NECDF Hydrolysate Disposal

PMATA Briefing for:
National Research Council
Committee On Review And Evaluation
Of The Army Chemical Stockpile Disposal Program
26 June 2003

Accelerated Newport Hydrolysate Disposal Status

U.S. ARMY CHEMICAL MATERIALS AGENCY

- Perma-fix Conducting Biodegradability Testing to Verify Treatment Process
  - Meet All Permit Requirements
  - Schedule 2 Compounds Present in Effluent at Concentrations Below 0.1 Percent by Weight.

- Demonstration Testing Completed 20 June

- Parsons has agreed to a Perma-Fix recommendation to use the Perma-Fix process for treating hydrolysate based on testing with old hydrolysate. This testing has commenced. Shipment of the fresh hydrolysate is on hold pending resolution of VX analytical method issues.

Accelerated Newport TSDF Treatment Process Options

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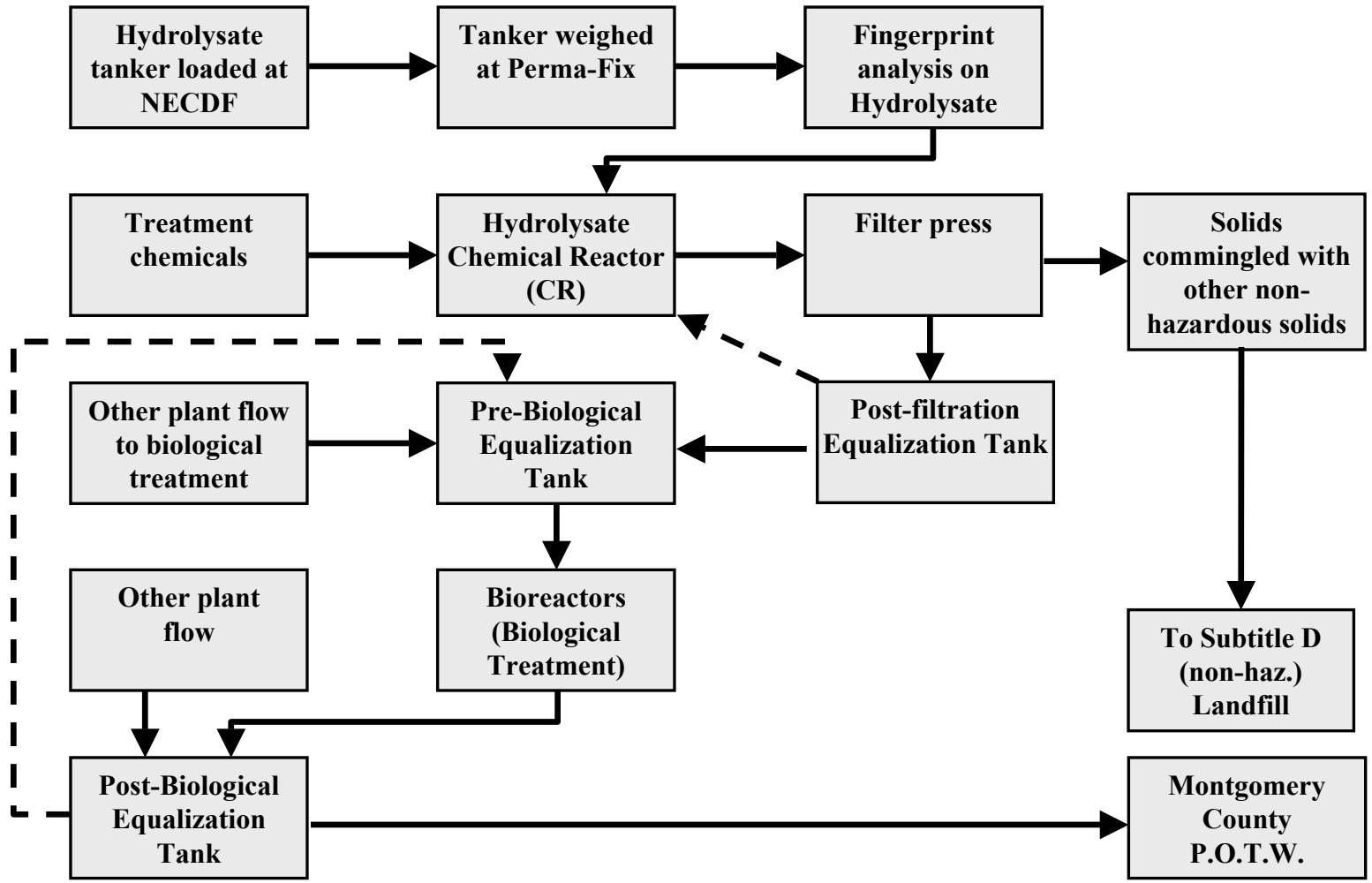
- **TENTATIVE PROCESS:**
  - **Peroxide Oxidation to Convert Thiolamine to Insoluble Disulfide (No Prior Ph Adjustment Used)**
  - **Oxidative destruction of Disulfides to Organic Sulfates and Phosphonates to Phosphates Using Fenton's Reagent.**
  - **Precipitated Phosphate (Ferric Phosphate) removed through filterpress Commingles With Other Plant Solids (e.g., waste activated sludge) and Disposed in Regional Class D Landfill**
  - **The filtrate commingles with other plant flow in the Pre-Biological Equalization Tank before being added to Bioreactors (Sequencing Batch Reactor) for Biological Treatment.**

Accelerated Newport Perma-Fix Full-Scale Process Flow Diagram



PMATA NRC JUN 2003

Accelerated Newport Hydrolysate Disposal Alternatives

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- On-site storage (storage of greater than 90-days requires hazardous waste/environmental permitting) until subsequent treatment and disposal in the Dayton area facility can be accomplished.

