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CHARACTERIZATION AND NEUTRALIZATION OF ARSENICAL-BASED WWII ERA CHEMICAL MUNITION FILLS

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14. ABSTRACT
The purpose of this work was to select, optimize, and validate a reagent for neutralization of arsenical fills contained in WWII era non-stockpile munitions. The work focused on the neutralization of arsinol, a mixture of diphenylchloroarsine (DA), phenyldichloroarsine (PD), triphenylarsine (TPA), and arsenic trichloride.

15. SUBJECT TERMS

Arsinol	German Traktor Rocket	Neutralization	Permanganate
Arsenic	Emergency Destruction System	Oxidation	Diphenylchloroarsine
EDS	PD	DA	Phenyldichloroarsine

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EXECUTIVE SUMMARY

This report summarizes efforts to develop and validate a neutralization chemistry for the arsenical fills found in WWII era German Traktor Rockets. These munitions are believed to make up approximately 40% of the Pine Bluff Arsenal recovered chemical warfare (CW) materiel inventory and must be destroyed in accordance with Chemical Materials Agency guidance. Destruction in accordance with the provisions of the Chemical Weapons Convention is currently being clarified, but as a worst-case basis, the criteria for this destruction were also considered during this study. The data generated during this study will be used to support design, systemization, and operation of a non-stockpile demilitarization process of the German Traktor Rockets using the Explosive Destruction System at Pine Bluff Arsenal. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at other 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 implemented 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 arsenical fills found in German Traktor Rockets. In lab-scale and full-scale Explosive Destruction System testing, the aqueous permanganate consistently produced neutralents that had residual agent levels well below the treatment goal of 50 mg/L (ppm). The reaction products included inorganic pentavalent arsenate and various pentavalent organo-arsenicals, with inorganic arsenate concentration positively correlated with reaction temperature. 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 January 2003 and completed in March 2005.

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This work would not have been possible without the efforts of CBARR, and the authors gratefully acknowledge CBARR for downloading the chemical fills from the rocket, and operating the EDS during full-scale testing.

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CHARACTERIZATION AND NEUTRALIZATION OF ARSENICAL-BASED WWII ERA CHEMICAL MUNITION FILLS

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. To support the recovered chemical weapons mission, the PMNSCM will chemically neutralize and destroy approximately 439 German Type 41 Traktor Rockets (GTRs) that were recovered after WWII and are currently in storage at Pine Bluff Arsenal (PBA), AR.[1] These rockets were also tested or disposed of at other sites in the United States, and may be recovered at these locations in the future. A variety of chemical warfare agents (CWAs) and other chemicals have been identified as possible fills in the stored GTRs,[1,2] but the focus of this effort is on the neutralization of arsenical fills. The potential arsenical fills include (2-chlorovinyl)arsine (L), diphenylchloroarsine (DA), phenyldichloroarsine (PD), triphenylarsine (TPA), and arsenic trichloride. The TPA and arsenic trichloride, while not chemical warfare agents, are chemicals used and/or produced in the synthesis of the arsenical chemical warfare agents.[3] The term arsenal (or arsine oil) is used to describe the crude mixtures obtained during synthesis of the phenyl-arsenical CWAs, and is a liquid containing approximately 50% PD, 35% DA, 5% TPA, and 5% arsenic trichloride.[3] Selected properties of the potential arsenical fills are summarized in Table 1, and the structures are illustrated in Figure 1.

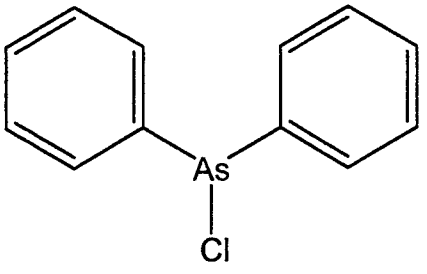
In December 2002, seven GTRs in storage at PBA were individually containerized using Department of Transportation and U.S. Army approved containers, and transferred from PBA to Edgewood Chemical and Biological Center (ECBC), located at Aberdeen Proving Ground, MD. Samples of each fill were then transported to ECBC laboratories for both characterization of the fill materiels, and treatability studies. A schematic of a GTR is illustrated in Figure 2, and a photograph of a GTR taken during fill downloading operations is included as Figure 3. Two of the GTRs were determined to contain tris(2-chloroethyl)amine (HN-3, CAS No. 555-77-1), while five of the rockets were determined to contain arsenical-based fill materiels.[1]

Table 1. Select Properties of Possible Arsenicals Contained in GTRs. The data was collected from a variety of sources.[3-6]

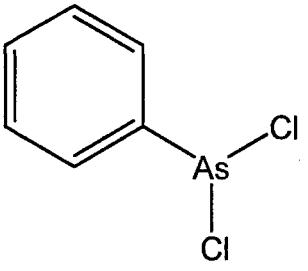
Property	Arsenical Chemical				
	L	DA	PD	TPA	Arsenic Trichloride
Chemical Formula	$C_2H_2AsCl_3$	$C_{12}H_{10}AsCl$	$C_6H_5AsCl_2$	$C_{18}H_{15}As$	$AsCl_3$
Molecular Weight	207.35	264.5	222.92	306.24	181.28
CAS Number	541-25-3	712-48-1	696-28-6	603-32-7	7784-34-1
Boiling Point (°C)	190	333 (decomposes)	252 to 255	NDA[b]	130
Vapor Pressure (mm Hg)	0.394 @ 20 °C	0.0036 @ 45 °C	0.033 @25 °C	NDA[b]	10 @ 23.5 °C
Volatility (mg/m^3)	4,480 @ 20 °C	48 @ 45 °C	390 @ 25 °C	NDA[b]	NDA[b]
Vapor Density[a]	7.1	Forms no appreciable vapor	7.7	Forms no appreciable vapor	6.3
Liquid Density	1.89 @ 20 °C	1.387 @ 50 °C	1.65 @ 25 °C	1.22[c]	2.15

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

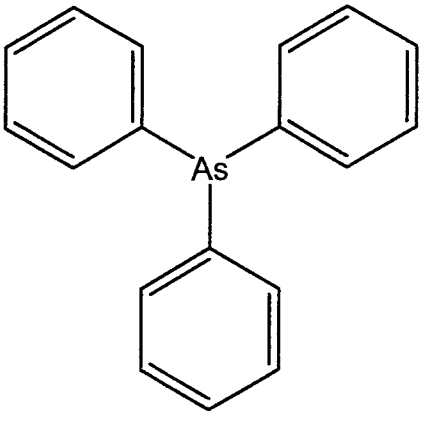
Diphenylchloroarsine



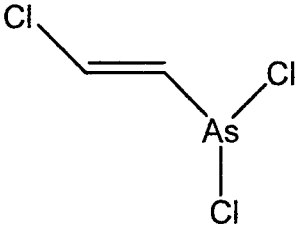
Phenylchloroarsine



Triphenylarsine



(2-chlorovinyl)arsine



Arsenic trichloride

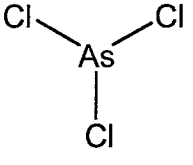


Figure 1. Structures of Potential Arsenicals Contained in GTRs.

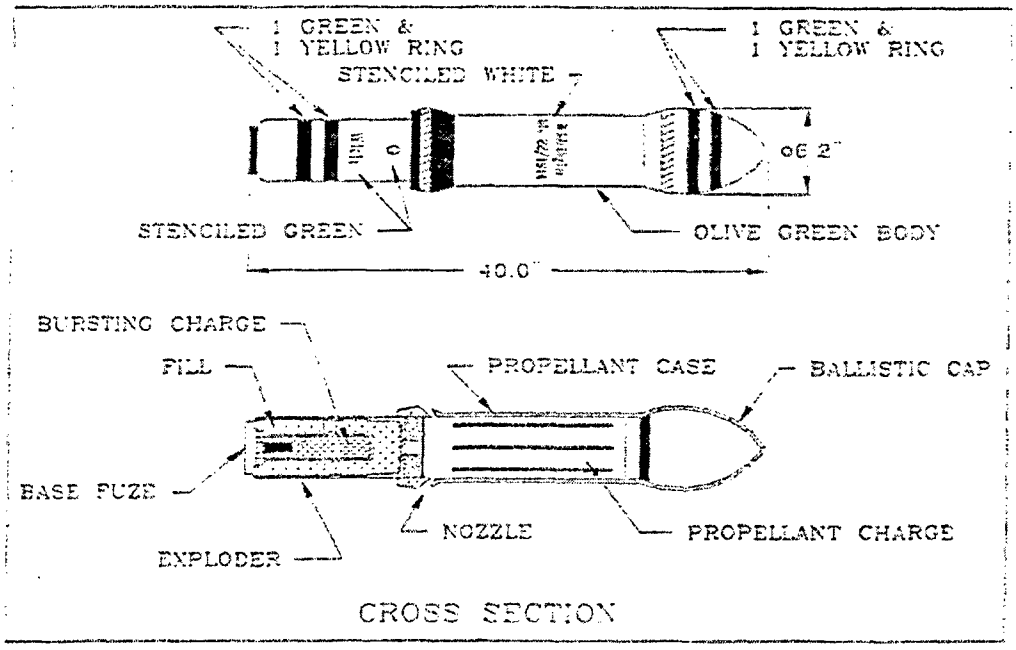


Figure 2. GTR Schematic.[7]

Figure 3. Photograph of GTR CA-0178. A section of the casing has been cut away, revealing the burster well, and the compartment which holds the chemical fill.

1.2 Study Objectives.

The purpose of this testing was to develop and validate a neutralization chemistry for the arsenical fills (particularly arsenal, a mixture of DA, PD, TPA, and $AsCl_3$) stored at Pine Bluff Arsenal. These munitions are believed to make up approximately 40% of the PBA recovered chemical warfare materiel inventory and must be destroyed in accordance with Chemical Materiels Agency (CMA) guidance. Destruction in accordance with the provisions of the Chemical Weapons Convention (CWC) is currently being clarified, but as a worst-case basis, the criteria for this destruction were also considered during this study. 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 the GTRs at Pine Bluff Arsenal. 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 other locations, including Aberdeen Proving Ground, Maryland.

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, N_2 gas was purged through the reactor headspace at a rate of 1-2 mL/min, and was vented through the condenser. The N_2 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-in. 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 Large-Scale Lab Reaction Studies.

The large-scale reactions were conducted using either a stainless steel reactor, or a glass reaction flask. The stainless steel reactor system was used to produce samples for the neutralent storage study, while the glass reaction flask was used to produce neutralent for Resource Conservation and Recovery Act (RCRA) waste characterization and corrosion testing.

The stainless steel reactor was a Parr Model 5100 series low pressure reactor, with a 0.6 L 316 stainless steel reaction vessel and a 1 L pressure pipet. The reactor was equipped with a mechanical stirrer, utilizing a turbine type impeller. Heating was accomplished by the use of an electric heating mantle, with temperature control maintained by using a Parr Model 4842 controller. In a typical run, a piece of copper (1/8 inch copper tubing, approximately 2.5 g) and common steel (wire, approximately 15 g) were suspended in the reaction vessel by means of a Teflon string, and then 10 mL of arsinol was added. The reactor was then sealed, and charged to 5-8 psi with nitrogen. Five hundred milliliters of pre-warmed reagent (approximately 40 °C) was added through the pipet, using a 25-30 psi nitrogen push. Once all the reagent was added, stirring was started, and the reaction temperature set-point raised to the desired temperature. Neutralent samples were removed from the reactor at various time points via a sampling valve.

The glass reaction flasks were 2 L Erlenmeyer type flasks, equipped with air cooled condensers. Stirring was accomplished by use of a TFE coated stir bar, and a combination magnetic stir plate/hot plate, with the reaction stirred at moderate speed throughout the reaction. Prior to any runs being conducted, hot plate settings were calibrated to desired temperatures by using 1,000 mL of deionized water in the flask. In a typical run, a piece of copper (1/8 inch copper tubing, approximately 5 g) and common steel (wire, approximately 30 g) were suspended in the reaction vessel by means of a Teflon string, and then 1,000 mL of reagent was added, and the temperature adjusted to 40 °C. Once the temperature stabilized, 20 mL of arsinol was quickly added as a single bolus. Approximately 15 min after the arsinol was added to the reactor, the temperature was adjusted to the desired level, and the reaction was allowed to proceed to completion.

2.4 Standards.

The DA and PD were synthesized in-house using an established procedure,[10] which involved reacting phenylmagnesium bromide with arsenic trichloride in the presence of ether, then isolating the DA and PD by vacuum distillation. The purities of DA and PD were determined using an established ^{13}C-NMR technique,[11] and were found to be 96.8 wt% and 95.2 wt%, respectively. The diphenylarsinic acid (DPAOA) was synthesized using an established procedure,[3] which involved refluxing DA in 20% HNO_3 for 3 hr. After cooling to ice bath temperature, the crude crystals of DPAOA were isolated by vacuum filtration, and further purified by re-crystallizing from methanol/water. The purity of the DPAOA was determined using an established quantitative ^{13}C-NMR technique,[11] and was found to be 91.7 wt% DPAOA. All other standards used in this project were obtained from commercial sources, and were of the highest available purity.

2.5 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] The method, for DA/PD/TPA only, was successfully validated by two other laboratories.[13,14] A detailed method description, in Standard Operating Procedure (SOP) format,[15] is attached as the Appendix.

2.5.1 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 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 2.6, 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.

2.5.2 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.

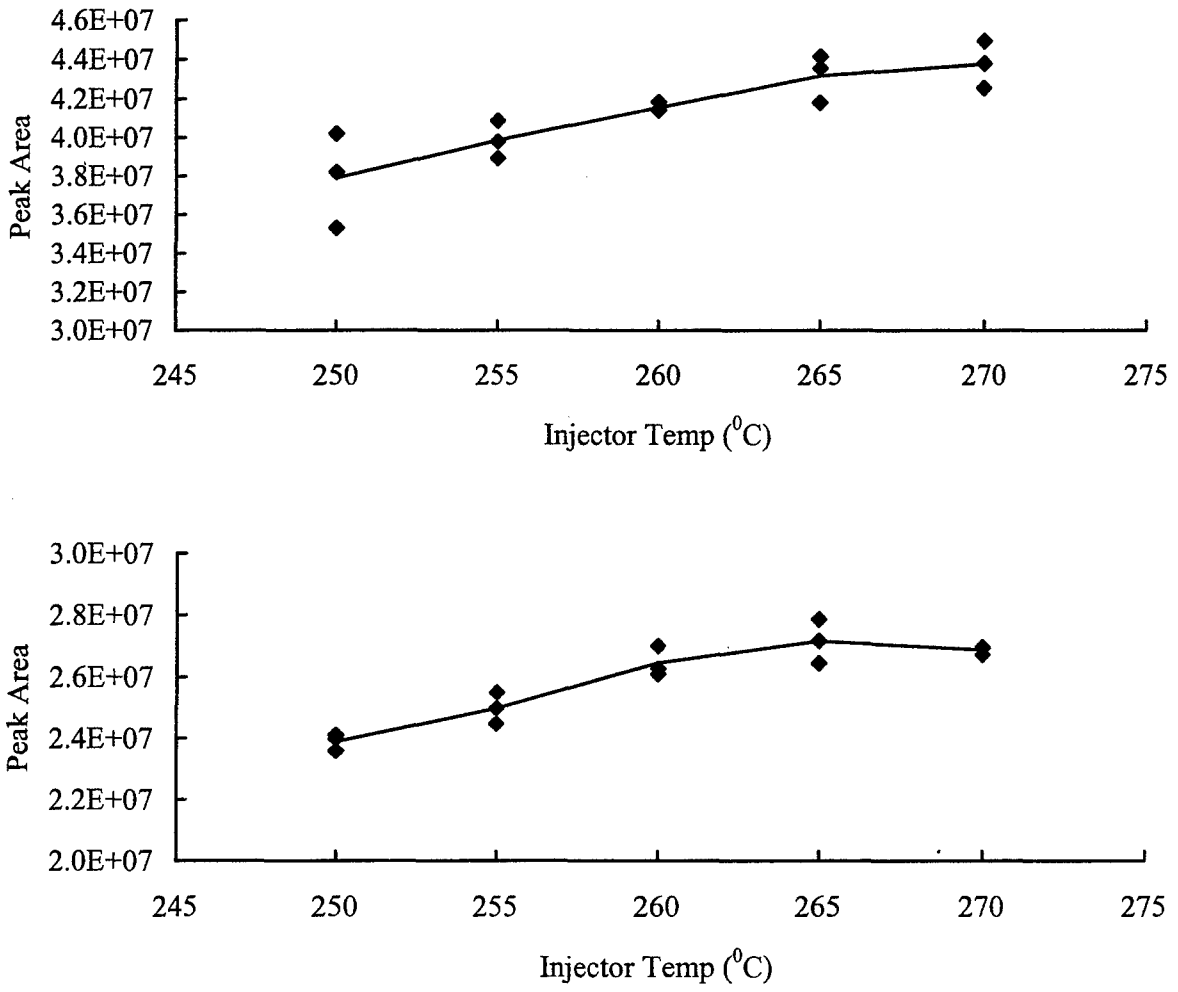


Figure 4. Peak Area as a Function of Injector Temperature for Three Target Analytes. The upper panel is DA, the middle panel is HD, and the bottom panel is TPA.

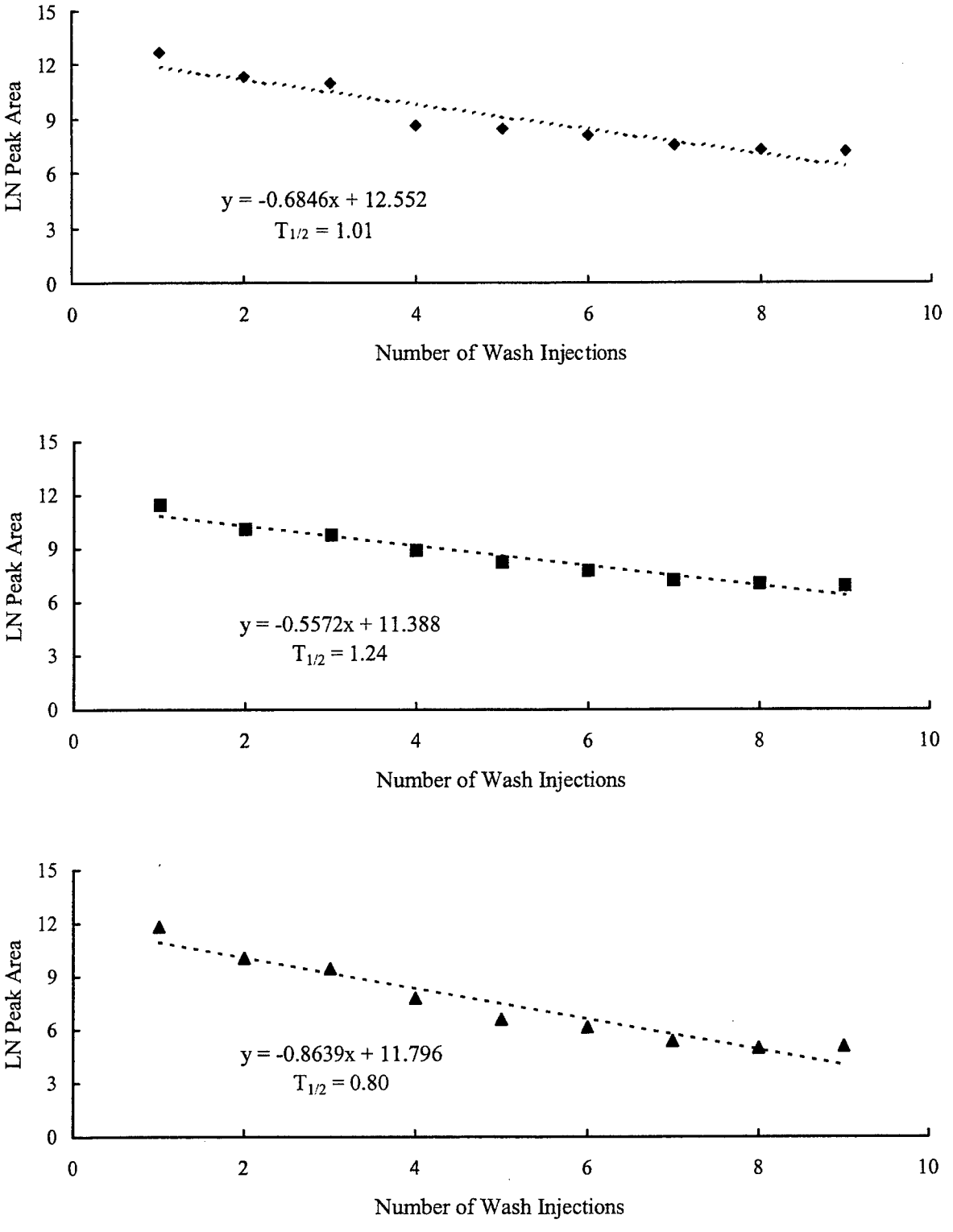
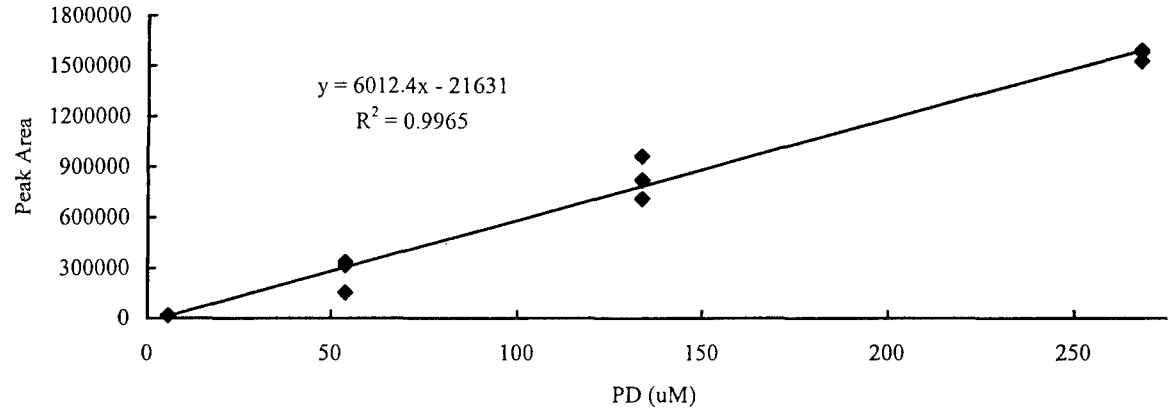
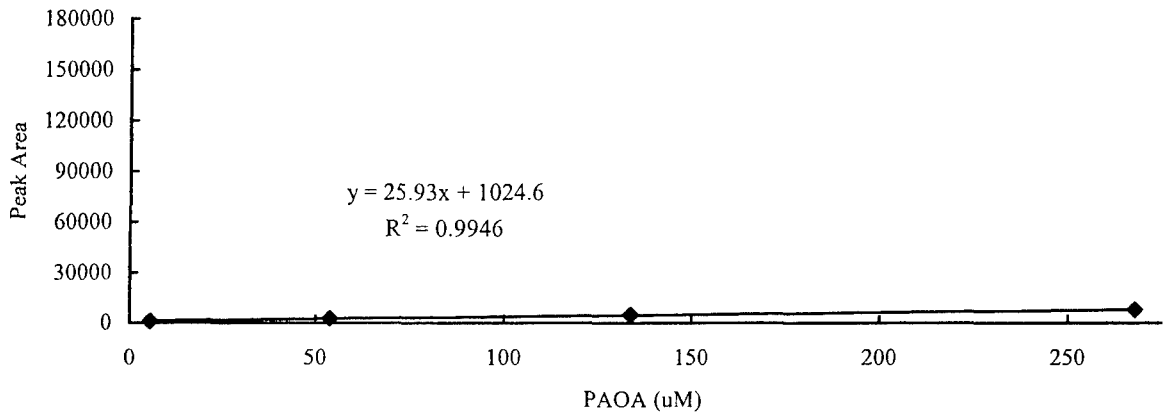


Figure 5. Carry Over as a Function of Number of Wash Vial Injections for DA, PD, and TPA. The upper panel is DA, the middle panel is PD, and the bottom panel is TPA.





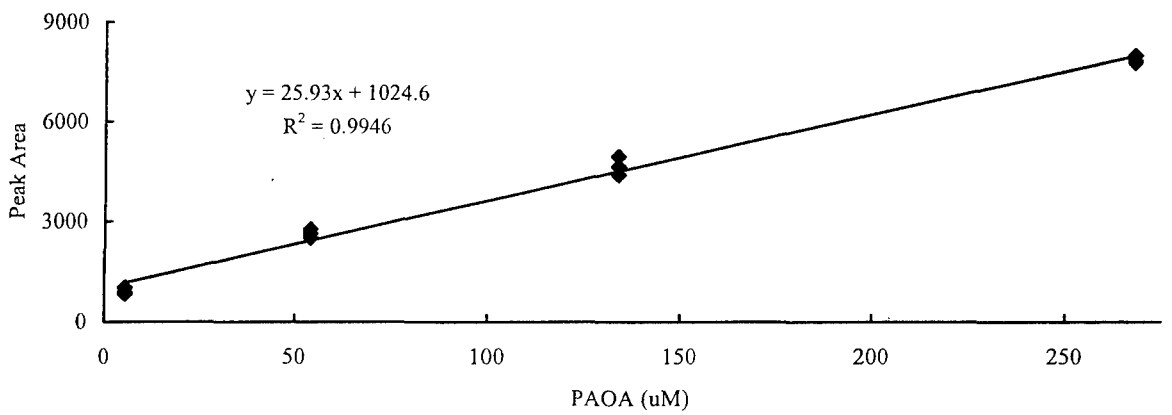


Figure 6. Comparison of Peak Area Response as a Function of Concentration for the Organo-Arsenicals Derivatized with Ethanethiol. The upper panel is PD (As^{+3}), the middle panel is phenylarsonic acid (As^{+3}) on the same Y-scale as PD, and the bottom panel is phenylarsonic acid (As^{+5}), with the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

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.

