Reference 7
HD/water hydrolysate	Sulfonium ion	ERDEC NMR method	Reference 12
Hydrolysate	Density at 77°F (25°C) g/mL	ASTM D 1217-86	Reference 7
Hydrolysate	Viscosity at 77°F (25°C) (cSt)	ASTM D 445-88	Reference 7
Offgas trap	CHC composition	ATP HN-07	Reference 7
Distillate from hydrolysate	CHC composition	ATP HN-09	Reference 7
Hydrolysate	CHC composition	ATP E-02	Reference 7
HD spiked with CHCs	HD assay	ATP A-01	Reference 7
HD heel hydrolysate	Elemental analysis	ATP A-02	Reference 7

NOTES:
ASTM = American Society for Testing and Materials
CHC = chlorinated hydrocarbon
NMR = Nuclear Magnetic Resonance
TDG = Thiodiglycol
cSt = centistokes
g/mL = grams per milliliter

SECTION 3
SUBTESTS

3. SUBTESTS

3.1 Mustard Agent/Sodium Hydroxide Process Subtest No. 1: Mustard Agent Addition to Sodium Hydroxide

The first subtest used the same ton container (no. D94102) of HD that was used in conducting Mettler testing. The subtest consists of two replicate runs at 16.7 wt % HD loading and is a basis for comparison with subtest nos. 2 and 4.

3.1.1 Specific Objectives of Test. The objectives were to: (1) obtain reproducible analyses of the products of HD/NaOH hydrolysis run at 16.7 wt % loading; (2) collect and analyze volatiles from the hydrolysis reactions. The results also serve as controls for subtest nos. 2 and 4.

3.1.2 Test Criteria. The criteria/data requirements stated in the test plan are: the temperature shall have been held to within 194(+/-9)°F [90(+/-5)°C]; (2) the stirring speed shall have been kept within 200(+/-50) revolutions per minute (rpm); (3) the agent addition rate shall have been maintained at a constant rate within +/-10 percent; (4) a sample shall have been withdrawn for analysis at 30 minutes after agent addition; (5) offgases shall have been trapped for analysis; and (6) the final pH shall be above 10.0, assuring that a sufficient base was used.

The specified stirring speed was increased from 200(+/-50) to 800(+/-50) rpm, because in the earliest run with this setup (HD/water subtest no. 1, run no. 3), 200 rpm was insufficient to disperse the HD. The allowable agent addition rate deviation was changed to +/-20 percent to conform with experimental capability.

3.1.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture. The HD batch was from ton container no. D94012, the same as that used in the subtests run under the Mettler test plan.

3.1.4 Test Procedure.

Step 1. Add the amount of distilled water shown in table 3-1 to the reactor. Add the amount of 50 wt % NaOH, EM Science-certified, shown in table 3-1 to the reactor via a dropping funnel under nitrogen atmosphere, with stirring until dissolved. Heat solution to 194(+/-9)°F [90(+/-5)°C].

Step 2. Add the amount of HD shown in table 3-1 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm and maintaining jacket temperature at 194(+/-4)°F [90(+/-2)°C].

Table 3-1. Test Parameters for HD/NaOH Subtest No. 1

Measurement	Specified	Run No. 1	Run No. 2
Weight of HD (g)	142.9	142.7	142.8
Weight of 50% NaOH (g)	151.0	151.0	151.0
Weight of water added (g)	561.8	561.9	561.8
Total weight of reactants (g)	855.6	855.6	855.6
Ton container no.	D94102	D94102	D94102
Agent addition rate (mL/minute)	1.87(+/-0.37)	1.81(+/-0.65)	1.22(+/-0.70)
Wt % of HD	16.7	16.7	16.7
Agent addition time (minutes)	60	62	90
Stirring speed (rpm)	800(+/-50)	800	800
Reaction temperature (°C)	90(+/-5)	90(+/-4)	90(+/-4)
Condenser temperature (°C)	NA	12-13	12-14
Offgas trap temperature (°C)	NA	-77 to -79	-78 to -79
Final pH	>10	14	13
Offgas trap weight change (g)	NA	-6.3[b]	Note[b]
Mass balance (% recovery[a])	>95	99.6	98.5
Date performed	N/A	11 Oct 1995	12 Oct 1995

NOTES:
[a] noncompositional: weight-in versus weight-out
[b] methanol backed up into line

g = grams

Step 3. After addition of HD is complete, continue heating and stirring for 60 minutes. Remove a 25-mL sample for analysis at 15-minute intervals, by means of a syringe, and chill to 32° to 39°F (0° to 4°C) by placing in precooled vials. Keep refrigerated until analyzed, with the actual temperature recorded.

Step 4. Continue stirring and cool to a temperature of 68° to 77°F (20° to 25°C).

Step 5. Weigh the final product and measure pH. Withdraw samples for analysis and physical properties.

Step 6. Collect and weigh the volatiles in the cold trap to 0.1g, transfer to a vial chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed.

3.1.5 Test Results. Table 3-1 lists the test parameters. The long addition time in run no. 2 was due to difficulty in adjusting the agent addition. Mass recoveries, HD destruction efficiency, and final pH are within the desired ranges.

Deviations from the test plan specifications and other observations reported for run no. 1 are as follows.

- Nitrogen was introduced into the reactor headspace during the reaction. Because of a leak around the stirrer shaft, the flow had to be increased to provide bubbling in the methanol trap.
- An exothermic reaction [as evidenced by a temperature rise from 196.5° to 200.8°F (91.6° to 93.8°C)] was noted when HD was first added to the solution.
- The black-colored HD disappeared immediately upon addition. The solution changed to an amber color upon initial agent addition. As the agent addition proceeded, the solution became a cloudy dark orange. Near the end of agent addition, the solution became dark brown with a heavy precipitate. No change in viscosity, as indicated by stirrer power requirement, was noted.
- In the HD analysis of the hydrolysate, the large amount of particulate matter made the filtration of the chloroform extract difficult.

Deviations from the test plan specifications and other observations reported for run no. 2 were the same as in subtest no. 1, run no. 1, except for the following.

- The total addition time for the specified amount of HD was 90 minutes.

Analytical results for the two runs are listed in tables C-1 and C-2 (appendix C), rather than the originally specified two samples at 30 and 60 minutes after the end of agent addition, a Test Change specified taking samples in duplicate at 15, 30, 45, and 60 minutes after the end of the agent addition (appendix D-2). One of each duplicate sample was spiked to 0.20 parts per million (ppm) HD. The spiked sample was analyzed for HD in the same manner as the unspiked sample to provide a measure of the chloroform extraction efficiency of HD in the analytical method.

3.1.6 Analysis of Test Results. The process neutralized HD in less than 15 minutes after the end of agent addition, with a major product being TDG, as summarized in table 3-2. The reported detectable amount of HD in the final product of run no. 2 is an unexplained result and can be discounted in view of the analysis of the earlier samples.

Based on the weight of HD charged, its purity of 91.3 percent, the TDG content of the product and its density, the conversion to TDG is calculated to be 26 percent for run no. 1 and 19 percent for run no. 2. Other organosulfur compounds detected, were 1,4-dithiane and 1,4-oxathiane at concentrations shown in table 3-2.

All of the HD spike recoveries were within the specified 50- to 150-percent range. There was no trend of recoveries as a function of sampling time; thus, there is no evidence of an analytical bias attributable to differences in chloroform extraction efficiency of solutions differing in their organic content.

The offgases were found to contain CHCs as shown in table 3-3.

3.2 Mustard Agent Process Subtest No. 2: Effect of Impurities in Mustard Agent

The lot of HD used for earlier ERDEC tests (reference 3) contained 89 wt % HD, four major impurities (1 to 10 wt %), and three trace impurities (0.1 to 0.9 wt %). The "Spring Valley" HD contained 64 wt % HD, six major impurities (1 to 12 wt %) and seven trace impurities (0.1 to 0.9 wt %). Residues referred to as heels and gels have been observed. Gels are higher molecular weight compounds that result largely from polymers intentionally added to thicken HD and are not expected to occur in the stockpile HD (reference 8). Heels are solid residues that remain inside the ton container when it is drained.

Run nos. 1 and 2 of this subtest used HD from ton container no. D94041, which had the highest concentration of impurities as determined in the ton container survey (appendix D-4).

The test plan originally specified that run nos. 3 and 4 use a high-viscosity ton container of HD, but none of significantly high viscosity was identified in the ton container survey. The hydrolysis of a heel from the bottom of an HD ton container is of more interest. Accordingly, the test plan was amended to use a portion of heel obtained in the ton

Table 3-2. Hydrolysate Analysis for HD/NaOH Subtest No. 1[c]

Sample Source[a]	Analysis[b]	Result (Run No. 1)	Result (Run No. 2)
15-minute	HD, mg/L	<0.02	0.15
30-minute	HD, mg/L	<0.02	<0.02
45-minute	HD, mg/L	<0.02	<0.02
60-minute	HD, mg/L	<0.02	<0.02
Final	HD, mg/L	<0.02	0.18
Final	TDG, mg/L	33160	23990
Final	1,4-Dithiane mg/L	668	431
Final	1,4-Oxathiane mg/L	1605	1114

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L [20 parts per billion (ppb)]; lower values and nondetectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

Table 3-3. Offgas Analysis for HD/NaOH Subtest No. 1

	Concentration in Methanol (mg/mL)		Amount in Offgas in Wt % of HD Charged[a]	
Compound	Run No. 1	Run No. 2	Run No. 1	Run No. 2
1,2-Dichloroethane	10681	6904	0.1120	0.0724
Trichloroethylene	30	10	0.0003	0.0001
Tetrachloroethylene	47	32	0.0005	0.0003

NOTE:

[a] compound as percent of HD charged = (mg compound/L MeOH) x (15 mL MeOH) x (10^{-3} L/mL) x (10^{-3} g/mg) x (100/143g HD)

container cleanout study from ton container no. D93734, which had the highest amount of heel as determined by nondestructive evaluation (NDE) (appendix D-4).

3.2.1 Specific Objectives of Test. The objective was to determine whether HD/NaOH hydrolysis results vary if the HD purity varies. Hydrolyses were run with HD from the ton container having the lowest amount of HD (highest total impurities) and with a heel from the cleanout of the ton container having the highest amount of heel. Tests were run in duplicate by adding HD or HD heel at 16.7 wt % loading. Results are compared with those of HD/NaOH subtest no. 1.

3.2.2 Test Criteria. See paragraph 3.1.2.

3.2.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture.

An analysis of ton container no. D94041 (used in run nos. 1 and 2) is given in appendix D-4. Samples of heel from ton container no. D93734 (used in run nos. 3 and 4) have been analyzed as discussed in appendix D-5 and found to be primarily composed of iron, HD, and the cyclic "Q" sulfonium ion $S(CH_2CH_2)_2S^+(CH_2CH_2)Cl$; the more solid-like the heel, the more sulfonium ion is present and the more jelly-like the heel the more HD is present.

3.2.4 Test Procedures. The following procedure was used for run nos. 1 and 2, weighing all materials and samples as they were added or removed from the reactor to provide a weight-in weight-out material balance.

> *Step 1.* Add the amount of distilled water shown in table 3-4 to the reactor. Add the amount of 50 wt % NaOH, EM Science-certified, shown in table 3-4 to the reactor via a dropping funnel under nitrogen atmosphere, with stirring until dissolved. Heat solution to 194(+/-4)°F [90(+/-2)°C].
>
> *Step 2.* Add the amount of HD shown in table 3-4 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm, and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].
>
> *Steps 3 through 6* were identical to subtest 1.

The following procedure was used for run nos. 3 and 4.

> *Step 1.* Add 562g of distilled water to the reactor. Add 713g of 50 wt % NaOH, EM Science-certified, to the reactor via a dropping funnel under nitrogen atmosphere, with stirring until dissolved. Withdraw 100 mL of the NaOH solution and place under dry nitrogen for use in step 2. Heat the NaOH solution remaining in the reactor to 194(+/-4)°F [90(+/-2)°C].

Table 3-4. Test Parameters for HD/NaOH Subtest No. 2

Measurement	Specified for Run Nos. 1 and 2	Run No. 1	Run No. 2	Specified for Run Nos. 3 and 4	Run No. 3	Run No. 4
Weight of HD (g)	142.9	143.7	143.2	142.9	129.1[c]	129.9[c]
Weight of 50% NaOH (g)	151.0	151.0	151.0	151.0	138.0[c]	147.3[c,d]
Weight of water added (g)	561.8	561.9	561.4	561.8	511.0[c]	500.8[c,d]
total weight of reactants (g)	855.6	855.6	855.6	855.6	778.1	778.0
Ton container no.	D94041	D94041	D94041	D93734 heel	D93734 heel	D93734 heel
Agent addition rate (mL/minute)	1.87 (+/-0.37)	1.88 (+/-0.17)	1.63 (+/-0.20)	Note [b]	Note [b]	Note [b]
Wt % of HD	16.7	16.8	16.7	16.7	16.6	16.7
Agent addition time (minutes)	60	60	69	60	60	60
Stirring speed (rpm)	800 (+/-50)	800	800	800 (+/-50)	800	800
Reaction Temperature (°C)	90(+/-5)	90(+/-4)	90(+/-3)	90(+/-5)	90(+/-4)	90(+/-4)
Condenser Temperature (°C)	N/A	12-13	13-14	N/A	12-14	12-13
Offgas trap temperature (°C)	N/A	-76 to -78	-78	N/A	-77 to -78	-79 to -80
Final pH	>10	14	14	>10	14	14
Offgas trap weight change (g)	N/A	+0.7	+0.6	N/A	+1.1	0.0
Mass balance (% recovery [a])	>95	99.0	99.2	>95	98.2	98.0
Date performed	N/A	19 Oct 1995	20 Oct 1995	N/A	7 Feb 1996	9 Feb 1996

NOTES:

[a] noncompositional: weight-in versus weight-out

[b] added to the reactor in six equal portions at 10-minute intervals

[c] Quantities of HD, NaOH, and water were scaled down because of the limited amount of heel (HD) available.

[d] Quantities of NaOH and water were adjusted to compensate for the low NaOH assay of 45.9 wt %.

Step 2. Add 143g of solid HD heel to the reactor by scooping it from the HD container into the reactor vessel. The solid HD is added through an open port in the top of the vessel using a common spatula and a wide-mouth funnel fitted to the port. The addition is over 1 hour, adding approximately six equal portions at 10-minute intervals. After each incremental addition, seal the introduction port with a ground-glass stopper and begin stirring at 800 rpm. After all the HD is added, take the 100-mL portion of NaOH solution withdrawn in step 1 and rinse any HD that may have stuck to the sides of the HD container, funnel, or walls of the reactor and add the NaOH solution to the reactor. Weigh the HD container and funnel to account for any mass of HD or NaOH solution that did not make it into the reactor and record these values to adjust the final mass balance.

Steps 3 through 6 were identical to subtest 1.

3.2.5 Test Results. Table 3-4 lists the test parameters specified. The agent addition rates were constant, although slower than specified in run no. 2. Because of a shortage of HD heel, the amounts of all materials were decreased by about 10 percent in run nos. 3 and 4.

Deviations from test plan specifications and other observations reported in run no. 1 were the same as in subtest no. 1, run no. 1, except for the following.

- The specified amount of HD was completely added in 60 minutes.

Deviations from the test plan specifications and other observations reported in run no. 2 were the same as subtest no. 1, run no. 1, except for the following.

- The specified amount of HD required a total addition time of 69 minutes.

Deviations from test plan specifications and other observations reported in run no. 3 were the same as in subtest no. 2, run no. 1, except for the following.

- Nitrogen was introduced into the reactor headspace during the reaction to provide a flow rate at the offgas trap of about 8 mL/minute (increased over earlier runs to improve control of flow and assure that an adequate amount of offgas product could be collected).

- The amount of HD heel was modified from the requested 142.9 g to 129.9 g because of a shortage of heel from the Chemical Transfer Facility (CTF) sample. The amounts of water and NaOH were adjusted to maintain the required 16.7 wt % HD loading.

- The HD heel (HD/sludge 5348-CTF-N-2) was a black chunky solid material with very little associated moisture. The heel broke into smaller chunks upon transfer from the CTF vessel to a beaker, from which it was added to the reactor in six equal portions of about 21.7 g at 10 minute intervals. Most of the solid heel dissolved immediately upon addition to form a black solution, with smaller chunks remaining for about 30 seconds. After 30 minutes of heel addition, a white crystalline solid was observed to form at the bottom of the condenser and a 1 g portion was collected for analysis. At the conclusion of the heel addition, the reaction mixture was a black solution containing black precipitate. No change in viscosity, as indicated by stirrer power requirement, was noted.

- As soon as each portion of heel was added the temperature rose to 201°F (94°C), remaining there for up to 7.5 minutes. After the last portion of heel was added, the final portion of NaOH was added to rinse the funnel, resulting in a 45°F (7°C) decrease in temperature.

- All samples withdrawn for analysis during the hour of heating after the end of agent addition were unavailable for analysis because they leaked from their containers and required a decontamination procedure.

Deviations from test plan specifications and other observations reported in run no. 4 were the same as in subtest no. 2, run no. 4, except for the following.

- The amount of HD heel was modified from the requested 142.9 g to 129.9 g because of a shortage of heel from the CTF sample. The amounts of water and NaOH were adjusted to maintain the required 16.7 wt % HD loading. In addition, the nominal 50 percent NaOH had a measured assay of 45.93 percent, so the relative amounts of water and NaOH had to be further adjusted. To 511.4 g of water was added 138 g of the 45.93 wt % NaOH. Then, 100 mL (111g) of the resulting solution was withdrawn for rinsing. To the remaining solution in the flask, the HD heel was added in six portions at 10 minute intervals. After the fifth portion, an additional 12.2 g of 45.93 wt % NaOH was added. After the final portion of HD was added, 87.8 mL (97.5 g) of the rinsing solution was added. The calculated total amount of 45.93 percent NaOH used is 147.3 g and the calculated total amount of water used is 500.8 g.

Analytical results for the four runs are reported in tables C-3 to C-6 (appendix C). Rather than the originally specified two samples at 30 and 60 minutes after the end of the agent addition, a Test Change specified taking samples in duplicate at 15, 30, 45, and 60 minutes after the end of agent addition (appendix D-2). One of each duplicate sample in run nos. 1 and 2 was spiked to 0.20 ppm HD. The spiked sample was analyzed for HD in the same manner as the unspiked sample to provide a measure of the chloroform extraction efficiency of HD in the analytical method.

3.2.6 Analysis of Test Results. The process neutralized the low-purity HD (run nos. 1 and 2) in less than 15 minutes after the end of the agent addition, with a major product being TDG, as summarized in table 3-5.

Based on the weight of HD charged, its purity of 85.4 percent, the TDG content of the product, and its density, the conversion to TDG for run no. 1 is calculated to be 26 percent and for run no. 2, the conversion is calculated to be 25 percent. This compares to 26 and 19 percent conversions obtained in subtest no 1. Other organosulfur compounds detected were 1,4-dithiane and 1,4-oxathiane.

The majority of the HD spike recoveries were within the specified 50- to 150-percent range. There was no trend of recoveries as a function of sampling time; thus, there is no evidence for an analytical bias attributable to differences in chloroform extraction efficiency of solutions differing in their organic content.

The process also neutralized the HD in the heel (run nos. 3 and 4). The resulting amount of TDG, as summarized in table 3-5, was much less than in hydrolysis of liquid HD, reflecting the lower HD content of the heel.

Analysis of chloroform extracts of the heel hydrolysates (run nos. 3 and 4) for other organosulfur compounds showed larger amounts of dithiane than in hydrolyses using the same loading of liquid HD (subtest no. 1, and subtest no. 2, run nos. 1 and 2). This result is in accordance with ERDEC's finding of high concentrations in HD heels of "Q" sulfonium ion, which hydrolyzes to 1,4-dithiane (appendix D-5).

The white crystalline solid collected as condensate in run no. 3 was analyzed by gas chromatography (GC)/mass spectrometry (MS) and was found to contain 34 wt % 1,4-dithiane and 7 wt % of 1,4-oxathiane, with the remainder unknown.
The heel hydrolysates (run nos. 3 and 4) were also analyzed by inductively coupled plasma (ICP) for metals and other elements. The concentrations of iron and sulfur in the hydrolysate were back-calculated to give their corresponding concentrations in the agent charged, as shown in appendix D-12. Iron was calculated at concentrations of 5.2 and 4 wt % of the heel, indicating a high concentration in the heel. Sulfur was calculated at 7.9 and 9.5 wt % of the heel (compared to 20.1 wt % calculated for pure HD), indicating a low concentration in the heel.

The offgases from all four runs were found to contain CHCs as shown in table 3-6.

Table 3-5. Hydrolysate Analysis for HD/NaOH Subtest No. 2[c]

Sample Source[a]	Analysis[b]	Result (Run No. 1)	Result (Run No. 2)	Result (Run No. 3)	Result (Run No. 4)
15-minute	HD, mg/L	<0.02	<0.02		1.99
30-minute	HD, mg/L	<0.02	<0.02		
45-minute	HD, mg/L	<0.02	<0.02		<0.1
60-minute	HD, mg/L	<0.02	<0.02		
Final	HD, mg/L	<0.02	<0.02	<0.02	<0.02
Final	TDG, mg/L	31570	30230	8400	5100
Final	1,4-dithiane (mg/L)	724	750	2015	2114
Final	1,4-thioxane (mg/L)	1267	1317	152	204

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

Table 3-6. Offgas Analysis for HD/NaOH Subtest No. 2

	1,2-Dichloroethane		Trichloroethylene	
Run No.	Concentration in Methanol (mg/L)	Amount in Offgas as Wt % of HD Charged[b]	Concentration in Methanol (mg/L)	Amount in Offgas as Wt % of HD Charged[a]
1	3311	0.0385	48	0.0006
2	4761	0.0554	46	0.0006
3	1990	0.0231	47	0.0005
4	1076	0.0125	nd	nd

NOTES:

[a] Offgas analysis was performed according to Method ATP HN07 (reference 7).

[b] (Compound as wt % of HD charged) = (mg compound/L MeOH) x (15 mL MeOH) x (10^{-3} L/mL) x (10^{-3} g/mg) x (100/g HD)

nd = not detected (detection limit 10 mg/L)

3.3 Mustard Agent/Sodium Hydroxide Process Subtest No. 4: Mustard Agent Spiked With Chlorinated Hydrocarbons

The purpose of this subtest is to determine the fate of certain CHCs that occur in one or more of the HD lots in the ton container survey. These compounds are of concern in the ultimate disposal of the effluent from the HD hydrolysis because they are listed in the Resource Conservation and Recovery Act (RCRA) land disposal restrictions (LDRs) which specify the maximum allowable concentrations in the final effluent. In the 27 individual ton containers analyzed (appendix D-4), these CHCs occurred as shown in table 3-7.

This subtest used the same ton container (no. D94102) of HD that was used in subtest no. 1. The HD was spiked with an amount of each CHC component to give a final concentration in the HD that approximated the maximum occurring concentration, except that the trichloroethylene amount was increased to 0.5 percent because 0.02 percent would have been too small to analyze accurately.

3.3.1 Specific Objectives of Test. The objectives were: (1) to determine the transfer (and possibly the reaction) of the following five CHCs during HD hydrolysis by NaOH at 16.7 wt % HD loading: 1,2-dichloroethane (0.5 percent), trichloroethylene (0.5 percent), tetrachloroethylene (1.5 percent), 1,1,2,2-tetrachloroethane (1 percent), and hexachloroethane (2.5 percent); (2) to determine whether the presence of these compounds affects the hydrolysis of HD; and (3) to determine whether vinyl chloride (a possible hydrolysis product of 1,2-dichloroethane) is formed during the hydrolysis. The subtests were run in duplicate in a 1-L stirred glass reactor employing a total reactant volume of 750 mL, using the same procedure as HD/NaOH subtest no. 1. At the end of the hydrolysis, the hydrolysate was distilled until about 5 percent of it was collected as condensate.

3.3.2 Test Criteria. Same as paragraph 3.1.2 plus (7) distillate was collected and (8) analyses for volatile components were required within 14 days of the hydrolysis.

3.3.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture. At the end of the hydrolysis, the setup was modified to allow distillation of 5 percent of the hydrolysate. The reflux condenser was replaced with a distilling head consisting of a three-way 75-degree angle connection tube, a downward-leading water-cooled Liebig condenser with the water temperature monitored, a 105-degree angle distilling adapter with sidearm leading to the offgas trap, and a receiving flask for the condensate. The modified setup is illustrated in appendix B.

Nitrogen flow was provided through the reactor during agent addition and subsequent heating sufficient to provide 15 to 20 bubbles per minute in the offgas trap.

Table 3-7. CHC Contents from Ton Container Survey

Component	Boiling Point (°C)	Number of Occurrences	Maximum Concentration (wt %)
1,2-dichloroethane	83	27	0.67
trichloroethylene	87	1	0.02
tetrachloroethylene	121	10	1.55
1,1,2,2-tetrachloroethane	147	4	0.84
hexachloroethane	187	2	3.03

Spiked HD was prepared from HD from ton container no. D94102 by adding CHCs (Aldrich Chemical Company) in the following amounts with stirring at 68° to 77°F (20° to 25°C) in an Erlenmeyer flask until dissolved.

Component	Wt %	Weight (g)
HD (including impurities)	94.0	580.7
1,2-dichloroethane	0.5	3.3
trichloroethylene	0.5	3.7
tetrachloroethylene	1.5	9.3
1,1,2,2-tetrachloroethane	1.0	6.2
hexachloroethane	2.5	15.4
Total	100.0	618.6

No adjustment in concentration was made for CHCs already present, which in the case of ton container no. D94102 consist of only 1,2-dichloroethane. The spiked HD was labeled L-241-01-HN-3385.

3.3.4 Test Procedures.

a. *Preparation and Storage of Spiked HD.*

Step 1. Send the required number of agent storage containers (Erlenmeyer flasks of borosilicate glass with glass stoppers) to the CTF for preconditioning, filling with HD, and transferring to building E3510, room 2, for storage. When needed, transport the HD from there to the laboratory [in accordance with operation no. 2 of the Standing Operating Procedure (SOP)].

Step 2. Place a stir plate in a surety hood behind the 20-cm line. Place a stir bar in a 1000-mL Erlenmeyer flask on the stir plate. Add the required amount of HD to the flask by pipetting or metering from the agent containers. Purge the empty agent containers with ultrapure nitrogen and replace the stoppers. Turn on the stirrer in the flask and adjust the speed to mix the HD.

Step 3. Working behind the 20-cm line in the hood, open and weigh out the specified amounts of the CHC spike chemicals. Add the spike chemicals to the HD in the flask with stirring at ambient temperature. Continue stirring for at least 10 minutes after the final spike chemical is added. Securely close the spike chemicals after use, triple-bag, and store under refrigeration.

Step 4. Open the original agent storage containers and transfer the required amount of spiked HD for each subtest into them by pipetting or metering from the Erlenmeyer flask. Purge the headspace of the agent storage containers with ultrapure nitrogen and seal with a stopper covered with Parafilm.

Step 5. Place the agent storage containers containing the spiked HD in an agent storage container filled partially with vermiculite and add additional vermiculite to cover. Place the lid on the container and seal with electrical tape. Transport the agent storage container to building E3510, room 2, according to operation no. 2 of the SOP. Have agent custodian sign DD Form 1911 for custody of the samples.

b. *Hydrolysis*

The following hydrolysis procedure was repeated for a total of two runs, weighing all materials and samples as they were added or removed from the reactor to provide a weight-in weight-out material balance.

Step 1. Add the amount of distilled water shown in table 3-8 to the reactor. Add the amount of 50 wt % NaOH, EM Science-certified, shown in table 3-8 to the reactor via a dropping funnel under nitrogen atmosphere, with stirring until dissolved. Heat solution to 194(+/-4)°F [90(+/-2)°C].

Step 2. Add the amount of HD shown in table 3-8 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm, and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].

Table 3-8. Test Parameters for HD/NaOH Subtest No. 4

Measurement	Specified	Run No. 1	Run No. 2
Weight of HD (g)	142.9	142.9	142.9
Weight of 50% NaOH (g)	151.0	151.0	151.0
Weight of water added (g)	561.8	561.8	562.0
total weight of reactants (g)	855.6	855.6	855.8
Ton container no.	D94102	D94102	D94102
Agent addition rate (mL/minute)	1.87(+/-0.37)	1.87(+/-0.39)	1.87(+/-0.67)
Wt % of HD	16.7	16.7	16.7
Agent addition time (minutes)	60	60	65
Stirring speed (rpm)	800(+/-50)	800	800
Reactor temperature (°C)	90(+/-5)	90(+/-4)	90(+/-3)
Condenser temperature (°C)	N/A	12-16	12-15
Offgas trap temperature (°C)	N/A	-77 to -79	-78 to -80
Final pH	>10	14	14
Distillate collected (wt % of hydrolysate before distillation)	5	3.8	4.8
Offgas trap (before distillation) weight change (g)	N/A	-3.4	+0.5
Offgas trap (after distillation) weight change (g)	N/A	0.0	+0.4
Mass balance (% recovery[a])	>95	96.0	96.4
Date performed	N/A	5 Dec 1995	7 Dec 1995

NOTE:

[a] noncompositional: weight-in versus weight-out

Step 3. After addition of HD is complete, continue heating and stirring for 60 minutes. Remove 25-mL samples for analysis at 15-minute intervals by means of a syringe and extract immediately for HD analysis. If samples need to be stored prior to analysis, chill to 32° to 39°F (0° to 4°C) by placing in a precooled vial and keep refrigerated until analyzed, with the actual temperature recorded.

Step 4. Collect and weigh the volatiles in the cold trap to 0.1g, transfer to a vial chilled to 32° to 39°F (0° to 4°C) and keep refrigerated until analyzed. Replenish the cold trap with fresh methanol. Change the reactor setup to that for distillation as shown in the addendum for appendix B.

Step 5. Raise jacket temperature to 248°F (120°C) and decrease the stirring speed to 200(+/-50) rpm. Continue stirring, heating, and offgas collection until an amount of condensate is collected in the receiving flask that is equal to 5(+/-1) percent of the calculated weight of hydrolysate in the reactor after accounting for samples removed.

Step 6. Continue stirring and cool to a temperature of 68° to 77°F (20° to 25°C). Weigh the final product and measure pH. Withdraw samples for analysis. Weigh the condensate in the receiving flask to 0.1g, transfer to a container chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed. Collect and weigh the volatiles in the cold trap to 0.1g, transfer to a vial chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed.