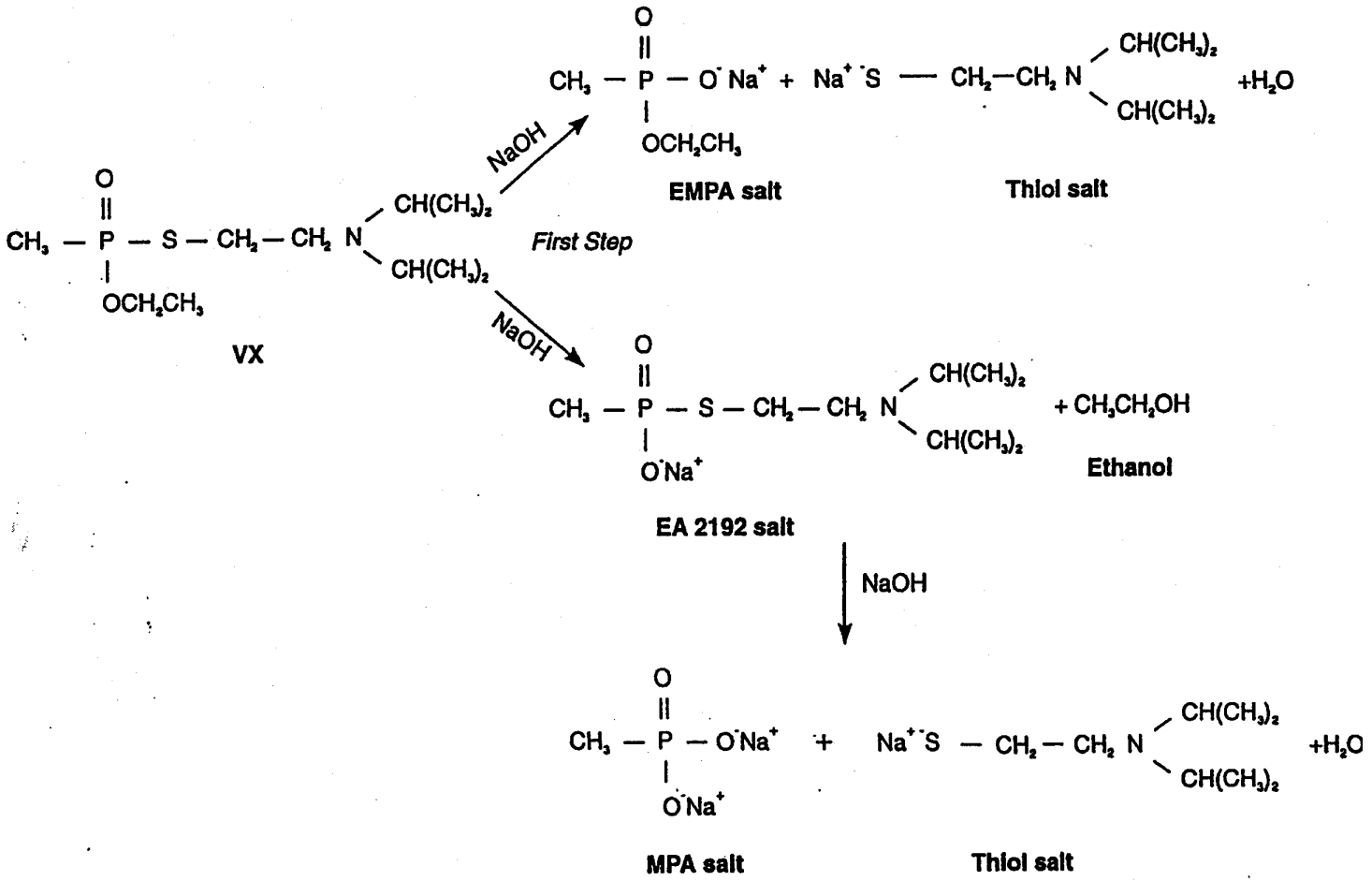
- Identification, selection, and use of an off-site treatment, storage, and disposal facility (in a different geographic area) to replace the Dayton area facility.

- On-site long-term storage (greater than 90-days) with subsequent on-site treatment. The on-site treatment alternatives include, but are not limited to, chemical and physical pre-treatment of the hydrolysate followed by on-site or off-site biological treatment; chemical and physical treatment; or super-critical water oxidation.

VX Analytical Method Issues at Less Than 20 ng/mL

VX Detection Above the MDL on the Saturn 2200

VX Caustic Neutralization



PMATA Criteria for Release of Hydrolysate

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Composite Sample:

- **VX MDL < 20 ng/mL**
- **[VX] < MDL (Non-Detect)**

Acidified Composite Sample:

[EA2192 Salt] < 20 µg/mL

Note: EA2192 was Measured to Confirm Thorough Mixing. Acidification Makes the Sample Homogeneous for NMR Analysis.

HAE and SPE

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Hexane Acid Extraction

- Combined Hydrolysate
- Hexane Extract
- 0.1 N HCl Wash (RSH Removal)
- 1.0 N HCl Wash (VX Removal)
- Adjust to pH 11
- Hexane Extraction
- GC-ITMS

Solid Phase Extraction

- Combined Hydrolysate
- Hexane Extract
- C2 Column
- Hexane Wash
- Methylene Chloride Elution
- GC-ITMS

CAMDS Results & NECDF Challenge

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CAMDS:

- HAE GC-ITMS Cleared 25 Batches of Hydrolysate for SCWO Testing
- SPE GC-ITMS Required to Clear the One Batch Produced from VX Stabilized with Diisopropyl Carbodiimide (DICDI)

NECDF

Question: Does the Stabilizer make a Difference?