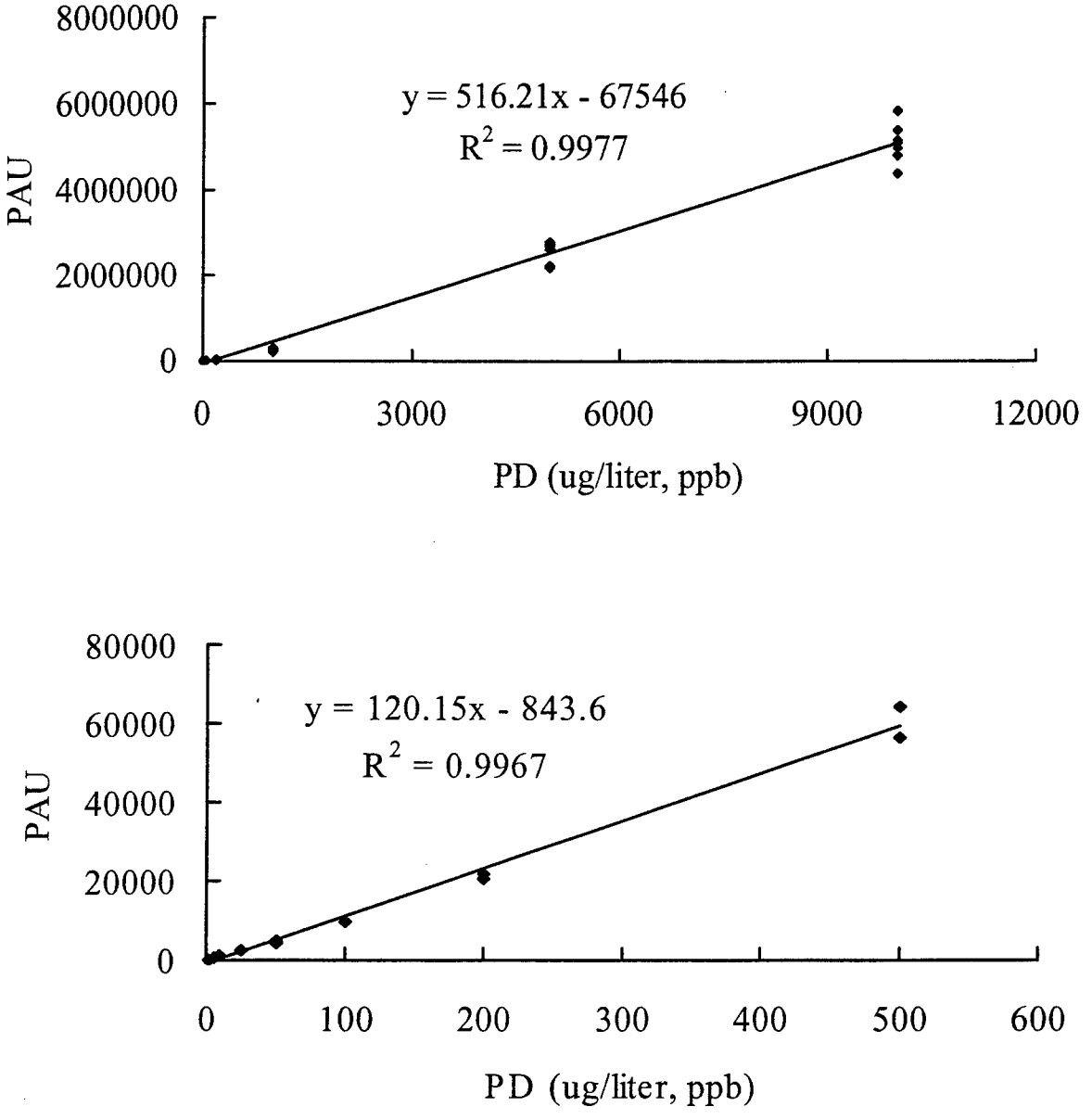


Figure 7. Example External Calibration Curves for PD. The upper panel is the entire range evaluated during the validation process, and the lower panel is the typical working calibration range used during the spike recovery and MDL experiments. The data is based on the extracted m/z ion 274.

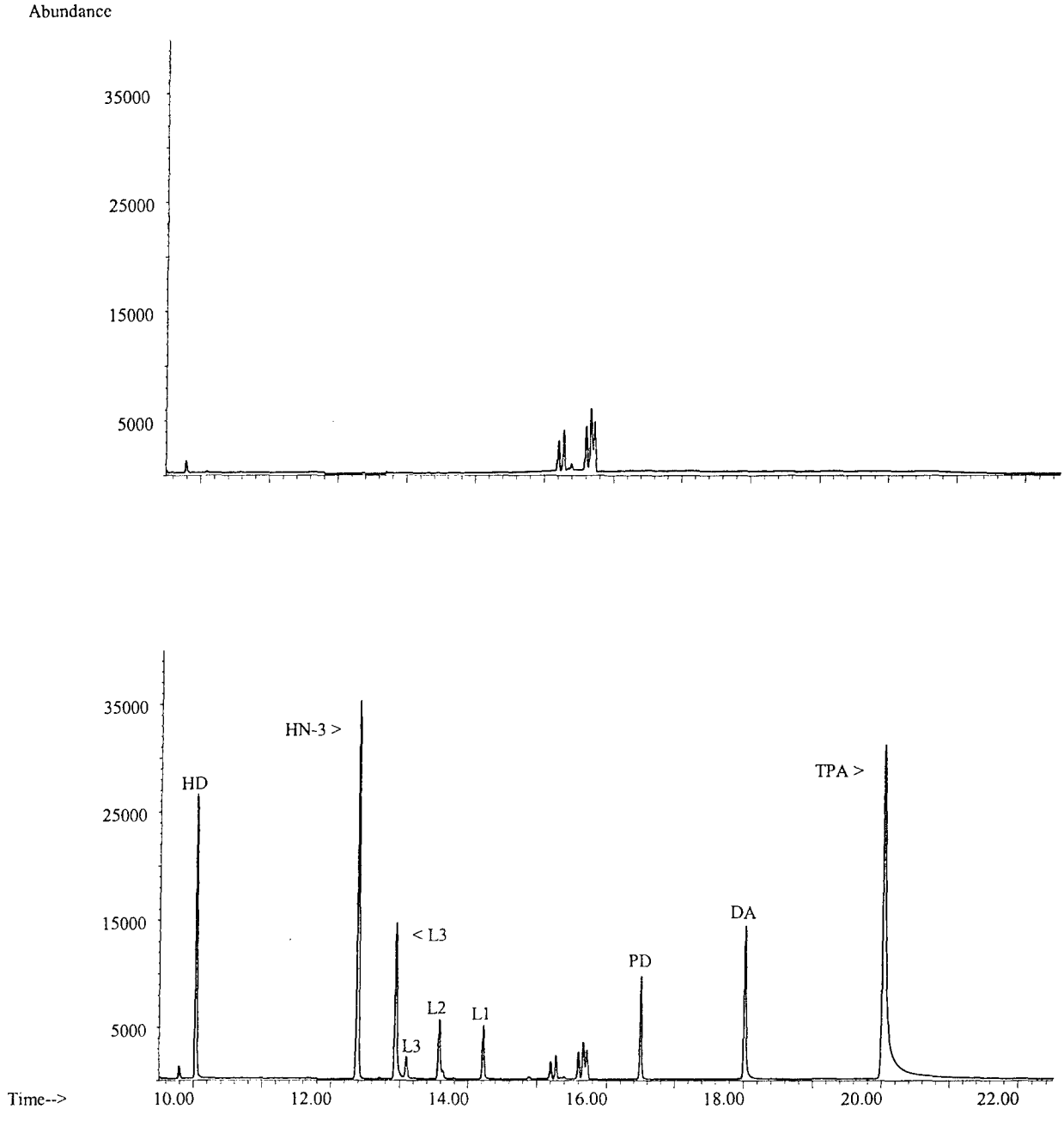


Figure 8. Example Chromatograms. The upper panel is an extraction blank, and the bottom panel is a 500 µg/L mixed standard. The time axis has been zoomed into the region of interest. L1, L2, DA, and PD are the ethanethiol derivatives.

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

2.5.3 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 (Section 3.7.3).

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.

2.5.4 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[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.

2.6 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] and the characterization of sulfur mustard and lewisite degradation products.[27-29]

2.6.1 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).

2.6.2 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.

2.6.3 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. Arsinol degradation products analyzed for by CE with direct UV detection include phenylarsine oxide (PAO), triphenylarsine oxide (TPAO), phenylarsonic acid (PAOA) and diphenylarsinic acid (DPAOA). Other arsenic-containing degradation products analyzed for by CE include the inorganic components, arsenate (AsO_4) and m-arsenite (AsO_2). 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.

2.6.4 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/de-ionized 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)[a]
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
Phenylarsonic acid	98-05-5	$C_6H_7AsO_3$	$C_6H_5AsO_3^{-2}$	0.5
Diphenylarsinic acid	4656-80-8	$C_{12}H_{11}AsO_2$	$C_{12}H_{10}AsO_2^-$	0.5
Phenylarsine oxide	637-03-6	C_6H_5AsO	C_6H_5AsO	1.0
Triphenylarsine oxide	1153-05-5	$C_{18}H_{15}AsO$	$C_{18}H_{15}AsO$	0.5
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

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

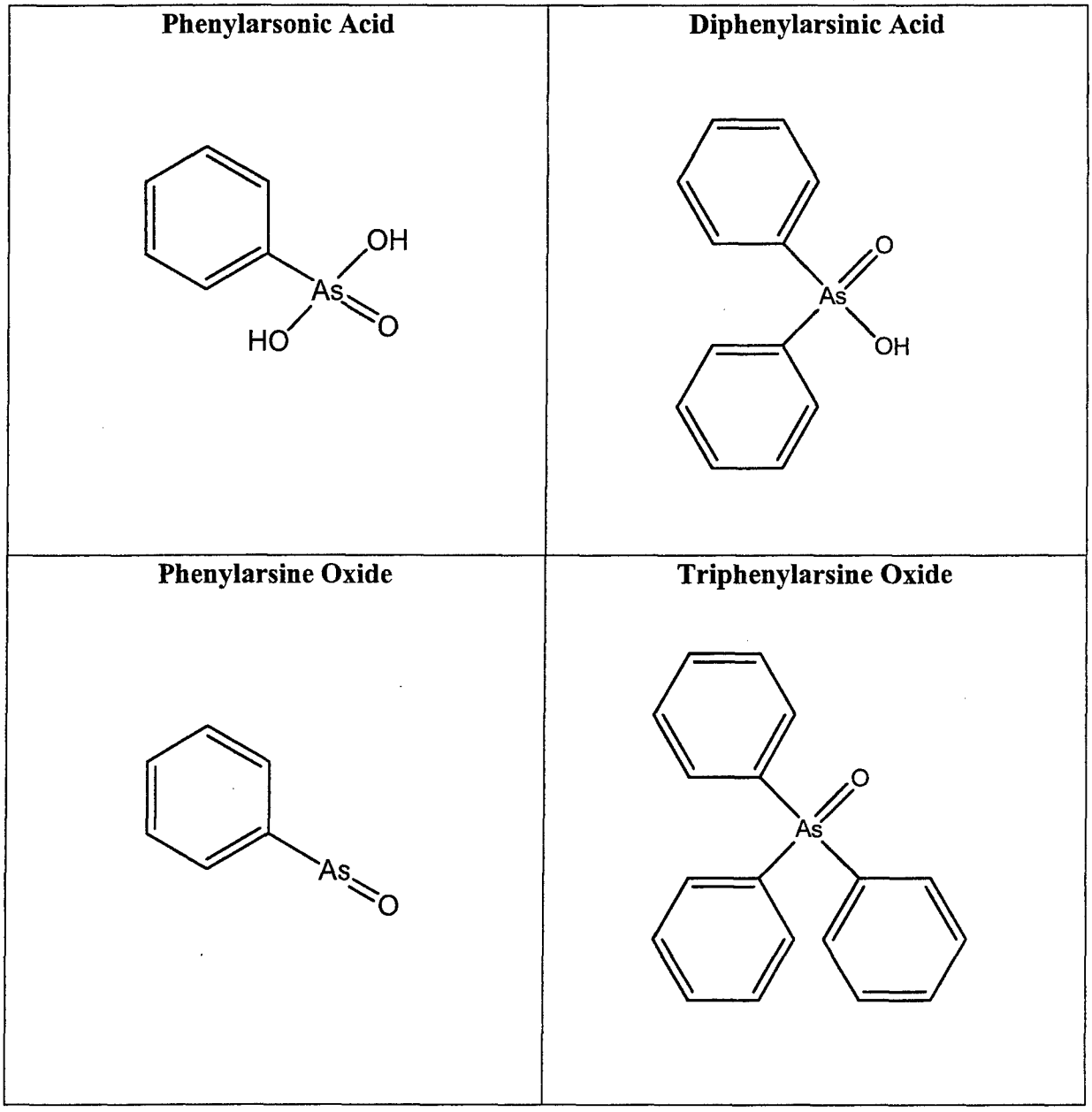


Figure 9. Structures of the Organo-Arsenicals Determined by the CE Methods.

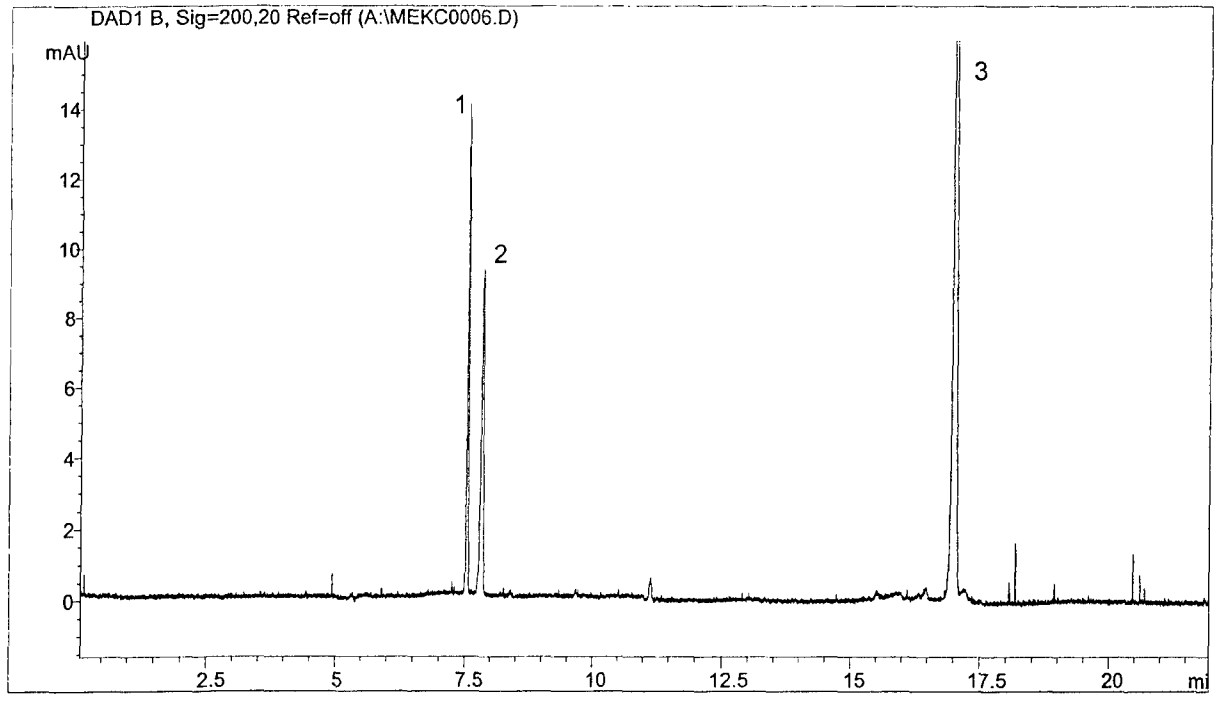


Figure 10. Electropherogram Generated from the Analysis of Standards Using MEKC with Direct UV Detection. Analytes are: 1 = DPAOA, 2 = PAO and 3 = TPAO.

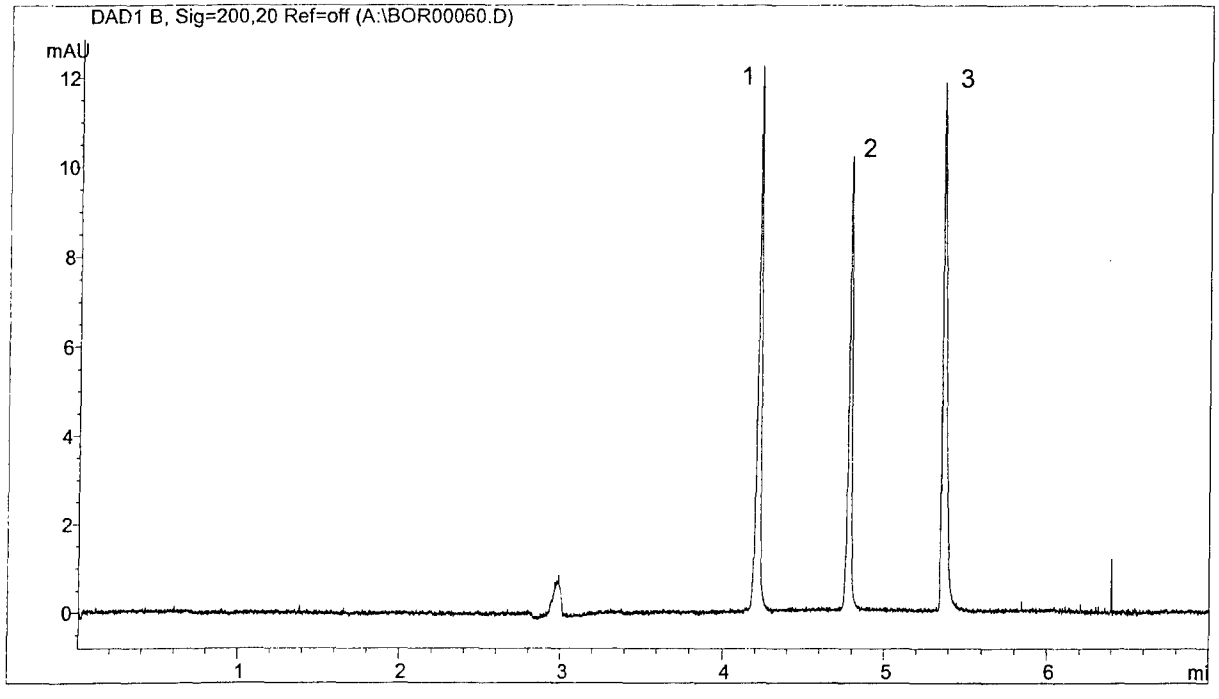


Figure 11. Electropherogram Generated from the Analysis of Standards Using CZE with Direct UV Detection. Analytes are: 1 = DPAOA, 2 = PAOA and 3 = CVAOA.

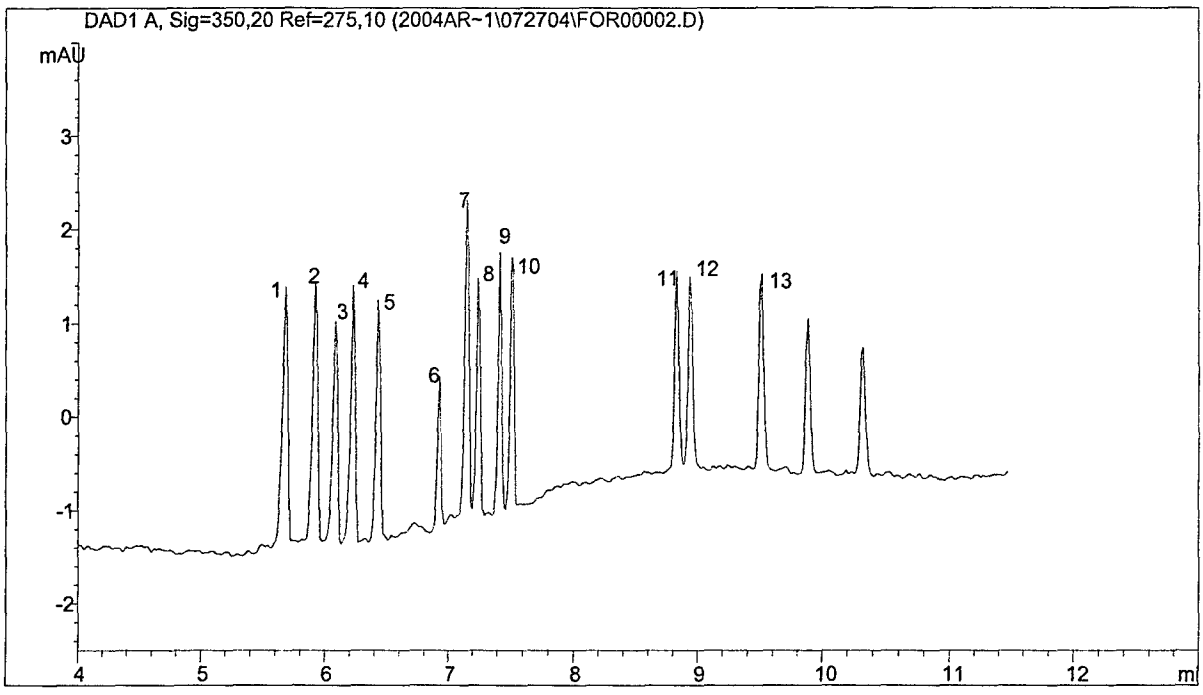


Figure 12. Electropherogram Generated from the Analysis of Standards Using a Modified CZE Method with Indirect UV Detection. Analytes are: 1 = chloride, 2 = nitrite, 3 = nitrate, 4 = sulfate, 5 = oxalate, 6 = carbonate, 7 = fluoride, 8 = formate, 9 = arsenate, 10 = phosphate, 11 = acetate, 12 = glycolate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

2.7 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= 4 EDS runs), the iron concentration was determined to be 1,690 mg/L, and the chloride concentration was determined to be 6,470 mg/L. Considering the sample dilution factor, both of these chemicals will be <1 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.

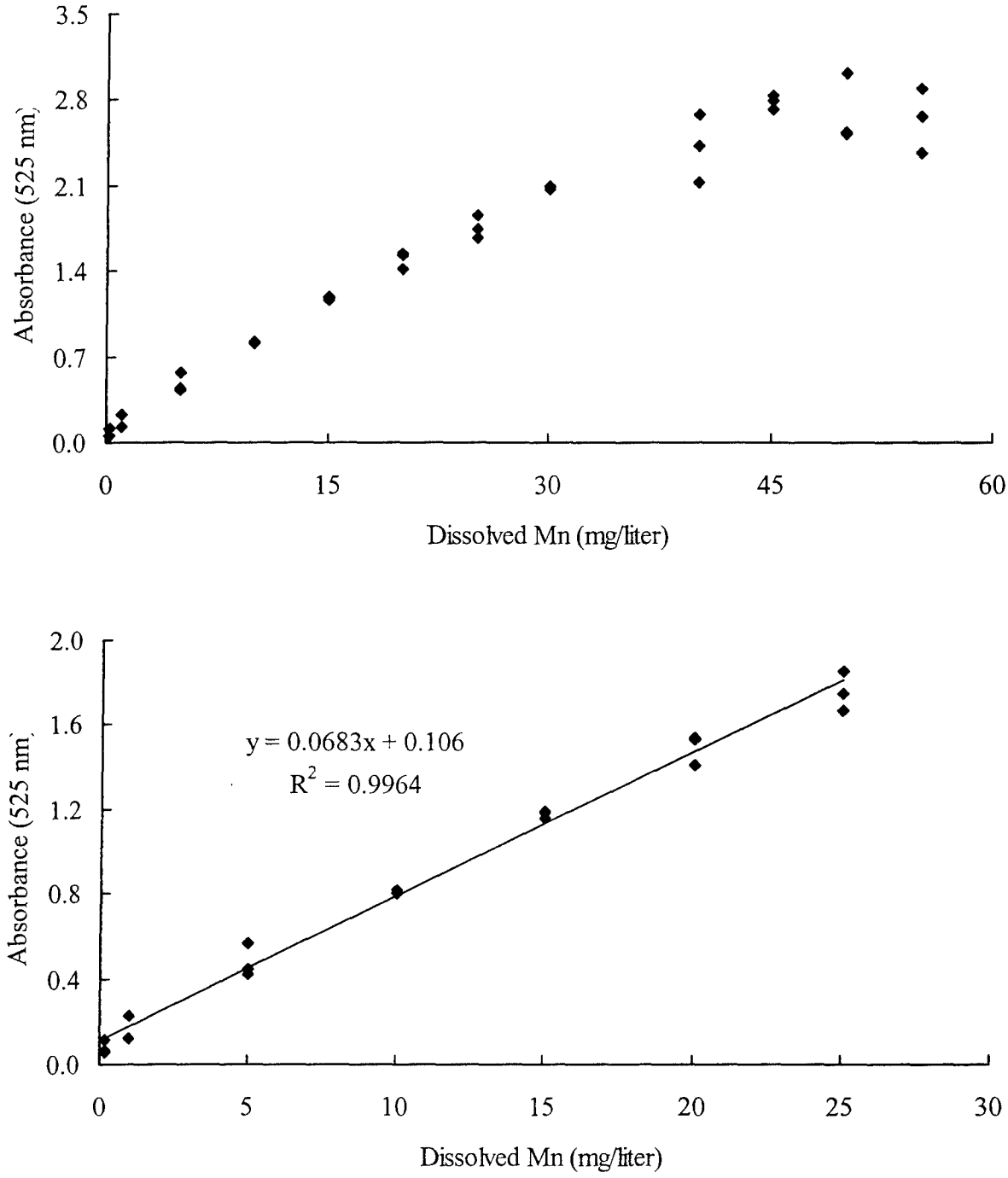


Figure 13. Response Curve (upper panel) and Linear Range (lower panel) of Dissolved Manganese.

3. RESULTS AND DISCUSSION

3.1 Identification 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.

In December 2002, seven GTRs in storage at PBA were individually containerized using Department of Transportation and U.S. Army approved containers, and transferred from PBA to Edgewood Chemical and Biological Center, located at Aberdeen Proving Ground, MD. Samples of each fill were then transported to ECBC laboratories for both characterization of the fill materiels, and treatability studies. Identification of GTRs, fill assignments based on non-intrusive sampling, and fill descriptions are summarized in Table 8. Two of the GTRs were determined (after intrusive sampling) to contain tris(2-chloroethyl)amine (HN-3, CAS No. 555-77-1), while five of the rockets were determined to contain arsenical-based fill materiels. Only results from the arsenical-based fill materiels are summarized in this report.

Table 8. Summary of GTR Identification, Fill Assignments Derived from Non-Intrusive Sampling,[1] and Description of Fill Materiel

GTR Identification Number	PINS[a] Fill Assessment	Description of Fill Materiel
CA-0173	Probable HN-3	Clear, tan in color
CA-0175	High confidence Winterlost[b]	Opaque, greenish/black in color
CA-0178	High confidence Winterlost[b]	Two phases: solid was yellow/green crystals; liquid was opaque, greenish/black in color
CA-0230	Possible Winterlost[b]	Opaque, greenish/black in color
CA-0276	High confidence Winterlost[b]	Opaque, greenish/black in color
CA-0279	Possible HN-3	Clear, tan in color
CA-0280	High confidence Winterlost[b]	Opaque, greenish/black in color

a. Portable Isotopic Neutron Spectroscopy.
b. Winterlost is a mixture of sulfur mustard and arsenical chemical warfare agents.

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 Hewlett-Packard (HP) 5890 GC with BioRad 5965B Fourier Transform Infrared Detector coupled in series with a HP 5971 mass spectral detector operating in electron impact ionization mode. This configuration allows separation and near-simultaneous collection of mass spectra and vapor-phase infrared spectra of the individual chemicals passing through the GC column. The GC was equipped with a HP-5 column which was 25m X 0.32 mm ID, with a phase thickness of 0.17 μm. Infrared spectra were collected in a range from 550 to 4000 cm^{-1} at an optical resolution of 8 cm^{-1}. 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 sample preparation scheme, 5 μL (or 5 mg of solid sample) of GTR fill materiel was mixed with 5 mL of acetonitrile, the sample was vortexed to dissolve, then filtered through a PTFE Acrodisc™ (0.45 μm) prior to analysis. In the second sample preparation scheme, 5 μL (or 5 mg of solid sample) of GTR fill materiel was mixed with 5 mL of hexane, the sample was vortexed to dissolve, then the solvent was backwashed with 1 mL of pH 7 buffer (See Appendix). The hexane extract was then filtered through a PTFE Acrodisc™ (0.45 μm) prior to analysis. The third approach was similar to the second, except 10 μL of neat ethanethiol was added to the hexane.

The results of the GC analyses are summarized in Table 9, and structures of the identified chemicals are illustrated in Figure 14. Mass spectra and infrared spectra of the identified chemicals are illustrated in Figures 15 and 16. Peak assignments were based on comparison to reference spectra,[35] comparison to external standards, and spectral interpretation.[36] While all the major peaks were identified, each sample had multiple (3-8) peaks which were not identified. These unidentified peaks were small (<1 area percent each), and were not standard agents or degradation products of standard agents. A specific search was made for HD and mustard related chemicals (oxidized forms of HD, 1,4-dithiane, 1,4-thioxane, Q, and T), and none were detected. While not rigorously established, the detection limits for these mustard related chemicals is 20-30 mg/L, under the conditions employed. Compounds VI and VII were not in the original fill, but are artifacts of the GC method. The formation of esters at high temperatures (as experienced in the injection port), in the presence of an alcohol (2-propanol was used to wash the syringe), under acidic conditions is well documented, and is used extensively to intentionally esterify various chemicals prior to chromatographic analyses.[37]

Table 9. Summary of Compounds Detected by Gas Chromatographic Experiments.

