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CHARACTERIZATION AND NEUTRALIZATION OF RECOVERED LEWISITE MUNITIONS

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This report summarizes efforts to characterize the lewisite contained in recovered munitions and validate a neutralization chemistry for lewisite fill materiel. The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found to be effective in destroying the lewisite. In lab-scale and full-scale Explosive Destruction System testing, the aqueous permanganate consistently produced terminal neutralents that had residual lewisite levels well below the treatment goal of 50 mg/L (ppm). The reaction products included inorganic pentavalent arsenate and various pentavalent organo-arsenicals. Solid manganese dioxide was also produced during the reaction and was successfully managed in the full-scale Explosive Destruction System testing.

15. SUBJECT TERMS

Lewisite	4.2 inch mortar	Neutralization	Permanganate
Arsenic	Emergency Destruction System	Oxidation	L2
EDS	105 mm round	L1	L3

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EXECUTIVE SUMMARY

This report summarizes efforts to characterize and neutralize lewisite fills contained in recovered munitions. The data generated during this study will be used to support design, systemization, and operation of a non-stockpile demilitarization process for the disposal of lewisite containing munitions. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at various locations.

In support of the primary focus of this effort, an analytical method for the quantitative multi-residue analysis of neutralents was developed, optimized, and validated. The method was validated using a method detection limit approach, with method detection limits ranging from 0.01 to 0.04 mg/L (ppm), depending on the analyte. Precision and accuracy experiments were performed at spike levels of 0.05 and 0.10 mg/L (ppm) in a surrogate matrix, as the actual neutralent was too reactive. The overall precision (as percent relative standard deviation) ranged from 2.4 to 13.7 %, depending on the analyte. The overall accuracy (as percent recovery) ranged from 66 to 110 %, depending on the analyte. The method was further validated when two independent laboratories were able to implement the method, and certified performance using their own validation protocols.

The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found to be effective in destroying the lewisite fills found in recovered munitions. In lab-scale and full-scale Explosive Destruction System testing, the aqueous permanganate consistently produced terminal neutralents that had residual lewisite levels well below the treatment goal of 50 mg/L (ppm). The reaction products included inorganic pentavalent arsenate and various pentavalent organo-arsenicals. Solid manganese dioxide was also produced during the reaction, and was successfully managed in the full-scale Explosive Destruction System testing.

The selected neutralization reagent is commercially available in bulk and is stable in storage. The reagent is aqueous based and non-flammable. However, the reagent is a strong oxidizer, and appropriate procedures must be followed when working with this reagent. The reagent is compatible with a wide range of stainless steels and was also found to be compatible with ethylene propylene diene monomer, which is used in the Explosive Destruction System.

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PREFACE

The work described in this report was authorized under Contract No. DAAD13-03-D-0017. This work was started in July 2004 and completed in April 2005.

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This work would not have been possible without the efforts of CBARR, and the authors gratefully acknowledge CBARR for obtaining lewisite samples from the munitions and operating the Emergency Destruction System (EDS) during full-scale testing.

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CONTENTS

FIGURES

TABLES

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CHARACTERIZATION AND NEUTRALIZATION OF RECOVERED LEWISITE MUNITIONS

1. INTRODUCTION

1.1 Background.

The U.S. Army has the mission to provide centralized management and direction to the Department of Defense (DoD) for the safe destruction of all U.S. non-stockpile chemical materiel (NSCM) as defined in Public Law 102-484, 23 October 1992. Destruction of NSCM, including recovered chemical warfare materiel (RCWM), will be in accordance with federal laws, policies, regulations, and directives, as well as applicable state and local laws and regulations. The Army is the DoD focal point for the coordination of all matters relating to NSCM destruction. This is accomplished by developing, constructing, fielding, and supporting the necessary capabilities and materiel used to characterize, contain, transport, store, treat, and dispose of NSCM, both for routine and emergency response scenarios.

RCWM consist of older chemical munitions that have been recovered outside the controlled chemical stockpile. Historically, upon discovery of chemical warfare materiel (CWM), explosive ordnance disposal technicians would identify and assess the condition of the munition and determine whether the ordnance was filled with toxic chemicals and if it was safe for transportation and storage. Chemical munitions that were determined to be safe were overpacked (placed into a container with packing material as appropriate) and stored onsite or transported by the U.S. Army Technical Escort Unit (now known as the 22nd Chemical Battalion) to an appropriate chemical storage facility. Those RCWM items that could not be transported or stored due to unacceptable risks were destroyed onsite using emergency destruction procedures.

The U.S. Army Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) is responsible for the destruction of several categories of chemical warfare materiel in a safe, cost effective, environmentally sound manner and in compliance with the Chemical Weapons Convention. A variety of chemical warfare agents (CWAs) and other chemicals have been identified as possible fills in recovered munitions,[1,2] but the focus of this effort was on the neutralization of lewisite fills. The potential arsenic-containing chemicals found in lewisite fills include dichloro(2-chlorovinyl)arsine (L1), bis(2-chlorovinyl)chloroarsine (L2), tris(2-chlorovinyl)arsine (L3), and arsenic trichloride. The arsenic trichloride, while not a chemical warfare agent, is a chemical used in the synthesis of lewisite.[3] Selected properties of the potential arsenic-containing chemicals are summarized in Table 1, and the structures are illustrated in Figure 1.

Two lewisite munitions in storage at Dugway Proving Ground (DPG) were individually containerized using Department of Transportation and U.S. Army approved containers, and transferred from DPG to Edgewood Chemical and Biological Center (ECBC), located at Aberdeen Proving Ground, MD. Samples of each fill were then transported to ECBC laboratories for characterization. Photographs of the two munitions are illustrated in Figures 2 and 3.

Table 1. Select Properties of Possible Arsenic-Containing Chemicals Contained in Lewisite. The data was collected from a variety of sources.[3-6]

Property	Arsenic-Containing Chemicals			
	L1	L2	L3	Arsenic Trichloride
Chemical Formula	$C_2H_2AsCl_3$	$C_4H_4AsCl_3$	$C_6H_6AsCl_3$	$AsCl_3$
Molecular Weight	207.35	233.36	259.39	181.28
CAS Number	541-25-3	40334-69-8	40334-70-1	7784-34-1
Boiling Point (°C)	190	230	260	130
Vapor Pressure (mm Hg)	0.394 @ 20°C	NDA[b]	NDA[b]	10 @ 23.5°C
Volatility (mg/m^3)	4,480 @ 20°C	NDA[b]	NDA[b]	NDA[b]
Vapor Density[a]	7.1	NDA[b]	NDA[b]	6.3
Liquid Density	1.89 @ 20°C	1.69 @ 20°C	1.58 @ 20°C	2.15

a. Relative to air, with air being one.
b. No data available.

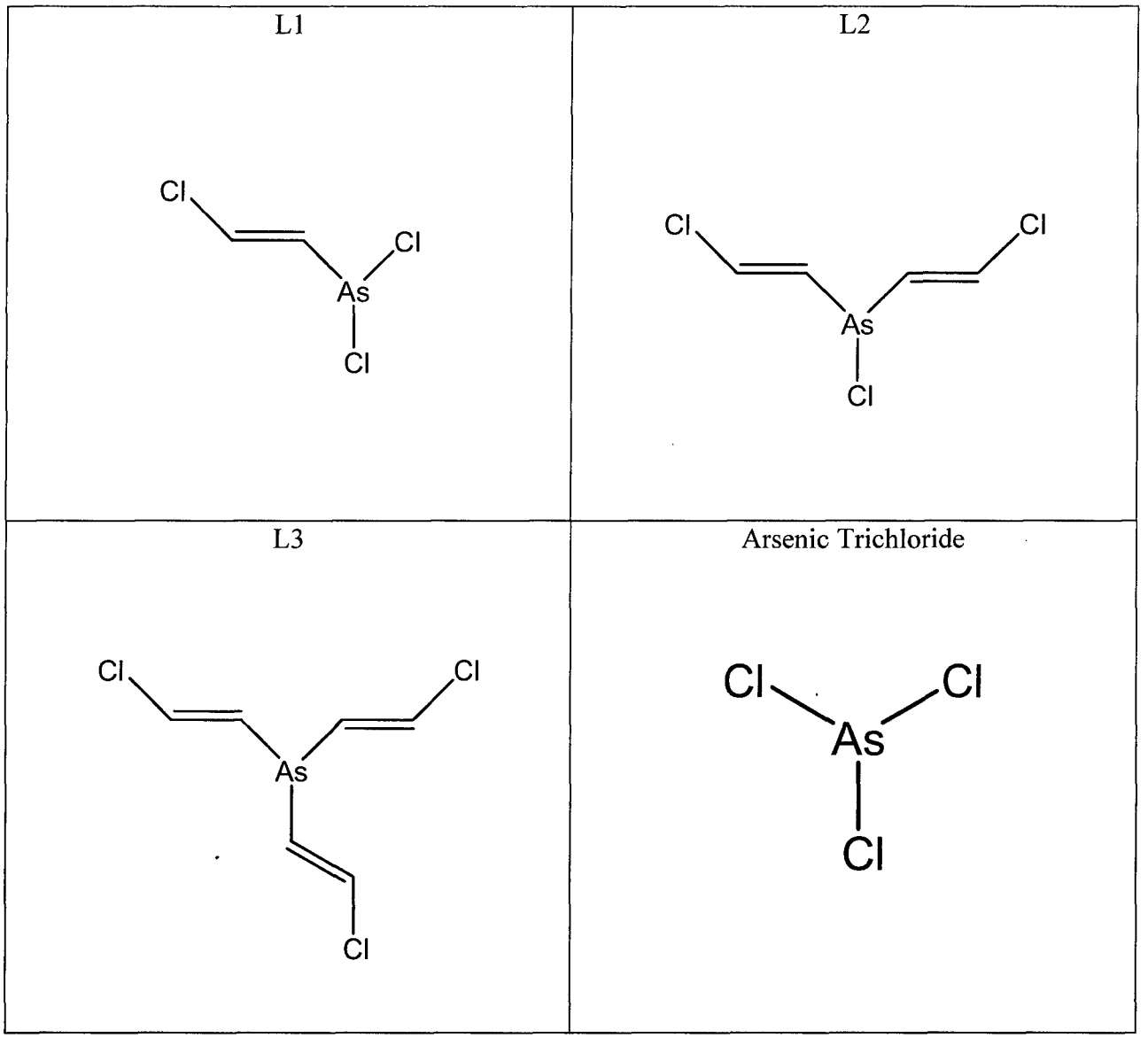

Figure 1. Structures of the Primary Arsenic-Containing Chemicals Anticipated in the Lewisite Fill Materiels.

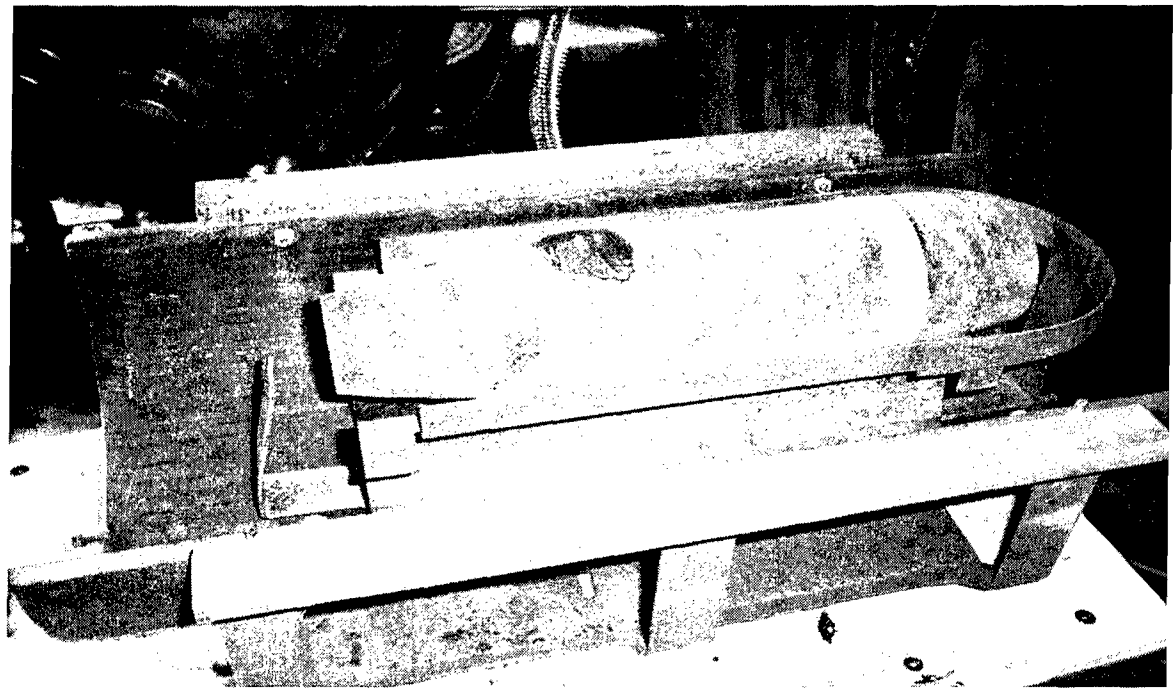

Figure 2. Photograph of the 105 mm Round (DPG-94-055) Just Prior to Being Loaded into the EDS.[7]

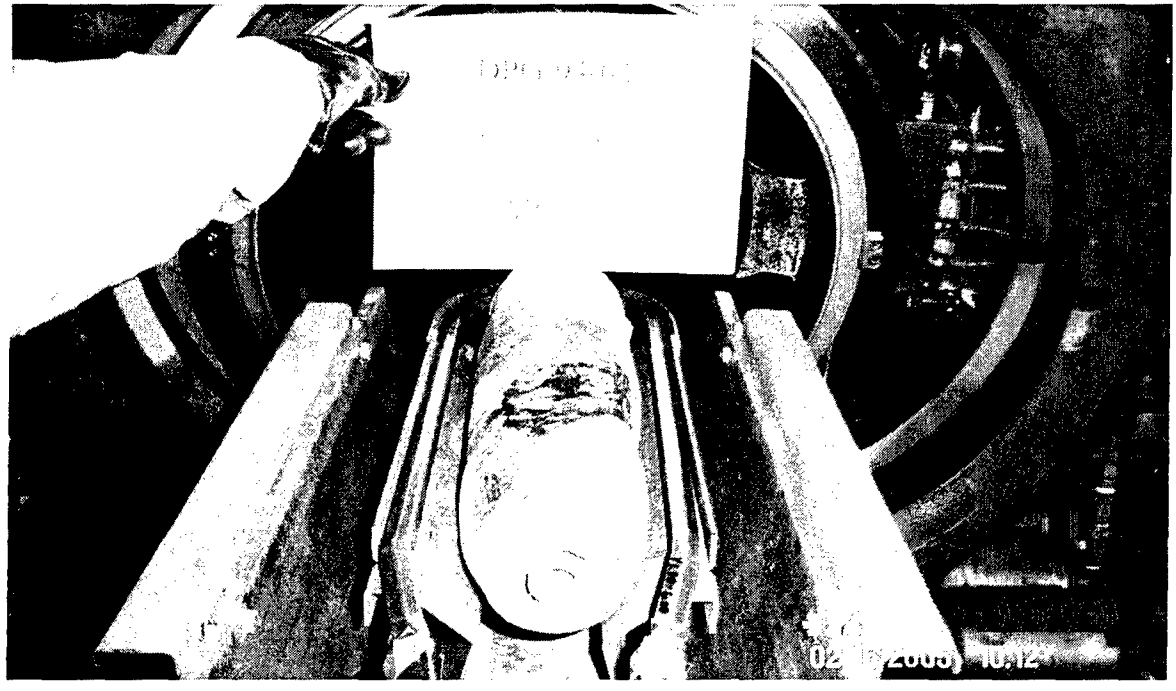

Figure 3. Photograph of the 4.2 Inch Mortar Round (DPG-94-028) Just Prior to Being Loaded into the EDS.[7]

1.2 Study Objectives.

The primary purpose of this testing was to demonstrate and validate a neutralization chemistry for the lewisite fills contained in recovered munitions. The data generated from the present study will be used to support design, systemization and operation of a non-stockpile demilitarization process for the destruction of recovered lewisite munitions. Presently, this includes the use of PMNSCM's Explosive Destruction System (EDS), a transportable stainless steel vessel used for the enclosed detonation and chemical neutralization of RCWM. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at various locations. A secondary objective of this work was to characterize lewisite fill materiels recovered from actual munitions.

A reagent, if it is to be used in demilitarization operations, should have the following characteristics:

- The reagent should be non-flammable, relatively non-toxic, compatible with standard reactor materials of construction, and commercially available in bulk.

- The reagent should be stable, and have a reasonable shelf-life.

- The reagent must maintain effectiveness in the presence of explosive residues, and large amounts of metallic copper and iron.

- The reagent must be capable of meeting the required OPCW chemical agent treatment goal of 1,000 mg/L, and should meet the desired CMA treatment goal of 50 mg/L.

- The treatment goals must be met under relatively mild reaction temperatures ($\leq$ 100 °C), short reaction times (5-6 hr), and high loadings of agent to reagent.

2. EXPERIMENTAL PROCEDURES

This section describes the in-house experimental procedures and analytical methods utilized during this project. Described are incremental reaction studies and related experimental activities used to select and evaluate neutralization chemistries against arsenal chemical fills. Analyses performed using standard methods and methods published in the open literature are referenced in the results section of this report.

2.1 Micro-Scale Reaction Studies.

The approach of screening reaction chemistries and reaction conditions on a micro-scale was used to quickly eliminate chemistries from consideration, and obtain information on the most efficacious reaction conditions. Additionally, the use of this micro-scale approach drastically reduced the use of hazardous chemicals, minimizing the danger to personnel

performing the reactions. The volume of waste was also drastically reduced by using this micro-scale approach. While conditions were varied depending on the experiment, the basic procedure was the same throughout this study. In a typical experiment, 500 μL of reagent was added to a 15 mL glass vial, a Teflon® (TFE) coated stir flea (8 X 1.5 mm) was added, then an aliquot of the agent feedstock was added. The vial was then capped, and placed on a hot plate with magnetic stirring capabilities. In most cases, the contents of the vial were vigorously stirred during the reaction. At an appropriate time, the vials were removed from the hot plate, and analyzed.

In addition to the time and cost savings realized using this approach, the residual agent data was not subjected to sampling issues, particularly when the final neutralent was heterogeneous. This is because the extraction/derivatization was carried out in the same vial the reaction was performed in. It is well documented that trace level organics may adsorb to glass surfaces/solids, requiring the sample bottle to be extracted with organic solvent to obtain reliable results.[8,9]

2.2 Small-Scale Lab Reaction Studies.

The small-scale reactions were carried out in a four neck, 250 mL round bottom glass flask, equipped with an air-cooled condenser and TFE coated thermocouple. Stirring was accomplished by use of a TFE coated stir bar, and a magnetic stir plate, with the reaction stirred at moderate speed throughout the reaction. Heating was accomplished by the use of an electric heating mantle, with temperature control maintained by using a J-KEM temperature controller. Throughout all steps of the reaction, N2 gas was purged through the reactor headspace at a rate of 1-2 mL/min, and was vented through the condenser. The N2 gas was then passed through two caustic-filled impingers, connected in series to the condenser. Each impinger contained 3 mL of 0.1N NaOH(aq).

In a typical run, 100 mL of reagent was added to the reactor, stirring and N_2 purge started, and the temperature adjusted to the desired temperature. If the run was to have added copper and iron to simulate metals present within the EDS reaction vessel, a piece of copper (1/8 inch copper tubing, approximately 0.5 g) and common steel (wire, approximately 5 g) were suspended in the reagent by means of a Teflon string. Once the temperature stabilized, the arsenal was quickly added as a single bolus, and the reaction was allowed to proceed. Neutralent samples were removed from the reactor at various times after the arsinol was added. The neutralent time points were removed from the reactor using a pipet, with the pipet tip maintained approximately ¾ of an inch below the liquid surface. Impinger samples were only collected after the run was terminated.

2.3 Standards.

The L1 and L2 were recovered from munitions grade lewisite, using vacuum distillation. The L3 was synthesized in-house using an established procedure,[10] which involved reacting acetylene with arsenic trichloride, then *immediately* isolating the L3 by vacuum distillation. The purities of L1, L2, and L3 were determined using an established ^{13}C-NMR technique,[11] and were found to be 92.7 wt% , 84.5 wt%, and 92.6 wt%, respectively. The 2-chlorovinyl arsonic acid (CVAOA) and bis(2-chlorovinyl)arsenic acid (BCVAOA) were

synthesized using an established procedure,[3] which involved separately refluxing L1 and L2 in 10% HNO_3 for three hr. After cooling to ice bath temperature, the crude crystals of CVAOA and BCVAOA were isolated by vacuum filtration, and further purified by re-crystallizing from methanol/water. The purity of the CVAOA and BCVAOA were determined using an established quantitative ^{13}C-NMR technique,[11] and were found to be 93.4 wt% and 96.8 wt%, respectively. The stock solutions of 2-chlorovinyl arsonous acid (CVAA) and bis(2-chlorovinyl)arsinous acid (BCVAA) were prepared by separately mixing a known amount of L1 or L2 in 0.1% aqueous HCl, mixing, and storing under reducing conditions. All other standards used in this project were obtained from commercial sources, and were of the highest available purity.

2.4 Residual Agent Method.

This section describes the experiments conducted during the development, optimization, and validation of a method for the multi-residue analysis of permanganate based neutralent samples. This method was validated for the simultaneous determination of trace levels of HD, HN-3, DA, PD, TPA, L1, L2, and L3, and is based on previous work.[12,13] The method, for arsenicals only, was successfully validated by two other laboratories.[14,*] A detailed method description, in Standard Operating Procedure (SOP) format,[15] is attached as the Appendix.

2.4.1 Optimization Experiments.

The injection temperature was systematically evaluated, to maximize analyte transfer through the injector, while minimizing analyte degradation. A mixed standard solution containing 5,000 µg/L of each target analyte was prepared, and split into 5 GC vials. Using a random number table,[16] the order of injector temperature was randomized, with injection temperatures of 250, 255, 260, 265, and 270 °C evaluated. Three injections were made at each injector temperature, with one vial used per temperature, and wash vials were used between treatments. The injector temperature was allowed to equilibrate for 3 hr before making any injections. In general, there was a linear upward trend in peak area from 250 through 265 °C for each analyte. In the temperature range of 265 through 270 °C, peak areas for some analytes decreased, indicating degradation, while others stabilized, indicating maximum throughput was achieved. An injection temperature of 265 °C was selected as the optimum temperature; selected data is illustrated in Figure 4.

Previous studies using gas chromatographic techniques to analyze phenyl-arsenicals noted the potential for carry-over during the analysis of these chemicals.[17,18] An experiment was conducted to evaluate both the efficacy of various syringe wash solutions, and the efficacy of injecting 2.5% ethanethiol solution as a system wash vial. A mixed standard was prepared at a concentration of 50 mg/L for each analyte (twice the concentration of the highest anticipated working standard), and was then split between two GC vials. The experiment

* Battelle Memorial Institute, June 2003, subject: Chemical Oxidation of Non-Stockpile Chemical Materiel Neutralents Laboratory-Scale Test Report – Phase IC: German Traktor Rocket Fill Material, unpublished data December 2006.

consisted of making three injections of the mixed standard, followed by three injections of trimethylpentane, then followed by nine injections of 2.5% ethanethiol in trimethylpentane. This experimental sequence was repeated twice, with the first sequence using 2-propanol as the first syringe wash solvent, followed by methanol as the second syringe wash solvent. The second experiment utilized 1-methyl-2-pyrrolidinole (NMP) as the first syringe wash solvent, followed by methanol as the second syringe wash solvent.

In all cases, there was no carry-over observed for HD, HN-3, L1, L2, or L3 in any of the experimental treatments. There was carry-over observed for DA, PD, and TPA, with no difference between syringe wash solvent treatments. In the worst case, the peak areas observed in the first trimethylpentane wash injection were <0.01% of the average standard peak area response. There was also carry-over observed for DA, PD, and TPA during the injection sequence of 2.5% ethanethiol in trimethylpentane. In the worst case, the peak areas observed in the first injection were <0.5% of the average standard peak area response. The carry-over of DA, PD, and PD as a function of wash injections is illustrated in Figure 5. The results of this experiment resulted in the use of 2-propanol/methanol as syringe wash solvents, and the periodic injection of 2.5% ethanethiol in trimethylpentane during an analytical sequence.

The analytical method utilizes ethanethiol to derivatize some of the arsenical species, and there was concern the thiol could reduce the pentavalent organo-arsenical reaction products (not detected by the GC method) to the trivalent form, resulting in false positive results for DA and PD. Individual standards of PD (As^{+3}), phenylarsine oxide (As^{+3}), and phenylarsonic acid (As^{+5}) were prepared in concentration from 5.40 to 268 μM (corresponds to 1 to 50 mg/L), and analyzed using the method described in the Appendix. The data are illustrated in Figure 6, and demonstrate, under the analytical conditions employed, the ethanethiol is not reducing the pentavalent phenylarsonic acid. The phenylarsonic acid was analyzed using the capillary electrophoresis technique described in Section 2.5, and found to contain traces of phenylarsine oxide. The impurity of phenylarsine oxide in the phenylarsonic acid accounts for the trivalent form detected when the phenylarsonic acid standards were analyzed. Another experiment was conducted to examine whether the solids generated during the permanganate neutralization of arsenicals could facilitate reduction of phenylarsonic acid to the trivalent form. Approximately 50 mg of sludge isolated from the reaction of lewisite with permanganate was added to a vial, and the phenylarsonic acid experiment described above was repeated. In all cases, there was no increase in the detection of trivalent species. This data suggests the solids encountered in actual reactor runs will not facilitate the reduction of reaction products, under the analytical conditions employed.

2.4.2 Calibration Model.

The external calibration model was established by preparation and analysis of a mixed set of standards, in accordance with the procedures contained in the Appendix. Each standard concentration was injected seven times, in a randomly assigned order. The order was established by use of a random number table.[16] A total of eight concentrations (0, 5, 10, 50, 200, 1,000, 5,000, and 10,000 μg/L (ppb) were analyzed during this modeling effort. This calibration range, assuming 100% recovery of analyte, corresponds to sample concentrations of 0.050 to

10 mg/L (ppm). In practice, a narrower range of standards (0 through 500 μg/L (ppb)) was used during method detection limit experiments, and a wider range of standards (0 through 25,000 μg/L) was used during analysis of actual reactor samples. In all cases, the range utilized was linear. The regression equations for each analyte (5 through 10,000 μg/L) are summarized in Table 2, example calibration curves are illustrated in Figure 7, and example chromatograms are illustrated in Figure 8. In all cases, there were no analytes detected in any of the blanks, and the blank data were not included in the regression models. The peak to peak signal to noise at the 5 μg/L level ranged from 8 to 54, depending on the analyte. There was no correlation of peak width or retention time with concentration of standard.

The peak are data from the calibration model experiment was subjected to lack of fit and zero intercept statistical analyses in accordance with established statistical protocols.[19,20] The lack of fit test is a statistical technique used to judge the linearity of a set of data. The mean square of the lack of fit is divided by the mean square of the total error to produce an F-ratio. This value is compared to the critical F-ratio value at a 95% confidence interval. If the calculated F-ratio is greater than the critical value, there is statistically significant lack of fit and the data are not linear. In all cases, the calculated F-ratios were less than the critical values, indicating the data do not significantly deviate from linearity at the 95% confidence interval.

The zero intercept test is used to determine if the intercept is statistically different from zero. Calibration curves are expected to have intercepts not statistically different from zero. Again, an F-ratio is used for comparison. In all cases, the calculated F-ratios were less than the critical values, indicating the Y-intercepts were not significantly different from zero at the 95% confidence interval.

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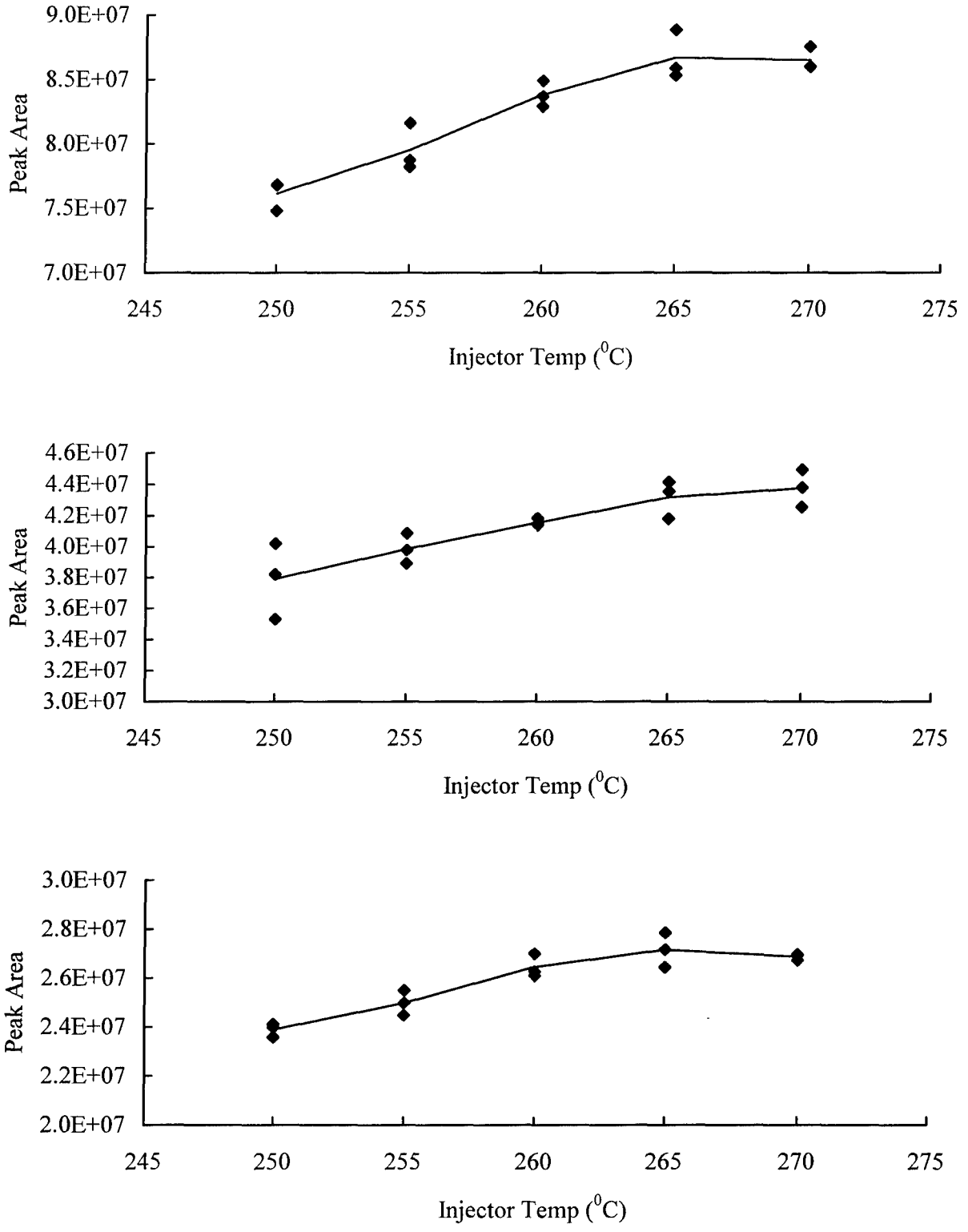
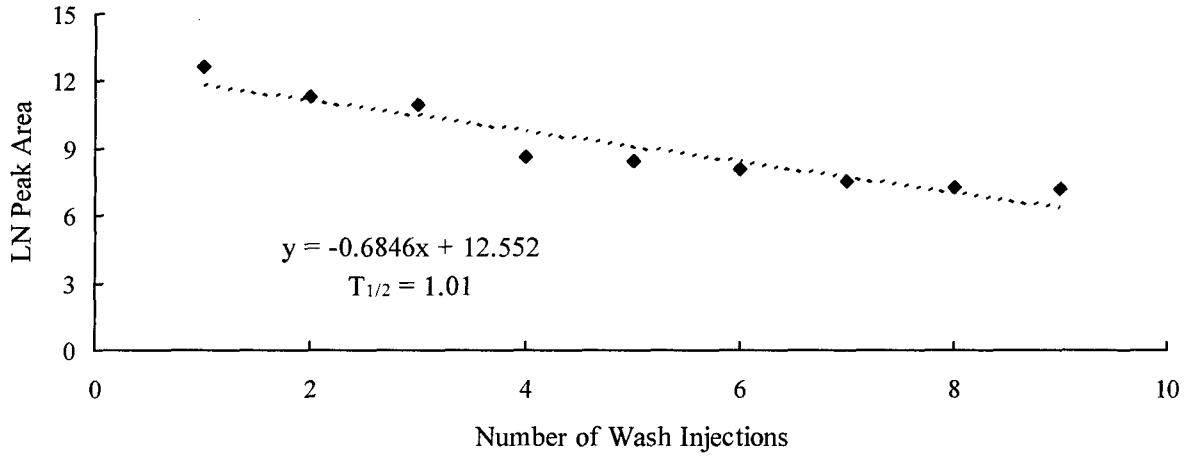
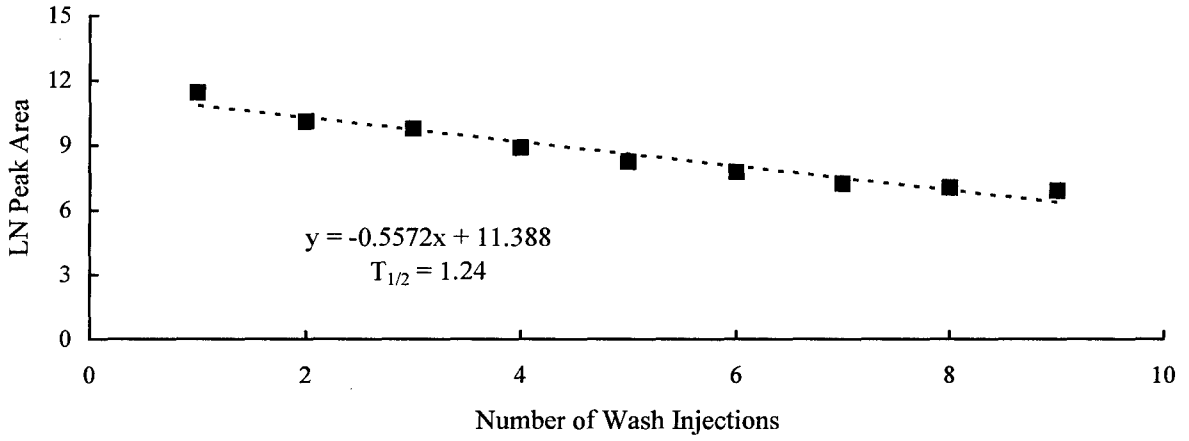


Figure 4. Peak Area as a Function of Injector Temperature for Three Target Analytes. The upper panel is DA, the middle panel is HD, and the bottom panel is TPA.