3.3.5 Test Results. Samples of the spiked HD were withdrawn on the day of each hydrolysis run for analysis (labeled L-241-01-HN-3395 and L-241-01-HN-3415) but were not analyzed until 4 months later. The results are presented in appendix D-9. The concentrations of CHCs in the two samples showed good replication but differed somewhat from the expected concentrations as prepared. The high concentrations of 1,2-dichloroethane are partially explainable because the HD already contained some before spiking. There were no unexpectedly low analyzed concentrations of any CHCs that could help explain their low recoveries from the hydrolysis reactions.

Table 3-8 lists the specified test parameters. The runs are considered satisfactory.

Deviations from the test plan specifications and other observations reported in run no. 1 were the same as in subtest no. 1, run no. 1, except for the following.

- The total addition time for the specified amount of HD was 60 minutes.

- Samples withdrawn at 30 and 60 minutes after the end of the agent addition showed three phases upon standing: the bottom was a reddish brown precipitate, the middle was a sandy precipitate, and the top was a liquid.

- The distillation was conducted at a jacket temperature of 248°F (120°C) and a pot temperature of 219° to 222°F (104° to 106°C). A time of between 3 to 4 hours was required to deliver 32 mL of distillate. The distillation was interrupted for about 5 minutes to fix a leaky seal between the reactor and the 75-degree angle connection tube to the condenser. The final distillate consisted of two phases: a bottom oily phase (4 mL) and a top opaque liquid phase (28 mL). The final reactor product had an oily surface and a heavy precipitate.

Deviations from the test plan and other observations reported in run no. 2 were the same as in subtest no. 3, run no. 1, except for the following.

- The total addition time for the specified amount of HD was 65 minutes.

- The distillation was conducted at a jacket temperature of 248°F (120°C) and a pot temperature of 219° to 222°F (104° to 106°C). The distillate was obtained in a much shorter time than in run no. 1. The final distillate consisted of two phases: a bottom oily phase (4 mL) and a top opaque liquid phase (30 mL). The final reactor product had an oily surface and a heavy precipitate.

Analytical results for the two runs are reported in tables C-7 to C-10 (appendix C).

Although the test plan requested analysis of the offgases for vinyl chloride, the analysis could not be run soon enough to prevent possible loss of vinyl chloride by volatilization.

3.3.6 Analysis of Test Results. Based on the weight of spiked HD charged, the HD purity of 84.8 percent, the TDG content of the product, and the product density, the conversion to TDG before distillation for run no. 1 is calculated to be 28 percent. For run no. 2, the conversion to TDG is 29 percent. This compares to 26 and 19 percent conversions obtained in subtest no 1. After distillation, the conversion is 26 percent for run no. 1 and 26 percent for run no. 2. Other organosulfur compounds detected were 1,4-dithiane and 1,4-oxathiane in concentrations as shown in table 3-9.

The added CHCs did not interfere with the HD hydrolysis. The hydrolysate before distillation contained 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene, and significant amounts of each were also found in the trapped offgases. Distillation of 5 percent of the hydrolysate removed most of the remaining 1,2-dichloroethane,

Table 3-9. Hydrolysate Analysis for HD/NaOH Subtest No. 4[c]

Sample Source[a]	Analysis[b]	Result (Run No. 1)	Result (Run No. 2)
30-minute	HD (mg/L)	<0.02	<0.02
60-minute	HD (mg/L)	<0.02	<0.02
60-minute	TDG (mg/L)	34220	35170
After distillation	HD (mg/L)	<0.02	<0.02
After distillation	TDG (mg/L)	32720	33220
After distillation	1,4-dithiane (mg/L)	66	58
After distillation	1,4-thioxane (mg/L)	57	39

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and nondetectable results are reported as <0.1 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

trichloroethylene, and tetrachloroethylene but did not completely eliminate them from the hydrolysate. The total recovery of CHCs was well below 100 percent.

Component	Without Distillation	With Distillation
1,2-dichloroethane	24 to 26 percent	35 to 61 percent
trichloroethylene	54 to 79 percent	98 to 103 percent
tetrachloroethylene	3 to 7 percent	46 percent
1,1,2,2-tetrachloroethane	0 percent	0 percent
hexachloroethane	1 to 7 percent	1 to 2 percent

A likely explanation for the absence of 1,1,2,2-tetrachloroethane and the relatively high recovery of trichloroethylene is that the former may have been dehydrochlorinated to the latter under the basic conditions of the hydrolysis. A possible explanation for the low recovery of hexachloroethane is that it sublimed into places where it was not available to be analyzed. A possible explanation for the higher recoveries with distillation is that the analytical methods used for the offgases and distillate may measure most of the CHC in the sample, whereas the method used for the hydrolysate (which involves a purge-and-trap step) may measure significantly less than the full amount of the CHC in the sample.

As summarized in table 3-9, run no. 1 showed equivalent HD neutralization efficiency to the unspiked HD of subtest no. 1. The conclusion is that the CHCs do not interfere with the HD hydrolysis.

3.4 Mustard Agent Water Process Subtest No. 1: Mustard Agent Addition to Water

The first subtest compares the products from 8.6 and 1.3 wt % HD loadings in which HD is added to water. The product was adjusted to basic pH by addition of NaOH at the end of the hydrolysis. Sulfonium ions were analyzed both before and after pH adjustment. The subtest also serves as a control for the impurity subtest (no. 2).

ERDEC has run feasibility tests at the 1.3 wt % HD loading and found almost complete conversion to TDG with no residual sulfonium ion concentration (reference 4). At 12 wt % loading of HD, a large concentration of sulfonium ions has been reported by ERDEC (appendix D-11). However, they are expected to decompose to TDG if the product is subsequently treated with NaOH.

3.4.1 Specific Objectives of Test. The objectives were to obtain reproducible analyses of the products of the HD/water hydrolysis process at 8.6 and 1.3 wt % HD loadings (two runs at each loading) and to collect and analyze offgases.

3.4.2 Test Criteria. See section 3.1.2.

3.4.3 Test Setup. See section 3.1.3.

3.4.4 Test Procedure. The following procedure was used for each of the four runs, weighing all materials and samples as they were added or removed from the reactor to provide a weight-in weight-out material balance.

> *Step 1.* Add the amount of distilled water shown in table 3-10 to the reactor and heat to 194(+/-4)°F [90(+/-2)°C].
>
> *Step 2.* Add the amount of HD shown in table 3-10 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm, and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].
>
> *Step 3 through 6* are identical to section 3.1.4.

3.4.5 Test Results. Table 3-10 lists the test parameters specified and actual. The runs were satisfactorily completed. The agent addition rates were difficult to control in run nos. 1 and 3, resulting in somewhat shorter-than-normal addition times. The actual HD loading in run no. 1 was 9.1 percent instead of 8.6 percent, but the difference is not regarded as invalidating the result. During the initial attempt to conduct run no. 3 at the originally specified 200 rpm (the first run of the entire test plan), HD globules were observed to form in the reactor. The run was repeated with a stirring speed of 800 rpm,

Table 3-10. Test Parameters for HD/Water Subtest No. 1

Measurement	Specified for Run Nos. 1 and 2	Run No. 1	Run No. 2	Specified for Run Nos. 3 and 4	Run No. 3	Run No. 4
Weight of HD (g)	65.7	69.8	66.5	9.5	9.5	10.8
Weight of water added (g)	698.3	698.3	698.3	742.5	742.5	742.5
total weight of reactants (g)	764.0	768.1	764.8	752.0	752.0	753.3
Ton container no.	D94102	D94102	D94102	D94102	D94102	D94102
Agent addition rate (mL/minute)	0.86 (+/-0.17)	1.12	0.87	0.125 (+/-0.025)	0.168	0.142
Wt % of HD	8.60	9.09	8.7	1.27	1.28	1.43
Agent addition time (minutes)	60	49	60	60	45	60
Stirring speed (rpm)	800 (+/-50)[a]	800	800	800 (+/-50)[a]	800	800
Reactor temperature (°C)	90(+/-5)	90	90(+/-4)	90(+/-5)	90	90
Condenser temperature (°C)	N/A	13-14	12-14	NA	11-12	12-15
Offgas trap temperature (°C)	N/A	-77 to -80	-77 to -79	NA	-77 to -78	-78 to -79
pH adjustment (g of 50% NaOH)	66.0	64.6	64.5	9.6	9.6	9.6
Final pH	>10	13	14	>10	12	12
Offgas trap weight change (g)	NA	-0.1	-0.8	NA	-0.7	0.0
Mass balance (% recovery[a])	>95	98.5	96.4	>95	97.8	96.0
Date performed	N/A	21 Sep 1995	26 Sep 1995	N/A	28 Sep 1995	19 Sep 1995

NOTE:
[a] noncompositional: weight-in versus weight-out

which provided satisfactory dispersion of the HD. The 800 rpm speed was, therefore, employed in all of the subtests.

Deviations from the test plan and other observations reported in both run nos. 1 and 2 are as follows.

- No nitrogen blanket was employed during the hydrolysis, although an offgas trap was employed. Only occasional bubbling in the offgas trap was observed.
- The agent addition pump was at a constant setting during the addition time.
- The black-colored HD disappeared immediately upon addition, but no significant color change occurred in the solution. No change in viscosity, as indicated by stirrer power requirement, was noted.
- Upon cooling to 140°F (60°C) for the NaOH addition, it was noted that the stirrer shaft and impeller become coated with a black material. Upon NaOH addition, the color of the solution changed from straw to black.

Deviations from the test plan and other observations in run no. 3 are as follows. (Observations were the same as in subtest no. 4, run nos. 1 and 2, except for the following.)

- Upon NaOH addition, the color of the solution changed from straw to golden amber.

Deviations from the test plan and other observations in run no. 4 are as follows. (Observations were the same as in subtest no. 4, run nos. 1 and 2, except for the following.)

- Upon NaOH addition, the color of the solution changed from straw to black. The stirrer shaft and impeller became coated with a black material.

Analytical results for the four runs are reported in tables C-11 to C-14 (appendix C). Rather than the originally specified two samples at 30 and 60 minutes after the end of the agent addition, a Test Change specified taking samples in duplicate at 15, 30, 45, and 60 minutes after the end of the agent addition (appendix D-3). One of each duplicate sample was spiked to 0.15 ppm HD. The spiked sample was analyzed for HD in the same manner as the unspiked sample to provide a measure of the hexane extraction efficiency of HD in the analytical method.

3.4.6 Analysis of Test Results. As summarized in table 3-11 HD is destroyed to below 0.02 mg/L. The time for agent destruction appears to be delayed at higher loadings because of the impact of sulfonium ions on the low level analytical method for HD. The sulfonium ions present during the first half hour after agent addition either alter the extraction efficiency of HD or they are converted to HD upon heating in the gas

Table 3-11. Hydrolysate Analysis for HD/Water Subtest No. 1[c]

Sample Source[a]	Analysis[b]	8.6 to 9.1 wt % Loading Result (Run 1)	 Result (Run 2)	1.3 wt % Loading Result (Run 3)	 Result (Run 4)
15 minute	HD, mg/L	0.28	0.25	<0.02	<0.02
30 minute	HD, mg/L	0.21	0.11	<0.02	<0.02
45 minute	HD, mg/L	<0.02	<0.02	<0.02	<0.02
60 minute	HD, mg/L	<0.02	<0.02	<0.02	<0.02
Final	HD, mg/L	<0.02	<0.02	<0.02	<0.02
Final	TDG, mg/L	35490	31500	6500	7100
Final	1,4-dithiane, mg/L	160	11	24	33
Final	1,4-thioxane, mg/L	15	4	0.3	0.3

NOTES:

[a] Sample times after end of agent addition.

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and non-detectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

chromatograph (reference 16 and 17). Spike recovery data (reference 2) showed no trends in extraction efficiency versus reaction time. Forty five minutes after agent addition the sulfonium ions are significantly reduced and the analysis is no longer affected.

The conversion to TDG (after NaOH addition at the end of hydrolysis) has been calculated and summarized as follows.

Run No.	HD Loading (wt %)	HD Conversion to TDG (percent)
1	9.1	59
2	8.6	55
3	1.3	74
4	1.3	72

A somewhat higher conversion to TDG is obtained at the lower HD loading than at the higher loading. Other organosulfur compounds detected were 1,4-dithiane and 1,4-oxathiane concentrations as shown in table 3-11.

NMR analyses (proton and carbon) on samples of hydrolysate, before and after addition of NaOH to adjust pH, were used to determine the sulfonium ion content, as well as an estimate of TDG and other organic components (table C-15 of appendix C). Stable sulfonium ions occurred as 10 to 13 mole percent of the organic content at 8.6 percent HD loading but were absent at 1.3 percent HD loading. Addition of NaOH destroys most but not all sulfonium ions, forming additional TDG and non-TDG products. Conversion to TDG increased as HD loading decreased. The TDG values by NMR can be used for comparison with each other but cannot be directly compared to the analyses by GC/MSD.

No CHCs were detected in the offgas trap in any of the four runs.

As summarized in table 3-11, neutralization to below 100 ppm HD required less than 15 minutes after the end of the addition at the 1.3 wt % HD loading (runs 3 and 4), but required 30 to 45 minutes after the end of the agent addition at the 8.6 wt % HD loading (runs 1 and 2).

3.5 Mustard Agent/Water Process Subtest No. 2: Effect of Impurities in Mustard Agent

HD from the stockpile may contain three classes of impurities: major impurities, trace impurities, and gels and heels. Each impurity is presumed to behave differently in the hydrolysis reaction and its effect on the product analysis must be established. The lot of HD used for earlier ERDEC tests (reference 3) contained 89 wt % HD, four major impurities (10 to 1 wt %) and three trace impurities (0.9 to 0.1 wt %). The "Spring Valley" HD contained 64 wt % HD, six major impurities (12 to 1 wt %), and seven trace impurities (0.9 to 0.1 wt %). Gels are higher molecular weight compounds that are dispersed in the HD. Gels have been reported to result largely from polymers intentionally added to thicken HD and are not expected to occur in the stockpile HD. Heels are solid residues that remain inside the ton container when it is drained.

Run nos. 1 and 2 of this subtest used HD from ton container no. D94041, which had the highest concentration of impurities as determined in the ton container survey (appendix D-4).

The test plan originally specified that run nos. 3 and 4 use a high-viscosity ton container of HD but none of significantly high viscosity was identified in the ton container survey. Of more interest is the hydrolysis of a heel from the bottom of an HD ton container. Accordingly, the test plan was amended to use a portion of heel obtained in the cleanout study from ton container no. D93734, which had the highest amount of heel as determined by NDE (appendix D-4).

3.5.1 Specific Objectives of Test. The objective was to determine whether HD/water hydrolysis results vary if the HD purity varies. Hydrolyses were run with the HD batch from the ton container having the lowest amount of HD (highest total impurities) and with a heel from the cleanout of the ton container having the highest amount of heel. Tests were run in duplicate by adding HD or HD heel at 8.6 wt % loading, with NaOH added at the end of the reaction. Results are compared with those of HD/water subtest no. 1.

3.5.2 Test Criteria. See paragraph 3.1.2.

3.5.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture.

3.5.4 Test Procedures

Step 1. Add the amount of distilled water shown in table 3-12 to the reactor and heat to 194(+/-4)°F [90(+/-2)°C].

Step 2. Add the amount of HD shown in table 3-12 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm, and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].

Step 3 through 6 are identical to section 3.1.4.

The following procedure was specified for run nos. 3 and 4.

Step 1. Add 598.0g of distilled water (100 mL less than the total amount) to reactor and heat to 194(+/-4)°F [90(+/-2)°C].

Step 2. Add 65.7g of solid HD heel to the reactor by scooping it from the HD container into the reactor vessel. The solid HD is added through an open port in the top of the vessel using a common spatula and a wide-mouth funnel fitted to the port. The addition is over 1 hour, adding approximately six equal portions at 10-minute intervals. After each incremental addition, seal the introduction port with a ground glass stopper and begin stirring at 800 rpm. After all the HD is added, take the 100-mL portion of water not used in step 1 and rinse any HD, which may have stuck to the sides of the HD container, funnel, or walls of the reactor and add the NaOH solution to the reactor. Weigh the HD container and funnel to account for any mass of HD or NaOH solution that did not make it into the reactor and record these values to adjust the final mass balance.

Step 3 through 6 are identical to paragraph 3.1.4.

3.5.5 Test Results. Table 3-12 lists the specified test parameters. The runs are considered satisfactory. The agent addition rate varied in run no. 1 and the addition time was shorter than 60 minutes. Although HD feed rates were outside of the specification, the subtest runs are acceptable because the HD apparently dissolved as rapidly as it was added.

Table 3-12. Test Parameters for HD/Water Subtest No. 2

Measurement	Specified for Run Nos. 1 and 2	Run No. 1	Run No. 2	Specified for Run Nos. 3 and 4	Run No. 3	Run No. 4
Weight of HD (g)	65.7	65.8	66.0	65.7	65.6	65.8
Weight of water added (g)	698.3	698.7	698.7	698.3	698.3	698.1
total weight of reactants (g)	764.0	764.5	764.7	764.0	763.9	763.9
Ton container no.	D94041	D94041	D94041	D93734	D93734	D93734
Agent addition rate (mL/minute)	0.86(+/-0.17)	1.016	0.81	heel Note[c]	heel Note[c]	heel Note[c]
Wt % of HD	8.60	8.61	8.63	8.60	8.59	8.61
Agent addition time (minutes)	60	51	64	60	60	60
Stirring speed (rpm)	800(+/-50)[a]	800	800	800(+/-50)	800	800
Reactor temperature (°C)	90(+/-5)	90(+/-1.4)	90(+/-1.1)	90(+/-5)	90(+/-6)	90(+/-6)
Condenser temperature (°C)	N/A	11-13	11-12	NA	12-15	11-14
Offgas trap temperature (°C)	N/A	-74 to -79	-76 to -78	NA	-78 to -79	-74 to -80
pH adjustment (g of 50% NaOH)	66.0	66.0	66.0	66.0	66.0	66.0
Final pH	>10	14	14	>10	14	14
Offgas trap weight change (g)	N/A	-0.6	Note[b]	N/A	-0.3	-0.4
Mass balance (% recovery[b])	>95	98.3	99.6	>95	98.1	97.2
Date performed	NA	17 Oct 1995	18 Oct 1995	N/A	30 Jan 1996	1 Feb 1996

NOTES:

[a] noncompositional: weight-in versus weight-out

[b] Methanol backed up into line.

[c] Added to the reaction in six equal portions of about 11g at 10-minute intervals.

Deviations from the test plan and other observations reported in run no. 1 were as follows.

- No nitrogen flow was employed during the hydrolysis, although an offgas trap was employed. Visible bubbling occurred at the 50-minute time of agent addition.
- The black-colored HD disappeared immediately upon addition. The solution became yellow upon initial agent addition. As the HD agent addition proceeded, the solution became darker yellow, and near the end of the run, greenish yellow. The stirrer shaft and impeller became coated with a black material during agent addition. No change in viscosity, as indicated by stirrer power requirement, was noted.
- Upon NaOH addition, the color of the solution turned very black.

Deviations from the test plan and other observations reported in run no. 2 were the same as for run no. 1, except for the following:

- The specified amount of HD was completely added in 60 minutes.

Deviations from the test plan and other observations reported in run nos. 3 and 4 were as follows.

- No nitrogen purge or blanket was used, although a methanol trap was employed to collect offgases. No bubbling was observed in the trap until after the addition of the final portion of water, after which bubbling occurred for about 30 minutes [possibly related to the temperature rising back to 194°F (90°C) from 183°F (84°C)].
- The HD heel (HD/sludge 5348-CTF-N-2) was a black chunky solid material with very little associated moisture. The heel broke into smaller chunks upon transfer from the CTF vessel to a beaker, from which it was added to the reactor in six equal portions of about 11g at 10-minute intervals. Most of the solid heel dissolved immediately upon addition to form a reddish-brown solution, with smaller chunks remaining for about 30 seconds. After the last portion of heel was added, the final portion of water was added to rinse the funnel, resulting in a 44°F (6°C) decrease in temperature. At the conclusion of the heel addition the reaction mixture was a yellowish solution and by the end of the reaction some black precipitate had formed. No change in viscosity, as indicated by stirrer power requirement, was noted.
- After 30 minutes of heel addition a white crystalline solid was observed to form at the bottom of the condenser and continued to form as the reaction progressed. An 0.6-g sample was collected but not analyzed. (A similar

material from HD/NaOH subtest no. 2, run no. 3 was found to contain 1,4-dithiane and 1,4-oxathiane.)

- When NaOH was added, the color of the solution became very black.

Analytical results are reported in tables C-16 to C-20 (appendix C). Rather than the originally specified two samples at 30 and 60 minutes after the end of agent addition, during run nos. 1 and 2, samples were taken in duplicate at 15-minute intervals. One of each duplicate sample was spiked to 50 ppm HD. The spiked sample was analyzed for HD in the same manner as the unspiked sample to provide a measure of the hexane extraction efficiency of HD in the analytical method.

3.5.6 Analysis of Test Results. As summarized in table 3-13, the process neutralized the low-purity HD (run nos. 1 and 2) in 30 to 45 minutes after the end of agent addition, about the same as with the higher purity lot of HD used in subtest no. 1. The major product was TDG.

Based on the weight of HD charged, its purity of 84.8 percent, the TDG content of the product (after pH adjustment with NaOH), and its density, the conversion to TDG for run no. 1 is calculated to be 64 percent and for run no. 2, 71 percent. This compares to 59 and 55 percent conversions obtained in subtest no 1. Other organosulfur compounds detected were 1,4-dithiane and 1,4-oxathiane in concentrations as shown in table 3-13.

In the HD spike recovery experiment designed to test hexane extraction efficiency, the recoveries varied from 46 to 171 percent, with values apparently unrelated to the time of sampling. The majority of the HD spike recoveries were within the specified 50- to 150-percent range. This suggests there is no analytical bias attributable to extraction efficiency.

The process also neutralized the HD heel (run nos. 3 and 4) as summarized in table 3-13. Although the HD disappeared more slowly in run no. 4, the resulting amount of TDG was much less than in the hydrolysis of liquid HD, reflecting the lower HD content of the heel. Analysis of hexane extracts of the final hydrolysates of run nos. 3 and 4 for other organosulfur compounds showed larger amounts of dithiane than in hydrolyses using the same loading of liquid HD (subtest no. 1, run nos. 1 and 2; subtest no. 2, run nos. 1 and 2). This result is in accordance with ERDEC's finding of high concentrations in HD heels of "Q" sulfonium ion, which hydrolyzes to 1,4-dithiane (appendix D-5).

The heel hydrolysates (run nos. 3 and 4) were also analyzed by ICP for metals and other elements. The concentrations of iron and sulfur in the hydrolysate were back-calculated to give their corresponding concentrations in the agent charged, as shown in appendix D-12. Iron was calculated at concentrations of 5 and 2.1 wt % of the

Table 3-13. Hydrolysate Analysis for HD/Water Subtest No. 2[c]

		High-Impurity HD		HD Heel	
Sample Source[a]	Analysis[b]	Result (Run No. 1)	Result (Run No. 2)	Result (Run No. 3)	Result (Run No. 4)
15-minute	HD (mg/L)	0.25	0.29	0.37	0.68
30-minute	HD (mg/L)	0.14	0.20	0.13	0.50
45-minute	HD (mg/L)	<0.02	<0.02	<0.02	0.22
60-minute	HD (mg/L)	<0.02	<0.02	<0.02	0.14
Final	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
Final	TDG (mg/L)	33530	37510	8300	6500
Final	1,4-dithiane (mg/L)	311	219	353	676
Final	1,4-thioxane (mg/L)	19	14	24	20

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

heel, indicating a high concentration in the heel. Sulfur was calculated at 12.9 and 10.9 wt % of the heel (compared to 20.1 wt % calculated for pure HD), indicating a low concentration in the heel.

NMR analyses (proton and carbon) on samples of hydrolysate of each of the four runs before and after addition of NaOH to adjust pH were used to determine the sulfonium ion content, as well as an estimate of TDG and other organic components (appendix C, table C-20). Product compositions in run nos. 1 and 2 were similar to those from the higher purity HD of subtest no. 1. The sulfonium ions, present at 11 to 12 mole percent of the organic content, were mostly, but not completely decomposed by the NaOH with formation of both TDG and non-TDG products. The hydrolysis products of the HD heel (run nos. 3 and 4) showed a small sulfonium ion content (2 to 3 mole percent of the organic content) both before and after NaOH treatment.

In all four runs only 1,2-dichloroethane was detected in the offgas trap, as shown in table 3-14.

Table 3-14. Offgas Analysis for HD/Water Subtest No. 2[c]

Run No.	1,2-Dichloroethane[a] Concentration in Methanol (mg/L)	1,2-Dichloroethane[a] Amount in Offgas as Wt % of HD Charged[b]
1	616	0.0140
2	1085	0.0246
3	37	0.0008
4	63	0.0014

NOTES:

[a] Trichloroethylene and tetrachloroethylene were not detected (detection limit 10 mg/L).

[b] (Compound as wt % of HD charged) = (mg compound/L MeOH) x (15 mL MeOH) x (10^{-3} L/mL) x (10^{-3} g/mg) x (100/66g HD)

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

3.6 Mustard Agent/Water Process Subtest No. 3: Mustard Agent Addition to Sodium Hydroxide

This subtest uses 8.6 and 1.3 wt % loadings of HD added to a 5 percent stoichiometric excess of aqueous NaOH, so it is actually the HD/NaOH process at low HD loadings. This subtest is included in the HD/water process test series to compare the results with those of subtest no. 1 in which NaOH is added after the hydrolysis. If the product analysis is similar, the procedure would be simpler than that of subtest no. 1 to prepare a product for biotreatment.

ERDEC's earlier tests of the addition of HD at a 1.3 wt % loading to NaOH gave a lower TDG yield than the same HD loading added to water (reference 4). This subtest was designed to confirm those results at the 1.3 wt % HD loading and extend them to the 8.6 wt % loading.

3.6.1 Specific Objectives of Test. The objective was to determine whether neutralization of HD by addition to excess NaOH results in a different product composition than when HD is added to water, as in subtest no. 1. Loadings of 8.6 wt % and 1.3 wt % HD (two runs at each loading) were used.

3.6.2 Test Criteria. See paragraph 3.1.2.

3.6.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture. The HD batch was from ton container no. D94012, the same as that used in subtest no. 1.

3.6.4 Test Procedure. The following procedure was used, weighing all materials and samples as they were added or removed from the reactor in order to provide a weight-in weight-out material balance.

> *Step 1.* Add the amount of distilled water shown in table 3-15 to the reactor. Add the amount of 50 wt % NaOH, EM Science-certified, shown in table 3-13 to the reactor via a dropping funnel under nitrogen atmosphere, with stirring until dissolved. Heat solution to 194(+/-4)°F [90(+/-2)°C].
>
> *Step 2.* Add the amount of HD shown in table 3-15 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].
>
> *Step 3 through 6* are identical to paragraph 3.1.4.

3.6.5 Test Results. Table 3-15 lists the specified test parameters. Although HD feed rates were outside of the specification, the subtest runs are acceptable because the HD apparently dissolved as rapidly as it was added. It was decided that run no. 4 should be repeated, since the original NaOH should have been in sufficient excess to keep the pH basic without additional adjustment, no samples from the first 60 minutes after end of agent addition were analyzed, the reaction was run for an excess of 60 minutes over that specified, and mass recovery was below the 95 percent specified. The runs were designated 4a and 4b, and only 4b is used in the analysis of test results.

Deviations from the test plan and other observations reported in run nos. 1, 2, and 3 were as follows.

- Nitrogen flow through the reactor headspace was provided during the NaOH addition only and not during the hydrolysis.
- The black-colored HD disappeared immediately upon addition and the reaction mass became amber color almost immediately. As agent addition was continued, the reaction became very turbid and was reddish brown at the end of the agent addition. The stirrer shaft and impeller were not coated with black as in subtest no. 1. No change in viscosity, as indicated by stirrer power requirement, was noted.

Deviations from the test plan and other observations in run no. 4a were the same as in run nos. 1, 2, and 3, except for the following.

- The sample removed at 60 minutes after completion of agent addition unexpectedly had a pH of 2, so samples already taken were discarded, additional NaOH (1 to 2g of 50 percent NaOH) was added, which brought the pH to 13. After the addition of the NaOH, the color changed to amber.

Table 3-15. Test Parameters for HD/Water Subtest No. 3

Measurement	Specified for Run Nos. 1 and 2	Run No. 1	Run No. 2	Specified for Run Nos. 3 and 4	Run No. 3	Run No. 4a	Run No. 4b
Weight of HD (g)	69.2	68.2	71.1	9.5	9.5	9.9	9.5
Weight of 50% NaOH added (g)	73.1	73.2	73.8	10.1	10.0	12.1	10.1
Weight of water added (g)	661.4	661.4	661.6	738.4	738.5	738.5	738.9
total weight of reactants (g)	803.7	802.8	806.5	758.0	758.0	760.5	758.5
Ton container no.	D94102	D94102	D94102	D94102	D94102	D94102	D94102
Agent addition rate (mL/minute)	0.908 (+/-0.0182)	0.895	0.933	0.125 (+/-0.025)	0.115	0.110	0.134 (+/-0.166)
Wt % of HD	8.60	8.50	8.82	1.27	1.25	1.30	1.25
Agent addition time (minutes)	60	60	60	60	65	71	55
Stirring speed (rpm)	800(+/-50)	800	800	800(+/-50)	800	800	800
Reactor temperature (°C)	90(+/-5)	90(+/-1.1)	90(+/-3.5)	90(+/-5)	90	90	90 (+/-1)
Condenser fluid temperature (°C)	N/A	12	13-14	N/A	13-14	11-14	13-14
Offgas trap temperature (°C)	N/A	-77 to -78	-77	N/A	-69 to -77	-77 to -78	-78 to -80
Final pH	>10	13	14	>10	12	2/13	12
Offgas trap weight change (g)	N/A	-0.9	-0.3	N/A	-0.5	-0.9	+0.1
Mass balance (% recovery[a])	>95	98.9	98.1	>95	99.2	93.0	99.4
Date run	N/A	3 Oct 1995	4 Oct 1995	N/A	5 Oct 1995	10 Oct 1995	4 Jan 1996

NOTE:

[a] noncompositional: weight-in versus weight-out

The reaction was continued for an additional 60 minutes during which additional samples were removed. The stirrer shaft and impeller were not changed in color as in subtest no. 1. No change in viscosity, as indicated by stirrer power requirement, was noted.

Deviations from the test plan and other observations in run no. 4b were the same as in run nos. 1, 2, and 3, except for the following.