GTR ID	Preparation Method	Compounds Identified[a]
	Acetonitrile Extraction	II and III
CA-0175	Hexane Extraction	III, VI, and VII
	Ethanethiol Derivitization	V, IV, and III
	Acetonitrile Extraction	II, and III
CA-0178[b]	Hexane Extraction	III
	Ethanethiol Derivitization	V and III
	Acetonitrile Extraction	II and III
CA-0230	Hexane Extraction	VII, VI, and III
	Ethanethiol Derivitization	V, IV, and III
	Acetonitrile Extraction	II and III
CA-0276	Hexane Extraction	III
	Ethanethiol Derivitization	V, IV, and III
	Acetonitrile Extraction	II and III
CA-0280	Hexane Extraction	III
	Ethanethiol Derivitization	V, IV, and III

a. See Figure 14 for structures.
b. Solid fraction.

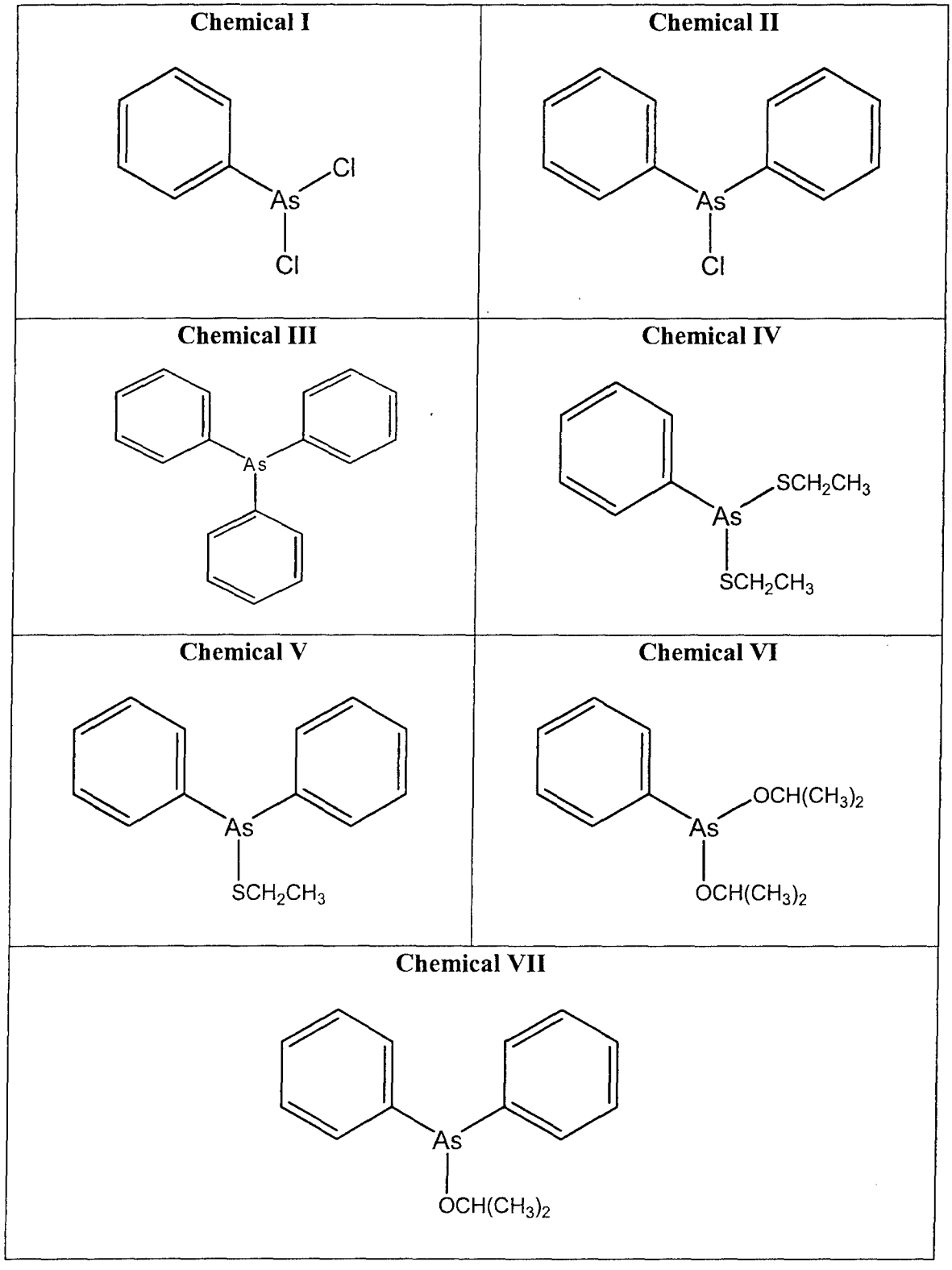


Figure 14. Structures of Chemicals Detected During the Gas Chromatographic Analyses.

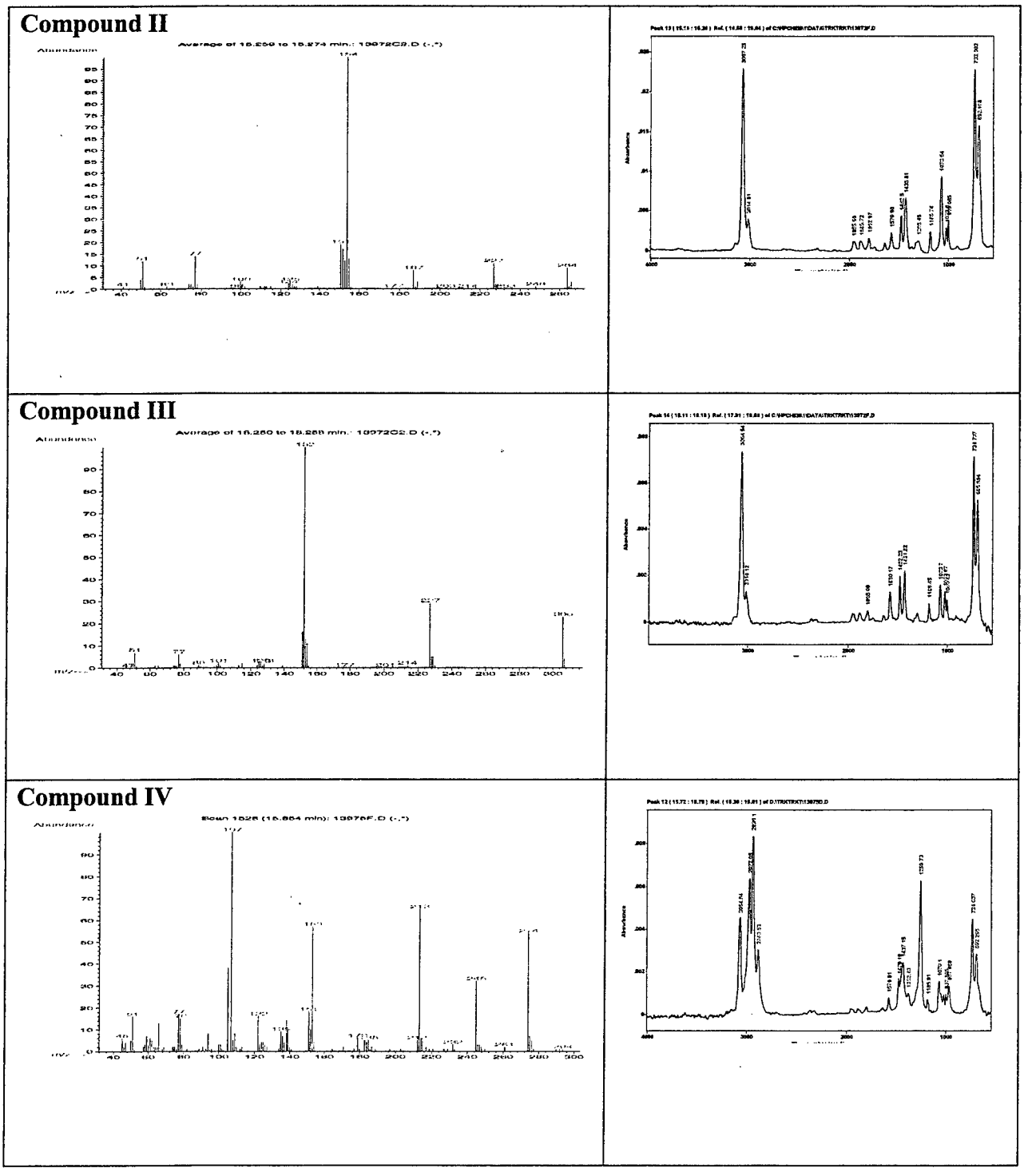


Figure 15. Mass and Infrared Spectra of Chemicals Identified During the Gas Chromatographic Analyses.

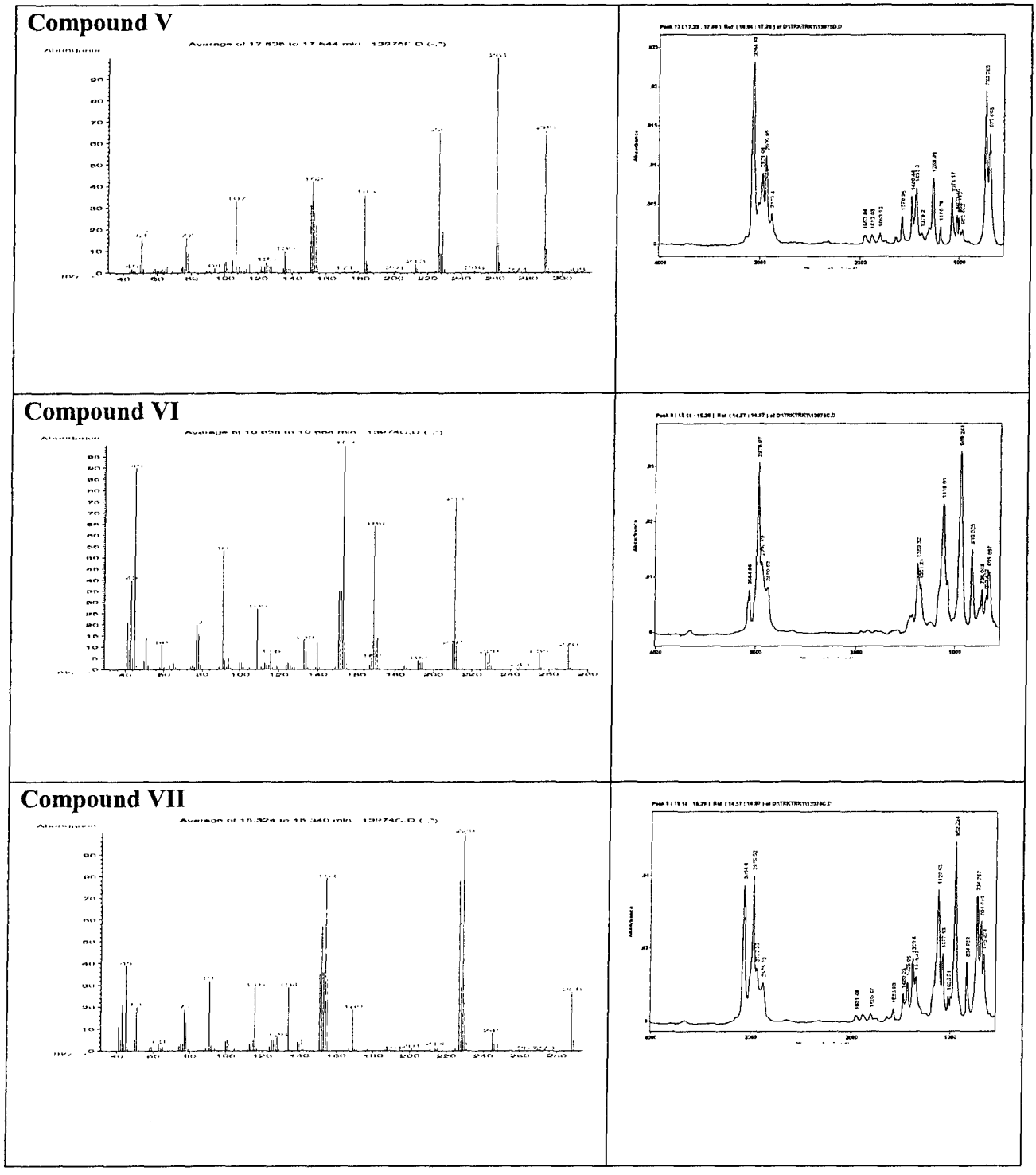


Figure 16. Mass and Infrared Spectra of Chemicals Identified During the Gas Chromatographic Analyses.

3.1.2 Qualitative NMR Experiments.

Qualitative NMR analyses were performed in accordance with established procedures.[1] All NMR experiments were performed on a Bruker Avance 300-MHz NMR with a 5 mm QNP probe. The acquisition parameters are provided in Table 10. Samples for NMR analyses were prepared by adding 100 µL of the liquid GTR fill, or approximately 100 mg of the solid fill, to 1 mL of $CDCl_3$. In all cases, the samples completely dissolved, and there was no need to filter the samples. In addition to the 1-D experiments acquiring data on ^{1}H, ^{13}C, and ^{31}P nuclei for all the samples, a single sample (CA-0276) was also analyzed using Distortionless Enhancement by Polarization Transfer (DEPT) pulse sequences. The DEPT pulse sequences make different carbons respond in different fashions, depending on how many protons are attached.[38] The DEPT 45 experiment produces a positive peak for every carbon with attached protons (CH, CH_2, CH_3). The DEPT 90 experiment produces peaks for only carbons with one proton attached (CH), with C_0, CH_2, and CH_3 carbons not being visualized during this experiment. In the DEPT 135 experiment, carbons with two protons attached (CH_2) yield negative peaks, while carbons with one or three protons attached (CH and CH_3) produce positive peaks.

In all cases, there were no peaks detected during the ^{31}P-NMR analyses. The lack of phosphorus (as agent or degradation products) eliminated the possibility of the entire nerve agent class of chemical warfare agents being contained in the rockets. While not rigorously determined, the estimated detection limit, under the conditions employed, is 20 mg/L of phosphorus. This corresponds to 100 mg/L of ethyl N,N-dimethylphosphoramidocyanidate (GA, CAS No. 77-81-6), a nerve agent typical of the WWII era.

In all cases, there were no unassigned peaks detected during the ^{1}H-NMR analyses. Except for solvent peaks, all the peaks were in the phenyl shift range, supporting the assignments made from the GC analyses (Section 3.1.1). Example ^{1}H-NMR spectra are illustrated in Figure 17. While not rigorously determined, the estimated detection limit, under the conditions employed, is ~ 300 mg/L.

In all cases, there were no unassigned peaks detected during the ^{13}C-NMR analyses. Except for solvent peaks, all the peaks were in the phenyl shift range, supporting the assignments made during the GC analyses (Section 3.1.1). Example ^{13}C-NMR spectra are illustrated in Figures 18 through 22, and are in good agreement with published reference and predicted spectra for DA and TPA,[35,39] and predicted spectra for PD.[39] The DEPT experiments confirmed all detected carbons had only one proton attached, with the DEPT 90 and DEPT 135 producing identical spectra, as illustrated in Figure 23. A sample was spiked with TPA, and reanalyzed using DEPT 90 acquisition parameters. A comparison of the unspiked and spiked samples is illustrated in Figure 24, and further supports assignment of the TPA peaks.

In all cases, NMR analyses support the GC assignments (Section 3.1.1), with no unassigned peaks detected in any of the NMR analyses. Four of the GTR fills were identified as being mixtures of DA, PD, and TPA, supporting identification of these fills as mixtures of DA and arsinol. The fifth GTR fill materiel (GTR CA-0178) was solid, and was predominantly DA.

The liquid fraction of CA-0178 was not available during these qualitative analyses, but was found to be a mixture of DA and arsinol (Section 3.2.1).

Table 10. Qualitative NMR Acquisition Parameters.

Acquisition Parameter	NMR Nuclei		
	^{1}H	^{13}C	^{31}P
Tip Angle	30°	90°	90°
90° Pulse	10 μsec	8 μsec	7.5 μsec
Sweep Width	4,496 Hz	22,675 Hz	48,661 Hz
File Size	32k	32k	32k
FID Resolution	0.068 Hz	0.7 Hz	0.25 Hz
Transients	128	512	256
Line Broadening	0.3 Hz	0.5 Hz	1.0 Hz

3.2 Quantitation of Fill Components.

The liquid GTR fills, on average, were found to contain 58.7 wt% DA, 29.4 wt% PD, and 4.00 wt% TPA by quantitative ^{13}C-NMR. The solid fraction from GTR CA-0178 was found to contain 94.1 wt% DA, with no PD or TPA detected by quantitative ^{13}C-NMR. The fills were also analyzed for total metals, and water soluble anions. All analyses support identification of these GTR fills as being mixtures of DA and arsinol.

3.2.1 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 delay of 4-5 times the longest T_1 must be used when acquiring quantitative NMR spectra.[38] Using fill materiel from GTR CA-0276, 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. The stacked T_1 plot for GTR fill CA-0276 is illustrated in Figure 25, and the graphed data is presented in Figure 26. On average, the ^{13}C T1's were determined to be: internal standard, 0.65 sec; DA, 0.73 sec; PD, 0.95 sec; and TPA, 0.76 sec. Since PD had the longest T_1 of 0.95 sec, a relaxation time of 10 sec was selected for acquisition of quantitative ^{13}C-NMR spectra.

Text continues on page 41.

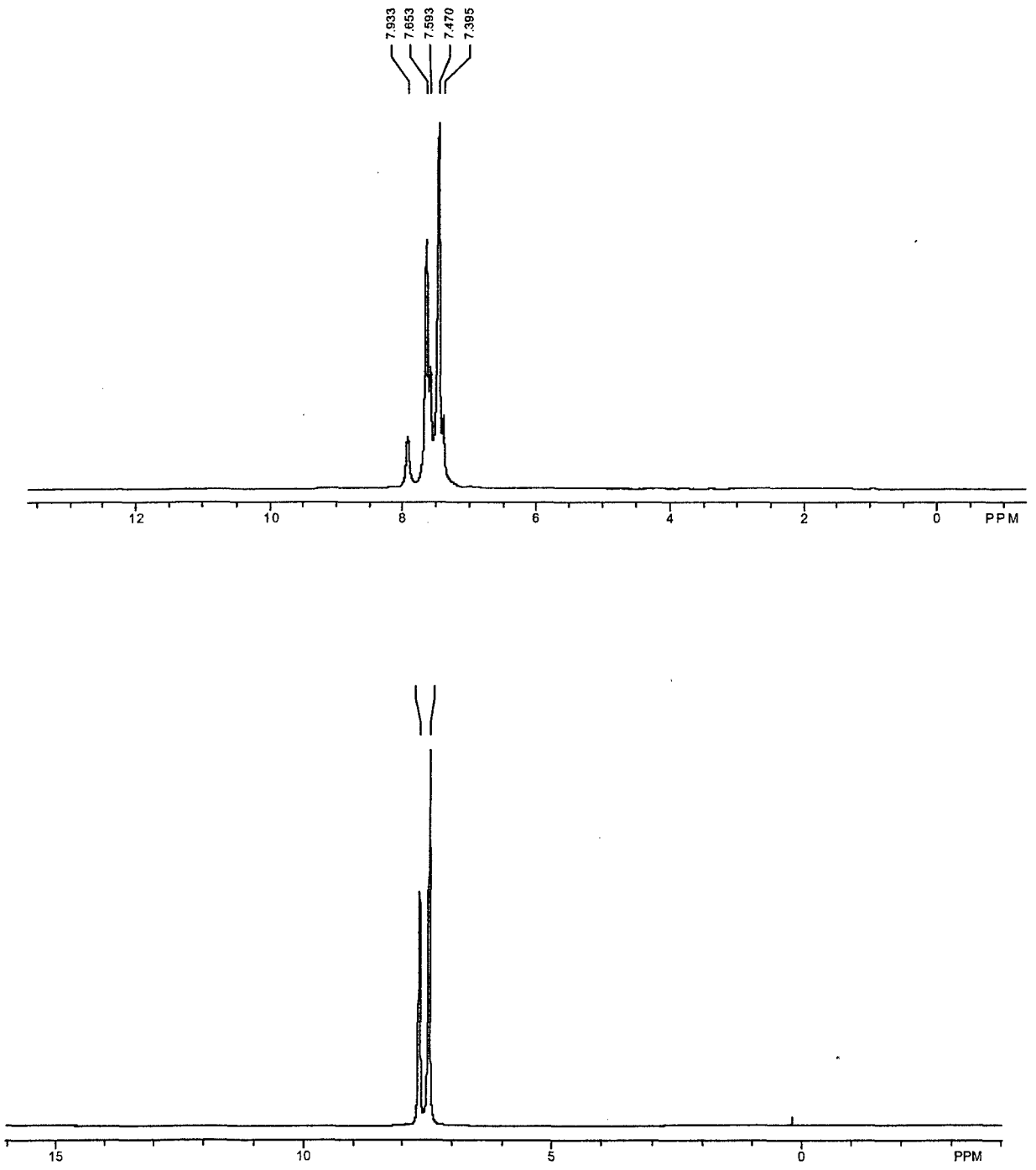


Figure 17. Example ^{1}H-NMR Spectra of GTR Fill Materiels. The upper panel is the ^{1}H-NMR spectrum of GTR CA-0276, and the bottom panel is the ^{1}H-NMR spectrum of GTR CA-0278 (solid fraction).

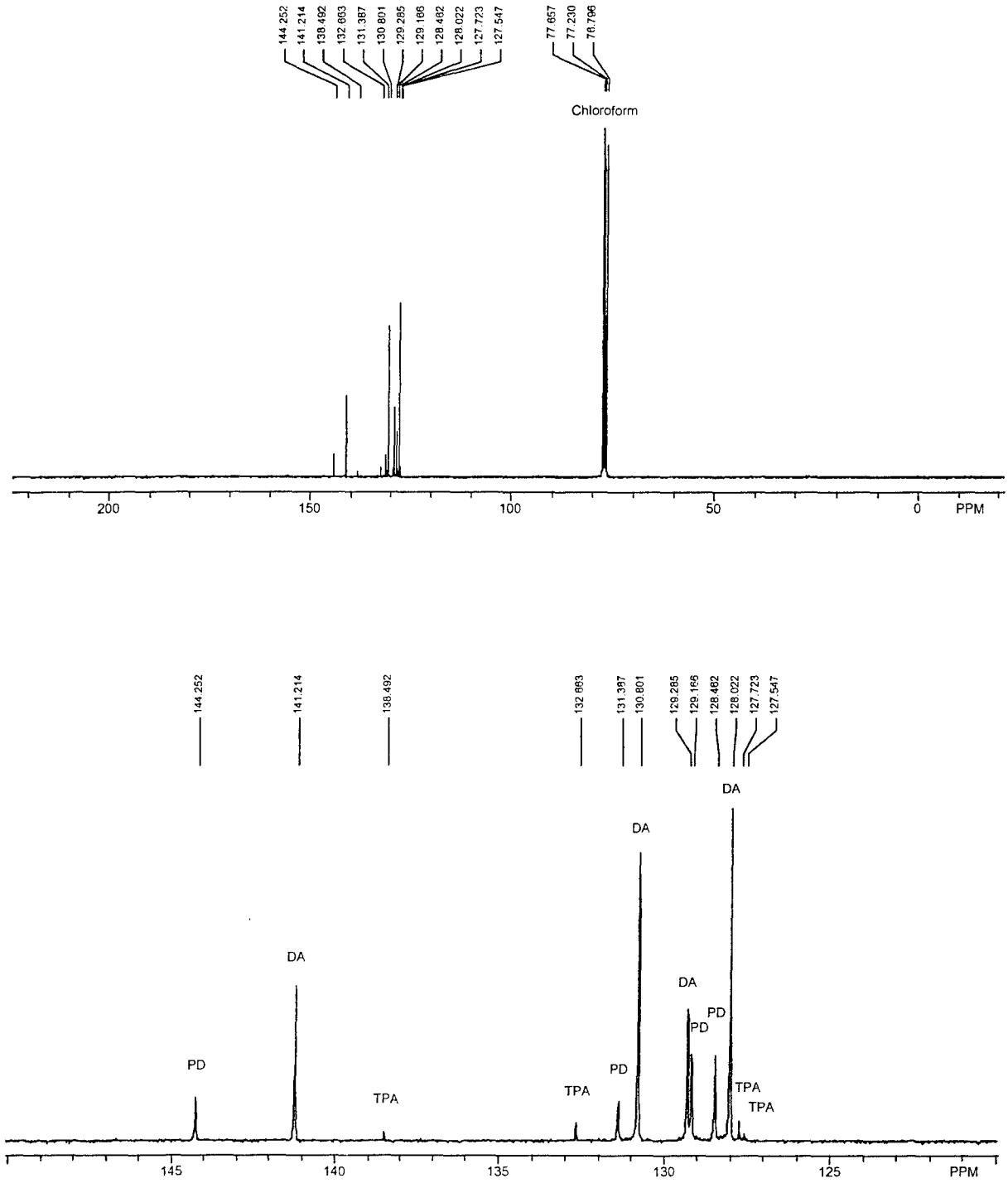


Figure 18. ^{13}C-NMR Spectra of Fill Materiel from GTR CA-0175. The upper panel is the full shift range, and the lower panel is zoomed into the phenyl-carbon shift range.