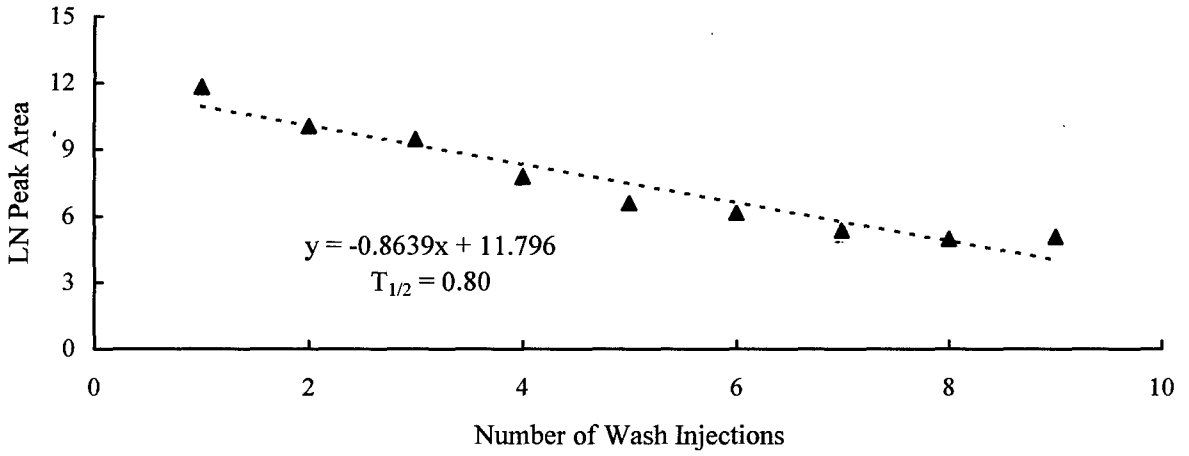


Figure 5. Carry Over as a Function of Number of Wash Vial Injections for DA, PD, and TPA. The upper panel is DA, the middle panel is PD, and the bottom panel is TPA.

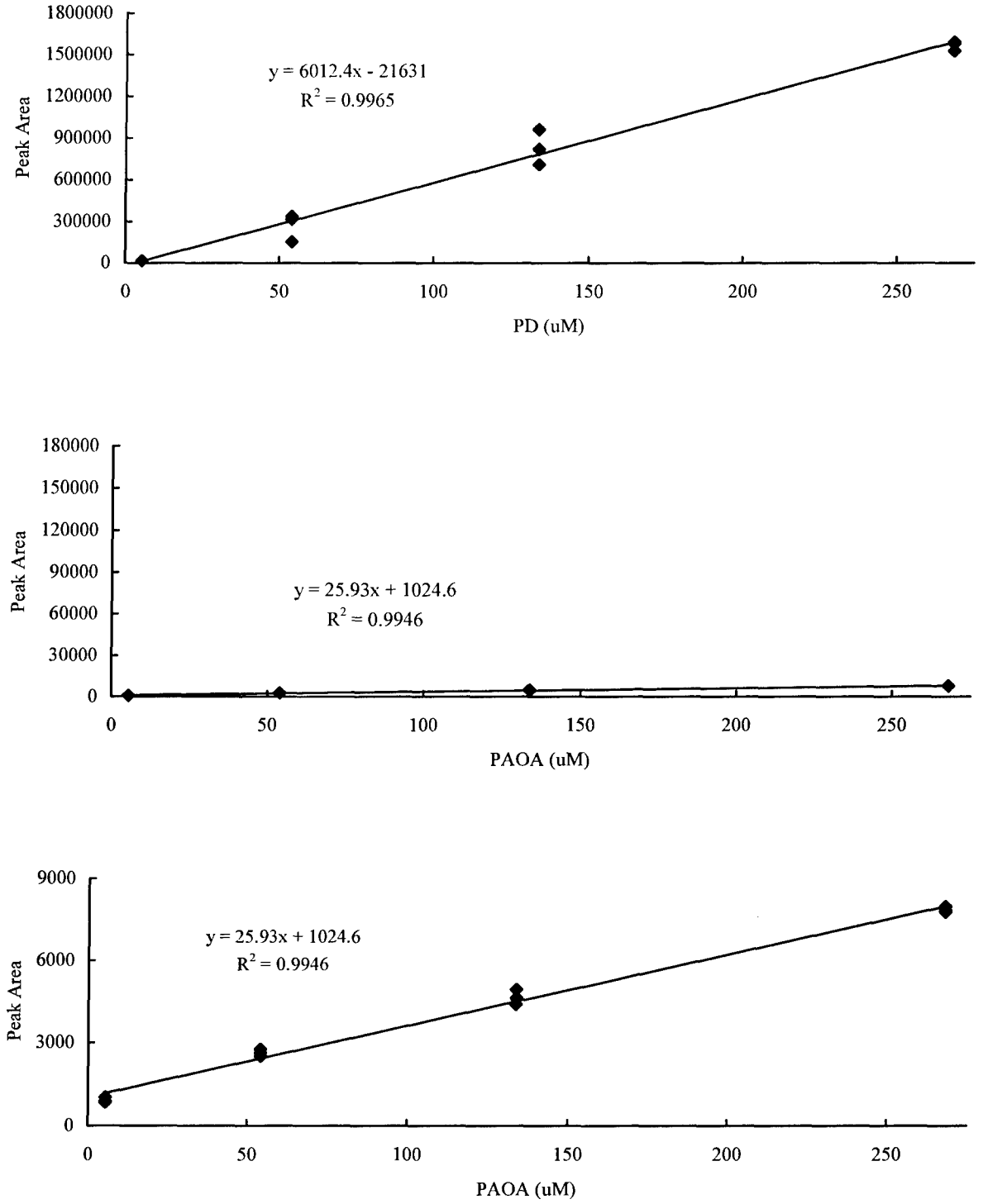
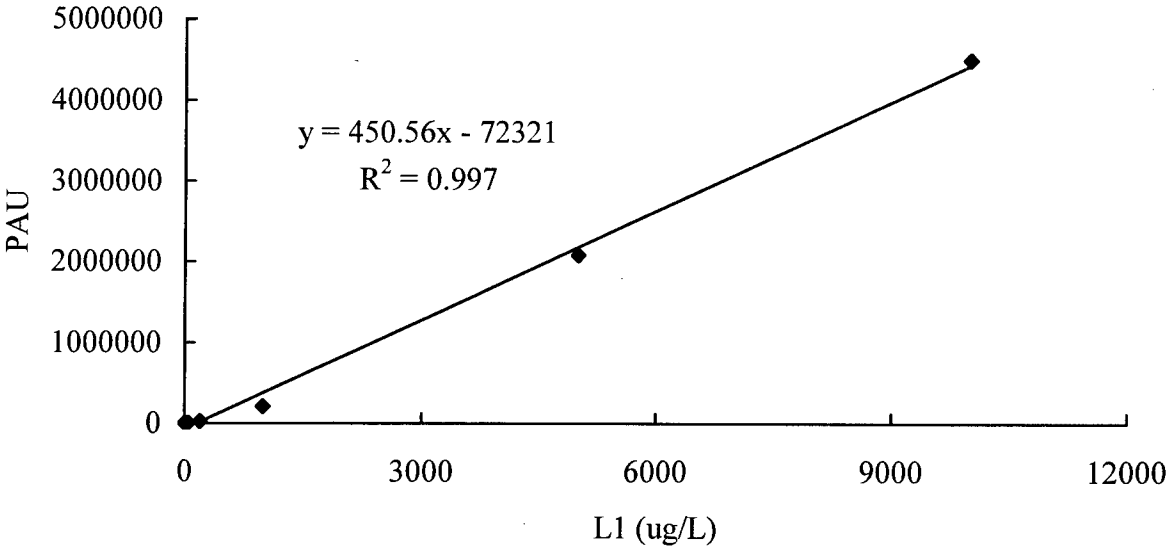


Figure 6. Comparison of Peak Area Response as a Function of Concentration for the Organo-Arsenicals Derivatized with Ethanethiol. The upper panel is PD (As^{+3}), the middle panel is phenylarsonic acid (As^{+3}) on the same Y-scale as PD, and the bottom panel is phenylarsonic acid (As^{+5}), with the Y-scale zoomed in.



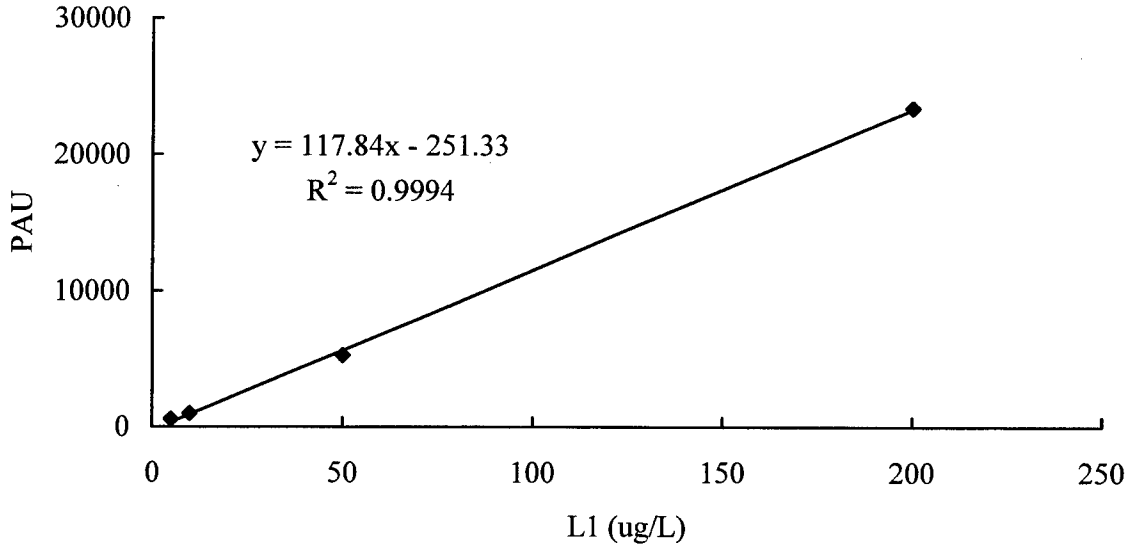


Figure 7. Example External Calibration Curves for L1. The upper panel is the entire range evaluated during the validation process, and the lower panel is the typical working calibration range used during the spike recovery and MDL experiments. The data is based on the extracted m/z ion 136.

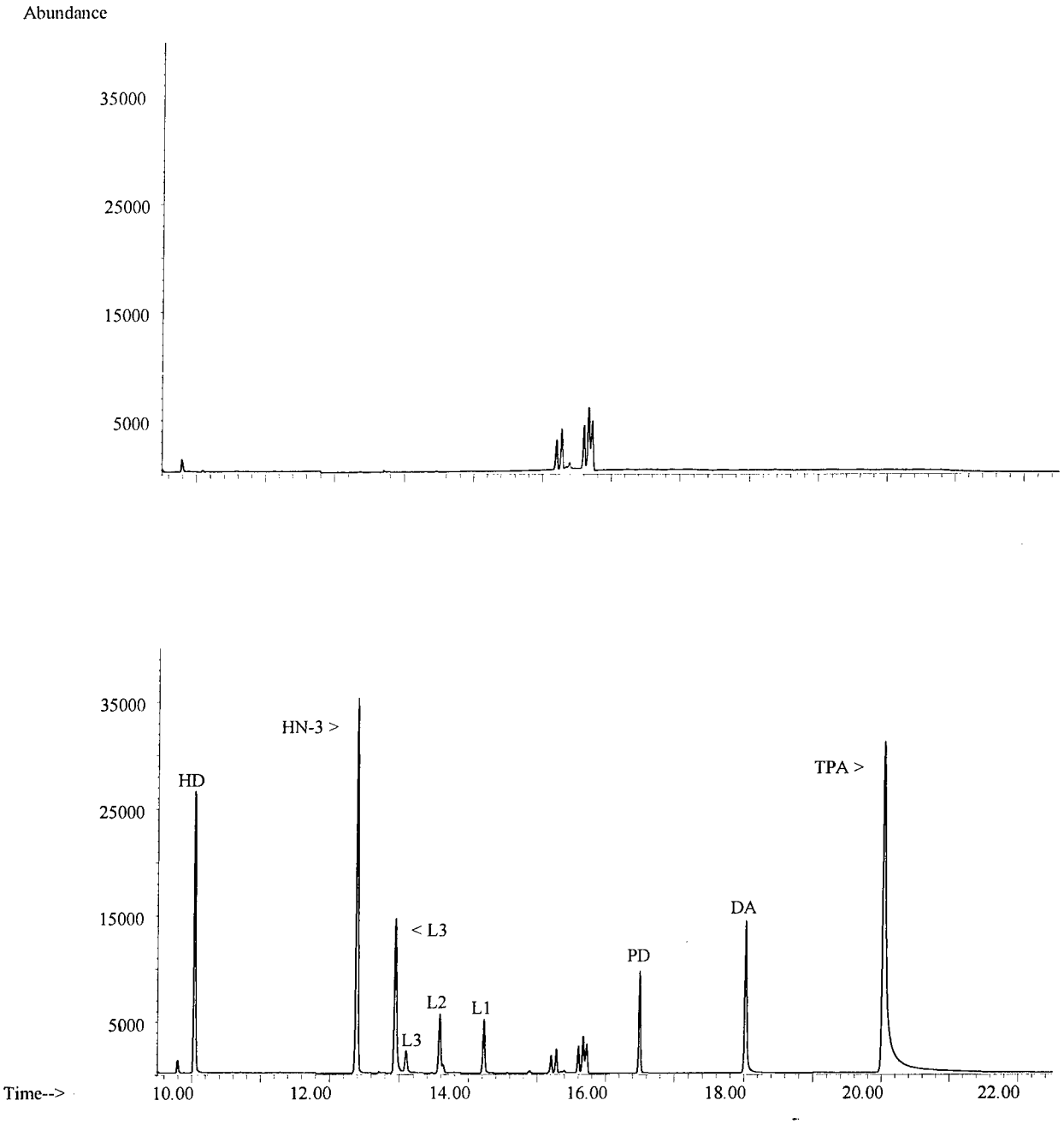


Figure 8. Example Chromatograms. The upper panel is an extraction blank, and the bottom panel is a 500 µg/L mixed standard. The time axis has been zoomed into the region of interest. L1, L2, DA, and PD are the ethanethiol derivatives.

Table 2. Summary of Linear Regression Parameters for Each of the Targeted Analytes in the 5 to 10,000 μg/L Range. The linear model is represented by y=mx+b.

Target Analyte	Linear Regression Parameters		
	m	b	R^2
HD	699.08	-39,331	0.9993
HN-3	91.072	-8,137.8	0.9980
L1	450.56	-72,321	0.9970
L2	353.0	-56,856	0.9965
L3	428.99	-35,595	0.9991
DA	1,085.3	-153,618	0.9979
PD	516.21	-67,546	0.9977
TPA	2835.8	-307,843	0.9987

2.4.3 Method Precision and Accuracy.

Precision and accuracy of analytical measurements are defined in several different ways by various regulatory agencies. In general, accuracy is defined as the degree to which a measured value approaches its true value, and is most often expressed as percent recovery.[21] Precision is commonly defined as the standard deviation of multiple measurements at a given concentration level.[22] This approach adheres to EPA guidance on determining precision and accuracy in waste streams. This approach requires multiple replicates of spiked sample matrix be prepared and analyzed at a spike level at, or below the reporting limit. A minimum of seven spike replicates and one unspiked matrix blank must be prepared. The EPA guidelines suggest a recovery in the range of 70 to 130 % is acceptable, but recoveries outside this range are acceptable in instances where the analyte is unstable or the sample matrix is reactive.

Initial attempts were made to perform spike recovery experiments in 20 wt% $NaMnO_4$ solutions, but spikes up to 5,000 μg/L were not recovered. A spike recovery experiment was performed using 0.25 wt% $NaMnO_4$, with a spike level of 1,000 μg/L. A series of seven replicates were prepared, and analyzed using the sample preparation and analysis method described in the Appendix. The sample extraction process was started within 2 min of the sample matrix being spiked. In all replicates, HD, HN3, L1, L2, and L3 were all non-detect. The DA and PD gave similar recoveries, with an average recovery less than 2%. The TPA was the most resistant to oxidation, with an average recovery of 11%. The reactivity of permanganate solution towards these analytes led to the use of a surrogate matrix being used for spike recovery experiments. This surrogate matrix was 6,500 mg/L chloride (as NaCl) in distilled, deionized water. The chloride concentration approximates the average chloride determined to be in the neutralents generated during full-scale EDS testing evaluating the efficacy of permanganate solutions against arsinol-based materiels.[13]

Precision and accuracy data were generated by spiking the mixed agents into either surrogate matrix, or deionized water, and applying the sample preparation and analysis method described in the Appendix. Multiple replicates (n=7) were independently prepared and analyzed at spike levels of 50 and 100 μg/L in surrogate matrix, and 500 and 1,000 μg/L in deionized water. In addition to the spiked samples, two blanks were also prepared and analyzed with each set of data. In all cases, there were no agents detected in any of the blank samples (n=8). The precision data is summarized in Table 3, and the accuracy data is summarized in Table 4. The precision and accuracy data indicate the analytical method is under control, and suitable for quantitative analysis of residual agents in these sample matrices. There are no clear trends in accuracy with agent concentration, suggesting the spike levels evaluated are all within a linear recovery range.

Table 3. Summary of Method Precision, as Measured by Standard Deviation of Found Agent Concentration.

Sample Matrix	Spike (μg/L)	Method Precision (μg/L)							
		HD	HN-3	L1	L2	L3	DA	PD	TPA
Surrogate	50	4.37	2.42	7.94	13.7	7.64	9.71	17.8	5.96
Surrogate	100	4.76	7.10	3.34	4.60	8.19	6.10	5.40	5.77
Deionized	500	3.99	4.92	4.41	1.71	2.37	2.44	4.64	2.09
Deionized	1,000	5.79	10.1	10.4	5.02	8.30	3.50	10.1	8.92

a. Surrogate matrix: 6,500 mg/L chloride in distilled, deionized water.
b. Distilled, deionized water.

Table 4. Summary of Method Accuracy, as Measured by Percent Recovery. The values in the table are means of seven replicate determinations. Recoveries were determined on mixed samples.

Sample Matrix	Spike (μg/L)	Method Accuracy (%)							
		HD	HN-3	L1	L2	L3	DA	PD	TPA
Surrogate[a]	50	86.2	65.9	107	112	93.5	110	133	98.5
Surrogate[a]	100	80.8	57.4	90.4	79.2	73.1	79.6	89.6	84.2
Deionized[b]	500	59.6	54.6	87.3	84.5	83.1	86.4	87.7	84.8
Deionized[b]	1,000	53.0	50.6	84.0	90.8	96.9	89.8	81.5	79.0

a. Surrogate matrix: 6,500 mg/L chloride in distilled, deionized water.
b. Distilled, deionized water.

2.4.4 Method Detection Limit.

In accordance with CMA's Laboratory and Monitoring Quality Assurance Plan (LMQAP),[23] waste screening methods require spike and recovery determinations as a means of method validation and certification. A useful approach for demonstrating detection limit is that used by EPA[24] to estimate a method detection limit (MDL). Multiple replicates (a minimum of seven) are prepared and processed using the method. The standard deviation is calculated, and then multiplied by the appropriate one-tailed Student's t statistic at the 99% confidence interval; the resulting value is the MDL. The MDL is defined as the minimum response that leads to detection of the analyte as determined from the analysis of a matrix that contains the analyte. The MDL does not provide quantitative information, but is based on statistics and reports with a 99% confidence level that the concentration of the analyte is greater than zero.

Method detection limit data were generated by spiking the mixed agents into surrogate matrix, and applying the sample preparation and analysis method described in the Appendix. Multiple replicates (n=7) were independently prepared and analyzed at spike levels of 50 and 100 μg/L. In addition to the spiked samples, two blanks were also prepared and analyzed with each set of data. In all cases, there were no agents detected in any of the blank samples (n=4). The method detection limits are summarized in Table 5, and the peak to peak signal to noise ratios are summarized in Table 6. The MDLs, with the exception of PD, were all calculated using the 50 μg/L spike data. The MDL for PD was calculated using the 100 μg/L spike data, because the MDL calculated using the 50 μg/L data was 55.9 μg/L, which is above the spike level, and therefore not valid per EPA protocol.[24] The MDL data indicate the analytical method is under control, and suitable for quantitative analysis of residual agents in these sample matrices. In the worst case, for L2, the MDL is more than 1,000 times below the desired treatment goal of 50 mg/L.

Table 5. Method Detection Limits of the Targeted Analytes. The spike recovery studies were performed in surrogate matrix. The Student's T value (n=7) was 3.143. The spike level was 100 μg/L for PD, and 50.0 μg/L for all other analytes.

Target Analyte	Found Concentration (μg/L)								MDL[b] (μg/L)
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	SD[a]	
HD	44.3	41.7	43.8	46.3	46.2	45.6	33.9	4.37	13.7
HN-3	30.5	31.0	30.8	36.3	32.8	36.1	33.1	2.44	7.67
L1	55.0	66.8	48.5	55.5	57.2	50.4	41.4	7.93	24.9
L2	82.4	57.0	47.9	53.9	62.4	49.5	39.4	13.70	43.1
L3	59.6	53.7	43.8	46.9	43.8	43.1	36.4	7.65	24.0
DA	64.6	62.0	62.9	60.3	49.3	48.2	39.0	9.71	30.5
PD	96.2	89.2	96.4	85.3	84.7	83.5	91.6	5.38	16.9
TPA	51.0	61.2	49.9	47.6	43.8	47.9	43.5	5.97	18.8

a. Standard deviation of found concentration.
b. Method detection limit.

Table 6. Peak-to-Peak Signal to Noise Ratios of the Targeted Analytes. The analytes were all spiked at 50.0 μg/L in surrogate matrix.

Target Analyte	Peak to Peak Signal to Noise Ratio							Average SNR*
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	
HD	7.2	10.0	7.0	11.1	11.9	11.6	10.4	10
HN-3	12.0	13.2	14.1	20.8	20.5	20.6	19.8	17
L1	14.0	11.0	9.0	8.0	5.2	5.6	5.4	8
L2	3.5	2.8	4.0	4.8	2.5	2.8	3.4	3
L3	3.8	6.9	7.8	10.2	9.8	7.8	8.4	8
DA	3.1	4.1	5.7	8.6	5.4	8.3	8.6	6
PD	11.4	16.8	14.3	14.5	20.9	20.0	29.0	18
TPA	3.7	5.7	4.8	13.2	11.3	12.9	9.3	9

* Signal to noise ratio.

2.5 Reaction Product Method.

Capillary electrophoresis (CE) with direct and indirect photometric detection was used to further characterize the samples generated during this study. Specifically, capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC), two particular disciplines of CE, were coupled with ultraviolet (UV) detection to determine arsinol degradation products. The technique of arsenic speciation by CE with direct UV detection for both organoarsenicals and inorganic arsenic-containing compounds was first reported at the 1997 ERDEC Scientific Conference on Chemical and Biological Defense Research.[25] Prior to that, CE methods were established in the literature for a number of chemical weapons agents' degradation products to include the detection of 2-chlorovinyl arsonic acid (CVAOA) by CE in 1995,[26] the characterization of sulfur mustard and lewisite degradation products,[27-29] and the characterization of phenyl-arsenical reaction products and impurities.[13]

2.5.1 Instrumentation.

These analyses were performed using a Hewlett-Packard 3D Capillary Electrophoresis system (Agilent Technologies, Wilmington, DE, USA) with an ultraviolet (deuterium lamp) diode array detector. The separation capillary was a piece of bare-fused silica with an external polyimide coating; removed at the optical window. Two capillaries, each of different dimensions, were used for three distinct methods. The capillary dimensions were 64.5 cm (L_{tot}) x 75 μm ID for an MEKC and a CZE method with direct UV detection, and 112 cm (L_{tot}) x 50 μm ID for a CZE method with indirect detection. This CE system uses an internal air compressor to drive all mechanical functions and to deliver pressure for hydrodynamic injections. The CE systems currently used are PC-driven and all data analyses were evaluated using HP ChemStation (Revision A.09.03 or A.10.02).

2.5.2 Reagents.

All chemicals obtained were of the highest purity available. Boric acid (H_3BO_3, 99.999%) [CAS No. 10043-35-3] and sodium dodecyl sulfate (SDS, 99+%) [CAS No. 151-21-3] were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Volumetric solutions of sodium hydroxide (NaOH) [CAS No. 1310-73-2] at 2.5 N and 0.1 N were obtained from J. T. Baker (Phillipsburg, NJ, USA) and Sigma-Aldrich, respectively. All buffers and aqueous solutions were prepared in distilled/de-ionized water (18 Mohm, Nanopure, Barnstead, Dubuque, IA, USA). A proprietary buffer (Part No. 5064-8209) for the separation of anions was purchased from Agilent Technologies.

2.5.3 Targeted Analytes.

The target analytes investigated by CE include the more polar, non-volatile chemicals resulting from degradation of starting feedstock or impurities in the starting feedstock or reagent. Lewisite degradation products analyzed for by CE with direct UV detection include CVAA, CVAOA, BCVAA and BCVAOA. Other arsenic-containing degradation products analyzed for by CE include the inorganic components arsenate (AsO_4) and m-arsenite (AsO_2), and other organo-arsenicals related to the degradation of arsinol mixtures. These were analyzed by indirect UV detection. Capillary electrophoresis with indirect UV detection was also used to analyze for common anions, such as chloride, sulfate, fluoride, and nitrate, and low-molecular weight organics such as, formic, oxalic, and glycolic acids. A summary of the targeted analytes is provided in Table 7, and the structures of the targeted organo-arsenicals are illustrated in Figure 9.

2.5.4 Procedure.

Three distinct CE methods were performed on all samples. Two methods used direct UV detection and the third used indirect detection. The three methods in combination used different strategies of separation from simple capillary zone electrophoresis to the use of additives in micellar electrokinetic chromatography.

MEKC and CZE were used with direct UV detection. A UV wavelength of 200 nm was used in all measurements; however, full UV spectra were collected. During separation in MEKC, the capillary was maintained at 28.5 °C, and the applied voltage was 17.5 kV. The final electrolyte composition was 10 mM borate/100 mM SDS at a pH of 8.9. For CZE, the capillary was also maintained at 28.5 °C, but the applied voltage was 30kV. The final electrolyte composition was 250 mM borate at a pH of 7.0. A modified CZE method was used with indirect UV detection. For indirect detection, a UV-absorbing component is added to the electrolyte allowing for a displacement by a non-UV-absorbing target analyte. The displacement is viewed electrophoretically as a detectable peak. The capillary was maintained at 30.0 °C, and the applied voltage was 20.5 kV. Example electropherograms, for each CE method, are illustrated in Figures 10 through 12.

Throughout the study, quantitative capabilities were maintained using the combined CE techniques. Calibration curves and accuracy measurements were generated for all

of the target analytes. Calibration curves were established for each target analyte, with from 4 to 7 concentration levels. Correlation coefficients exceeded 0.99960 for all target analytes except TPAO, which was 0.99889. Mid-level check standard analyses were performed on a daily basis. In most cases, acceptance criteria for each externally calibrated target analyte were for an accuracy measurement of 75-125%. For analyte standards prone to variability from short-term storage, mid-level check standards served as a migration correction.

Prior to CE analysis, samples were determined or known to have high concentrations of potassium permanganate ($KMnO_4$) and/or sodium hydroxide (NaOH). To adjust these matrices to improve their amenability to CE, all samples were diluted in distilled/ deionized water. Common dilution values included 10, 100 and 1000 times dilution of the original sample. The reporting limits (Table 7) for target analytes found in the samples must be multiplied by the dilution factor. Since the CE analytical procedure includes a sample preparation step involving sample dilution, final concentrations of target analytes, their limits of detection (LODs) and the LODs of not found target analyzed must be raised by the dilution factor. Furthermore, samples may be diluted for both matrix effects and/or reporting high concentration target analytes to within their measured linear range. However, every attempt is made to analyze the smallest dilution possible (10X) to maintain the lowest possible LOD for each target analyte in each sample.

Table 7. Summary of Targeted Analytes Quantitated by the CE Methods.

Chemical Name	CAS Number	Chemical Formula	Analyte Formula	CE Reporting Limit (mg/L)*
Sodium arsenite	1327-53-3	$NaAsO_2$	AsO_2^-	3.3
Potassium arsenate	7784-41-0	KH_2AsO_4	$HAsO_4^-$	1.6
Sodium chloride	7647-14-5	NaCl	Cl^-	3.8
Potassium fluoride	7789-23-3	KF	F^-	0.7
Potassium nitrate	7757-79-1	KNO_3	NO_3^-	4.9
Potassium sulfate	7778-80-5	K_2SO_4	SO_4^{-2}	4.5
CVAA	85090-33-1	$C_2H_4AsClO_2$	$C_2H_3AsClO_2^-$	2.3
CVAOA	64038-44-4	$C_2H_4AsClO_3$	$C_2H_2AsClO_3^{-2}$	1.0
BCVAA	Not Available	$C_4H_5AsCl_2O$	$C_4H_4AsCl_2O^-$	1.0
BCVAOA	Not Available	$C_4H_5AsCl_2O_2$	$C_4H_4AsCl_2O_2^-$	1.0
Ammonium acetate	631-61-8	$NH_4(C_2H_3O_2)$	$C_2H_3O_2^-$	1.6
Ammonium formate	540-69-2	$NH_4(CHO_2)$	CHO_2^-	1.5
Fumaric acid	110-17-8	$C_4H_4O_4$	$C_4H_2O_4^{-2}$	1.5
Glycolic acid	79-14-1	$C_2H_4O_3$	$C_2H_3O_3^-$	2.0
Potassium oxalate, monohydrate	6487-48-5	$K_2C_2O_4 \bullet H_20$	$C_2O_4^{-2}$	3.8
Succinic acid	110-15-6	$C_4H_6O_4$	$C_4H_4O_4^{-2}$	2.0

* Reporting limit at the instrument; does not include dilution factor of the sample.

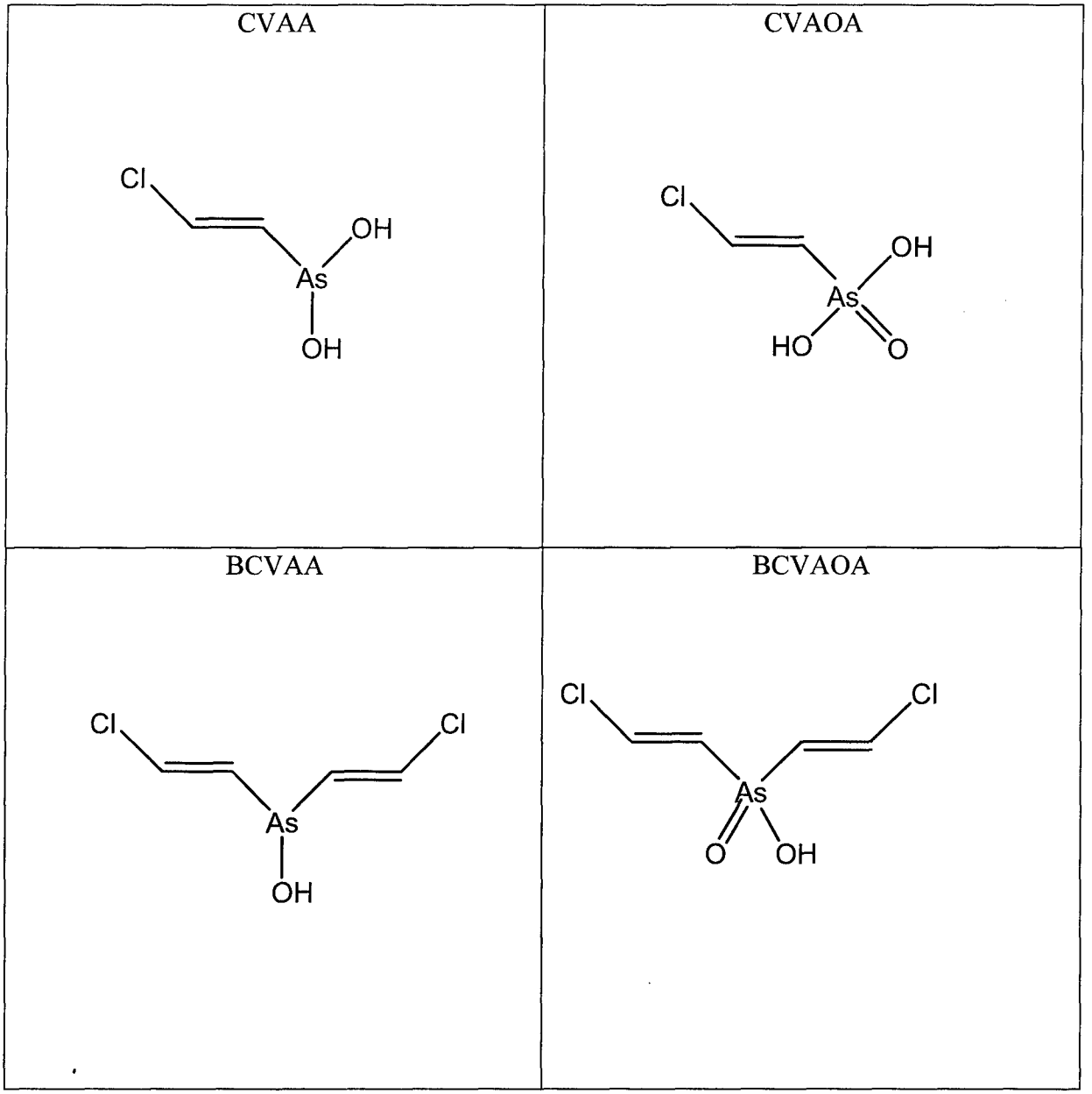


Figure 9. Structures of the Lewisite Related Organo-Arsenicals Determined by the CE Methods.

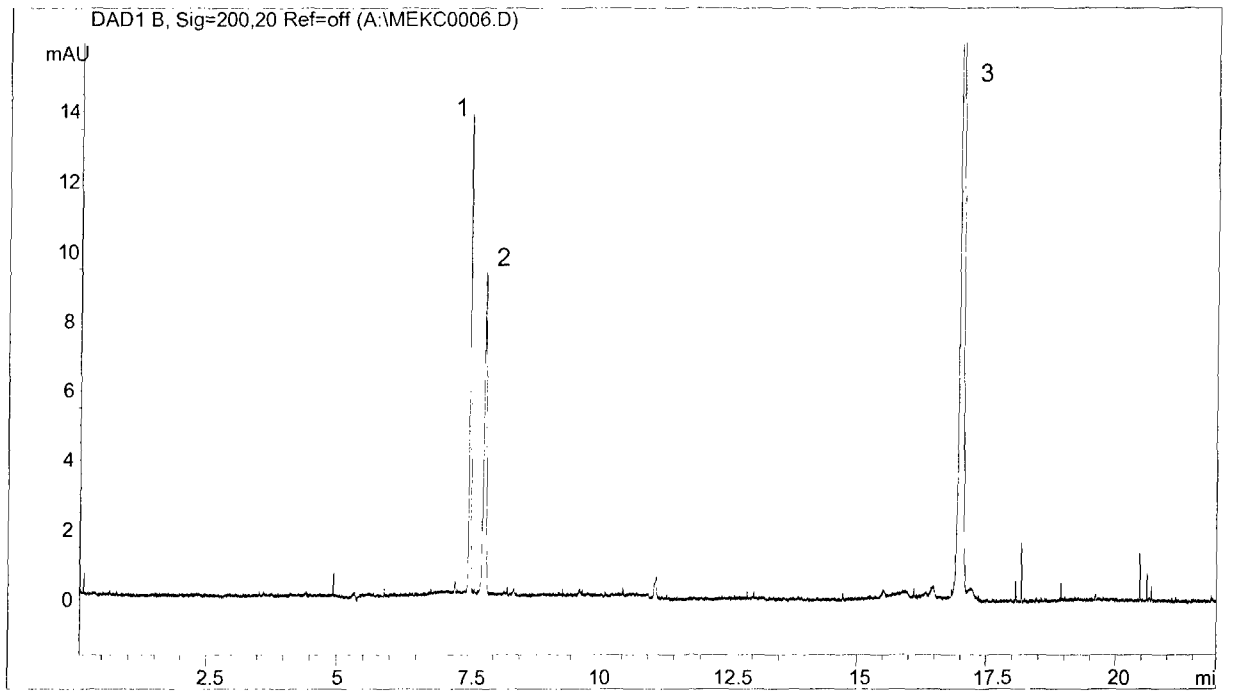


Figure 10. Electropherogram Generated from the Analysis of Standards Using MEKC with Direct UV Detection. Analytes are: 1 = DPAOA, 2 = PAO and 3 = TPAO.