- Nitrogen flow was provided during the hydrolysis with flow at the offgas trap measured at 5 mL/minute.

Analytical results for the runs are reported in tables C-21 to C-26 (appendix C). Rather than the originally specified two samples at 30 and 60 minutes after the end of agent addition, a Test Change specified taking samples in duplicate at 15, 30, 45, and 60 minutes after the end of agent addition (appendix D-3). One of each duplicate sample was spiked to 0.20 ppm HD. The spiked sample was analyzed for HD in the same manner as the unspiked sample to provide a measure of the hexane extraction efficiency of HD in the analytical method.

3.6.6 Analysis of Test Results. As shown in table 3-16 the HD destruction was faster than in the corresponding HD/water hydrolyses of subtest no. 1.

As summarized in table 3-16, neutralization to below 100 ppm HD required less than 15 minutes after the end of the addition at both HD loadings. By contrast, for agent addition to water (subtest no. 1), neutralization required 30 to 45 minutes after the end of the agent addition at the 8.6 wt % HD loading.

From the weight of HD charged, its purity of 91.3 percent, the TDG content (by GC/MSD) of the product, and its density, the conversion to TDG (after NaOH addition) has been calculated as follows (run no. 4a has not been included since its pH condition was abnormal).

Run No.	HD Loading (wt %)	HD Conversion to TDG (percent)
1	8.5	55
2	8.8	56
3	1.3	67
4b	1.3	67

As summarized in table 3-16, neutralization to below 100 ppm HD required less than 15 minutes after the end of the addition at both HD loadings. By contrast, for agent addition to water (subtest no. 1), neutralization required 30 to 45 minutes after the end of the agent addition at the 8.6 wt % HD loading.

Table 3-16. Hydrolysate Analysis for HD/Water Subtest No. 3[c]

Sample Source[a]	Analysis[b]	8.6 Wt % Loading Result (Run No. 1)	8.6 Wt % Loading Result (Run No. 2)	1.3 Wt % Loading Result (Run No. 3)	1.3 Wt % Loading Result (Run No. 4b)
15-minute	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
30-minute	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
45-minute	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
60-minute	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
Final	HD (mg/L)	<0.02	<0.02	<0.02	<0.02
Final	TDG (mg/L)	34250	35990	5900	5900
Final	1,4-dithiane (mg/L)	253	292	39	34
Final	1,4-thioxane (mg/L)	800	889	37	7

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

Results were fairly reproducible and higher conversions to TDG were obtained at the lower HD loading. Other organosulfur compounds detected were 1,4-dithiane and 1,4-oxathiane in concentrations as shown in table 3-16.

All of the HD spike recoveries were within the specified 50- to 150-percent range. There was no trend of recoveries as a function of sampling time; thus, there is no evidence for an analytical bias attributable to differences in hexane extraction efficiency of solutions differing in their organic content.

NMR analyses (proton and carbon) on samples of hydrolysate were used to determine the sulfonium ion content, as well as an estimate of TDG and other organic components (appendix C, table C-26). No sulfonium ions were detected in any of the runs.

No CHCs were detected in the offgas trap in any of the four runs.

3.7 Mustard Agent/Water Process Subtest No. 5: Mustard Agent Spiked With Chlorinated Hydrocarbons

The purpose of this subtest is to determine the fate of certain CHCs that occur in one or more of the HD lots in the ton container survey. These compounds are of concern in the ultimate disposal of the effluent from the HD hydrolysis because they are listed in the RCRA LDRs, which specify the maximum allowable concentrations of each in the final effluent.

In the 27 individual ton containers analyzed (appendix D-4), these CHCs occurred as shown in table 3-7 (paragraph 3.4). This subtest was added by a test change (appendix D-13); often, the original test plan was approved.

This subtest used HD from the same ton container (no. D94102) that was used in subtest no. 1. The HD was spiked with an amount of each CHC component to give a final concentration in the HD that approximated the maximum occurring previously, except that the trichloroethylene amount was increased to 0.5 percent because 0.02 percent would have been too small to analyze accurately.

3.7.1 Specific Objectives of Test. The objectives were: (1) to determine the transfer (and possibly the reaction) of the following CHCs during HD hydrolysis by water at 8.6 wt % HD loading: 1,2-dichloroethane (0.5 percent), trichloroethylene (0.5 percent), tetrachloroethylene (1.5 percent), 1,1,2,2-tetrachloroethane (1 percent), and hexachloroethane (2.5 percent); (2) to determine whether the presence of these compounds affects the hydrolysis of HD; and (3) to determine whether vinyl chloride (a possible hydrolysis product of 1,2-dichloroethane) is formed during hydrolysis. The subtests were run in triplicate in a 1-L stirred glass reactor employing a total reactant volume of 750 mL using the same procedure as HD/water subtest no. 1. (A third run was made because of the delay in analysis of the CHCs in one run.) At the end of hydrolysis, the hydrolysate was distilled until about 5 percent of it was collected as condensate.

3.7.2 Test Criteria. See paragraph 3.4.2.

3.7.3 Test Setup. The reactions were run in a 1-L reactor, as illustrated in appendix B. The cold trap contained 15 mL of methanol to collect offgases and was cooled by a methanol/dry ice mixture. At the end of the hydrolysis the setup was modified to allow distillation of 5 percent of the hydrolysate. The reflux condenser was replaced with a distilling head consisting of a three-way 75-degree angle connection tube, a downward-leading water cooled Liebig condenser with the water temperature monitored, a 105-degree angle distilling adapter with sidearm leading to the offgas trap, and a receiving flask for the condensate. The distillation setup is illustrated in appendix B.

Nitrogen flow was provided through the reactor during the agent addition and subsequent heating sufficient to provide 15 to 20 bubbles per minute in the offgas trap, with the actual rate measured by a flowmeter at the offgas trap.

Spiked HD was prepared from HD from ton container no. D94102, by adding CHCs (Aldrich Chemical Company) in the following amounts, with stirring at 68° to 77°F (20° to 25°C) in an Erlenmeyer flask until dissolved.

Component	Wt %	Weight (g)
HD (including impurities)	94.0	252.0
1,2-dichloroethane	0.5	1.3
trichloroethylene	0.5	1.3
tetrachloroethylene	1.5	4.0
1,1,2,2-tetrachloroethane	1.0	2.7
hexachloroethane	2.5	6.7
Total	100.0	268.0

No adjustment in concentration was made for CHCs already present, which in the case of ton container no. D94102, consist only of 1,2-dichloroethane. The spiked HD was labeled L-351-01-HW-3135.

3.7.4 Test Procedures.

a. *Preparation and Storage of spiked HD*

Step 1. Send the required number of agent storage containers (Erlenmeyer flasks of borosilicate glass with glass stoppers) to the CTF for preconditioning, filling with HD and transferring to building E3510, room 2 for storage. When needed, transport the HD from there to the laboratory (in accordance with operation no. 2 of SOP).

Step 2. Place a stir plate in a surety hood behind the 20-centimeter (cm) line. Place a stir bar in a 1000-mL Erlenmeyer flask on the stir plate. Add the required amount of HD to the flask by pipetting or metering from the agent containers. Purge the empty agent containers with ultrapure nitrogen and replace the stoppers. Turn on the stirrer in the flask and adjust the speed to mix the HD.

Step 3. Working behind the 20-cm line in the hood, open and weigh out the specified amounts of the CHC spike chemicals. Add the spike chemicals to the HD in the flask with stirring at ambient temperature. Continue stirring for at least 10 minutes after the final spike chemical is added. Securely close the spike chemicals after use, triple-bag, and store under refrigeration.

Step 4. Open the original agent storage containers and transfer the required amount of spiked HD for each subtest into them by pipetting or metering from the Erlenmeyer flask. Purge the headspace of the agent storage containers with ultrapure nitrogen and seal with a stopper covered with Parafilm.

Step 5. Place the agent storage containers containing the spiked HD in an agent storage container filled partially with vermiculite and add additional vermiculite to cover. Place the lid on the container and seal with electrical tape. Transport the agent storage container to building E3510, room 2 according to operation no. 2 of the SOP. Have agent custodian sign DD Form 1911 for custody of the samples.

b. *Hydrolysis*

The following procedure was repeated for a total of two runs, weighing all materials and samples as they were added or removed from the reactor in order to provide a weight-in weight-out material balance.

Step 1. Add the amount of distilled water shown in table 3-17 to the reactor and heat to 94(+/-4)°F [90(+/-2)°C].

Step 2. Add the amount of spiked HD shown in table 3-17 to the reactor at a constant rate over 1 hour by a metering pump, with stirring at 800 rpm, and maintaining jacket temperature at 194(+/-9)°F [90(+/-5)°C].

Step 3. After addition of HD is complete, continue heating and stirring for 60 minutes. Remove 25-mL samples for analysis at 15-minute intervals by means of a pipette and extract immediately for HD analysis. If samples need to be stored prior to analysis, chill to 32° to 39°F (0° to 4°C) by placing in a precooled vial and keep refrigerated until analyzed, with the actual temperature recorded.

Step 4. After the 60-minute sample is removed, continue stirring, cool to 140°F (60°C), and add the amount of NaOH shown in table 3-17. Continue stirring for 10 minutes, then remove a sample for analysis. Collect and weigh the volatiles in the cold trap to 0.1g, transfer to a vial chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed. Replenish the cold trap with fresh methanol. Change the reactor setup to that for distillation as shown in appendix B.

Step 5. Raise jacket temperature to 248°F (120°C) and decrease the stirring speed to 200(+/-50) rpm. Continue stirring, heating, and offgas collection until an amount of condensate is collected in the receiving flask that is equal to 5(+/-1) percent of the calculated weight of hydrolysate in the reactor after accounting for samples removed.

Table 3-17. Test Parameters for HD/Water Subtest No. 5

Measurement	Specified	Run No. 1a	Run No. 1b	Run No. 2
Weight of HD (g)	65.7	65.7	65.7	65.8
Weight of water added (g)	698.3	698.3	698.3	698.4
Total weight of reactants (g)	764.0	764.0	764.0	764.2
Ton container no.	D94102	D94102	D94102	D94102
Agent addition rate (mL/minute)	0.86 (+/-0.17)	0.86 (+/-0.45)	0.86 (+/-0.50)	0.86 (+/-0.83)
Wt % of HD	8.60	8.60	8.60	8.60
Agent addition time (minutes)	60	52	60	54
Stirring speed (rpm)	800(+/-50)	800	800	800
Reactor temperature (°C)	90(+/-5)	90(+/-2)	90(+/-2)	90(+/-1)
Condenser temperature (°C)	N/A	12-17	13-19	12-17
Offgas trap temperature (°C)	N/A	-77 to -79	-77 to -79	-73 to -78
pH adjustment (g of 50% NaOH)	66.0	66.0	66.0	66.0
Final pH	>10	14	14	14
Distillate collected (wt % of hydrolysate) (before distillation)	5	5.2	5.1	4.6
Offgas trap (before distillation) weight change (g)	N/A	-0.2	-0.2	-0.5
Offgas trap (after distillation) weight change (g)	N/A	-1.5	+0.4	-0.1
Mass balance (% recovery[a])	>95	85.5	94.1	96.7
Date performed	N/A	13 Nov 1995	28 Nov 1995	30 Nov 1995

NOTE:

[a] noncompositional: weight-in versus weight-out

Step 6. Continue stirring and cool to a temperature of 68° to 77°F (20° to 25°C). Weigh the final product and measure pH. Withdraw samples for analysis. Weigh the condensate in the receiving flask to 0.1g, transfer to a container chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed. Collect and weigh the volatiles in the cold trap to 0.1g, transfer to a vial chilled to 32° to 39°F (0° to 4°C), and keep refrigerated until analyzed.

3.7.5 Test Results. Samples of the spiked HD were withdrawn on the day of each hydrolysis run for analysis (labeled L-351-01-HW-3175, L-351-01-HW-3325, and L-351-01-HW-3345) but were not analyzed until four months later. The results are presented in appendix D-9. The concentrations of CHCs found in the three samples showed fair replication. The high concentration of 1,2-dichloroethane is partially explainable because the HD already contained some before spiking. The absence of trichloroethylene and 1,1,2,2-tetrachloroethane in the analyses of the HD is not explained; a substantial recovery of trichloroethylene occurred in the hydrolysis reactions indicating that it was indeed present in the spiked HD or was formed by hydrolysis of 1,1,2,2-tetrachloroethane. There were no unexpectedly low analyzed concentrations in the HD of the other three CHCs that could help explain their low recoveries from the hydrolysis reactions.

Table 3-17 lists the test parameters specified and actual. Although HD feed rates were outside of the specification, the subtest runs are acceptable because the HD apparently dissolved as rapidly as it was added. The agent addition times in run nos. 1a and 2 were shorter than 60 minutes.

Deviations from the test plan and other observations reported in run no. 1a were as follows.

- A flow of nitrogen was provided into the reactor headspace, which delivered a flow rate at the offgas trap during the reaction of between 1 and 15 mL/minute (mostly 4 to 6 mL/minute).

- The total addition time for the specified amount of HD was 52 minutes.

- The black-colored HD disappeared immediately upon addition. The solution changed to a light green color upon initial agent addition. As the agent addition proceeded, the solution remained light green. No change in viscosity, as indicated by stirrer power requirement, was noted. After pH adjustment, the reaction product was completely black and the stirring shaft and impeller had a black coating.

- The distillation was conducted at a jacket temperature of 248°F (120°C) and a pot temperature of 217°F (103°C).

- Samples were held for 2 weeks under refrigeration before analyses could be performed; therefore, the run was repeated as run no. 1b to determine the effect of sample storage time on the CHC analyses.

The low mass recovery (85.5 percent) is attributed to water loss by vaporization during the changeover from reflux to distillation mode. This was the first run of this procedure, and the reactor was left open at elevated temperature for several minutes.

Deviations from the test plan and other observations reported in run no. 1b were the same as in run no. 1a, except for the following:

- The HD inlet was located above the surface of the liquid in the reactor.
- During the hydrolysis, a white crystalline solid material formed on the top of the reactor around the joints. A portion was collected and analyzed by GC and found to contain a substantial portion of hexachloroethane.
- The condensate appeared to have a crystalline material suspended within the clear liquid portion.

Deviations from the test plan and other observations reported in run no. 2 were the same as in run no. 1a, except for the following.

- During the hydrolysis, a white crystalline solid material formed in the top of the reactor around the joints. The liquid associated with the crystals turned M-8 paper red, an indication of the presence of HD.

Analytical results are reported in tables C-27 through C-33 (appendix C).

3.7.6 Analysis of Test Results. Although the test plan requested analysis of the offgases for vinyl chloride (a possible hydrolysis product of 1,2-dichloroethane), the analysis was not performed because the procedure was not setup in time to analyze the samples soon enough to prevent possible loss of vinyl chloride by volatilization.

HD and TDG data are presented in table 3-18. The presence of HD in the early samples is believed to be the affect of sulfonium ions on the analytical method rather than reaction rate difference between HD/NaOH and HD/Water processes. The sulfonium ions present during the first half hour after agent addition either alter the extraction efficiency of HD or they are converted to HD upon heating in the gas chromatograph (reference 16 and 17). Spike recovery data showed no trends in extraction efficiency versus reaction time.

Table 3-18. Hydrolysate Analysis for HD/Water Subtest No. 5[c]

		8.6 Wt % Loading		
Sample Source[a]	Analysis[b]	Result (Run No. 1a)	Result (Run No. 1b)	Result (Run No. 2)
30-minute	HD (mg/L)	0.22	<0.02	0.16
60-minute	HD (mg/L)	0.11	<0.02	<0.02
60-minute	TDG (mg/L)	39440	36920	37180
After pH adjustment	HD (mg/L)	<0.02	<0.02	<0.02
After pH adjustment	TDG (mg/L)	41510	38190	31600
After distillation	HD (mg/L)	<0.02	<0.02	<0.02
After distillation	TDG (mg/L)	41780	40900	26400
After distillation	1,4-dithiane (mg/L)	6.3	7.6	6.9
After distillation	1,4-thioxane (mg/L)	2.3	3.0	3.5

NOTES:

[a] sample times after end of agent addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results are reported as <0.02 mg/L.

[c] Analytical methods are listed in table 2-2; HD via HN01, TDG via HN-05A, and sulfur compounds (last two) by HN04 (see table 2-2 for references).

Based on the weight of spiked HD charged, its purity of 85.8 percent, the TDG content of the product, and its density (estimated to be 1.0), the conversion to TDG can be calculated as follows.

	Run No. 1a (%)	Run No. 1b (%)	Run No. 2 (%)
Before pH adjustment	66	62	63
After pH adjustment	77	71	58
After distillation	73	72	47

For comparison, conversions obtained in subtest no. 1 after pH adjustment were 59 and 55 percent. The changes in TDG upon pH adjustment and distillation were not consistent among the three runs, so no conclusions can be drawn. Other organosulfur compounds detected were 1,4-dithiane and 1,4 oxathine in concentrations as shown in table 3-18.

NMR analyses on samples of hydrolysate of each of the three runs before pH adjustment, after pH adjustment, and after distillation were used to determine the sulfonium ion content, as well as an estimate of TDG and other organic components (appendix C, table C-33). Product compositions were similar to those from the unspiked HD of subtest no. 1. The sulfonium ions, present at 9 to 13 mole percent of the organic content, were completely decomposed by NaOH with formation of both TDG and non-TDG products.

The CHC analyses of the three replicate runs gave only fair reproducibility. However, there was no evidence for CHC loss due to a delay (caused by the Government shut down) in the analysis for 2 weeks (run no. 1a). The hydrolysates before distillation contain significant amounts of 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene, but only 1,2-dichloroethane occurred in a significant amount in the trapped offgases. Distillation of 5 percent of the hydrolysate removed most of the remaining 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene but did not completely eliminate them from the hydrolysate. Total recovery of CHCs was much below 100 percent.

	Before Distillation (%)	After Distillation (%)
1,2-dichloroethane	28 to 34	27 to 51
trichloroethylene	7 to 64	9 to 43
tetrachloroethylene	1 to 3	1 to 10
1,1,2,2-tetrachloroethane	0	0
hexachloroethane	0 to 95	0 to 44

The CHC recoveries calculated after distillation are not significantly different than before distillation; this result is in contrast to the higher recoveries after distillation calculated in the corresponding HD/NaOH subtest as reported in paragraph 3.4.6. The explanation for the absence of 1,1,2,2-tetrachloroethane proposed for the HD/NaOH hydrolysis (paragraph 3.4.6) was that it may have been dehydrochlorinated to the latter under the basic conditions of the hydrolysis. Under the acidic conditions of the HD/water process, the hydrolysis of 1,1,2,2-tetrachloroethane seems less plausible. However, the hydrolysate sample had been pH-adjusted by adding NaOH followed by heating at 140°F (60°C) for 10 minutes. A likely explanation for the variable concentration of hexachloroethane is its sublimation onto cooler portions of the reactor, as observed in two of the subtest runs.

SECTION 4
SUMMARY OF TEST RESULTS

4. SUMMARY OF TEST RESULTS

Table 4-1 summarizes the test conditions for all the hydrolysis subtests and runs.

4.1 Mustard Agent Destruction Efficiency

Table 4-2 summarizes the residual HD in hydrolysate samples taken at 15-minute intervals after the end of the HD addition. The analytical method detection limit was <0.02 mg/L (20 ppb).

Both the HD/NaOH and HD/water processes destroyed HD to a level below 0.02 mg/L (0.02 ppm) within 60 minutes after the end of the HD addition.

In HD/water runs using 1.3 wt % HD loadings (subtest no. 1, run nos. 3 and 4), destruction of HD to a level below 0.02 mg/L was achieved within 30 minutes after the end of the HD addition. In contrast, HD/water runs using 8.6 wt % HD loadings showed detectable levels of HD in the 30-minute samples but had dropped to <0.02 mg/L in the 45-minute samples (subtest no. 1 run nos. 1 and 2).

Using an HD ton container of low purity had no effect on HD destruction efficiency by either the HD/NaOH process or the HD/water process (subtest no. 2, run nos. 1 and 2). HD in heels taken from the ton container having the highest heel level was also completely hydrolyzed by both processes (subtest no. 2, run nos. 3 and 4), although in run no. 4 of each subtest the HD destruction efficiency for the heel was slower compared to subtests using liquid HD. Spiking of the HD with five CHCs had no effect on the HD destruction efficiency by either process (HD/NaOH subtest no. 4 and HD/water subtest no. 5).

Results of the HD spiking recoveries are reported in table 4-3. In matrix spike recovery experiments, recoveries in the range of 50 to 150 percent were considered acceptable. There were no trends in the spike recoveries that were related to the time of sampling, indicating that comparison of HD concentrations at the different sampling times is valid.

4.2 Thiodiglycol

Table 4-4 summarizes the TDG analyses of the hydrolysates. Analyses by GC/MS were used to calculate an estimated conversion of the original HD to TDG. The calculations, shown in appendix D-6, required use of an HD assay of the original agent and corrections for samples removed and NaOH added after the end of the hydrolysis. The deviations in results from replicate experiments (nine sets of duplicate runs and one set of triplicate runs) ranged from 0 to 26 percent; if the two results of HD/water subtest no. 5, run no. 2 are excluded, the deviations are only 0 to 7 percent. These deviations can be used in comparing the following results of experiments that tested different variables.

In general, conversions to TDG increase with decreasing HD loading. However, the TDG conversions of 72 to 74 percent obtained at the 1.3 wt % HD loadings of this report were well below the 90 to 95 percent values obtained at 1.3 wt % HD loadings in the earlier ERDEC results and at 1 to 3 wt % HD loadings in the HD/water 2-L Mettler tests. At the 1.3 wt % loading, conversion to TDG was slightly lower when NaOH was used in place of water.

At the 8.6 wt % loading, conversion to TDG was not adversely affected by use of NaOH in place of water, nor by use of low-purity HD or by the presence of CHCs.

There were no significant variations in conversions of HD to TDG resulting from using low-purity HD (subtest no. 2, run nos. 1 and 2) or HD spiked with CHCs (subtest no. 4).

4.3 Other Organosulfur Compounds

Table 4-5 summarizes the other organosulfur compounds in the hydrolysates of all of the subtests. The analyses were done by ATP Method HN-04, which analyzes the chloroform or hexane extracts of the hydrolysates. The results do not include any organosulfur compounds that may remain in the aqueous phase, such as water-soluble TDG oligomers or hydrolysis products of higher molecular-weight analogs of HD. Only 1,4-dithiane and 1,4-oxathiane were found. Other smaller peaks were observed but could not be identified using a spectral library. The results show good reproducibility for replicate runs, one exception being that the 1,4-dithiane concentration in HD/water subtest no. 3.1, run no. 2 seems to be too low.

4.4 Sulfonium Ion Content

Samples of HD/water hydrolysate were submitted for sulfonium ion analysis by NMR. Table 4-6 shows the sulfonium ion content of hydrolysate from the HD/water subtests before and after pH adjustment with NaOH. The results are expressed both as mole percent of organic and "percent HD that went to," the percent of the loaded agent (HD) converted to the component. The "percent HD that went to" calculation is based on the area percent of the total protons, including all triplets from mustard and mustard impurities but excluding any peaks that are identifiable as not originating from the HD, such as solvent contaminants. When sulfonium ions are present in the hydrolysate, they are accounted for by adjusting for the fact that each sulfonium ion came from two or three molecules of HD. The two sulfonium ions found were:

CHTG: $HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$

H2TG: $(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$.

In subtest no. 1, the analyses showed that stable sulfonium ions occurred with 8.6 percent HD loading but not with 1.3 percent HD loading. With low-purity HD (subtest no. 2, run nos. 1 and 2), the analyses showed sulfonium ion concentrations similar to the higher purity HD of subtest no. 1, run no. 2. The sulfonium ions, present at 11 to 12 mole percent of the organic content, were mostly but not completely decomposed by the NaOH. The hydrolysis products of the HD heel (run nos. 3 and 4) showed a small sulfonium ion content (2 to 3 mole percent of the organic content) both before and after NaOH treatment. In subtest no. 3, where HD was added to NaOH for the hydrolysis, no sulfonium ions were detected in the product. When HD spiked with CHCs was hydrolyzed (subtest no. 5) the sulfonium ion concentrations before NaOH were similar to those of subtest no. 1. Addition of NaOH destroyed the sulfonium ions.

4.5 Elemental Analysis

Elemental analyses by ICP were made only on the hydrolysates of the two subtests using the HD heel. In the HD/NaOH process (subtest no. 2, run nos. 3 and 4), iron was calculated at concentrations of 5.2 and 4 wt %. Sulfur was calculated at 7.9 and 9.5 wt %. In the HD/water process (subtest no. 2, run nos. 3 and 4), iron was calculated at concentrations of 5 and 2.1 wt %. Sulfur was calculated at 12.9 and 10.9 wt % of the heel. Variations among the four runs can be attributed to the fact that the heel was not uniform and the portions used in different runs may have differed in composition.

4.6 Offgases

Offgases were collected in all subtests in a cooled bubbler containing methanol located at the outlet of the condenser. The HD/NaOH subtests employed a nitrogen flow, while most of the HD/water runs did not. The methanol was analyzed for CHCs, specifically 1,2-dichloroethane, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, and hexachloroethane. Table 4-7 summarizes the offgas analyses. The only compounds detected were 1,2-dichloroethane and traces of trichloroethylene and tetrachloroethylene. The nondetectable amounts in most of the HD/water subtests can be attributed to the low HD loadings and the absence of nitrogen flow. With the low-purity HD (ton container no. D94041), the amount of 1,2-dichloroethane present in the initial agent is 0.67 wt % (table D-4); thus, the amount in the offgases from HD/NaOH hydrolysis (subtest no. 2, run nos. 1 and 2) represents a 6 to 8 percent recovery and the amount in the offgases from HD/water hydrolysis (subtest no. 2, run nos. 1 and 2) represents a 2 to 4 percent recovery.

4.7 Recovery of Chlorinated Hydrocarbons from HD

Table 4-8 shows the recovery of CHCs that were added by spiking the HD in HD/NaOH subtest no. 4 and HD/water subtest no. 5. The 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene were distributed between the hydrolysate and the offgases. Distillation greatly decreased but did not completely eliminate CHCs observed in the initial hydrolysates.

The total recoveries varied considerably from CHC to CHC and from run to run. The recovery for 1,2-dichloroethane ranged from 24 to 88 percent; these values are likely to be high because the calculation does not include the amount present in the unspiked HD. The recovery of trichloroethylene ranged from 8 to 103 percent; the high percents probably include amounts formed by hydrolysis of 1,1,2,2-tetrachloroethane, which was not detected in any samples. Tetrachloroethylene recoveries varied from 1 to 46 percent. Hexachloroethane recoveries varied from 0 to 95 percent; a likely explanation for the variable concentration of hexachloroethane is its sublimation onto cooler portions of the reactor, as observed in two of the subtest runs, where it was unavailable for analysis.

4.8 Physical Properties

The hydrolysate product densities at 77°F (25°C) and viscosities at 77°F (25°C) were measured as reported in the individual test result tables in appendix C. Small differences occurred that were related to the process and the HD loading shown as follows:

Process	HD Loading (wt %)	Density at 25°C (g/mL)	Viscosity at 25°C (cSt)
HD/NaOH	16.7	1.08 to 1.10	1.4-1.5
HD/NaOH	8.6	1.04	1.1
HD/NaOH	1.3	1.00	0.9
HD/water	8.6	1.04 to 1.05	1.1-1.2
HD/water	1.3	1.00 to 1.05	0.9-1.1

The densities were used in the calculation of TDG conversions from the TDG concentrations. The low viscosities show that the products would have no associated transfer problems.

Table 4-1. Summary of Hydrolysis Reaction Conditions

Subtest Name and No.	Subtest No. in Test Plan and Test Data	Report Section	Agent Ton Container No.	HD Loading (wt %)[a]	CHC Spiking of HD	NaOH Addition Time
HD/NaOH subtest no. 1, run nos. 1&2	2.1	3.1	D94102	16.7	No	Initially
HD/NaOH subtest no. 2, run nos. 1&2	2.2	3.2	D94041	16.7	No	Initially
HD/NaOH subtest no. 2, run nos. 3&4	2.2	3.2	D93734 Heel	16.7	No	Initially
HD/NaOH subtest no. 4, run nos. 1&2	2.4	3.4	D94102	16.7	Yes	Initially
HD/water subtest no. 1, run nos. 1&2	3.1	3.5	D94102	8.6	No	After hydrolysis
HD/water subtest no. 1, run nos. 3&4	3.1	3.5	D94102	1.3	No	After hydrolysis
HD/water subtest no. 2, run nos. 1&2	3.2	3.6	D94041	8.6	No	After hydrolysis
HD/water subtest no. 2, run nos. 3&4	3.2	3.6	D93734 Heel	8.6	No	After hydrolysis
HD/water subtest no. 3, run nos. 1&2[b]	3.3	3.7	D94102	8.6	No	Initially
HD/water subtest no. 3, run nos. 3&4[b]	3.3	3.7	D94102	1.3	No	Initially
HD/water subtest no. 5, run nos. 1&2	3.5	3.9	D94102	8.6	Yes	After hydrolysis

NOTES:

[a] Nominal loading; actual loading varied slightly as reported in section 3.

[b] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

Table 4-2. Residual HD in Hydrolysate

		HD Concentration (mg/L) at Times After End of HD Addition[a]				
Subtest Name and No.	Run No.	15 minutes	30 minutes	45 minutes	60 minutes	Final
HD/NaOH subtest no. 1	1	<0.02	<0.02	<0.02	<0.02	<0.02
	2	0.15	<0.02	<0.02	<0.02	0.18
HD/NaOH subtest no. 2	1	<0.02	<0.02	<0.02	<0.02	<0.02
	2	<0.02	<0.02	<0.02	<0.02	<0.02
HD/NaOH subtest no. 2	3	NA	NA	NA	NA	<0.02
	4	1.99	NA	<0.02	NA	<0.02
HD/NaOH subtest no. 4	1	NA	<0.02	NA	<0.02	<0.02
	2	NA	<0.02	NA	<0.02	<0.02
HD/water subtest no. 1	1	0.28	0.21	<0.02	<0.02	<0.02
	2	0.25	0.11	<0.02	<0.02	<0.02
HD/water subtest no. 1	3	<0.02	<0.02	<0.02	<0.02	<0.02
	4	<0.02	<0.02	<0.02	<0.02	<0.02
HD/water subtest no. 2	1	0.25	0.14	<0.02	<0.02	<0.02
	2	0.28	0.20	<0.02	<0.02	<0.02
HD/water subtest no. 2	3	0.37	0.13	<0.02	<0.02	<0.02
	4	0.68	0.50	0.22	0.14	<0.02
HD/water subtest no. 3[b]	1	<0.02	<0.02	<0.02	<0.02	<0.02
	2	<0.02	<0.02	<0.02	<0.02	<0.02
HD/water subtest no. 3[b]	3	<0.02	<0.02	<0.02	<0.02	<0.02
	4b	<0.02	<0.02	<0.02	<0.02	<0.02
HD/water subtest no. 5	1a	NA	0.22	NA	0.11	<0.02
	1b	NA	<0.02	NA	<0.02	<0.02
	2	NA	0.16	NA	<0.02	<0.02

NOTES:

[a] HD analyses of the hydrolysate are reported down to a level of 0.02 mg/L (0.02 ppm); lower values and nondetectable results are reported as <0.02 mg/L.