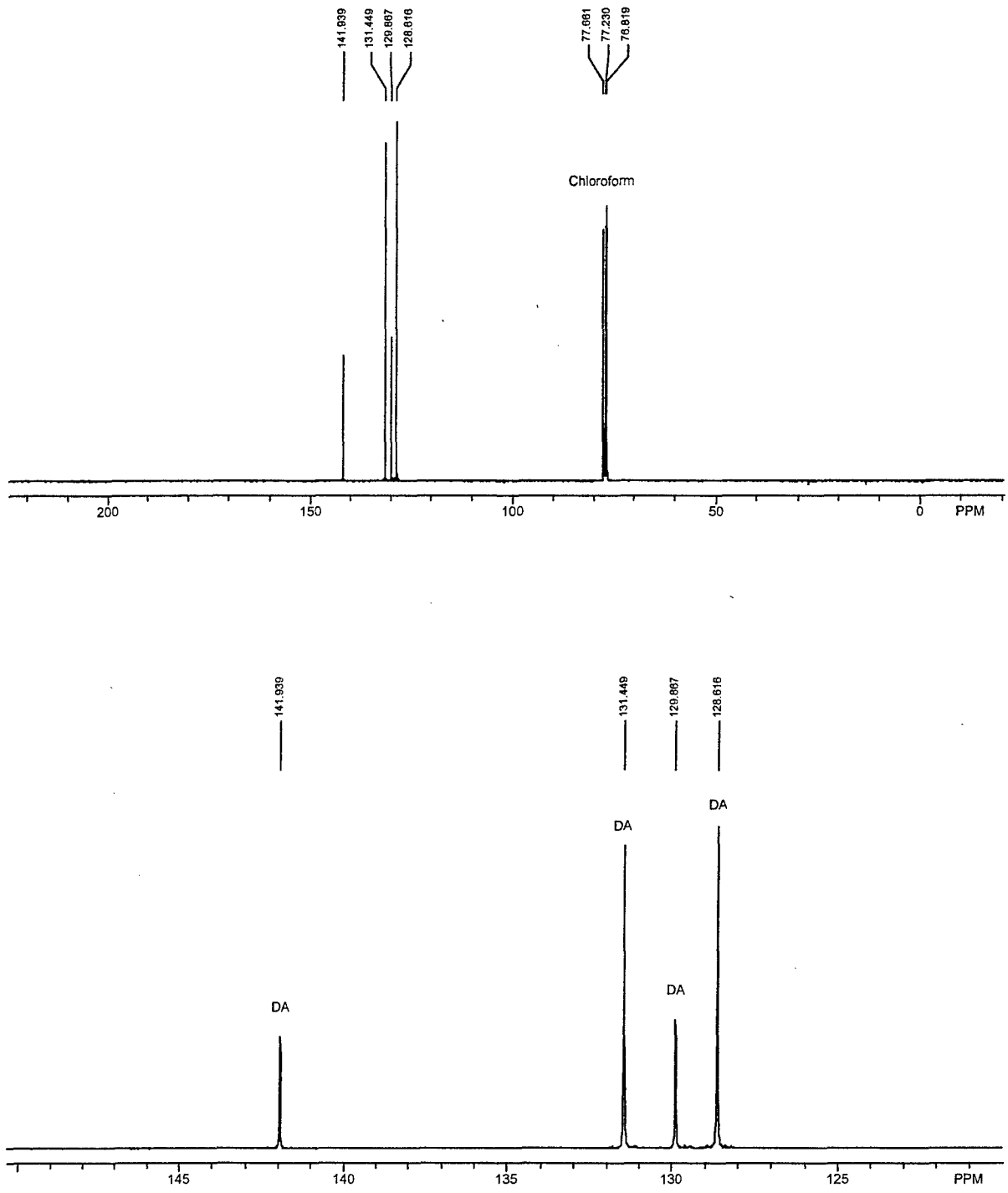


Figure 19. ^{13}C-NMR Spectra of Fill Materiel from GTR CA-0178, Solid Fraction. The upper panel is the full shift range, and the lower panel is zoomed into the phenyl-carbon shift range.

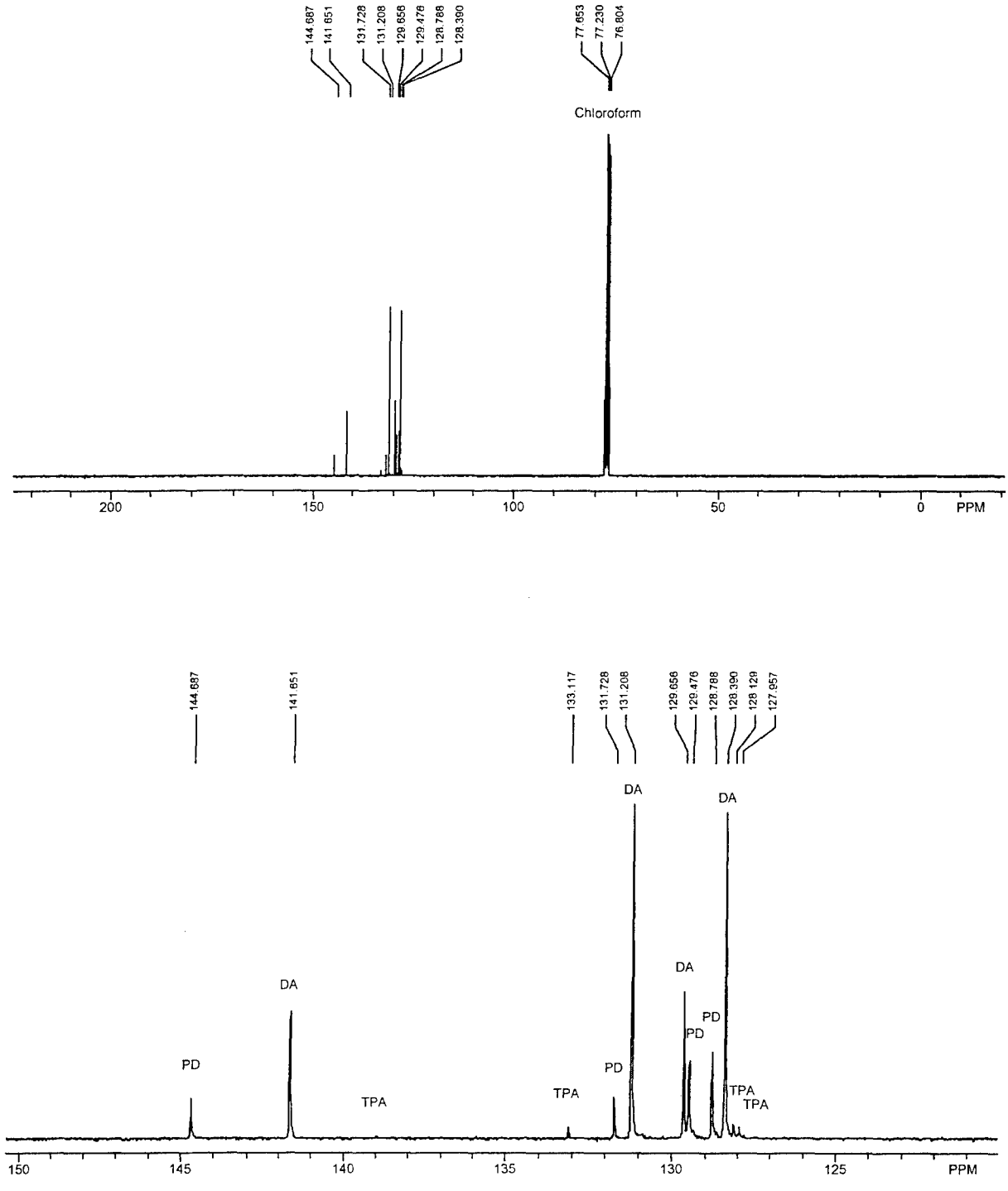


Figure 20. ^{13}C-NMR Spectra of Fill Materiel from GTR CA-0230. The upper panel is the full shift range, and the lower panel is zoomed into the phenyl-carbon shift range.

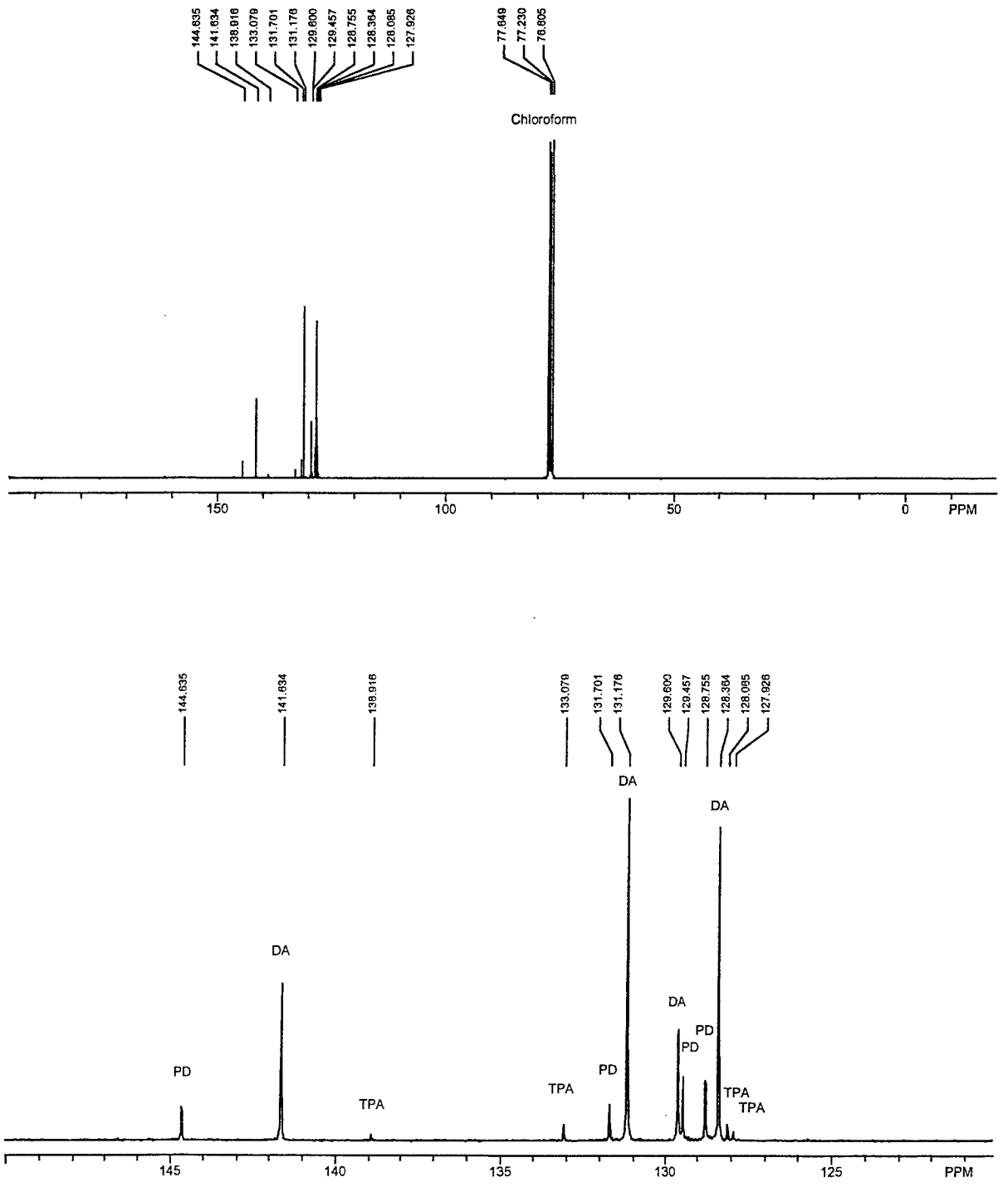


Figure 21. ^{13}C-NMR Spectra of Fill Materiel from GTR CA-0276. The upper panel is the full shift range, and the lower panel is zoomed into the phenyl-carbon shift range.

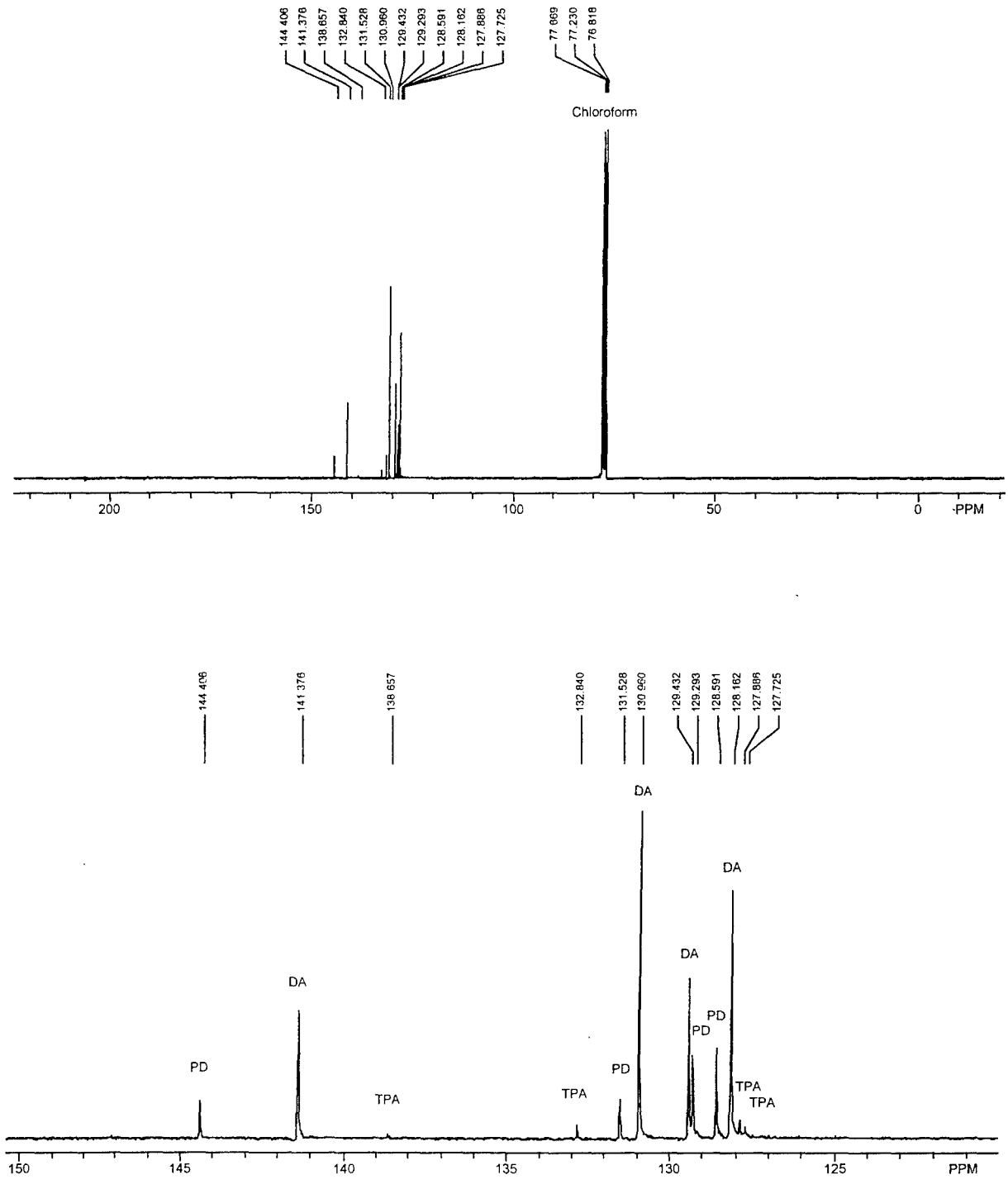


Figure 22. ^{13}C-NMR Spectra of Fill Materiel from GTR CA-0280. The upper panel is the full shift range, and the lower panel is zoomed into the phenyl-carbon shift range.

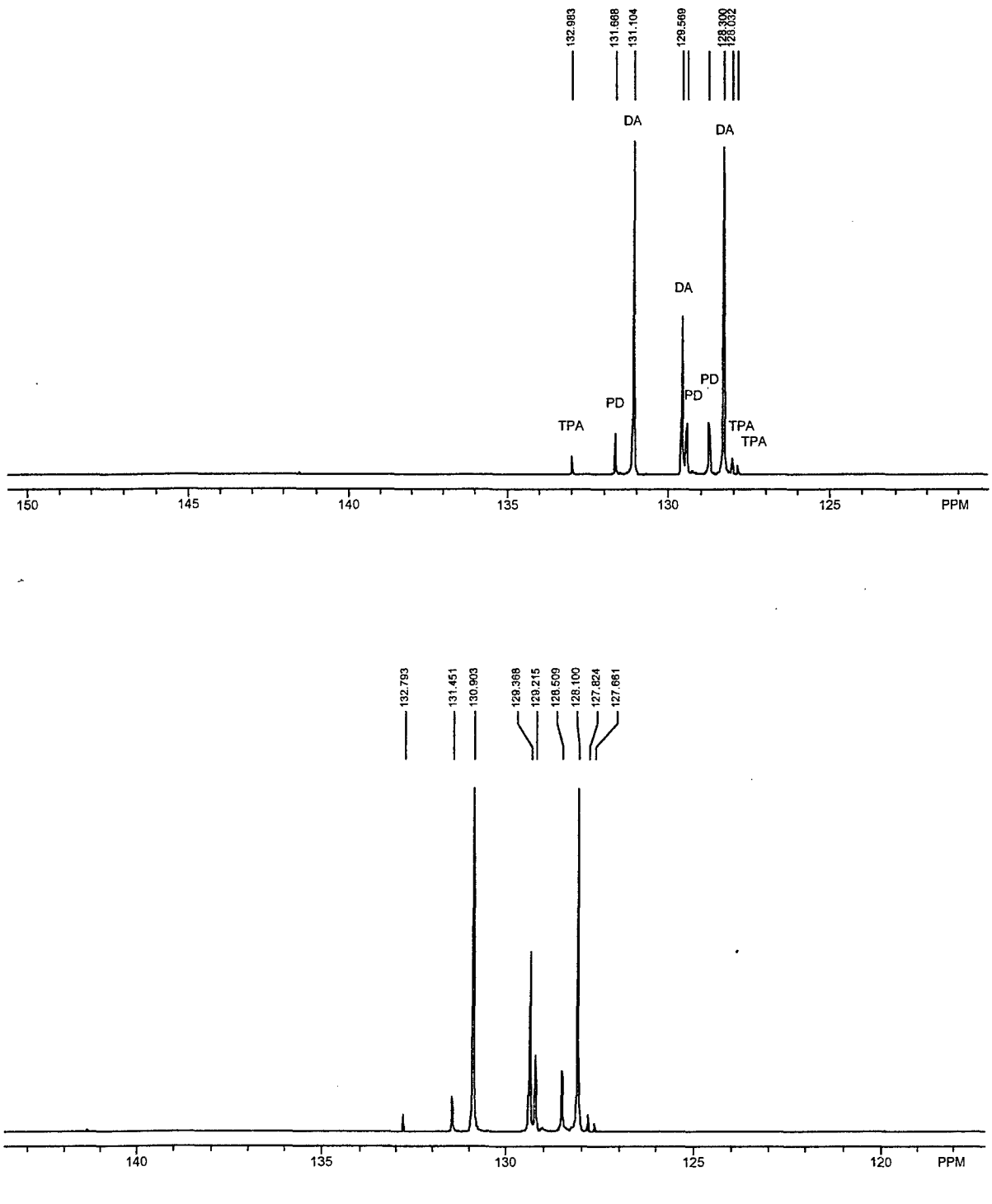


Figure 23. Qualitative NMR Spectra of Fill Materiel from GTR CA-0276. The upper panel is the DEPT 90 spectrum, and the lower panel is the DEPT 135 spectrum.

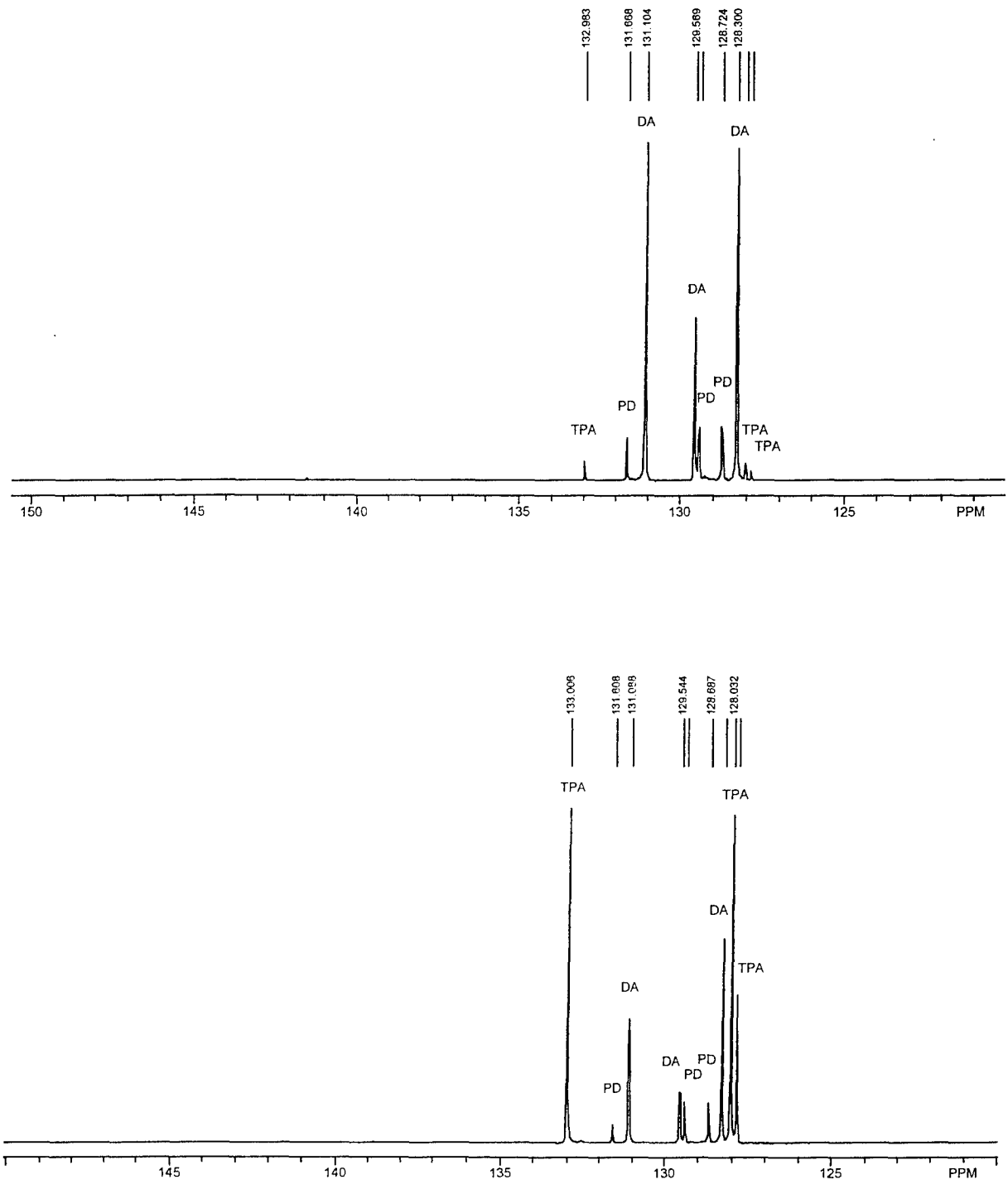


Figure 24. Qualitative NMR Spectra of Fill Materiel from GTR CA-0276. The upper panel is the DEPT 90 spectrum, and the lower panel is the DEPT 90 spectrum after spiking the sample with TPA.

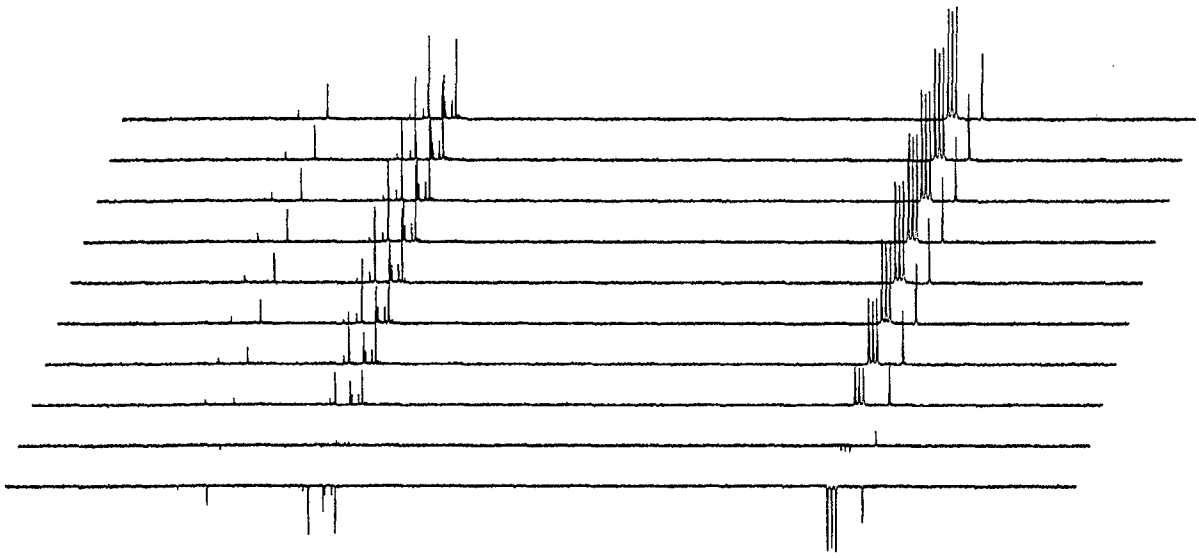


Figure 25. Stacked T_1 Plot for Fill Materiel from GTR CA-0276.

Samples of the neat GTR fill materiels were individually analyzed by an established quantitative ^{13}C-NMR technique to confirm identity, and determine weight percent purity of the individual agents.[11,40] Each sample was prepared in triplicate, and NMR data was acquired in triplicate to confirm stability. In addition, the two largest peaks for each chemical were integrated, to provide additional assurance there were no overlapping peaks. Approximately 150 mg (exact weight recorded) of neat GTR fill materiel was weighed into a 4 mL glass vial, and then approximately 160 mg (exact weight recorded) of 1,1,2,2 tetrachloroethane (internal standard, CAS No. 79-34-5) was weighed into the vial. One-milliliter 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.[11,40] The data are summarized in Tables 11 through 13.

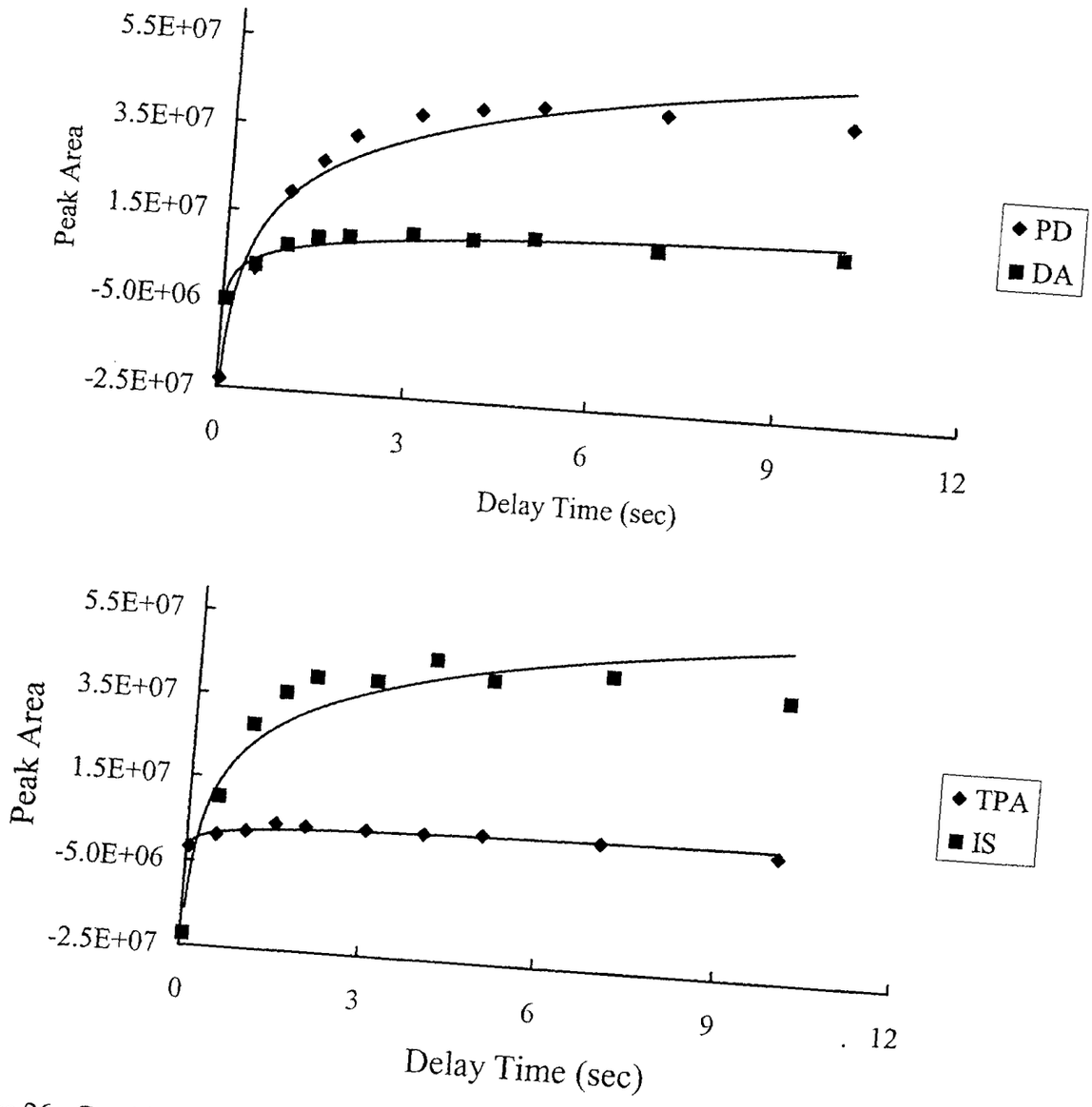


Figure 26. Graphical Data from the Determination of T_1's for Fill Materiel from GTR CA-0276. The upper panel is the DA and PD data, and the lower panel is the TPA and internal standard (IS) data.