In Additional Testing HAE has not Recovered VX or VX Spikes in DICDI-Stabilized VX Caustic Hydrolysates. So, SPE is preferred, but Residual VX or Interferant Seen using the Saturn 2200 does not Meet Clearance Criteria:

Non Detect = [VX] < MDL

Varian Saturn 4D and Saturn 2200

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Saturn 4D

- Instrument Introduced to the Project in 1996 and used at CAMDS in 1999-2000
- One Stage Isolation
  - 2 atomic mass units (amu)
  - Intially used a 1 amu window
- Chemical Ionization followed by electron impact in the ion trap

Saturn 2200

- Introduced in 2002
- Two Stage Isolation
  - 268 +/- 10 amu
  - 268 +/- 2 amu
- Chemical Ionization followed by electron impact in the ion trap

SPE AND HAE MDLs

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Table 20 Comparison of Saturn 2200 and Saturn 4D MDL Studies
(Performed on Unstabilized Hydrolysate HXVX03-31-03 that was heated on April 9, 2003)

Sample Preparation Procedure	Saturn 2200				Saturn 4D			
	Early April[1]		Late April		Early April[1]		Late April	
	MDL	Spike Level	MDL	Spike Level	MDL	Spike Level	MDL	Spike Level
SPE	48.9 ppb	56.8 ppb	11.9 ppb[4]	22.7 ppb	27 ppb	56.8 ppb	13.5ppb[4]	22.7 ppb
HAE	28.0 ppb	56.5 ppb	5.7 ppb[2]	NS	2.2 ppb	56.5 ppb	ND[3]	NS

Saturn 2200 Calibration Data

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Table 3. VX Calibration Performed on 03-28-03 Using the Saturn 2200 GC/ITMS (2-Step Isolation)

Calibration Curve For the Analysis of Samples

File Name	Std ID	VX Concentration ug/mL	128 ion Area	Calc. VX Conc. ug/mL	Difference %
XVX-032503-1-2.27ug-3-28-2003001	XVX-032503-1	2.27	341646	2.266	-0.18
XVX-032503-2-1.14ug-3-28-2003	XVX-032503-2	1.14	160297	1.163	2.02
XVX-032503-3-0.57ug-3-28-2003004	XVX-032503-3	0.568	69851	0.562	-1.06
XVX-032503-4-0.22ug-3-28-2003	XVX-032503-4	0.227	14399	0.172	-24.2
XVX-032503-5-0.11ug-3-28-2003	XVX-032503-5	0.114	2906	0.090	-21.1
XVX-032503-6-0.05ug-3-28-2003	XVX-032503-6	0.057	1174	0.077	35.1
XVX-032503-8-0.02ug-3-28-2003	XVX-032503-8	0.023	143	0.069	200.0
XVX-03503-7-0.01ug-3-28-2003	XVX-032503-7	0.011	ND	#VALUE!	#VALUE!
QC Checks					
XVX-032503-3-0.57ug-3-28-2003005	XVX-032503-3	0.568	62855	0.514	-9.5
XVX-032503-3-0.57ug-3-28-2003006	XVX-032503-3	0.568	51727	0.436	-23.2
Calibration Check Performed 04/01/03					
Pre SPE Analysis					
XVX-032503-3-0.57ug-4-1-2003003	XVX-032503-3	0.568	83152	0.653	15.0
XVX-032503-5-0.11ug-4-1-2003	XVX-032503-5	0.114	6025	0.112	-1.8
XVX-032503-5-0.11ug-4-1-2003001	XVX-032503-5	0.114	4649	0.102	-10.5
Post SPE / Pre HAE Analysis					
XVX-032503-3-0.57ug-4-1-2003004	XVX-032503-3	0.568	93102	0.720	26.8

Saturn 4D: Less Sensitivity?

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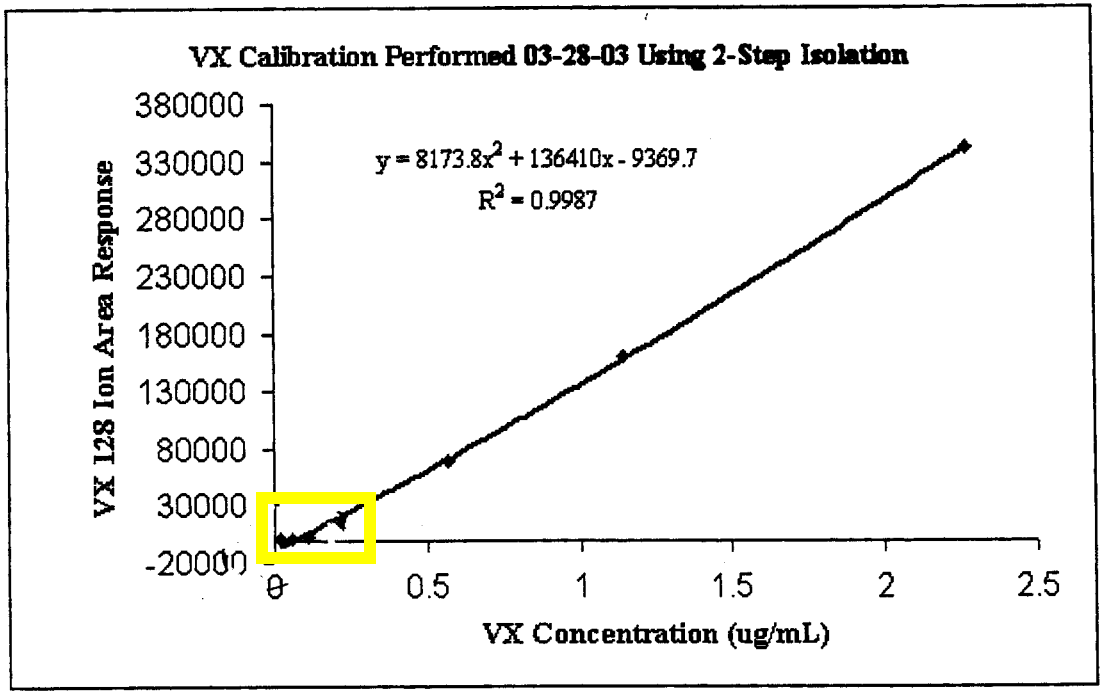
Table 6. VX Calibration Performed on 04-04-03 Using the Saturn 4D GC/ITMS