[b] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

NA = not available because sample was not taken or sample container leaked

Table 4-3. HD Spike Recovery

		HD Spike Recovery (percent) at Times After End of HD Addition			
Subtest Name and No.	Run No.	15 minutes	30 minutes	45 minutes	60 minutes
HD/NaOH subtest no. 1	1	63	63	66	73
	2	69	114	61	130
HD/NaOH subtest no. 2	1	155	81	124	135
	2	171	81	108	84
HD/water subtest no. 1	1	19	11	59	61
	2	84	87	56	55
HD/water subtest no. 1	3	61	71	80	70
HD/water subtest no. 2	1	46	100	103	117
	2	171	102	113	91
HD/water subtest no. 2	3	79	99	51	41
	4	32	59	168	82
HD/water subtest no. 3[b]	1	86	84	77	65
	2	65	69	61	59
HD/water subtest no. 3[b]	3	85	85	90	79
	4b	70	114	127	118

NOTES:

[a] percent recovery = (concentration of spiked sample - concentration of unspiked sample) x 100/(concentration of matrix spike added)

[b] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

NA = not available because sample was not taken or sample container leaked

Table 4-4. TDG Analyses

Subtest Name and No.	Test Parameters (and sample time)	Run No.	HD Loading (wt %)	By GC/MS TDG Concentration (mg/L)	By GC/MS TDG/HD Conversion (mole %)
HD/NaOH subtest no. 1	Ton container no. D94102 (final)	1	16.7	33160	26
		2	16.7	23990	19
HD/NaOH subtest no. 2	Low-purity HD (final)	1	16.8	31570	26
		2	16.7	30230	25
HD/NaOH subtest no. 2	HD heel (final)	3	16.6	8400	NA
		4	16.7	5100	NA
HD/NaOH subtest no. 4	HD spiked with CHC (before distillation)	1	16.7	34220	28
		2	16.7	35170	29
HD/NaOH subtest no. 4	HD spiked with CHC (after distillation)	1	16.7	32720	26
		2	16.7	33220	26
HD/water subtest no. 1	Ton container no. D94102 (final)	1	9.1	35490	59
		2	8.7	31500	55
HD/water subtest no. 1	Ton container no. D94102 (final)	3	1.3	6500	74
		4	1.4	7100	72
HD/water subtest no. 2	Low-purity HD (final)	1	8.6	33530	64
		2	8.6	37510	71
HD/water subtest no. 2	HD heel (final)	3	8.6	8300	NA
		4	8.6	5900	NA
HD/water subtest no. 3[a]	HD added to NaOH (final)	1	8.5	34250	55
		2	8.8	35990	56
HD/water subtest no. 3[a]	HD added to NaOH (final)	3	1.3	5900	67
		4b	1.3	5900	NA
HD/water subtest no. 5	HD spiked with CHC (before distillation)	1a	8.6	41510	NA
		1b	8.6	38190	NA
		2	8.6	31600	NA
HD/water subtest no. 5	HD spiked with CHC (after distillation)	1a	8.6	41780	NA
		1b	8.6	40900	NA
		2	8.6	26400	NA

NOTES:

[a] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

NA = not available

Table 4-5. Other Organosulfur Analyses

Subtest Name and No.	Test Parameters (and sample time)	Run No.	HD Loading (wt %)	1,4-Oxathiane (mg/L)	1,4-Dithiane (mg/L)
HD/NaOH subtest no. 1	Ton container no. D94102 (final)	1	16.7	1605	668
		2	16.7	1114	431
HD/NaOH subtest no. 2	Low-purity HD (final)	1	16.8	1267	724
		2	16.7	1317	750
HD/NaOH subtest no. 2	HD heel (final)	3	16.6	152	2015
		4	16.7	204	2114
HD/NaOH subtest no. 4	HD spiked with CHC (after distillation)	1	16.7	57	66
		2	16.7	39	58
HD/water subtest no. 1	Ton container no. D94102 (final)	1	9.1	15	160
		2	8.7	3.9	11
HD/water subtest no. 1	Ton container no. D94102 (final)	3	1.3	0.3	24
		4	1.4	0.3	33
HD/water subtest no. 2	Low-purity HD (final)	1	8.6	19	311
		2	8.6	14	219
HD/water subtest no. 2	HD heel (final)	3	8.6	24	353
		4	8.6	20	676
HD/water subtest no. 3[a]	HD added to NaOH (final)	1	8.5	800	253
		2	8.8	889	292
HD/water subtest no. 3[a]	HD added to NaOH (final)	3	1.3	37	39
		4b	1.3	7.0	34
HD/water subtest no. 5	HD spiked with CHC (after distillation)	1a	8.6	2.3	6.3
		1b	8.6	3.0	7.6
		2	8.6	3.5	6.9

NOTES

[a] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

NA = not available

Table 4-6. Sulfonium Ion Analyses[a]

Subtest Name and No.	Test Parameters (and sample time)	Run No.	HD Loading (wt %)	CHTG (mole percent)	CHTG (percent HD that went to)	H2TG (mole percent)	H2TG (percent HD that went to)
HD/water subtest no. 1	Ton container no. D94102 (before NaOH)	1	9.1	10.6	NA	1.7	NA
		2	8.7	9.0	NA	1.4	NA
HD/water subtest no. 1	Ton container no. D94102 (final)	1	9.1	2.8	NA	nd	NA
		2	8.7	0.6	NA	nd	NA
HD/water subtest no. 1	Ton container no. D94102 (before NaOH)	3	1.3	nd	NA	nd	NA
		4	1.4	nd	NA	nd	NA
HD/water subtest no. 1	Ton container no. D94102 (final)	3	1.3	nd	NA	nd	NA
		4	1.4	nd	NA	nd	NA
HD/water subtest no. 2	Low-purity HD (before NaOH)	1	8.6	9.5	16.4	1.6	4.1
		2	8.6	10.4	17.6	1.2	3.2
HD/water subtest no. 2	Low-purity HD (final)	1	8.6	2.5	4.5	0.7	1.9
		2	8.6	1.0	4.0	nd	NA
HD/water subtest no. 2	HD heel (before NaOH)	3	8.6	nd	NA	nd	NA
		4	8.6	2.6	NA	nd	NA
HD/water subtest no. 2	HD heel (final)	3	8.5	3.0	NA	nd	NA
		4	8.8	2.3	NA	nd	NA
HD/water subtest no. 3[b]	HD added to NaOH	1	8.5	nd	NA	nd	NA
		2	8.8	nd	NA	nd	NA
HD/water subtest no. 3[b]	HD added to NaOH	3	1.3	nd	NA	nd	NA
		4b	1.3	0.3	0.7	nd	NA
HD/water subtest no. 5	HD spiked with CHC (before NaOH)	1a	8.6	11.8	21.3	1.8	5.0
		1b	8.6	8.1	15.0	1.1	3.0
		2	8.6	8.0	15.0	1.6	4.4
HD/water subtest no. 5	HD spiked with CHC (after NaOH)	1a	8.6	nd	NA	nd	NA
		1b	8.6	nd	NA	nd	NA
		2	8.6	nd	NA	nd	NA

NOTES:

[a] Sulfonium ions were measured by the ERDEC NMR method (reference 12).

[b] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

NA = not available
nd = not detected; limit of detection 0.5 mole percent
CHTG = $HOCH_2CH_2SCH_2CH_2S^+(CH2CH2OH)_2$
H2TG = $(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$

Table 4-7. Offgas Analyses

Subtest Name and No.[a]	Test Parameters	Run No.	HD Loading (wt %)	Nitrogen Flow (mL/minute)[c]	Amount in Offgas as Percent of Agent Charged		
					1,2-dichloro-ethane	Trichloro-ethylene	Tetrachloro-ethylene
HD/NaOH subtest no. 1	Ton container no. D94102	1	16.7	Note[d]	0.1120	0.0003	0.0005
		2	16.7	Note[d]	0.0724	0.0001	0.0001
HD/NaOH subtest no. 2	Low-purity HD	1	16.8	4	0.0385	0.0006	nd
		2	16.7	4	0.0554	0.0006	nd
HD/NaOH subtest no. 2	HD heel	3	16.6	8	0.0231	0.0005	nd
		4	16.7	8	0.0125	nd	nd
HD/water subtest no. 1	Ton container no. D94102	1	9.1	none	nd	nd	nd
		2	8.7	none	nd	nd	nd
HD/water subtest no. 1	Ton container no. D94102	3	1.3	none	nd	nd	nd
		4	1.4	none	nd	nd	nd
HD/water subtest no. 2	Low-purity HD	1	8.6	none	0.0140	nd	nd
		2	8.6	none	0.0246	nd	nd
HD/water subtest no. 2	HD heel	3	8.6	none	0.0008	nd	nd
		4	8.6	none	0.0014	nd	nd
HD/water subtest no. 3[b]	HD added to NaOH	1	8.5	none	nd	nd	nd
		2	8.8	none	nd	nd	nd
HD/water subtest no. 3[b]	HD added to NaOH	3	1.3	none	nd	nd	nd
		4b	1.3	5	nd	nd	nd

NOTES:

[a] Results of subtests using HD spiked with CHCs (HD/NaOH subtest no. 4 and HD/water subtest no. 5) are results are reported in paragraph 4.7.

[b] Because HD was added to NaOH in this subtest, it is actually the HD/NaOH process.

[c] measured at offgas trap

[d] initially 3 to 6 mL/minute, then increased due to leaks in reactor

nd = not detected at level of 10 mg/L in methanol of trap

Table 4-8. Analysis of Hydrolysate of CHC-Spiked HD

Product Fraction and Name of CHC	Percent of CHC Recovered				
	HD/NaOH Subtest No. 4		HD/Water Subtest No. 5		
	Run No. 1	Run No. 2	Run No. 1a	Run No. 1b	Run No. 2
Samples after hydrolysis					
1,2-dichloroethane	0.8	1.2	4.3	1.0	7.0
Trichloroethylene	3.8	7.8	9.6	1.1	5.7
Tetrachloroethylene	0.6	0.1	0.2	0.0	1.9
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	1.0	0.1	14.3	0.0	0.0
Hydrolysate, initial					
1,2-dichloroethane	5.1	7.6	27.9	6.4	44.5
Trichloroethylene	25.0	51.0	62.0	6.6	36.3
Tetrachloroethylene	4.3	0.9	1.0	0.0	12.2
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	6.2	0.6	91.9	0.0	0.1
Offgases from hydrolysis					
1,2-dichloroethane	19.6	15.0	33.7	49.8	7.6
Trichloroethylene	25.3	20.6	0.1	0.0	12.2
Tetrachloroethylene	1.8	1.4	0.2	1.1	0.0
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	0.0	0.0	0.0	0.0	0.0
Samples after pH adjustment					
1,2-dichloroethane	...	...	2.1	0.5	3.5
Trichloroethylene	...	...	4.6	0.5	2.8
Tetrachloroethylene	...	...	0.1	0.0	1.0
1,1,2,2-tetrachloroethane	...	...	0.0	0.0	0.0
hexachloroethane	...	...	6.8	0.0	0.0

Table 4-8. Analysis of Hydrolysate of CHC-Spiked HD (Continued)

	Percent of CHC Recovered				
	HD/NaOH Subtest No. 4		HD/Water Subtest No. 5		
Product Fraction and Name of CHC	Run No. 1	Run No. 2	Run No. 1a	Run No. 1b	Run No. 2
Hydrolysate after distillation					
1,2-dichloroethane	0.9	2.3	1.9	0.6	5.4
Trichloroethylene	2.2	16.1	1.9	5.8	3.9
Tetrachloroethylene	0.7	2.4	0.1	0.0	0.6
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	0.1	0.1	0.2	0.1	0.1
Condensate and offgases from distillation					
1,2-dichloroethane	40.1	16.8	28.3	2.9	64.4
Trichloroethylene	66.8	58.9	14.2	3.8	32.4
Tetrachloroethylene	42.3	42.5	2.1	0.4	6.2
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	1.3	1.1	0.0	0.0	0.0
Totals without distillation					
1,2-dichloroethane	25.5	23.7	65.9	57.2	59.1
Trichloroethylene	54.1	79.4	71.7	7.9	42.0
Tetrachloroethylene	6.7	2.5	1.4	1.1	14.2
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	7.2	0.7	106.2	0.0	0.2
Totals with distillation					
1,2-dichloroethane	61.4	35.3	70.4	54.8	87.9
Trichloroethylene	98.2	103.4	30.5	11.4	44.9
Tetrachloroethylene	45.5	46.4	2.6	1.5	9.7
1,1,2,2-tetrachloroethane	0.0	0.0	0.0	0.0	0.0
hexachloroethane	2.3	1.3	21.3	0.1	0.2

SECTION 5
CONCLUSIONS

5. CONCLUSIONS

The HD/NaOH process destroys HD to a level below 0.02 milligrams per liter (mg/L) within 30 minutes after the end of the agent addition. Likewise, the HD/Water process destroys HD to a level below 0.02 mg/L. The time for agent destruction in the HD/Water process appears to be delayed at higher loadings because of the impact of sulfonium ions on the low level analytical method for HD. The sulfonium ions present during the first half hour after agent addition either alter the extraction efficiency of HD or they are converted to HD upon heating in the gas chromatograph (references 16 and 17). Spike recovery data showed no trends in extraction efficiency versus reaction time. Forty five minutes after agent addition the sulfonium ions are significantly reduced and the analysis is no longer affected. At lower agent loadings in HD/Water and in the HD/NaOH process sulfonium ion concentrations are not significant, so the analysis is not affected.

Low HD loadings give the highest conversions of HD to TDG. At the same HD loadings, the HD/water process gives a higher conversion to TDG than the HD/NaOH process. The maximum conversions to TDG were obtained in the HD/water process at a 1.3 wt % HD loading, with adjustment to basic pH made after the hydrolysis. These conclusions support the earlier experiments by ERDEC (references 3 and 4) and the HD/bench 2-L Mettler tests (references 15 and 16).

In both the HD/NaOH and HD/water processes, HD destruction and conversion to TDG were not adversely affected by use of HD of lower purity. Similarly, hydrolysis of a heel sample from the ton container having a high residue level proceeded without difficulty.

The HD/water process at the higher HD loading (8.6 percent) resulted in stable sulfonium ions, which were converted to TDG upon pH adjustment with NaOH. At the lower HD loading (1.3 percent) no sulfonium ions were detected.

The five landbanned CHCs found in some HD ton containers are partially evolved in the offgas stream and partially retained in the hydrolysate. They do not appear to interfere with the HD hydrolysis. Distilling part of the hydrolysate (stripping) can be used to remove most of the remaining CHCs for their potential separate treatment.

SECTION 6
RECOMMENDATIONS AND LESSONS LEARNED

6. RECOMMENDATIONS AND LESSONS LEARNED

6.1 Recommendations

HD/water hydrolysis at a 1.3 wt % HD loading, with pH adjustment after the hydrolysis, is a process that affords a product suitable for subsequent biotreatment, where the higher conversion to TDG is needed. At higher HD loading, post-hydrolysis addition of NaOH to reduce sulfonium ions is recommended.

6.2 Lessons Learned

The HD analytical method is capable of detecting HD down to a level of 0.02 mg/mL. The original reports with a detection level of 0.1 mg/mL were not adjusted for concentration of HD on extraction and recovery in the extraction process (appendix D).

APPENDIX A
ACRONYMS/ABBREVIATIONS

APPENDIX A
ACRONYMS/ABBREVIATIONS

ADE	agent destruction efficiency
APG	Aberdeen Proving Ground
ARC	accelerating rate calorimeter
ASTM	American Society for Testing and Materials
ATP	Alternative Technology Program
CHC	chlorinated hydrocarbon
CTF	Chemical Transfer Facility
DA	Department of the Army
DAB	Defense Acquisition Board
ERDEC	Edgewood Research, Development, and Engineering Center
GC	gas chromatography
HD	mustard agent
HPLC	high-performance liquid chromatography
ICP	inductively coupled plasma
LDR	land disposal restriction
MEA	monoethanolamine
MS	mass spectrometry
MSD	mass selective detector
NDE	nondestructive evaluation
NMR	Nuclear Magnetic Resonance
PMAT&A	Product Manager for Alternative Technologies and Approaches
PMCD	Program Manager for Chemical Demilitarization
R&D	research and development
RCRA	Resource Conservation and Recovery Act
rpm	revolutions per minute
SOP	Standing Operating Procedure
TDG	thiodiglycol
TEMP	Test and Evaluation Master Plan
TOA	trade-off analysis

USACDRA	U.S. Army Chemical Demilitarization and Remediation Activity
VX	nerve agent

APPENDIX B
FIGURES

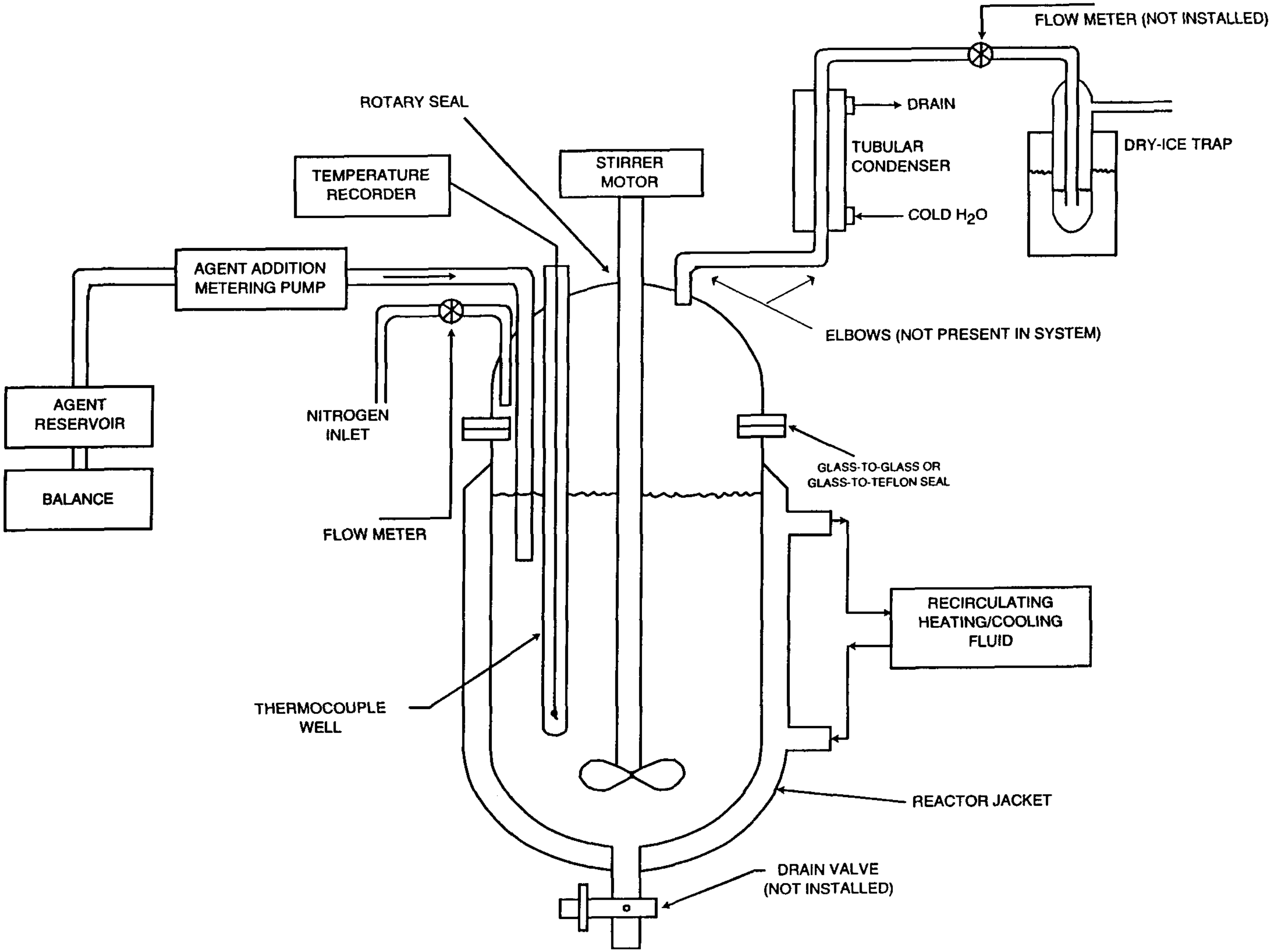

Figure B-1. Lab Reactor

1070>-appbfigs.pre

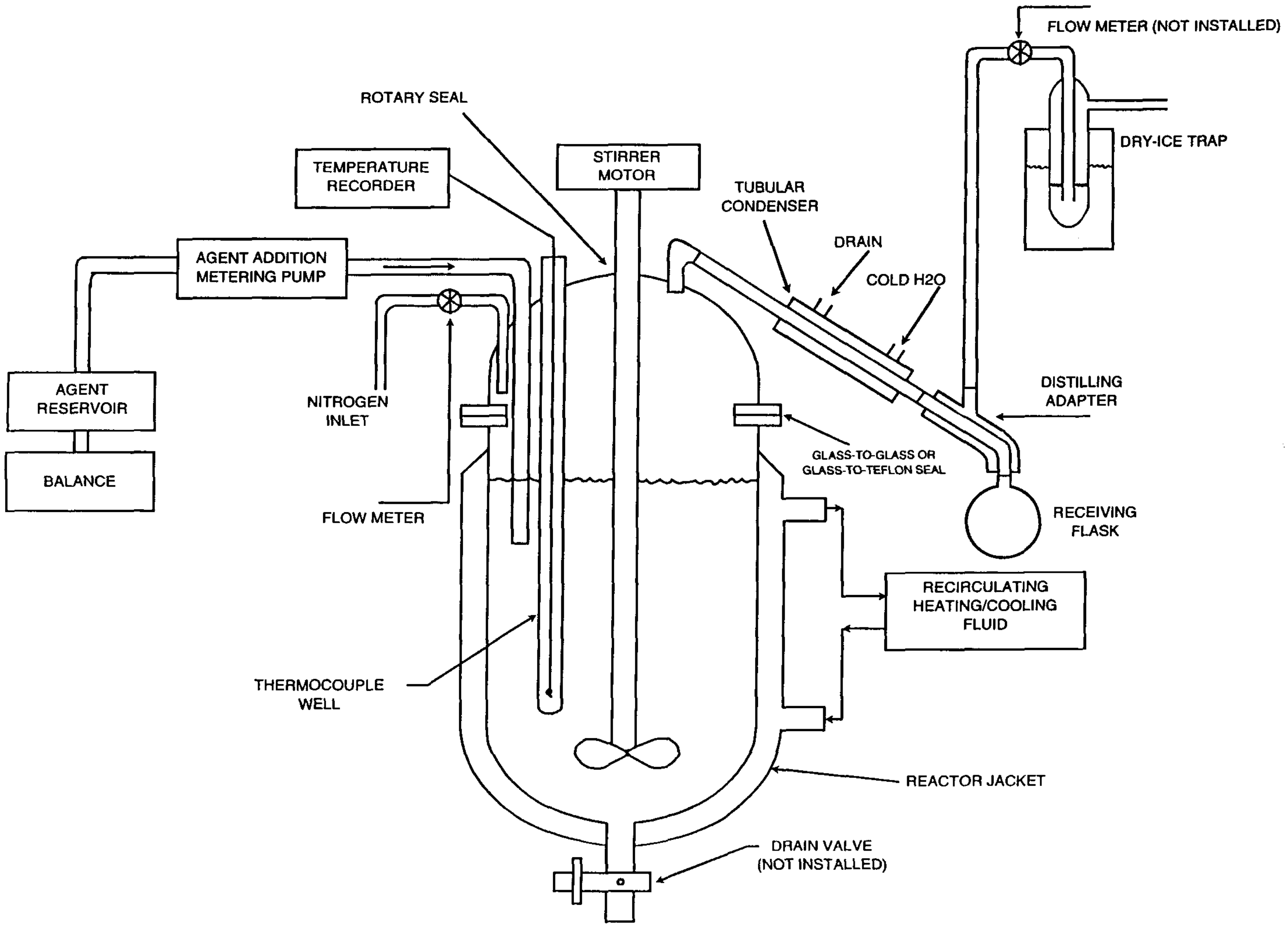

Figure B-2. Lab Reactor With Distillate Collection

APPENDIX C
ANALYTICAL DATA COLLECTED

Table C-1. HD/NaOH Subtest No. 1, Run No. 1 Analyses

Sample No. (nn of L-211-nn-HN-2845)	Sample Source[a]	Analysis	Method	Result
01	15 minutes	HD concentration	ATP HN-01	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01	63 %
03	30 minutes	HD concentration	ATP HN-01	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01	63%
05	45 minutes	HD concentration	ATP HN-01	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01	66%
07	60 minutes	HD concentration	ATP HN-01	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01	73%
10	Final	HD concentration	ATP HN-01	<0.1 mg/L
10	Final	TDG	ATP HN-05A	33160 mg/L
10	Final	1,4-Dithiane	ATP HN-04	668 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	1605 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0814 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	1.459 cSt
12	Offgases	1,2-Dichloroethane	ATP HN-07	10681 mg/L
12	Offgases	Trichloroethylene	ATP HN-07	30 mg/L
12	Offgases	Tetrachloroethylene	ATP HN-07	47 mg/L

NOTES:

[a] sample times are after completion of HD addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and nondetectable results are reported as <0.1 mg/L.

[c] Detection limit for offgas components is 10 mg/L in methanol of trap.

FOR REFERENCE METHODS, SEE TABLE C-34 ON PAGE C-34.

Table C-2. HD/NaOH Subtest No. 1, Run No. 2 Analyses

Sample No. (nn of L-212-nn-HN-2855)	Sample Source[a]	Analysis	Method	Result[b]
01	15 minutes	HD concentration	ATP HN-01	0.15 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01	69%
03	30 minutes	HD concentration	ATP HN-01	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01	114%
05	45 minutes	HD concentration	ATP HN-01	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01	61%
07	60 minutes	HD concentration	ATP HN-01	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01	130%
10	Final	HD concentration	ATP HN-01	0.18 mg/L
10	Final	TDG	ATP HN-05A	23990 mg/L
10	Final	1,4-Dithiane	ATP HN-04	431 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	1114 mg/L
11	Final	Density at 25°C, g/mL	ASTM D 1217-86	1.0954
11	Final	Viscosity at 25°C, cSt	ASTM D 445-88	1.385
12	Offgases	1,2-Dichloroethane	ATP HN-07	6904 mg/L
12	Offgases	Trichloroethylene	ATP HN-07	10 mg/L
12	Offgases	Tetrachloroethylene	ATP HN-07	32 mg/L

NOTES:

[a] Sample times are after completion of HD addition.

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-3. HD/NaOH Subtest No. 2, Run No. 1 Analyses

Sample No. (nn of L-221-nn-HN-2925)	Sample Source[a]	Analysis	Method	Result[b]
01	15 minutes	HD concentration	ATP HN-01	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01	155%
03	30 minutes	HD concentration	ATP HN-01	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01	81%
05	45 minutes	HD concentration	ATP HN-01	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01	124%
07	60 minutes	HD concentration	ATP HN-01	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01	135%
10	Final	HD concentration	ATP HN-01	<0.1 mg/L
10	Final	TDG	ATP HN-05A	31570 mg/L
10	Final	1,4-Dithiane	ATP HN-04	724 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	1267 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0937 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	1.368 cSt
12	Offgases	1,2-Dichloroethane	ATP HN-07	3311 mg/L
12	Offgases	Trichloroethylene	ATP HN-07	48 mg/L
12	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-4. HD/NaOH Subtest No. 2, Run No. 2 Analyses

Sample No. (nn of L-222-nn-HN-2935)	Sample Source[a]	Analysis	Method	Result[b]
01	15 minutes	HD concentration	ATP HN-01	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01	171%
03	30 minutes	HD concentration	ATP HN-01	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01	81%
05	45 minutes	HD concentration	ATP HN-01	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01	108%
07	60 minutes	HD concentration	ATP HN-01	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01	84%
10	Final	HD concentration	ATP HN-01	<0.1 mg/L
10	Final	TDG	ATP HN-05A	30230 mg/L
10	Final	1,4-Dithiane	ATP HN-04	750 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	1317 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.1004 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	1.394 cSt
12	Offgases	1,2-Dichloroethane	ATP HN-07	4761 mg/L
12	Offgases	Trichloroethylene	ATP HN-07	46 mg/L
12	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-5. HD/NaOH Subtest No. 2, Run No. 3 Analyses

Sample No. (nn of L-223-nn-HN-0386)	Sample Source[a]	Analysis	Method	Result[b]
01	21 minutes	HD concentration	ATP HN-01	Note [c]
02	36 minutes	HD concentration	ATP HN-01	Note [c]
03	51 minutes	HD concentration	ATP HN-01	Note [c]
04	66 minutes	HD concentration	ATP HN-01	Note [c]
05	Final	HD concentration	ATP HN-01	<0.1 mg/L
05	Final	TDG	ATP HN-05A	8400 mg/L
05	Final[d]	1,4-dithiane	HN-04	2015 mg/L
05	Final[d]	1,4-oxathiane	HN-04	152 mg/L
06	Final	Density at 25°C	ASTM D 1217-86	1.0903 g/mL
06	Final	Viscosity at 25°C	ASTM D 445-88	1.219 cSt
07	Offgases	1,2-Dichloroethane	ATP HN-07	1990 mg/L
07	Offgases	Trichloroethylene	ATP HN-07	47 mg/L
07	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

[c] Samples were unavailable for analysis because they leaked from their containers and required a decontamination procedure.

[d] A white crystalline solid that condensed on the bottom of the condenser was collected as L-223-11-HW-0386 (1.0 g); analysis by GC/MS showed 335 mg of 1,4-dithiane and 7 mg of 1,4-oxathiane, with the remainder unknown.