Table 11. Summary of DA Weight Percent Values in GTR Fill Materiels.

GTR Identification	DA Concentration in Original Fill Materiel (wt%)			
	Replicate 1 (n=6)	Replicate 2 (n=6)	Replicate 3 (n=6)	Overall (n=18)
CA-0175				
Mean	60.3	53.1	53.9	55.8
SD	0.06	0.01	0.001	4.52
%RSD	0.098	0.011	0.003	8.11
CA-0178[a]				
Mean	68.7	NA	NA	NA
SD	0.02	NA	NA	NA
%RSD	0.029	NA	NA	NA
CA-0178[b]				
Mean	93.9	94.3	94.3	94.1
SD	0.001	0.027	0.021	1.41
%RSD	0.001	0.028	0.022	1.49
CA-0230				
Mean	58.2	56.9	58.7	57.9
SD	0.010	0.003	0.002	0.97
%RSD	0.017	0.006	0.004	1.68
CA-0276				
Mean	62.7	58.4	60.2	60.5
SD	0.02	0.01	0.01	2.14
%RSD	0.026	0.014	0.016	3.53
CA-0280				
Mean	56.9	56.6	58.0	57.2
SD	0.003	0.006	0.007	0.77
%RSD	0.005	0.010	0.011	1.35

a. Liquid fraction; only prepared and analyzed a single replicate.
b. Solid fraction.

Table 12. Summary of PD Weight Percent Values in GTR Fill Materiels.

GTR Identification	PD Concentration in Original Fill Materiel (wt%)			
	Replicate 1 (n=6)	Replicate 2 (n=6)	Replicate 3 (n=6)	Overall (n=18)
CA-0175				
Mean	31.7	31.7	30.0	31.1
SD	0.003	0.008	0.004	0.98
%RSD	0.011	0.024	0.013	3.15
CA-0178[a]				
Mean	21.4	NA	NA	NA
SD	0.03	NA	NA	NA
%RSD	0.140	NA	NA	NA
CA-0178[b]				
Mean	ND[c]	ND[c]	ND[c]	NA
SD	NA	NA	NA	NA
%RSD	NA	NA	NA	NA
CA-0230				
Mean	32.5	30.4	30.4	31.1
SD		0.003	0.001	1.04
%RSD	0.001	0.008	0.004	3.34
CA-0276				
Mean	27.3	30.3	27.2	28.3
SD	0.004	0.003	0.004	1.58
%RSD	0.015	0.008	0.014	5.61
CA-0280				
Mean	29.7	29.6	30.1	29.8
SD	0.002	0.004	0.002	0.32
%RSD	0.006	0.013	0.007	1.07

a. Liquid fraction; only prepared and analyzed a single replicate.
b. Solid fraction.
c. Not detected.

Table 13. Summary of TPA Weight Percent Values in GTR Fill Materiels.

GTR Identification	TPA Concentration in Original Fill Materiel (wt%)			
	Replicate 1 (n=6)	Replicate 2 (n=6)	Replicate 3 (n=6)	Overall (n=18)
CA-0175				
Mean	3.62	3.84	3.34	3.60
SD	0.006	0.001	0.002	0.36
%RSD	0.158	0.029	0.060	10.1
CA-0178[a]				
Mean	2.30	NA	NA	NA
SD	0.010	NA	NA	NA
%RSD	0.435	NA	NA	NA
CA-0178[b]				
Mean	ND[c]	ND[c]	ND[c]	NA
SD	NA	NA	NA	NA
%RSD	NA	NA	NA	NA
CA-0230				
Mean	4.48	4.65	4.48	4.54
SD	0.006	0.004	0.002	0.37
%RSD	0.132	0.080	0.034	8.12
CA-0276				
Mean	3.96	4.63	3.79	4.13
SD	0.003	0.004	0.002	0.460
%RSD	0.073	0.080	0.040	11.1
CA-0280				
Mean	4.00	4.50	4.43	4.31
SD	0.009	0.005	0.002	0.59
%RSD	0.237	0.106	0.037	13.6

a. Liquid fraction; only prepared and analyzed a single replicate.
b. Solid fraction.
c. Not detected.

3.2.2 Water Soluble Products.

The GTR fill materiels were analyzed for water-soluble products using the anion capillary electrophoresis method described in Section 2.6. 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. There was not enough sample of the solid fraction from GTR CA-0178, and this sample was not analyzed using this approach. 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 Table 14. **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 soluble arsenite (AsO_2^-) ranged from trace to 4,520 mg/kg in the GTR 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 trace (reporting limit of 1,080 mg/kg) to 7,660 mg/kg in the GTR fill materiels. It is not known whether the arsenite determined to be in the GTR fill materiels is solely from the hydrolysis of arsenic trichloride, solely present as an impurity of synthesis, or some combination of the two processes.

The soluble chloride ranged from 124,000 to 151,000 mg/kg in the GTR fill materiels. Assuming chloride is a conservative tracer, the expected neutralent concentrations would range from 3,670 to 4,470 mg/L for a 1:50 reactor loading, and 7,340 to 8,940 mg/L for a 1:25 reactor loading. Using a density of 1.16, this corresponds to 3,160 to 3,850 and 6,330 to 7,710 mg/kg.

The soluble glycolate ($C_2H_3O_3^-$) ranged from 755 to 2,130 mg/kg in the GTR fill materiels. Assuming this glycolate (an oxidative reaction product of DA, PD, and TPA) did not react during the neutralization GTR fills, the expected neutralent concentrations would range from 20 to 60 mg/L for a 1:50 reactor loading, and 40 to 120 mg/L for a 1:25 reactor loading. Using a density of 1.16, this corresponds to 17 to 52 and 34 to 103 mg/kg.

3.2.3 Total Metals.

The total metal analyses were performed on duplicate digests of the neat GTR fill materiel The digests for total mercury were prepared according to the procedure specified in SW-846, Method 7470A,[41] while the digests for the other metals were prepared according to the procedure specified in SW-846, Method 3010A.[42] The digests prepared specifically for mercury analyses were analyzed using EPA Method 245.1,[43] which is a cold vapor atomic adsorption based method. The other digests were analyzed by two different methods, EPA Method 200.7,[44] or EPA Method 200.8.[45] 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 15. 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 GTR fill materiels during the total metal testing.

Table 14. Water Extractable Products in GTR Fill Materiels. All data reported in the original fill materiel, with units of mg/kg. These results are on the sample extracted with deionized water, 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 of 501.9 mg.

Target Analyte	Concentration in Original Fill Materiel (mg/kg)				
	CA-0175	CA-0178[a]	CA-0230	CA-0276	CA-0280
Arsenite (AsO_2^-)	Trace[b]	4,520	1,390	2,010	Trace[b]
Arsenate ($HAsO_4^{-2}$)	ND[c] (638)	ND[c] (638)	ND[c] (638)	ND[c] (638)	ND[c] (638)
Chloride (Cl^-)	141,000	124,000	138,000	140,000	151,000
Fluoride (F^-)	ND[c] (279)	ND[c] (279)	ND[c] (279)	ND[c] (279)	ND[c] (279)
Nitrate (NO_3^-)	ND (1,950)	ND (1,950)	ND (1,950)	ND (1,950)	ND (1,950)
Sulfate (SO_4^{-2})	ND (1,790)	ND (1,790)	ND (1,790)	ND (1,790)	ND (1,790)
Acetate ($C_2H_3O_2^-$)	Trace[b]	Trace[b]	668	Trace[b]	Trace[b]
Formate (CHO_2^-)	ND[c] (598)	ND[c] (598)	ND[c] (598)	ND[c] (598)	ND[c] (598)
Fumarate ($C_4H_2O_4^{-2}$)	ND[c] (797)	ND[c] (797)	ND[c] (797)	ND[c] (797)	ND[c] (797)
Glycolate ($C_2H_3O_3^-$)	1,870	2,130	1,010	755	859
Oxalate ($C_2O_4^{-2}$)	ND (1,510)	ND (1,510)	ND (1,510)	ND (1,510)	ND (1,510)
Succinate ($C_4H_4O_4^{-2}$)	ND[c] (797)	ND[c] (797)	ND[c] (797)	ND[c] (797)	ND[c] (797)

a. Liquid fraction.

b. Peak detected, but less than reporting limit.

c. No peak was detected.

The relatively high levels of sulfur in the GTR 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 SO_4^{-2} concentration in the liquid GTR fills would range from 7,100 to 18,700 mg/kg. The CE analyses of the liquid GTR fills did not detect any SO_4^{-2} (Table 14), with an estimated detection limit of 1,790 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. While the sulfur could be in the form of an organic chemical, there were no unassigned peaks in the NMR analyses (Section 3.1.2), suggesting the sulfur is in an inorganic form, or distributed between many organic forms, as to be below the NMR detection limits.

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 16. There is good agreement between the total arsenic determined by ICP, and the arsenic determined as individual chemicals, with an average percent difference of 3.94%. This agreement suggests there were no significant levels of arsenic species not accounted for in the characterization of these GTR fill materiels.

3.2.4 Bulk Density of Fill Materiels.

The densities of liquid fills from individual rockets were determined using a density-bottle approach,[46] using 1 mL Class A volumetric flasks as the density bottle. The density determinations were made at a temperature of 25 °C. The bulk GTR fill materiels were equilibrated at temperature in a water bath for 3 hr, then were purged with N_2 gas for 5 min prior to aliquoting into temperature equilibrated density bottles. The density bottles were then allowed to equilibrate for an additional 30 min, and the fill level was brought to the mark. The density bottles were then removed from the water bath, dried, and weighed. The data are summarized in Table 17. The grand average density of the arsinol-based liquid GTR fill materiels was determined to be 1.4797 g/mL at 25 °C.

3.3 Selection of Neutralization Reagent.

Initial work examined the micro-scale performance of the oxidative reagent HPO_2™ against commonly used chemical agent decon solutions containing NaOH, monoethanolamine (MEA) and/or bleach. Subsequent micro-scale work evaluated HPO_2™ and other oxidizers with and without added organic co-solvent. This was followed by small-scale screening evaluations of HPO_2™ reagent and HNO_3. It was at this point a basic change in the GTR disposal technology redirected evaluations towards the selected neutralization reagent—sodium permanganate.

3.3.1 Micro-Scale Screening of Reagent Candidates.

In a previous study examining the bulk neutralization of HL, an oxidative-based reagent was found to be extremely effective in the bulk neutralization of HL.[12,47,48] This reagent, designated as HPO_2™, is a proprietary mixture, and is aqueous-based. Since a large body of data had been accumulated on this reagent, it was decided to evaluate the efficacy of HPO_2™ against the arsinol-based GTR fill materiels.

Using the micro-scale screening approach outlined in Section 2.1, a preliminary experiment investigating the efficacy of HPO_2™ reagent, 20 wt% NaOH, 80%MEA/20%NaOH, and commercial bleach was conducted using fill materiel from GTR CA-0276. The last three reagents were evaluated as they are commonly used in demil operations,[49] so as to establish a baseline for comparison to HPO_2™ reagent. In this experiment, the loading ratio of fill materiel

to reagent was 1:50, the reactions were stirred and allowed to proceed for 5 hr at 75 °C, and each reaction was conducted in triplicate. The residual agent results are summarized in Table 18, and indicate HPO_2™ reagent was the most efficacious of the reagents evaluated. In addition to the residual agent data, reaction behavior was also noted. The addition of the fill materiel to the bleach was very exothermic, and would potentially be hard to control on a large-scale. The addition of fill materiel to the 20% NaOH resulted in a large amount of white precipitate being formed, and NMR and MS/MS analyses confirmed it was the dimer of DA.[18,50] An example of the ^{13}C-NMR spectrum is illustrated in Figure 27. While the addition of the fill materiel to the MEA/NaOH reagent did not cause an exotherm, or generate a precipitate, by the end of the reaction period the neutralent was a gelatinous mass. This solidification of the neutralent would present a challenge in large-scale operations. In contrast, the reaction of the fill materiel with HPO_2™ reagent was well behaved, with no noticeable exotherm. The final neutralent was homogeneous, with only a small amount of fine white solids.

The next series of micro-scale experiments focused on three different oxidizers, with and without the addition of a co-solvent (10%, v:v) to help solubilize the hydrophobic arsinol fill materiel. The oxidizers were HPO_2™ reagent, 25 % sodium persulfate, and an aqueous solution saturated with sodium percarbonate. The co-solvent was 1-methyl-2-pyrrolidinone (NMP, CAS No. 872-50-4), which has been demonstrated to be useful in helping with the neutralization of thickened CWAs.[51] The reactions were conducted using fill materiel from GTR CA-0276, at 75 and 90 °C, with stirring, and the reactions allowed to proceed for 5 hr. The volume to volume loading of arsinol to reagent was 1:40. The residual agent results are summarized in Tables 19 and 20, and suggest $Na_2S_2O_8$ as being the best reagent based on apparent efficacy. However, observations made during the reactions suggested otherwise. In all the runs conducted using 25% $Na_2S_2O_8$, a black, tarry residue coated the inside of the reactor. It is believed the relatively low residual agent levels detected in solution resulted from the agents being trapped inside this residue. The persulfate reactions conducted using NMP supported this conclusion. The reaction with NMP resulted in the solubilization of most of the tarry substance and significantly higher agent concentrations in the final solution. The HPO_2™ reagent, of the oxidizers evaluated, was therefore the most efficacious under the experimental conditions utilized.

Table 15. Total Metals in GTR Fill Materiels. The data is reported in units of mg/kg, and is in the original fill materiel. The reported results are the averages of duplicate digestions, and have been corrected for the digestion blank.

Total Metal	Concentration in GTR Fill (mg/kg) GTR Fill Identification					
	CA-0175	CA-0178[a]	CA-0178[b]	CA-0230	CA-0276	CA-0280
Aluminum	ND	14.5	78.6	ND	ND	ND
Antimony	268	324	58.6	238	221	242
Arsenic	307,000	276,000	257,000	286,000	278,000	289,000
Barium	ND	ND	3.21	ND	ND	ND
Beryllium	ND	ND	ND	ND	ND	ND
Cadmium	ND	ND	ND	ND	ND	ND
Calcium	ND	ND	ND	ND	ND	ND
Chromium	4.58	40.1	167	3.38	4.66	4.43
Cobalt	1.33	11.5	18.9	1.05	0.886	0.978
Copper	168	414	143	132	129	154
Iron	7,690	16,000	74,200	4,270	4,970	6,580
Lead	4.28	15.8	5.70	9.01	6.70	12.8
Magnesium	ND	ND	ND	ND	ND	ND
Manganese	7.24	49.9	344	4.45	12.1	18.0
Mercury[c]	1.55	3.07	0.267	1.28	1.23	1.38
Mercury[d]	1.00	1.91	0.448	0.982	0.947	0.931
Nickel	1.89	9.21	129	ND	3.02	3.54
Potassium	ND	ND	ND	ND	ND	ND
Selenium	8.35	13.5	ND	7.79	8.82	8.56
Silver	5.05	6.80	ND	4.20	4.00	4.58
Sodium	ND	ND	ND	ND	ND	ND
Sulfur	2,970	6,250	601	2,670	2,370	2,650
Thallium	ND	ND	ND	ND	ND	ND
Tin	ND	ND	ND	ND	ND	ND
Vanadium	ND	ND	ND	ND	ND	ND
Zinc	63.4	ND	14.9	ND	41.0	44.3

a. Liquid fraction of GTR CA-0178.
b. Solid fraction of GTR CA-0178.
c. Analyzed using ICP-MS method.
d. Analyzed using CVAA method after separate digestion.

Table 16. Comparison of Total Arsenic as Determined by ICP to Total Arsenic as Determined by Dimensional Analysis.

GTR Identification	Total As By ICP (mg/kg)	Total As by Dimensional Analysis (mg/kg)[a]	Percent Difference (%)[b]
CA-0175	307,000	271,000	12.4
CA-0178[c]	276,000	275,000	0.363
CA-0178[d]	257,000	266,000	3.44
CA-0230	286,000	281,000	1.76
CA-0276	278,000	278,000	0.00
CA-0280	289,000	273,000	5.69

a. Sum of DA, PD, TPA, and arsenite as arsenic.
b. (x-y/(x+y/2))*100
c. Liquid fraction.
d. Solid fraction

Table 17. Bulk Density of Liquid GTR Fill Materiels at 25 °C.

Replicate Number	Mass (grams) GTR Fill Identification				
	CA-0175	CA-0178*	CA-0230	CA-0276	CA-0280
One	1.4805	1.4826	1.4798	1.4764	1.4847
Two	1.4745	1.4783	1.4738	1.4829	1.4810
Three	1.4792	1.4807	1.4825	1.4784	1.4797
Average	1.4781	1.4805	1.4787	1.4792	1.4818
SD	0.00316	0.00215	0.00445	0.00333	0.00259
%RSD	0.214	0.146	0.301	0.225	0.175

*Liquid fraction.

Table 18. Summary of the Efficacy of Four Reagent Systems Against an Arsinol-Based GTR Fill Materiel. Reaction conducted at 75 °C for 5 hr. The reported data are the averages of triplicate reactions. The initial agent concentrations were 17,900 mg/L DA; 8,380 mg/L PD; and 1,210 mg/L TPA.

Reaction Chemistry	Concentration in Neutralent (mg/L)		
	DA	PD	TPA
HPO_2™	36.5	28.1	12.8
20% NaOH	9,340	1,580	986
80% MEA/20% NaOH[a]	1,870	985	606
Commercial Bleach[b]	4,680	2,960	947

a. 80% by volume MEA and 20% by volume of 20 wt% NaOH
b. Commercial bleach solution; nominally 5% Na°Cl

Table 19. Summary of the Efficacy of Six Reagent Systems Against an Arsinol-Based GTR Fill Materiel. Reaction conducted at 75 °C for 5 hr. The reported data are the averages of duplicate reactions. The initial agent concentrations were 22,400 mg/L DA; 10,500 mg/L PD; and 1,520 mg/L TPA.

Reaction Chemistry	Concentration in Neutralent (mg/L)		
	DA	PD	TPA
Sodium Persulfate	8.18	7.26	2.24
Sodium Persulfate with NMP	8,210	3,400	714
HPO_2™	202	17.9	58.3
HPO_2™ with NMP	181	17.0	40.1
Sodium Percarbonate	4,590	1,060	1,060
Sodium Percarbonate with NMP	894	31.8	599

Table 20. Summary of the Efficacy of Six Reagent Systems Against an Arsinol-Based GTR Fill Materiel. Reaction conducted at 90 °C for 5 hr. The reported data are the averages of duplicate reactions. The initial agent concentrations were 22,400 mg/L DA; 10,500 mg/L PD; and 1,520 mg/L TPA.

Reaction Chemistry	Concentration in Neutralent (mg/L)		
	DA	PD	TPA
Sodium Persulfate	26.3	6.54	1.80
Sodium Persulfate with NMP	7,880	2,910	654
HPO_2™	167	12.3	34.9
HPO_2™ with NMP	238	18.5	50.3
Sodium Percarbonate	4,890	1,280	1,130
Sodium Percarbonate with NMP	901	9.67	594

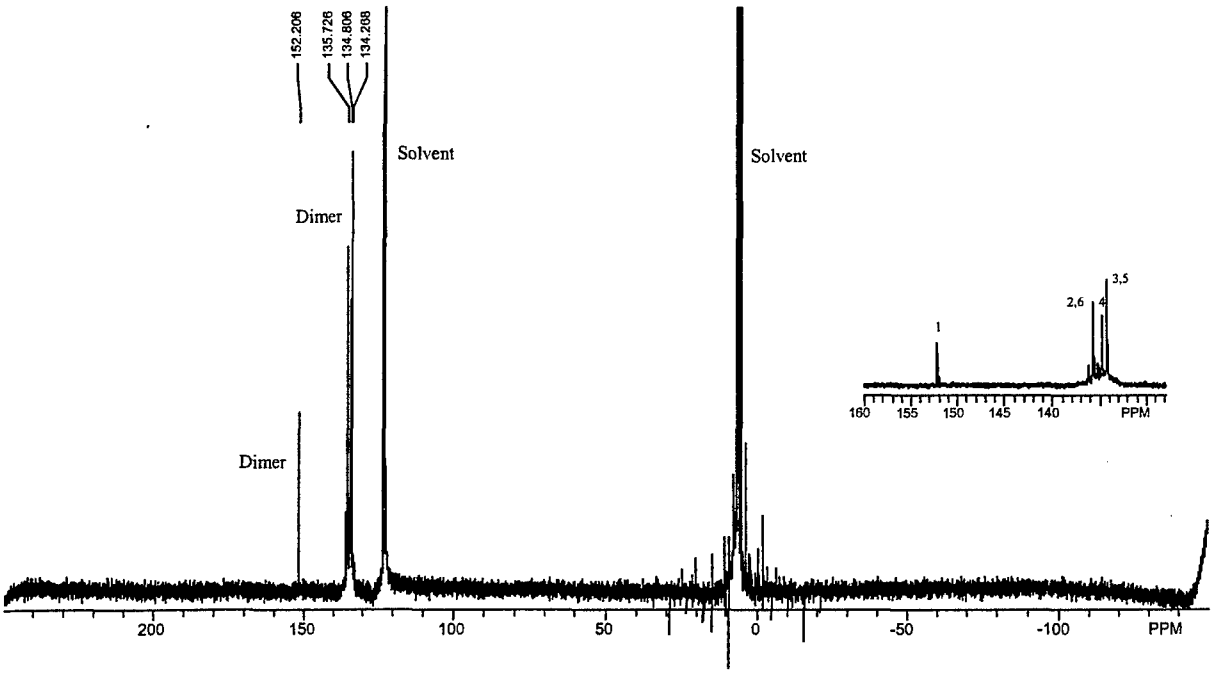


Figure 27. ^{13}C-NMR Spectrum of the Solid Isolated from the Reaction of Arsinol Fill Materiel with 20% Caustic Solution. The inset is zoomed into the region of interest.

3.3.2 Small-Scale Screening of Reagent Candidates.

The micro-scale reagent screening (Section 3.3.1) confirmed the efficacy of HPO_2™ reagent, and indicated further study was warranted. In addition, 35% HNO_3 was also selected for evaluation, as another group had reported success using this reagent.[52] These reactions were conducted in the 250 mL glass reactor system described in Section 2.2, and were all conducted at a loading (v:v) of 1:50 feedstock to reagent. The impinger solutions described in Section 2.2 were not analyzed during this effort. In all cases, the feedstock was an arsenical CWA, which had been drained from a WWII era German Traktor Rocket. This rocket was identified as "CA-0230", and the fill materiel had been previously analyzed (Sections 3.1 and 3.2). The fill material was analyzed using quantitative ^{13}C-NMR,[11,53] and was determined to contain 57.9 wt% DA, 31.1 wt% PD, and 4.5 wt% TPA as the bulk chemical constituents. In addition, the fill materiel was digested, and determined to contain 28.6 wt% total arsenic.

The residual agent and reaction product data are summarized in Tables 21 and 22, and the time course of residual agent data is illustrated in Figure 28. The results indicate the modified HPO_2™ reagent (modified by adding $NaHCO_3$) was very effective in destroying the agents, while the 35% HNO_3 was less effective in destroying the agents. Another significant difference between the reagents is the degree to which the organo-arsenicals are mineralized to inorganic arsenate. This is illustrated in Figure 29. The 35% HNO_3 was not very effective at cleaving the carbon-arsenic bond, as evidenced by the accumulation of pentavalent organo-arsenical species. In addition to the differences noted in the analysis of the neutralent, the reaction performed using 35% HNO_3 generated a thick film on the inside of the reactor.

Some of this residue was wiped off the reactor surface, and analyzed by quantitative ^{13}C-NMR.[11,53] While a total weight of residue on the reactor surface was not obtained, the relative composition of DA, PD, and TPA in the film was approximately that of the starting fill materiel. The residual agent values reported for the 35% HNO_3 reagent might be underestimated due to formation of this film.

Table 21. Summary of Analytical Results for the Modified HPO_2™ Reagent. 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 milligrams/liter. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hours)			
	1	2	3	6
Diphenylchloroarsine (DA)	3.61	1.45	0.984	0.691
Phenyldichloroarsine (PD)	2.93	1.04	1.23	0.745
Triphenylarsine (TPA)	5.68	2.15	1.86	0.106
Arsenite (AsO_2^-)	1,320	1,040	838	504
Arsenate ($HAsO_4^{-2}$)	8,340	10,900	11,400	12,300
Chloride (Cl^-)	3,980	4,200	4,600	5,000
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	160	Trace[b] (50.0)	ND[a] (50.0)	ND[a] (50.0)
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	95.4	ND[a] (50.0)	ND[a] (50.0)	ND[a] (50.0)
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	984	1,150	1,540
Formate (CHO_2^-)	Trace[b] (150)	3,180	2,850	1,730
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	5,870	998	365	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	3,940	1,480	1,240	1,130
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 22. Summary of Analytical Results for the Nitric Acid Reagent. 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 milligrams/liter. The values in parentheses are reporting limits.

Target Analyte	Reaction Time (hours)			
	1	2	3	6
Diphenylchloroarsine (DA)	412	342	326	481
Phenyldichloroarsine (PD)	91.7	155	117	164
Triphenylarsine (TPA)	54.5	57.4	47.6	50.1
Arsenite (AsO_2^-)	ND* (330)	ND* (330)	ND* (330)	ND* (330)
Arsenate ($HAsO_4^{-2}$)	96.8	88.3	144	121
Chloride (Cl^-)	5,900	5,270	5,400	5,940
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	12,100	11,900	9,990	12,100
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	20,900	20,400	17,800	21,400
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 ($C_2H_3O_3^-$)	6,400	6,400	5,980	6,230
Oxalate ($C_2O_4^{-2}$)	2,960	2,910	3,420	3,950
Succinate ($C_4H_4O_4^{-2}$)	ND* (200)	ND* (200)	ND* (200)	ND* (200)

*No peak was detected.