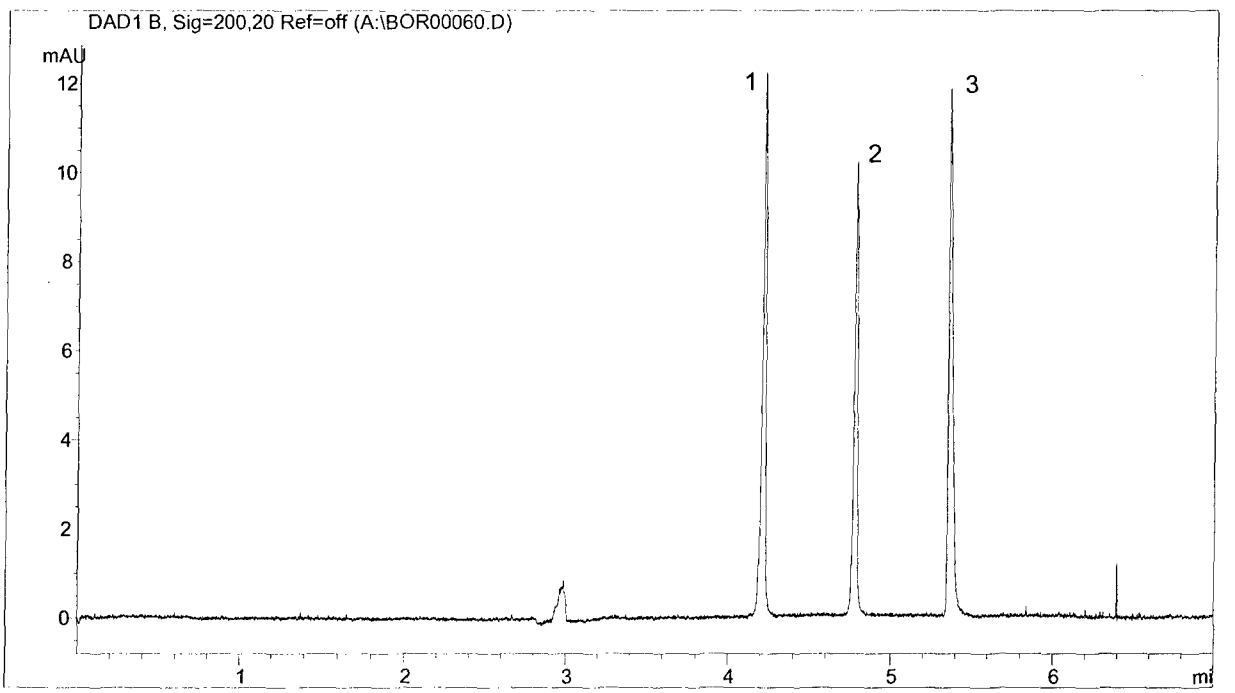


Figure 11. Electropherogram Generated from the Analysis of Standards Using CZE with Direct UV Detection. Analytes are: 1 = DPAOA, 2 = PAOA and 3 = CVAOA.

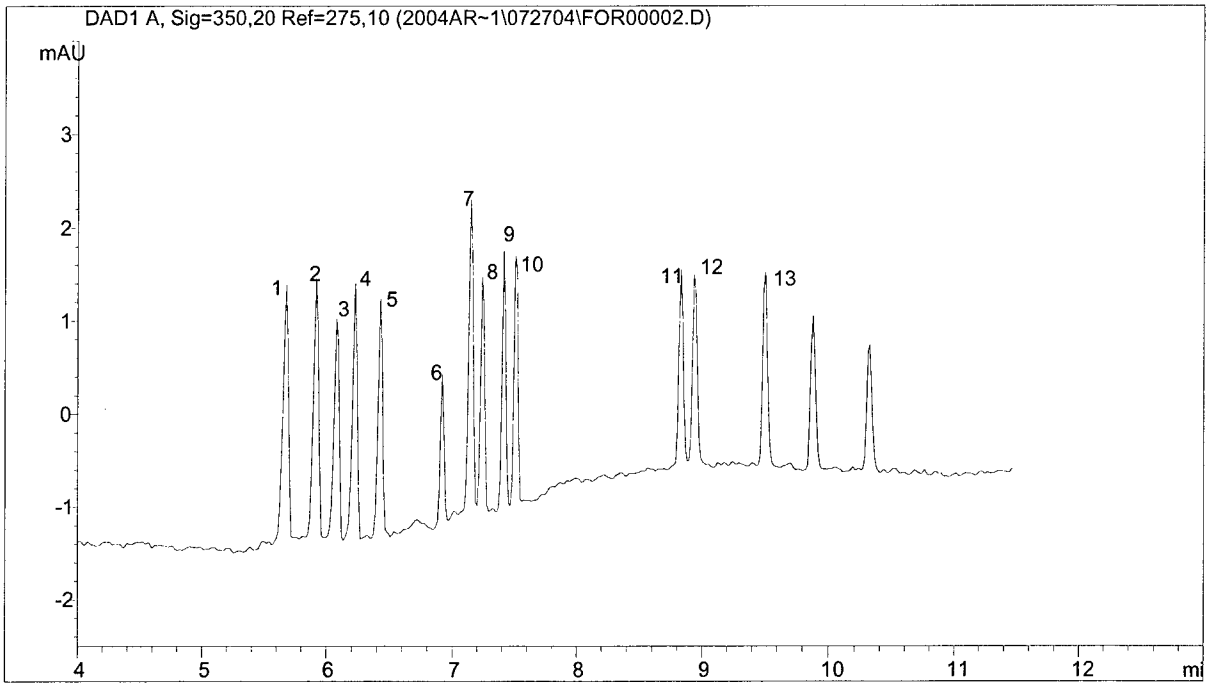


Figure 12. Electropherogram Generated from the Analysis of Standards Using a Modified CZE Method with Indirect UV Detection. Analytes are: 1 = chloride, 2 = nitrite, 3 = nitrate, 4 = sulfate, 5 = oxalate, 6 = carbonate, 7 = fluoride, 8 = formate, 9 = arsenate, 10 = phosphate, 11 = acetate, 12 = glycolate and 13 = meta-arsenite. The two peaks after m-arsenite are system peaks related to borate species.

2.6 Determination of Residual Permanganate.

An attempt to determine residual permanganate in neutralent samples was made using a titration assay provided by a manufacturer of 20 wt% permanganate solutions,[30] but the method could not be successfully implemented. Apparently, the high background levels of arsenic interfered with the assay.

A Hach Chemical Company method (Method 8034) for the analysis of dissolved manganese,[31] was modified to quantitate residual permanganate in neutralent samples generated during this study. In the unmodified method, manganese in the sample is oxidized to the purple permanganate ion by sodium periodate, after buffering the sample with citrate. The absorbance at 525 nm is measured, and is directly proportional to manganese concentration. In the method, calcium (≥700 mg/L), chloride (≥70,000 mg/L), iron (≥5 mg/L), magnesium (≥100,000 mg/L), and pH extremes are the only listed potential interferences. The calcium and magnesium concentrations in the neutralents were not determined, but it is not likely there will be any significant levels of calcium or magnesium in the neutralent samples. On average (n= 2 EDS runs), the iron concentration was determined to be 9,6350 mg/L, and the chloride concentration was determined to be 15,300 mg/L. Considering the typical sample dilution factor of 10,000, both of these chemicals will be <2 mg/L at the instrument, and should not interfere with the assay. The modification was the elimination of the oxidizing reagent from the sample preparation. A response curve ranging from 0.200 to 55.0 mg/L manganese (corresponds to

0.516 to 142 mg/L NaMnO4) was generated during the initial stages of development. The entire response curve, and the linear range (0.200 to 25.0 mg/L manganese), is illustrated in Figure 13.

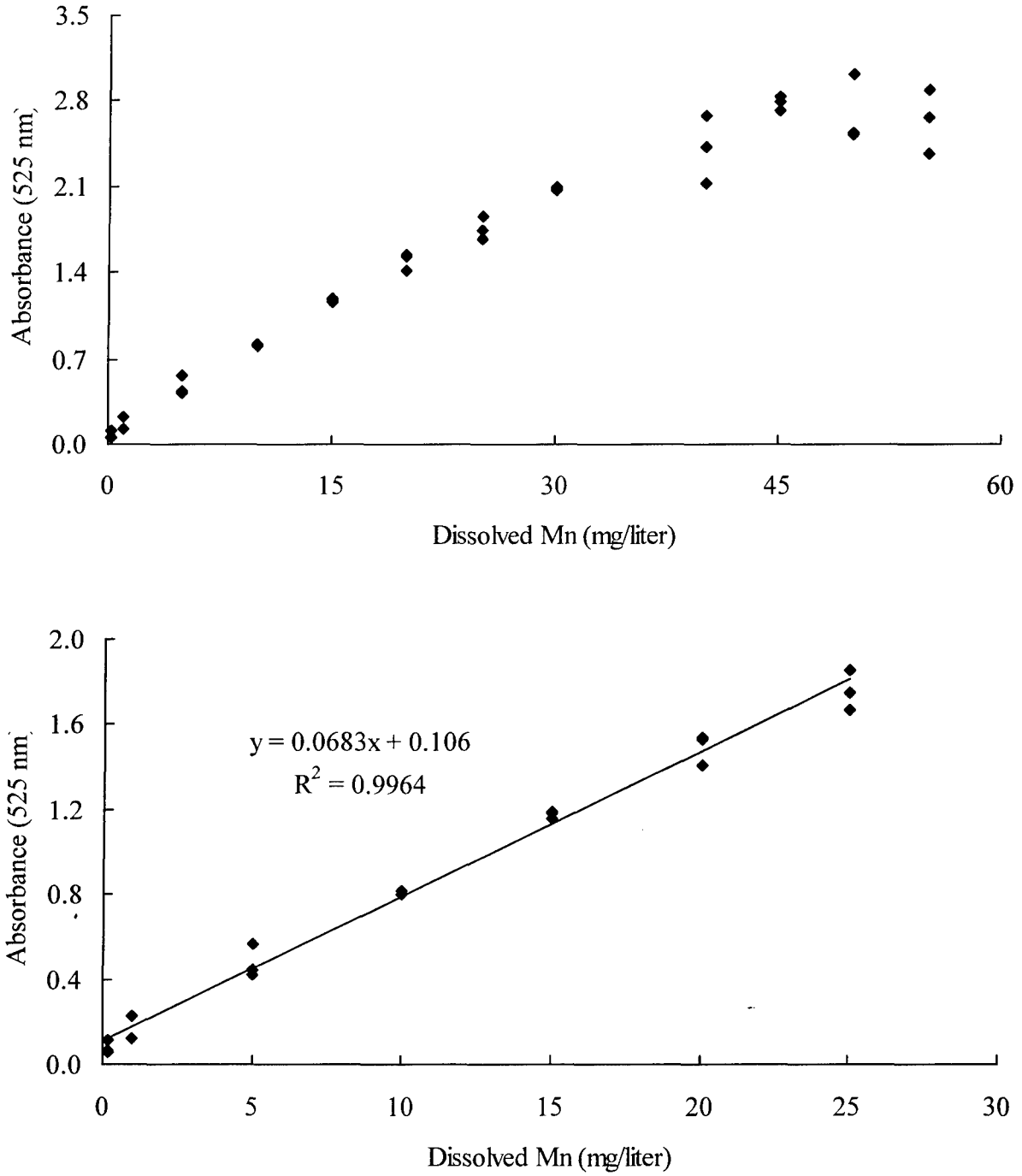


Figure 13. Response Curve (upper panel) and Linear Range (lower panel) of Dissolved Manganese.

3. RESULTS AND DISCUSSION

3.1 Characterization of Fill Components.

In previous studies involving the characterization of unknown materiels recovered from chemical munitions,[32] and ton containers,[33,34] the use of multiple analytical techniques was found to be essential to successful identification and quantitation of the sample components. This multi-disciplinary approach was used in this study, to provide a high degree of confidence in both identification and quantitation of the fill components.

Two lewisite munitions in storage at Dugway Proving Ground (DPG) were individually containerized using Department of Transportation and U.S. Army approved containers, and transferred from DPG to Edgewood Chemical and Biological Center (ECBC), located at Aberdeen Proving Ground, MD. These munitions were identified as "DPG-94-028", which was an M2 4.2 inch mortar, and "DPG-94-055", which was a 105 mm round. Samples of each fill were then transported to ECBC laboratories for characterization. In addition to the two fill materiels recovered from actual munitions, a bulk munition grade lewisite (L-U-6095-CTF-N-5) used in the lab-scale testing (Section 3.2) and EDS testing (Section 3.4) was also characterized. In all cases, the fill materiels were greenish-black in color, with fine black particulates which stayed suspended in the materiel.

The three fill materiels, on average, were found to contain 64.0 wt% L1, 28.5 wt% L2, and 0.177 wt% L3. The fill materiels were also analyzed for semi-volatiles, total metals, and water soluble anions. The results from all analyses conducted on these fills are consistent with the materiels being munitions grade lewisite.

3.1.1 Qualitative Gas Chromatographic Experiments.

Qualitative gas chromatographic analyses were performed in accordance with established procedures.[33,34] Gas chromatographic analysis of these samples was performed on a Agilent Model 6890 GC with an Agilent Model 5973 mass spectral detector operating in electron impact ionization mode. The GC was equipped with an HP-5 column which was 50m X 0.32mm ID, with a phase thickness of 1 μm. Mass spectra were acquired at a range of m/z 40-400.

Samples for GC analyses were prepared using three different approaches. In the first approach, 10 μL of fill materiel was added to 10 mL of trimethylpentane (TMP), the sample was vortexed to dissolve, then filtered through a PTFE Acrodisc™ (0.45 μm) prior to analysis. In the second approach, 10 μL of fill materiel was added to 10 mL of dichloromethane (MCL), the sample was vortexed to dissolve, then filtered through a PTFE Acrodisc™ (0.45 μm) prior to analysis. In the third approach, 10 μL of fill materiel was added to 10 mL of 1% ethanethiol inTMP, the sample was vortexed to dissolve, allowed to react for 15 min, then filtered through a PTFE Acrodisc™ (0.45 μm) prior to analysis.

The results of the GC analyses using sample preparation approaches one and two are summarized in Table 8, and mass spectra of the peaks are illustrated in Figures 14 through 18. A total of 20 peaks were selected as being significant, based on area percent values being greater than 0.1 %. Five of the peaks were hydrocarbons, with good spectral matches (>95%) for four of the peaks. These hydrocarbons were only detected in one of the fill samples (DPG-94-028), and might be from lubricants used during drilling when the sample was obtained. Eight of the peaks were not identified during library searches of the spectra, but contain m/z ions 145, 161, 171, and 197. These ions are suggestive of chemicals related to lewisites, as demonstrated in a previous study.[35] These lewisite related peaks were found in each of the three fill materiels. Two of the peaks were positively identified as L3, by comparison to reference spectra and spiking of the extracts with L3. Five of the peaks were not assigned, with no matches obtained during searches of multiple MS spectra databases.

The results of the GC analyses using sample preparation approach three support all three materiels as being munitions grade lewisite. The most striking difference is no detectable dichloro(1-chlorovinyl)arsine (commonly referred to as geminal-L1) in the fill obtained from the munition identified as "DPG-94-028". The assignment of this peak as g-L1 is supported by spectral interpretation,[36] and comparison of these results to those obtained in a previous study.[37] In addition to confirming the presence of L1, L2 and L3 in all three fill materiels, derivatized trivalent arsenic (triethyl ester of arsenotrithious acid or thioarsenous acid, CAS No. 34666-79-0) was also detected in all three fill materiels. The peak assignments of t-L1, t,t-L2, L3, and the triester were confirmed by comparison to reference spectra, and spiking of the extract with authentic standards. The mass spectra of t-L1, g-L1, t,t-L2, and the triester are illustrated in Figure 19. It is not known whether the triester was formed by the reaction of ethanethiol with arsenic trichloride, inorganic arsenite ion, or some combination of both chemicals.

Text continues on page 34.

Table 8. Summary of Compounds Detected by Gas Chromatographic Experiments. Blank peaks were not included. The samples prepared using trimenthylpentane are identified as "TMP", and the samples prepared using methylene chloride are identified as "MCL".

Peak Identification	Area Percent		
	L-U-6095-CTF-N	DPG-94-028	DPG-94-055
1	TMP = 2.43 MCL = ND[a]	TMP = 3.04 MCL = ND[a]	TMP = 3.73 MCL = ND[a]
2	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = ND[a]	TMP = 1.14 MCL = ND[a]
3	TMP = 19.6 MCL = ND[a]	TMP = 58.7 MCL = 1.49	TMP = 40.9 MCL = 1.26
4 (L-Related)	TMP = 0.865 MCL = 1.56	TMP = 1.95 MCL = 2.16	TMP = 1.70 MCL = 4.07
5 (L-Related)	TMP = 0.643 MCL = ND[a]	TMP = 2.49 MCL = ND[a]	TMP = 1.71 MCL = ND[a]
6	TMP = ND[a] MCL = ND[a]	TMP = 0.659 MCL = 1.09	TMP = 0.160 MCL = ND[a]
7 (L3)	TMP = 46.5 MCL = 58.9	TMP = 2.11 MCL = 4.10	TMP = 1.47 MCL = 3.29
8 (L3)	TMP = 17.4 MCL = 19.6	TMP = 0.807 MCL = 1.81	TMP = 0.404 MCL = 1.92
9 (Pentadecane)	TMP = ND[a] MCL = ND[a]	TMP = 0.749 MCL = 1.35	TMP = ND[a] MCL = ND[a]
10 (Hexadecane)	TMP = ND[a] MCL = ND[a]	TMP = 0.536 MCL = 0.905	TMP = ND[a] MCL = ND[a]
11 (Heptadecane)	TMP = ND[a] MCL = ND[a]	TMP = 0.653 MCL = 0.944	TMP = ND[a] MCL = ND[a]
12 (L-Related)	TMP = 1.42 MCL = 1.81	TMP = ND[a] MCL = ND[a]	TMP = 3.03 MCL = 3.47
13 (L-Related)	TMP = 6.51 MCL = 9.75	TMP = 16.3 MCL = 46.7	TMP = 30.9 MCL = 45.5
14 (L-Related)	TMP = 3.52 MCL = 4.35	TMP = 10.5 MCL = 24.4	TMP = 13.5 MCL = 17.2
15 (L-Related)	TMP = 0.868 MCL = 1.37	TMP = 1.44 MCL = 3.05	TMP = 3.28 MCL = 1.27
16	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = 0.402	TMP = ND[a] MCL = 0.727
17 (Dodecane)	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = 0.701	TMP = ND[a] MCL = ND[a]
18 (Hydrocarbon)	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = 0.231	TMP = ND[a] MCL = ND[a]
19 (L-Related)	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = ND[a]	TMP = ND[a] MCL = 0.581
20 (L-Related)	TMP = ND[a] MCL = 2.68	TMP = ND[a] MCL = 10.6	TMP = ND[a] MCL = 20.8

a. No peak was detected.