Table C-6. HD/NaOH Subtest No. 2, Run No. 4 Analyses

Sample No. (nn of L-224-nn-HN-0406)	Sample Source[a]	Analysis	Method	Result[b]
01	19 minutes	HD concentration	ATP HN-01	1.99 mg/L
02	32 minutes	HD concentration	ATP HN-01	Note [c]
03	47 minutes	HD concentration	ATP HN-01	<0.1 mg/L
04	62 minutes	HD concentration	ATP HN-01	Note [c]
05	Final	HD concentration	ATP HN-01	<0.1 mg/L
05	Final	TDG	ATP HN-05A	5100 mg/L
05	Final	1,4-dithiane	HN-04	2114 mg/L
05	Final	1,4-oxathiane	HN-04	204 mg/L
06	Final	Density at 25°C	ASTM D 1217-86	1.1102 g/mL
06	Final	Viscosity at 25°C	ASTM D 445-88	1.280 cSt
07	Offgases	1.2-Dichloroethane	ATP HN-07	1076 mg/L
07	Offgases	Trichloroethylene	ATP HN-07	ND
07	Offgases	Tetrachloro-ethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

[c] Samples were unavailable for analysis because they leaked from their containers and required a decontamination procedure.

Table C-7. HD/NaOH Subtest No. 4, Run No. 1 Analyses

Sample No. (nn of L-242-nn-HN-3395)	Sample Source[a]	Analysis	Method	Result[b]
01	30 minutes	HD concentration	ATP HN-01	<0.1 mg/L
02	60 minutes	HD concentration	ATP HN-01	<0.1 mg/L
02	60 minutes	TDG	ATP HN-05A	34220 mg/L
04	Final	HD concentration	ATP HN-01	<0.1 mg/L
04	Final	TDG	ATP HN-05A	32720 mg/L
04	Final	1,4-Dithiane	ATP HN-04	66 mg/L
04	Final	1,4-Oxathiane	ATP HN-04	57 mg/L

NOTES:

[a] Sample times are after completion of HD addition

[b] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-8. HD/NaOH Subtest No. 4, Run No. 2 Analyses

Sample No. (nn of L-242-nn-HN-3415)[a]	Sample Source[b]	Analysis	Method	Result[c]
01	30 minutes	HD concentration[c]	ATP HN-01	<0.1 mg/L
02	60 minutes	HD concentration[c]	ATP HN-01	<0.1 mg/L
02	60 minutes	TDG	ATP HN-05A	35170 mg/L
04	Final	HD concentration[c]	ATP HN-01	<0.1 mg/L
04	Final	TDG	ATP HN-05A	33220 mg/L
04	Final	1,4-Dithiane	ATP HN-04	58 mg/L
04	Final	1,4-Oxathiane	ATP HN-02	39 mg/L

NOTES:

[a] The L-242 prefix was inadvertently was used instead of the L-243 prefix assigned by the test plan.

[b] Sample times are after completion of HD addition

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L.

Table C-9. HD/NaOH Subtest No. 4, Run No. 1 CHC Analyses

HD/NaOH subtest 4 run 1: CHC Analysis (See appendix D-10 for calculations)

Spiked HD Composition	Wt%	Grams Added	Portion	mL
HD	94.00	134.33	Reaction	778
1,2-dichloroethane	0.50	0.71	Offgas trap (60-min)	14.1
trichloroethylene	0.50	0.71	Samples removed	103
tetrachloroethylene	1.50	2.14	Condensate (top)	28
1,1,2,2-tetrachloroethane	1.00	1.43	Condensate (bot)	4
hexachloroethane	2.50	3.57	Hydrolysate, final	643
Total	100.00	142.90	Offgas trap (final)	13.9

Sample Number	Sample Source	Analysis	Method	Conc., mg/L	Total Produced, g	% of Added
	Samples after hydrolysis	Volatiles	Calculated from sample 2			
		1,2-dichloroethane		54	0.0056	0.8
		trichloroethylene		265	0.0273	3.8
		tetrachloroethylene		135	0.0139	0.6
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		330	0.0340	1.0
L-242-02-HN-3395	Hydrolysate before distn.	Volatiles	ATP E-02			
		1,2-dichloroethane		54	0.0365	5.1
		trichloroethylene		265	0.1789	25.0
		tetrachloroethylene		135	0.0911	4.3
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		330	0.2228	6.2
L-242-03-HN-3395	Offgas (60-minute)	Composition	ATP HN-07			
		1,2-dichloroethane		9952	0.1403	19.6
		trichloroethylene		12815	0.1807	25.3
		tetrachloroethylene		2679	0.0378	1.8
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-242-04-HN-3395	Hydrolysate, final	Volatiles	ATP E-02			
		1,2-dichloroethane		10	0.0064	0.9
		trichloroethylene		25	0.0161	2.2
		tetrachloroethylene		25	0.0161	0.7
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		3	0.0019	0.1
L-242-05-HN-3395	Condensate (Top)	Composition	ATP HN-09			
		1,2-dichloroethane		120	0.0034	0.5
		trichloroethylene		52	0.0015	0.2
		tetrachloroethylene		78	0.0022	0.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
	Condensate (Bottom)	Composition	ATP HN-09			
		1,2-dichloroethane		22771	0.0911	12.7
		trichloroethylene		92824	0.3713	52.0
		tetrachloroethylene		211401	0.8456	39.4
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		11718	0.0469	1.3
L-242-06-HN-3395	Offgas (final)	Composition	ATP HN-07			
		1,2-dichloroethane		13793	0.1917	26.8
		trichloroethylene		7518	0.1045	14.6
		tetrachloroethylene		4307	0.0599	2.8
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		35	0.0005	0.0
	CHC Balance Without Distillation					
		1,2-dichloroethane				25.5
		trichloroethylene				54.1
		tetrachloroethylene				6.7
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				7.2
	CHC Balance With Distillation					
		1,2-dichloroethane				61.4
		trichloroethylene				98.2
		tetrachloroethylene				45.5
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				2.3

Table C-10. HD/NaOH Subtest No. 4, Run No. 2 CHC Analyses

HD/NaOH subtest 4 run 2: CHC Analysis (See appendix D-10 for calculations)

Spiked HD Composition	Wt%	Grams Added	Portion	mL
HD	94.00	134.33	Reaction	778
1,2-dichloroethane	0.50	0.71	Offgas trap (60-min)	14.3
trichloroethylene	0.50	0.71	Samples removed	103
tetrachloroethylene	1.50	2.14	Condensate (top)	30
1,1,2,2-tetrachloroethane	1.00	1.43	Condensate (bot)	4
hexachloroethane	2.50	3.57	Hydrolysate, final	641
Total	100.00	142.90	Offgas trap (final)	14.2

Sample Number	Sample Source	Analysis	Method	Conc., mg/L	Total Produced, g	% of Added
	Samples after hydrolysis	Volatiles	Calculated from sample 2			
		1,2-dichloroethane		80	0.0082	1.2
		trichloroethylene		540	0.0556	7.8
		tetrachloroethylene		30	0.0031	0.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		30	0.0031	0.1
L-242-02-HN-3415	Hydrolysate before distn.	Volatiles	ATP E-02			
		1,2-dichloroethane		80	0.0540	7.6
		trichloroethylene		540	0.3645	51.0
		tetrachloroethylene		30	0.0203	0.9
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		30	0.0203	0.6
L-242-03-HN-3415	Offgas (60-minute)	Composition	ATP HN-07			
		1,2-dichloroethane		7487	0.1071	15.0
		trichloroethylene		10292	0.1472	20.6
		tetrachloroethylene		2147	0.0307	1.4
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-242-04-HN-3415	Hydrolysate, final	Volatiles	ATP E-02			
		1,2-dichloroethane		26	0.0167	2.3
		trichloroethylene		180	0.1154	16.1
		tetrachloroethylene		80	0.0513	2.4
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		6	0.0038	0.1
L-242-05-HN-3415	Condensate (Top)	Composition	ATP HN-09			
		1,2-dichloroethane		232	0.0070	1.0
		trichloroethylene		ND	0.0000	0.0
		tetrachloroethylene		203	0.0061	0.3
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
	Condensate (Bottom)	Composition	ATP HN-09			
		1,2-dichloroethane		21291	0.0852	11.9
		trichloroethylene		86091	0.3444	48.2
		tetrachloroethylene		209325	0.8373	39.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		9822	0.0393	1.1
L-242-06-HN-3415	Offgas (final)	Composition	ATP HN-07			
		1,2-dichloroethane		1989	0.0282	4.0
		trichloroethylene		5388	0.0765	10.7
		tetrachloroethylene		4701	0.0668	3.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
	CHC Balance Without Distillation					
		1,2-dichloroethane				23.7
		trichloroethylene				79.4
		tetrachloroethylene				2.5
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				0.7
	CHC Balance With Distillation					
		1,2-dichloroethane				35.3
		trichloroethylene				103.4
		tetrachloroethylene				46.4
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				1.3

Table C-11. HD/Water Subtest No. 1, Run No. 1 Analyses

Sample No. (nn of L-313-nn-HW-2645)[a]	Sample Source[b]	Analysis	Method	Result[d]
01	15 minutes	HD concentration	ATP HN-01[c]	0.28 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01[c]	19 %
03	30 minutes	HD concentration	ATP HN-01[c]	0.21 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01[c]	11%
05	45 minutes	HD concentration	ATP HN-01[c]	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01[c]	59%
07	60 minutes	HD concentration	ATP HN-01[c]	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01[c]	61%
10	Final	HD concentration	ATP HN-01[c]	<0.1 mg/L
10	Final	TDG	ATP HN-05A	35490 mg/L
10	Final	1,4-Dithiane	ATP HN-04	160 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	15 mg/L
07	60 minutes	Density at 25°C	ASTM D 1217-86	1.0466 g/mL
07	Final	Viscosity	ASTM D 445-88	1.161 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] The L-313 prefix was inadvertently used instead of the L-311 prefix assigned by the test plan.

[b] Sample times are after completion of HD addition.

[c] Battelle modification used hexane as extraction solvent in place of chloroform.

[d] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-12. HD/Water Subtest No. 1, Run No. 2 Analyses

Sample No. (nn of L-313-nn-HW-2695)[a]	Sample Source[b]	Analysis	Method	Result[d]
01	15 minutes	HD concentration	ATP HN-01[c]	0.25 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01[c]	84 %
03	30 minutes	HD concentration	ATP HN-01[c]	0.11 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01[c]	87%
05	45 minutes	HD concentration	ATP HN-01[c]	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01[c]	56%
07	60 minutes	HD concentration	ATP HN-01[c]	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01[c]	55%
10	Final	HD concentration	ATP HN-01[c]	<0.1 mg/L
10	Final	TDG	ATP HN-05A	31500 mg/L
10	Final	1,4-Dithiane	ATP HN-04	11 mg/L
10	Final	1,4-Oxathine	ATP HN-04	4 mg/L
10	Final	Density at 25°C	ASTM D 1217-86	1.0476 g/mL
10	Final	Viscosity at 25°C	ASTM D 445-88	1.142 cSt
11	Offgases	1,2-Dichloroethane	ATP HN-07	ND
11	Offgases	Trichloroethylene	ATP HN-07	ND
11	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] The L-313 prefix was inadvertently used instead of the L-312 prefix assigned by the test plan.

[b] Sample times are after completion of HD addition.

[c] Battelle modification used hexane as extraction solvent in place of chloroform.

[d] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-13. HD/Water Subtest No. 1, Run No. 3 Analyses

Sample No. (nn of L-313-nn-HW-2715)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	61 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	71%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	80%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	70%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	6500
10	Final	1,4-Dithiane	ATP HN-04	24 mg/L
10	Final	1,4-Oxathine	ATP HN-04	0.3 mg/L
10	Final	Density at 25°C	ASTM D 1217-86	0.9977 g/mL
10	Final	Viscosity at 25°C	ASTM D 445-88	0.926 cSt
11	Offgases	1,2-Dichloroethane	ATP HN-07	ND
11	Offgases	Trichloroethylene	ATP HN-07	ND
11	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-14. HD/Water Subtest No. 1, Run No. 4 Analyses

Sample No. (nn of L-313-nn-HW-2625)[a]	Sample Source[b]	Analysis	Method	Result[e]
01	15 minutes[c]	HD concentration	ATP HN-01[d]	<0.1 mg/L
03	30 minutes[c]	HD concentration	ATP HN-01[d]	<0.1 mg/L
05	45 minutes[c]	HD concentration	ATP HN-01[d]	<0.1 mg/L
06	60 minutesc	HD concentration	ATP HN-01[d]	<0.1 mg/L
07	Final	HD concentration	ATP HN-01[d]	<0.1 mg/L
07	Final	TDG	ATP HN-05A	7100
07	Final	1,4-Dithiane	ATP HN-04	33 mg/L
07	Final	1,4-Oxathiane	ATP HN-04	0.3 mg/L
07	Final	Density at 25°C	ASTM D 1217-86	0.9988 g/mL
07	Final	Viscosity at 25°C	ASTM D 445-88	0.941 cSt
08	Offgases	1,2-Dichloroethane	ATP HN-07	ND
08	Offgases	Trichloroethylene	ATP HN-07	ND
08	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] The L-313 prefix was inadvertently used instead of the L-314 prefix assigned by the test plan.

[b] Sample times are after completion of HD addition.

[c] HD spike recoveries were not ruin.

[d] Battelle modification used hexane as extraction solvent in place of chloroform.

[e] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L.

Table C-15. HD/Water Subtest No. 1 NMR Analyses

Run No.	HD Loading	Sampling Time	Sample No.	Mole Percent of Organic TDG	CHTG	H2TG	Q-OH	Acetone	Other
1	9.1	before NaOH	L-313-09-HW-2645	65.4	10.6	1.7		0.7	21.7
		after NaOH	L-313-11-HW-2645	76.9	2.8			0.2	20.1
2	8.7	before NaOH	L-313-09-HW-2695	77.3	9.0	1.4			12.4
		after NaOH	L-313-10-HW-2695	81.2	0.6			0.1	18.1
3	1.3	before NaOH	L-313-09-HW-2715	92.7	ND	ND	3.7	0.02	3.6
		after NaOH	L-313-10-HW-2715	92.9	ND	ND	3.3	0.2	3.6
4	1.4	before NaOH	L-313-06-HW-2625	75.1 92.8*	ND	ND	2.5 3.1*	19.1	3.3 4.1*
		after NaOH	L-313-07-HW-2625	72.4 92.8*	ND	ND	2.8 3.6*	22.0	2.8 3.6*

NOTES:
* Corrected by excluding acetone

Q-OH = $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$
CHTG = $HOCH_2CH_2SCH_2CH_2S^+(CH2CH2OH)_2$
H2TG = $(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$

Table C-16. HD/Water Subtest No. 2, Run No. 1 Analyses

Sample No. (nn of L-321-nn-HW-2905)	Sample Source(a)	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	0.25 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	46 %
03	30 minutes	HD concentration	ATP HN-01(b)	0.14 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	100%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	103%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	117%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	33530 mg/L
10	Final	1,4-Dithiane	ATP HN-04	311 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	19 mg/L
12	Final	Density at 25°C	ASTM D 1217-86	1.0487 g/mL
12	Final	Viscosity at 25°C	ASTM D 445-88	1.053 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	616 mg/L
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-17. HD/Water Subtest No. 2, Run No. 2 Analyses

Sample No. (nn of L-322-nn-HW-2915)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	0.28 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	171%
03	30 minutes	HD concentration	ATP HN-01(b)	0.20 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	102%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	113%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	91%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	37510 mg/L
10	Final	1,4-Dithiane	ATP HN-04	219 mg/L
10	Final	1,4-Oxathine	ATP HN-04	14 mg/L
12	Final	Density at 25°C	ASTM D 1217-86	1.0496 g/mL
12	Final	Viscosity at 25°C	ASTM D 445-88	1.128 cSt
11	Offgases	1,2-Dichloroethane	ATP HN-07	1085
11	Offgases	Trichloroethylene	ATP HN-07	ND
11	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-18. HD/Water Subtest No. 2, Run No. 3 Analyses

Sample No. (nn of L-323-nn-HW-0306)	Sample Source[a]	Analysis	Method	Result[c]
01	16 minutes	HD concentration	ATP HN-01[b]	0.37 mg/L
01	16 minutes	HD recovery	ATP HN-01[b]	79 percent
01	16 minutes	TDG	ATP HN-05A	10500 mg/L
02	31 minutes	HD concentration	ATP HN-01[b]	0.13 mg/L
02	31 minutes	HD recovery	ATP HN-01[b]	99 percent
02	31 minutes	TDG	ATP HN-05A	10888 mg/L
03	47 minutes	HD concentration	ATP HN-01[b]	<0.1 mg/L
03	47 minutes	HD recovery	ATP HN-01[b]	51 percent
03	47 minutes	TDG	ATP HN-05A	11000 mg/L
04	61 minutes	HD concentration	ATP HN-01[b]	<0.1 mg/L
04	61 minutes	HD recovery	ATP HN-01[b]	41 percent
04	61 minutes	TDG	ATP HN-05A	19200 mg/L
07	Final	HD concentration	ATP HN-01[b]	<0.1 mg/L
07	Final	TDG	ATP HN-05A	8300 mg/L
07	Final	1,4-dithiane	HN-04	353 mg/L
07	Final	1,4-oxathiane	HN-04	24 mg/L
08	Final	Density at 25°C	ASTM D 1217-86	1.0296 g/mL
08	Final	Viscosity at 25°C	ASTM D 445-88	1.023 cSt
09	Offgases	1,2-Dichloroethane	ATP HN-07	37 mg/L
09	Offgases	Trichloroethylene	ATP HN-07	ND
09	Offgases	Tetrachloro-ethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-19. HD/Water Subtest No. 2, Run No. 4 Analyses

Sample No. (nn of L-324-nn-HW-0326)	Sample Source[a]	Analysis	Method	Result[c]
01	16 minutes	HD concentration	ATP HN-01[b]	0.68 mg/L
01	16 minutes	HD recovery	ATP HN-01[b]	32 percent
01	16 minutes	TDG	ATP HN-05A	7000 mg/L
02	30 minutes	HD concentration	ATP HN-01[b]	0.50 mg/L
02	30 minutes	HD recovery	ATP HN-01[b]	59 percent
02	30 minutes	TDG	ATP HN-05A	6700 mg/L
03	45 minutes	HD concentration	ATP HN-01[b]	0.22 mg/L
03	45 minutes	HD recovery	ATP HN-01[b]	168 percent
03	45 minutes	TDG	ATP HN-05A	7200 mg/L
04	63 minutes	HD concentration	ATP HN-01[b]	0.14 mg/L
04	63 minutes	HD recovery	ATP HN-01[b]	82 percent
04	63 minutes	TDG	ATP HN-05A	6500 mg/L
07	Final	HD concentration	ATP HN-01[b]	<0.1 mg/L
07	Final	TDG	ATP HN-05A	5900 mg/L
07	Final	1,4-dithiane	HN-04	676 mg/L
07	Final	1,4-oxathiane	HN-04	20 mg/L
08	Final	Density at 25°C	ASTM D 1217-86	1.0498 g/mL
08	Final	Viscosity at 25°C	ASTM D 445-88	1.004 cSt
09	Offgases	1,2-Dichloroethane	ATP HN-07	63 mg/L
09	Offgases	Trichloroethylene	ATP HN-07	ND
09	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-20. HD/Water Subtest No. 2 NMR Analyses

Run No.	HD Loading	Sampling Time	Sample No.	Mole Percent of Organic and (Percent of HD That Went To)					
				TDG	CHTG	H2TG	Q-OH	Methanol	Other
1	8.6	before NaOH	L-321-09-HW-2905	80.9 (70.1)	9.5 (16.4)	1.6 (4.1)			8.1 (9.4)
		after NaOH	L-321-11-HW-2905	79.3 (72.0)	2.5 (4.5)	0.7 (1.9)			17.5 (21.6)
2	8.6	before NaOH	L-322-09-HW-2915	79.0 (67.1)	10.4 (17.6)	1.2 (3.2)			9.4 (12.2)
		after NaOH	L-322-11-HW-2915[a]	51.4 (77.0)	1.0 (4.0)			39.8	7.9 (19.0)
3	8.6	before NaOH	L-323-05-HW-0306		ND	ND			
		after NaOH	L-323-06-HW-0306		3.0	ND			
4	8.6	before NaOH	L-324-05-HW-0326		2.6	ND			
		after NaOH	L-324-06-HW-0326		2.3	ND			

NOTE:

[a] 1H and ^{13}C NMR

CHTG = $HOCH_2CH_2SCH_2CH_2S^+(CH2CH2OH)_2$
ND = not detected; limit of detection 0.5 mole percent
H2TG = $(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$
Q-OH = $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$

Table C-21. HD/Water Subtest No. 3, Run No. 1 Analyses

Sample No. (nn of L-331-nn-HW-2765)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	86 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	84%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	77%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	65%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	34250 mg/L
10	Final	1,4-Dithiane	ATP HN-04	253 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	800 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0444 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	1.080 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloro-ethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-22. HD/Water Subtest No. 3, Run No. 2 Analyses

Sample No. (nn of L-332-nn-HW-2775)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	65 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	69%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	61%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	59%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	35990 mg/L
10	Final	1,4-Dithiane	ATP HN-04	292 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	8889 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0422 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	1.049 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-23. HD/Water Subtest No. 3, Run No. 3 Analyses

Sample No. (nn of L-333-nn-HW-2785)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	85 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	85%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	90%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	79%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	5900
10	Final	1,4-Dithiane	ATP HN-04	39 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	37 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	0.9988 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	0.920 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloro-ethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-24. HD/Water Subtest No. 3, Run No. 4a Analyses

Sample No. (nn of L-334-nn-HW-2835)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	97 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	88%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	91%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	90%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	6600
10	Final	1,4-Dithiane	ATP HN-04	25 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	30 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0001 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	0.916 cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-25. HD/Water Subtest No. 3, Run No. 4b Analyses

Sample No. (nn of L-334-nn-HW-0046)	Sample Source[a]	Analysis	Method	Result[c]
01	15 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
02	15 minutes, spiked with HD	HD recovery	ATP HN-01(b)	70 %
03	30 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
04	30 minutes spiked with HD	HD recovery	ATP HN-01(b)	114%
05	45 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
06	45 minutes spiked with HD	HD recovery	ATP HN-01(b)	127%
07	60 minutes	HD concentration	ATP HN-01(b)	<0.1 mg/L
08	60 minutes, spiked with HD	HD recovery	ATP HN-01(b)	118%
10	Final	HD concentration	ATP HN-01(b)	<0.1 mg/L
10	Final	TDG	ATP HN-05A	5900
10	Final	1,4-Dithiane	ATP HN-04	34 mg/L
10	Final	1,4-Oxathiane	ATP HN-04	7 mg/L
11	Final	Density at 25°C	ASTM D 1217-86	1.0055 g/mL
11	Final	Viscosity at 25°C	ASTM D 445-88	0.922cSt
13	Offgases	1,2-Dichloroethane	ATP HN-07	ND
13	Offgases	Trichloroethylene	ATP HN-07	ND
13	Offgases	Tetrachloroethylene	ATP HN-07	ND

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-26. HD/Water Subtest No. 3 NMR Analyses

Run No.	HD Loading	Sampling Time	Sample No.	Mole Percent of Organic and (Percent of HD That Went To)					
				TDG	CHTG	H2TG	Q-OH	Unsat Cpds.	Other
1	8.5	END	L-331-09-HW-2765		ND	ND			
			Same by ^{13}C	(59)	ND	ND		(5)	(36)
2	8.8	END	L-332-09-HW-2775	(58)	ND	ND		(5)	(37)
			Same by ^{13}C	(49)	ND	ND		(5)	(46)
3	1.3	END	L-333-09-HW-2785	(78)	ND	ND		(2)	(20)
			Same by ^{13}C	(74)	ND	ND		(2)	(24)
4a	1.3	END	L-334-09-HW-2835	(79.7)	ND	ND			(20.3)
			Same by ^{13}C	(79.4)	ND	ND			(20.6)
4b	1.3	END	L-334-09-HW-0046	79.8 (78.7)	0.3 (0.7)				19.8 (20.7)

NOTES:
CHTG = $HOCH_2CH_2SCH_2CH_2S^+(CH2CH2OH)_2$
H2TG = $(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$
Q-OH = $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$

Table C-27. HD/Water Subtest No. 5, Run No. 1a Analyses

Sample No. (nn of L-352-nn-HW-3175)	Sample Source[a]	Analysis	Method	Result[c]
01	30-minute	HD	ATP HN-01[b]	0.22
02	60-minute	HD	ATP HN-01[b]	0.11
02	60-minute	TDG	ATP HN-05A	39440
03	After pH adjustment	HD	ATP HN-01[b]	<0.1 mg/L
03	After pH adjustment	TDG	ATP HN-05A	41510
03	After pH adjustment	Other organosulfur	BAT-02	TBD
05	Final reactor contents	HD	ATP HN-01[b]	<0.1 mg/L
05	Final reactor contents	TDG	ATP HN-05A	41780
05	Final reactor contents	1,4-Dithiane	ATP HN-04	6.3 mg/L
05	Final reactor contents	1,4-Oxathine	ATP HN-04	2.3 mg/L

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-28. HD/Water Subtest No. 5, Run No. 1a CHC Analyses

HD/Water subtest 5 Run 1a: CHC Analysis (See appendix D-10 for calculations)

Spiked HD Composition	Wt%	Grams Added
HD	94.00	61.76
1,2-dichloroethane	0.50	0.33
trichloroethylene	0.50	0.33
tetrachloroethylene	1.50	0.99
1,1,2,2-tetrachloroethane	1.00	0.66
hexachloroethane	2.50	1.64
Total	100.00	65.70

Portion	Weight, g
Reaction	764.0
Samples after hydr.	102.7
Hydrolysate, initial	661.3
pH adjustment soln.	66.0
Hydrolysate, pH adj.	727.3
Samples after pH	54.2
Offgas trap (60-min)	11.2
Condensate	35.2
Hydrolysate, final	637.9
Offgas trap (final)	11.2

Sample Number	Sample Source	Analysis	Method	Conc., mg/L	Total Produced, g	% of Added
	Samples after hydrolysis	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		139	0.0142	4.3
		trichloroethylene		308	0.0316	9.6
		tetrachloroethylene		15	0.0016	0.2
		1,1,2,2-tetrachloroethane		0	0.0000	0.0
		hexachloroethane		2282	0.2344	14.3
L-352-03-HW-3175	Hydrolysate, pH adjusted	Volatiles	ATP E-02			
		1,2-dichloroethane		126	0.0916	27.9
		trichloroethylene		280	0.2036	62.0
		tetrachloroethylene		14	0.0102	1.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		2075	1.5091	91.9
L-352-04-HW-3175	Offgas (60-minute)	Composition	ATP HN-07			
		1,2-dichloroethane		7808	0.1107	33.7
		trichloroethylene		14	0.0002	0.1
		tetrachloroethylene		118	0.0017	0.2
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
	Samples after pH adj.	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		126	0.0068	2.1
		trichloroethylene		280	0.0152	4.6
		tetrachloroethylene		14	0.0008	0.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		2075	0.1125	6.8
L-352-05-HW-3175	Hydrolysate, final	Volatiles	ATP E-02			
		1,2-dichloroethane		10	0.0064	1.9
		trichloroethylene		10	0.0064	1.9
		tetrachloroethylene		2	0.0013	0.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		4	0.0026	0.2
L-352-06-HW-3175	Condensate	Composition	ATP HN-09			
		1,2-dichloroethane		673	0.0237	7.2
		trichloroethylene		56	0.0020	0.6
		tetrachloroethylene		96	0.0034	0.3
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-352-07-HW-3175	Offgas (final)	Composition	ATP HN-07			
		1,2-dichloroethane		4896	0.0694	21.1
		trichloroethylene		3159	0.0448	13.6
		tetrachloroethylene		1191	0.0169	1.7
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		11	0.0002	0.0
	CHC Balance Without Distillation					
		1,2-dichloroethane				65.9
		trichloroethylene				71.7
		tetrachloroethylene				1.4
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				106.2
	CHC Balance With Distillation					
		1,2-dichloroethane				70.4
		trichloroethylene				30.5
		tetrachloroethylene				2.6
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				21.3

Table C-29. HD/Water SubtestNo. 5, No. Run No. 1b Analyses

Sample No. (nn of L-352-nn-HW-3325)	Sample Source[a]	Analysis	Method	Result[c]
01	30-minute	HD	ATP HN-01[b]	<0.1 mg/L
02	60-minute	HD	ATP HN-01[b]	<0.1 mg/L
02	60-minute	TDG	ATP HN-05A	36920
03	After pH adjustment	HD	ATP HN-01[b]	<0.1 mg/L
03	After pH adjustment	TDG	ATP HN-05A	38190
05	Final reactor contents	HD	ATP HN-01[b]	<0.1 mg/L
05	Final reactor contents	TDG	ATP HN-05A	40900
05	Final reactor contents	1,4-Dithiane	ATP HN-04	7.6 mg/L
05	Final reactorcontents	1,4-Oxathiane	ATP HN-04	3.0 mg/L

NOTES:

[a] Sample times are after completion of HD addition.

[b] Battelle modification used hexane as extraction solvent in place of chloroform.