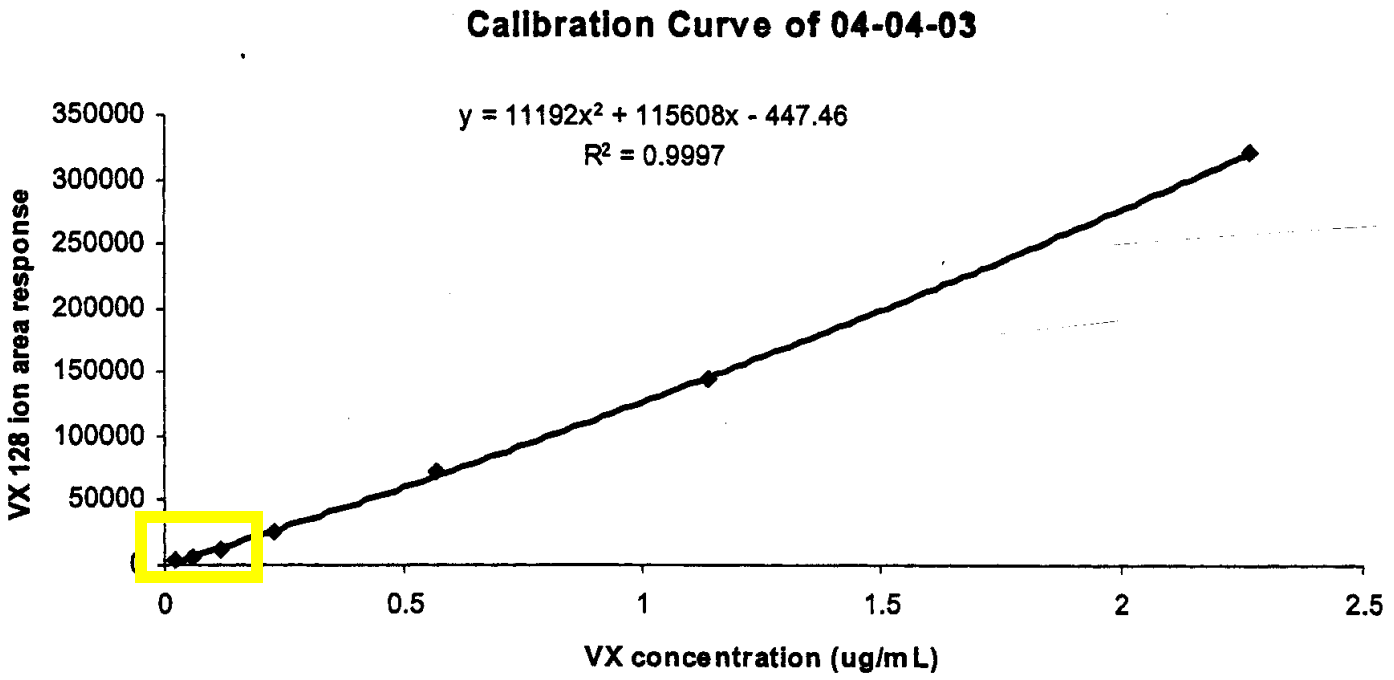
File Name	Std ID	VX Concentration ug/mL	128 ion Area	Cal. VX Conc. ug/mL	Difference %	Comment
04040306	XVX-032503-1	2.27	319967	2.27	0.00	
04040307	XVX-032503-2	1.14	143815	1.13	-0.88	
04040308	XVX-032503-3	0.568	72418	0.60	5.63	
04040309	XVX-032503-4	0.227	25381	0.219	-3.52	
04040310	XVX-032503-5	0.114	11458	0.102	-10.53	
04040311	XVX-032503-6	0.057	5948	0.055	-3.51	
04040312	XVX-032503-8	0.023	3033	0.030	30.43	
Continuing QC Checks						
Pre Sample Analysis						
04080301	XVX-032503-3	0.568	85481	0.696	22.54	QC Ck
04080302	XVX-032503-5	0.114	13019	0.115	0.88	QC Ck
Mid Sample Analysis						
04080311	XVX-032503-3	0.568	98547	0.795	39.96	QC Ck
04080312	XVX-032503-3	0.568	95126	0.769	35.39	QC Ck
Post Sample Analysis						
04080316	XVX-032503-3	0.568	99905	0.805	41.73	QC Ck
04080317	XVX-032503-3	0.568	94080	0.762	34.15	QC Ck
04080318	XVX-032503-5	0.114	13945	0.123	7.89	QC Ck

Regression Equation, Quadratic 2nd Order: $y = 11192x2 + 115608x - 447.46$; $R^2 = 0.9997$; Created on 04/04/03 See Logbook C31794 P.20

Saturn 2200 Calibration Curve



Saturn 4D


Calibration Curve of 04-04-03
y = 11192x² + 115608x - 447.46
R² = 0.9997
VX 128 ion area response
350000
300000
250000
200000
150000
100000
50000
0
0.5
1
1.5
2
2.5
VX concentration (ug/mL)

Saturn 2200:
Greater Sensitivity and Interferants?