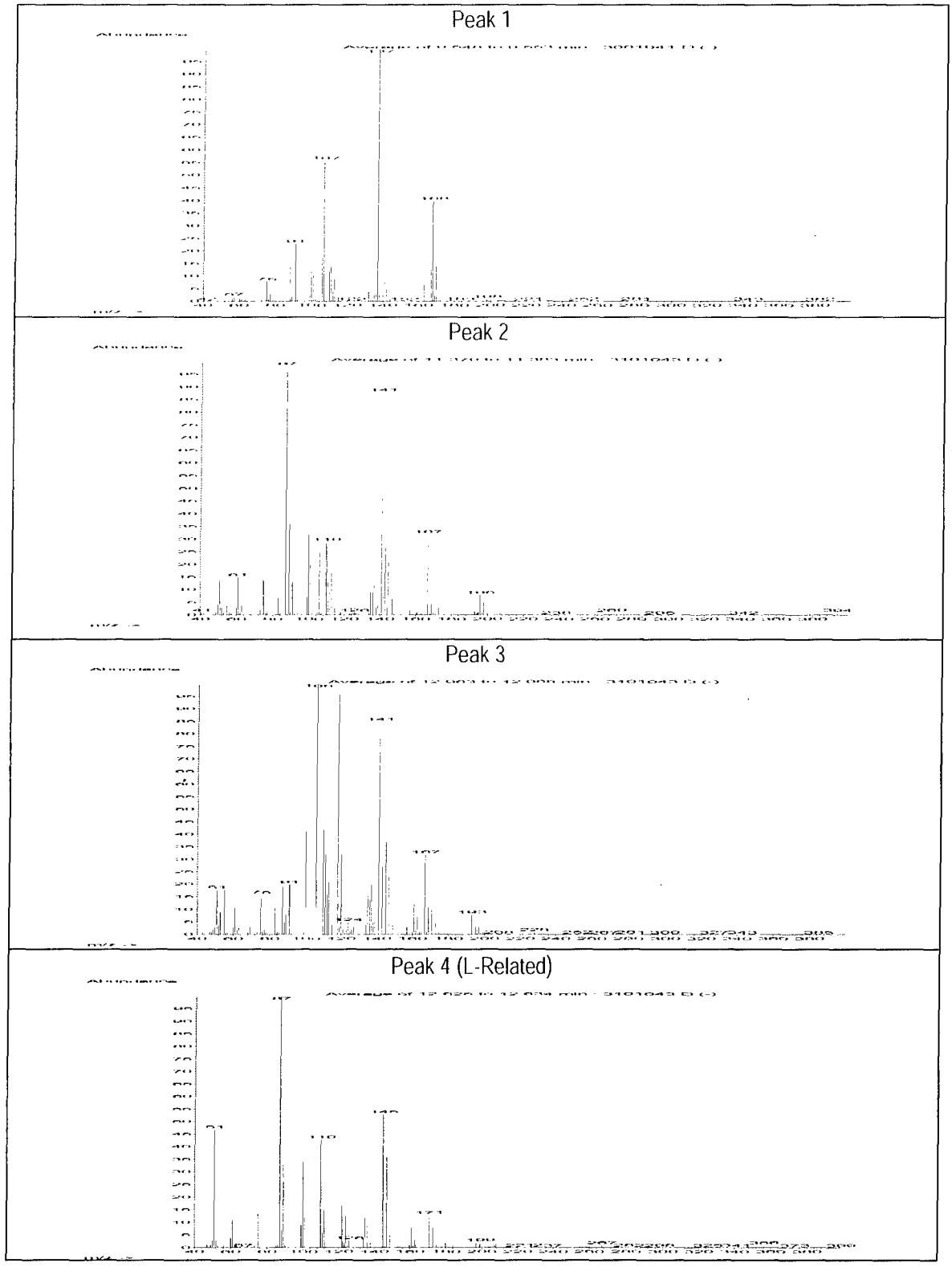


Figure 14. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

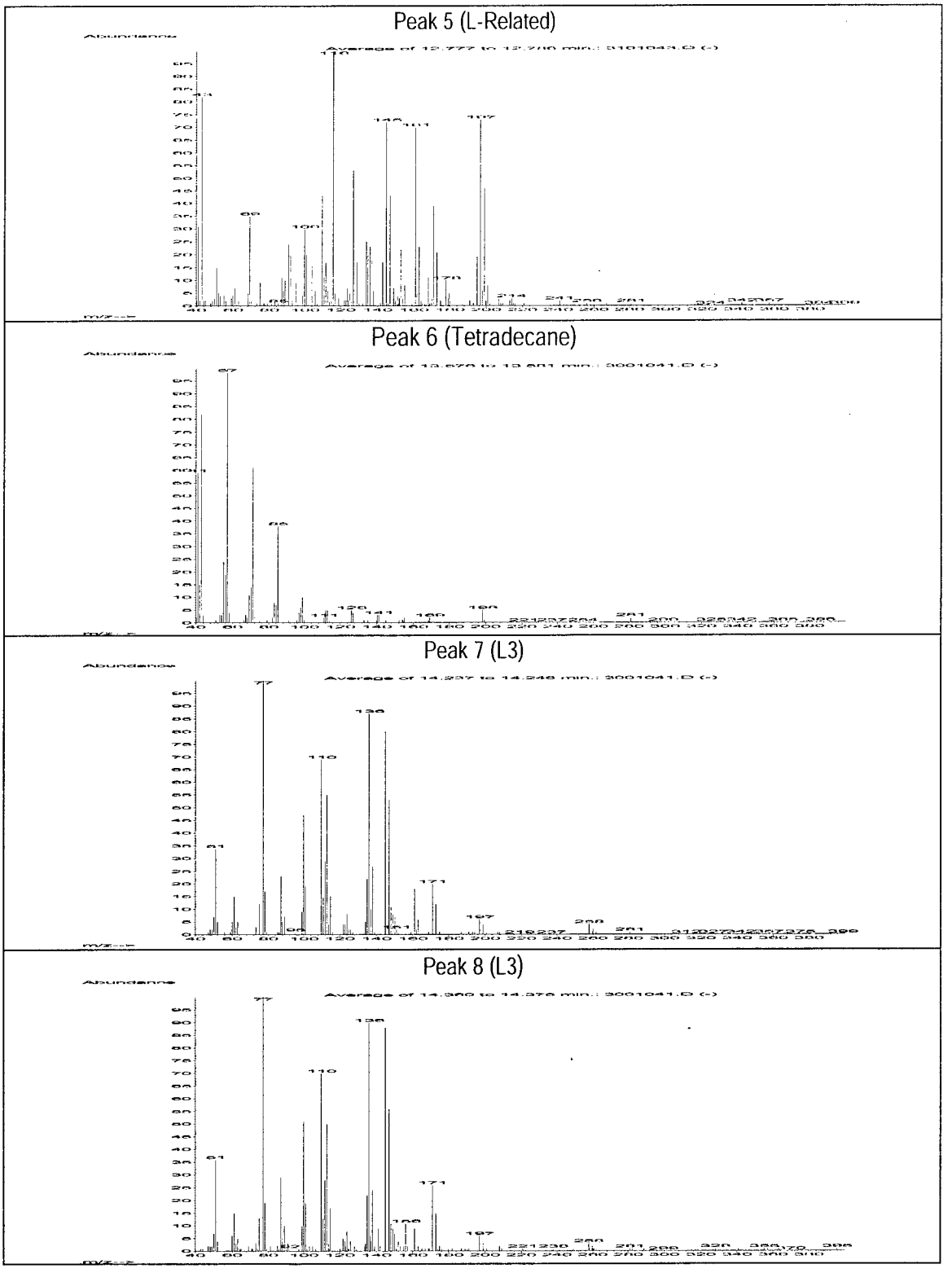


Figure 15. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

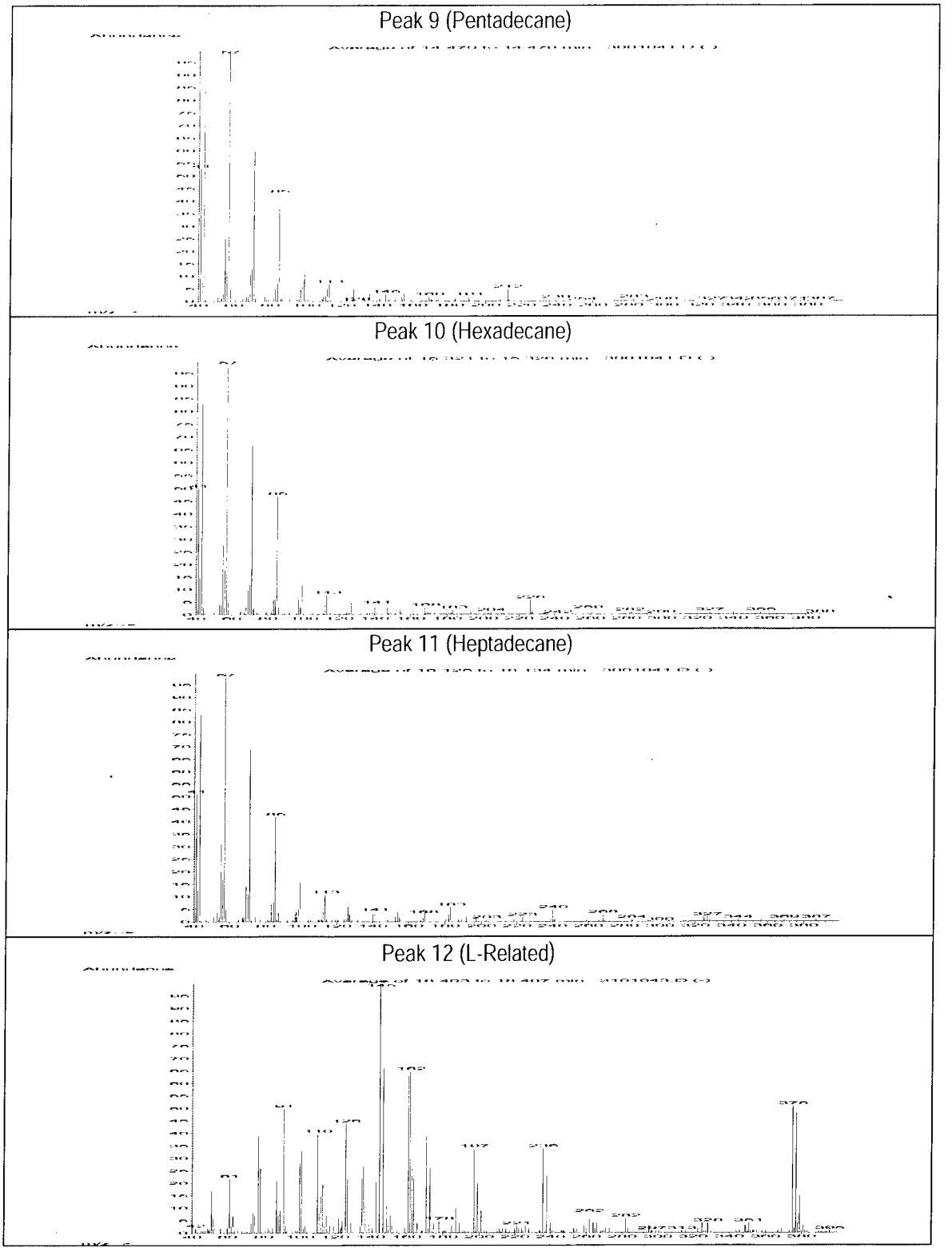


Figure 16. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

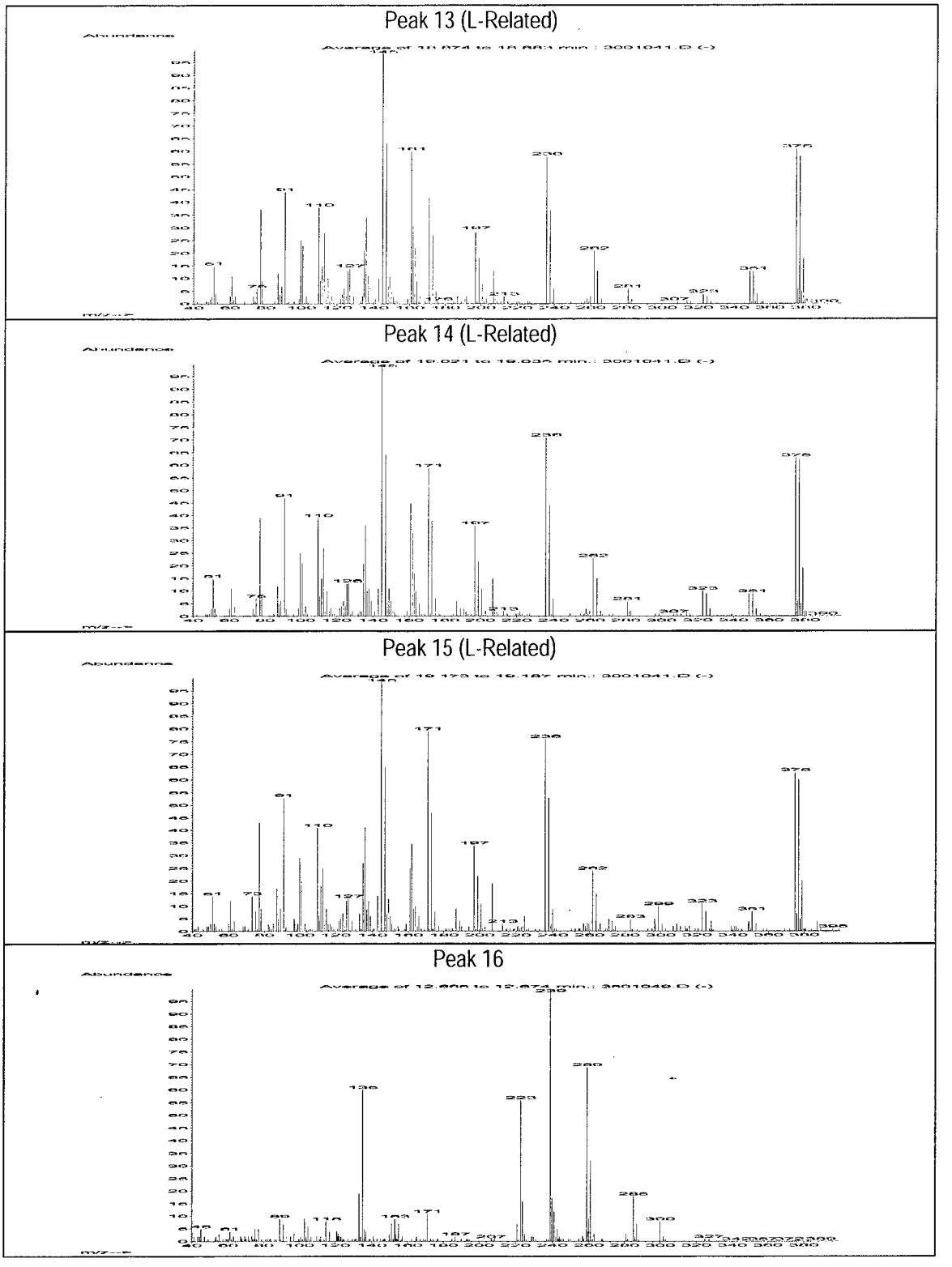


Figure 17. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

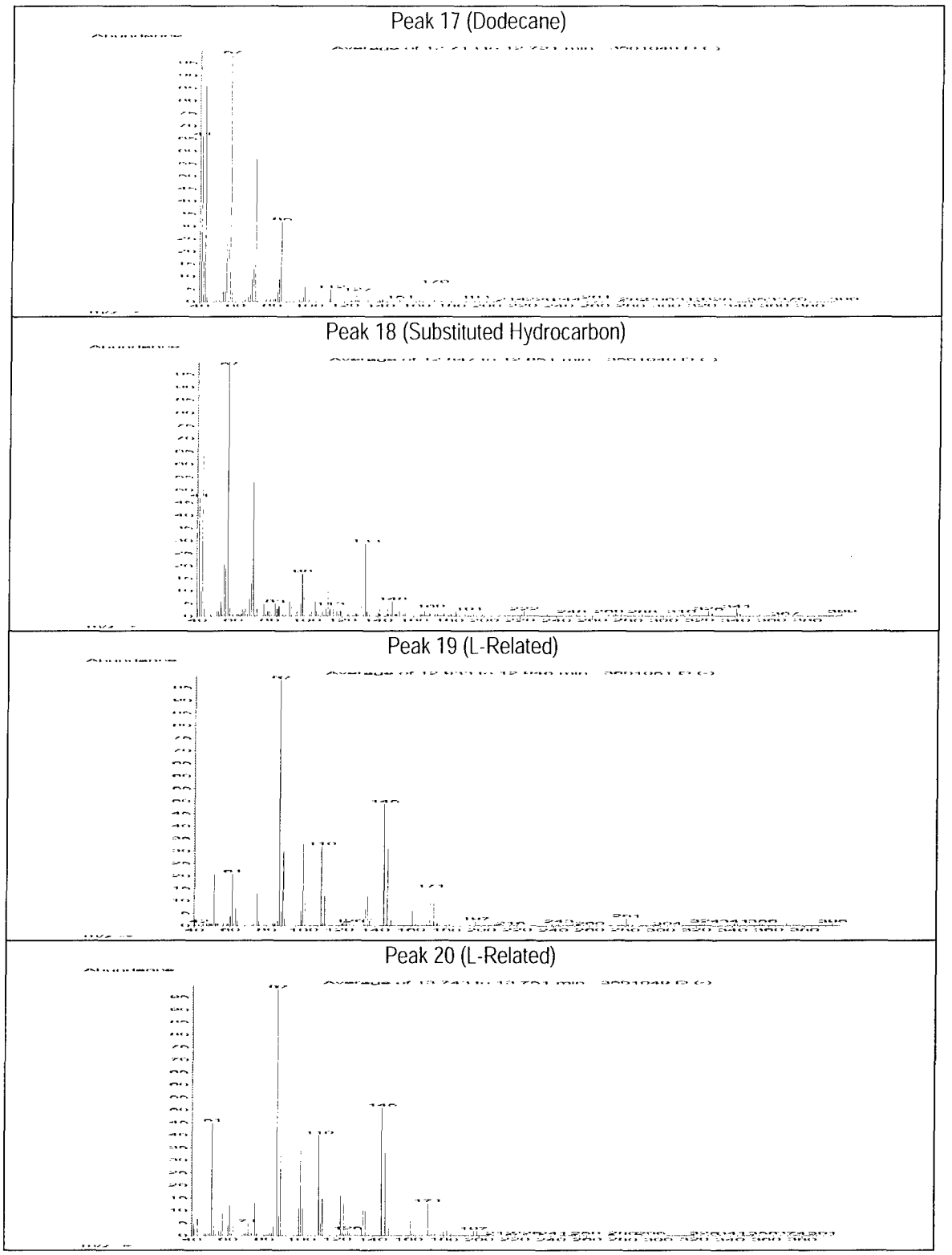


Figure 18. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

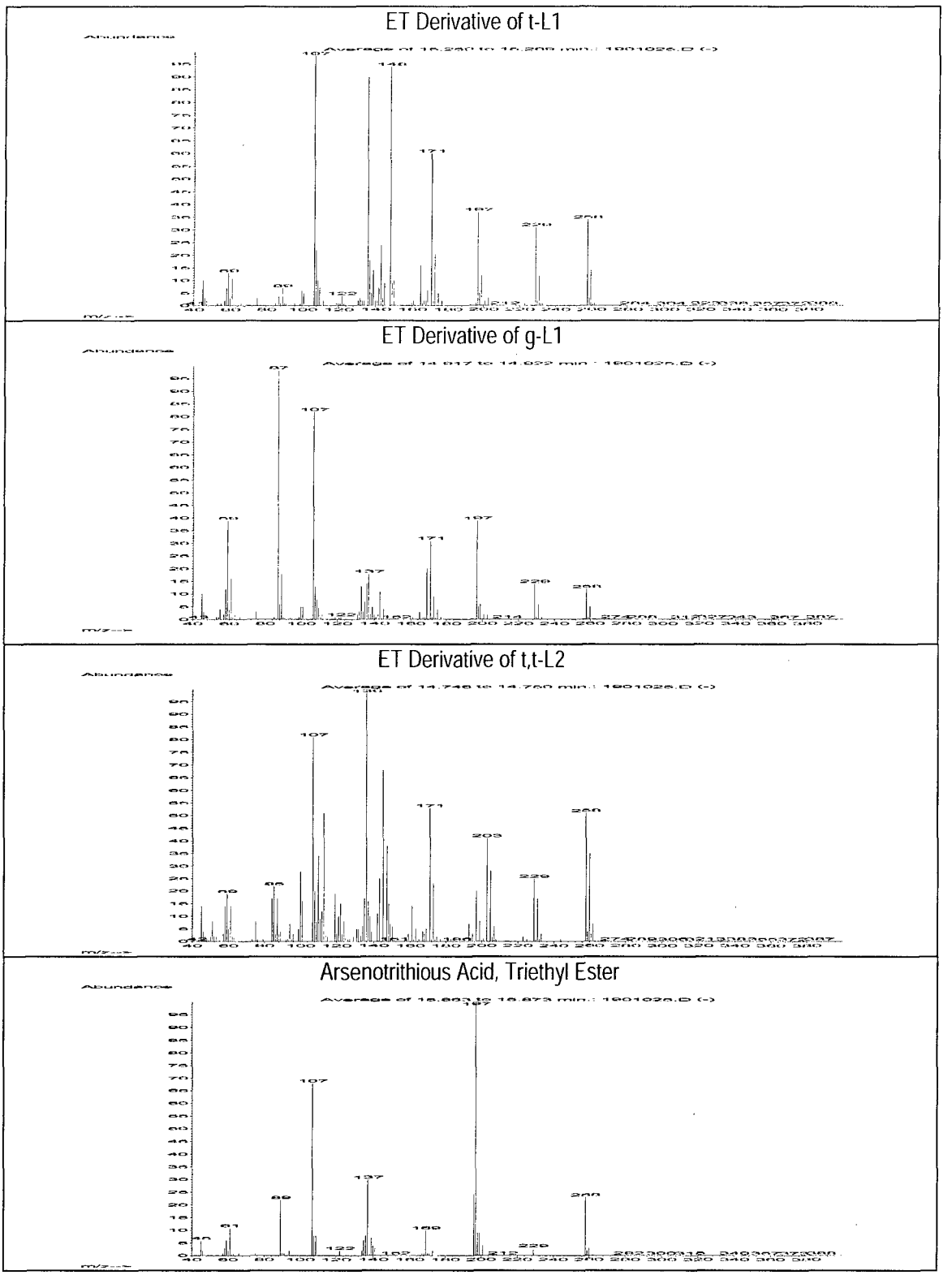


Figure 19. Mass Spectra of Chemicals Detected during the Gas Chromatographic Analyses. All spectra have been normalized to the largest mass equal to 100%.

3.1.2 Bulk Composition by NMR.

It was necessary to measure the spin-lattice relaxation times (T_1) of each chemical to be determined, to allow for an appropriate relaxation time between NMR pulses. To allow complete relaxation of magnetization between NMR pulses, a minimum delay of 4-5 times the longest T_1 must be used when acquiring quantitative NMR spectra.[38] Using fill materiel from each munition, 100 µL of fill materiel, 100 µL of 1,1,2,2 tetrachloroethane (internal standard, CAS No. 79-34-5), and 1 mL of deuterated solvent ($CDCl_3$, 99.8 atom % D) was added to a 4 mL glass vial. After mixing, the solution was transferred to a glass NMR tube, and T_1's were determined for each peak. On average, the ^{13}C T_1's were determined to be: internal standard, 0.58 sec; t-L1, 0.85 sec; g-L1, 0.76 sec; t,t-L2, 0.93 sec; and unassigned peaks ranged from 0.62 to 1.25 sec. Since on e of the unassigned peaks had the longest T_1 of 1.25 sec, a relaxation time of 12 sec was selected for acquisition of quantitative ^{13}C-NMR spectra.

Samples of each fill materiel were individually analyzed by an established quantitative ^{13}C-NMR technique to confirm identity, and determine weight percent purity of the individual agents.[11,39] Each sample was prepared once, but NMR data were acquired in triplicate to confirm stability. Approximately 150 mg (exact weight recorded) of neat fill materiel was weighed into a 4 mL glass vial, and then approximately 160 mg (exact weight recorded) of internal standard was weighed into the vial. One mL of deuterated solvent ($CDCl_3$, 99.8 atom %D) was then added, the vial capped, and mixed. An aliquot was then transferred to a glass NMR tube per established procedures.[11,39] The standard acquisition time was five hr, but it was necessary to acquire data for 25 hr in order to obtain reliable integration of the g-L1 peaks. The data are summarized in Table 9, and example spectra are illustrated in Figures 20 through 22. There were five or six (depending on fill) unassigned peaks in the chloro-vinyl shift region of the spectra. Similar peaks, also unassigned, were found in WWII era lewisite analyzed in another study.[35]

Table 9. Summary of Lewisite Weight Percent Values in the Fill Materiels.

Fill Identification	Concentration in Fill Materiel (wt%)		
	t-L1	g-L1	t,t-L2
L-U-6095-CTF-N			
Mean	80.6	1.75[a]	3.77
SD	5.16	NA	0.526
%RSD	6.40	NA	13.9
DPG-94-028			
Mean	51.7	ND[a]	14.7
SD	3.59	NA	1.23
%RSD	6.94	NA	8.37
DPG-94-055			
Mean	59.6	1.25[a]	10.0
SD	5.21	NA	0.754
%RSD	8.74	NA	7.54

a. Determined using a longer acquisition time; only one replicate analyzed

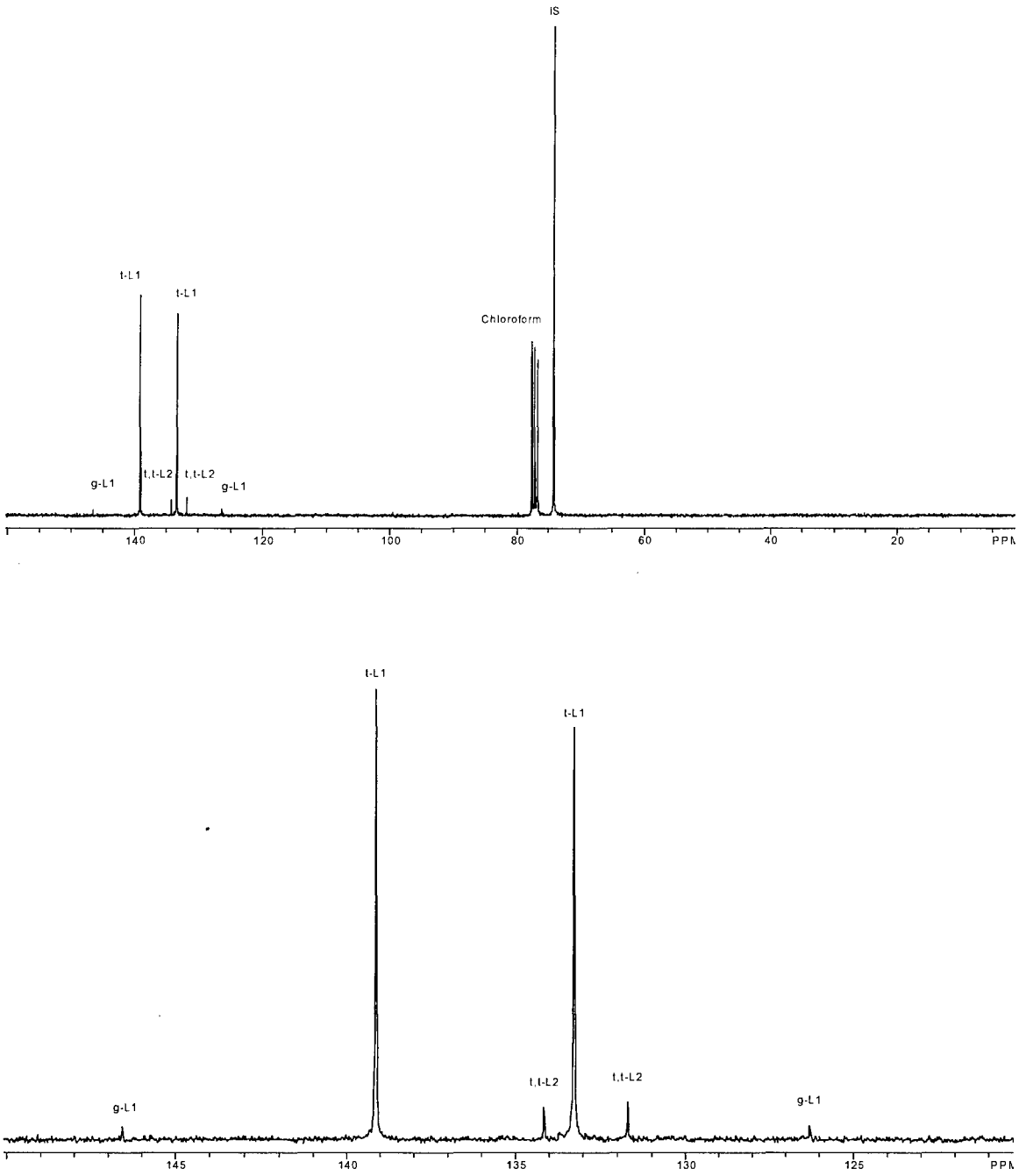


Figure 20. ^{13}C-NMR Spectra of L-U-6095-CTF-N. The upper panel is the full shift range, and the lower panel is zoomed into the chlorovinyl-carbon shift range. Data acquired using a 25 hour sampling time.

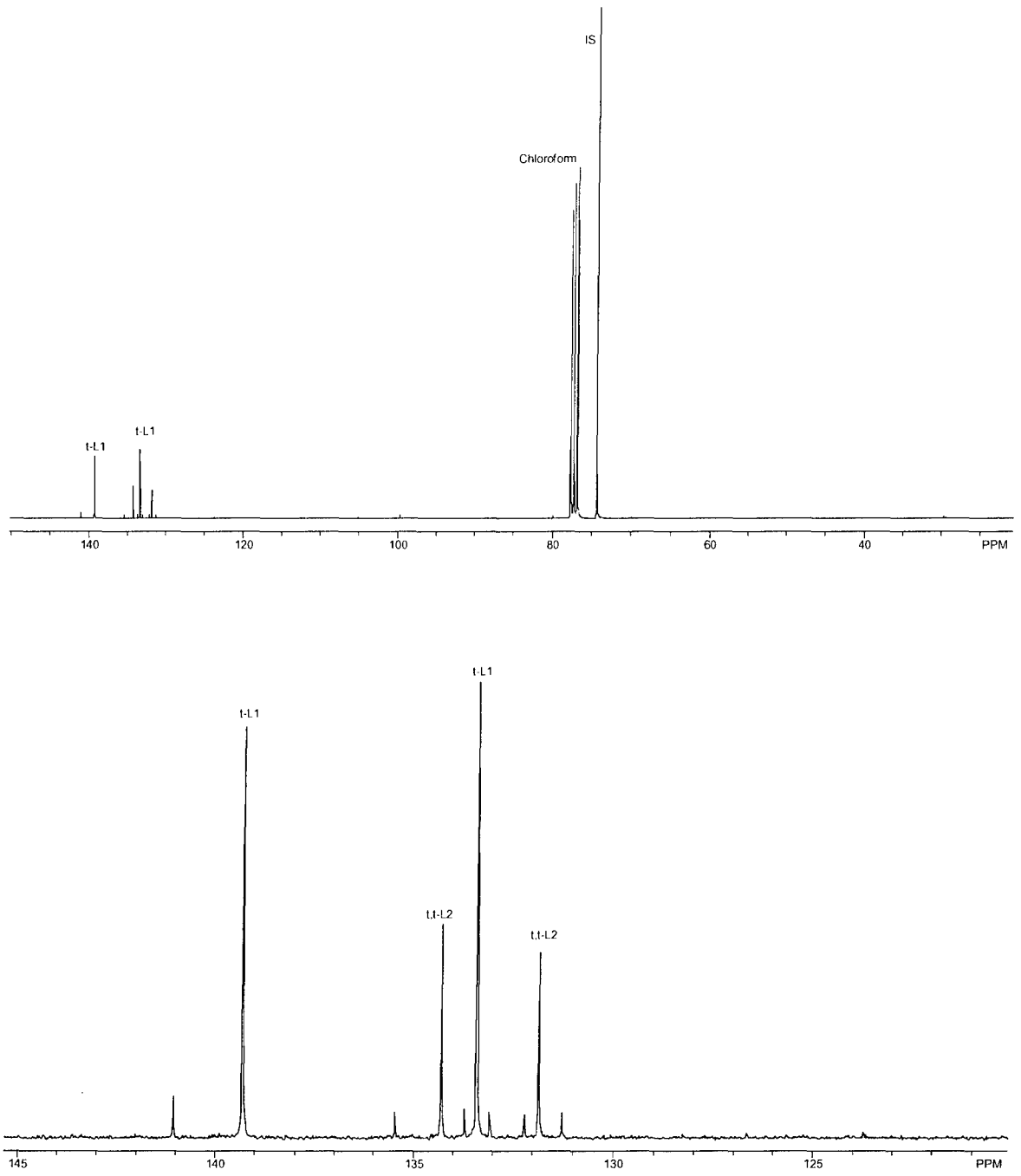


Figure 21. ^{13}C-NMR Spectra of Fill Materiel from DPG-94-028. The upper panel is the full shift range, and the lower panel is zoomed into the chlorovinyl-carbon shift range. Data acquired using a 25 hour sampling time.

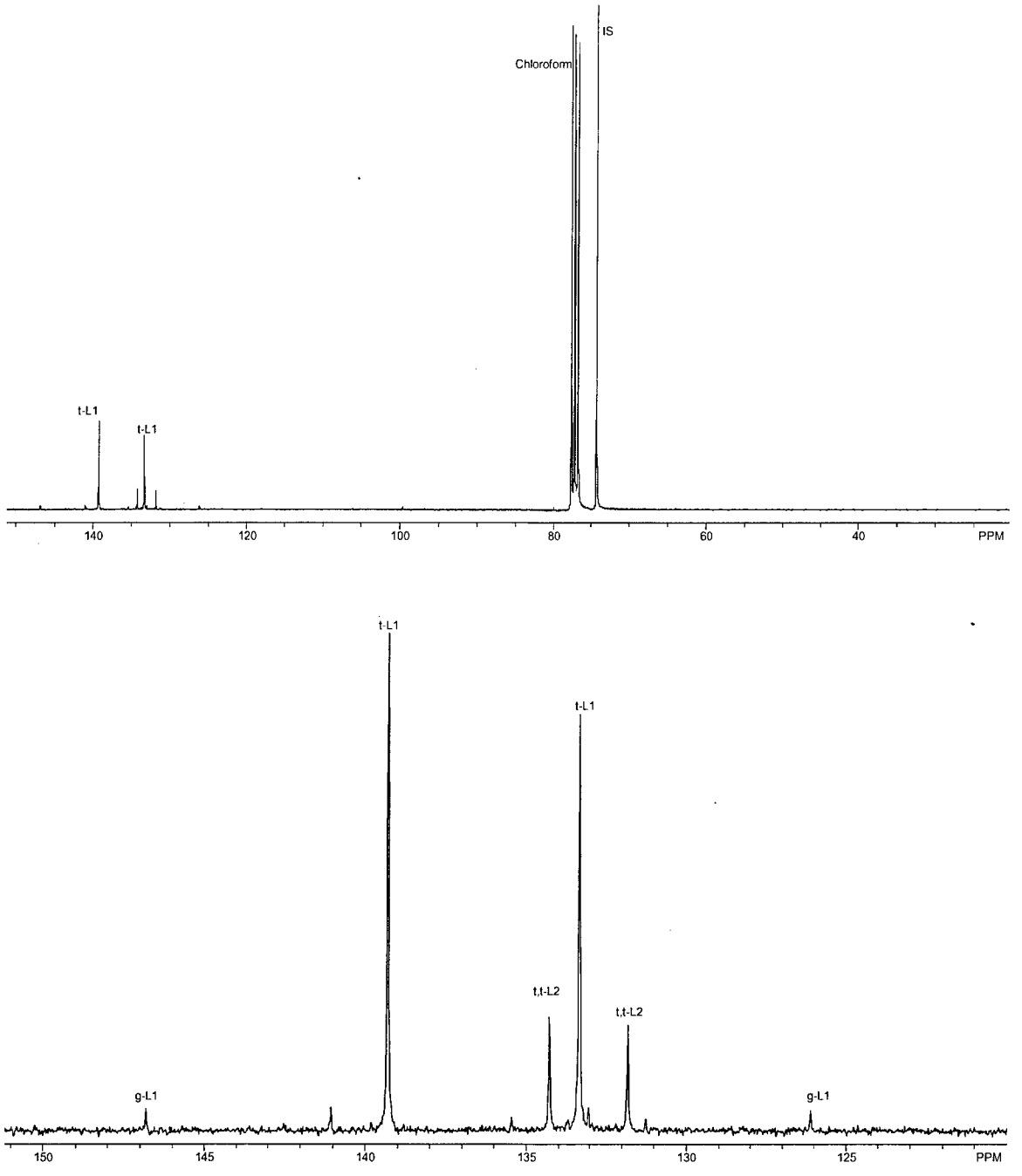


Figure 22. ^{13}C-NMR Spectra of Fill Materiel from DPG-94-055. The upper panel is the full shift range, and the lower panel is zoomed into the chlorovinyl-carbon shift range. Data acquired using a 25 hour sampling time.

3.1.3 Quantitation of L3.

Samples of each fill materiel were individually analyzed by an established quantitative GC/MSD technique to determine the amount of L3 in each fill.[13] Each sample was prepared in triplicate, and quantitation was accomplished using an external calibration model, with a complete set of standards analyzed at the start, and at the end of each sequence analyzing sample extracts. Concurrently with analysis of these samples, extraction blanks (n=2) and laboratory control spikes (1.00 mg/L spike level, n=2) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The average recovery from laboratory control spikes was 93.7 % for L3. The L3 results summarized in Table 10, and there were no anomalies during the preparation or analysis of these samples.

Table 10. Summary of L3 Concentrations in the Fill Materiels.

Data Summary	L3 in Fill Materiel (mg/kg)		
	L-U-6095-CTF	DPG-94-028	DPG-94-055
Mean	104	2,920	2,290
SD	15.2	219.4	87.4
%RSD	14.6	7.51	3.82

3.1.4 Water Soluble Products.

The lewisite fill materiels were analyzed for water-soluble products using the anion capillary electrophoresis method described in Section 2.5. The water-soluble products were determined after samples were prepared using a water extraction approach. Approximately 500 mg (exact weight recorded) of sample was weighed into a 7 mL glass vial, then 2 mL of deionized water was added to the vial, and the vial capped. The vial was then vigorously shaken for 60 sec, and allowed to sit undisturbed for 10 min. The vial was then shaken again, allowed to sit undisturbed for 10 min, and an aliquot of the water layer was filtered (0.45 μm, PTFE Acrodisc™) prior to analysis. Samples were prepared in duplicate. Quantitation was accomplished using an external calibration model, with calibration check standards and laboratory blanks analyzed at the start, and at the end of the sequence analyzing sample extracts. In all cases, there were no analytes detected in any of the laboratory blanks, and all check standards were within acceptable limits. The water soluble product data is summarized in Table 11. **The reported values represent that fraction of chemical which was extractable under the conditions employed, and might not accurately reflect the total concentration in the fill materiel.**

The water soluble arsenite (AsO_2^-) ranged from 19,100 to 43,900 mg/kg in the lewisite fill materiels. Using dimensional analysis, and assuming all the arsenite was from the hydrolysis of arsenic trichloride during sample preparation, the arsenic trichloride concentrations would range from 32,400 to 74,400 mg/kg in the lewisite fill materiels. It is not known whether the arsenite determined to be in the water extract is solely from the hydrolysis of arsenic

trichloride, solely present as an impurity of synthesis, or some combination of the two processes. The presence of oxidized forms of L1 and L2 (CVAOA and BCVAOA) is consistent with aged lewisite, and has been previously reported.[35]

Table 11. Water Extractable Products in Lewisite Fill Materiels. All data reported in the original fill materiel, with units of milligrams/kilograms. These results are on the sample extracted with deionized water, and then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are estimated detection limits based on the average sample weight.

Target Analyte	Concentration in Fill Materiel (mg/kg)		
	L-U-6095-CTF-N	DPG-94-028	DPG-94-055
Arsenite (AsO_2^-)	19,100	43,900	29,100
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	295,000	280,000	306,000
Fluoride (F^-)	ND[a] (28)	ND[a] (28)	ND[a] (28)
Nitrate (NO_3^-)	ND[a] (194)	ND[a] (194)	ND[a] (194)
Sulfate (SO_4^{-2})	ND[a] (179)	ND[a] (179)	ND[a] (179)
CVAA	Present[b]	Present[b]	Present[b]
CVAOA	ND[a] (55)	1,340	1,860
BCVAA	Present[b]	Present[b]	Present[b]
BCVAOA	ND[a] (40)	597	613
Acetate ($C_2H_3O_2^-$)	ND[a] (64)	ND[a] (64)	ND[a] (64)
Formate (CHO_2^-)	ND[a] (60)	ND[a] (60)	ND[a] (60)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)
Glycolate ($C_2H_3O_3^-$)	ND[a] (79)	ND[a] (79)	ND[a] (79)
Oxalate ($C_2O_4^{-2}$)	ND[a] (151)	ND[a] (151)	ND[a] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)

a. No peak was detected.
b. A peak was present, but it was above the calibration range.

3.1.5 Total Metals.

The total metal analyses were performed on duplicate digests of the neat lewisite fill materiel. The digests for total mercury were prepared according to the procedure specified in SW-846, Method 7470A,[40] while the digests for the other metals were prepared according to the procedure specified in SW-846, Method 3010A.[41] The digests prepared specifically for mercury analyses were analyzed using EPA Method 245.1,[42] which is a cold vapor atomic adsorption based method. The other digests were analyzed by two different methods, EPA Method 200.7,[43] or EPA Method 200.8.[44] The 200 series methods are both inductively coupled plasma (ICP) based, but Method 200.7 utilizes optical detection, and Method 200.8 utilizes mass detection. The results are summarized in Table 12. The concurrently run quality control (QC) samples, such as the laboratory control spikes and sample matrix spikes (of the targeted analytes), were all within the acceptable quality limits. There were no deviations or anomalies reported during the digestion or analysis of the lewisite fill materiels during the total metal testing.

The relatively high levels of sulfur in two of the fill materiels was at first surprising, but an examination of the early literature describing the synthesis of arsenical CWAs detailed the use of various sulfur-containing chemicals (SO_2, Na_2SO_3, and $(CH_3)_2SO_4$) in the preparation of these arsenicals.[3] Using dimensional analysis, and assuming all the sulfur was in the form of sulfate (SO_4^{-2}), the average SO_4^{-2} concentration in the lewisite fills would be 2,860 mg/kg. The CE analyses of the liquid lewisite fills did not detect any SO_4^{-2} (Table 11), with an estimated detection limit of 179 mg/kg. However, the CE analyses would only detect water soluble forms of SO_4^{-2} (or SO_3^{-2}, which is not resolved from SO_4^{-2}), and the SO_4^{-2} might be in an insoluble salt form.

Using dimensional analysis, a comparison of the arsenic contained in the various arsenic-containing chemicals as determined by NMR and CE was made to the total arsenic determined by ICP. This comparison is summarized in Table 13. There is good agreement between the total arsenic determined by ICP, and the arsenic determined as individual chemicals, with an average percent difference of 9.62 %. This agreement suggests there were no significant levels of arsenic species not accounted for in the characterization of these lewisite fill materiels.

Table 12. Total Metals in Lewisite Fill Materiels. The data is reported in units of milligrams/kilograms, and is in the original fill materiel. The reported results are the averages of duplicate digestions, and have been corrected for the digestion blank.

Target Analyte	Concentration in Fill Materiel (mg/kg)		
	L-U-6095-CTF-N	DPG-94-028	DPG-94-055
Aluminum	4.74	16.6	7.68
Antimony	2.61	7.25	1.69
Arsenic	366,000	237,000	261,000
Barium	ND	ND	ND
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Calcium	ND	ND	ND
Chromium	12.6	0.880	0.540
Cobalt	ND	ND	ND
Copper	3.54	15.4	9.90
Iron	265	531	492
Lead	2.34	ND	8.95
Magnesium	ND	ND	ND
Manganese	0.451	ND	ND
Mercury	103	140	81.5
Nickel	1.46	ND	ND
Potassium	ND	ND	ND
Selenium	4.29	ND	1.05
Silver	ND	ND	ND
Sodium	ND	ND	ND
Sulfur	997	910	ND
Thallium	ND	ND	ND
Tin	17.8	417	438
Vanadium	ND	ND	0.342
Zinc	4.18	ND	0.850

Table 13. Comparison of Total Arsenic as Determined by ICP to Total Arsenic as Determined by Dimensional Analysis.

Lewisite Identification	Total As By ICP (mg/kg)	Total As by Dimensional Analysis (mg/kg)[a]	Percent Difference (%)[b]
L-U-6095-CTF-N	366,000	323,000	12.5
DPG-94-028	237,000	266,000	11.5
DPG-94-055	261,000	274,000	4.86

a. Sum of L1, L2, L3, and other arsenic-containing chemicals as arsenic.
b. Absolute value of (x-y/(x+y/2))*100.

3.2 Selection of Neutralization Reagent.

Initial work examined the small-scale performance of 22 wt% Oxone® (potassium peroxymonosulfate, CAS No. 37222-66-5) and 20 wt% NaOH, with and without metals added to mimic EDS conditions. The metals added to the reaction quickly degraded the Oxone® reagent, rendering it ineffective. While the 20 wt% NaOH was not affected by the presence of added metals, the initial reaction was violent, with a large release of acetylene. In addition, the lewisite feedstock used in these experiments had a low level of L3, and previous studies demonstrated 20 wt% caustic would not be effective against elevated levels of L3.* This was followed by micro and small-scale screening evaluations of permanganate reagent (U.S. Patent pending), which was previously demonstrated to be effective for neutralizing phenyl-arsenical CWAs under EDS conditions.[13]

3.2.1 Small-Scale Screening of Reagent Candidates.

These reactions were conducted in the 250 mL glass reactor system described in Section 2.2, and were conducted at loadings (v:v) of 1:50 and 1:40 feedstock to reagent. The reactions were conducted with and without metals added to the reaction. The impinger solutions described in Section 2.2 were not analyzed during this effort. In all cases, the feedstock was "L-U-6095-CTF-N", which was a munitions grade lewisite obtained from bulk storage. The fill material was analyzed using quantitative ^{13}C-NMR and GC/MSD techniques,[13,40] and was determined to contain 80.6 wt% t-L1, 1.75 wt% g-L1, 3.77 wt% t,t-L2, 0.0104 wt% L3 as the bulk chemical constituents. In addition, the fill materiel was digested, and determined to contain 36.6 wt% total arsenic.

* Morrissey, K.M. Development and Validation of a Reagent for the Neutralization of Arsenical-Based Sludges Contained in Ton Containers; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, unpublished data, June 2006.

The reactions conducted with Oxone® were all well behaved, with no foaming or bumping observed at any time during the reactions. On average, there was a 25 °C exotherm at a rate of 1.7 °C/min when the lewisite was added to the reagent. The Oxone® based neutralent remained acidic (pH 0.5-1.0) throughout the reaction. Oxidizing capacity was exhausted (starch-iodide paper negative) after 1 hour of reaction when metals were present, and after 2 hr of reaction without metals added. The reactions conducted with NaOH generated large amounts of foam when the Lewisite was added; presumably from the formation of acetylene and vinyl chloride. On average, there was a 10 °C exotherm at a rate of 6.7 °C/min when the lewisite was added to the NaOH solution. The NaOH based neutralents remained alkaline (pH 13-14) throughout the reaction. Example temperature data collected during two runs are illustrated in Figures 23 and 24.

The residual agent and reaction product data are summarized in Tables 14 through 19. The results indicate the Oxone® reagent was very effective in destroying the agents when no metals were added, however, the presence of metals quickly degraded performance. The Oxone® reagent was quickly decomposed by the copper and iron added to simulate metals contained in the linear shape charge (LSC) and fragmentation suppression shield (FSS) portions of the EDS, and lost efficacy. The rapid loss of oxidizing capacity when Oxone® was used in the presence of copper and iron, rendered it unsuitable for use in the EDS. The generation of large amounts of acetlyene and vinyl chloride during the neutralization of lewisite with NaOH posed safety issues during EDS operations. These safety issues, and the lack of efficacy against high levels of L3,* eliminated NaOH from further consideration for application in the EDS.

Text continues on page 52.

* Morrissey, K.M. Development and Validation of a Reagent for the Neutralization of Arsenical-Based Sludges Contained in Ton Containers; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, unpublished data June 2006.