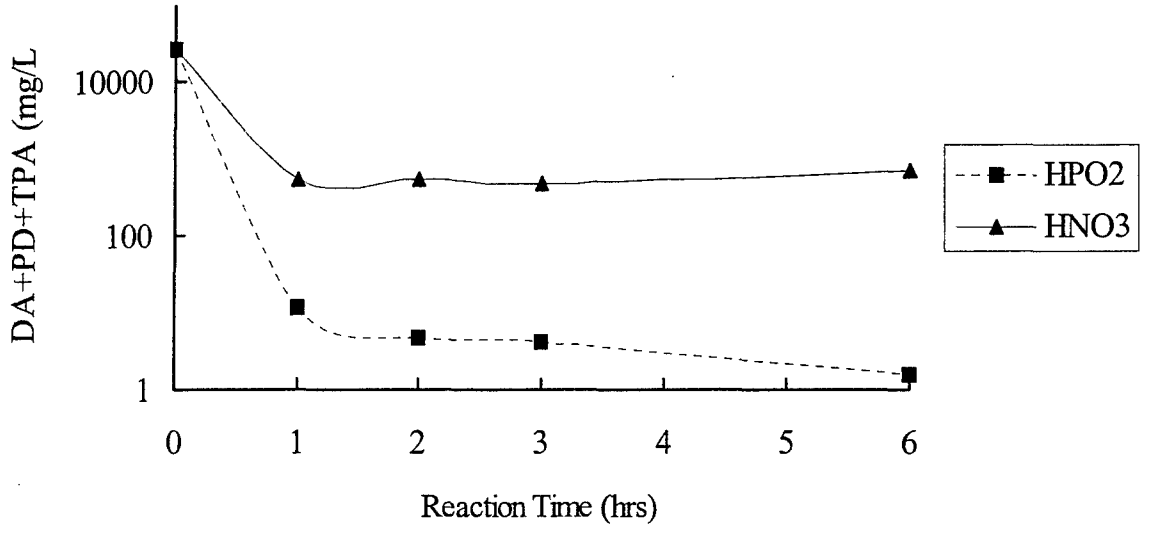


Figure 28. Residual Agents over Time for Each of the Reagents. The Y-axis is the sum of residual DA, PD, and TPA. Note the Y-scale is logarithmic.

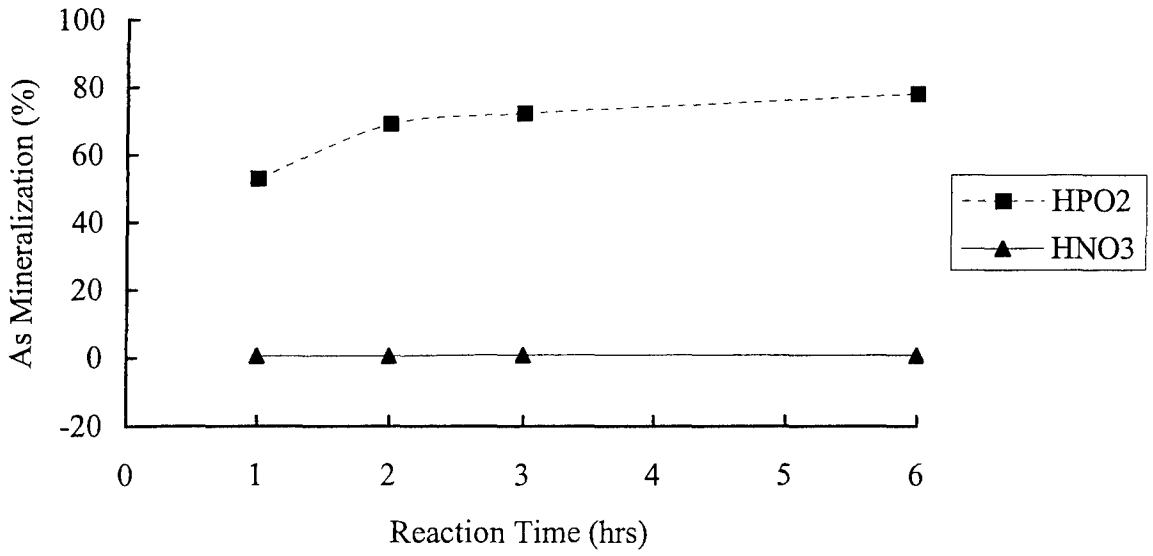


Figure 29. Mineralization of Arsenic Based on Formation of the Pentavalent Arsenate Species. Note the Y-Scale starts at –20 to allow visualization of the arsenate values obtained using the 35% HNO_3 reagent.

While the most efficacious chemistry was modified HPO_2™ reagent, additional data was collected using 35% HNO_3. These chemistries were selected for further evaluation based on both efficacy of destruction and generation of no, or minimal, solids during the neutralization process. A series of small-scale reactions were conducted to examine loading ratios, reaction times, and reaction temperatures, and the results are summarized in separate reports.[54,55] Near the end of this reactor campaign, a decision was made to move away from a punch and drain operation, to an EDS based operation to dispose of the GTRs.[56] While the initial results looked promising for both the modified HPO_2™ reagent and 35% HNO_3, neither could be used in the EDS. The HPO_2™ reagent was quickly decomposed by the copper and iron contained in the linear shape charge (LSC) and fragmentation suppression shield (FSS) portions of the EDS, and lost efficacy.[54,55] The design engineers decided 35% HNO_3 was not compatible with the materials of construction of the EDS, and had concerns about the NO_x emissions.[57]

3.3.3 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% $NaMnO_4$ could effectively neutralize the lewisite residues.[58] Sodium permanganate was considered as an oxidizing reagent for this project,[59] but was initially rejected because of the formation of solids (MnO_2) which would have caused problems in pumping. The programmatic change from a punch and drain to an EDS operation, allowed for the management of generated solids.

Using the micro-scale screening approach outlined in Section 2.1, a preliminary experiment investigating the efficacy 20 wt% $NaMnO_4$ was conducted using fill materiel from GTR CA-0276. In this experiment, the loading of fill materiel to reagent was 1:40, the reactions were

stirred and reaction temperatures were 55, 75, and 90 °C. Individual reaction vials were harvested at 2, 4, 6, and 24 hr, with each treatment conducted in duplicate. The residual agent results are illustrated in Figure 30, and indicate 20 wt% $NaMnO_4$ is very efficacious, resulting in residual agent levels well below the 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% $NaMnO_4$ with an arsinol fill materiel. 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), additional argon was pumped into the vial, and the vial heated to 60 °C. A 10 µL aliquot of neat arsinol from GTR CA-0276 (1:50 loading) was introduced through the septa, and the reaction allowed to proceed. Two hundred microliters of headspace gases were removed at 15, 60, 120, and 180 min after the arsinol was added, and analyzed by GC/MSD in full SCAN mode. The predominant gases generated during the reaction of arsinol with 20 wt% $NaMnO_4$ was oxygen and carbon dioxide, with traces of acetylene and 1-propene also detected. The acetylene and 1-propene detected in the headspace are ubiquitous background, and were also detected in ambient laboratory air samples. There were no additional gases detected at the longer time points, and peak area response stayed fairly constant over time.

Based on previous experience using 20 wt% $NaMnO_4$ to neutralize lewisite residues,[55] and the micro-scale work described above, it was decided to advance this reagent to small-scale laboratory 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 it's properties.

3.4 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.

3.4.1 General Properties of Permanganate Reagent.

Concentrated sodium permanganate solutions are strong oxidizers, and need to be handled with appropriate precautions.[60,61] A summary of general properties, taken from the open literature,[60,61] is provided in Table 23. The oxidative strength of permanganate, as compared to other common oxidizers, is summarized in Table 24.[62]

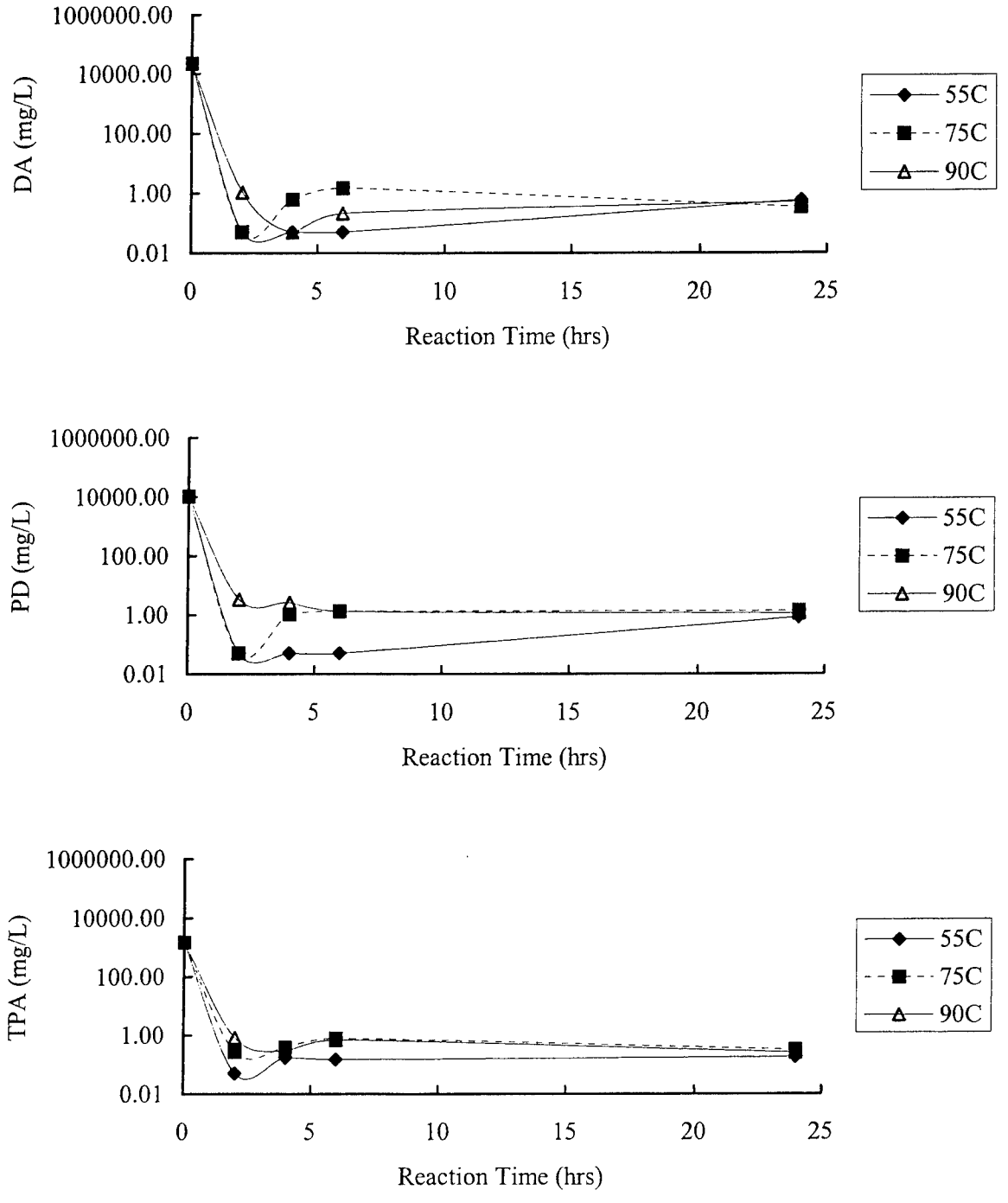


Figure 30. Residual Agent Concentrations as a Function of Reaction Time. The upper panel is DA, the middle panel is PD, and the bottom panel is TPA. The plotted values are the averages of duplicate reactions, and "ND" values are plotted as 0.05 mg/L. Note the Y-scale is logarithmic.

Table 23. Summary of Properties of 20 wt% $NaMnO_4$ Solutions. Data from references 60 and 61.

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[a]	18 months
Specific Gravity	1.16 g/mL

a. Storage conditions not specified.

Table 24. Relative Oxidizing Strength of Common Oxidizers. All data is relative to chlorine being rated as 1.0. Data from reference 62.

Oxidative Species	Relative Oxidizing Strength[a]
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

a. Relative to chlorine being 1.00

3.4.2 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.[63-66] 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.[67] 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.[68,69] 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% $NaMnO_4$.[68,69] Titanium, gold, and platinum were also reported to perform well in permanganate solutions, with corrosion rates of 2 mpy or less.[63]

Nylons, polyesters, acrylics, styrenes, furans, nitrile, natural rubber, SBR, and isoprene are not compatible with aqueous permanganate solutions.[70-73] Fluoropolymers (PTFE, PVDF, ETFE, and E-CTFE), EP, and EPDM are considered to be compatible under a variety of conditions.[70-73]

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,[74] 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,[75] 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. This 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.[76] The materials compatibility study was conducted in accordance with standard NACE and ASTM test methods.[77,78]

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 (Section 3.6.6) were also performed at 60 and 80 °C. There were no significant differences observed in EPDM performance when neutralent or unused reagent was used to perform the compatibility studies.

3.4.3 Reaction Mechanism.

Permanganate solutions are used in the remediation of contaminated groundwater,[79-81] disinfection and pre-oxidation of drinking water,[82-84] treatment of industrial wastewaters,[85,86] and in organic synthesis reactions.[87,88] A general description of the reaction mechanism, obtained from a literature source related to groundwater remediation,[79] 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."*

Text continues on page 67.

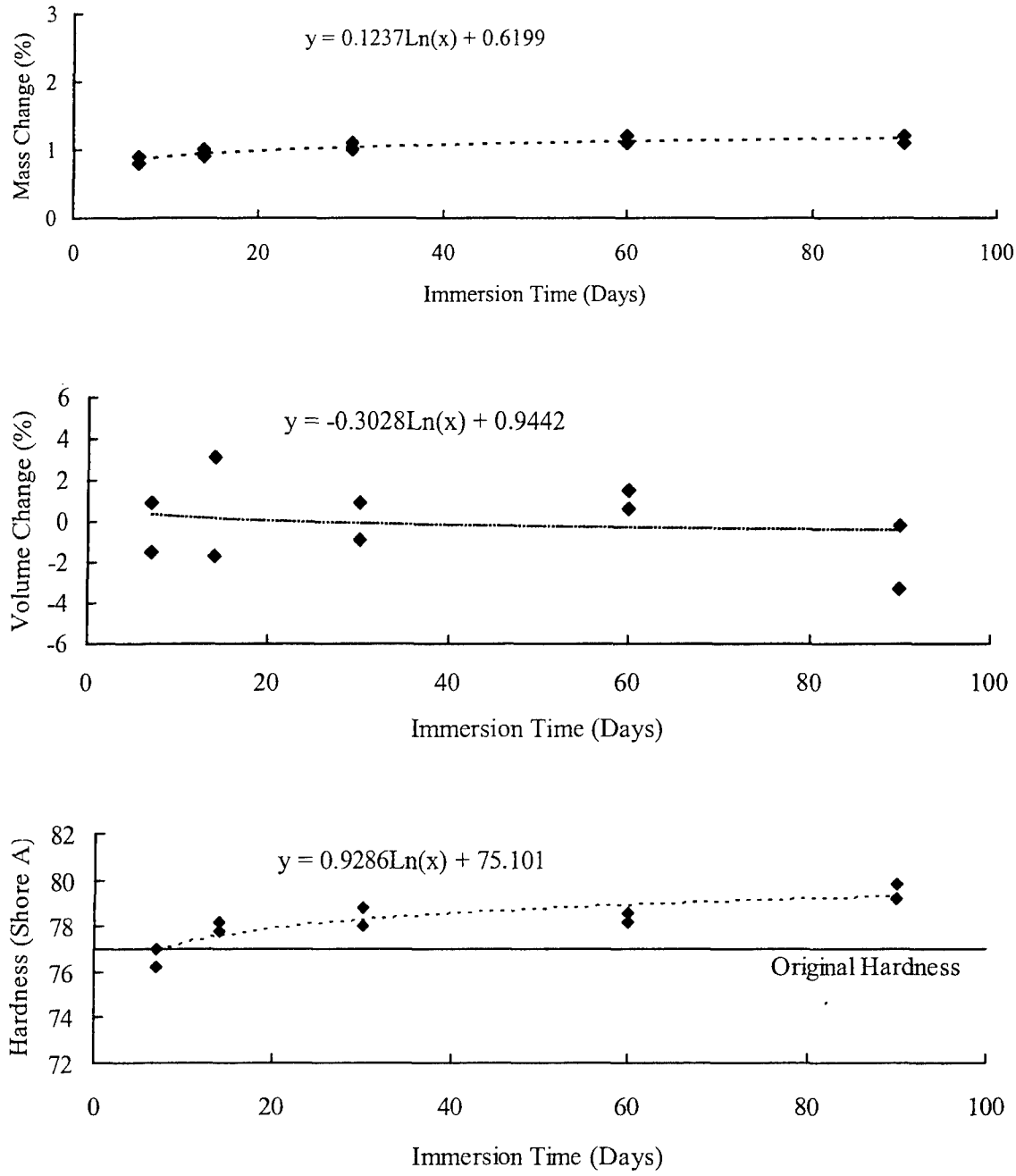


Figure 31. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 60 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness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

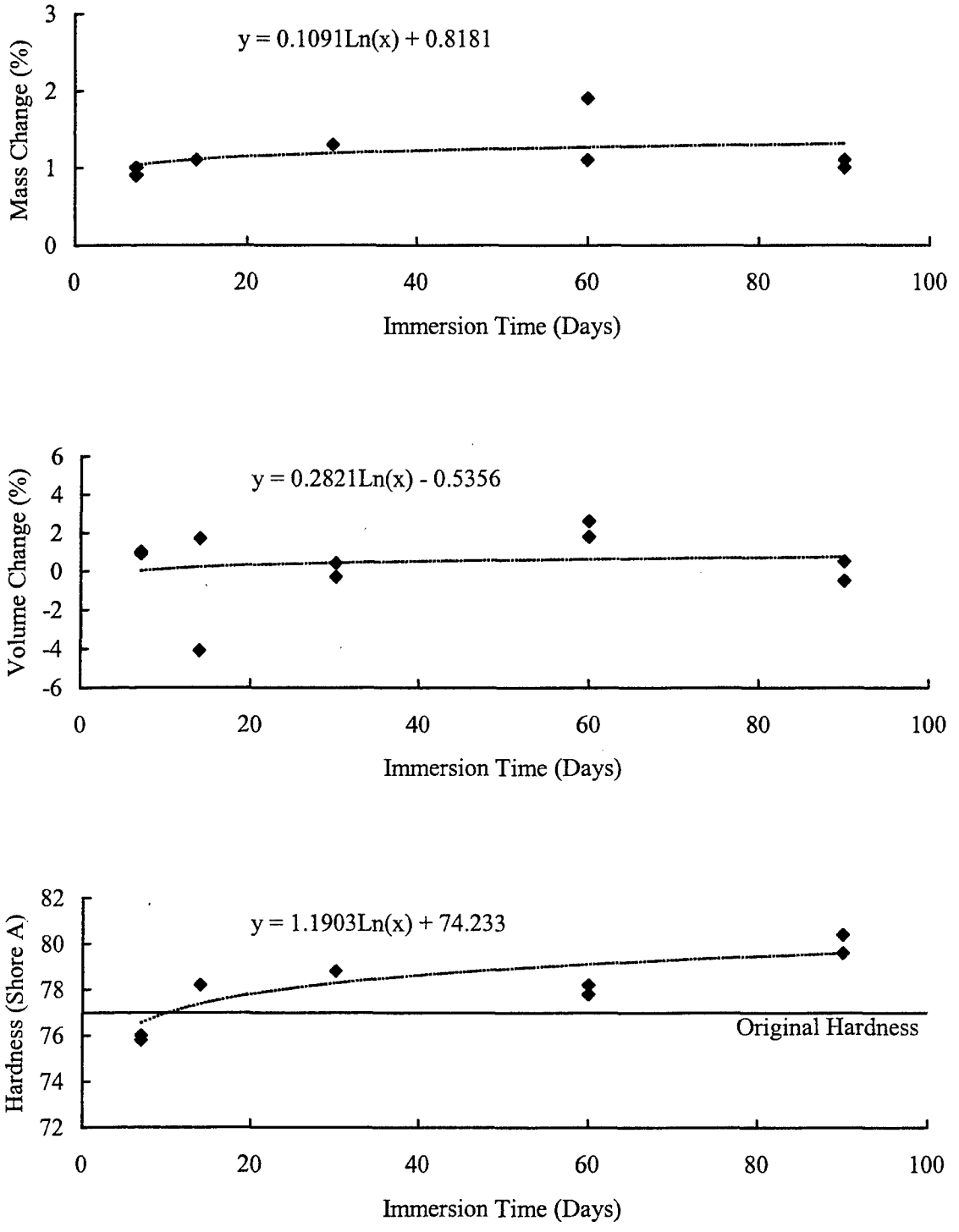
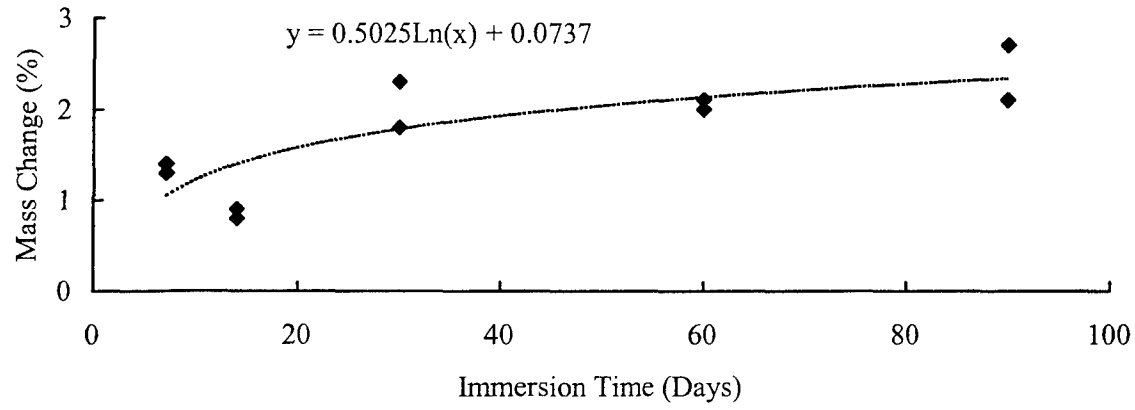
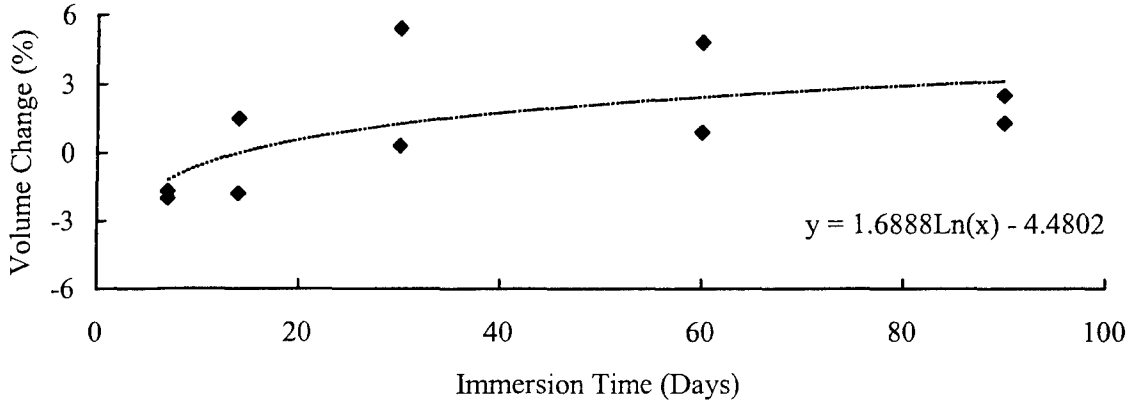


Figure 32. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 80 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness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





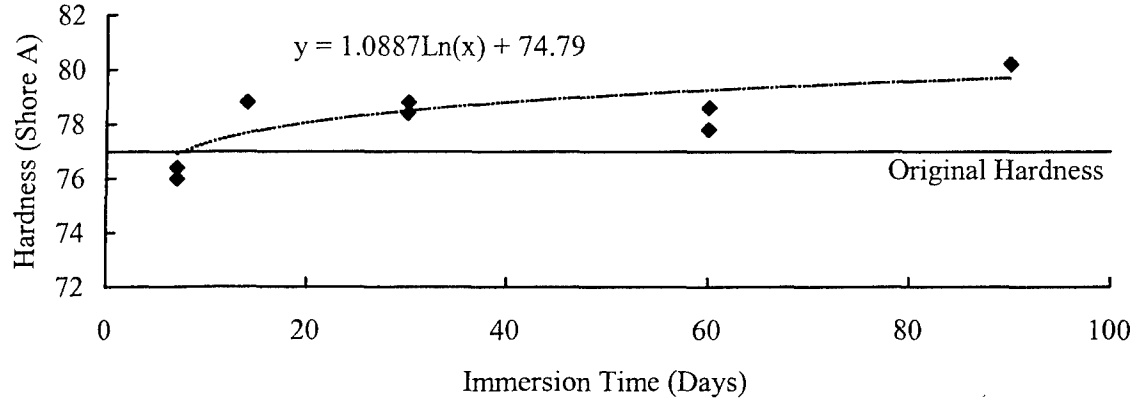


Figure 33. Changes in EPDM over Time when Immersed in 20 wt% $NaMnO_4$ Solution at 100 °C. The upper panel is the percent change in mass relative to the initial mass, the middle panel is the percent change in volume relative to the initial volume, and the lower panel is the change in hardness. The hardness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

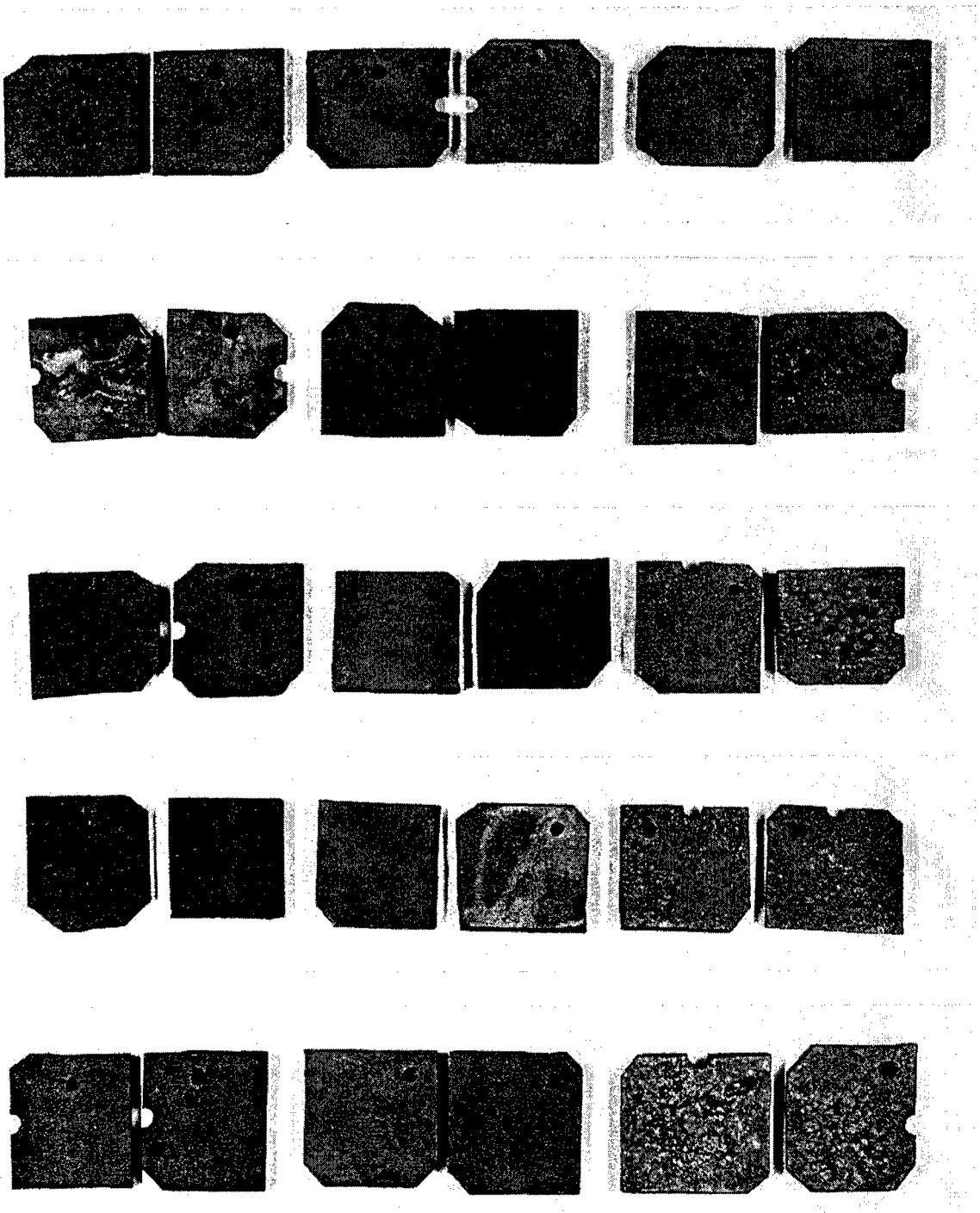


Figure 34. Cleaned Test Specimens after Exposure to 20% $NaMnO_4$ at Three Different Temperatures. The top panel is the test specimens after seven days of exposure, the next panel down is after 14 days, the third panel down is after 30 days, the fourth panel down is after 60 days, and the bottom panel 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.