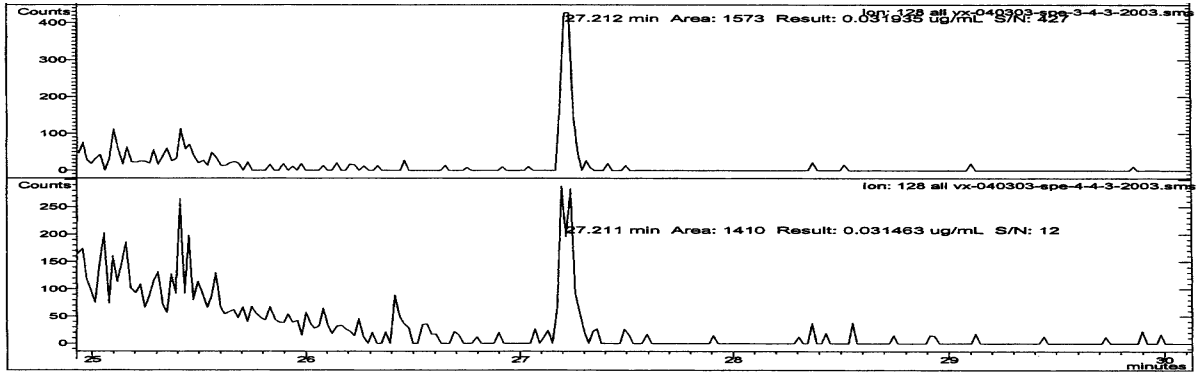


Figure 3. Saturn 2200 GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) Before Additional Heating; SPE MDL Samples Nos. 1 - 4; Unspiked

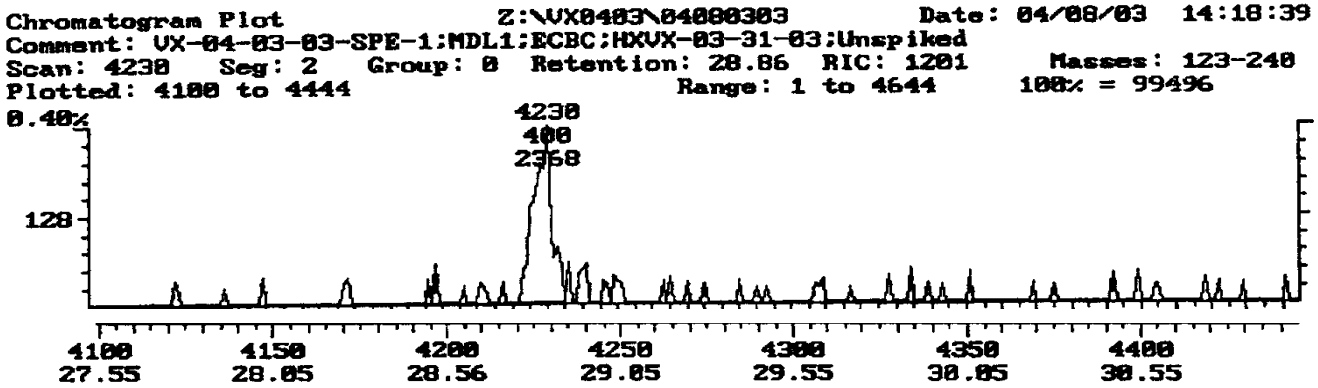


Figure 7. Saturn 4D GC/ITMS Chromatograms from ECBC Hydrolysate (Alion Lot No. HXVX-03-31-03) Prepared using Unstabilized VX. Before Additional Heating; SPE MDL Samples No. I Unspiked; Analyzed on April 8, 2003

Saturn 2200: After 3 Hr. Additional Heating Interferant?

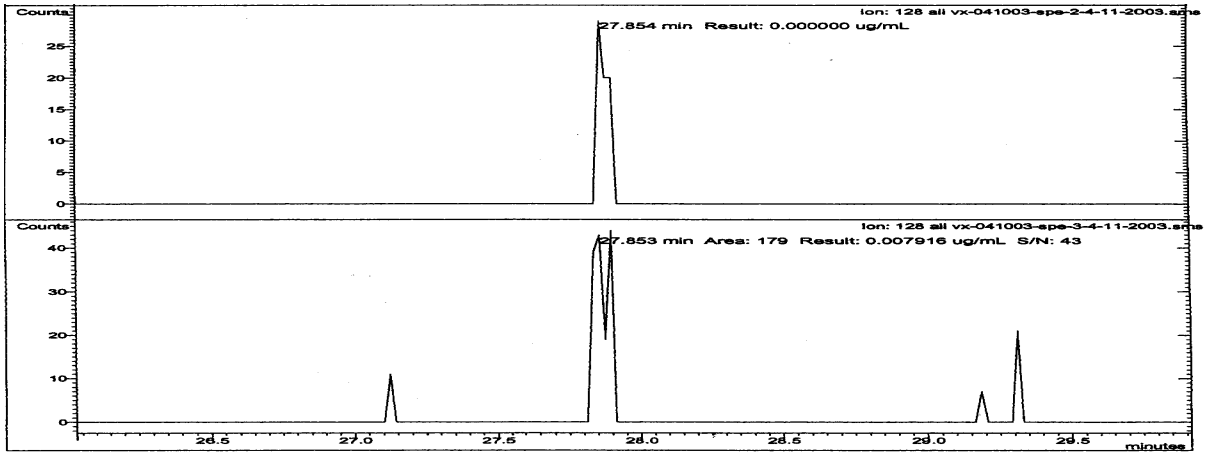


Figure 12. Saturn 2200 GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) After an Additional 3 Hours of Heating at ~90°C; SPE Unspiked MDL Samples Nos.1-3.