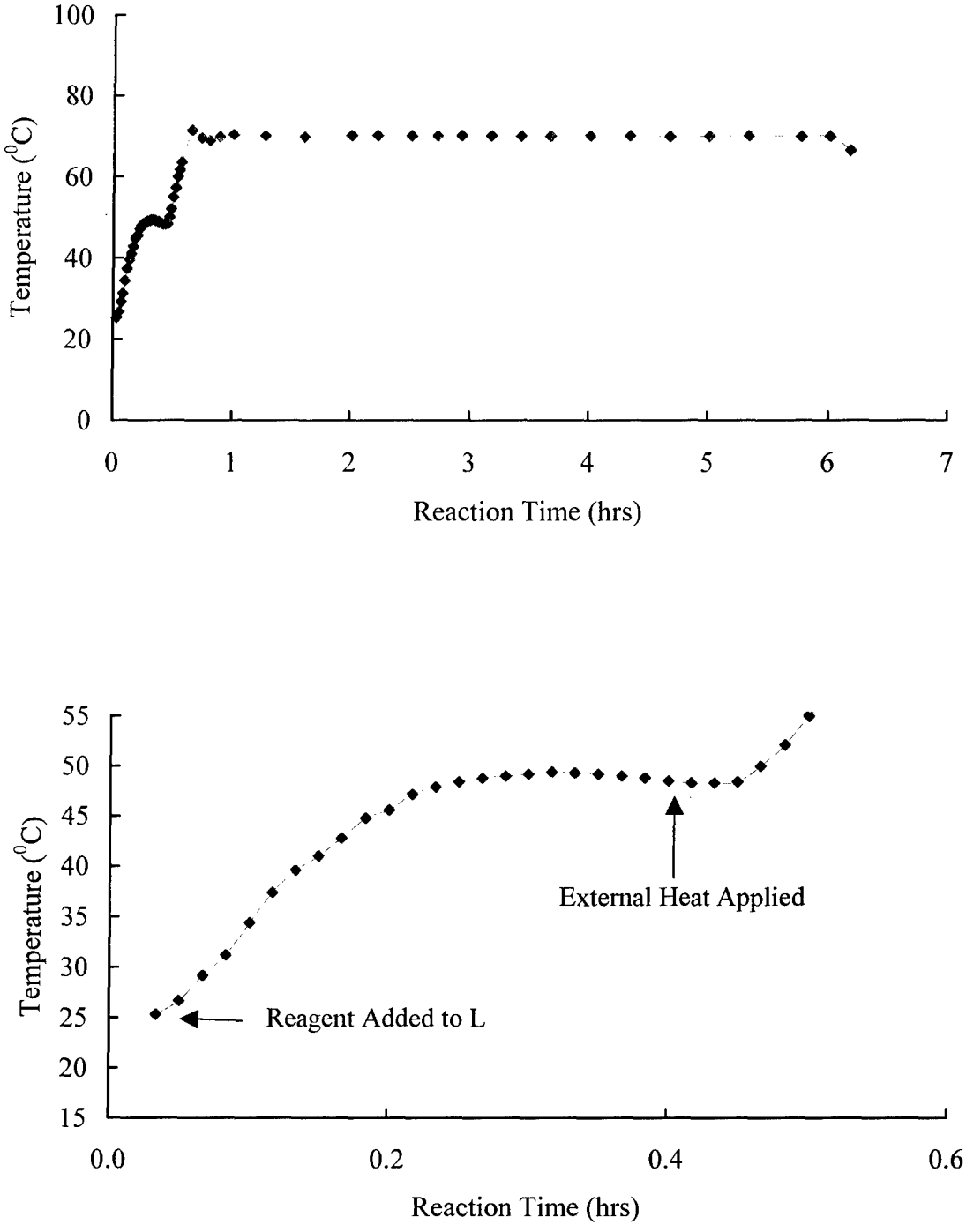


Figure 23. Example Temperature Versus Time Data for Oxone® Run Conducted at 70 °C. The reaction was conducted at a loading of 1:40, and metals were added. The upper panel is the full range of data, and the lower panel is zoomed into the timeframe when the lewisite was added to the reagent.

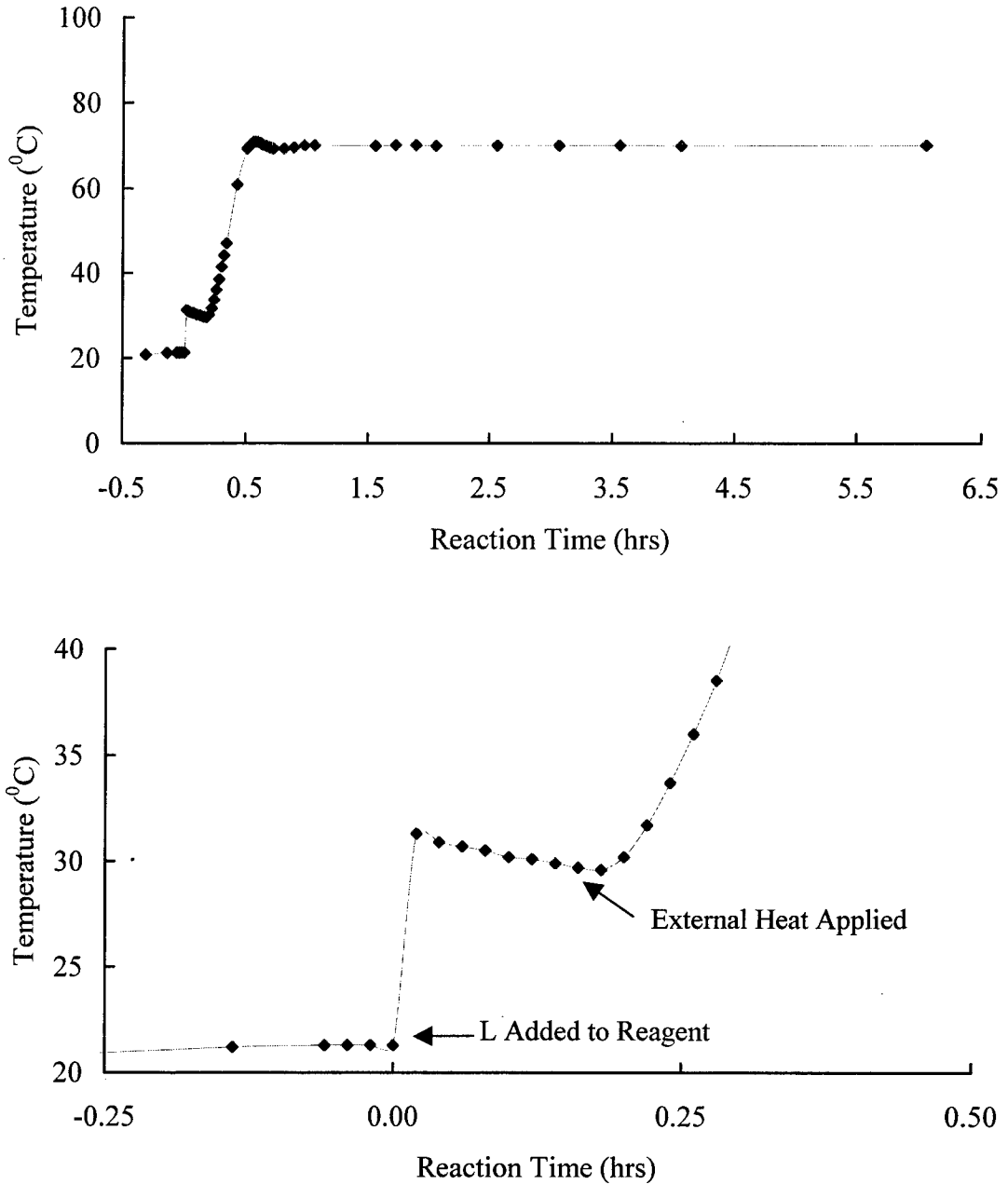


Figure 24. Example Temperature Versus Time Data for NaOH Run Conducted at 70 °C. The reaction was conducted at a loading of 1:40, and metals were added. The upper panel is the full range of data, and the lower panel is zoomed into the timeframe when the lewisite was added.

Table 14. Summary of Analytical Results for the Oxone® Reagent at 70 °C, 1:40 Loading, and with Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	680	1,730	2,460	2,760
L2	12.7	15.1	19.7	22.4
L3	27.0	27.3	34.8	35.6
Arsenite (AsO_2^-)	854	769	940	1,080
Arsenate ($HAsO_4^{-2}$)	15,100	12,500	13,000	12,100
Chloride (Cl^-)	7,800	6,820	7,390	7,170
CVAA ($C_2H_2O_2AsCl^{-2}$)	921	1,500	2,050	2,350
CVAOA ($C_2H_2O_3AsCl^{-2}$)	16,500	15,100	16,200	16,200
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	1,130	851	921	1,030
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	783	484	324	258
Oxalate ($C_2O_4^{-2}$)	Int[c]	Int[c]	Int[c]	Int[c]
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected.
b. Peak detected, but less than reporting limit.
c. Interference from large sulfate peak prevented detection of this analyte. Sulfate from decomposition of Oxone®.

Table 15. Summary of Analytical Results for the Oxone® Reagent at 85 °C, 1:40 Loading, and with Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	1,810	2,000	2,250	2,220
L2	43.3	45.0	63.1	52.0
L3	200	131	145	145
Arsenite (AsO_2^-)	2,940	3,550	3,290	3,560
Arsenate ($HAsO_4^{-2}$)	13,000	11,200	12,700	12,700
Chloride (Cl^-)	5,000	5,670	6,450	5,630
CVAA ($C_2H_2O_2AsCl^{-2}$)	1,570	2,240	1,940	1,980
CVAOA ($C_2H_2O_3AsCl^{-2}$)	13,900	13,800	14,900	13,800
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	1,150	1,340	1,170	1,270
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	598	239	Trace[b] (200)	Trace[b] (200)
Oxalate ($C_2O_4^{-2}$)	Int[c]	Int[c]	Int[c]	Int[c]
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected.
b. Peak detected, but less than reporting limit.
c. Interference from large sulfate peak prevented detection of this analyte. Sulfate from decomposition of Oxone®.

Table 16. Summary of Analytical Results for the Oxone® Reagent at 70 °C, 1:40 Loading, and without Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	3.04	1.62	1.39	8.66
L2	9.25	2.42	1.78	7.19
L3	3.85	2.26	1.33	3.28
Arsenite (AsO_2^-)	ND[a] (160)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Arsenate ($HAsO_4^{-2}$)	12,200	15,900	16,000	14,600
Chloride (Cl^-)	2,880	3,050	3,400	4,090
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)	ND[a] (230)	ND[a] (230)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	18,600	17,900	16,800	14,700
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	573	485	493	291
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	1,140	937	788	468
Oxalate ($C_2O_4^{-2}$)	Int[c]	Int[c]	Int[c]	Int[c]
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected.
b. Peak detected, but less than reporting limit.
c. Interference from large sulfate peak prevented detection of this analyte. Sulfate from decomposition of Oxone®.

Table 17. Summary of Analytical Results for the NaOH Reagent at 70 °C, 1:40 Loading, and with Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	65.3	59.9	60.4	64.8
L2	3.59	1.36	0.443	0.237
L3	ND[a] (0.05)	ND[a] (0.05)	ND[a] (0.05)	ND[a] (0.05)
Arsenite (AsO_2^-)	22,600	23,700	22,500	22,500
Arsenate ($HAsO_4^{-2}$)	275	332	344	423
Chloride (Cl^-)	27,000	27,000	28,700	27,200
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)	ND[a] (230)	ND[a] (230)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	ND[a] (150)	ND[a] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	ND[a] (380)	ND[a] (380)	ND[a] (380)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected.
b. Peak detected, but less than reporting limit.

Table 18. Summary of Analytical Results for the NaOH Reagent at 80 °C, 1:50 Loading, and with Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	2.95	3.25	3.07	4.12
L2	ND* (0.05)	ND* (0.05)	ND* (0.05)	ND* (0.05)
L3	ND* (0.05)	ND* (0.05)	ND* (0.05)	ND* (0.05)
Arsenite (AsO_2^-)	18,100	21,700	20,700	20,300
Arsenate ($HAsO_4^{-2}$)	199	294	263	339
Chloride (Cl^-)	20,100	20,300	23,200	19,500
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND* (230)	ND* (230)	ND* (230)	ND* (230)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
BCVAA ($C_4H_4OAsCl_2^-$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
Acetate ($C_2H_3O_2^-$)	ND* (160)	ND* (160)	ND* (160)	ND* (160)
Formate (CHO_2^-)	ND* (150)	ND* (150)	ND* (150)	ND* (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)
Glycolate ($C_2H_3O_3^-$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)
Oxalate ($C_2O_4^{-2}$)	ND* (380)	ND* (380)	ND* (380)	ND* (380)
Succinate ($C_4H_4O_4^{-2}$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)

* No peak was detected.

Table 19. Summary of Analytical Results for the NaOH Reagent at 90 °C, 1:50 Loading, and with Metals Added. The GC results (residual agents) are reported as the mean of duplicate determinations, and the CE results (reaction products) are a single replicate. All data reported in the original neutralent, with units of mg/L. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hr)			
	1	2	4	6
L1	2.79	2.95	3.12	3.19
L2	ND* (0.05)	ND* (0.05)	ND* (0.05)	ND* (0.05)
L3	ND* (0.05)	ND* (0.05)	ND* (0.05)	ND* (0.05)
Arsenite (AsO_2^-)	18,500	18,200	19,800	20,100
Arsenate ($HAsO_4^{-2}$)	254	325	430	461
Chloride (Cl^-)	20,700	21,100	20,500	20,800
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND* (230)	ND* (230)	ND* (230)	ND* (230)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
BCVAA ($C_4H_4OAsCl_2^-$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND* (100)	ND* (100)	ND* (100)	ND* (100)
Acetate ($C_2H_3O_2^-$)	ND* (160)	ND* (160)	ND* (160)	ND* (160)
Formate (CHO_2^-)	ND* (150)	ND* (150)	ND* (150)	ND* (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)
Glycolate ($C_2H_3O_3^-$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)
Oxalate ($C_2O_4^{-2}$)	ND* (380)	ND* (380)	ND* (380)	ND* (380)
Succinate ($C_4H_4O_4^{-2}$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)

* No peak was detected.

3.2.2 Initial Investigations into the Efficacy of Sodium Permanganate.

A previous study examining the neutralization of sludge materiels from ton containers containing weight percent levels of lewisites concluded that 20 wt% $NaMnO_4$ (U.S. Patent pending) could effectively neutralize the lewisite residues.* In addition, a recent evaluation of the efficacy of 20 wt% $NaMnO_4$ (U.S. Patent pending) against phenyl-arsenical CWAs in actual EDS operations also concluded 20 wt% $NaMnO_4$ could effectively neutralize the phenyl-arsenicals, and could be implemented in the EDS.[13]

Using the micro-scale screening approach outlined in Section 2.1, a preliminary experiment investigating the efficacy 20 wt% $NaMnO_4$ was conducted using munitions grade lewisite (L-U-6095-CTF-N). In this experiment, the loading of neat lewisite to reagent was 1:40 and 1:20, the reactions were stirred and reaction temperatures were 55 and 75 °C. Individual reaction vials were harvested at 2, 4, and 6 hr, with each treatment conducted in duplicate. The residual agent results are summarized in Table 20, and indicate 20 wt% $NaMnO_4$ is very efficacious, resulting in total (sum L1, L2, L3) residual agent levels well below the individual treatment goal of 50 mg/L In addition to the residual agent data, reaction behavior was also noted. In all cases, reactions were well behaved, with no apparent exotherms.

Micro-scale experiments were conducted to determine the gases produced during the reaction of 20 wt% $NaMnO_4$ and 18 wt% NaOH with munitions grade lewisite. In these experiments, 500 µL of reagent was added to a 5 mL reaction vessel, and the headspace blanketed with argon. The vial was sealed (septa cap), and additional argon was pumped into the vial. A 25 µL aliquot of neat lewisite (L-U-6095-CTF-N, 1:20 loading) was introduced through the septa, and the reaction allowed to proceed at room temperature. Two hundred µL of headspace gases were removed at 10, 60, and 120 min after the lewisite was added, and analyzed by GC/MSD in full SCAN mode. Chromatograms comparing the two reagents after 10 min of reaction are illustrated in Figures 25 and 26. The predominant gases generated during the reaction of lewisite with 18 wt% caustic were acetylene, with some vinyl chloride. The gases produced during the caustic reaction were expected, and are consistent with previous studies.[45,46] The predominant gases generated during the reaction of lewisite with 20 wt% $NaMnO_4$ were CO_2 and O_2. The acetylene and 1-propene detected in the gas above the 20 wt% $NaMnO_4$ reaction appear to be background, as they are also found in the ambient lab air background.

Additional micro-scale experiments, focused on detection and quantitation of acetylene, were also performed. In these experiments, 500 µL of 20 wt% $NaMnO_4$ was added to a 5 mL reaction vessel, and the headspace blanketed with argon. The vial was sealed (septa cap), and additional argon pumped into the vial. A 10 µL of neat lewisite (L-U-6095-CTF-N, 1:50 loading) was introduced through the septa, and the reaction allowed to proceed at 60 °C. Two hundred µL of headspace gases were removed at 15, 60, and 120 min after the lewisite was

* Morrissey, K.M. Development and Validation of a Reagent for the Neutralization of Arsenical-Based Sludges Contained in Ton Containers; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, unpublished data June 2006.

added, and analyzed by GC/MSD in SIM mode. An additional sample was collected at 180 min, and analyzed by GC/MSD in full SCAN mode. In addition to the lewisite/$NaMnO_4$ reaction, the headspace above just 20 wt% $NaMnO_4$ (also heated at 60 °C) was also analyzed over time. Chromatograms from the full SCAN runs are illustrated in Figures 27 and 28. The predominant gases generated from the reaction of lewisite with 20 wt% NaMnO4 are CO_2 and O_2. Note the chromatographic method does not resolve N_2, O_2, and Ar. The spectra of the unresolved peak indicate it is predominantly Ar and O_2, with a small amount of N_2. The 1-propene is ubiquitous, and is also found in the ambient laboratory air. This background of 1-propene is thought to be off-gassing from plastics found in the environment and in the septa used to seal the vial. Chromatograms comparing the acetylene region of various chromatograms are illustrated in Figure 29 and 30. This data supports the observation that there is no significant amount of acetylene generated during the reaction of lewisite with 20 wt% $NaMnO_4$. The acetylene peak observed in these reactions is from ambient laboratory air background, or a co-eluting interferent with the same spectra.

Based on previous experience using 20 wt% $NaMnO_4$ to neutralize lewisite residues and phenyl-arsenical CWAs,[13,*] and the micro-scale work described above, it was decided to advance this reagent to full-scale EDS testing. In order to reduce the logistical burden of EDS field operations, it was decided not to pursue optimization of the basic 20 wt% $NaMnO_4$ reagent to enhance performance. Such optimization would have included addition of co-solvents, catalysts, and adjustment of pH. The use of unmodified 20 wt% $NaMnO_4$ has several logistical advantages over a modified or mixed reagent system. These include: the commercial availability of 20 wt% $NaMnO_4$ in bulk, it's stability in storage, and ready availability of data on many of its properties.

Table 20. Summary of Residual Agent Results from the Reaction of Munitions Grade Lewisite with 20 wt% $NaMnO_4$. The results are reported as the mean of duplicate reactions, and all data is reported in the original neutralent. The data is presented as the sum of L1, L2, and L3.

Reaction Conditions	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
1:40 loading at 55 °C	ND[a]	ND[a]	ND[a]
1:40 loading at 75 °C	ND[a]	ND[a]	ND[a]
1:20 loading at 55 °C	2.71	5.21	4.88
1:20 loading at 75 °C	6.11	4.62	2.49

a. Detection limit is estimated to be 0.05 mg/L.

* Morrissey, K.M. Development and Validation of a Reagent for the Neutralization of Arsenical-Based Sludges Contained in Ton Containers; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, unpublished data June 2006.

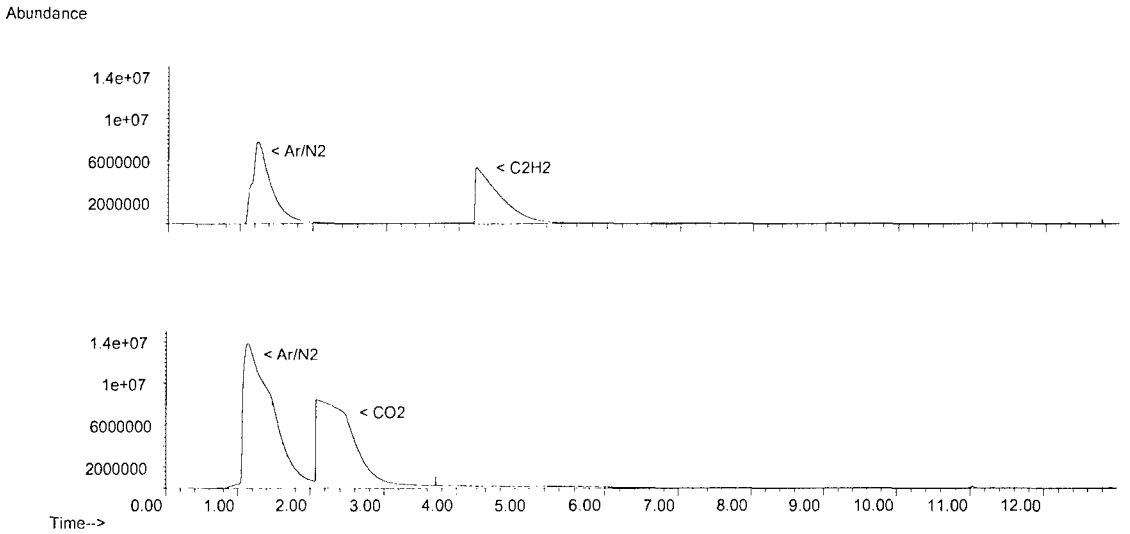


Figure 25. Comparison of the Headspace Gases Above a Lewisite/Caustic Reaction (upper panel) and a Lewisite/Permanganate Reaction (bottom panel). The data was acquired by GC/MSD-EI, in full SCAN mode. The samples were both obtained 10 min after the lewisite was added to the sealed reaction vial. The Ar was introduced into the vial, and is not a product gas.

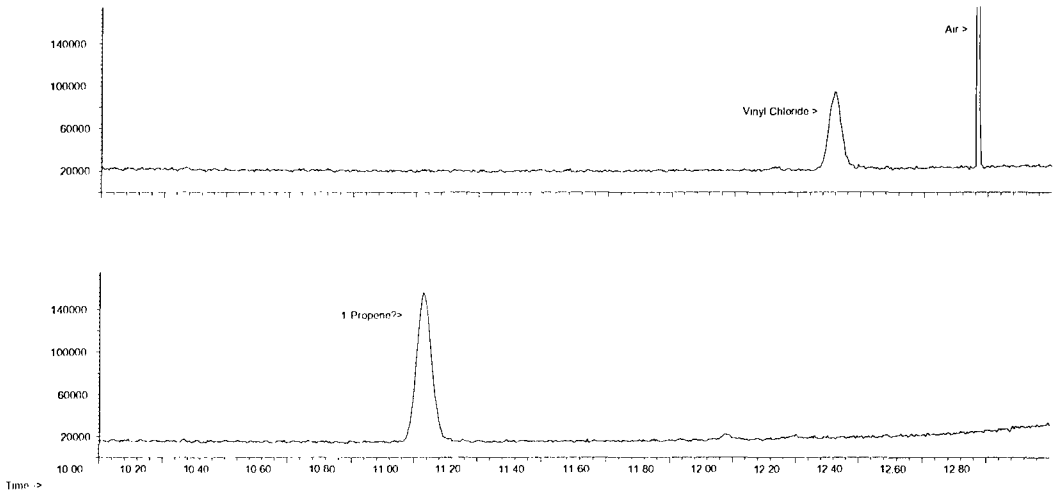


Figure 26. Comparison of the Headspace Gases Above a Lewisite/Caustic Reaction (upper panel) and a Lewisite/Permanganate Reaction (bottom panel). The data was acquired by GC/MSD-EI, in full SCAN mode. The samples were both obtained 10 min after the lewisite was added to the sealed reaction vial. The scales have been zoomed in to see the trace level chemicals.

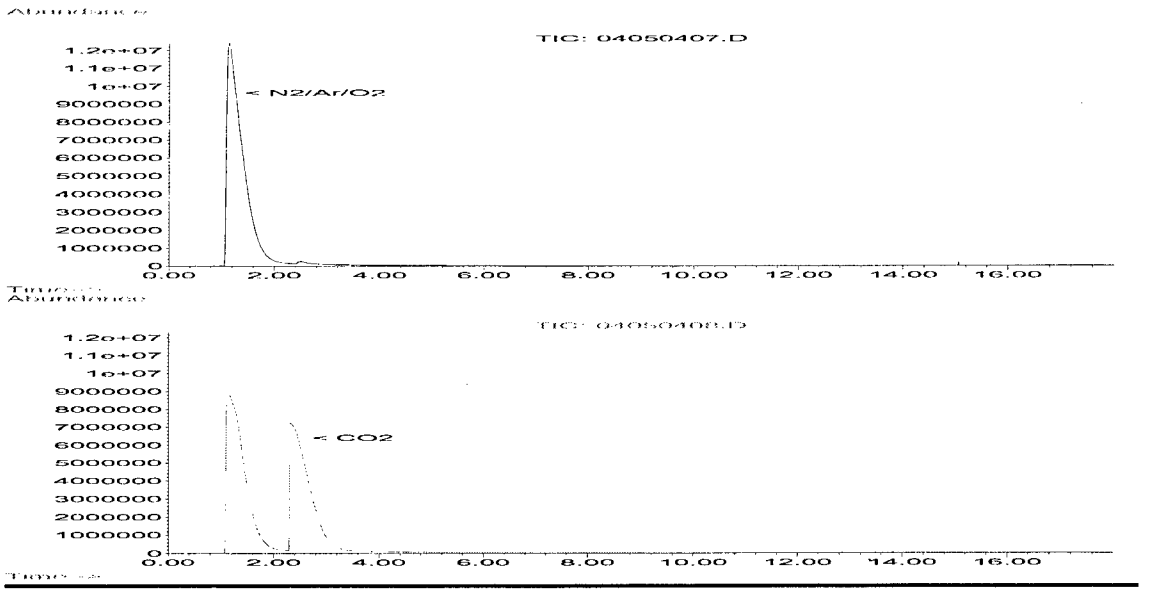


Figure 27. Comparison of the Headspace Gases Above a 20 wt% $NaMnO_4$ Reagent Blank (upper panel) and a Lewisite/Permanganate Reaction (bottom panel). The data was acquired by GC/MSD-EI, in full SCAN mode. The samples were both obtained after 3 hr at 60 °C.

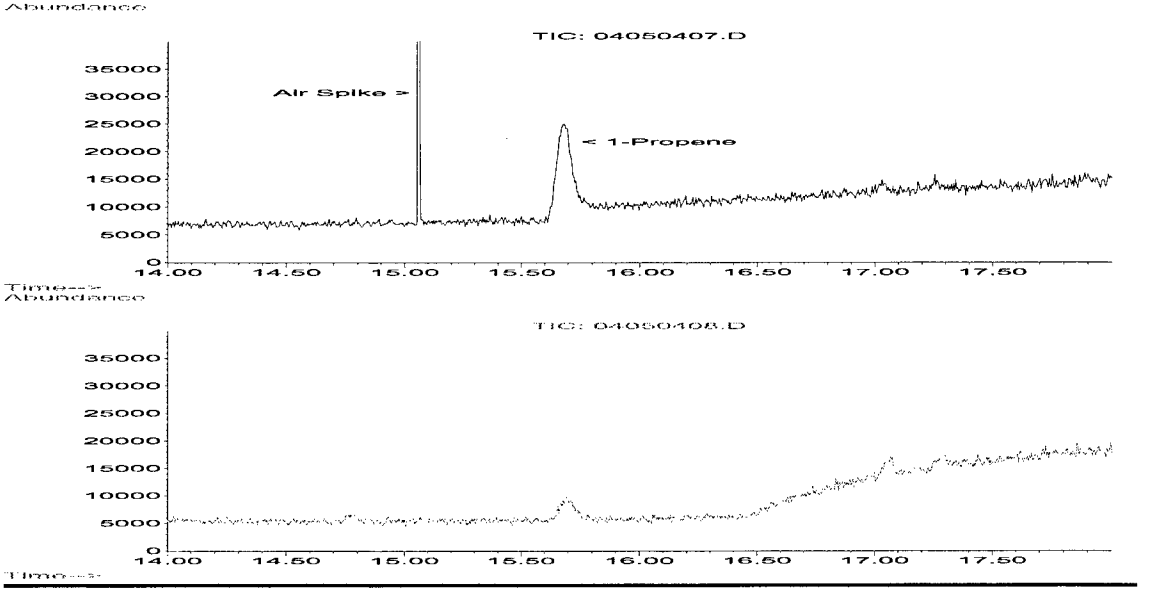


Figure 28. Comparison of the Headspace Gases Above a 20 wt% $NaMnO_4$ Reagent Blank (upper panel) and a Lewisite/Permanganate Reaction (bottom panel). The data was acquired by GC/MSD-EI, in full SCAN mode. The samples were both obtained after 3 hr at 60 °C. The scales have been zoomed in to see the trace level chemicals.

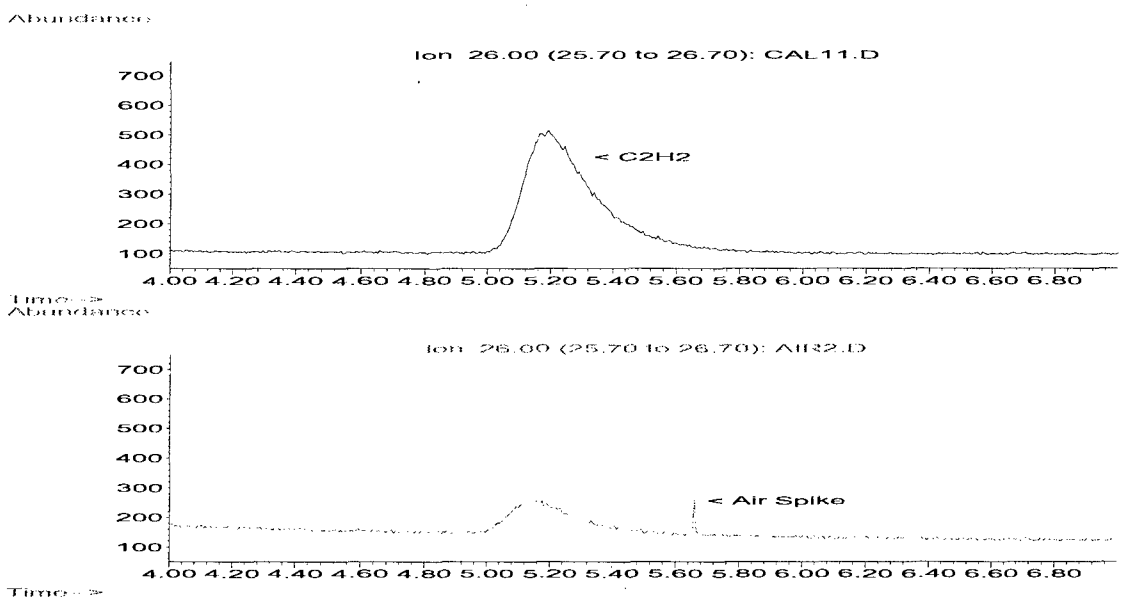


Figure 29. Comparison of a 14.2 ppm Acetylene Standard (top panel) and Ambient Laboratory Air (bottom panel). The data was acquired by GC/MSD-EI, in SIM mode. The scales have been zoomed in to see the acetylene region of the chromatogram.

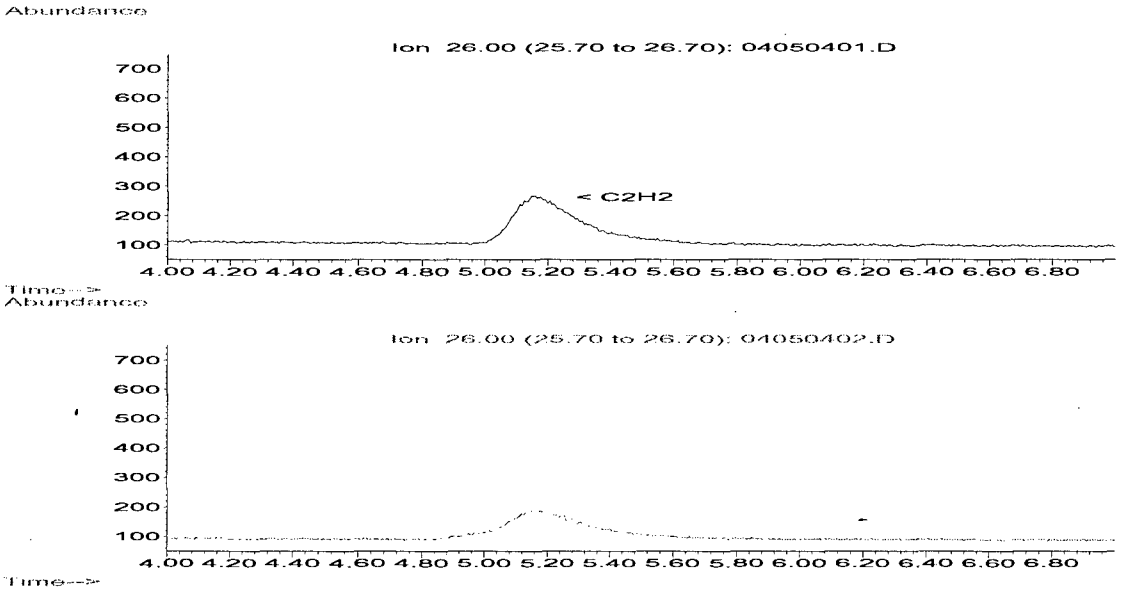


Figure 30. Comparison of the Headspace Gases Above a 20 wt% $NaMnO_4$ Reagent Blank (upper panel) and a Lewisite/Permanganate Reaction (bottom panel). The data was acquired by GC/MSD-EI, in SIM mode. The samples were both obtained after 15 min at 60 °C. The scales have been zoomed in to see the acetylene region of the chromatogram.

3.3 Preparation and Characterization of Permanganate Reagent.

The reagent used in the laboratory studies was prepared from reagent grade 40 wt% $NaMnO_4$ solution by making a 1:1 dilution (by weight) of the starting reagent with deionized water. The resulting reagent was 20 wt% $NaMnO_4$. The reagent was stored in a glass reagent bottle, at ambient temperature.

3.3.1 General Properties of Permanganate Reagent.

Concentrated sodium permanganate solutions are strong oxidizers, and need to be handled with appropriate precautions.[47,48] A summary of general properties, taken from the open literature,[47,48] is provided in Table 21. The oxidative strength of permanganate, as compared to other common oxidizers, is summarized in Table 22.[49]

Table 21. Summary of Properties of 20 wt% $NaMnO_4$ Solutions. Data from references 49 and 50.

Parameter	Value
Appearance and Odor	Dark purple solution; odorless
Boiling Point (760 mm)	>101°C
Freezing Point	-6°C
Insoluble Matter	100-1,900 ppm
pH	6-9
Shelf-Life*	18 months
Specific Gravity	1.16 g/mL

* Storage conditions not specified.

Table 22. Relative Oxidizing Strength of Common Oxidizers. All data is relative to chlorine being rated as 1.0.[51]

Oxidative Species	Relative Oxidizing Strength*
Fluorine	2.23
Hydroxyl Radical	2.06
Atomic Oxygen	1.78
Hydrogen Peroxide	1.31
Perhydroxyl Radical	1.25
Permanganate	1.24
Hypobromous Acid	1.17
Chlorine Dioxide	1.15
Hypochlorous Acid	1.10
Hypoiodous Acid	1.07
Chlorine	1.00
Bromine	0.80
Iodine	0.54

* Relative to chlorine being 1.00

3.3.2 Materials Compatibility.

A literature search was conducted to collect data relating to the compatibility of 20 wt% $NaMnO_4$ solutions with a variety of materials. This effort included searching relevant books published by the American Society for Metals (ASM), the American Society for Testing and Materials (ASTM) and the National Association of Corrosion Engineers (NACE); searches of electronic databases of published technical works; contacting chemical suppliers of $NaMnO_4$; and internet searches using several search engines.