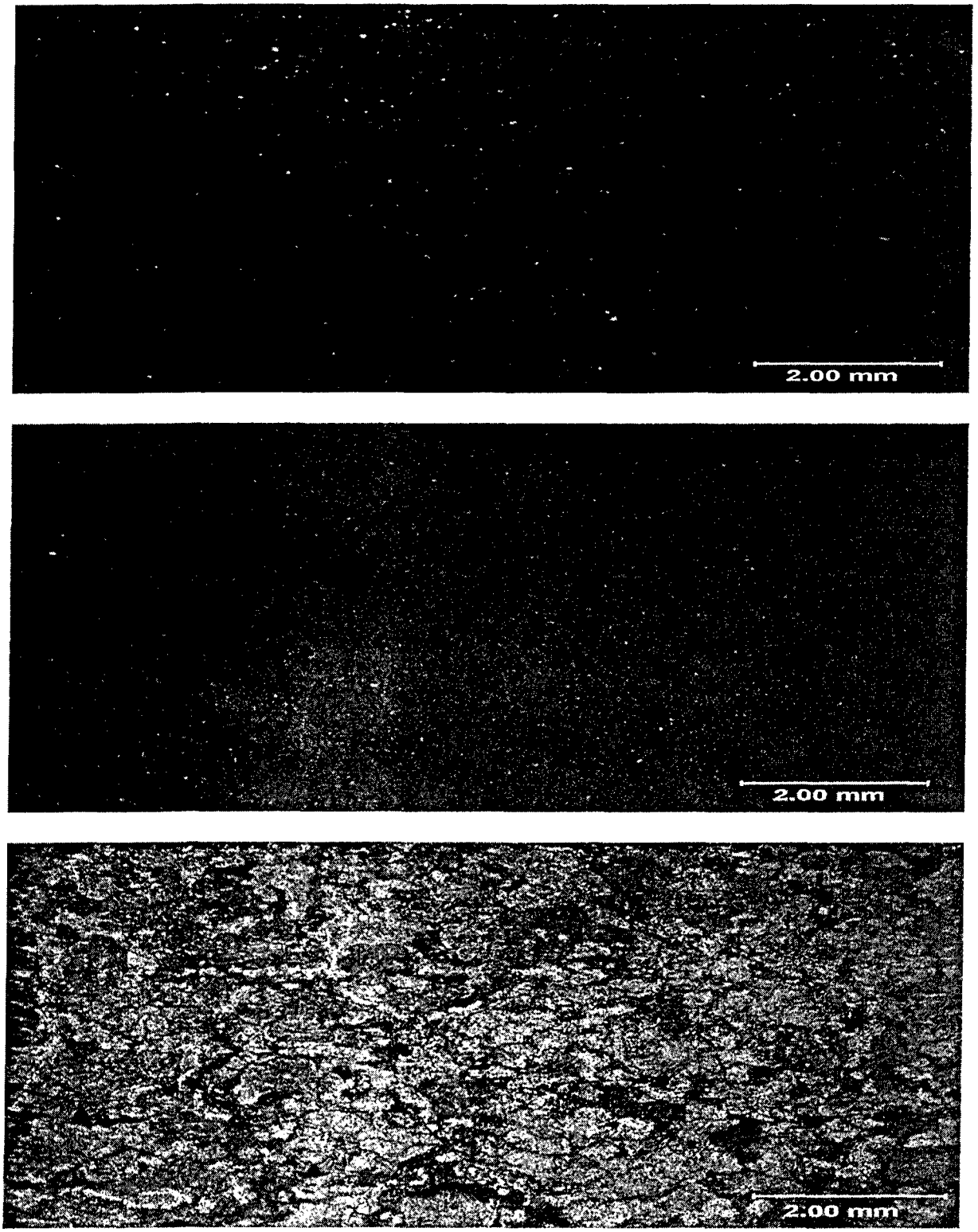


Figure 35. Surface Features of Unexposed EPDM (upper panel), Test Specimen After 90 Days of Exposure at 60 °C (middle panel), and Test Specimen After 90 Days of Exposure at 100 °C (lower panel). Surfaces are magnified 11 times. Note deposits on surface of specimens exposed at 100 °C.

The reaction pathways and kinetics of the oxidation of trichloroethylene (TCE) by aqueous permanganate solutions has been extensively studied,[80,81,89,90] and the process has been determined to proceed in three sequential steps.[89] 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.[91,92] 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.[92] 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.

3.5 Small-Scale Laboratory Demonstration of Permanganate Reagent.

A series of small-scale (100 mL) reactions were conducted to investigate the influence of reaction temperature, reaction time, and arsinol loading on the efficacy of 20 wt% $NaMnO_4$ reagent against liquid arsinol GTR fill materiels. This investigation was conducted using a single GTR fill (CA-0230) to eliminate variability due to different fill materiels. Additional reactions were conducted using all the different liquid arsinol fills, under reaction conditions thought to be most suitable for EDS operations (60 °C and 1:50 arsinol to reagent loading) to examine efficacy as a function of different GTR fills.

3.5.1 Reaction Conditions.

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, N_2 gas was purged through the reactor headspace at a rate of 1-2 mL/min, and was vented through the condenser. The N_2 gas was then passed through two caustic-filled impingers, connected in series to the condenser. Each impinger contained 3 mL of 0.1N $NaOH_{(aq)}$.

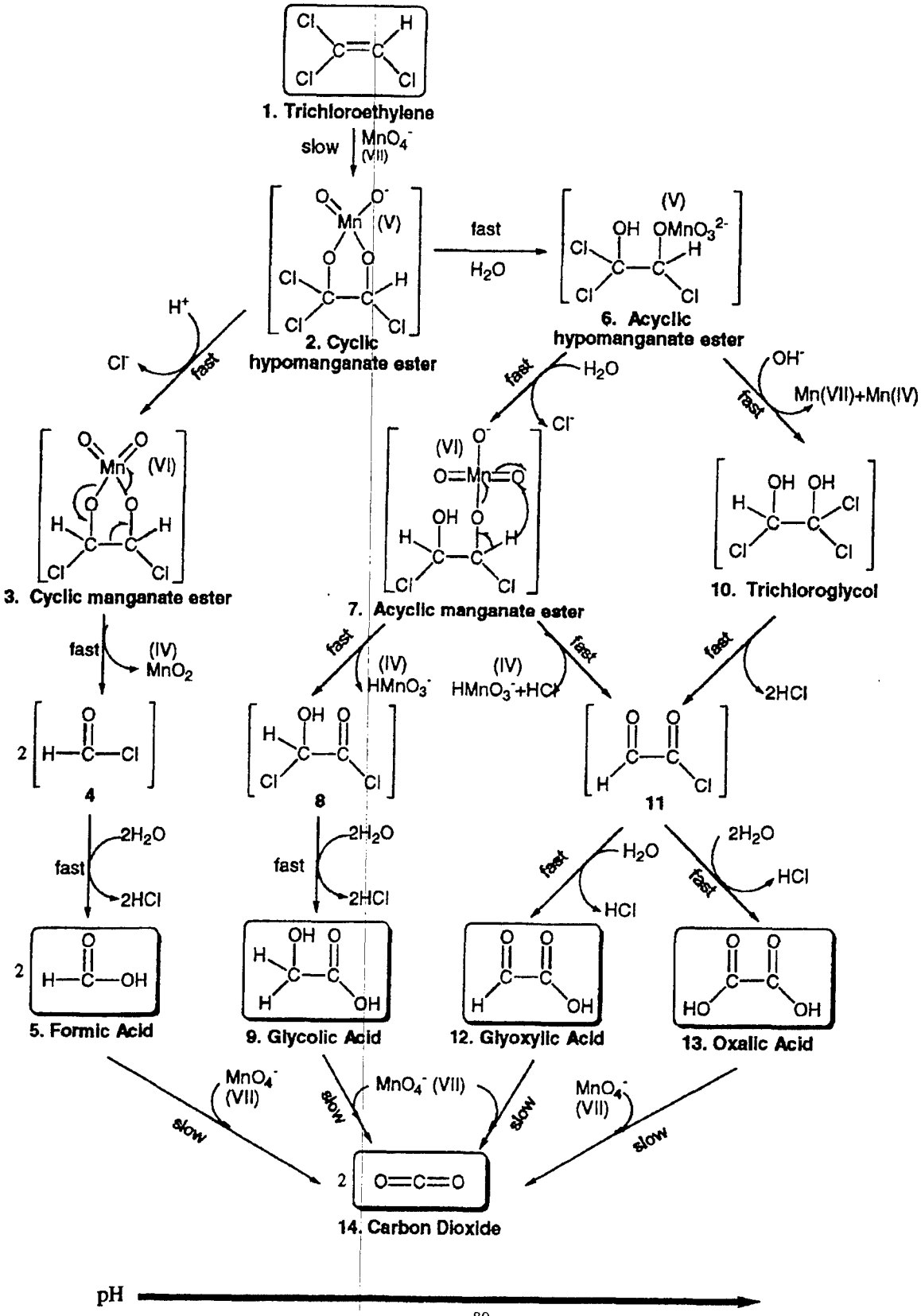


Figure 36. Trichloroethylene Oxidation Pathways.[89]

In these runs, 100 mL of reagent was added to the reactor, stirring and N_2 purge started, and the temperature set-point adjusted to 40 °C. A piece of copper (1/8-in. 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 at 40 °C, the arsinol (2.0 or 4.0 mL) was quickly added as a single bolus, and the reaction was allowed to proceed for 15 min. Fifteen minutes after the arsinol was added, the temperature set-point was adjusted to the desired reaction temperature. Neutralent samples were removed from the reactor at 2, 4, and 6 hr after the desired reaction temperature was achieved. 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. A summary of reaction conditions is presented in Table 25.

In addition to the runs described above, two additional reactions were performed. These reactions were conducted in the glass reactor system previously described, used fill materiel from GTR CA-0230, used 100 mL of 20 wt% $NaMnO_4$, and were conducted at an initial arsinol to reagent loading of 1:50. The first reaction examined the potential for agent reformation if the neutralent was quenched with an aqueous solution of sodium thiosulfate. This reformation experiment was conducted at a reaction temperature of 60 °C, with a reaction time of 3.5 hr. After 3.5 hr of reaction at 60 °C, a sample was removed from the reactor for agent analyses, and the temperature set-point changed to 50 °C. Once the temperature equilibrated to 50 °C, 100 mL of 10 wt% sodium thiosulfate was slowly added over a period of 30 min. Once all the thiosulfate solution had been added, the reaction was allowed to proceed for 30 min, and another sample was pulled for agent analyses.

The second run was performed to evaluate how much arsinol could be added, before the 20 wt% $NaMnO_4$ reagent failed. This force to failure experiment was conducted at a reaction temperature of 80 °C, with an initial arsinol loading of 1:50. After 2 hr of reaction at 80 °C, a sample was removed from the reactor for agent analyses, and another aliquot of arsinol was added to the reactor. The cycle of sampling, then adding additional arsinol continued, for a total addition of 11 mL of arsinol. Samples were also collected at 3 and 5 hr after the last addition of arsinol. This corresponds to an arsinol to reagent loading of 1:9, based on the initial 100 mL of reagent. There was a power failure in the middle of the experiment, with the reaction temperature dropping to room temperature (~23 °C) for approximately 8 hr.

3.5.2 Temperature Profiles and Observations.

The reactions described in Table 25 were all well behaved, with no significant exotherm or off-gassing observed when the arsinol was added to the 20 wt% $NaMnO_4$ reagent. There was a slight exotherm when the arsinol was added, with a maximum rise of 5-6 °C observed during the reactions. During the first hour of reaction, there was a crust that developed on top of the neutralent, but this crust was mostly dissolved by the second hour of reaction.

Example temperature profiles are illustrated in Figures 37 and 38. While not continuously monitored during the runs, pH was determined on each of the terminal neutralents. The terminal pH values ranged from 7.59 to 9.62, and were positively correlated with reaction temperature. This correlation is, most likely, due to enhanced degradation of MnO_4^- to MnO_2 at the higher reaction temperatures. For reference, the pH of the starting 20 wt% $NaMnO_4$ reagent was determined to be 7.82. In all runs, except one, the terminal neutralent was dark purple in color, indicating there was still MnO_4^- available in the neutralent. The terminal neutralent from the 1:25 loading experiment conducted at 100 °C was tan in color, indicating the oxidizer had become exhausted at some point during the reaction.

Table 25. Summary of Reaction Conditions for the Small-Scale Laboratory Reactor Runs.

Reaction Temperature (°C)	20 wt% $NaMnO_4$ Reagent (mL)	GTR Fill Used	Agent:Reagent Loading (v:v)	Initial Agent (mg/L)
60	100	CA-0230	1:50	DA = 17,100
80	100	CA-0230	1:50	PD = 9,200
100	100	CA-0230	1:50	TPA = 1,330
60	100	CA-0230	1:25	DA = 34,300
80	100	CA-0230	1:25	PD = 18,400
100	100	CA-0230	1:25	TPA = 2,660
60	100	CA-0175	1:50	See Note a
60	100	CA-0178	1:50	See Note b
60	100	CA-0230	1:50	See Note c
60	100	CA-0276	1:50	See Note d
60	100	CA-0280	1:50	See Note e

a. DA = 16,500, PD = 9,210, and TPA = 1,070 mg/L.
b. DA = 20,300, PD = 6,330, and TPA = 681 mg/L.
c. DA = 17,100, PD = 9,200, and TPA = 1,330 mg/L.
d. DA = 17,900, PD = 8,380, and TPA = 1,220 mg/L.
e. DA = 16,900, PD = 8,820, and TPA = 1,280 mg/L.

The reactor run examining the quenching of neutralent with aqueous thiosulfate solution was well behaved, with no vigorous off-gassing or foaming taking place during the quenching step. There was a 10 °C exotherm, even with the large dilution by room temperature thiosulfate solution. The temperature profile is illustrated in Figure 39. While not continuously monitored during the run, pH was determined on the terminal neutralent, after being quenched with thiosulfate solution. The terminal pH value was determined to be 7.95. The neutralent was not completely quenched, as evidenced by the light purple color of the neutralent.

The reactor run examining the capacity of the 20 wt% $NaMnO_4$ reagent was well behaved, with no vigorous off-gassing or foaming taking place during the additions of arsinol.

There was a slight exotherm after each addition, with the magnitude of the exotherm decreasing with each addition of arsinol. The largest exotherm was approximately 5 °C, and occurred after the second addition of arsinol. The temperature profile is illustrated in Figure 40. The development of the crust on top of the neutralent was more pronounced in this run, but it mostly dissolved within 1 hr after the last addition of arsinol. While not continuously monitored during the run, pH was determined on the terminal neutralent, and found to be 7.22. The terminal neutralent was still a dark purple color, suggesting the oxidative capacity of the reagent had not been exhausted.

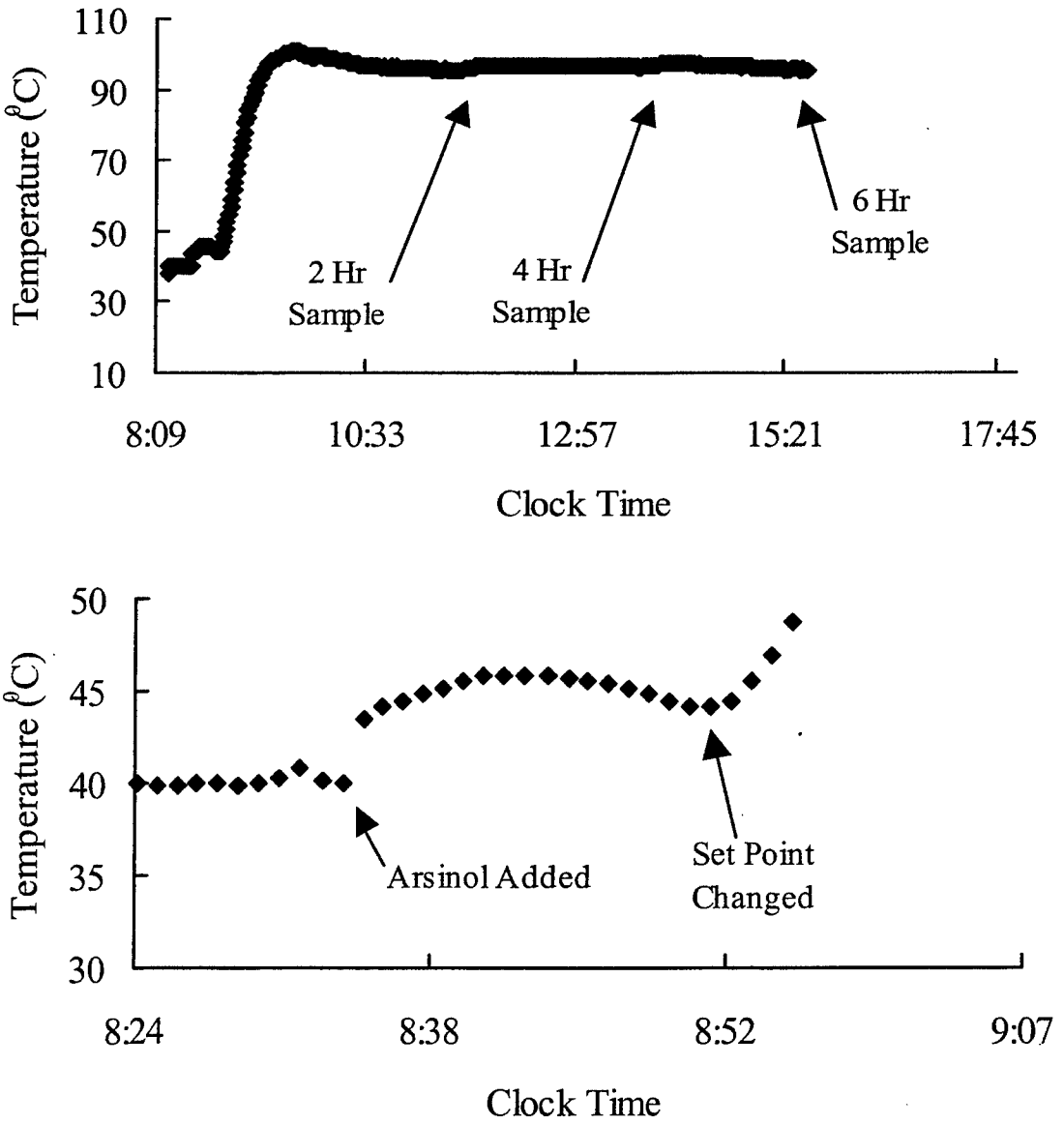


Figure 37. Temperature Profile for the 1:50 Loading Reactor Run, with a Final Temperature of 100 °C. The upper panel is full-scale, and the lower panel is zoomed into the arsinol addition time-frame.

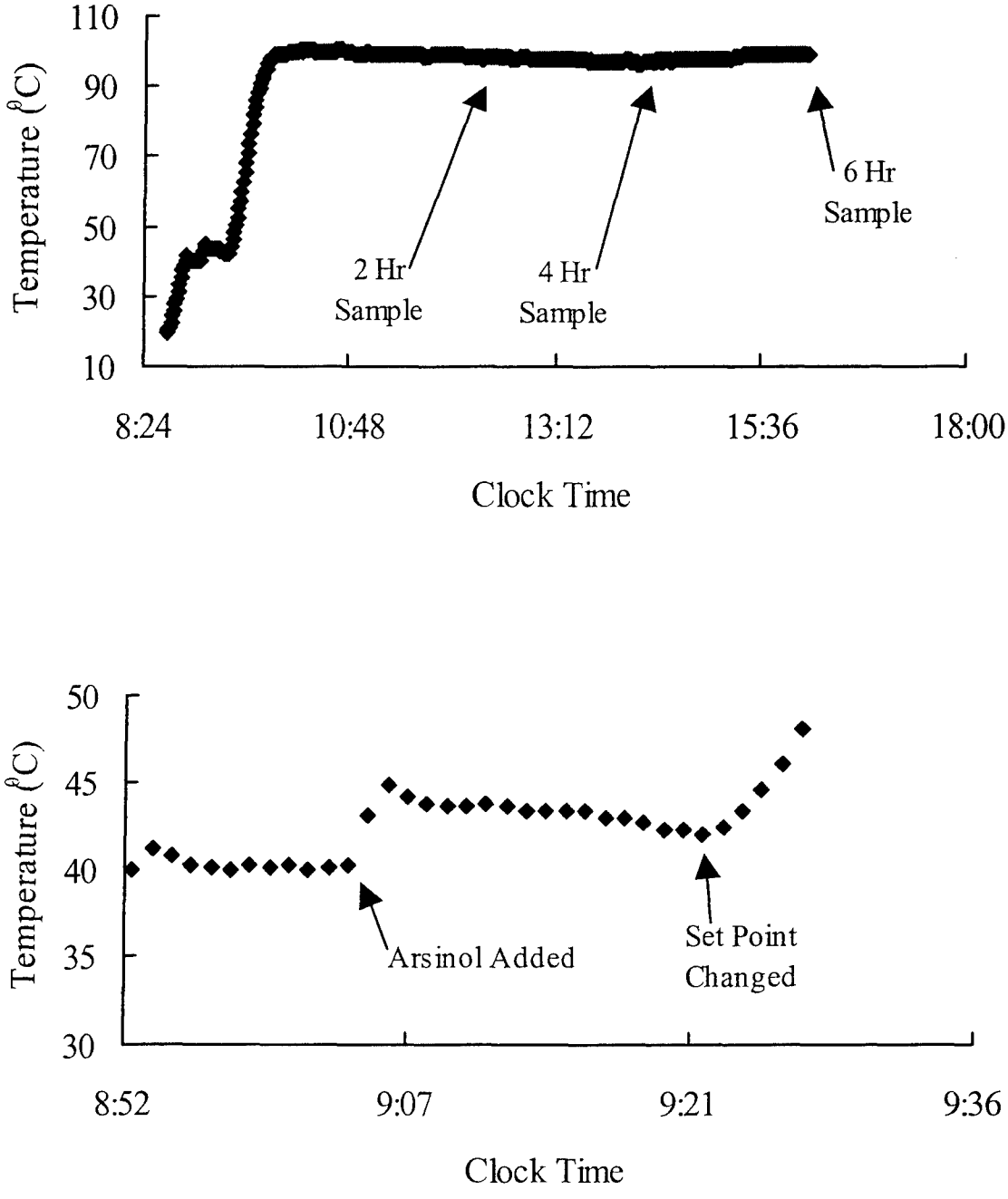


Figure 38. Temperature Profile for the 1:25 Loading Reactor Run, with a Final Temperature of 100 °C. The upper panel is full-scale, and the lower panel is zoomed into the arsinol addition time-frame.

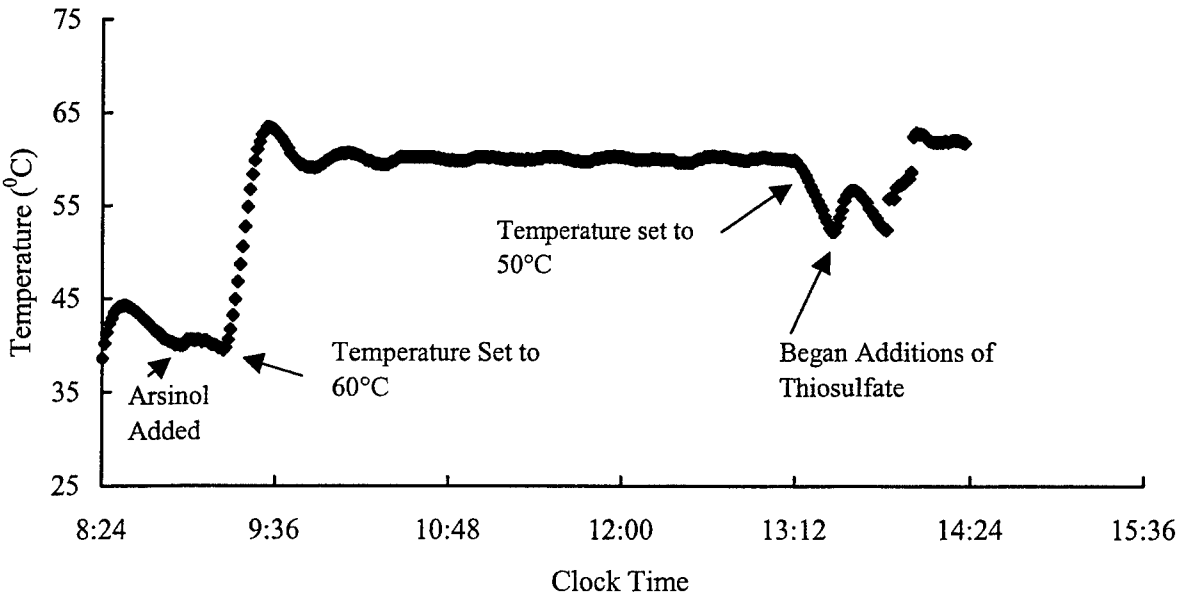


Figure 39. Temperature Profile for the Thiosulfate Quenching Reactor Run.

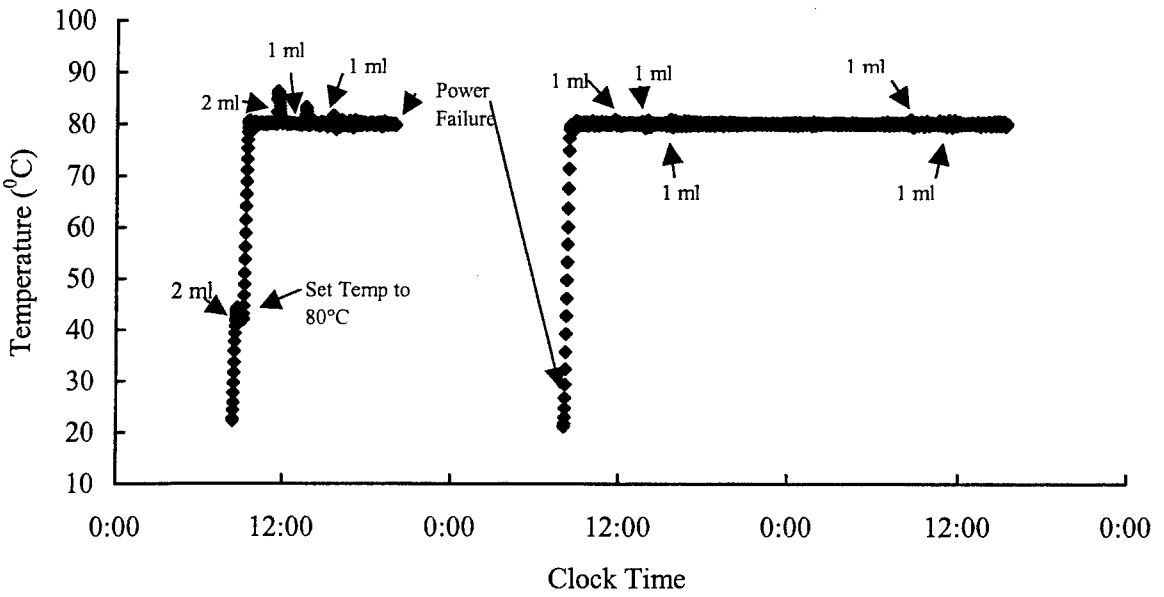


Figure 40. Temperature Profile for the Force to Failure Reactor Run. The indicated volumes refer to additions of fill materiel from GTR CA-0230.