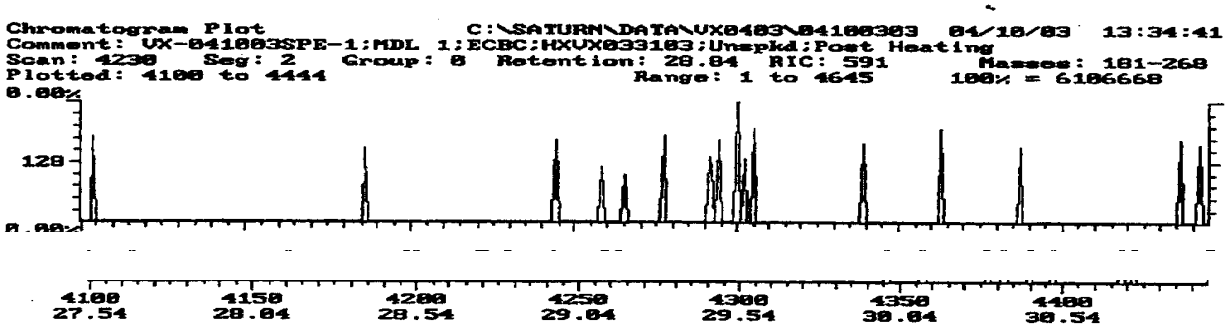


Figure 17. Saturn 4D GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) After Additional Heating. SPE MDL Samples Nos. 1 – 3; Unspiked

Saturn 2200: Previous Sample Spiked

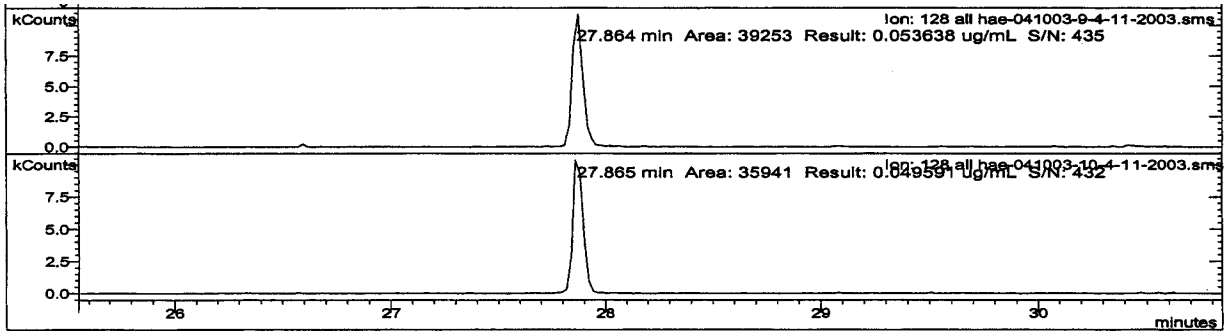


Figure 11. Saturn 2200 GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) After an Additional 3 Hours of Heating at ~90°C; HAE Spiked (56.5ppb) MDL Samples Nos. 4 -10.

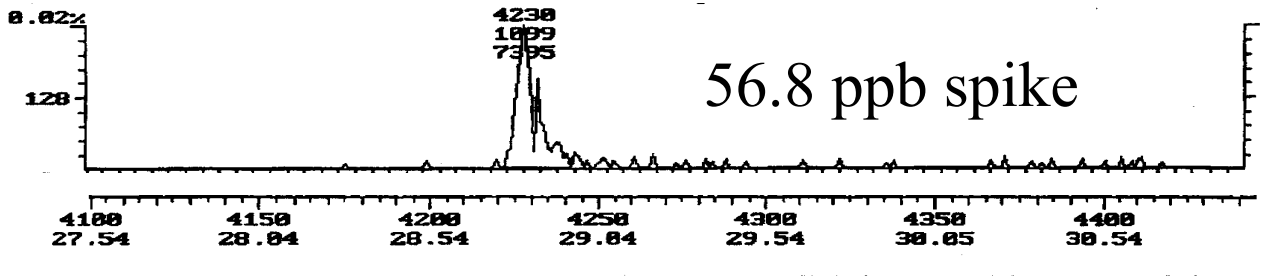


Figure 18. Saturn 4D GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) After Additional Heating; SPE MDL Samples Nos. 4 – 5; 56.8 ppb VX Spike

Varian Saturn 4D vs. Saturn 2200 GC-ITMS

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Questions:

1. Is the Saturn 2200 more Sensitive than the 4D?

- Yes
- MDLs determined for SPE and HAE do not appear to be significantly different
- MDLs on the Saturn 4D and the Saturn 2200 are not significantly different
- In DICDI stabilized VX Hydrolysate, HAE does not Work
- In DICID Stabilized VX Hydrolysate, Additional Heating does not appear to reduce the "VX residual"

2. Is an Interferant Present and Contributing to the Residual VX?

Yes

Further Questions?