Based on the data collected, many metal alloys are considered compatible with 20% permanganate solutions at room temperature, and near neutral or slightly alkaline pH values.[50-53] These include carbon steel, aluminum alloys, copper alloys, stainless steels, and nickel alloys. Compatibility of these materials is defined as having corrosion rates between 2 and 20 mils per year (mpy). Compatibility in acidic solutions varies significantly depending on the acidic species present.

Stainless steels (304 and 316) are recommended by Carus Chemical Corporation for use in pumps and piping components that are typically operated at, or slightly above, room temperature.[54] Carus warns that the presence of chlorides in the permanganate solution will accelerate attack to stainless steels. Higher alloyed stainless steels (Alloy 20, 904L, or the 6% Mo super austenites) may offer better corrosion resistance when chlorides are present, but there is little published data to support this.[55-56] Among nickel alloys, the C family (C, C276, C22, C2000) of nickel alloys is intended for exposure to oxidizing environments, and are expected to

perform well in an oxidizing environment such as 20 wt% $NaMnO_4$.[55,56] Titanium, gold, and platinum were also reported to perform well in permanganate solutions, with corrosion rates of 2 mpy or less.[50]

Nylons, polyesters, acrylics, styrenes, furans, nitrile, natural rubber, SBR, and isoprene are not compatible with aqueous permanganate solutions.[59-62] Fluoropolymers (PTFE, PVDF, ETFE, and E-CTFE), EP, and EPDM are considered to be compatible under a variety of conditions.[57-60]

The data collected during the literature search indicates there are numerous materials compatible with aqueous permanganate solutions. However, most of the data was based on exposure to dilute (<5%) solutions of $KMnO_4$, not 20 wt% $NaMnO_4$. Although the sodium salt form is expected to behave similarly, no specific data concerning exposure to 20 wt% $NaMnO_4$ was found. The collected data also indicates that compatibility of many materials is dependent on temperature, pH, and the presence of halides, especially chloride. The lack of specific exposure data suggests material compatibility studies should be performed using 20 wt% $NaMnO_4$, and in the expected temperature range of EDS operations.

The sodium permanganate reagent proposed for the detoxification of CWAs in the EDS will come into contact with various materials during the processing and handling steps,[61] so a baseline evaluation of the materials compatibility of the reagent was conducted. An initial short-term evaluation (4 to 12 hr) was performed by another laboratory,[62] and found no compatibility issues with using 20 wt% $NaMnO_4$ at 60 °C in contact with EPDM, 316 stainless steel, and 304 stainless steel. The evaluation performed during this study focused on ethylene propylene diene monomer (EPDM), as the literature search indicated the stainless steels to be generally compatible with the reagent itself. In addition, EDS engineers were most concerned with how well the EPDM gaskets in the EDS would perform with 20 wt% $NaMnO_4$ as the reagent.[63] The materials compatibility study was conducted in accordance with standard NACE and ASTM test methods.[64,65]

The baseline compatibility of sodium permanganate reagent with EPDM was conducted at three temperatures: 60, 80, and 100 °C. The EPDM coupons were approximately 1" X 1" X 0.125 ", and the average initial weight was 3.193 g. In each test, a sample of EPDM was fully immersed in the reagent, with each treatment being conducted in duplicate. Care was taken that none of the sample coupons were touching each other during the test. After 7, 14, 30, 60, and 90 days, test specimens were removed, and after cleaning the specimens, measurements were made on mass, dimensions, and hardness. The data are summarized in Figures 31 through 33, and photographs of the test specimens are illustrated in Figures 34 and 35.

The changes in measured properties suggest EPDM is compatible with 20% $NaMnO_4$ at temperatures up to 80 °C, with little or no deterioration observed after 90 days of immersion. At 100 °C, deposits (presumably MnO_2) started forming on the EPDM test specimens after seven days of immersion. These deposits were tightly adherent, and very difficult to remove, even with scraping. The small increases in mass and hardness suggest the EPDM was being slowly deteriorated at 100 °C. The increase in hardness combined with the deposit formation would require EPDM gaskets be replaced more often if the reactions were

conducted above 80 °C. Short-term (5 day) exposure studies using actual neutralent generated from the reaction of 20 wt% $NaMnO_4$ and phenyl-arsenicals were also performed at 60 and 80 °C. In another study, there were no significant differences observed in EPDM performance when neutralent or unused 20 wt% $NaMnO_4$ was used to perform the compatibility studies.[13]

3.3.3 Reaction Mechanism.

Permanganate solutions are used in the remediation of contaminated groundwater,[66-68] disinfection and pre-oxidation of drinking water,[69-71] treatment of industrial wastewaters,[72,73] and in organic synthesis reactions.[74,75] A general description of the reaction mechanism, obtained from a literature source related to groundwater remediation,[66] is provided below:

> *"Permanganate has a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups. As an electrophile, the permanganate ion is strongly attracted to the electrons in carbon-carbon double bonds found in chlorinated alkenes, borrowing electron density from these bonds to form a bridged, unstable oxygen compound known as the hypomanganate diester. This intermediate product further reacts by a number of mechanisms including hydroxylation, hydrolysis or cleavage. Under most naturally occurring subsurface pH and temperature conditions, the carbon-carbon double bonds of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion."*

The reaction pathways and kinetics of the oxidation of trichloroethylene (TCE) by aqueous permanganate solutions has been extensively studied,[67,68,76,77] and the process has been determined to proceed in three sequential steps.[76] These steps are illustrated in Figure 36. The first step is the formation of the cyclic hypomanganate ester, which was found to be independent of pH in the range studied (pH 4-8 @ 21 °C). The second step is the decomposition of the cyclic ester to various organic acids. This second step was found to be dependent on pH, with formic acid being the predominant acid formed at pH of 4. Oxalic glycolic, and glyoxylic acids were the major products formed at pH values of 6 and 8. The final step is the oxidation of organic acids to CO_2, which proceeds relatively slowly, and is dependent on pH. The rate of oxidation to CO_2 increases with decreasing pH.

The oxidation of trivalent arsenic to pentavalent arsenic by aqueous permanganate solutions and manganese dioxide has also been studied.[78,79] The majority of these studies were related to drinking water remediation, and focused on the inorganic forms of arsenic. In aqueous solution, the oxidation of arsenite to arsenate with potassium permanganate was very fast, with >95% of the arsenite converted to arsenate in less than 1 min.[79] This study included interferents such as elevated levels of iron, sulfide, dissolved manganese, dissolved organic carbon, and pH ranging between 6.3 to 8.3. These interferents did not significantly impede the oxidation of arsenite. While the majority of the tests were performed at ambient temperature (~24 °C), several experiments were performed at 5 °C, with no significant slowing of the oxidation of arsenite to arsenate observed.

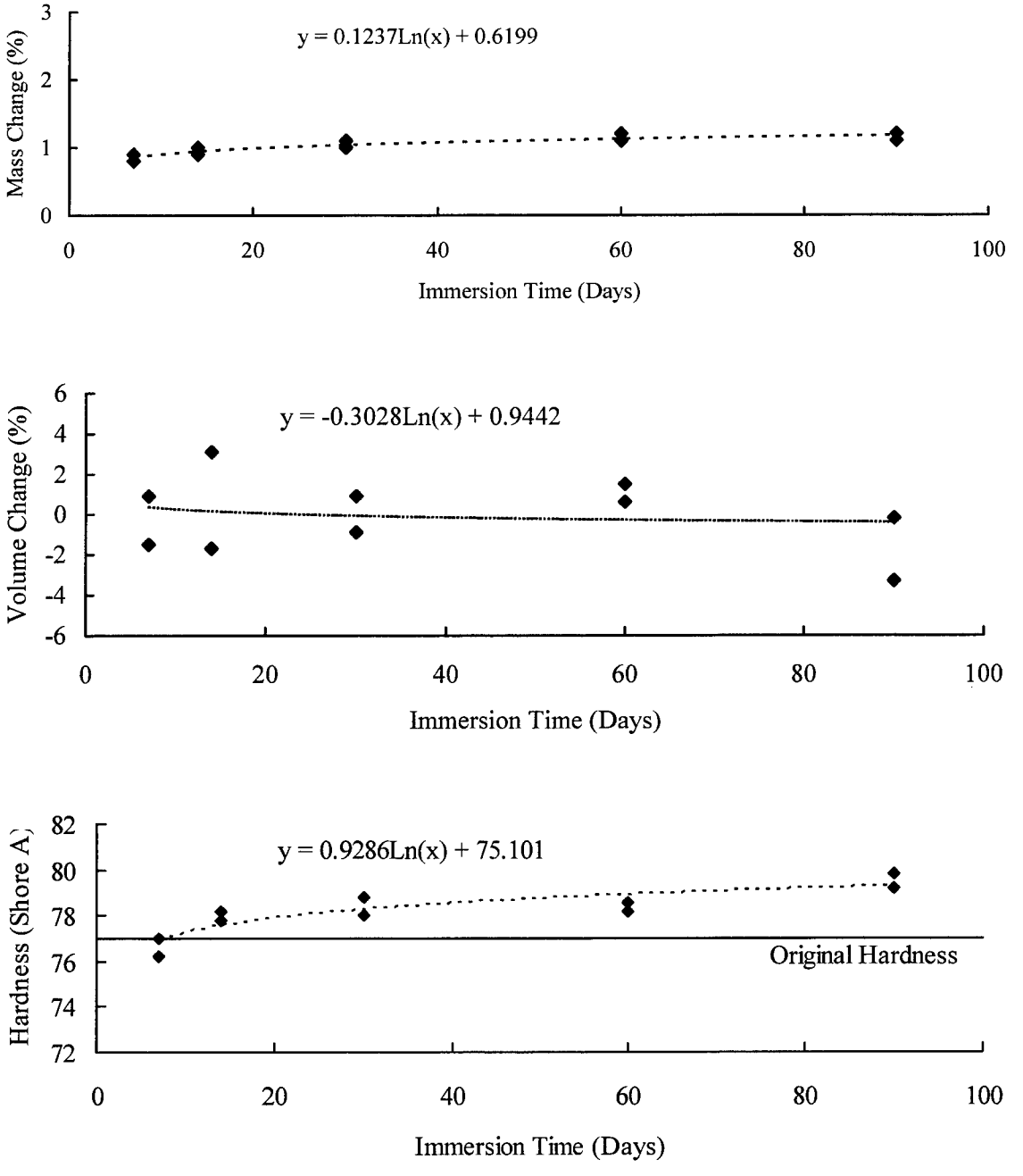


Figure 31. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 60 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness values are averages of five readings from each test specimen.

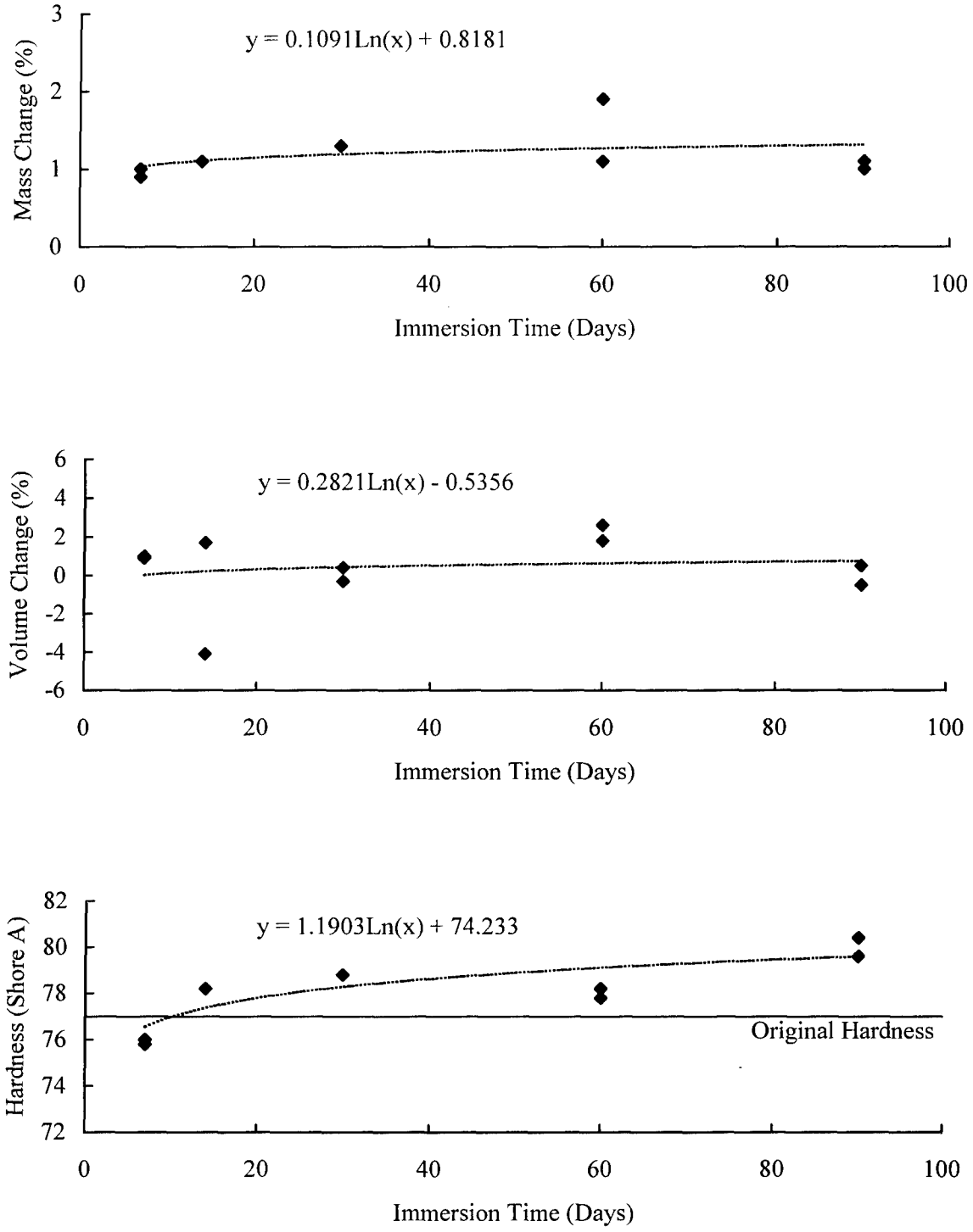


Figure 32. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 80 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness values are averages of five readings from each test specimen.

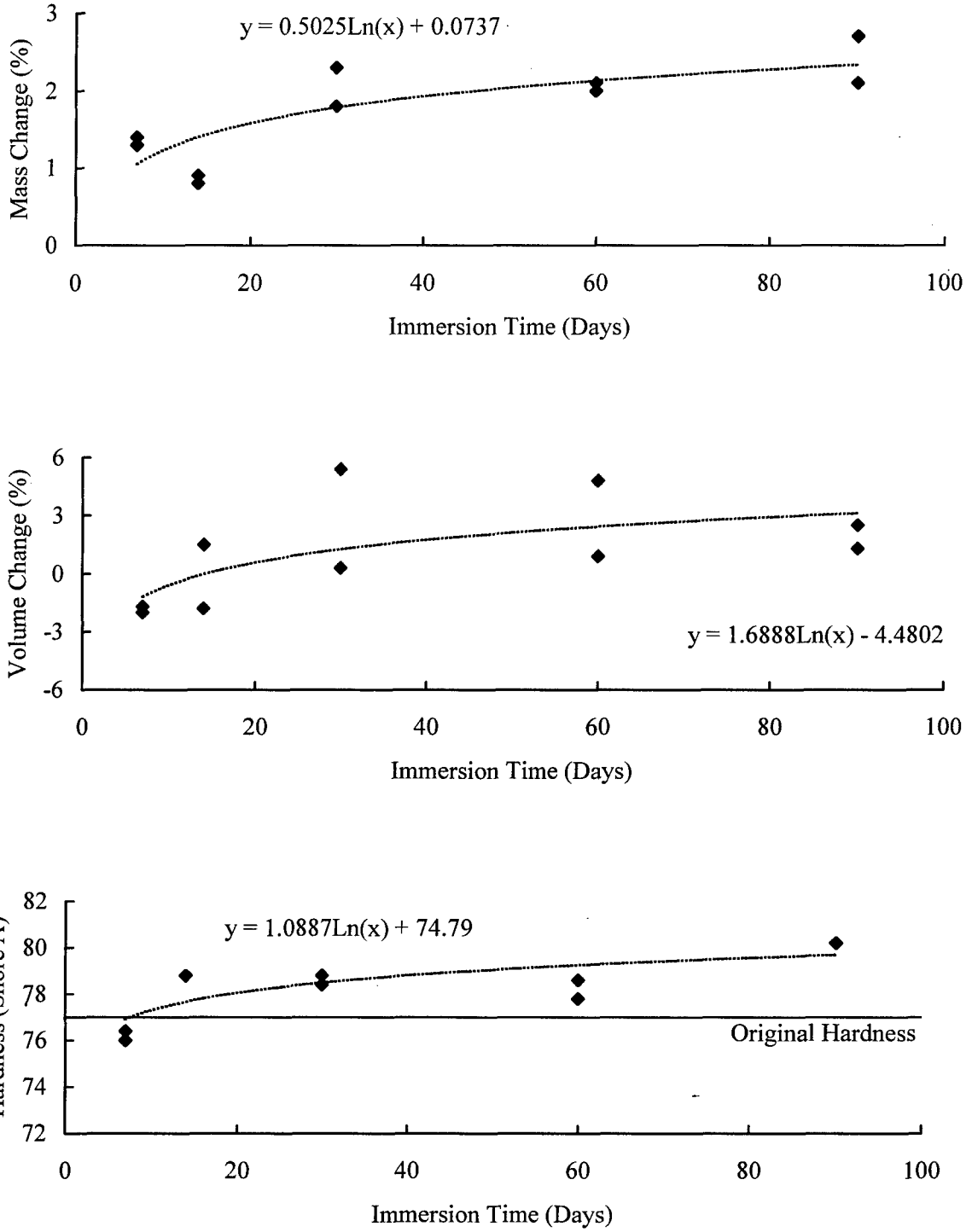


Figure 33. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 100 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness values are averages of five readings from each test specimen.

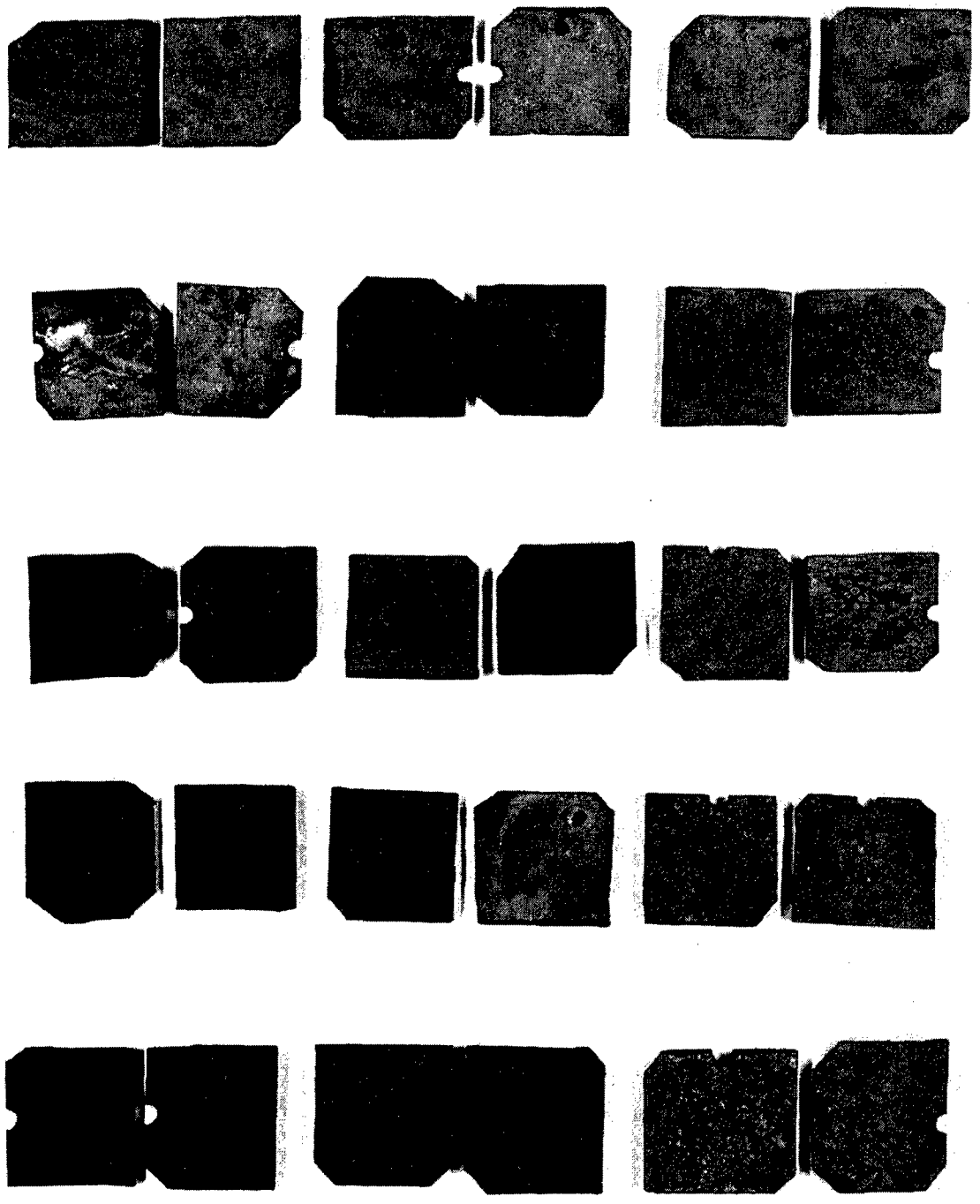


Figure 34. Cleaned Test Specimens after Exposure to 20% $NaMnO_4$ at Three Different Temperatures. The top panel is the test specimens after seven days of exposure, the next panel down is after 14 days, the third panel down is after 30 days, the fourth panel down is after 60 days, and the bottom panel is after 90 days. In all cases, the left two specimens were exposed at 60 °C, the middle two specimens were exposed at 80 °C, and the right two specimens were exposed at 100 °C.

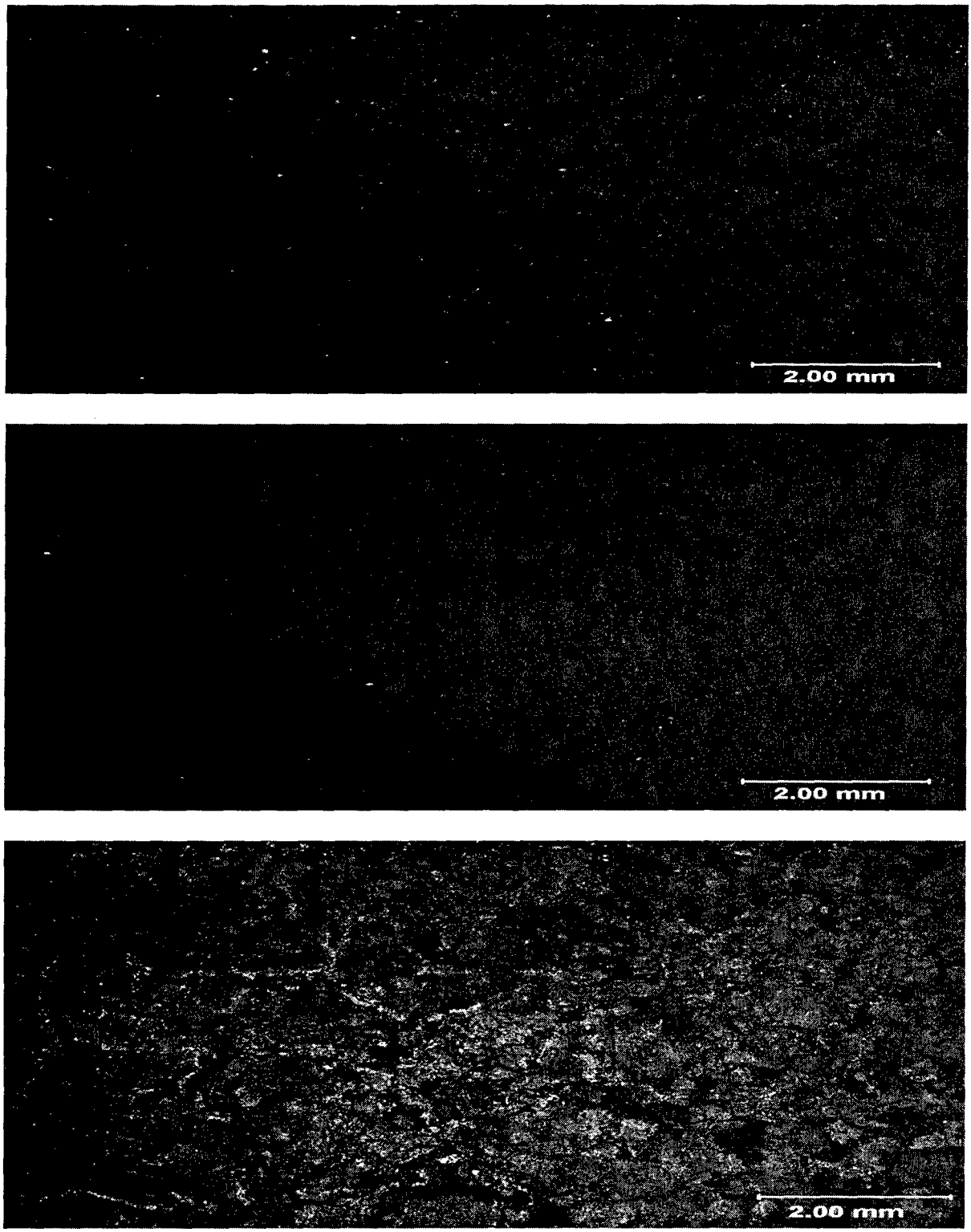


Figure 35. Surface Features of Unexposd EPDM (upper panel), Test Specimen After 90 Days of Exposure at 60 °C (middle panel), and Test Specimen After 90 Days of Exposure at 100 °C (lower panel). Surfaces are magnified 11 times. Note deposits on surface of specimens exposed at 100 °C.

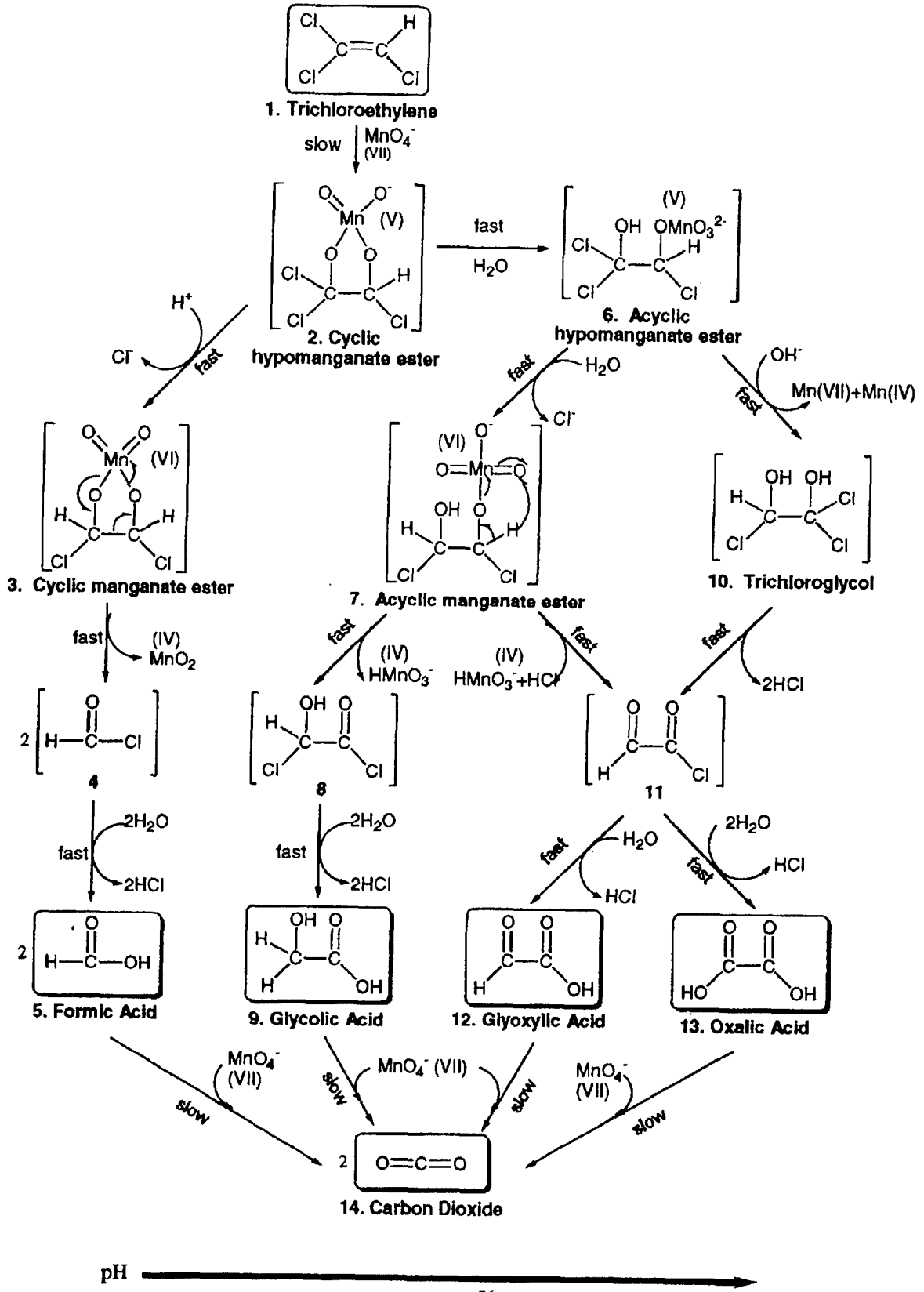


Figure 36. Trichloroethylene Oxidation Pathways.[76]

3.4 Full-Scale Validation of Permanganate Reagent.

The Explosive Destruction System, is a trailer-mounted system designed to safely neutralize a variety of chemical munitions.[80,81] It employs explosive-shaped charges to breach the munition's wall, exposing the chemical fill, while containing the chemical fill at the same time. Once the fill is exposed, chemical reagents are added, and the vessel is agitated and heated. After neutralization, waste materials are removed from the reaction vessel and transported to a treatment, storage, and disposal facility (TSDF) for final disposal.

This section describes the chemical characterization of samples obtained during four full-scale trials examining the efficacy of 20 wt% $NaMnO_4$ reagent against actual arsinol fills neutralized using an EDS. This section focuses on the chemical composition of the resulting samples and waste streams, and not on operational issues associated with the testing. Operational effectiveness is described in a separate report.[7]

3.4.1 Reaction Conditions.

The reaction conditions are summarized in Table 23, and were obtained from a separate report describing operational effectiveness of the reagent.[7] Procedural details can also be found in the same report.[7] In summary, the DOT bottle or munition containing lewisite was placed into the EDS vessel, and explosive charges attached to the DOT bottle or munition. Once the charges were attached, the EDS vessel was sealed, and the charges detonated. After detonation, the 20 wt% $NaMnO_4$ reagent was pumped into the reactor, and temperature adjusted to the required set point. After the reaction was completed, the resulting neutralent was drained from the reactor, then tap water was pumped into the reactor to rinse the vessel. On average, 81 L of tap water was used, at ambient temperature (13-20 °C) during the first rinse. The first rinse was then drained from the reaction vessel, and a second rinse performed. On average, 65 L was used for the second rinse, and it was also conducted at ambient temperature. After rinsing the reactor, a cleaning solution was used to clean the reactor prior to the next run; this cleaning procedure was only used during EDS runs two and three. Two different cleaning solutions were used; a peroxide/acetic acid solution was used for the second run, and a dilution of HPO_2™ reagent was used after the third run. The HPO_2™ reagent is a proprietary (U.S. Patent Number 6,960,701; all rights reserved), oxidative-based reagent,[82] recently demonstrated to be effective in the detoxification of arsenical-based CWAs.[13] During the reactor campaign, multiple samples were collected at various times during the experiment. The identity and description of the samples are summarized below:

- *Three- Hour Neutralent:* Sample of neutralent removed from the reactor after 3 hr of reaction.

- *Six-Hour Neutralent:* Sample of neutralent removed from the reactor after 6 hr of reaction.

- *Twenty-One--Hour Neutralent:* Sample of neutralent removed from the reactor after 21 hr of reaction.

- *Rinse:* Sample of the first rinse solution removed from the reactor.

- *Sludge:* Sample of solids remaining in reactor after the second rinse was drained from the reactor.

- *Cleaning Solution:* Sample collected from the first waste drum. This drum contains the neutralent drained from the reactor.

Table 23. Summary of Reaction Conditions.[7]

EDS Run Number	Lewisite Fill Materiel		Reagent Added (L)	Reaction Temperature (°C)
	Amount (L)[a]	Composition (wt%)		
One	1.82[b]	L1 = 80.6 L2 = 3.77 L3 = 0.0104	110	60
Two	Unknown[c]	L1 = 59.6 L2 = 10.0 L3 = 0.229	85	60
Three	1.82[d]	L1 = 51.7 L2 = 14.7 L3 = 0.292	110	60

a. Used average density of 1.89 to convert weight to volume.
b. DOT bottle with 7.6 pounds of lewisite, L-U-6095-CTF-N. Sub-test L-DOT(P1)-02.
c. 105 mm round, estimated at 80% full. DPG-94-055.
d. 4.2 inch mortar, 7.6 pounds, DPG-94-028.

3.4.2 Residual Agents.

Samples were received after being screened by another laboratory,[7,83] and then analyzed for residual L1, L2, and L3 using the method described in the Appendix. In all cases, the samples were not extracted/derivatized for several days after the reactions were completed. The delay in processing ranged from five to six days, depending on the run. Prior to being analyzed, the samples were stored at –20 °C. Quantitation was accomplished using an external calibration model, with a complete set of standards analyzed at the start, and at the end of each sequence analyzing sample extracts. Concurrently with analysis of these samples, extraction blanks (n=2) and laboratory control spikes (1.0 mg/L spike level, n=2) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The average recoveries from laboratory control spikes were: L1 93.6 %, L2 78.2 % , and L3 97.3 %. The neutralent time point data is summarized in Table 24, and the rinse, cleaning solution, and sludge data is summarized in Table 25. Example chromatograms are illustrated in Figure 37. There were no anomalies during the preparation or analysis of these samples.

Table 24. Residual Agents in Neutralent Time Point Samples. All data reported in the original neutralent, with units of mg/L. These reported results are the averages of duplicate analyses.

Target Analyte	Concentration in Neutralent (mg/L)*		
	@ 3 hr	@ 6 hr	@ 21 hr
	EDS Run Two		
L1	1.66	0.701	0.139
L2	1.55	0.986	0.333
L3	0.196	0.209	0.075
	EDS Run Three		
L1	3.44	5.96	4.72
L2	2.09	3.46	1.08
L3	1.16	1.76	0.582

* Reported values are the averages of two derivatization/extraction duplicates.