[c] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-30. HD/Water Subtest No. 5, Run No. 1b CHC Analyses

HD/Water subtest 5 Run 1b: CHC Analysis (See appendix D-10 for calculations)

Spiked HD Composition	Wt%	Grams Added
HD	94.00	61.76
1,2-dichloroethane	0.50	0.33
trichloroethylene	0.50	0.33
tetrachloroethylene	1.50	0.99
1,1,2,2-tetrachloroethane	1.00	0.66
hexachloroethane	2.50	1.64
Total	100.00	65.70

Portion	Weight, g
Reaction	764.0
Samples after hydr.	104.6
Hydrolysate, initial	659.4
pH adjustment soln.	66.0
Hydrolysate, pH adj.	725.4
Samples after pH	57.3
Offgas trap (60-min)	11.0
Condensate	33.9
Hydrolysate, final	634.2
Offgas trap (final)	11.0

Sample Number	Sample Source	Analysis	Method	Conc., mg/L	Total Produced, g	% of Added
	Samples after hydrolysis	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		32	0.0033	1.0
		trichloroethylene		33	0.0035	1.1
		tetrachloroethylene		0	0.0000	0.0
		1,1,2,2-tetrachloroethane		0	0.0000	0.0
		hexachloroethane		0	0.0000	0.0
L-352-03-HW-3175	Hydrolysate, pH adjusted	Volatiles	ATP E-02			
		1,2-dichloroethane		29	0.0210	6.4
		trichloroethylene		30	0.0218	6.6
		tetrachloroethylene		0.2	0.0001	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-352-04-HW-3175	Offgas (60-minute)	Composition	ATP HN-07			
		1,2-dichloroethane		11748	0.1636	49.8
		trichloroethylene		43	0.0006	0.2
		tetrachloroethylene		791	0.0110	1.1
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		18	0.0003	0.0
	Samples after pH adj.	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		29	0.0017	0.5
		trichloroethylene		30	0.0017	0.5
		tetrachloroethylene		0.2	0.0000	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-352-05-HW-3175	Hydrolysate, final	Volatiles	ATP E-02			
		1,2-dichloroethane		3	0.0019	0.6
		trichloroethylene		30	0.0190	5.8
		tetrachloroethylene		ND	0.0000	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		2	0.0013	0.1
L-352-06-HW-3175	Condensate	Composition	ATP HN-09			
		1,2-dichloroethane		137	0.0046	1.4
		trichloroethylene		ND	0.0000	0.0
		tetrachloroethylene		ND	0.0000	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-352-07-HW-3175	Offgas (final)	Composition	ATP HN-07			
		1,2-dichloroethane		354	0.0049	1.5
		trichloroethylene		897	0.0125	3.8
		tetrachloroethylene		273	0.0038	0.4
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		27	0.0004	0.0
	CHC Balance Without Distillation					
		1,2-dichloroethane				57.2
		trichloroethylene				7.9
		tetrachloroethylene				1.1
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				0.0
	CHC Balance With Distillation					
		1,2-dichloroethane				54.8
		trichloroethylene				11.4
		tetrachloroethylene				1.5
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				0.1

Table C-31. HD/Water Subtest No. 5, Run No. 2 Analyses

Sample No. (nn of L-352-nn-HW-3345[a]	Sample Source[b]	Analysis	Method	Result[d]
01	30-minute	HD	ATP HN-01[c]	0.16 mg/L
02	60-minute	HD	ATP HN-01[c]	<0.1 mg/L
02	60-minute	TDG	ATP HN-05A	37180
03	After pH adjustment	HD	ATP HN-01[c]	<0.1 mg/L
03	After pH adjustment	TDG	ATP HN-05A	31600
05	Final reactor contents	HD	ATP HN-01[c]	<0.1 mg/L
05	Final reactor contents	TDG	ATP HN-05A	26400
05	Final reactor contents	1,4-Dithiane	ATP HN-04	6.9 mg/L
05	Final reactor contents	1,4-Oxathine	ATP HN-04	3.5 mg/L

NOTES:

[a] The L-352 prefix was inadvertently used instead of the L-353 prefix assigned by the test plan.

[b] Sample times are after completion of HD addition.

[c] Battelle modification used hexane as extraction solvent in place of chloroform.

[d] HD analyses of the hydrolysate are reported down to a level of 0.1 mg/L (0.1 ppm); lower values and non-detectable results are reported as <0.1 mg/L. Detection limit for offgas components is 10 mg/L in methanol of trap.

Table C-32. HD/Water Subtest No. 5, Run No. 2 CHC Analyses

HD/Water subtest 5 Run 2: CHC Analysis (See appendix D-10 for calculations)

Spiked HD Composition	**Wt%**	**Grams Added**
HD	94.00	61.76
1,2-dichloroethane	0.50	0.33
trichloroethylene	0.50	0.33
tetrachloroethylene	1.50	0.99
1,1,2,2-tetrachloroethane	1.00	0.66
hexachloroethane	2.50	1.64
Total	100.00	65.70

Portion	**Weight, g**
Reaction	764.2
Samples after hydr.	103.5
Hydrolysate, initial	660.7
pH adjustment soln.	66.0
Hydrolysate, pH adj.	726.7
Samples after pH	57.0
Offgas trap (60-min)	11.5
Condensate	30.8
Hydrolysate, final	638.9
Offgas trap (final)	11.2

Sample Number	**Sample Source**	**Analysis**	**Method**	**Conc., mg/L**	**Total Produced, g**	**% of Added**
	Samples after hydrolysis	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		221	0.0229	7.0
		trichloroethylene		180	0.0187	5.7
		tetrachloroethylene		183	0.0189	1.9
		1,1,2,2-tetrachloroethane		0	0.0000	0.0
		hexachloroethane		3	0.0003	0.0
L-352-03-HW-3175	Hydrolysate, pH adjusted	Volatiles	ATP E-02			
		1,2-dichloroethane		201	0.1461	44.5
		trichloroethylene		164	0.1192	36.3
		tetrachloroethylene		166	0.1206	12.2
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		3	0.0022	0.1
L-352-04-HW-3175	Offgas (60-minute)	Composition	ATP HN-07			
		1,2-dichloroethane		1723	0.0251	7.6
		trichloroethylene		ND	0.0000	0.0
		tetrachloroethylene		ND	0.0000	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
	Samples after pH adj.	Volatiles	Calculated from sample 3			
		1,2-dichloroethane		201	0.0115	3.5
		trichloroethylene		164	0.0093	2.8
		tetrachloroethylene		166	0.0095	1.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		3	0.0002	0.0
L-352-05-HW-3175	Hydrolysate, final	Volatiles	ATP E-02			
		1,2-dichloroethane		28	0.0179	5.4
		trichloroethylene		20	0.0128	3.9
		tetrachloroethylene		9	0.0058	0.6
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		3	0.0019	0.1
L-352-06-HW-3175	Condensate	Composition	ATP HN-09			
		1,2-dichloroethane		520	0.0160	4.9
		trichloroethylene		ND	0.0000	0.0
		tetrachloroethylene		ND	0.0000	0.0
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		ND	0.0000	0.0
L-352-07-HW-3175	Offgas (final)	Composition	ATP HN-07			
		1,2-dichloroethane		13793	0.1955	59.5
		trichloroethylene		7518	0.1066	32.4
		tetrachloroethylene		4307	0.0611	6.2
		1,1,2,2-tetrachloroethane		ND	0.0000	0.0
		hexachloroethane		35	0.0005	0.0
	CHC Balance Without Distillation					
		1,2-dichloroethane				59.1
		trichloroethylene				42.0
		tetrachloroethylene				14.2
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				0.2
	CHC Balance With Distillation					
		1,2-dichloroethane				87.9
		trichloroethylene				44.9
		tetrachloroethylene				9.7
		1,1,2,2-tetrachloroethane				0.0
		hexachloroethane				0.2

Spiked HD Composition	Wt%	Analysis correction	Grams added
HD	94.00	93.74	61.59
1,2-dichloroethane	0.50	0.76	0.50
trichloroethylene	0.50	0.50	0.33
tetrachloroethylene	1.50	1.50	0.99
1,1,2,2-tetrachloroethane	1.00	1.00	0.66
hexachloroethane	2.50	2.50	1.64
Total	100.00	100.00	65.70

Table C-33. HD/Water Subtest No. 5 NMR Analyses

Run No.	HD Load	Sampling Time	Sample No.	Mole Percent of Organic and (Percent of HD That Went To) TDG	CHTG	H2TG	Q-OH	Methanol	Other
1a	8.6	before NaOH	L-352-02-HW-3175	75.7 (68.2)	11.8 (21.3)	1.8 (5.0)		5.9	4.8 (5.5)
		after NaOH	L-352-03-HW-3175	67.2 (68.4)				4.5	28.3 (31.6)
		after distn.	L-352-10-HW-3175	76.0 (74.9)				1.5	22.5 (25.1)
1b	8.6	before NaOH	L-352-02C-HW-3325	77.6 (72.4)	8.1 (15.0)	1.1 (3.0)			13.2 (9.6)
		after NaOH	L-352-03C-HW-3325	81.3 (82.4)					18.7 (17.6)
		after distn.	L-352-05B-HW-3325	69.6 (72.1)					30.4 (27.9)
2	8.6	before NaOH	L-352-02C-HW-3345	76.6 (71.5)	8.0 (15.0)	1.6 (4.4)			13.8 (9.2)
		after NaOH	L-352-03C-HW-3345	72.1 (75.1)					27.9 (24.9)
		after distn.	L-352-05B-HW-3345	70.8 (71.7)					29.2 (28.3)

NOTES:
CHTG = $HOCH_2CH_2SCH_2CH_2S^+(CH2CH2OH)_2$
H2TG = $HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$
Q-OH = $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$

Table C-34. Analytical Methods

Sample Source	Analysis	Method	Reference
HD/NaOH hydrolysate	HD concentration	ATP HN-01	Reference 7
HD/NaOH hydrolysate, spiked with HD	HD recovery	ATP HN-01	Appendix D-2
HD/water hydrolysate	HD concentration	ATP HN-01 with hexane extraction	Appendix D-1
HD/water hydrolysate, spiked with HD	HD recovery	ATP HN-01 with hexane extraction	Appendixes D-1 and D-3
Hydrolysate	TDG	ATP HN-05A, BAT-01	Reference 7
Hydrolysate	Organosulfur compounds	ATP HN-04	Reference 7
HD/water hydrolysate	Sulfonium ion	ERDEC NMR method	Reference 12
Hydrolysate	Density at 77°F (25°C) g/mL	ASTM D 1217-86	Reference 7
Hydrolysate	Viscosity at 77°F (25°C) (cSt)	ASTM D 445-88	Reference 7
Offgas trap	CHC composition	ATP HN-07	Reference 7
Distillate from hydrolysate	CHC composition	ATP HN-09	Reference 7
Hydrolysate	CHC composition	ATP E-02	Reference 7
HD spiked with CHCs	HD assay	ATP A-01	Reference 7
HD heel hydrolysate	Elemental analysis	ATP A-02	Reference 7

NOTES:
ASTM = American Society for Testing and Materials
CHC = chlorinated hydrocarbon
NMR = Nuclear Magnetic Resonance
TDG = Thiodiglycol
cSt = centistokes
g/mL = grams per milliliter

APPENDIX D
PROCEDURES AND CALCULATIONS

APPENDIX D
PROCEDURES AND CALCULATIONS

D-1 Battelle adaption of ATP Method HN-01 to analyze HD in HD/water hydrolysate by GC/MSD.

D-2 Test Change to evaluate solvent extraction efficiency in HD/NaOH subtests.

D-3 Test Change to evaluate solvent extraction efficiency in HD/water subtests.

D-4 HD Ton Container Survey - Summary of Impurity Weight Percents, Heel Levels and Viscosities.

D-5 Preliminary Report on The Composition of The TC HD Heels, L.L. Szafraniec, et. al., 19 March 1996.

D-6 TDG Calculations from Analyses by GC/MS (ATP method HN-05A).

D-7 Test change to hydrolyze HD heel in HD/NaOH subtest no. 2.

D-8 Test change to hydrolyze HD heel in HD/water subtest no. 2.

D-9 Analysis of HD spiked with CHCs.

D-10 Formulas for calculating CHC concentrations in hydrolysis products.

D-11 Y-C. Yang in ERDEC Alt Tech Highlights, 20-23 March 1995.

D-12 Heel Hydrolysate Analyses by ICP

D-13 Test change to add two new subtests using HD spiked with chlorinated hydrocarbons.

D-1 Battelle adaption of ATP Method HN-01 to analyze HD in HD/water hydrolysate by GC/MSD.

- ## Appendix To Low-Level HD in Mustard Agent/Sodium Hydroxide Neutralization Product (ATP Method HN-01)

The following deviations are used to adapt ATP Method HN-01 for the analysis of low level HD in mustard agent/water neutralization product by GC/MSD:

Section 3.1.5 Test Procedure For Sample Extraction.

a. Sample Extraction Procedure.

(2) 25 mL of neutralization product extracted.

1.0 (+/- 0.1) g of NaCl is dissolved into the HD/water neutralization product.

(3) pH adjustment of the HD/water neutralization product will be accomplished with 2N NaOH.

(4) The HD/water neutralization product is extracted with one 2 mL aliquot of Hexane (C_6H_{14}).

(5) Not applicable.

b. Calibration Standard Preparation.

(2) Secondary dilution standards are prepared in Hexane (C_6H_{14}).

d. GC/MSD Analysis.

Injection volume: 1.0 µL.

f. Calibration of the GC/MSD.

(1) 1.0 µL injections.

g. 1.0 µL injection

h Quantitation.

$$\text{concentration in } \mu g/mL = \frac{\text{concentration from the calibration curve} \times 2}{25 \text{ mL}}$$

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MEMORANDUM FOR: DISTRIBUTION

FROM: Dr. William G. Kavanagh, SAIC wgk

DATE: 4 September 1996

SUBJECT: HD-Water Agent Destruction Efficiency Summary (BK-96-932)

The attached HD-Water Agent Destruction Efficiency Summary (4 September 1996) was prepared at the request of PMAT&A to clarify agent destruction efficiency data for the HD-Water neutralization process at 3.8 weight percent HD loading. The summary has been reviewed by PMAT&A, ERDEC and SAIC personnel and by participating subcontract scientists. Consensus on the content has been achieved among these reviewers. The document is provided for your information as an aide to understanding the conclusion that HD-Water neutralization at 3.8 percent HD loading reliably destroys HD to greater than 99.9999 percent agent destruction efficiency.

cf: DO 170 File

HD - Water Agent Destruction Efficiency Summary (4 September 1996)

1. OBJECTIVE: The objective of this paper is to confirm the achievement of an agent destruction efficiency (ADE) of > 99.9999 for 2 L through 114 L scale design case tests for HD-Water Neutralization.

2. HD-Water NEUTRALIZATION: HD-Water Neutralization design case specifies the addition of HD (3.8 weight percent) to water at 90 °C followed by pH adjustment with sodium hydroxide prior to cooling. Adjusted for agent purity, the ADE objective is an HD concentration of less than 35 ~~m~~μg/L or 35 parts per billion (ppb).

3. HD-Water NEUTRALIZATION PRODUCT: In all design case tests, HD was non detect at the method detection limit or target reporting level. Any ADE calculations based on these results must be flagged as "greater than" (>). In other words the calculated value is a worst case estimate of the ADE.

4. ANALYTICAL METHODS:
   a. Target Reporting Levels (TRL): Target reporting levels are the levels used in the class II precision and accuracy studies. These levels have been shown to produce reliable positive results and no false negative results. These levels are method and matrix specific.
   b. Method Detection Limits (MDL) are estimated or calculated limits below which the agent can not be detected using the applied method which includes an extraction solvent, the matrix under evaluation, gas chromatographic conditions including the column, and the specific detector.
   c. Detectors: The detectors used for HD are the flame photometric detector (FPD) in sulfur mode or the mass selective detector (MSD) in selective ion monitoring (SIM) mode.
   d. Solvents: Solvents used were chloroform or hexane.
   e. Methods (Reference 1):
      i. HNO1: Chloroform + GC - MSD(SIM); TRL = 50 ppb
      ii. HNO2: Hexane + GC - FPD(S); TRL = 10 ppb

   Discussion: In the course of the early HD-Water Mettler (2L) tests, the FPD was found to give spurious results for the middle reaction course samples. The presence of interfering sulfonium ions or phase separations were considered as possible causes. Analysts switched to the mass selective detector for the greater specificity needed. Analytical data using the MSD on hexane extracts of the HD-Water matrix are summarized in table 1. Analytical data using the MSD on chloroform extracts of the HD-Water matrix is expected this week.

   When the decision to switch to the MSD was made the potential loss in sensitivity or a higher target reporting level of 50 ppb was not a problem, because the HD loading for HD water at that time was 8.6 weight percent with and ADE six-nines objective concentration of about 80 ppb. When the design case loading was dropped to 3.8 weight percent HD, the ADE six-nines calculation could not be made without a new class II P&A study or presentation of MDL data (enclosure 1) that confirms analytical sensitivity at < 35 ppb.

5. METTLER AND CHAMBER TESTING RESULTS (Table 1):

a. Two Liter Mettler ADE Results:
The Analytical Chemistry Team (ACT) performed most of the analyses on the 2 L Mettler design case testing of the HD-Water matrix. The ACT provided MDL data on their HN02 based method which uses hexane extraction (performed in Bldg 3510) followed by GC-MSD(SIM) in bldg E3300.

The Battelle laboratory assisted with some 2 L Mettler testing (tests 17 and 18). They used a 0.1 mg/mL standard in hexane as their low standard in their HN02 based method which uses hexane extraction (performed in Bldg 3510) followed by GC-MSD(SIM) in bldg E3510. This equates to an instrument detection limit (IDL) of 8 ppb in the hydrolysate. Matrix recovery data is necessary to calculate a method detection limit, but typical recoveries of greater than 75 percent would support an MDL/TRL of < 35 ppb. Estimation of the method detection limit is discussed further in inclosure 1.

b. Twelve Liter Mettler ADE Results:
The Analytical Chemistry Team (ACT) performed most of the analyses on the 12 L Mettler design case testing (tests 9 through 13) of the HD-Water matrix. The ACT provided MDL data on their HN02 based method which uses hexane extraction (performed in Bldg 3510) followed by GC-MSD(SIM) in bldg E3300.

The Battelle laboratory assisted with some 12 L Mettler design case testing (tests 15 through 17). As above, they used a 0.1 mg/mL standard in hexane as their low standard in their HN02 based method which uses hexane extraction (performed in Bldg 3510) followed by GC-MSD(SIM) in bldg E3510.

c. One Hundred Fourteen Liter Chamber ADE Results
The MDL for the method modification using $CHCl_3$ extraction (per HN01) of the HD-Water matrix was initiated on 26 August 1996. That data will be available this week.

d. Forty Gallon Reactor Results
The ACT used their 50:1 off post shipping method for low level HD in the forty gallon reactor test series. The MDLs for the forty gallon reactor results were based on 100 percent recovery of the low standard that ACT ran with each batch of samples.

HD - Water Agent Destruction Efficiency Summary (4 September 1996)

6. DISCUSSION: An HD ADE greater than six nines was repeatedly achieved in 2 and 12 liter Mettler tests and in chamber 114 liter tests. This success was achieved at HD loadings from one to nine weight percent loads. When the design case HD loading was lowered to 3.8 weight percent, some of the analytical reporting limits did not support calculations of ADE's > 99.9999 for 3.8 weight percent loadings. Two 2L Mettler 3 weight percent loads had ADE's > 99.9999. Eight 12 L Mettler loads at 3.8 weight percent achieved ADE's > 99.9999. Three 114 L chamber runs achieved and ADEs of > 99.999. Determination of the MDL for the analytical method used in the chamber laboratory is expected to allow calculation of the an ADE greater than the current five nines at the chamber level. Evaluation of HD recovery data in hexane extractions of the HD-Water matrix confirms that all 3.8 weight percent design case tests in the 12 L Mettler reactor achieved an ADE > 99.9999.

7. REFERENCE:
   1. US Army PMCD, HD Onsite Sample Analysis Test Plan, 1 March 1996, pp. 3-1 to 3-32.

Table 1.

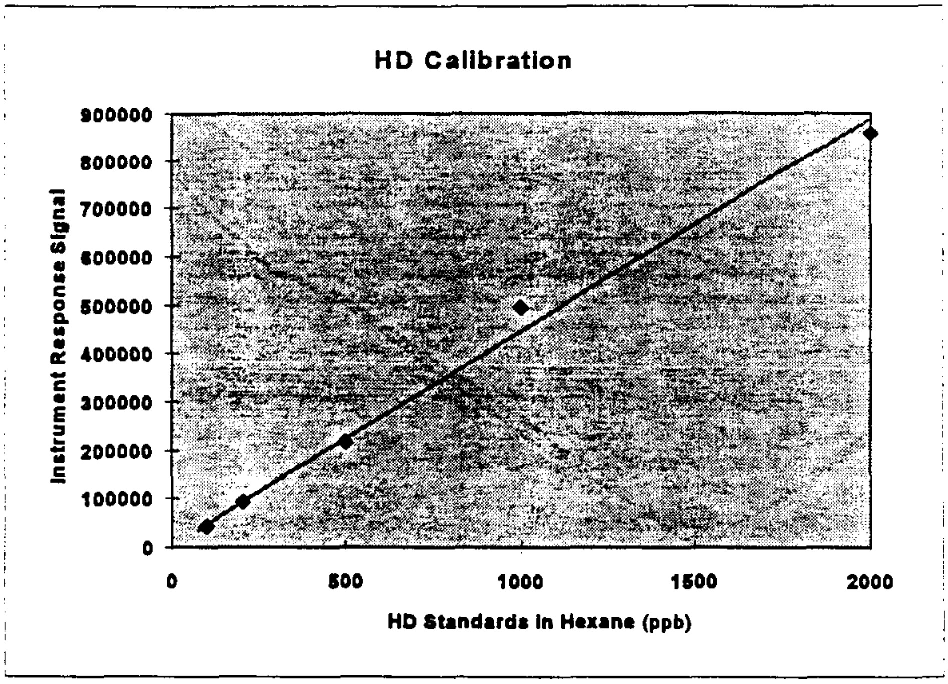
HD-Water Neutralization
Agent Destruction Efficiency

Reactor Size	HD Loading (wt pecent)	Subtest	Sample # (s)	Agitator (RPM)	HD Weight (kg)	HD Final Conc (ppb)	Lab	Method	Low Standard in Hexane (ppb)	Conc Factor	MDL (1) (ppb)	TRL	ADE (%)	
2 Liter	3.2	2	5 & 20	950	0.051	ND	ACT	HN02	100	12.5		10	>99.9999	
	3.1	3 DRAFT	5 & 20	950	0.05	ND	ACT	HNO2	100	12.5		10	>99.9999	
	6.3	4 DRAFT	5	950	0.153	ND	ACT	HNO2	100	12.5		10	>99.9999	
	9.3	5 DRAFT	5	950	0.102	ND	ACT	HN02	100	12.5		10	>99.9999	
	9.3	6 DRAFT	5 & 20	950	0.152	ND	ACT	HN02	100	12.5		10	>99.9999	
	8.6	5	5 & 20	950	0.152	ND	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	6	5	950	0.14	60	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	7	4	300	0.14	ND	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	8	4	625	0.14	ND	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	9	5	825	0.14	ND	ACT	HNO2	100	12.5		10	>99.9999	
	9.3	10	5	950	0.15	ND	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	14	5	950	0.14	ND	ACT	HNO2	100	12.5		10	>99.9999	
	1	15	5	950	0.14	ND	ACT	HNO2	100	12.5		10	>99.9999	
	8.6	8A	5	625	0.14	60	ACT	Hex-MSD	100	12.5	< 20		>99.9999	
	8.6	8B	4	625	0.106	ND	ACT	Hex-MSD	100	12.5	< 20		>99.9999	
	1	15A	4	950	0.0159	ND	ACT	Hex-MSD	100	12.5	< 20		>99.9999	
	1.3	15B	3	950	0.0151	ND	ACT	Hex-MSD	100	12.5	< 20		>99.9999	
	3.8	17	4 & 5	700 + Pressure	0.049	ND	Battelle	Hex-MSD	100	12.5	< 20		>99.9999	
	8.6	18	4 & 5	700 + Pessure	0.117	ND	Battelle	Hex-MSD	100	12.5	< 20		>99.9999	
			Static Mixer/NaOH											
12 Liter	3.8	9	NO/NO	100	0.384	ND	ACT	Hex-MSD	1000	12.5	< 20		>99.9999	
	3.8	10	YES/NO	100	0.385	ND	ACT	Hex-MSD	1000	12.5	< 20		>99.9999	
	3.8	11	YES/NO	100	0.384	ND	ACT	Hex-MSD	1000	12.5	< 20		>99.9999	
	3.8	12	NO/YES	100	0.384	ND	ACT	Hex-MSD	700	12.5	< 20		>99.9999	
	3.8	13	YES/YES	100	0.384	ND	ACT	Hex-MSD	700	12.5	< 20		>99.9999	
	3.8	15	YES/YES	100	0.382	ND	Battelle	Hex-MSD	100	12.5	< 20		>99.9999	
	3.8	16	YES/YES	100	0.382	ND	Battelle	Hex-MSD	100	12.5	< 20		>99.9999	
	3.8	17	YES/YES	100	0.382	ND	Battelle	Hex-MSD	100	12.5	< 20		>99.9999	
114 Liter	3.8	19	End of Run	350	3.6	ND	Chbr Lab	CHCl3-MSD	100	5			>99.999	
	3.8	20	End of Run	350	3.68	ND	Chbr Lab	CHCl3-MSD	100	5			>99.999	
	3.8	21	End of Run	350	3.62	ND	Chbr Lab	CHCl3-MSD	100	5			>99.999	
40 Gallon	3.8	5354-CTF	OTH-29495	1750	11	ND	ACT	ACT `50:1	1000	12.5 $CHCl_3$	80		>99.9999	
	8.6	6003-CTF	OTH-00996	1750	21.4	ND	ACT	ACT `40:1	1000	40 $CHCl_3$	22		>99.9999	
	3.8	6078-CTF	OTH-08196	1750	11.6	ND	ACT	ACT `50:1	4400	50	88		>99.999	
	3.8	6100-CTF	OTH-09696	1750	11.6	ND	ACT	ACT `50:1	933	50	19		>99.9999	
	3.8	6183-CTF	OTH-15996-5	1750	11.5	ND	ACT	ACT `50:1	900	50	18		>99.9999	

Note 1: Where < 20 ppb is entered a 50 percent HD recovery in hexane was assummed. In the 40 gallon reactor data the detection limit was based on 100 percent recovery of the low standard assayed in the analytical batch.

9/4/9610:52 AM

Discussion of Concentration Factors and Estimated Method Detection Limits for Low Level HD Extracted into Hexane (HNO2) and Detected using GC-MSD (HN01). (Reference 1)



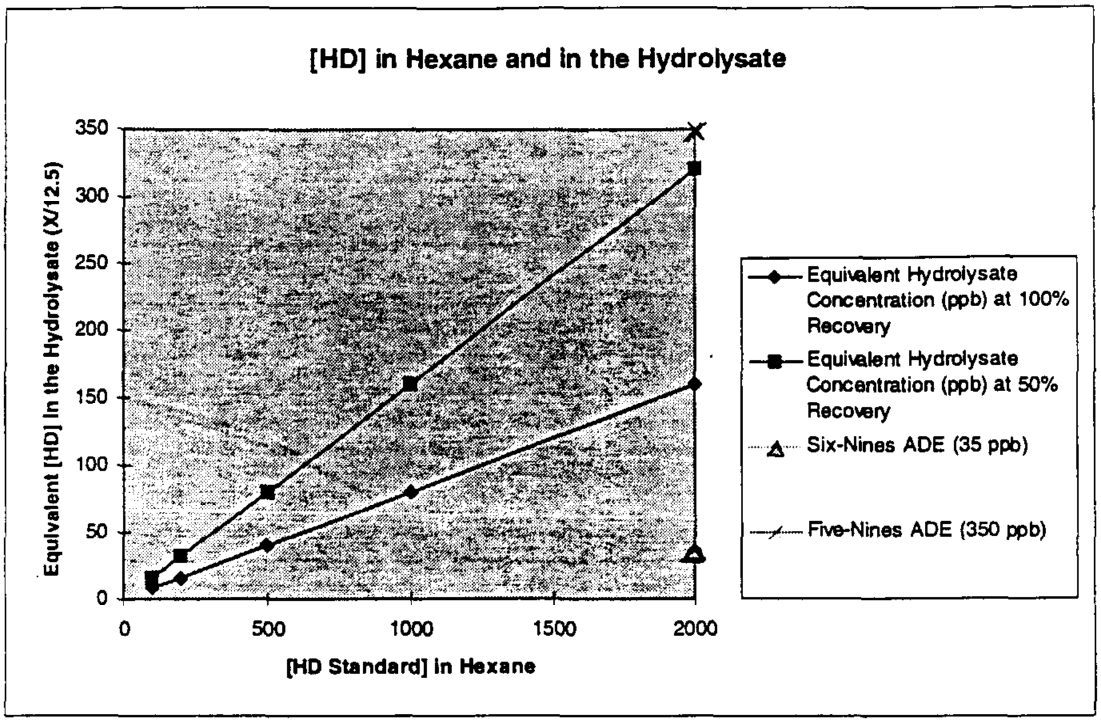
The GC-MSD is calibrated using standards prepared in hexane. The standards are in parts per billion (ppb) of HD in hexane. A hypothetical standard curve for the standard levels required by HNO2 is shown in the above figure. The calibration establishes the relationship between instrument response and known amounts of HD in hexane. A known volume (usually 1 uL) of hexane extract is injected into the GC-MSD to determine the amount of HD present in the extract. The extract HD concentration is then converted to the hydrolysate concentration using known experimental factors.

In the analysis of the HD-Water hydrolysate, a 25 mL aliquot of hydrolysate is taken and extracted with 2 mL of hexane. The transfer of HD to the hexane results in a 12.5 fold (25 divided by 2) concentration of HD. Method development studies demonstrated a better than 75 percent recovery of HD in hexane under conditions specified in Alternative Technology Method HN02.

The following figure shows the hydrolysate concentration to hexane standard relationships for 100 percent recovery and a worst case recovery of 50 percent.

For example: A hydrolysate contains 30 ppb HD. Analysis at 100 percent recovery would produce an extract with 375 ppb HD. Analysis at 50 percent recovery would produce an extract with 190 ppb HD.

Inclosure 1.



We have estimated the method detection limit for this method to be < 20 ppb in the hydrolysate by assuming a worst case 50 percent recovery of HD. With HD at 20 ppb in the hydrolysate, the extract at 50 percent recovery would have 125 ppb HD. The low standard in hexane is 100 ppb, so we have a standard that can be compared with what we observe. If the HD is non detect in a test sample in the same analytical batch as a check standard at 100 ppb HD is within 25 percent of its instrument response signal, we assert that the HD is non detect at < 20 ppb. That is, if the check standard gets the required response and the test sample is non detect we assert that the test sample is non detect at < 20 ppb.

Reference 1. US Army PMCD, HD Onsite Sample Analysis Test Plan, 1 March 1996, pp. 3-1 to 3-32.

Inclosure 1.

D-2 Test Change to evaluate solvent extraction efficiency in HD/NaOH subtests.

TEST CHANGE FORM

TO: Test Evaluation Team and Test Plan Signers

FROM: Marcia Middleton, SAIC **PHONE:** 273-1030

DATE: 5 October 1995

TEST PLAN: HD/NaOH Laboratory (MM-95-430) **SUBTEST:** Section 2, subtests 1 and 2

EVALUATION: (1) The analytical procedure for offgas analysis specifies a nitrogen flow through the cold trap. A step to assure an appropriate nitrogen flow needs to be added to the neutralization procedure of the subtest.