- Does SPE Introduce an Interferent and or Participate in Agent Formation?
- Is VX Formed in the Organic Extraction Step?
- Is the Lack of a Static Mixer in Lab Scale Reactors a Problem?
- What about the DICDI Stabilized VX Hydrolysate?

Back Up Slides

Thanks to Contributors 1994 thru 2003

U.S. ARMY CHEMICAL MATERIALS AGENCY

- PM Alternative Technologies and Approaches (PMATA)
- Edgewood Chemical and Biological Center (ECBC)
- PM Assembled Chemical Weapons Assessment (ACWA)
- Chemical Agent Munitions Disposal System (CAMDS)
- SAIC
- ALION (formerly IITRI)
- SwRI
- NECDF – Parsons
- Stone and Webster – Shaw Group

Liquid Back Extraction vs. Solid Phase Extraction

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Liquid Back Extraction

- MDL < 20 ppb
- Unspiked Hydrolysate [VX] < MDL
- No Background Correction Required
- Low Recovery (10-40%)
- No VX Formation in Extract Observed

Solid Phase Extraction

- MDL < 20 ppb
- Unspiked Hydrolysate [VX] > 20 ppb
- Correction for recovery reduces [VX] to < 20 ppb
- Recovery (40 to 150%)
- Residual [VX] > 20 ppb suggestive of VX Formation in Extract

Hexane-Acid-Hexane Extraction Pre-CAMDS MDL Results

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IITRI

Run 1

- Spiked at 100 ppb
- MDL = 24 ppb
- Unspiked Hydrolysate Triplicates all < MDL

Run 2

- Spiked at 100 ppb
- "MDL" = 14 ppb
  - QC Failure-Check Standard >25%
- Unspiked Hydrolysate Triplicates all < MDL

Run 3

- Spiked at 61 ppb
- MDL = 19 ppb
- Unspiked Hydrolysate Triplicates all < MDL

ECBC

One Run

- Spiked at 60 ppb
- MDL 25 ppb
- Unspiked Hydrolysate Triplicates [VX] < MDL

Method Review Background

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- **Chloroform Extraction-Syringe Spike GC/ITMS Method was Selected from Protocols used by ECBC to Certify Liquid Agent Non-Detect in Decontaminated Liquids for Shipment to a TSDF**
- **During Neutralization Studies in February 1998 Introduction of VX from a "dead leg" Resulted in Toxic Levels of VX in Samples Sent for Toxicology Studies.**
- **This Event Prompted Detailed Process and Analytical Method Review**

Saturn 2200 HAE Before Heating

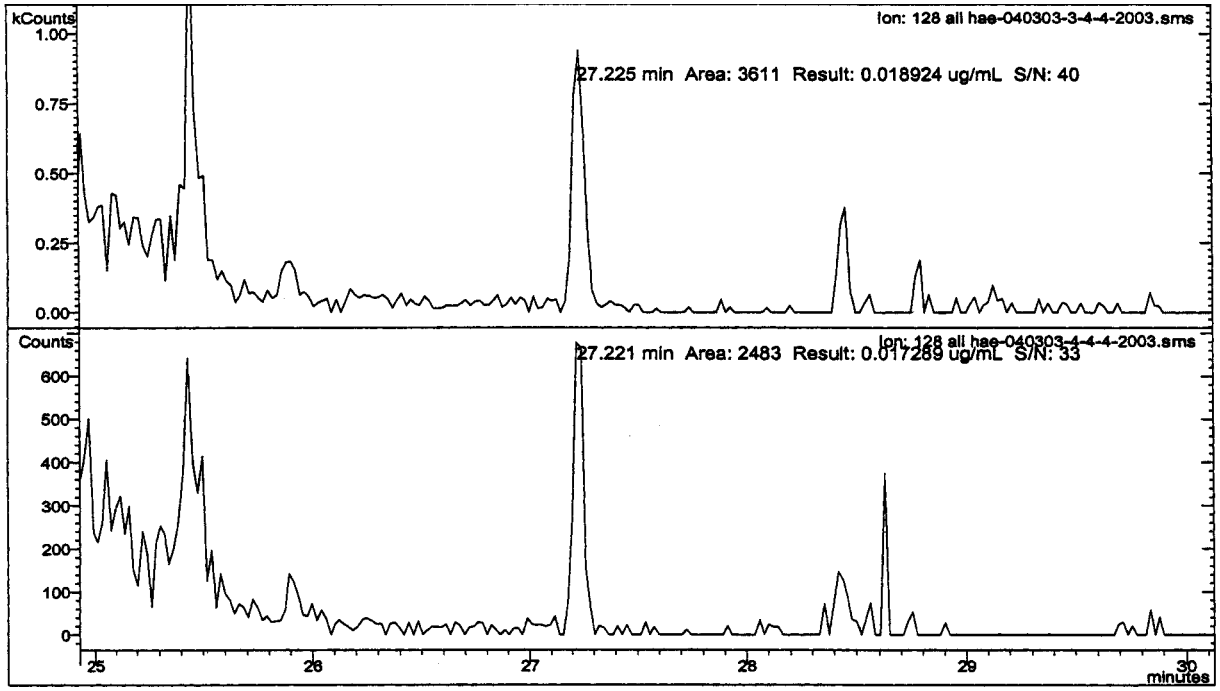

Figure 1. Saturn 2200 GC/ITMS Chromatograms from ECBC Hydrolysate Prepared using Unstabilized VX (Alion No. HXVX-03-31-03) Before Additional Heating;
HAE MDL Samples Nos. 1 - 4; Unspiked