Table 25. Residual Agents in Rinse, Cleaning Solution, and As-Received Sludge Samples. All data reported in the original sample, with units of milligrams/liter for liquids, and milligrams/kilograms for the sludges. These reported results are the averages of duplicate analyses.

Target Analyte	Concentration in Sample (mg/L)[a]		
	Rinse	Cleaning Solution	Sludge[b]
	EDS Run Two		
L1	41.1	0.071	52.6
L2	24.3	0.223	30.6
L3	14.5	0.126	47.2
	EDS Run Three		
L1	28.0	ND[c]	49.6
L2	5.82	ND[c]	21.1
L3	6.59	ND[c]	26.6

a. Reported values are the averages of two derivatization/extraction duplicates.
b. Units are mg/kg.
c. Peak not detected.

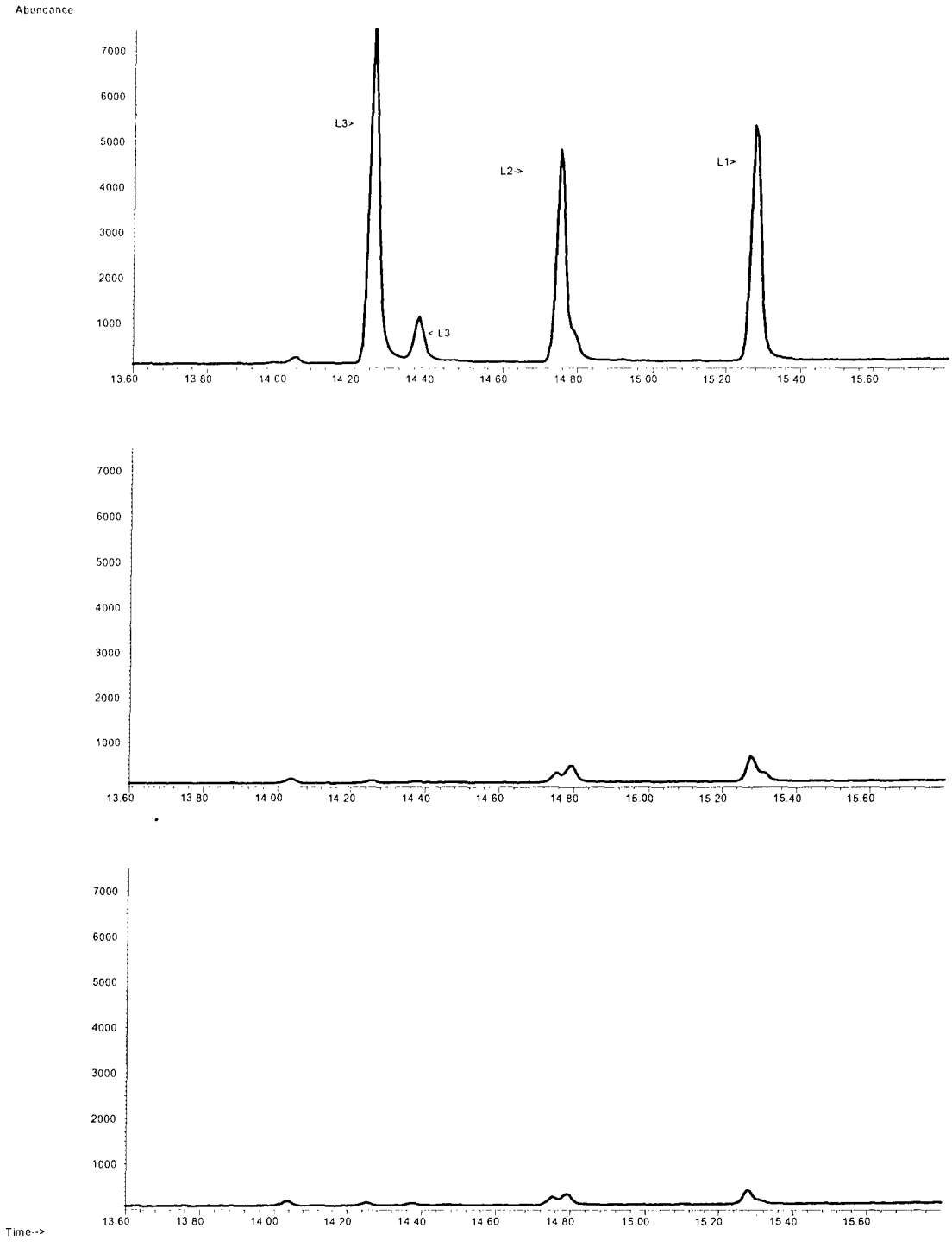


Figure 37. Example Chromatograms for Samples from EDS Run Number Two. The upper panel is a 1.00 mg/L mixed standard, the middle panel is a three hour neutralent sample, and the bottom panel is a six hour neutralent sample. Data was acquired by GC/MSD-EI, in SIM mode; L1 and L2 are ethanethiol derivatives.

3.4.3 Quantitation of Reaction Products.

The samples were analyzed for reaction products using the capillary electrophoresis methods described in Section 2.5. The reaction products were determined after samples were prepared using two different methods. The first method involved filtering the samples (0.45 μm, PTFE Acrodisc™), and then analyzing the filtrate. All the neutralent time point samples, the rinse sample, and the two cleaning solution samples were prepared using this approach. The second method involving extracting the sample with a dilute solution of NaOH. Approximately 500 mg (exact weight recorded) of sample was weighed into a 4 mL glass vial, then 2 mL of 0.1wt% NaOH(aq) was added to the vial, and the vial capped. The vial was then heated in a constant temperature bath (75 °C) for 30 min, then sonicated for 15 min. After sonication, an aliquot was filtered (0.45 μm, PTFE Acrodisc™) prior to analysis. Only the neutralent time point, rinse samples, and the sludge from EDS run one were prepared using this second approach. There was not enough sample of the sludge from runs two and three, and cleaning solution samples to perform the caustic extraction. The reaction product data is summarized in Tables 26 through 33. Samples (n=6) of 20 wt% $NaMnO_4$ reagent prepared in the laboratory was found to contain 472 mg/L of Cl^-, 250 mg/L F^-, and trace levels of SO_4^{-2}, formate, and oxalate. All other targeted analytes were non-detect in the laboratory prepared 20 wt% $NaMnO_4$ reagent.

The reaction products determined to be in the samples generated during the full-scale EDS runs were similar to those found during analysis of samples generated during the neutralization of phenyl-arsenicals.[13] The predominant arsenic species in the neutralent samples was inorganic arsenate, though recoveries of arsenic (as arsenate) were low compared to the total arsenic determined by ICP (Section 3.4.4). The average recovery was 3.9 %, and ranged from 2.4 to 4.9 %. The F^- and SO_4^{-2} concentrations in the filtered neutralents generated during EDS testing were somewhat elevated relative to the micro-scale runs, but the differences can be explained. The tests conducted in the EDS used $NaMnO_4$ from a different vendor, and background levels of F^- and SO_4^{-2} might have been higher in this reagent. Also, tap water was used during the EDS tests, while deionized water was used in the micro-scale testing. These two differences could easily account for the observed differences. The filtered neutralents generated during EDS testing also had traces of NO_3^- relative to the laboratory testing. The most likely explanation for this is explosives were used in the EDS runs, but were not used in the laboratory testing.

Text continues on page 80.

Table 26. Summary of Neutralent Results for EDS Run One. All concentration data reported in the original sample. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are estimated detection limits.

Target Analyte	Concentration in Sample (mg/L)			
	3 Hour Neutralent	6 Hour Neutralent	21 Hour Neutralent	As-Received Sludge[a]
Arsenite (AsO_2^-)	ND[b] (160)	ND[b] (160)	ND[b] (160)	ND[b] (64)
Arsenate ($HAsO_4^{-2}$)	ND[b] (160)	ND[b] (160)	ND[b] (160)	1,590
Chloride (Cl^-)	20,600	16,900	10,100	589
Fluoride (F^-)	236	408	419	360
Nitrate (NO_3^-)	Trace[c] (490)	Trace[c] (490)	Trace[c] (490)	ND[b] (194)
Sulfate (SO_4^{-2})	959	905	868	ND[b] (179)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[b] (100)	Trace[c] (100)	Trace[c] (100)	1,150
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[b] (230)	ND[b] (230)	ND[b] (230)	ND[b] (91)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[b] (40)	ND[b] (40)	ND[b] (40)	ND[b] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[b] (100)	ND[b] (100)	ND[b] (100)	ND[b] (40)
Acetate ($C_2H_3O_2^-$)	ND[b] (160)	ND[b] (160)	ND[b] (160)	ND[b] (64)
Formate (CHO_2^-)	ND[b] (150)	ND[b] (150)	ND[b] (150)	ND[b] (60)
Fumarate ($C_4H_2O_4^{-2}$)	ND[b] (200)	ND[b] (200)	ND[b] (200)	ND[b] (79)
Glycolate ($C_2H_3O_3^-$)	ND[b] (200)	ND[b] (200)	ND[b] (200)	ND[b] (79)
Oxalate ($C_2O_4^{-2}$)	Trace[c] (380)	ND[b] (380)	ND[b] (380)	ND[b] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[b] (200)	ND[b] (200)	ND[b] (200)	ND[b] (79)

a. Concentration units for sludge is mg/kg.
b. No peak was detected in the electropherogram.
c. A peak was detected, but below the estimated detection limit.

Table 27. Summary of Neutralent Results for EDS Run Two. All data reported in the original neutralent, with units of mg/L. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are estimated detection limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenite (AsO_2^-)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	9,730	9,220	8,870
Fluoride (F^-)	Trace[b] (70)	Trace[b] (70)	Trace[b] (70)
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	Trace[b] (490)
Sulfate (SO_4^{-2})	702	550	1,010
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (100)	ND[a] (100)	ND[a] (100)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)	ND[a] (230)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Acetate ($C_2H_3O_2^-$)	Trace[b] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	Trace[b] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	Trace[b] (380)	Trace[b] (380)	Trace[b] (380)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the estimated detection limit.

Table 28. Reaction Products in Rinse and Cleaning Solution Samples from EDS Run Two. All data reported in the original sample, with units of mg/L. These results are on the filtered (0.45 μm) sample. The values in parentheses are estimated detection limits. The cleaning solution was a mixture of hydrogen peroxide and acetic acid.

Target Analyte	Concentration in Sample (mg/L)	
	Rinse	Cleaning Solution
Arsenite (AsO_2^-)	ND[a] (160)	ND[a] (160)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	582	Trace[b] (380)
Fluoride (F^-)	74.0	ND[a] (70)
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	ND[a] (450)	ND[a] (450)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (100)	ND[a] (100)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (40)	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	85,500
Formate (CHO_2^-)	ND[a] (150)	452
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	ND[a] (200)	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	ND[a] (380)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the estimated detection limit.

Table 29. Reaction Products in Neutralent Time Point Samples from EDS Run Two. All data reported in the original sample, with units of milligrams/kilograms. These results are on the sample extracted with 0.1wt% NaOH, then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are estimated detection limits based on the average sample weight.

Target Analyte	Concentration in Neutralent (mg/kg)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenite (AsO_2^-)	ND[a] (64)	ND[a] (64)	ND[a] (64)
Arsenate ($HAsO_4^{-2}$)	1,100	1,070	920
Chloride (Cl^-)	7,150	6,680	5,900
Fluoride (F^-)	266	294	282
Nitrate (NO_3^-)	Trace[b] (194)	Trace[b] (194)	Trace[b] (194)
Sulfate (SO_4^{-2})	349	278	310
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (91)	ND[a] (91)	ND[a] (91)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
Acetate ($C_2H_3O_2^-$)	Trace[b] (64)	Trace[b] (64)	ND[a] (64)
Formate (CHO_2^-)	ND[a] (60)	ND[a] (60)	ND[a] (60)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)
Glycolate ($C_2H_3O_3^-$)	Trace[b] (79)	ND[a] (79)	ND[a] (79)
Oxalate ($C_2O_4^{-2}$)	ND[a] (151)	ND[a] (151)	Trace[b] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the estimated detection limit.

Table 30. Summary of Neutralent Results for EDS Run Three. All data reported in the original neutralent, with units of mg/L. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are estimated detection limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenite (AsO_2^-)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	Trace[b] (160)
Chloride (Cl^-)	17,900	19,800	16,700
Fluoride (F^-)	266	403	398
Nitrate (NO_3^-)	Trace[b] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	610	580	526
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (100)	ND[a] (100)	ND[a] (100)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)	ND[a] (230)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Acetate ($C_2H_3O_2^-$)	201	209	209
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	Trace[b] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	Trace[b] (380)	ND[a] (380)	ND[a] (380)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.

Table 31. Reaction Products in Rinse and Cleaning Samples from EDS Run Three. All data reported in the original sample, with units of mg/L. These results are on the filtered (0.45 μm) sample. The values in parentheses are estimated detection limits. The cleaning solution was a dilution of HPO_2® reagent, which generates sulfate as a decomposition product.

Target Analyte	Concentration in Sample (mg/L)	
	Rinse	Cleaning Solution
Arsenite (AsO_2^-)	ND[a] (160)	ND[a] (160)
Arsenate ($HAsO_4^{-2}$)	165	ND[a] (160)
Chloride (Cl^-)	1,740	Trace[b] (380)
Fluoride (F^-)	169	Trace[b] (70)
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b] (450)	27,000
CVAOA ($C_2H_2O_3AsCl^{-2}$)	151	ND[a] (100)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (230)	ND[a] (230)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	803	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (100)	ND[a] (100)
Acetate ($C_2H_3O_2^-$)	Trace[b] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	ND[a] (200)	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	ND[a] (380)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the estimated detection limit.

Table 32. Reaction Products in Neutralent Time Point Samples from EDS Run Three. All data reported in the original sample, with units of milligrams/kilograms. These results are on the sample extracted with 0.1wt% NaOH, then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are estimated detection limits based on the average sample weight.

Target Analyte	Concentration in Neutralent (mg/kg)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenite (AsO_2^-)	ND[a] (64)	ND[a] (64)	ND[a] (64)
Arsenate ($HAsO_4^{-2}$)	2,790	2,400	1,910
Chloride (Cl^-)	12,700	13,900	10,700
Fluoride (F^-)	341	306	315
Nitrate (NO_3^-)	Trace[b] (194)	Trace[b] (194)	Trace[b] (194)
Sulfate (SO_4^{-2})	452	420	391
CVAOA ($C_2H_2O_3AsCl^{-2}$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (91)	ND[a] (91)	ND[a] (91)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (40)	ND[a] (40)	ND[a] (40)
Acetate ($C_2H_3O_2^-$)	155	161	164
Formate (CHO_2^-)	ND[a] (60)	Trace[b] (60)	Trace[b] (60)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)
Glycolate ($C_2H_3O_3^-$)	ND[a] (79)	ND[a] (79)	ND[a] (79)
Oxalate ($C_2O_4^{-2}$)	316	239	188
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79)	ND[a] (79)	ND[a] (79)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.

Table 33. Reaction Products in Rinse Samples from EDS Runs Two and Three. All data reported in the original sample, with units of milligrams/kilograms. These results are on the sample extracted with 0.1wt% NaOH, then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are estimated detection limits based on the average sample weight.

Target Analyte	Concentration in Rinse (mg/L)	
	Run Two	Run Three
Arsenite (AsO_2^-)	ND[a] (64)	ND[a] (64)
Arsenate ($HAsO_4^{-2}$)	1,930	2,880
Chloride (Cl^-)	420	1,010
Fluoride (F^-)	205	118
Nitrate (NO_3^-)	ND[a] (194)	ND[a] (194)
Sulfate (SO_4^{-2})	Trace[b] (179)	Trace[b] (179)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	507	914
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (91)	ND[a] (91)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	2,410	1,750
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (40)	ND[a] (40)
Acetate ($C_2H_3O_2^-$)	ND[a] (64)	ND[a] (64)
Formate (CHO_2^-)	Trace[b] (60)	67.4
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79)	ND[a] (79)
Glycolate ($C_2H_3O_3^-$)	ND[a] (79)	ND[a] (79)
Oxalate ($C_2O_4^{-2}$)	ND[a] (151)	ND[a] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79)	ND[a] (79)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.

3.4.4 Total Metals.

The total metal analyses were performed on duplicate digests of the neutralent, rinse, cleaning solution and sludge samples. The digests were prepared according to the procedure specified in SW846, Methods 3010A and 7471A.[41] The digests were analyzed using three different methods; EPA 200.7 for iron, sodium, and sulfur;[43] EPA 200.8 for arsenic, copper, and manganese,[44] and EPA 245.1 for mercury.[42] The EPA 200.7 method uses ICP, with optical detection, and EPA 200.8 and 245.1 uses ICP, with mass detection. In addition to the EDS samples, duplicate samples of 20 wt% $NaMnO_4$ reagent and digests of a SARM soil (NIST 2710, Montana Soil) were also performed. The results are summarized in Tables 34 through 38. The concurrently run QC samples, such as the laboratory control spikes and sample matrix spikes (of the targeted analytes), were all within the acceptable quality limits. There were no deviations or anomalies reported during the digestion or analysis of the samples during the total metal testing. During the mercury digestion of the samples from EDS run one, there were small amounts of solids remaining after the digestion process. In all other cases, the samples were completely digested, with no visible solids remaining. The SARM soil controls, however, were not completely dissolved during the digestion process. The lack of complete dissolution of the SARM soil accounts for sodium not being detected, although the SARM contained 11,400 mg/kg of sodium.

Laboratory prepared 20 wt% $NaMnO_4$ was also analyzed for total metals (n=2), and was found to contain: 900 mg/kg copper; 40.8 mg/kg iron; 76,300 mg/kg manganese; 34,900 mg/kg sodium; and no detectable arsenic or sulfur. The estimated sample detection limits are 36.5 mg/kg for arsenic, and 910 mg/kg for sulfur. Using dimensional analysis, and not accounting for any impurities, 20 wt% $NaMnO_4$ should contain 32,400 mg/kg of sodium, and 77,400 mg/kg of manganese. The experimental values obtained for sodium and manganese are in good agreement with the theoretical values.

Table 34. Total Metals in the SARM Soil Control. The data are reported in the original sample, with units of milligrams/kilograms. The reported results are averages of two digestions, and have been corrected for the digestion blank. The value in parentheses is the estimated reporting limit, based on the average sample weight of 172.0 mg.

Total Metal	Mean Value (mg/kg)	Percent Recovery		
		Mean	SD	Percent RSD
Arsenic	557	89.0	7.53	8.47
Copper	2,660	90.1	5.02	5.58
Iron	23,300	68.9	1.87	2.71
Manganese	7,130	67.3	5.93	8.81
Sodium	ND[a] (145)	NA[b]	NA[b]	NA[b]
Sulfur	2,120	88.1	1.61	1.83
Mercury[c]	1,090	104	6.0	5.79

a. Not detected in digest.
b. Not applicable.
c. Average sample weight for Hg analysis was 11.8 mg.

Table 35. Total Metals in Neutralent Time Point Samples from EDS Run Two. All data reported in the original sample, with units of milligrams/kilograms. These reported results are the averages of duplicate digestions, and have been corrected for the digestion blank. The value in parentheses is the estimated reporting limit, based on the average sample weight of 53.1 mg.

Total Metal	Concentration in Original Neutralent (mg/kg)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenic	25,100	23,500	12,400
Copper	5,540	5,610	2,680
Iron	11,900	11,500	5,760
Manganese	107,000	114,000	93,800
Sodium	34,300	33,500	32,000
Sulfur	ND[a] (942)	ND[a] (942)	ND[a] (942)
Mercury[b]	5.56	4.68	3.28

a. Not detected in digest.
b. Average sample weight for Hg analyses was 593.6 mg.

Table 36. Total Metals in Rinse, Cleaning Solution, and Sludge Samples from EDS Run Two. All data reported in the original sample, with units of milligrams/kilograms. These reported results are the averages of duplicate digestions, and have been corrected for the digestion blank. The value in parentheses is the estimated reporting limit, based on the average sample weight of 53.1 mg.

Total Metal	Concentration in Original Sample (mg/kg)		
	Rinse	Cleaning Solution	As-Received Sludge
Arsenic	14,500	26.8	28,000
Copper	3,650	13.4	11,600
Iron	12,700	30.3	35,100
Manganese	49,000	744	89,200
Sodium	5,220	250	8,300
Sulfur	ND[b] (942)	ND[b] (16)	ND[b] (942)
Mercury	1.85[c]	0.0070[d]	5.70[c]

a. Average weight for cleaning solution was 3.09 g.
b. Not detected in digest.
c. Average sample weight for Hg was 593.6 mg.
d. Average sample weight was 20.0 g.

Table 37. Total Metals in Neutralent Time Point Samples from EDS Run Three. All data reported in the original sample, with units of milligram/kilogram. These reported results are the averages of duplicate digestions, and have been corrected for the digestion blank. The values in parentheses are the estimated reporting limits, based on the average sample weight.

Total Metal	Concentration in Original Neutralent (mg/kg)		
	@ 3 hr	@ 6 hr	@ 21 hr
Arsenic	30,700	26,700	20,800
Copper	2,710	2,940	2,020
Iron	7,580	10,400	8,950
Manganese	130,000	134,000	110,000
Sodium	37,100	38,500	35,900
Sulfur	ND[a] (942)	ND[a] (942)	ND[a] (942)
Mercury[b]	40.6	38.3	41.3

a. Not detected in digest.
b. Average sample weight for Hg analyses was 593.6 mg.

Table 38. Total Metals in Rinse, Cleaning Solution, and Sludge Samples from EDS Run Three. All data reported in the original sample, with units of milligram/kilogram. These reported results are the averages of duplicate digestions, and have been corrected for the digestion blank. The values in parentheses are the estimated reporting limits, based on the average sample weight.

Total Metal	Concentration in Original Sample (mg/kg)		
	Rinse	Cleaning Solution[a]	As-Received Sludge
Arsenic	20,600	13.1	27,100
Copper	2,540	4.69	4,300
Iron	16,900	13.5	23,600
Manganese	107,000	181	132,000
Sodium	17,200	ND[b] (40)	21,400
Sulfur	ND[b] (942)	7,700	ND[b] (942)
Mercury[c]	24.8	0.0235[d]	41.7

a. Average weight for cleaning solution was 3.09 g.
b. Not detected in digest.
c. Average sample weight for Hg was 593.6 mg.
d. Average sample weight was 4.15 g.

3.4.5 Qualitative Analyses by NMR.

The neutralent time points, rinse, and cleaning solution samples were qualitatively analyzed for bulk reaction products using a previously established NMR method.[13] The reaction products were determined after samples were prepared by mixing 1,000 μL of sample with 200 μL of D_2O, mixing, then filtering (0.45 μm, PTFE Acrodisc™) prior to analysis. In all cases, there were no detectable peaks. Example spectra from samples generated during EDS run two are illustrated in Figures 38 and 39. The lack of detectable peaks suggests the carbon-containing reaction products are bound to solids greater than 0.45 μm, and were filtered out of the sample prior to analysis by NMR. This is also supported by the CE data described in Section 3.4.3.

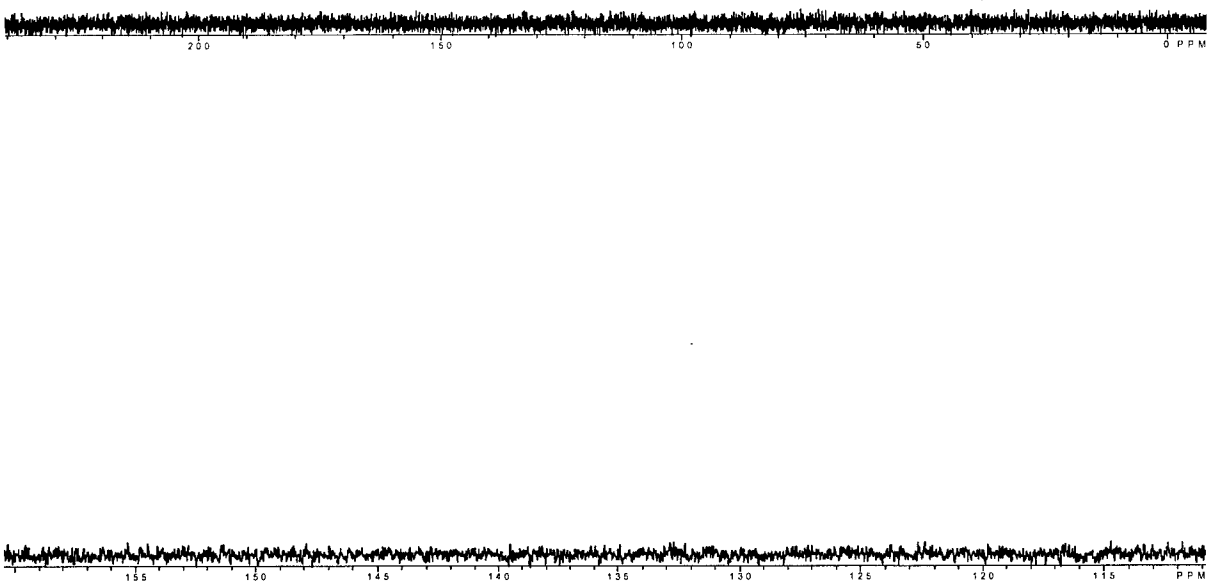


Figure 38. Example ^{13}C-NMR Spectra Obtained from the Analysis of the Three-Hour Neutralent Sample Generated During EDS Run Two. The upper panel is the full spectrum, and the lower panel is the spectrum zoomed into the chloro-vinyl shift region.

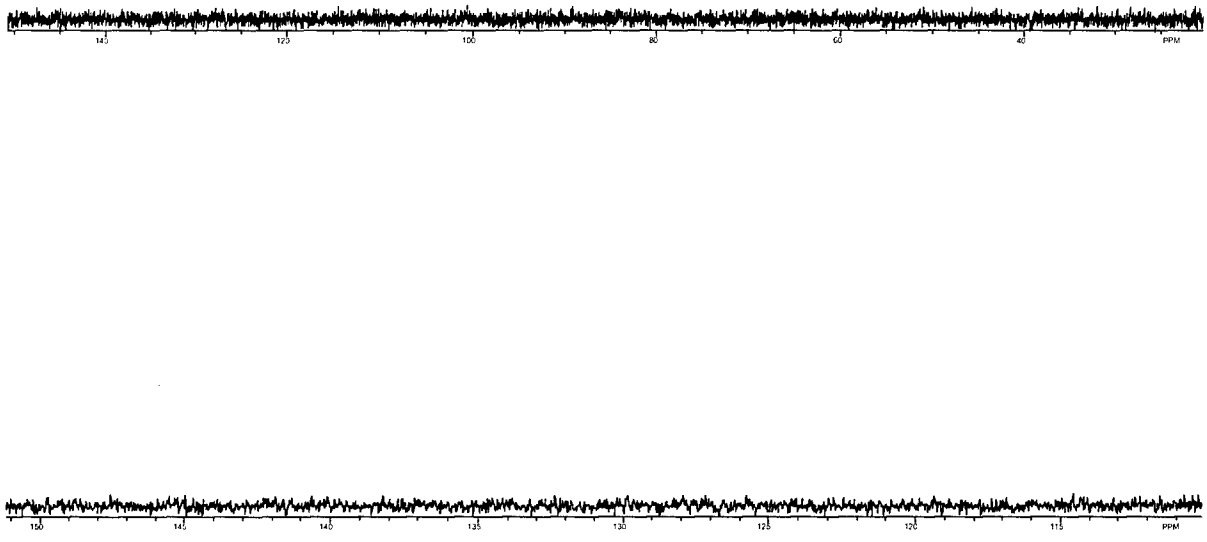


Figure 39. Example ^{13}C-NMR Spectra Obtained from the Analysis of the Rinse Sample Generated During EDS Run Two. The upper panel is the full spectrum, and the lower panel is the spectrum zoomed into the chloro-vinyl shift region.

3.4.6 Residual Sodium Permanganate.

The samples were analyzed for residual $NaMnO_4$ using the method described in Section 2.6. The neutralent time point and rinse samples were all analyzed, with each sample prepared and analyzed in triplicate. The residual $NaMnO_4$ data are summarized in Table 39. Calibration check standards (two concentrations) and positive controls (20 wt % $NaMnO_4$ reagent) were concurrently prepared and analyzed with each group of samples. There were no anomalies noted during the preparation or analysis of these samples.

The residual $NaMnO_4$ values reported in Table 39 are consistent with the initial reagent being 20 wt% $NaMnO_4$. In theory, there should be 232,000 mg/L of $NaMnO_4$ in 20 wt% $NaMnO_4$ reagent, assuming a density of 1.16. In all cases, the check standards were all within acceptance limits.

Table 39. Residual Sodium Permanganate Data from the Analysis of Neutralent Time Point and Rinse Samples. The reported values are the averages of triplicate determinations.

Sample Description	$NaMnO_4$ (mg/L)		
	EDS Run One	EDS Run Two	EDS Run Three
3 Hour Neutralent	176,000	232,000	151,000
6 Hour Neutralent	154,000	211,000	110,000
21 Hour Neutralent	156,000	219,000	125,000
Rinse	NA	12,600	29,000

3.4.7 Isolation and Characterization of Solids from Sludge Samples.

The solids contained in the sludge samples from EDS runs two and three were isolated, in order to characterize the solid fraction contained in these samples. There was not enough sample of the neutralent, rinse, or cleaning solution samples to perform this isolation. The solids were isolated by vacuum filtration through a 0.8 μm cellulose nitrate filter, after which 50 mL of ice-cold deionized water was used to wash the solids. After air drying overnight in a hood, the solids were stored in a desiccator for seven days prior to any analyses taking place. The solids lost 55.7 and 38.4 wt%, respectively, for EDS runs two and three. The weight loss was due to water, and volatile organics contained in the original samples. The solids were isolated at various times after the reaction occurred, which is important since the solid composition changes with time if not isolated from the bulk permanganate solution. This was demonstrated on a micro-scale, and is discussed in a previous report.[13] The time between start of reaction, and isolation of solids, was eight days for EDS run two, and five days for EDS run three.

Isolated solids were analyzed for residual L1, L2, and L3 using the method described in the Appendix. Approximately 50 mg (exact weight recorded) of solid was used for each derivitization/extraction, and each sample was prepared in duplicate. Quantitation was accomplished using an external calibration model, with a complete set of standards analyzed at the start, and at the end of the sequence analyzing sample extracts. Concurrently with analysis of these samples, extraction blanks (n=2) and laboratory control spikes (5 mg/L spike level, n=2) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The average recoveries were: L1 92.5%, L2 81.3%, and L3 101%. The residual agent data is summarized in Table 40, and there were no anomalies during the preparation or analysis of these samples.

The isolated solids were analyzed for reaction products using the capillary electrophoresis methods described in Section 2.5. The reaction products were determined after samples were prepared using a caustic extraction approach. Approximately 500 mg (exact weight recorded) of sample was weighed into a 4 mL glass vial, then 2 mL of 0.1wt% $NaOH_{(aq)}$ was added to the vial, and the vial capped. The vial was then heated in a constant temperature

bath (75 °C) for 30 min, then sonicated for either 15 min or 3 hr. After sonication, an aliquot was filtered (0.45 μm, PTFE Acrodisc™) prior to analysis. Quantitation was accomplished using an external calibration model, with calibration check standards and laboratory blanks analyzed at the start, and at the end of the sequence analyzing sample extracts. In all cases, there were no analytes detected in any of the laboratory blanks, and all check standards were within acceptable limits. The reaction product data is summarized in Tables 41 and 42.

The isolated solids were analyzed for total metals using the digestion procedure specified in SW846, Methods 3010A and 7471A,[41] and digestions were performed in duplicate. Approximately 50 mg of sample (exact weight recorded) was digested, and the final digest volume brought to 0.05 L. The digests were analyzed using three different methods; EPA 200.7 for iron, sodium, and sulfur;[43] EPA 200.8 for arsenic, copper, and manganese,[44] and EPA 245.1 for mercury.[42] The EPA 200.7 method uses ICP, with optical detection, and EPA 200.8 and 245.1 uses ICP, with mass detection. In addition to the isolated solids, concurrent digests of a SARM soil (NIST 2710, Montana Soil) were also performed. The results are summarized in Tables 43 and 44. The concurrently run QC samples, such as the laboratory control spikes and sample matrix spikes (of the targeted analytes), were all within the acceptable quality limits. There were no deviations or anomalies reported during the digestion or analysis of the samples during the total metal testing. In all cases, the isolated solid samples were completely digested, with no visible solids remaining. The SARM soil controls, however, were not completely dissolved during the digestion process. The lack of complete dissolution of the SARM soil accounts for sodium not being detected, although the SARM contained 11,400 mg/kg of sodium.

The isolated solids were qualitatively analyzed for bulk reaction products using an established NMR method.[13] Approximately 500 mg (exact weight recorded) of sample was weighed into a 4 mL glass vial, then 2 mL of $CDCl_3$ was added to the vial, and the vial capped. The vial was then heated in a constant temperature bath (75 °C) for 30 min, then sonicated for 15 min. After sonication, an aliquot was filtered (0.45 μm, PTFE Acrodisc™) prior to analysis. In all cases, there were no detectable carbon peaks in any of extracts; example spectra are illustrated in Figure 40. The reaction products appear to be bound to the solids, and not extracted under the conditions employed.

Using dimensional analysis, the extracted residual agent and reaction product concentrations were converted to extracted arsenic concentrations, and compared to the total arsenic concentrations determined by ICP. The overall recoveries of extracted arsenic ranged from 11.5 to 15.0 percent, with the longer extraction times giving slightly higher recoveries. Increasing the extraction time from 0.25 to 3 hr yielded an average increase of 2.5 percent. It is not known whether this increase is statistically significant, as only duplicate extractions were performed. The low recovery of extractable arsenic is consistent with a previous study examining the efficacy of permanganate solution against phenyl-arsenical CWAs,[13] and is believed to be due to the high levels of iron in these samples. This decrease in extraction efficiency has been demonstrated in other studies, which examined the binding affinity of arsenicals to soils and various metal oxides.[84-86]

Table 40. Residual Agents in Solids Isolated from Sludge Samples. All data reported in the isolated solid, with units of milligrams/kilograms. These reported results are the averages of duplicate analyses.