(2) An approved change in sampling procedure in the HD/water subtests is being used to evaluate solvent extraction efficiency of HD in the HD analytical method. Duplicate samples are being taken at each sampling time, and one sample from each pair is being spiked with a known quantity of HD. A similar change is proposed for the HD/NaOH subtests to evaluate chloroform extraction efficiency in the HD analytical method.

CHANGES: (1) A minimal nitrogen flow will be provided through the reactor during the HD addition and subsequent heating. The nitrogen flow will be sufficient to provide 15-20 bubbles per minute in the offgas trap, with the actual rate measured by a flow meter at the nitrogen inlet. A second flow meter at the offgas trap will assess possible leakage around the reactor joints.

(2) Instead of the planned HD analyses on two samples at 30-minute intervals, substitute four samples in duplicate at 15-minute intervals. One of each duplicate sample is to be spiked to 50 ppm HD. This spike would yield a 250 ppm value in the chloroform extract (5x dilution factor) at a 100% extraction efficiency. The spiking solution is a 5 mg/mL solution of HD in isopropyl alcohol. Add 0.25 mL of this solution to each 25 mL sample to be spiked. This spiking should be done in the reaction matrix after the pH adjustment described in HN-01. Extraction should be performed immediately after mixing the spiked, pH-adjusted reaction product. Tabulate the HD concentrations for the spiked and unspiked samples versus time.

CONCURRENCE: Your concurrence with this change is requested. Please sign and return.

Product Manager, Alternative Technologies and Approaches	Date
Test Director, PM ATA	Date
Team Leader, ERDEC	Date

D-3 Test Change to evaluate solvent extraction efficiency in HD/water subtests.

TEST CHANGE FORM

TO: Test Evaluation Team and Test Plan Signers

FROM: Marcia Middleton, SAIC **PHONE:** 273-1030

DATE: 20 September 1995

TEST PLAN: HD/Water Laboratory (MM-95-386) **SUBTEST:** Sampling and Analysis Plan

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EVALUATION: The peaking of HD concentration in the HD/water reaction was observed in the Mettler and Chamber level subtests. A change in hexane extraction efficiency has been proposed to explain these observations. The hexane extraction efficiency could be evaluated in the HD/water laboratory subtests by taking duplicate samples at each sampling time and spiking one sample from each pair with a known quantity of HD. The extractions would then be performed as planned and the hexane extraction efficiency quantified.

CHANGES: Change sampling procedure in HD-water subtests. Instead of the planned six samples at ten minute intervals, substitute four samples in duplicate at fifteen minute intervals. One of each duplicate sample is to be spiked to 50 ppm HD. This spike would yield a 625 ppm value in the hexane extract at a 100% extraction efficiency. The spiking solution is a 5 mg/mL solution of HD in isopropyl alcohol. Add 0.25 mL of this solution to each 25 mL sample to be spiked. This spiking should be done in the reaction matrix after the pH adjustment described in HN02. Extraction should be performed immediately after mixing the spiked, pH adjusted reaction product. Plot or tabulate the HD concentrations for the spiked and unspiked samples versus time.

CONCURRENCE: Your concurrence with this change is requested. Please sign and return.

Chief, Operations Division	Date
Chief, Applied Technologies Branch	Date
Test Director, Applied Technologies Branch	Date
Team Leader, ERDEC	Date

D-4 HD Ton Container Survey - Summary of Impurity Weight Percents, Heel Levels and Viscosities.

Appendix D-4. HD TC SURVEY - SUMMARY OF IMPURITY WEIGHT PERCENTS, HEEL LEVELS AND VISCOSITIES

TABLE COLUMN NUMBER		1	2	3	4	5	6	7	8	9
TON CONTAINER NUMBER		D78193	D77881	D78005	D92334	D93849	D84133	D84593	D92169	D93704
CTF LOT NUMBER		5163-1	5163-2	5163-3	5164-1	5164-2	5164-3	5164-4	5164-5	5164-6
	MW	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
HD	159	89.06	91.43	91.14	87.69	89.30	91.97	91.91	92.96	91.12
2-methyl-1-propene	56	0.00	0.02	0.00	0.00	0.04	0.01	0.02	0.00	0.02
thiirane	60	0.00	0.00	0.03	0.04	0.02	0.01	0.01	0.00	0.00
2-chlorobutane	93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-dichloroethane	99	0.34	0.33	0.19	0.06	0.49	0.20	0.16	0.46	0.26
1,4-oxathiane	104	0.09	0.24	0.09	0.09	0.00	0.02	0.01	0.03	0.02
1,4-dithiane	120	1.83	2.09	0.77	0.58	2.27	0.56	0.47	0.63	0.87
trichloroethylene	131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,5-trithiepane	152	0.00	0.00	0.10	0.04	0.28	0.00	0.00	0.00	0.19
tetrachloroethylene	166	**1.55**	0.00	0.04	0.17	0.00	0.00	0.00	0.24	0.00
1,1,2,2-tetrachloroethane	168	0.00	**0.84**	0.00	0.11	0.00	0.00	0.00	0.00	0.00
2-chloroethyl 3-chloropropyl sulfide	173	0.00	1.61	1.00	1.10	1.72	1.22	1.31	0.00	1.27
bis-3(chloropropyl) sulfide	187	0.67	0.49	0.62	0.43	0.25	0.21	0.29	0.41	0.17
C6H12Cl2S isomers	187	0.30	0.00	0.19	0.00	0.60	0.63	0.69	0.00	0.68
2-chloroethyl 4-chlorobutyl sulfide	187	1.41	0.47	0.87	0.28	1.46	0.93	1.01	0.65	1.34
bis-(2-chloroethyl) disulfide	191	0.62	0.00	0.32	**4.33**	0.00	0.40	0.36	0.39	0.72
2-chloroethyl 2-(chloroethoxy)ethyl sulfide	203	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-bis-(2-chloroethylthio)ethane ("Q")	219	2.90	2.47	4.23	1.42	3.34	3.73	3.65	4.23	3.34
bis-(2-chloroethyl) trisulfide	223	0.12	0.00	0.19	**0.63**	0.24	0.00	0.00	0.00	0.00
hexachloroethane	237	1.11	0.00	0.00	**3.03**	0.00	0.00	0.00	0.00	0.00
Unknown (MW is arbitrary)	200	0.00	0.00	**0.22**	0.00	0.00	0.10	0.12	0.00	0.00
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Subtotal of HD analogs, MW 173-223		6.02	5.05	7.42	8.19	7.60	7.13	7.30	5.68	7.52
Heel level, inches		5.0	4.0	4.0	na	4.0	6.3	10.9	7.8	8.0
Viscosity at 25 deg. C, cSt		3.96	3.67	3.69	3.16	**4.04**	3.50	3.45	3.34	3.63

CALCULATIONS:

Let H = HD purity % by GC/TCD = HD mole %
Let An = impurity area % by GC/MS
Let Cn = component mole %
Let Mn = component MW
Let Rn = component relative weight
Let Wn = component weight %
Cn = [An/sum(An)]*[100-H] ; C of HD = H
Rn = Mn*Cn
Wn = [Rn/sum(Rn)]*[100]

NOTES:

The "worst case" value for each component is boldfaced

Because of rounding, weight percent values shown may not add up to 100.00%

The calculations do not include any inorganic components, believed to be largely iron chlorides. Based on Fe analyses of the 27 ton containers, the concentration of iron (II) chloride averages 0.70 wt% and the'maximum is 1.39 wt%.

TABLE COLUMN NUMBER		10	11	12	13	14	15	16	17	18
TON CONTAINER NUMBER		D78004	D78271	D77877	D77949	D94515	D93382	D93608	D93565	D92221
CTF LOT NUMBER		5171-1	5171-2	5172-1	5172-2	5172-3	5172-4	5172-5	5172-6	5172-7
	MW	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
HD	159	89.26	91.26	92.99	92.15	94.98	93.79	95.19	94.66	91.15
2-methyl-1-propene	56	0.01	0.01	0.03	0.02	0.01	0.02	0.02	0.03	0.02
thiirane	60	0.01	0.01	0.00	0.02	0.00	0.02	0.01	0.02	0.03
2-chlorobutane	93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-dichloroethane	99	0.38	0.09	0.46	0.33	0.20	0.36	0.40	0.46	0.26
1,4-oxathiane	104	**0.27**	0.05	0.00	0.07	0.03	0.07	0.08	0.14	0.07
1,4-dithiane	120	1.19	0.99	2.36	1.54	0.57	1.77	1.56	1.83	2.27
trichloroethylene	131	**0.02**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,5-trithiepane	152	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.71**
tetrachloroethylene	166	0.13	0.31	0.32	0.06	0.00	0.16	0.00	0.61	0.00
1,1,2,2-tetrachloroethane	168	0.02	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00
2-chloroethyl 3-chloropropyl sulfide	173	1.49	1.43	0.00	**2.52**	2.04	0.00	0.00	0.00	0.22
bis-3(chloropropyl) sulfide	187	0.47	0.13	0.88	0.48	0.44	**1.04**	0.27	0.29	0.71
C6H12Cl2S isomers	187	0.22	0.87	0.41	0.38	0.33	0.66	0.68	0.53	0.54
2-chloroethyl 4-chlorobutyl sulfide	187	1.04	1.00	1.19	1.16	1.11	1.28	1.58	1.38	1.36
bis-(2-chloroethyl) disulfide	191	0.16	0.83	0.00	0.09	0.00	0.00	0.00	0.00	1.83
2-chloroethyl 2-(chloroethoxy)ethyl sulfide	203	**1.12**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-bis-(2-chloroethylthio)ethane ("Q")	219	4.16	2.83	1.36	1.15	0.28	0.83	0.21	0.06	0.82
bis-(2-chloroethyl) trisulfide	223	0.04	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
hexachloroethane	237	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown (MW is arbitrary)	200	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Subtotal of HD analogs, MW 173-223		8.70	7.21	3.84	5.78	4.20	3.81	2.74	2.26	5.48
Heel level, inches		4.4	6.9	7.3	5.4	8.5	7.5	7.7	6.7	4.3
Viscosity at 25 deg. C, cSt		3.94	3.82	3.66	3.65	3.26	3.49	3.28	3.27	3.80

TABLE COLUMN NUMBER		19	20	21	22	23	24	25	26	27
TON CONTAINER NUMBER		D94032	D93715	D93848	D94256	D92229	D93993	D93734	D93980	D94041
CTF LOT NUMBER		5177-1(2)	5177-2	5177-3	5177-4	5177-5	5178-1	5178-2	5178-3	5179-1
	MW	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
HD	159	88.92	89.46	92.28	91.65	90.36	89.45	89.42	88.01	**84.56**
2-methyl-1-propene	56	0.03	0.03	0.05	0.02	0.02	**0.06**	0.02	0.04	0.04
thiirane	60	0.01	0.04	0.01	0.01	0.02	0.00	0.02	**0.06**	0.04
2-chlorobutane	93	0.01	0.00	**0.03**	0.01	0.00	0.00	0.00	0.00	0.00
1,2-dichloroethane	99	0.37	0.40	0.57	0.31	0.34	0.65	0.37	0.46	**0.67**
1,4-oxathiane	104	0.03	0.05	0.06	0.03	0.08	0.07	0.02	0.04	0.10
1,4-dithiane	120	1.22	2.01	1.59	0.80	1.95	1.03	1.42	2.08	**3.68**
trichloroethylene	131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,5-trithiepane	152	0.20	0.24	0.00	0.00	0.23	0.00	0.28	0.29	0.51
tetrachloroethylene	166	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2,2-tetrachloroethane	168	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-chloroethyl 3-chloropropyl sulfide	173	1.74	1.09	1.34	1.32	1.34	2.08	1.24	1.44	1.44
bis-3(chloropropyl) sulfide	187	0.25	0.21	0.21	0.20	0.10	0.19	0.16	0.20	0.17
C6H12Cl2S isomers	187	**0.98**	0.79	0.79	0.80	0.55	0.88	0.72	0.89	0.85
2-chloroethyl 4-chlorobutyl sulfide	187	1.65	1.21	1.08	1.33	0.74	1.18	1.41	**1.75**	1.35
bis-(2-chloroethyl) disulfide	191	0.63	1.70	0.00	0.07	0.23	0.69	1.19	0.37	2.25
2-chloroethyl 2-(chloroethoxy)ethyl sulfide	203	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-bis-(2-chloroethylthio)ethane ("Q")	219	3.94	2.48	1.99	3.45	3.95	3.73	3.64	**4.25**	3.96
bis-(2-chloroethyl) trisulfide	223	0.00	0.31	0.00	0.00	0.09	0.00	0.08	0.12	0.38
hexachloroethane	237	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown (MW is arbitrary)	200	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Subtotal of HD analogs, MW 173-223		9.19	7.78	5.41	7.17	7.00	8.74	8.45	9.02	**10.41**
Heel level, inches		5.7	3.1	11.6	8.5	6.9	5.7	**13.5**	5.2	4.4
Viscosity at 25 deg. C, cSt		3.63	3.98	3.38	3.48	3.74	3.47	3.83	3.83	4.00

	MW	Mean Wt %	Worst Wt %
HD	159	90.97	84.56
2-methyl-1-propene	56	0.02	0.06
thiirane	60	0.02	0.06
2-chlorobutane	93	0.00	0.03
1,2-dichloroethane	99	0.35	0.67
1,4-oxathiane	104	0.07	0.27
1,4-dithiane	120	1.48	3.68
trichloroethylene	131	0.00	0.02
1,2,5-trithiepane	152	0.11	0.71
tetrachloroethylene	166	0.13	1.55
1,1,2,2-tetrachloroethane	168	0.04	0.84
2-chloroethyl 3-chloropropyl sulfide	173	1.11	2.52
bis-3(chloropropyl) sulfide	187	0.37	1.04
C6H12Cl2S isomers	187	0.55	0.98
2-chloroethyl 4-chlorobutyl sulfide	187	1.16	1.75
bis-(2-chloroethyl) disulfide	191	0.64	4.33
2-chloroethyl 2-(chloroethoxy)ethyl sulfide	203	0.04	1.12
1,2-bis-(2-chloroethylthio)ethane ("Q")	219	2.68	4.25
bis-(2-chloroethyl) trisulfide	223	0.09	0.63
hexachloroethane	237	0.15	3.03
Unknown (MW is arbitrary)	200	0.02	0.22
Total		na	na
Subtotal of HD analogs, MW 173-223		6.63	10.41
Heel level, inches		6.7	13.5
Viscosity at 25 deg. C, cSt		3.63	4.04

Mean weight percents include zero-value results.

D-5 Preliminary Report on the Composition of the TC HD Heels,
L.L. Szaframec, et. al. 19 March 1996.

<- type 62
(Message # 62: 4438 bytes, New)
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From: "Gerald P. Young" <gpyoung@cbda9.apgea.army.mil> To:
jjhavel@CDRA.APGEA.ARMY.MIL
Subject: [Linda L. Szafraniec: Composition of Ton Container HD Heels]
info
----- Forwarded message # 1:
Received: from cbda6.apgea.army.mil by cbda8.cbdcom.apgea.army.mil id aa20551;
19 Mar 96 12:52 EST
Date: Tue, 19 Mar 96 12:51:57 EST
From: Linda L. Szafraniec <llszafra@cbdcom.apgea.army.mil>
To: gpyoung@cbdcom.apgea.army.mil, jrward@cbdcom.apgea.army.mil,
jjnovad@cbdcom.apgea.army.mil, jarichmo@cbdcom.apgea.army.mil,
jdthomps@cbdcom.apgea.army.mil, sreckhau@cbdcom.apgea.army.mil,
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llszafra@cbdcom.apgea.army.mil, abbutrow@cbdcom.apgea.army.mil,
vmmchugh@cbdcom.apgea.army.mil
Subject: Composition of Ton Container HD Heels Message-ID:
<9603191251.aa28085@cbdcom.apgea.army.mil>

PRELIMINARY REPORT ON THE COMPOSITION OF THE TC HD HEELS
L.L. Szafraniec, W.T. Beaudry, and D.K. Rohrbaugh; Analytical Chem Team

Several HD heels have been examined using 1H and 13C NMR and GC/MS. The preliminary results from these analyses indicate that the HD heels are primarily composed of three components:

(1) Iron - The oxidation state of the iron has not yet been determined.

(2) HD - which appears to be part of the heel as well as "deposited on" and "occluded in" the heel from the surrounding HD solution.

(3) The cyclic Q sulfonium ion:
CH2-CH2
S S+ - CH2CH2Cl
CH2-CH2

It appears that the more "solid-like" the heel, the more of the sulfonium ion is present. The more "jelly-like" the heel, the more HD is present. To date, the amount of the cyclic sulfonium ion has ranged from 42 mole% to as much as 91 mole% of the sample.

The cyclic sulfonium ion was identified from its 1H and 13C NMR spectra [1H (D2O): SCH2: 3.20 (2H) and 3.25 (2H); CH2S+: 3.96 (2H) and 4.07 (2H); S+CH2: 3.94 (2H); CH2Cl: 3.64 (2H); and 13C (D2O): SCH2: 26.0 (2C); CH2S+: 40.3 (2C); S+CH2: 45.9 (1C); CH2Cl: 41.3 (1C)].

A GC/MS/CI spectrum of a sample containing 77 mole% of the cyclic sulfonium ion and 15 mole% HD showed that the sulfonium ion was not stable to GC/MS analysis (see below).

4.6 area%	1,2-dichloroethane
0.2	1,4-thioxane
16.8	1,4-dithiane
54.2	HD
7.4	ClCH2CH2SCH2CH2SCH=CH2
16.8	Q

However, an MS/APCI analysis with no corona current showed the following ions to be present, consistent with the cyclic sulfonium ion:

S(CH2CH2)2S+(CH2CH2Cl)	183,184,185
S(CH2CH2)2S+(CH=CH2)	147,148
(CH2CH2)S+(CH2CH2Cl)	123,124

Several samples of hydrolyzed HD heels have also been characterized by NMR and GC/MS. No degradation of the cyclic sulfonium ion occurs in water hydrolysis or acid hydrolysis of the HD heels. If base is added after water hydrolysis, the cyclic sulfonium was found to form the following compounds:

S(CH2CH2)2S+(CH2CH2OH)
S(CH2CH2)2S+(CH=CH2)
HOCH2CH2-S-CH2CH2-S-CH2CH2OH (Q-OH)

If the cyclic sulfonium ion is hydrolyzed under basic conditions, the following compounds are observed:

HOCH2CH2-S-CH2CH2-S-CH=CH2
Q-OH
1,4-dithiane (large amounts)

Studies are continuing to determine the ratios of sulfonium ion, HD and iron in the various heels and to determine the oxidation state of the iron. Also, Dr. Fu-Lian Hsu, Threat Agents Team, is in the process of preparing an authentic sample of the cyclic sulfonium ion for validation of the structure and for toxicity testing, if required.

A more complete report detailing the results for individual samples will be sent after the analyses have been completed. In the meantime, if there are any questions, please contact the undersigned.

D-6 TDG Conversion Calculations.

Table D-6. TDG Analyses by GC/MS (ATP Method HN-05A)

		Column	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
		Symbol				Wo	Sh	Wh	N	Sn	Wn	D	Wf	Cm	d	T			
Subtest and run	Sample No.	Sample Time	Wt HD charged	Wt water charged	Wt NaOH charged	Total weight	Samples> hydrolysis	Product> hydrolysis	NaOH for pH adj	Samples> pH adj	Product> pH adj	Distillate	Final product	TDG conc.	Product density	TDG in total	HD assay	TDG/HD conversion	HD loading
		Units	g	g	g	g	g	g	g	g	g	g	g	mg/L	g/mL	g	mole %	mole %	wt%
		Calculation				D+E+F		G-H			I+J-K		L-M			Eq. 1		Eq. 2	Eq. 3
2.1.1	L-211-10-HN-2845	Final	142.7	561.9	151.0	855.6	217.9	637.7			637.7		637.7	33160	1.081	26.2	91.3	26.2	16.68
2.1.2	L-212-10-HN-2855	Final	142.8	561.8	151.0	855.6	218.1	637.5			637.5		637.5	23990	1.095	18.7	91.3	18.7	16.69
2.2.1	L-221-10-HN-2925	Final	143.7	561.9	151.0	856.6	220.8	635.8			635.8		635.8	31570	1.094	24.7	84.8	26.4	16.78
2.2.2	L-222-10-HN-2935	Final	143.2	561.4	151.0	855.6	218.7	636.9			636.9		636.9	30230	1.100	23.5	84.8	25.2	16.74
2.4.1	L-242-02-HN-3395	before distn	142.9	561.8	151.0	855.7	113.0	742.7			742.7		742.7	34220	1.100	26.6	85.8	28.3	16.70
2.4.1	L-242-04-HN-3395	after distn	142.9	561.8	151.0	855.7	113.0	742.7			742.7	28.4	714.3	32720	1.100	24.5	85.8	26.0	16.70
2.4.2	L-242-02-HN-3415	before distn	142.9	562.0	151.0	855.9	112.8	743.1			743.1		743.1	35170	1.100	27.4	85.8	29.1	16.70
2.4.2	L-242-04-HN-3415	after distn	142.9	562.0	151.0	855.9	112.8	743.1			743.1	35.8	707.3	33220	1.100	24.6	85.8	26.2	16.70
3.1.1	L-313-10-HW-2645	Final	69.8	698.3		768.1	206.6	561.5	64.6		626.1		626.1	35490	1.047	29.0	91.3	59.4	9.09
3.1.2	L-313-10-HW-2695	Final	66.5	698.3		764.8	214.2	550.6	64.5		615.1		615.1	31500	1.048	25.7	91.3	55.1	8.70
3.1.3	L-313-10-HW-2715	Final	9.6	742.5		752.1	198.4	553.7	9.6		563.3		563.3	6500	0.998	5.0	91.3	74.1	1.28
3.1.4	L-313-07-HW-2625	Final	10.8	742.5		753.3	149.7	603.6	9.6		613.2		613.2	7100	0.999	5.4	91.3	71.9	1.43
3.2.1	L-321-10-HW-2905	Final	65.8	698.7		764.5	207.2	557.3	66.0		623.3		623.3	33530	1.049	27.3	84.8	63.9	8.61
3.2.2	L-322-10-HW-2915	Final	66.0	698.7		764.7	206.4	558.3	66.0		624.3		624.3	37510	1.050	30.6	84.8	71.2	8.63
3.3.1	L-331-10-HW-2765	Final	68.2	661.4	73.2	802.8	209.2	593.6			593.6		593.6	34250	1.044	26.3	91.3	55.1	8.50
3.3.2	L-331-10-HW-2775	Final	71.1	661.6	73.8	806.5	205.5	601.0			601.0		601.0	35990	1.042	27.9	91.3	55.9	8.82
3.3.3	L-331-10-HW-2785	Final	9.5	738.5	10.0	758.0	194.8	563.2			563.2		563.2	5900	0.999	4.5	91.3	67.3	1.25
3.3.4a	L-331-10-HW-2835	Final	9.9	738.5	14.1	762.5	350.3	412.2			412.2		412.2	6600	1.000	5.0	91.3	72.6	1.30
3.3.4b	L-331-10-HW-0046	Final	9.5	738.9	10.1	758.5	199.5	559.0			559.0		559.0	5900	1.006	4.5	91.3	66.9	1.25
3.5.1a	L-352-02-HW-3175	before pH adj	65.7	698.3		764.0	102.7	661.3			661.3		661.3	39440	1.050	28.7	85.8	66.3	8.60
3.5.1a	L-352-03-HW-3175	after pH adj	65.7	698.3		764.0	102.7	661.3	66.0		727.3		727.3	41510	1.050	33.2	85.8	76.8	8.60
3.5.1a	L-352-05-HW-3175	after distn	65.7	698.3		764.0	102.7	661.3	66.0	54.2	673.1	35.2	637.9	41780	1.050	31.7	85.8	73.3	8.60
3.5.1b	L-352-02-HW-3325	before pH adj	65.7	698.3		764.0	104.6	659.4			659.4		659.4	36920	1.050	26.9	85.8	62.1	8.60
3.5.1b	L-352-03-HW-3325	after pH adj	65.7	698.3		764.0	104.6	659.4	66.0		725.4		725.4	38190	1.050	30.6	85.8	70.7	8.60
3.5.1b	L-352-05-HW-3325	after distn	65.7	698.3		764.0	104.6	659.4	66.0	57.3	668.1	33.9	634.2	40900	1.050	31.1	85.8	71.8	8.60
3.5.2	L-352-02-HW-3345	before pH adj	65.8	698.4		764.2	103.5	660.7			660.7		660.7	37180	1.050	27.1	85.8	62.5	8.61
3.5.2	L-352-03-HW-3345	after pH adj	65.8	698.4		764.2	103.5	660.7	66.0		726.7		726.7	31600	1.050	25.3	85.8	58.4	8.61
3.5.2	L-352-05-HW-3345	after distn	65.8	698.4		764.2	103.5	660.7	66.0	57.0	669.7	30.8	638.9	26400	1.050	20.2	85.8	46.5	8.61
3.5	Average	before pH adj																63.6	
3.5	Average	after pH adj																68.6	
3.5	Average	after distn																63.9	

Equation 1 (columns) Q=O*N*(1+(K/L)+(H/I)+(K/L)*(H/I))/(1000000*P)
Equation 1 (symbols) T=Cm*Wf(1+(Sn/Wn)+(Sh/Wh)+(Sn*Sh)/(Wn*Wh))/(1000000*d) *DERIVATION ON SEPARATE PAGE*
Equation 2 S = 100*(Q/122)/((D/159)*(R/100))
Equation 3 T = 100*D/(D+E+F) *ASSUMES weight % HD = mole % HD from assay by GC/MSD*

Derivation of equation 1 for TDG total in table D-6:

Let:

Wo = wt (grams) of reactants added initially
Sh = wt (grams) of samples taken after hydrolysis
Wh = wt (grams) of hydrolysate after sampling
Ch = conc (wt fraction) of TDG in hydrolysate after sampling
N = wt (grams) of NaOH added for pH adj
Sn = wt (grams) of additional samples taken after pH adj
Wn = wt (grams) hydrolysate after pH adj and additional sampling
Cn = conc (wt fraction) of TDG in hydrolysate after pH adj and additional sampling
D = wt (grams) of distillate
Wf = wt (grams) of final hydrolysate
Cf = conc (wt fraction) of TDG in final hydrolysate
T = total wt (grams) of TDG produced
Cm = conc (mg/L) of TDG in final hydrolysate
d = density (g/mL) of final hydrolysate

Calculation of hydrolysate weights in terms of initial reactants weight, sample weights, NaOH weight and distillate weight:

$Wh = Wo - Sh$
$Wn = Wh + N - Sn = Wo - Sh + N - Sn$
$Wf = Wn - D = Wo - Sh + N - Sn - D$

Calculation of TDG concentrations in terms of final TDG concentration (concentration and dilution factors):

$Cn = Cf\ (Wf/Wn)$
$Ch = Cn\ (Wn + Sn)/Wh = Cf\ (Wf/Wn)(Wn + Sn)/Wh$

Calculation of TDG mass balance:

$T = CfWf + CnSn + ChSh$
$T = CfWf + Cf\ (Wf/Wn)\ Sn + CfSh(Wf/Wn)(Wn + Sn)/Wh$
$T = CfWf\ [1 + (Sn/Wn) + (Sh/Wh) + (SnSh/WnWh)]$

Conversion of TDG mass balance into terms of TDG concentration in mg/L:

$(Cf, g/g) = (Cm, mg/L)(g/mg)(L/mL)(mL/g)$
$Cf = Cm/(10^6 d)$
$T = (Cm/10^6 d)Wf\ [1 + (Sn/Wn) + (Sh/Wh) + (SnSh/WnWh)]$

D-7 Test change to hydrolyze HD heel in HD/NaOH subtest no. 2.

TEST CHANGE FORM

To: PMAT&A
From: Marcia Middleton, SAIC mam
Date: January 19, 1996
Test Plans: HD/NaOH Laboratory Test Plan (DB-96-627) **Subtests:** 2.2

CONTROLLED DOCUMENT
A34278-03
Document Number

Evaluation:
The purpose of this change is to specify the mustard agent (HD) to be used in Runs 3 and 4 of subtest 2.2 and to provide an alternative procedure for adding it to the 1-liter reactor used in the chemical neutralization reaction. The test plan originally specified the use of a high viscosity lot of HD, but none of significantly high viscosity was identified in the ton container survey. Of more interest is the hydrolysis of the heel commonly found in the bottom of the HD ton containers. The original test plan requires the HD to be added as a liquid which is pumped into the reactor continuously over a one hour period. An alternative procedure is needed to add HD which has partially or completely solidified. This procedure modifies and replaces that of the test plan subtest 2.2 Runs 3 and 4.

Changes: The procedure changes the introduction of HD into the reaction vessel to permit neutralization of partially or completely solidified HD, such as exists in the ton container heel. The heel will be obtained from the container-emptying experiment conducted at the CTF on ton container D93734 in December 1995.

The following procedure change replaces steps 1 and 2 of test plan section 2.2.5 in their entirety, which will now read:

Step 1. Prepare NaOH solution in 1-liter reactor by adding 713 grams of 50 wt% NaOH (amount of line 14 in table 2-1) to 562 grams of distilled water (amount of line 16 in table 2-1) with stirring until dissolved. Withdraw 100 mL of the NaOH solution and place under dry nitrogen for use in Step 2. Heat the NaOH solution remaining in the reactor to 194(±4)°F [90(±2)°C].

Step 2. Add 143 grams of solid HD (amount of line 2 of table 2-3) to the reactor by scooping it from a container into the reactor vessel. The solid HD will be added through an open port in the top of the vessel using a common spatula and a wide mouth funnel fitted to the port. The addition will be over one hour, adding 6 approximately equal portions at 10 minute intervals. After each incremental addition, seal the introduction port with a ground glass stopper and begin stirring at 800 rpm. After all the HD is added, take the 100 mL portion of NaOH solution withdrawn in Step 1 and rinse any HD which may have stuck to the sides of the HD container, funnel, or walls of the reactor and add the NaOH solution to the reactor. Weigh the HD container and funnel to account for any mass of HD or NaOH solution that did not make it into the reactor and record these values to adjust the final mass balance.

All other steps and sample requirements in Subtest 2.2 remain the same, except that the final hydrolysate will also be submitted for analysis of metals by ATP method E-04.

Concurrence: Your concurrence with these changes is requested. Please sign and return.