Saturn 4D HAE – No Stabilizer

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Table 9. HAE Procedure Performed 04-01-03 using ECBC-No Stabilizer Hydrolysate (Alion No. HXVX-03-31-03)

Samples analyzed using the Saturn 4D

HAE Samples Prepared on 4-1-03 and reanalyzed on 4-08-03

File Name	Sample ID	VX Spike, ug/mL	128 ion Area	VX Concentration (ug/mL)		Recovery, %
				Extract	Sample	
04080313	HAE-040103-1	NS	ND	#VALUE!	#VALUE!	NA
04080314	HAE-040103-2	NS	ND	#VALUE!	#VALUE!	NA
04080315	HAE-040103-3	NS	ND	#VALUE!	#VALUE!	NA
		Average	#DIV/0!	#VALUE!	#VALUE!	
		Std Dev	#DIV/0!	#VALUE!	#VALUE!	
		RSD, %	#DIV/0!	#VALUE!	#VALUE!	

NS = Not Spiked
ND = None Detected
NA = Not Applicable
BLS= Ion 128 area count is below lowest standard (0.023mg/mL)
Regression Equation, Quadratic 2nd Order: $y = 11192x2 + 115608x - 447.46$; $R^2 = 0.9997$; Created on 04/04/03 See Log C31794 P.20

Saturn 4D SPE – No Stabilizer

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Table 7. Results of SPE Procedure Performed 04-01-03 using ECBC-No Stabilizer Hydrolysate (Alion Lot No. HXVX-03-31-03)

Samples analyzed using the Saturn 4D

Samples prepared on 04/1/03 were reanalyzed on April 7, 2003

File Name	Sample ID	VX Spike, ug/mL	128 ion Area	VX Concentration (ug/mL)		Recovery, %
				Extract	Sample	
04070303	VX-040103-SPE-1	NS	9541	0.086	0.034	NA
04070304	VX-040103-SPE-2	NS	6256	0.058	0.023	NA
04070305	VX-040103-SPE-3	NS	ND	#VALUE!	#VALUE!	NA
		Average	7899	#VALUE!	#VALUE!	
		Std Dev	2323	#VALUE!	#VALUE!	
		RSD, %	29.4	#VALUE!	#VALUE!	

NS = Not Spiked

ND = None Detected

NA = Not Applicable

BLS= Ion 128 area count is below lowest standard (0.057mg/mL)

Regression Equation, Quadratic 2nd Order: $y = 11192x2 + 115608x - 447.46$; $R^2 = 0.9997$; Created on 04/04/03 See Log C31794 P.20

History of Low Level VX Analysis of Hydrolysate (1994 - 2000)

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Scale	Method	Detection Limits
Laboratory Glass Reactor < 2 Liters	NMR	1 - 20 ppm
Bench - 2 Liters Mettler Calorimeter	HPLC-MS-MS	100 ppb
Bench - 114 L Reactor - 12 L Mettler	Chloroform Extraction GC-ITMS	80-200 ppb DL
CAMDS - 100 Gallon Reactor	Hexane - Acid Hexane and C2	Less Than 20 ppb

Agent Formation in Methylene Chloride Extracts when pH is Adjusted

U.S. ARMY CHEMICAL MATERIALS AGENCY

- **ECBC Reported (1996) Formation of VX in Methylene Chloride Extracts of VX Caustic Hydrolysate when the Hydrolysate pH is reduced below pH 11.**

- **Residual VX is Found in Organic Extracts after Hydrolysate pH is Adjusted. Agent was Observed by NMR in the Extract, but not in the pH Adjusted Hydrolysate.**

Method Review Results

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PMATA adopted criteria from 40 CFR Part 136 Appendix B (Method Detection Limit) as a basis for future analytical method development

Saturn 2200

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Table 1. Analysis of VX in Unspiked Hydrolysate received 3-31-03, Alion Lot No HXVX03-31-03 (analyzed by the Saturn 2200 GC/ITMS)		
	HAE[1] Results, ppb	SPE[2] Results, ppb
Sample 1	31	31.4
Sample 2	28	30.2
Sample 3	27	31.6
Average	28.7	31.1
SD	2.1	0.7

[1] HAE: Hexane Acid Extraction procedure as per SOP C-Anal-100-05 (See appendix pg. 55-93).

[2] SPE: Solid Phase Extraction as per SOP C-Anal-108-02 (See appendix pg. 94-129).

Saturn 4D

U.S. ARMY CHEMICAL MATERIALS AGENCY

Table 2. Analysis of VX in Unspiked Hydrolysate received 3-31-03, Alion Lot No HXVX03-31-03 (analyzed by the Saturn 4D GC/ITMS)		
	HAE Results, ppb	SPE Results, ppb
Sample 1	Not Detected (ND)	34
Sample 2	ND	23
Sample 3	ND	ND
Average		
SD		

Samples were analyzed using the Saturn 4D on April 1, 7 and 8. The results of April 1 analysis were all non-detects for both the SPE and the HAE samples. Assessment of the calibration check standards indicated a drop in sensitivity. The column, liner and septa were replaced and the instrument was recalibrated. The HAE samples were reanalyzed on April 7 and 8. On both days the results was non-detect for VX. The SPE samples were re-analyzed on April 7 and those results are summarized in Table 2 above. Calibration data and sample calculations are shown in the following tables. Chromatograms from the three days are presented on appendix pages (See appendix pg. 159-205).

Carbodiimide Stabilizers

- Dicyclohexyl Carbodiimide (DCCDI)
- Diisopropyl Carbodiimide (DICDI)