Target Analyte	Concentration in Isolated Solids (mg/kg)	
	EDS Run Two	EDS Run Three
L1	206	41.8
L2	86.3	15.2
L3	43.3	7.62

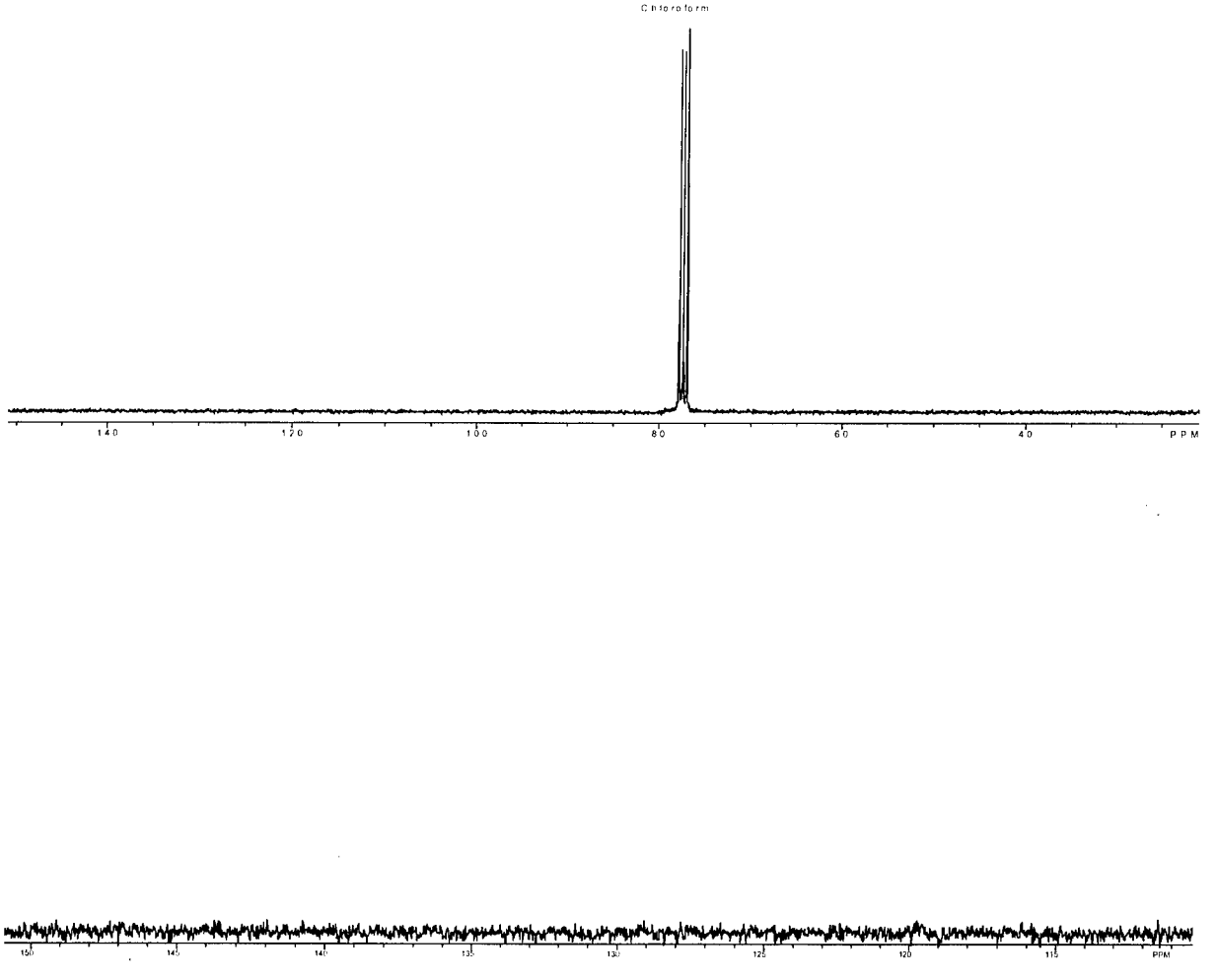


Figure 40. Example ^{13}C-NMR Spectra Obtained from the Analysis of the Isolated Sludge Solids from EDS Run Two. The upper panel is the full spectrum, and the lower panel is the spectrum zoomed into the chloro-vinyl shift region.

Table 41. Residual Reaction Products in Solids Isolated from EDS Run Two Sludge Samples. All data reported in the original sample, with units of milligrams/kilograms. These results are on the sample extracted with 0.1wt% NaOH, then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are reporting limits based on the average sample weight.

Target Analyte	Concentration in Isolated Solid (mg/kg)	
	15 Min Sonication	3 Hr Sonication
Arsenite (AsO_2^-)	ND[a] (64)	ND[a] (64)
Arsenate ($HAsO_4^{-2}$)	7,880	9,075
Chloride (Cl^-)	435	530
Fluoride (F^-)	182	178
Nitrate (NO_3^-)	ND[a] (197)	ND[a] (197)
Sulfate (SO_4^{-2})	Trace[b] (181)	Trace[b] (181)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	5,120	5,370
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (93)	ND[a] (93)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	10,100	11,300
BCVAA ($C_4H_4OAsCl_2^-$)	272	371
Acetate ($C_2H_3O_2^-$)	Trace[b] (64)	Trace[b] (64)
Formate (CHO_2^-)	Trace[b] (60)	73
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (80)	ND[a] (80)
Glycolate ($C_2H_3O_3^-$)	Trace[b] (80)	Trace[b] (80)
Oxalate ($C_2O_4^{-2}$)	ND[a] (153)	ND[a] (153)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (80)	ND[a] (80)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.

Table 42. Residual Reaction Products in Solids Isolated from EDS Run Three Sludge Samples. All data reported in the original sample, with units of milligrams/kilograms. These results are on the sample extracted with 0.1wt% NaOH, then filtered (0.45 μm). The reported data is the average of duplicate extractions, and have been corrected for the extraction blank. The values in parentheses are reporting limits based on the average sample weight.

Target Analyte	Concentration in Isolated Solid (mg/kg)	
	15 Min Sonication	3 Hr Sonication
Arsenite (AsO_2^-)	ND[a] (64)	ND[a] (64)
Arsenate ($HAsO_4^{-2}$)	6,610	9,300
Chloride (Cl^-)	265	316
Fluoride (F^-)	117	163
Nitrate (NO_3^-)	ND[a] (197)	ND[a] (197)
Sulfate (SO_4^{-2})	Trace[b] (181)	Trace[b] (181)
CVAOA ($C_2H_2O_3AsCl^{-2}$)	3,020	3,600
CVAA ($C_2H_2O_2AsCl^{-2}$)	ND[a] (93)	ND[a] (93)
BCVAOA ($C_4H_4O_2AsCl_2^-$)	4,700	6,000
BCVAA ($C_4H_4OAsCl_2^-$)	ND[a] (40)	ND[a] (40)
Acetate ($C_2H_3O_2^-$)	ND[a] (64)	Trace[b] (64)
Formate (CHO_2^-)	ND[a] (60)	Trace[b] (60)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (80)	ND[a] (80)
Glycolate ($C_2H_3O_3^-$)	ND[a] (80)	ND[a] (80)
Oxalate ($C_2O_4^{-2}$)	ND[a] (153)	ND[a] (153)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (80)	ND[a] (80)

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.

Table 43. Total Metals in the SARM Soil Control. The data are reported in the original sample, with units of milligrams/kilograms. The reported results are averages of two digestions per method, and have been corrected for the digestion blank. The value in parentheses is the estimated reporting limit, based on the average sample weight.

Total Metal	Mean Value (mg/kg)	Percent Recovery		
		Mean	SD	Percent RSD
Arsenic	557	89.0	7.53	8.47
Copper	2,660	90.1	5.02	5.58
Iron	23,300	68.9	1.87	2.71
Manganese	7,130	67.3	5.93	8.81
Sodium	ND[a] (145)	NA[b]	NA[b]	NA[b]
Sulfur	2,120	88.1	1.61	1.83
Mercury[c]	1,090	104	6.0	5.79

a. Not detected in digest.
b. Not applicable.
c. Average sample weight for Hg analysis was 11.8 mg.

Table 44. Total Metals in Solids Isolated from Sludge Samples. All data reported in the isolated solid, with units of milligrams/kilograms. These reported results are the averages of duplicate digestions, and have been corrected for the digestion blank. The value in parentheses is the estimated reporting limit, based on the average sample weight.

Total Metal	Concentration in Isolated Solid (mg/kg)	
	EDS Run Two	EDS Run Three
Arsenic	76,200	54,700
Copper	31,000	9,450
Iron	82,600	49,000
Manganese	255,000	288,000
Sodium	24,400	43,700
Sulfur	ND[a] (883)	ND[a] (883)
Mercury[b]	18.5	92.0

a. Not detected in digest.
b. Average sample weight for HG analyses was 449 mg.

4. CONCLUSIONS

The selected neutralization reagent, aqueous 20 wt% sodium permanganate (U.S. Patent pending), was found to be effective in destroying the lewisite fills under relatively mild reaction temperatures and short reaction times. In both lab-scale and full-scale Explosive Destruction System testing, the aqueous permanganate consistently produced neutralents which had residual lewisite levels below the treatment goal of 50 mg/L (ppm). The reaction products included inorganic pentavalent arsenate and various pentavalent organo-arsenicals. Solid manganese dioxide was also produced during the reaction, and was successfully managed in the full-scale Explosive Destruction System testing.

The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found not to generate acetylene or vinyl chloride as reaction by-products.

The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found to be non-flammable, relatively non-toxic, compatible with standard reactor materials of construction, and commercially available in bulk.

The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found to be stable, and have an estimated shelf-life of 18 months.

The selected neutralization reagent, aqueous 20 wt% sodium permanganate, was found to maintain effectiveness in the presence of explosive residues, and large amounts of copper and iron.

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APPENDIX
RESIDUAL AGENT METHOD DESCRIPTION IN SOP FORMAT

1. TITLE

Multi-Residue Quantitative Analysis of HD, HN3, Lewisite and Other Arsenical Chemical Warfare Agents in Permanganate-Based Demilitarization Waste Streams.

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3. KEYWORDS

Gas Chromatograph/Mass Selective Detector, GC/MSD, Arsenical CWA, HD, HN3, Lewisite, L1, L2, L3, PD, phenyldichloroarsine, DA, Diphenylchloroarsine
TPA, Triphenylarsine, Derivatization, Ethanethiol, Neutralent and Sludge.

4. REVISION HISTORY

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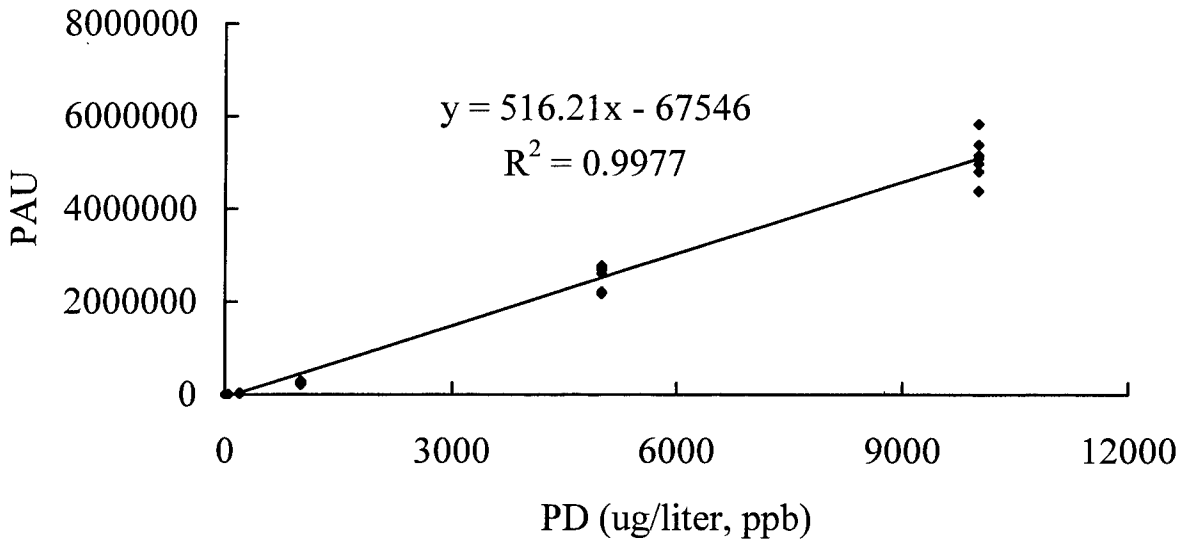
6. PURPOSE AND APPLICATION

The purpose of this method is to provide a means for the multi-residue quantitative analysis of HD, HN-3, L1, L2, L3, DA, PD, and TPA in demilitarization waste streams.

6.1 Analyte Concentration Range. The external calibration model was established by preparation and analysis of a mixed set of standards, in accordance with the procedures contained in Section 11.2. Each standard concentration was injected seven times, in a randomly assigned order. A total of eight concentrations (0, 5, 10, 50, 200, 1,000, 5,000, and 10,000 µg/L (ppb)) were analyzed during this modeling effort. This calibration range, assuming 100% recovery of analyte, corresponds to sample concentrations of 0.050 to 100mg/L (ppm), assuming a
500 µL sample size. In practice, a narrower range of standards (0 through 500 µg/L (ppb)) was used during method detection limit experiments, and a wider range of standards (0 through 25,000 µg/L) was used during analysis of actual reactor samples. In all cases, the range utilized was linear. The regression equations for each analyte (5 through 10,000 µg/L) are summarized in Table 1, and example calibration curves are illustrated in the Figure. The peak to peak signal to noise at the 5 µg/L level ranged from 8 to 54, depending on the analyte. There was no correlation of peak width or retention time with concentration of standard.

Table 1. Summary of Linear Regression Parameters for each of the Targeted analytes in the 5 to 10,000 µg/L range. The linear model is represented by y=mx+b.

Target Analyte	Linear Regression Parameters		
	m	b	R^2
HD	699.08	-39,331	0.9993
HN-3	91.072	-8,137.8	0.9980
L1	450.56	-72,321	0.9970
L2	353.0	-56,856	0.9965
L3	428.99	-35,595	0.9991
DA	1,085.3	-153,618	0.9979
PD	516.21	-67,546	0.9977
TPA	2835.8	-307,843	0.9987



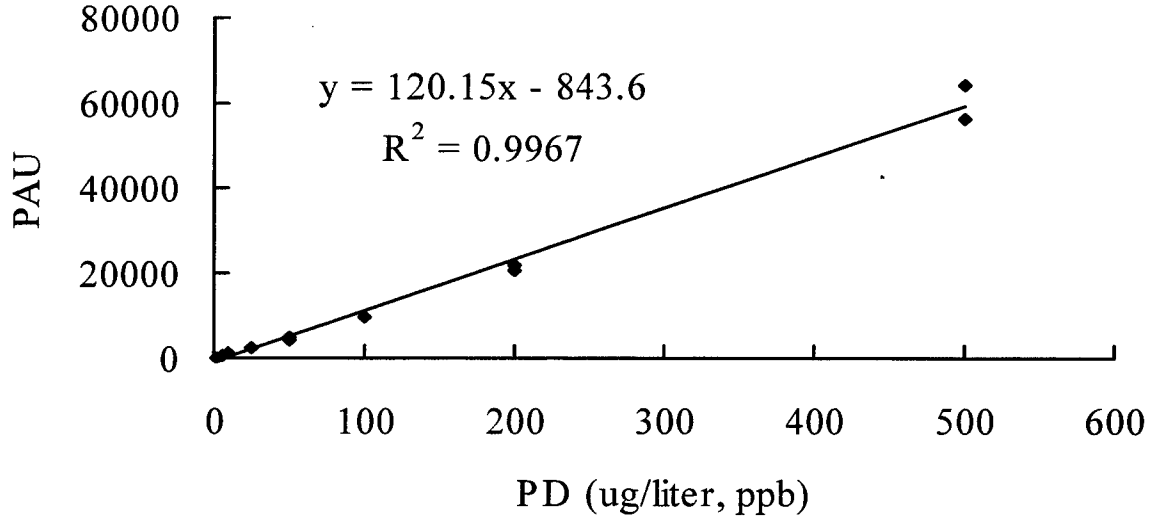


Figure. Example external calibration curves for PD. The upper panel is the entire range evaluated during the validation process, and the lower panel is the typical working calibration range used during the spike recovery and MDL experiments. The data is based on the extracted m/z ion 274.

6.2 Sample Matrices and Interferences. The primary sample matrix is neutralent produced from the reaction of 20 wt% $NaMnO_4$ with vesicant class chemical warfare agents. Additional matrices, such as isolated solids, sludges, rinses, and caustic solutions have also been successfully analyzed using this method.

6.3 Throughput. During the spike and recovery MDL study, a single operator was able to prepare 21 samples and the accompanying calibration standards and initiate the instrument

analysis in an 8-hr day. The instrumental analysis continued unattended during the night, and approximately 3-4 hr of analyst time was required to interpret and reduce the data.

7. RISK AND SAFETY ASSESSMENT

The sample matrix, which may contain significant levels of chemical agents, associated precursors, contaminants, arsenic or degradation products, can be a hazard to the analyst(s) if the sample is not properly handled and contained. This method is designed for the safe analysis of samples. Extracts will be contained in septum cap vials that can be pierced by an auto injector syringe. Lab coats, safety glasses, and appropriate gloves must be worn when handling samples. In the case of a spill, wipe up the area with absorbent paper and a towel wetted with bleach. A split vent trap must be attached to the Split/Splitless Inlet Vent and to the Septum Purge Vent on the Gas Chromatograph (GC) to trap the material that is purged away during analysis. The method developed is based on RDECOM Standing Operating Procedure (SOP) RNG-116,[1] which provides specific guidelines for all aspects of chemical surety materiel (CSM) operations. Hazard analysis is conducted for all SOPs prior to operations to ensure low risk levels and operator safety.

8. SCIENTIFIC BASIS

Gas chromatography is an analytical instrument method for the separation of components of a mixture. Separation takes place in a specifically designed column, and is based on the differences in component partition coefficients between the stationary and mobile phases. The detection of eluted components is accomplished using the MSD in selected ion mode (SIM) which allows for a comparison of retention time and ion ratios of detected analytes to the retention time and ion ratios of the reference standard material.

Lewisite, PD, and DA are thermally labile, and are therefore not amenable to direct analysis by GC techniques. Ethanethiol was used as a derivatizing reagent in all samples and standards in order to derivatize these analytes to a form that is amenable to analysis by gas chromatography.

9. TRAINING

The analyst(s) must have specific experience (or a combination of training by the manufacturer and 6 months of experience) in the operation of all required analytical instruments. These instruments include but are not limited to the Agilent 6890 Series gas chromatograph in conjunction with the 5973 MSD or the equivalent of this combination. The analyst must also be experienced in collection and interpretation of mass spectral data and must demonstrate competence in the use of the related software applications. The analyst(s) must be trained in the use of safety equipment and surety materials. In addition, the analyst(s) must have the training required in AR358-61[2] and the clearances specified in AR50-6[3] appropriate to the expected levels of chemical agents in the standards and samples to be analyzed.

10. APPARATUS

The instrumentation and equipment needed to perform this method are described as follows:

10.1 Instrumentation. Agilent Series GC/MS system - The analytical system should be equipped with a temperature-programmable Agilent 6890N gas chromatograph (or equivalent), configured with a split/splitless injection port, and an Agilent 5973N mass spectrometer capable of scanning from 35 to 550 amu every 1.0 second or less.

10.2 Column: DB-5MS analytical column, 30 m X 0.25 mm X 1.0 □m film thickness.

10.3 Data system: A computer system, interfaced to the MS, which allows for the continuous acquisition, analysis, and storage of all chromatographs and spectra obtained during each chromatographic run.

10.4 GC Consumable Supplies

- 4mm deactivated single taper injection port liners (**NO PACKING**)
- 11mm septum
- Ferrules
- O-rings
- Split Vent Traps

10.5 Glassware, Miscellaneous Equipment, and Supplies

- Safety glasses
- Lab coat
- Latex gloves
- Nitrile gloves
- Analytical balance, capable of measuring to ±0.0001g
- Pasteur transfer pipets, disposable with rubber bulbs
- ,Vial racks
- Labeling tape
- Parafilm™
- Manual or automatic pipettes, 10μL, 100-1000μL, 1-10mL
- Disposable pipet tips
- 10 μL syringes
- 15 mL vial, screw top solid cap with PTFE liner
- 7 mL vial, screw top solid cap with PTFE liner
- Autosampler vial, glass with screw top closures and septa

10.6 Source Details

Agilent Technologies, www.agilent.com/chem/supplies.
VWR Scientific, P.O. Box 626, Bridgeport, NJ 08014
Supelco, Inc., Supelco Park, Bellefont, PA 16823
Aldrich Chemical Company, 1001 W. St. Paul Ave., Milwaukee, WI 53233
Rainin Instruments Company, Mack Road, Woburn, MA 01801

10.7 Chemicals

10.7.1 Chemical Agent Standards. Primary stock standards are required for the preparation of all intermediate and calibration level standard solutions. Table 2 provides some pertinent chemical information for all target analytes covered by this method and gives a suggested concentration for each primary stock solution.

Table 2. Information on Analytes.

Chemical Name	Abbreviation	CAS Number	Chemical Formula	Primary Stock Concentration (ug/mL)
Bis(2-chloroethyl)sulfide	HD	505-60-2	$C_4H_8Cl_2S$	1000
Tris(2-chloroethyl)amine	HN3	555-77-1	$C_6H_{12}Cl_3N$	1000
2-Chlorovinyl arsine dichloride	L1	541-25-3	$C_2H_2AsCl_3$	1000
Bis-(2-chlorovinyl)chloroarsine	L2	40334-69-8	$C_4H_4AsCl_3$	1000
Tris-(2-chlorovinyl)arsine	L3	40334-70-1	$C_6H_6AsCl_3$	1000
Phenyldichloroarsine	PD	696-28-6	$C_6H_5AsCl_2$	1000
Diphenylchloroarsine	DA	712-48-1	$C_{12}H_{10}AsCl$	1000
Triphenylarsine	TPA	603-32-7	$C_{18}H_{15}As$	1000

10.7.2 Reagents. The following reagents are required for solution preparation and/or instrument analysis.

- Reagent water - 18Ω distilled/deionized water, demonstrated to be free of interferences and/or target analytes.
- 2,2,4-Trimethylpentane
- Isopropyl Alcohol
- Methyl Alcohol
- Ethanethiol
- K_2HPO_4
- KH_2PO_4

- NaCl
- Activated charcoal

11. PROCEDURE

11.1 Solution Preparation

11.1.1. 1% Ethanethiol in TMP – Add 1.0mL of neat ethanethiol to 99.0 mL of 2,2,4-TMP, mix well. Prepare fresh solution weekly. (Note: Stench. Store refrigerated in tightly capped amber glass bottle, doubly contained with activated charcoal in outer container to absorb odor.)

11.1.2. pH 7 buffer solution – Accurately weigh 43.5 g K_2HPO_4 and 20.5 g KH_2PO_4 and transfer to glass bottle or flask. Add 250mL deionized water, mix well until all salts are dissolved. Store at room temperature in tightly capped glass bottle.

11.1.3. Surrogate Sample Matrix – Dissolve 107mg NaCl in 10.0 mL deionized water. Store at room temperature in tightly capped glass bottle.

11.2 Calibration Standard Preparation.

Note: ***Accuracy in the derivitization of the calibration standards and samples is critical to the successful implementation of this method. It is critical that all standards and samples maintain a concentration of 1% ethanethiol in solution. Do not deviate from the procedures outlined below when preparing calibration standards.***

11.2.1 Intermediate Standard Solution, 50µg/mL. Prepare an intermediate cocktail solution containing the 8 compounds listed in Table 2 at a concentration of 50µg/mL in isopropyl alcohol.

For example, transfer 1 mL of isopropyl alcohol to a 5ml Class A volumetric flask. To this flask, add exactly 50.0µL of each of the 1000µg/mL stock solutions described in part 10.7.1. Dilute to the mark with addition isopropyl alcohol, cap and invert to mix.

Transfer solution to a 7mL glass vial with a screw top solid cap with PTFE liner. Reserve a portion of this stock solution to be used for a control spiking solution.

11.2.2 Derivatized Intermediate Calibration Standard Solution, 50µg/mL. Accurately transfer 2000µL of the intermediate standard solution from 11.2.1 to a 4mL glass vial. Carefully add exactly 20.0µL of neat ethanethiol. Cap tightly, mix well.

11.2.3 Initial Calibration Standards. Initial calibration standards should be prepared at a *minimum* of six different concentrations through the serial dilution of the derivatized intermediate calibration standard in 11.2.2. In order to maintain the 1% ethanethiol concentration in all serially diluted calibration standards, dilutions *must* be prepared using the 1% ethanethiol solution noted in 11.1.1 as the dilution solvent.

This method has demonstrated a linear response over the range of 5ppb to 10ppm. However, quantitation of responses at the lower end of this range may require a separate, tighter calibration range in order to eliminate the positive bias introduced by a large y –intercept.

The following are suggested calibration levels in ppb to cover both the wide range and low end calibration curves: 5,10,50,100,200,1000,5000 and 10000.

While these individual levels may be varied to the discretion of the analyst, **it is critical that regardless of analyte concentration, the 1% ethanethiol concentration must be maintained.**

11.2.4 Control Matrix Spiking Solution. Transfer 1-2 mLs of the Intermediate Standard Solution from 11.2.1 to a vial to be used as a spiking solution for extraction control samples.

11.3 Sample Preparation Steps

1. Transfer 500μL of each liquid sample, or 50 mg of solid sample, to an individual, labeled 15mL glass vial.

2. Prepare a laboratory control spike sample by transferring 500 μL of aqueous NaCl matrix (from 11.1.3) to separate 15mL vial. Spike exactly 50.0 μL of the control matrix spiking solution (11.2.4) directly into the NaCl matrix in the vial.

3. Add exactly 5.0mLs of 1% ethanethiol in TMP to all samples and control spikes. Initiate a method blank at this step by adding 5.0mLs of 1% ethanethiol in TMP to an empty 15mL glass vial.

4. Tightly cap the vials and vigorously shake each for 30 sec. Allow solution to settle briefly and loosen caps to release any pressure that may have built in vials.

5. Tighten caps and repeat the 30 second shaking sequence for a total of 3 shakes.

6. Open caps and accurately transfer 2.0mLs of pH 7 buffer solution to each vial.

7. Tightly cap and shake samples for an additional 3 replicates of 30 sec.

8. Allow samples to settle and the clear ethanethiol extract layer to form on the top of the solution.

9. Draw off an aliquot of the extract layer from the top and transfer to an autosampler vial for analysis. Transfer remaining ethanethiol in TMP to a 7mL vial. Store tightly capped, doubly contained with activated charcoal in the outer container at 6 °C.

11.4 Sample Analysis

11.4.1 Set up GC/MSD data acquisition method in SIM mode as follows:

Oven Parameters:
Initial temperature: 50 °C Maximum temp: 350 °C
Initial Time: 2.5 min Equilibration Time: 1.00 min
Ramps:

#	Rate(°C/min)	Final Temp(°C)	Final Time(min)
1	20.00	180	0.50
2	10.00	220	0.00
3	20.00	275	4.50
4	70.00	50	0.50
5	0.0 (Off)		

Post temp: 0 °C
Post time: 0.00 min
Run time: 24.46 min

Inlet (Split/Splitless)
Mode: Pulsed Splitless
Initial temp: 265 °C (On)
Pressure: 11.06 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 2.00 min
Purge Flow: 50.0 mL/min
Purge Time: 1.00 min
Total Flow: 54.2 mL/min
Gas Saver: On
Saver Flow: 20.0 mL/min
Saver Time: 3.00 min
Gas Type: Helium

Column
Capillary Column
Model Number: Agilent 122-5533
DB-5MS, 0.25mm X 30 meters X 1.0 □m
Max Temperature: 350 °C
Nominal Length: 30.0 m
Nominal Diameter: 250 nm
Nominal Film Thickness: 1.00 μm
Mode: constant flow
Initial Flow: 1.3 mL/min
Nominal Initial pressure: 11.07 psi
Average velocity: 42 cm/sec
Inlet: Front Inlet
Outlet: MSD

Outlet Pressure: vacuum

MSD Transfer Line Heater
Initial Temperature: 250 °C (On)
Initial Time: 0.00min

Injector

Sample Washes:	2
Sample Pumps:	2
Injection Volume:	1.0 µL
Syringe Size:	5.0 µL
Post Inj Solvent A Washes:	2 (Isopropyl alcohol)
Post Inj Solvent B Washes:	2 (Methanol)
Viscosity Delay:	0 sec
Plunger Speed:	Fast
PreInjection Dwell:	0.00 min
PostInjection Dwell:	0.00 min

MS Acquisition Parameters

General Information

Tune File:	ATUNE.U
Acquisition Mode:	SIM

MS Information

Solvent Delay:	6.00 min
EM Absolute:	False
EM Offset:	0

SIM Parameters

Resolution:	Low
Dwell Time:	100
HD Acquisition Ions:	**109**, 111, 158, and 160
HN3 Acquisition Ions:	154, **156**, and 158
L3 Acquisition Ions:	113, **136**, and 145
L2/L1 Acquisition Ions:	**136**, 145, and 258
Arsenite Acquisition Ions:	137, **197**, and 258
PD Acquisition Ions:	**213**, 245, and 274
DA Acquisition Ions:	227, **261**, and 290
TPA Acquisition Ions:	**152**, 227, and 306

The underlined ion in bold font is the recommended quantitation ion.

MS Zones

MS Quad: 150 °C
MS Source: 230 °C

11.4.2 Establish operating conditions as specified in Section 11.4.1 and perform a standard autotune. Follow the procedures, criteria, recommendations and trouble shooting detailed in the user's guide and hardware manual accompanying the instrument.

11.4.3 Introduce each calibration standard into the GC/MS using the same technique that will be used to introduce the actual samples. Following a successful initial calibration, analyze all samples, method blanks and spike control samples. Following all sample analysis, make a second injection of each calibration standard from a separate vial than that used for the initial calibration.
Contamination by carryover can occur when high-level and low-level samples are sequentially analyzed. To avoid contamination, instrument blanks should be analyzed between standards and samples and following any samples suspected to contain high concentrations of target analytes.

12. CALIBRATION AND QUANTIFICATION OF SAMPLES AND STANDARDS

Initial calibration and sample quantification is performed by using a linear regression analysis to establish the calibration curve. The instrument response is treated as the dependent variable (y) and the calibration standard "on-column" amount as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y=mx+b$$

where

y = Instrument response
m = slope of the line (also called the coefficient of x)
x = on-column amount of the calibration standard (in ng)
b = the y-intercept

The regression calculation will generate a correlation coefficient (R) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 is indicative of a "perfect" fit. The initial calibration curve should have a correlation coefficient (R) which is ≥0.995. (R^2 should be ≥ 0.990).

The quantified amount determined by sample analysis is calculated by solving the regression calculation for x, as follows:

$$x = (y-b)/m$$

13. METHOD VALIDATION

In accordance with CMA's Laboratory and Monitoring Quality Assurance Plan (LMQAP),[4] waste screening methods require spike and recovery determinations as a means of method validation and certification. A useful approach for demonstrating detection limit is that used by EPA to estimate a method detection limit (MDL).[5] Multiple replicates (a minimum of seven) are prepared and processed using the method. The standard deviation is calculated, and then multiplied by the appropriate one-tailed Student's t statistic at the 99% confidence interval; the resulting value is the MDL. The MDL is defined as the minimum response that leads to detection of the analyte as determined from the analysis of a matrix that contains the analyte. The MDL does not provide quantitative information, but is based on statistics and reports with a 99% confidence level that the concentration of the analyte is greater than zero.

Method detection limit data were generated by spiking the mixed agents into a surrogate matrix, and applying the sample preparation and analysis method described in Sections 11.3 and 11.4. Multiple replicates (n=7) were independently prepared and analyzed at spike levels of 50 and 100 μg/L. In addition to the spiked samples, two blanks were also prepared and analyzed with each set of data. In all cases, there were no agents detected in any of the blank samples (n=4). The method detection limits are summarized in Table 3, and the peak to peak signal to noise ratios are summarized in Table 4. The MDLs, with the exception of PD, were all calculated using the 50 μg/L spike data. The MDL for PD was calculated using the 100 μg/L spike data, because the MDL calculated using the 50 μg/L data was 55.9 μg/L, which is above the spike level, and therefore not valid per EPA protocol.[5] The MDL data indicate the analytical method is under control, and suitable for quantitative analysis of residual agents in these sample matrices. In the worst case, for L2, the MDL is more than 1,000 times below the desired treatment goal of 50 mg/L.

Table 3. Method detection limits of the targeted analytes. The spike recovery studies were performed in a surrogate matrix. The Student's T value (n=7) was 3.143. The spike level was 100 μg/L for PD, and 50.0 μg/L for all other analytes.

Target Analyte	Found Concentration (μg/L)								MDL[b] (μg/L)
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	SD[a]	
HD	44.3	41.7	43.8	46.3	46.2	45.6	33.9	4.37	**13.7**
HN-3	30.5	31.0	30.8	36.3	32.8	36.1	33.1	2.44	**7.67**
L1	55.0	66.8	48.5	55.5	57.2	50.4	41.4	7.93	**24.9**
L2	82.4	57.0	47.9	53.9	62.4	49.5	39.4	13.70	**43.1**
L3	59.6	53.7	43.8	46.9	43.8	43.1	36.4	7.65	**24.0**
DA	64.6	62.0	62.9	60.3	49.3	48.2	39.0	9.71	**30.5**
PD	96.2	89.2	96.4	85.3	84.7	83.5	91.6	5.38	**16.9**
TPA	51.0	61.2	49.9	47.6	43.8	47.9	43.5	5.97	**18.8**

a. Standard deviation of found concentration.
b. Method detection limit.

Table 4. Peak to peak signal to noise ratios of the targeted analytes. The analytes were all spiked at 50.0 μg/L in a surrogate matrix.

Target Analyte	Peak to Peak Signal to Noise Ratio							Average SNR[a]
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	
HD	7.2	10.0	7.0	11.1	11.9	11.6	10.4	10
HN-3	12.0	13.2	14.1	20.8	20.5	20.6	19.8	17
L1	14.0	11.0	9.0	8.0	5.2	5.6	5.4	8
L2	3.5	2.8	4.0	4.8	2.5	2.8	3.4	3
L3	3.8	6.9	7.8	10.2	9.8	7.8	8.4	8
DA	3.1	4.1	5.7	8.6	5.4	8.3	8.6	6
PD	11.4	16.8	14.3	14.5	20.9	20.0	29.0	18
TPA	3.7	5.7	4.8	13.2	11.3	12.9	9.3	9

a. Signal to noise ratio.

14. STATEMENT OF THE ANALYTICAL RESULT

If generated, hard copies of the chromatograms and spectra will be retained for each sample. All summary spreadsheets will be retained for each group of samples. All data will be labeled with a unique sample identification. Appropriate details and observations will be recorded in a

laboratory notebook. All electronic data files will be archived. The results will be reported in the sample as submitted to the laboratory, and data reports will adhere to client requirements.

15. REFERENCES

1. *Analytical Support to the Research Technologies Directorate Advanced Chemistry Team*, SOP RNG-116, U.S. Army Research Development and Engineering Command, 2005.

2. *The Army Toxic Chemical Agent Safety Program*, Army Regulation 358-61. Headquarters, Department of the Army, draft November 1992.

3. *Nuclear and Chemical Weapons and Materiel: Chemical Surety*, Army Regulation 50-6. Headquarters, Department of the Army, effective 01 March 1995.

4. *Programmatic Laboratory and Monitoring Quality Assurance Plan*, U.S. Army Chemical Materials Agency, Aberdeen Proving Ground, Maryland. Final June 2004, UNCLASSIFIED Report.

5. Definition and Procedure for the Determination of the Method Detection Limit. *Code of Federal Regulations,* Revision 1.11, 40, Part 136, Appendix B. 1 July 1989

16. SUMMARY OF REVISION CHANGES

1. Revision dated 03 February 2005: Preliminary working draft for internal review only.

2. Revision dated 10 May 2005: Draft submitted for external review.

3. Revision dated 15 June 2005: Draft final which incorporated reviewer comments. Suitable for distribution to outside laboratory