Product Manager for Alternative Technologies and Approaches

24 Jan 96
Date

Test Director, PMAT&A

19 JAN 96
Date

Team Leader, ERDEC

23 Jan 96
Date

D-8 Test change to hydrolyze HD heel in HD/water subtest no. 2.

TEST CHANGE FORM

To: PMAT&A
From: Marcia Middleton, SAIC mam
Date: January 19, 1996
Test Plans: HD/Water Laboratory Test Plan (DB-96-635) **Subtests:** 3.2

CONTROLLED DOCUMENT
A3427C-03
Document Number

Evaluation:
The purpose of this change is to specify the mustard agent (HD) to be used in Runs 3 and 4 of subtest 3.2 and to provide an alternative procedure for adding it to the 1-liter reactor used in the chemical neutralization reaction. The test plan originally specified the use of a high viscosity lot of HD, but none of significantly high viscosity was identified in the ton container survey. Of more interest is the hydrolysis of the heel commonly found in the bottom of the HD ton containers. The original test plan requires the HD to be added as a liquid which is pumped into the reactor continuously over a one hour period. An alternative procedure is needed to add HD which has partially or completely solidified. This procedure modifies and replaces that of the test plan subtest 3.2 Runs 3 and 4.

Changes: The procedure changes the introduction of HD into the reaction vessel to permit neutralization of partially or completely solidified HD, such as exists in the ton container heel. The heel will be obtained from the container-emptying experiment conducted at the CTF on ton container D93734 in December 1995.

The following procedure change replaces steps 1 and 2 of test plan section 3.2.5 in their entirety, which will now read:

Step 1. Add distilled water (100 mL less than the amount of line 8 of table 3-3) to reactor and heat to 194(±4)°F [90(±2)°C].

Step 2. Add solid HD (amount of line 2 of table 3-3) to the reactor by scooping it from a container into the reactor vessel. The solid HD will be added through an open port in the top of the vessel using a common spatula and a wide mouth funnel fitted to the port. The addition will be over one hour, adding 6 approximately equal portions at 10 minute intervals. After each incremental addition, seal the introduction port with a ground glass stopper and begin stirring at 800 rpm. After all the HD is added, take the 100 mL portion of water not used in step 1 and rinse any HD which may have stuck to the sides of the HD container, funnel, or walls of the reactor and add the water to the reactor. Weigh the HD container and funnel to account for any mass of HD or water that did not make it into the reactor and record these values to adjust the final mass balance.

All other steps and sample requirements in Subtest 3.2 remain the same, except that the final hydrolysate will also be submitted for analysis of metals by ATP method E-04.

Page 2 of 2
January 19, 1996
PMAT&A
HD/Water Laboratory Test Plan (DB-96-635)

Concurrence: Your concurrence with these changes is requested. Please sign and return.

Product Manager for Alternative Technologies and Approaches — 24 Jan 96
Date

Cheryl Lynn Maggio
Test Director, PMAT&A — 19 JAN 96
Date

Joseph J Novad
Team Leader, ERDEC — 23 Jan 96
Date

D-9 Analysis of HD spiked with CHCs.

Appendix D-9. Analysis of HD Spiked With Chlorinated Hydrocarbons

	L-351-01-HW-3135	L-351-01-HW-3135 Analysis			L-351-01-HW-3325 Analysis			L-351-01-HW-3345 Analysis		
	Prepared wt%	Area % by GC/TCD	Calc. Conc. mg/mL	**Calculated Wt %**	Area % by GC/TCD	Calc. Conc. mg/mL	**Calculated Wt %**	Area % by GC/TCD	Calc. Conc. mg/mL	**Calculated Wt %**
HD, neat	94.00									
HD, assay		84.35			83.47			85.69		
1,2-dichloroethane	**0.50**	1.45	23.79	**1.87**	1.57	26.59	**2.09**	1.40	19.47	**1.53**
trichloroethylene	**0.50**	nd	nd	**0.00**	<0.01	<0.50	**<0.04**	nd	nd	**0.00**
tetrachloroethylene	**1.50**	0.22	6.61	**0.52**	0.48	14.45	**1.14**	0.31	7.49	**0.59**
1,1,2,2-tetrachloroethane	**1.00**	nd	nd	**0.00**	nd	nd	**0.00**	nd	nd	**0.00**
hexachloroethane	**2.50**	1.32	33.74	**2.66**	1.26	34.06	**2.68**	1.23	27.23	**2.14**
Total	100.00	87.34			86.78			88.63		

	L-241-01-HN-3385	L-241-01-HN-3395 Analysis			L-241-01-HN-3415 Analysis		
	Prepared wt%	Area % by GC/TCD	Calc. Conc. mg/mL	**Calculated Wt %**	Area % by GC/TCD	Calc. Conc. mg/mL	**Calculated Wt %**
HD, neat	94.00						
HD, assay		86.23			86.27		
1,2-dichloroethane	**0.50**	1.33	19.47	**1.53**	1.44	19.75	**1.56**
trichloroethylene	**0.50**	0.77	12.51	**0.99**	0.74	11.20	**0.88**
tetrachloroethylene	**1.50**	1.49	38.79	**3.05**	1.58	38.56	**3.04**
1,1,2,2-tetrachloroethane	**1.00**	1.01	16.39	**1.29**	0.99	15.16	**1.19**
hexachloroethane	**2.50**	1.18	27.32	**2.15**	1.16	25.19	**1.98**
Total	100.00	92.01			92.18		

nd = not detected by either GC/TCD or GC/MSD
Area % by GC/TCD: from M. W. Ellzy analytical report of 12 April 1995
Calc. Conc. mg/mL: from M. W. Ellzy analytical report of 17 April 1995
Calculated Wt % = (mg/mL)*(1/1.27)*(100/1000) where 1.27 = density of HD

D-10 Formulas for calculating CHC concentrations in hydrolysis products.

A	A	B	C	D	E	F	G
1	Appendix D-10. Formulas Used in Calculating CHC Compositions in HD/NaOH subtest 4						
2							
3		**Spiked HD Composition**	**Wt%**	**Grams Added**		**Portion**	**mL**
4		HD	94.00	142.9*C4/100		Reaction	G4
5		1,2-dichloroethane	0.50	142.9*C5/100		Offgas trap (60-min)	G5
6		trichloroethylene	0.50	142.9*C6/100		Samples removed	G6
7		tetrachloroethylene	1.50	142.9*C7/100		Condensate (top)	G7
8		1,1,2,2-tetrachloroethane	1.00	142.9*C8/100		Condensate (bot)	G8
9		hexachloroethane	2.50	142.9*C9/100		Final	+G4-(G6+G7+G8)
10		Total	@SUM(C4..C9)	@SUM(D4..D9)		Offgas trap (final)	G10
11							
12	**Sample Number**	**Sample Source**	**Analysis**	**Method**	**Conc., mg/L**	**Total Produced, g**	**% of Added**
13							
14		Removed before 60-min	Volatiles	Calculated from sample 2			
15			1,2-dichloroethane		+E21	+E15*($G$6/10^6)	(F15/D5)*100
16			trichloroethylene		+E22	+E16*($G$6/10^6)	(F16/D6)*100
17			tetrachloroethylene		+E23	+E17*($G$6/10^6)	(F17/D7)*100
18			1,1,2,2-tetrachloroethane		+E24	+E18*($G$6/10^6)	(F18/D8)*100
19			hexachloroethane		+E25	+E19*($G$6/10^6)	(F19/D9)*100
20	L-242-02-HN-3395	60-minute	Volatiles	ATP E-02			
21			1,2-dichloroethane		E21	+E21*(G4-G6)/10^6	(F21/D5)*100
22			trichloroethylene		E22	+E22*(G4-G6)/10^6	(F22/D6)*100
23			tetrachloroethylene		E23	+E23*(G4-G6)/10^6	(F23/D7)*100
24			1,1,2,2-tetrachloroethane		E24	+E24*(G4-G6)/10^6	(F24/D8)*100
25			hexachloroethane		E25	+E25*(G4-G6)/10^6	(F25/D9)*100
26	L-242-03-HN-3395	Offgas (60-minute)	Composition	ATP HN-07			
27			1,2-dichloroethane		E27	+E27*(G5/10^6)	(F27/D5)*100
28			trichloroethylene		E28	+E28*(G5/10^6)	(F28/D6)*100
29			tetrachloroethylene		E29	+E29*(G5/10^6)	(F29/D7)*100
30			1,1,2,2-tetrachloroethane		E30	+E30*(G5/10^6)	(F30/D8)*100
31			hexachloroethane		E31	+E31*(G5/10^6)	(F31/D9)*100
32	L-242-04-HN-3395	Final reactor	Volatiles	ATP E-02			
33			1,2-dichloroethane		E33	+E33*(G9/10^6)	(F33/D5)*100
34			trichloroethylene		E34	+E34*(G9/10^6)	(F34/D6)*100
35			tetrachloroethylene		E35	+E35*(G9/10^6)	(F35/D7)*100
36			1,1,2,2-tetrachloroethane		E36	+E36*(G9/10^6)	(F36/D8)*100
37			hexachloroethane		E37	+E37*(G9/10^6)	(F37/D9)*100
38	L-242-05-HN-3395	Condensate (Top)	Composition	ATP HN-09			
39			1,2-dichloroethane		E39	+E39*(G7/10^6)	(F39/D5)*100
40			trichloroethylene		E40	+E40*(G7/10^6)	(F40/D6)*100
41			tetrachloroethylene		E41	+E41*(G7/10^6)	(F41/D7)*100
42			1,1,2,2-tetrachloroethane		E42	+E42*(G7/10^6)	(F42/D8)*100
43			hexachloroethane		E43	+E43*(G7/10^6)	(F43/D9)*100
44		Condensate (Bottom)	Composition	ATP HN-09			
45			1,2-dichloroethane		E45	+E45*(G8/10^6)	(F45/D5)*100
46			trichloroethylene		E46	+E46*(G8/10^6)	(F46/D6)*100
47			tetrachloroethylene		E47	+E47*(G8/10^6)	(F47/D7)*100
48			1,1,2,2-tetrachloroethane		E48	+E48*(G8/10^6)	(F48/D8)*100
49			hexachloroethane		E49	+E49*(G8/10^6)	(F49/D9)*100
50	L-242-06-HN-3395	Offgas (final)	Composition	ATP HN-07			
51			1,2-dichloroethane		E51	+E51*(G10/10^6)	(F51/D5)*100
52			trichloroethylene		E52	+E52*(G10/10^6)	(F52/D6)*100
53			tetrachloroethylene		E53	+E53*(G10/10^6)	(F53/D7)*100
54			1,1,2,2-tetrachloroethane		E54	+E54*(G10/10^6)	(F54/D8)*100
55			hexachloroethane		E55	+E55*(G10/10^6)	(F55/D9)*100
56							
57		CHC Balance Without Distillation					
58			1,2-dichloroethane				+G15+G21+G27
59			trichloroethylene				+G16+G22+G28
60			tetrachloroethylene				+G17+G23+G29
61			1,1,2,2-tetrachloroethane				+G18+G24+G30
62			hexachloroethane				+G19+G25+G31
63							
64		CHC Balance With Distillation					
65			1,2-dichloroethane				+G15+G27+G33+G39+G45+G51
66			trichloroethylene				+G16+G28+G34+G40+G46+G52
67			tetrachloroethylene				+G17+G29+G35+G41+G47+G53
68			1,1,2,2-tetrachloroethane				+G18+G30+G36+G42+G48+G54
69			hexachloroethane				+G19+G31+G37+G43+G49+G55

A	A	B	C	D	E	F	G
1	**Appendix D-10. Formulas Used in Calculating CHC Compositions in HD/water subtest 5**						
2							
3		**Spiked HD Composition**	**Wt%**	**Grams Added**		**Portion**	**Weight, g**
4		HD	94.00	65.7*C4/100		Reaction	G4
5		1,2-dichloroethane	0.50	65.7*C5/100		Samples after hydr.	G5
6		trichloroethylene	0.50	65.7*C6/100		Hydrolysate, initial	+G4-G5
7		tetrachloroethylene	1.50	65.7*C7/100		pH adjustment soln.	G7
8		1,1,2,2-tetrachloroethane	1.00	65.7*C8/100		Hydrolysate, pH adj.	+G6+G7
9		hexachloroethane	2.50	65.7*C9/100		Samples after pH	G9
10		Total	@SUM(C4..C9)	@SUM(D4..D9)		Offgas trap (60-min)	G10
11						Condensate	G11
12						Hydrolysate, final	+G8-G9-G11
13						Offgas trap (final)	G13
14							
15	**Sample Number**	**Sample Source**	**Analysis**	**Method**	**Conc., mg/L**	**Total produced, g**	**% of added**
16							
17		Samples after hydrolysis	Volatiles	Calculated from sample 3			
18			1,2-dichloroethane		+E24*($G$8/$G$6)	+E18*$G$5*10^-6	(F18/$D$5)*100
19			trichloroethylene		+E25*($G$8/$G$6)	+E19*$G$5*10^-6	(F19/$D$6)*100
20			tetrachloroethylene		+E26*($G$8/$G$6)	+E20*$G$5*10^-6	(F20/$D$7)*100
21			1,1,2,2-tetrachloroethane		+E27*($G$8/$G$6)	+E21*$G$5*10^-6	(F21/$D$8)*100
22			hexachloroethane		+E28*($G$8/$G$6)	+E22*$G$5*10^-6	(F22/$D$9)*100
23	L-352-03-HW-3175	Hydrolysate, pH adjusted	Volatiles	ATP E-02			
24			1,2-dichloroethane		E24	+E24*($G$8*10^-6)	(F24/$D$5)*100
25			trichloroethylene		E25	+E25*($G$8*10^-6)	(F25/$D$6)*100
26			tetrachloroethylene		E26	+E26*($G$8*10^-6)	(F26/$D$7)*100
27			1,1,2,2-tetrachloroethane		E27	+E27*($G$8*10^-6)	(F27/$D$8)*100
28			hexachloroethane		E28	+E28*($G$8*10^-6)	(F28/$D$9)*100
29	L-352-04-HW-3175	offgas (60-minute)	Composition	ATP HN-07			
30			1,2-dichloroethane		E30	+E30*($G$10/0.79)*10^-6	(F30/$D$5)*100
31			trichloroethylene		E31	+E31*($G$10/0.79)*10^-6	(F31/$D$6)*100
32			tetrachloroethylene		E32	+E32*($G$10/0.79)*10^-6	(F32/$D$7)*100
33			1,1,2,2-tetrachloroethane		E33	+E33*($G$10/0.79)*10^-6	(F33/$D$8)*100
34			hexachloroethane		E34	+E34*($G$10/0.79)*10^-6	(F34/$D$9)*100
35		Samples after pH adj.	Volatiles	Calculated from sample 3			
36			1,2-dichloroethane		+E24	+E36*$G$9*10^-6	(F36/$D$5)*100
37			trichloroethylene		+E25	+E37*$G$9*10^-6	(F37/$D$6)*100
38			tetrachloroethylene		+E26	+E38*$G$9*10^-6	(F38/$D$7)*100
39			1,1,2,2-tetrachloroethane		+E27	+E39*$G$9*10^-6	(F39/$D$8)*100
40			hexachloroethane		+E28	+E40*$G$9*10^-6	(F40/$D$9)*100
41	L-352-05-HW-3175	Hydrolysate, final	Volatiles	ATP E-02			
42			1,2-dichloroethane		E42	+E42*$G$12*10^-6	(F42/$D$5)*100
43			trichloroethylene		E43	+E43*$G$12*10^-6	(F43/$D$6)*100
44			tetrachloroethylene		E44	+E44*$G$12*10^-6	(F44/$D$7)*100
45			1,1,2,2-tetrachloroethane		E45	+E45*$G$12*10^-6	(F45/$D$8)*100
46			hexachloroethane		E46	+E46*$G$12*10^-6	(F46/$D$9)*100
47	L-352-06-HW-3175	Condensate	Composition	ATP HN-09			
48			1,2-dichloroethane		E48	+E48*$G$11*10^-6	(F48/$D$5)*100
49			trichloroethylene		E49	+E49*$G$11*10^-6	(F49/$D$6)*100
50			tetrachloroethylene		E50	+E50*$G$11*10^-6	(F50/$D$7)*100
51			1,1,2,2-tetrachloroethane		E51	+E51*$G$11*10^-6	(F51/$D$8)*100
52			hexachloroethane		E52	+E52*$G$11*10^-6	(F52/$D$9)*100
53	L-352-07-HW-3175	Offgas (final)	Composition	ATP HN-07			
54			1,2-dichloroethane		E54	+E54*($G$13/0.79)*10^-6	(F54/$D$5)*100
55			trichloroethylene		E55	+E55*($G$13/0.79)*10^-6	(F55/$D$6)*100
56			tetrachloroethylene		E56	+E56*($G$13/0.79)*10^-6	(F56/$D$7)*100
57			1,1,2,2-tetrachloroethane		E57	+E57*($G$13/0.79)*10^-6	(F57/$D$8)*100
58			hexachloroethane		E58	+E58*($G$13/0.79)*10^-6	(F58/$D$9)*100
59							
60		CHC Balance Without Distillation					
61			1,2-dichloroethane				+G18+G24+G30
62			trichloroethylene				+G19+G25+G31
63			tetrachloroethylene				+G20+G26+G32
64			1,1,2,2-tetrachloroethane				+G21+G27+G33
65			hexachloroethane				+G22+G28+G34
66							
67		CHC Balance With Distillation					
68			1,2-dichloroethane				+G18+G30+G36+G42+G48+G54
69			trichloroethylene				+G19+G31+G37+G43+G49+G55
70			tetrachloroethylene				+G20+G32+G38+G44+G50+G56
71			1,1,2,2-tetrachloroethane				+G21+G33+G39+G45+G51+G57
72			hexachloroethane				+G22+G34+G40+G46+G52+G58

D-11 Y-C. Yang in ERDEC Alt Tech Highlights, 20-23 March 1995.

<- type 3
(Message # 3: 15479 bytes, New)
Date: Tue, 28 Mar 95 13:55:41 EST
From: Jennifer L. O'Connor <jloconno@cbdcom.apgea.army.mil>
To: jjnovad@cbdcom.apgea.army.mil, jarichmo@cbdcom.apgea.army.mil, tchoff@cbdcom.apgea.army.mil, srharlac@cbdcom.apgea.army.mil, tlbrown@cbdcom.apgea.army.mil, rprhoads@cbdcom.apgea.army.mil, ajsapona@cbdcom.apgea.army.mil, wlhershf@cbdcom.apgea.army.mil, fjdipiet@cbdcom.apgea.army.mil, frschulz@cbdcom.apgea.army.mil, jdthomps@cbdcom.apgea.army.mil, lgfoust@cbdcom.apgea.army.mil, slandry@dan, jwlovric@cbdcom.apgea.army.mil, djpalugh@cbdcom.apgea.army.mil, jrward@cbdcom.apgea.army.mil, gpyoung@cbdcom.apgea.army.mil, vwelsh@dan, aeisen@dan
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Subject: ERDEC Alt Tech Highlights, 20-24 Mar 95

1. LABORATORY SCALE TESTING - Jim Richmond, 671-5524

a. NEUTRALIZATION:

1). Neutralization of 10 % HD in Water at 90 deg C (Y.-C. Yang)

At Dr. Yang's request, Mr. L. R. Procell of Decon/Demil Team conducted the following experiment in order to determine if the HD-water reaction at an increased HD loading would also produce high yields of thiodiglycol. 10% HD was used to assess the possibility of increasing the throughput of the HD-water reaction for Stand-Alone Neutralization.

$\frac{1.27\,g}{11.27\,g} = 11.3\%$
w/w

1mL of neat CASARM HD was added to 10mL deionized water at 88-90degC. The mixture was stirred gently in a closed reactor for about 65 minutes until all of the HD was completely dissolved. The reactor was then opened to the atmosphere and stirred vigorously for an additional 55 minutes. An aliqout of the mixture was then removed for NMR analysis (Szafraniec and Beaudry, Analytical Chem. Team). The following is their report.

1H and 13C NMR Results: Values reported as area percent (which is the same as "percent HD that went to ..."). We are reporting it this way because it takes more than 1 mole of HD to form the sulfonium ions and this gives a better indication of how much of HD was reacted to form the the sulfonium ions and these numbers are different from that expressed in mole percentages.

RUN 1, The sample was run shortly after the sample was received:

Compound	13C Data	1H Data
TDG	39.8	39.9
CHTG	39.8	36.1
H2TG	11.0	10.0
Other	9.4	13.9
	100	99.9

(Both CHTG and H2TG are sulfonium ions, see 1988 JOC paper by Yang et al for their chemical structures).

Run 2, Sample allowed to sit at 22 deg C and re-run after 4 days:

TDG	37.1	39.5
CHTG	42.2	39.7
H2TG	12.2	10.8
Other	8.5	10.0
	100	100

Within error of the method, the two analytical results are the same - no change in composition indicating no subsequent hydrolysis of the sulfonium ions at 22 deg C even after 4 days. However, it is conceivable that some of the sulfonium ion products hydrolyzed to TDG at 88-90 deg C during the 55 min reaction time in the reactor after all of the HD was dissovled in the hot water.

Major component of "Other" appears to be ether-type compounds. In contrast to the 1% HD in water hydrolysis which yields a clean product of TDG, the higher 10% HD hydrolysis yields a mixture of sulfonium salts which form from the reaction of TDG with HD or CH (chlorohydrin). There is no new mechanism or magic of the HD-water system as compared to what was already known and reported on the kinetics and mechanisms of the hydrolysis of HD.

D-12 Heel Hydrolysate Analyses by ICP

Table D-12a. Heel Hydrolysate Analyses by ICP

	Subtest/run	2.2 run 3	2.2 run 4	3.2 run 3	3.2 run 4
	Sample no.	L-223-09-HN-0386	L-224-09-HN-0406	L-323-11 HW-0306	L-324-11-HW-0326
	Units				
Wt of agent initial	g	129.1	129.9	65.6	65.8
Wt of reactants	g	778.1	778.0	763.9	763.9
Wt of samples after hydrolysis	g	225.9	232.9	207.4	208.1
Wt of product after sampling	g	552.2	545.1	556.5	555.8
Wt of NaOH added after sampling	g	0.0	0.0	66.0	66.0
Wt of product after NaOH	g	552.2	545.1	622.5	621.8
Wt of aqueous ICP sample	g	21.00	21.00	17.00	16.50
Density of aqueous ICP sample	g/mL	1.10	1.10	1.05	1.05
Wt of solid ICP sample	g	1.24	0.95	0.53	0.52
Wt of total ICP sample	g	22.24	21.95	17.53	17.02
Conc of Fe in aqueous ICP sample	mg/L	1.443	0.893	13.862	8.055
Conc of Fe in solid ICP sample	mg/kg	155469	153544	128622	53765
Wt of Fe in aqueous ICP sample	g	0.00003	0.00002	0.00022	0.00013
Wt of Fe in solid ICP sample	g	0.19	0.15	0.07	0.03
Wt of Fe in total ICP sample	g	0.19	0.15	0.07	0.03
Wt of Fe in product after NaOH	g	4.79	3.61	2.41	1.02
Wt of Fe in product after sampling	g	4.79	3.61	2.41	1.02
Wt of Fe in samples after hydrolysis	g	1.96	1.54	0.90	0.38
Wt of Fe in reactants	g	6.75	5.15	3.31	1.40
Fe as weight % of agent	**%**	**5.2**	**4.0**	**5.0**	**2.1**
Conc of S in aqueous ICP sample	mg/L	4620	6760	6178	5958
Conc of S in solid ICP sample	mg/kg	164604	230882	140450	94708
Wt of S in aqueous ICP sample	g	0.09	0.13	0.10	0.09
Wt of S in solid ICP sample	g	0.20	0.22	0.07	0.05
Wt of S in total ICP sample	g	0.29	0.35	0.17	0.14
Wt of S in product after NaOH	g	7.26	8.64	6.17	5.21
Wt of S in product after sampling	g	7.26	8.64	6.17	5.21
Wt of S in samples after hydrolysis	g	2.97	3.69	2.30	1.95
Wt of S in reactants	g	10.23	12.32	8.47	7.16
S as weight % of agent	**%**	**7.9**	**9.5**	**12.9**	**10.9**

The samples separated into an aqueous portion and a solid precipitate, which were analyzed separately.

A	A	B	C	D	E	F	G	H
1	**Table D-12b. Heel Hydrolysate Analyses by ICP - Calculation Formulas**							
2								
3								
4				Subtest/run	2.2 run 3	2.2 run 4	3.2 run 3	3.2 run 4
5				Sample no.	L-223-09- HN-0386	L-224-09- HN-0406	L-323-11 HW-0306	L-324-11- HW-0326
6				Units				
7	Wt of agent initial			g	129.1	129.9	65.6	65.8
8	Wt of reactants			g	778.1	778	763.9	763.9
9	Wt of samples after hydrolysis			g	225.9	232.9	207.4	208.1
10	Wt of product after sampling			g	+E8-E9	+F8-F9	+G8-G9	+H8-H9
11	Wt of NaOH added after sampling			g	0	0	66	66
12	Wt of product after NaOH			g	+E10+E11	+F10+F11	+G10+G11	+H10+H11
13								
14	Wt of aqueous ICP sample			g	21	21	17	16.5
15	Density of aqueous ICP sample			g/mL	1.1	1.1	1.05	1.05
16	Wt of solid ICP sample			g	1.2402	0.9469	0.5254	0.5173
17	Wt of total ICP sample			g	+E14+E16	+F14+F16	+G14+G16	+H14+H16
18								
19	*Conc of Fe in aqueous ICP sample*			mg/L	1.443	0.893	13.862	8.055
20	Conc of Fe in solid ICP sample			mg/kg	155469	153544	128622	53765
21	Wt of Fe in aqueous ICP sample			g	+E$14*E19*10^-6/E$15	+F$14*F19*10^-6/F$15	+G$14*G19*10^-6/G$15	+H$14*H19*10^-6/H$15
22	Wt of Fe in solid ICP sample			g	+E$16*E20*10^-6	+F$16*F20*10^-6	+G$16*G20*10^-6	+H$16*H20*10^-6
23	Wt of Fe in total ICP sample			g	+E21+E22	+F21+F22	+G21+G22	+H21+H22
24	Wt of Fe in product after NaOH			g	+E23*(E$12/E$17)	+F23*(F$12/F$17)	+G23*(G$12/G$17)	+H23*(H$12/H$17)
25	Wt of Fe in product after sampling			g	+E24	+F24	+G24	+H24
26	Wt of Fe in samples after hydrolysis			g	+E25*(E$9/E$10)	+F25*(F$9/F$10)	+G25*(G$9/G$10)	+H25*(H$9/H$10)
27	Wt of Fe in reactants			g	+E25+E26	+F25+F26	+G25+G26	+H25+H26
28	Fe as weight % of agent			%	100*(E27/E$7)	100*(F27/F$7)	100*(G27/G$7)	100*(H27/H$7)
29								
30	Conc of S in aqueous ICP sample			mg/L	4620	6760	6178	5958
31	Conc of S in solid ICP sample			mg/kg	164604	230882	140450	94708
32	Wt of S in aqueous ICP sample			g	+E$14*E30*10^-6/E$15	+F$14*F30*10^-6/F$15	+G$14*G30*10^-6/G$15	+H$14*H30*10^-6/H$15
33	Wt of S in solid ICP sample			g	+E$16*E31*10^-6	+F$16*F31*10^-6	+G$16*G31*10^-6	+H$16*H31*10^-6
34	Wt of S in total ICP sample			g	+E32+E33	+F32+F33	+G32+G33	+H32+H33
35	Wt of S in product after NaOH			g	+E34*(E$12/E$17)	+F34*(F$12/F$17)	+G34*(G$12/G$17)	+H34*(H$12/H$17)
36	Wt of S in product after sampling			g	+E35	+F35	+G35	+H35
37	Wt of S in samples after hydrolysis			g	+E36*(E$9/E$10)	+F36*(F$9/F$10)	+G36*(G$9/G$10)	+H36*(H$9/H$10)
38	Wt of S in reactants			g	+E36+E37	+F36+F37	+G36+G37	+H36+H37
39	S as weight % of agent			%	100*(E38/E$7)	100*(F38/F$7)	100*(G38/G$7)	100*(H38/H$7)

D-13 Test change to add two new subtests using HD spiked with chlorinated hydrocarbons.

FAX TRANSMITTAL # of pages ▶

To Marcia Middleton	From Cheryl Maggio
Dept./Agency	Phone #
Fax #	Fax #

NSN 7540-01-317-7368 5099-101 GENERAL SERVICES ADMINISTRATION

E FORM

n Signers

HONE: 273-1030

ATP
A3427-03
Document Number
CONTROLLED DOCUMENT

DATE: November 3, 1995

TEST PLAN: HD/NaOH and HD/Water Laboratory (MM-95-512) **SUBTEST:** New subtests

EVALUATION: The purpose of two new subtests is to determine the fate of certain chlorinated hydrocarbons that occur in one or more of the HD batches in the Ton Container Survey. These compounds are of concern in the ultimate disposal of the effluent from the HD hydrolysis because they are listed in the Resource Conservation and Recovery Act (RCRA) land disposal restrictions, which specify the maximum allowable concentrations of each in the final effluent.

The two new subtests are designed to: (a) determine the transfer (and possibly the reaction) of the following compounds during hydrolysis: 1,2-dichloroethane, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, and hexachloroethane; (b) determine whether the presence of these compounds affects the hydrolysis of HD; and (c) determine whether vinyl chloride (a possible hydrolysis product of 1,2-dichloroethane) is formed during the hydrolysis.

CHANGES: The two new subtests will use the same hydrolysis procedures as in the earlier subtests, but the HD will be spiked with amounts of the five chlorinated hydrocarbons that will give final concentrations in the HD that approximate the maximum concentration of each that was found in the Ton Container Survey. The spiked HD will be hydrolyzed in two replicate runs by the HD/NaOH process and in two replicate runs by the HD/water process.

In addition to following the course of the hydrolysis as in the earlier subtests, samples will be analyzed for volatiles to determine what happens to the five hydrocarbons. Further, the hydrolysate will be partially distilled to determine whether the chlorinated hydrocarbons can be isolated for potential separate treatment and disposal.

CONCURRENCE: Your concurrence with this change is requested. Please sign and return.

Product Manager, Alternative Technologies And Approaches — Date: 7 Nov 95

Cheryl Lyn Maggio
Test Director, PMAT&A — Date: 6 NOV 95

Joseph J. Novad
Team Leader, ERDEC — Date: 6 Nov 95

APPENDIX E
RERERENCES

APPENDIX E
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