3.5.3 Residual Agents.

Time-point samples were removed from the reactor, and analyzed for residual DA, PD, and TPA using the procedure described in Section 2.5. The three mL samples were removed from the reactor using a modified glass Pasteur pipet, with the tip of the pipet being approximately 3/4-inch below the surface of the neutralent. Once removed from the reactor, samples were placed into a 4 mL glass vial, and immediately placed into a water/ice bath to inhibit further reaction. 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=12) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. Concurrently with the analysis of these samples, a single spike recovery study was performed, using both 1 wt% $NaMnO_4$ solution, and deionized water as sample matrices. The spike level was 5.0 mg/L, and a total of seven replicates were prepared and analyzed in each matrix. Sample derivitization and extraction was started within 2 min of the sample being spiked, and extraction blanks (n=2) for each matrix were also processed. The recoveries of residual agents from the 1 wt% $NaMnO_4$ solution were all very low, ranging from 0.355 to 2.76 %, depending on the analyte. The recoveries from deionized water were much higher, and are consistent with the recoveries obtained during the method validation study (Section 2.5.3). On average (n=7) the recoveries were: 76.6 % for DA (SD = 1.93%), 83.1 % for PD (SD = 1.59%), and 95.1 % for TPA (SD = 1.62%).

The neutralent time point data is summarized in Tables 26 through 28. The residual agent data for the reaction time/reaction temperature/arsinol loading study is illustrated in Figure 41. The reaction of DA, PD, and TPA with 20 wt% $NaMnO_4$ proceeds very quickly, and appears to be independent of reaction temperature, arsinol loading, and GTR fill used. Using the average 2 hr results for each arsinol loading, the first order half-lives for DA and PD were calculated to be 8 min, at both arsinol loadings. The half-lives for TPA were calculated to be 11 min at the 1:50 arsinol loading, and 18 min at the 1:25 arsinol loading. The 1:25 loading experiment conducted at 100 °C exhausted all the MnO_4^-, as evidenced by the color change of the neutralent (See Section 3.5.2), and this accounts for the somewhat elevated levels of TPA found in samples from this reaction. The 20% $NaMnO_4$ reagent was very effective at destroying the agents, with average (across all reaction time/temperatures/loadings) destruction efficiencies calculated to be 99.988 % for DA, 99.990 % for PD, and 99.096 % for TPA. In the worst case reaction (1:25 loading at 100 °C), the destruction efficiencies were calculated to be 99.968 % for DA, 99.991 % for PD, and 95.387 % for TPA. In all cases, there were no agents detected in any of the impinger samples. The detection limit is estimated to be 0.0015 mg of agent being entrained in the impinger.

The terminal neutralent samples from the thiosulfate quenching experiment were analyzed for residual agents, using the previously described method. Prior to quenching, all three agents were not detected (≤0.05 mg/L). After addition of the thiosulfate solution, all three agents were detected in the neutralent. When the dilution factor is taken into consideration, the residual agent concentrations were determined to be: 0.292 mg/L DA, 0.582 mg/L PD, and 0.966 mg/L TPA. This corresponds to 6, 12, and 19 times above the values (≤0.05 mg/L) determined to be in

the unquenched neutralent. The use of reducing agents to quench these permanganate neutralents apparently reduces the pentavalent organo-arsenical forms of the agents back to their trivalent forms, and are then derivatized during sample processing.

The force to failure agent data is illustrated in Figure 42. In the initial sampling, the 50 mg/L treatment goal for each of the agents was exceeded after various additions of arsinol, and these are summarized as follows:

- For TPA, the 50 mg/L treatment goal was exceeded after 5 mL of arsinol was added. This is a volumetric loading of 1:20.

- For DA, the 50 mg/L treatment goal was exceeded after 7 mL of arsinol was added. This is a volumetric loading of 1:14.

- For PD, the 50 mg/L treatment goal was exceeded after 11 mL of arsinol was added. This is a volumetric loading of 1:9.

While the reaction chemistry failed to meet the desired treatment goal at a 1:20 loading for TPA, this is well above the anticipated 1:50 loading to be used in actual EDS operations. In addition, these samples were taken from the reactor after only 2 hr of reaction. Samples taken from the reactor (open symbols in Figure 42) at 3 and 5 hr after addition of the last aliquot of arsinol show a decreasing trend, suggesting increased reaction times could accommodate higher loadings of arsinol.

Table 26. Residual DA in Whole Neutralent Time Point Samples. The reported values are averages of duplicate determinations, and are in the original neutralent sample.

Reaction Conditions and GTR Fill Used	Residual DA in Neutralent (mg/L) Reaction Time		
	2 Hr	4 Hr	6 Hr
1:50 @ 60 °C, CA-0230	ND[a]	ND[a]	ND[a]
1:50 @ 80 °C, CA-0230	Trace[b]	ND[a]	0.259
1:50 @ 100 °C, CA-0230	1.15	0.933	0.779
1:25 @ 60 °C, CA-0230	0.375	Trace[b]	ND[a]
1:25 @ 80 °C, CA-0230	Trace[b]	ND[a]	ND[a]
1:25 @ 100 °C, CA-0230	3.32	11.6	17.6
1:50 @ 60 °C, CA-0175	Trace[b]	Trace[b]	Trace[b]
1:50 @ 60 °C, CA-0178	Trace[b]	Trace[b]	Trace[b]
1:50 @ 60 °C, CA-0230	Trace[b]	Trace[b]	Trace[b]
1:50 @ 60 °C, CA-0276	Trace[b]	Trace[b]	Trace[b]
1:50 @ 60 °C, CA-0280	Trace[b]	Trace[b]	Trace[b]

a. No peak was detected; estimated detection limit is 0.05 mg/L.
b. Peak was detected, but was less than 0.1 mg/L.

Table 27. Residual PD in Whole Neutralent Time Point Samples. The reported values are averages of duplicate determinations, and are in the original neutralent sample.

Reaction Conditions and GTR Fill Used	Residual PD in Neutralent (mg/L) Reaction Time		
	2 Hr	4 Hr	6 Hr
1:50 @ 60 °C, CA-0230	ND[a]	ND[a]	ND[a]
1:50 @ 80 °C, CA-0230	ND[a]	ND[a]	1.36
1:50 @ 100 °C, CA-0230	1.20	0.651	0.486
1:25 @ 60 °C, CA-0230	ND[a]	ND[a]	ND[a]
1:25 @ 80 °C, CA-0230	ND[a]	ND[a]	ND[a]
1:25 @ 100 °C, CA-0230	2.17	1.14	1.63
1:50 @ 60 °C, CA-0175	Trace[b]	ND[a]	ND[a]
1:50 @ 60 °C, CA-0178	ND[a]	ND[a]	ND[a]
1:50 @ 60 °C, CA-0230	ND[a]	ND[a]	ND[a]
1:50 @ 60 °C, CA-0276	ND[a]	ND[a]	ND[a]
1:50 @ 60 °C, CA-0280	ND[a]	ND[a]	ND[a]

a. No peak was detected; estimated detection limit is 0.05 mg/L.
b. Peak was detected, but was less than 0.1 mg/L.

Table 28. Residual TPA in Whole Neutralent Time Point Samples. The reported values are averages of duplicate determinations, and are in the original neutralent sample.

Reaction Conditions and GTR Fill Used	Residual TPA in Neutralent (mg/L) Reaction Time		
	2 Hr	4 Hr	6 Hr
1:50 @ 60 °C, CA-0230	Trace[a]	Trace[a]	ND[b]
1:50 @ 80 °C, CA-0230	0.375	0.222	0.444
1:50 @ 100 °C, CA-0230	1.53	0.280	0.202
1:25 @ 60 °C, CA-0230	5.01	4.99	5.15
1:25 @ 80 °C, CA-0230	6.63	6.16	6.31
1:25 @ 100 °C, CA-0230	71.1	116	181
1:50 @ 60 °C, CA-0175	Trace[a]	Trace[a]	Trace[a]
1:50 @ 60 °C, CA-0178	Trace[a]	Trace[a]	Trace[a]
1:50 @ 60 °C, CA-0230	0.115	0.236	0.125
1:50 @ 60 °C, CA-0276	0.104	Trace[a]	Trace[a]
1:50 @ 60 °C, CA-0280	Trace[a]	Trace[a]	Trace[a]

a. Peak was detected, but was less than 0.1 mg/L.
b. No peak was detected; estimated detection limit is 0.05 mg/L.

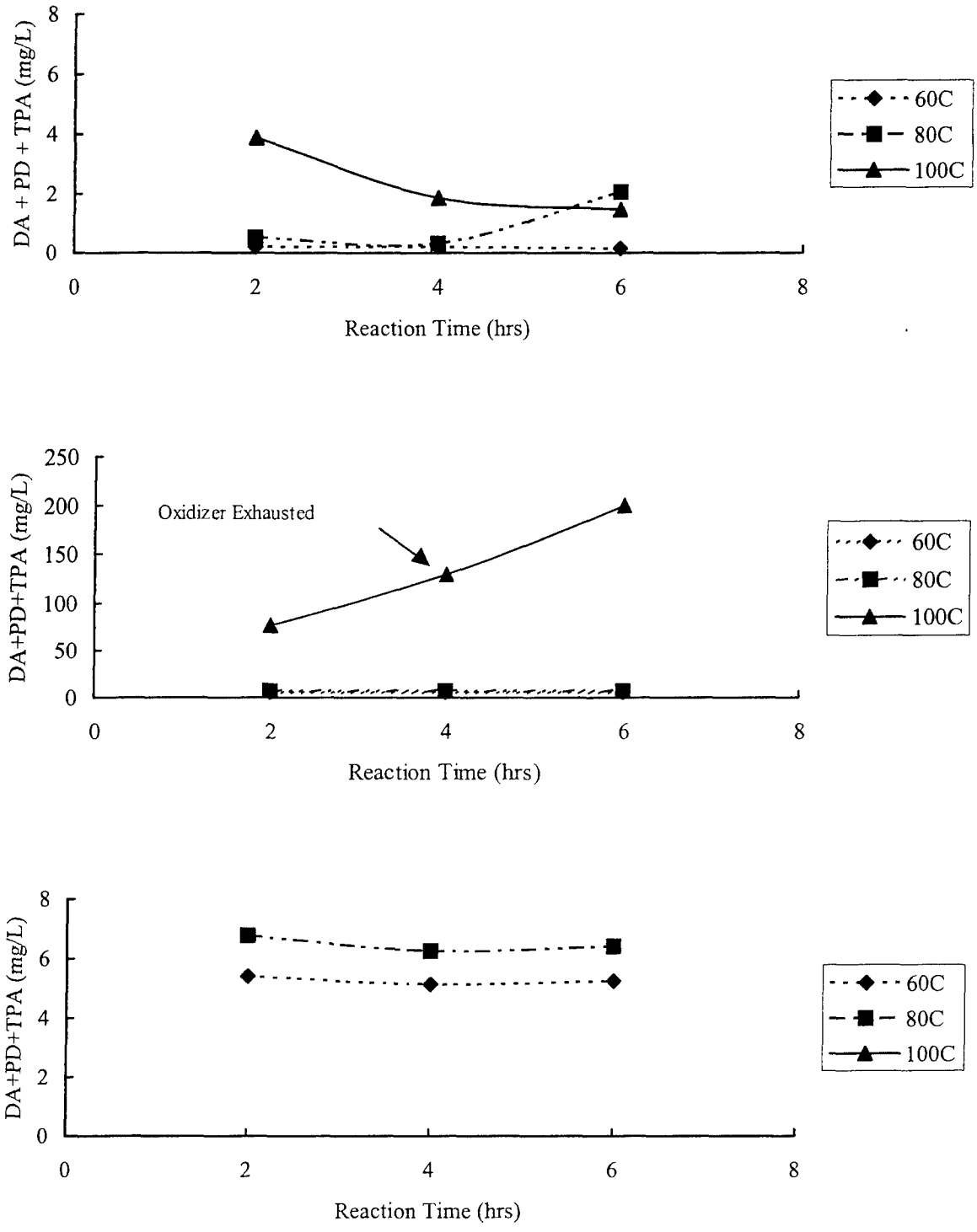


Figure 41. Residual Agent in the Neutralent as a Function of Time. The agents are plotted as the sum of DA, PD, and TPA to simplify the figure. The top panel is the 1:50 loading data, the middle panel is the 1:25 loading data, and the bottom panel is the 1:25 loading data zoomed in to show the 60 and 80 °C data.

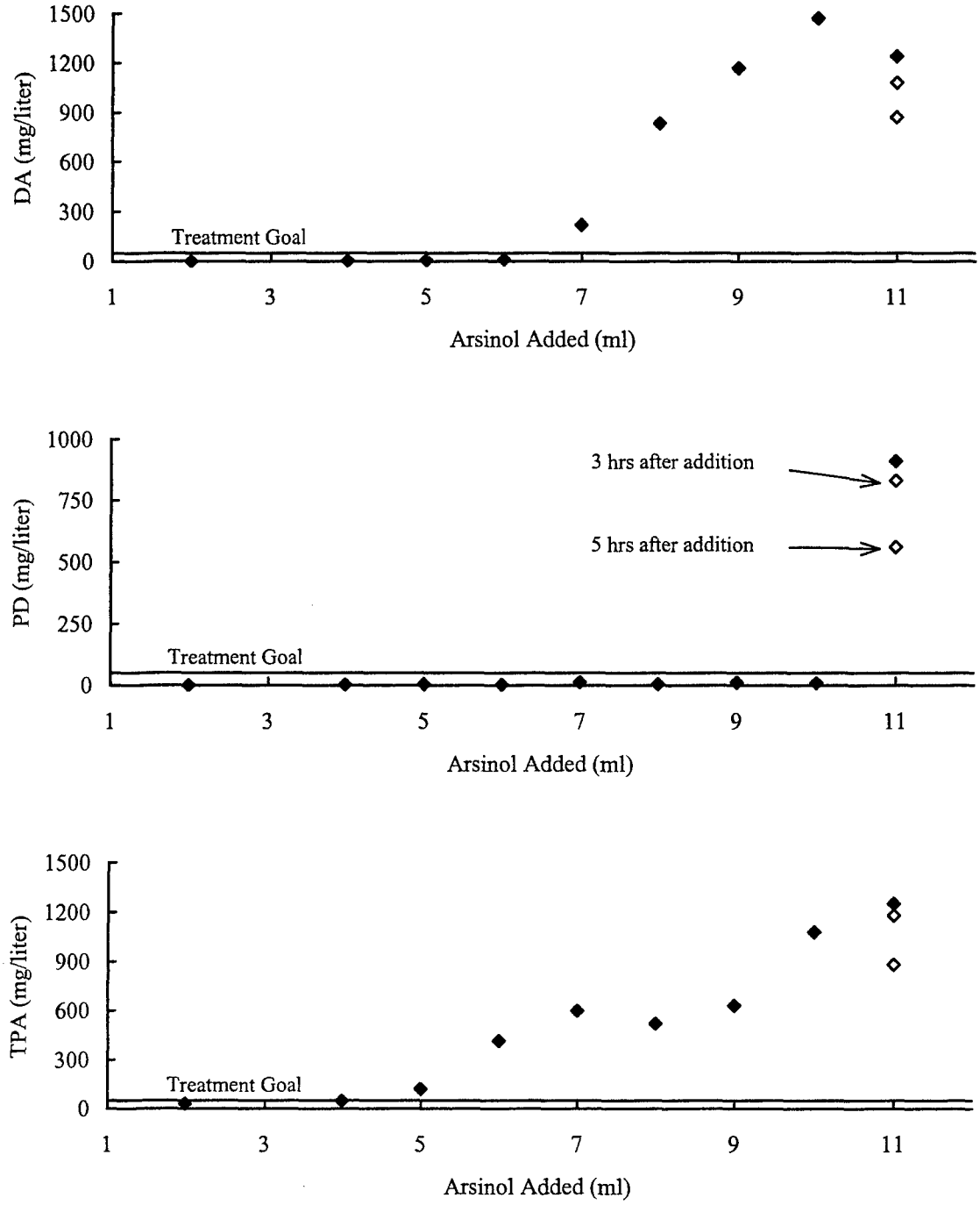


Figure 42. Residual Agent as a Function of Amount of Arsinol Added. Upper panel is DA, middle panel is PD, and lower panel is TPA. Reaction conducted at 80 °C using fill materiel from GTR CA-0230. The plotted values are the averages of duplicate determinations. The open symbols are samples taken 3 and 5 hr after the last addition of arsinol was made.

3.5.4 Quantitation of Reaction Products.

The neutralent samples were analyzed for reaction products using the capillary electrophoresis methods described in Section 2.6. The reaction products were determined after samples were filtered (0.45 μm, PTFE Acrodisc™), and then analyzing the filtrate. Only the neutralent samples from the reaction time/reaction temperature/arsinol loading experiment were analyzed for reaction products. 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 samples. 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 29 through 34. Samples (n=6) of initial 20 wt% $NaMnO_4$ reagent were also analyzed for the reaction products. On average, the 20 wt% $NaMnO_4$ reagent 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 initial 20 wt% $NaMnO_4$ reagent.

Graphs showing inorganic arsenate, the sum of pentavalent organo-arsenicals, and the sum of organic acids as a function of reaction time are illustrated in Figures 43 through 45. The arsenate concentrations ranged from non-detect to trace at the lower reaction temperatures of 60 and 80 °C, with higher concentrations obtained during the 100 °C reactions. The arsenate concentrations suggest mineralization rates of up to 10% (1:50 loading, 100 °C, 6-hr reaction), but these might be underestimates due to sorption of arsenate on the solids (MnO_2 and iron oxides) generated during the reaction.[93] These analyses were performed on filtered neutralent, without a caustic extraction as performed in later analyses (Section 3.7.3). The decrease in soluble arsenate during the 1:25 loading experiment conducted at 100 °C is, most likely, due to the enhanced formation of MnO_2 observed to take place during this experiment.

The pentavalent organo-arsenicals ranged from non-detect to trace at the 60 °C reaction temperature for both loadings, with moderate accumulations at the 80 °C reactions. In the 1:50 loading reaction conducted at 100 °C, the organo-arsenical concentration decreased with time, correlating well with the increase observed for inorganic arsenate. In the 1:25 loading reaction conducted at 100 °C, the organo-arsenical concentration increased with time, supporting observations (color was no longer purple) the permanganate had become exhausted. The organic acid concentrations correlated well with the pentavlent organo-arsenical data, further validating the analytical approach used to analyze these samples. The observed reaction products suggest a reaction pathway similar to that observed for the reaction of other organics with permanganate solutions (Section 3.4.3). While reaction temperature and loading had little effect on residual agent levels (Section 3.5.3), they had a significant influence on reaction product distribution. The more dilute 1:50 loading and higher 100 °C reaction temperature produced more inorganic arsenate (more mineralization), and a decreasing concentration of organic acids over time. This decrease in organic acid concentration indicates complete oxidation of the organic acids to CO_2, which is supported by other studies.[89,90]

Text continues on page 90.

Table 29. Summary of Analytical Results for the 1:50 Loading Performed at 60 °C. All data reported in the original neutralent, with units of milligrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	4,760	5,460	5,800
Fluoride (F^-)	253	225	254
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b]	Trace[b]	Trace[b]
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	ND[a] (50.0)	ND[a] (50.0)	ND[a] (50.0)
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	ND[a] (50.0)	ND[a] (50.0)	ND[a] (50.0)
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	ND[a] (50.0)	ND[a] (50.0)	ND[a] (50.0)
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	223	ND[a] (160)
Formate (CHO_2^-)	Trace[b]	Trace[b]	Trace[b]
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 ($C_2O_4^{-2}$)	386	Trace[b]	427
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

Table 30. Summary of Analytical Results for the 1:50 Loading Performed at 80 °C. All data reported in the original neutralent, with units of milligrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	Trace[b]	Trace[b]	250
Chloride (Cl^-)	9,410	8,920	8,350
Fluoride (F^-)	204	225	229
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b]	Trace[b]	485
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	625	3,230	4,210
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	710	4,860	4,920
Phenylarsine Oxide (C_6H_5AsO)	Trace[b]	Trace[b]	Trace[b]
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	63.8	77.4	80.6
Acetate ($C_2H_3O_2^-$)	Trace[b]	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b]	Trace[b]	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	676	1,650	2,700
Oxalate ($C_2O_4^{-2}$)	Trace[b]	637	754
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

Table 31. Summary of Analytical Results for the 1:50 Loading Performed at 100 °C. All data reported in the original neutralent, with units of millgrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	436	1,330	1,640
Chloride (Cl^-)	7,080	6,670	7,290
Fluoride (F^-)	334	347	383
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b]	Trace[b]	Trace[b]
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	9,600	11,300	10,500
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	7,130	4,330	2,950
Phenylarsine Oxide (C_6H_5AsO)	Trace[b]	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	Trace[b]	Trace[b]	ND[a] (50.0)
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b]	ND[a] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	6,010	6,360	4,920
Oxalate ($C_2O_4^{-2}$)	2,050	2,920	2,940
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

Table 32. Summary of Analytical Results for the 1:25 Loading Performed at 60 °C. All data reported in the original neutralent, with units of milligrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	10,500	11,900	13,200
Fluoride (F^-)	113	137	158
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b]	Trace[b]	Trace[b]
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	ND[a] (50.0)	54.0	209
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	ND[a] (50.0)	87.6	239
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	Trace[b]
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	ND[a] (50.0)	ND[a] (50.0)	Trace[b]
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b]	Trace[b]	Trace[b]
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]	Trace[b]	Trace[b]
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

Table 33. Summary of Analytical Results for the 1:25 Loading Performed at 80 °C. All data reported in the original neutralent, with units of milligrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	Trace[b]	Trace[b]
Chloride (Cl^-)	11,000	14,100	16,000
Fluoride (F^-)	202	257	275
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b]	Trace[b]	485
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	178	1,230	3,440
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	147	1,840	3,530
Phenylarsine Oxide (C_6H_5AsO)	Trace[b]	Trace[b]	Trace[b]
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	Trace[b]	60.8	71.0
Acetate ($C_2H_3O_2^-$)	Trace[b]	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	ND[a] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	Trace[b]	734	1,840
Oxalate ($C_2O_4^{-2}$)	Trace[b]	Trace[b]	429
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

Table 34. Summary of Analytical Results for the 1:25 Loading Performed at 100 °C. All data reported in the original neutralent, with units of milligrams/liter. The values in parentheses are estimated reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	2 hr	4 hr	6 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	509	1,210	982
Chloride (Cl^-)	16,000	19,700	23,400
Fluoride (F^-)	292	409	497
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	584	779	831
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	17,500	27,800	40,300
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	16,500	19,800	29,100
Phenylarsine Oxide (C_6H_5AsO)	Trace[b]	Trace[b]	119
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	127	166	317
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	ND[a] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	9,960	17,900	22,500
Oxalate ($C_2O_4^{-2}$)	3,520	3,000	1,380
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)

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

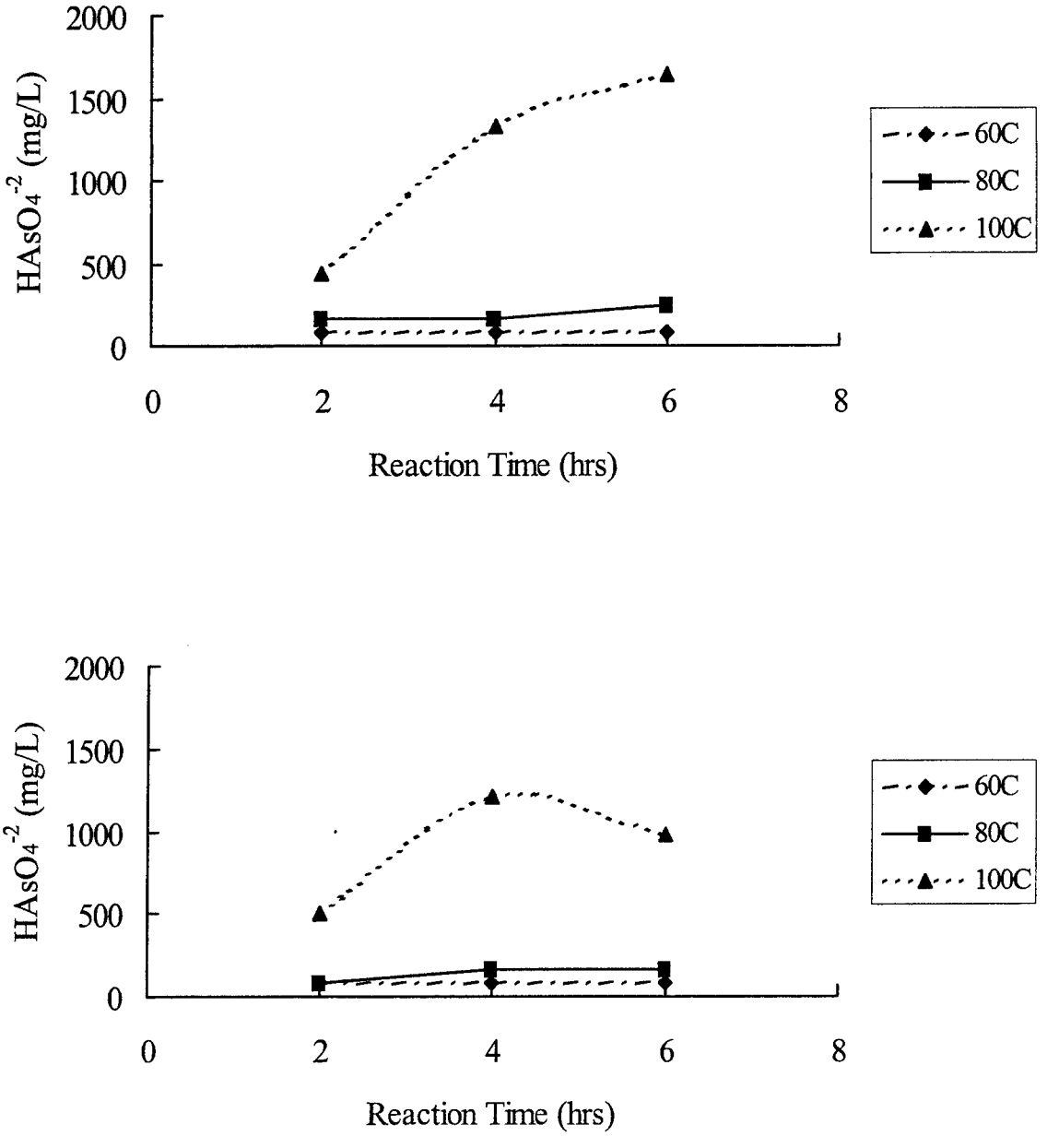


Figure 43. Dissolved Inorganic Arsenate Ion ($HAsO_4^{-2}$) as a Function of Reaction Time. The top panel is the 1:50 loading data, and the bottom panel is the 1:25 loading data. Non-detect values were plotted as 80 mg/L, and trace values were plotted as 160 mg/L.

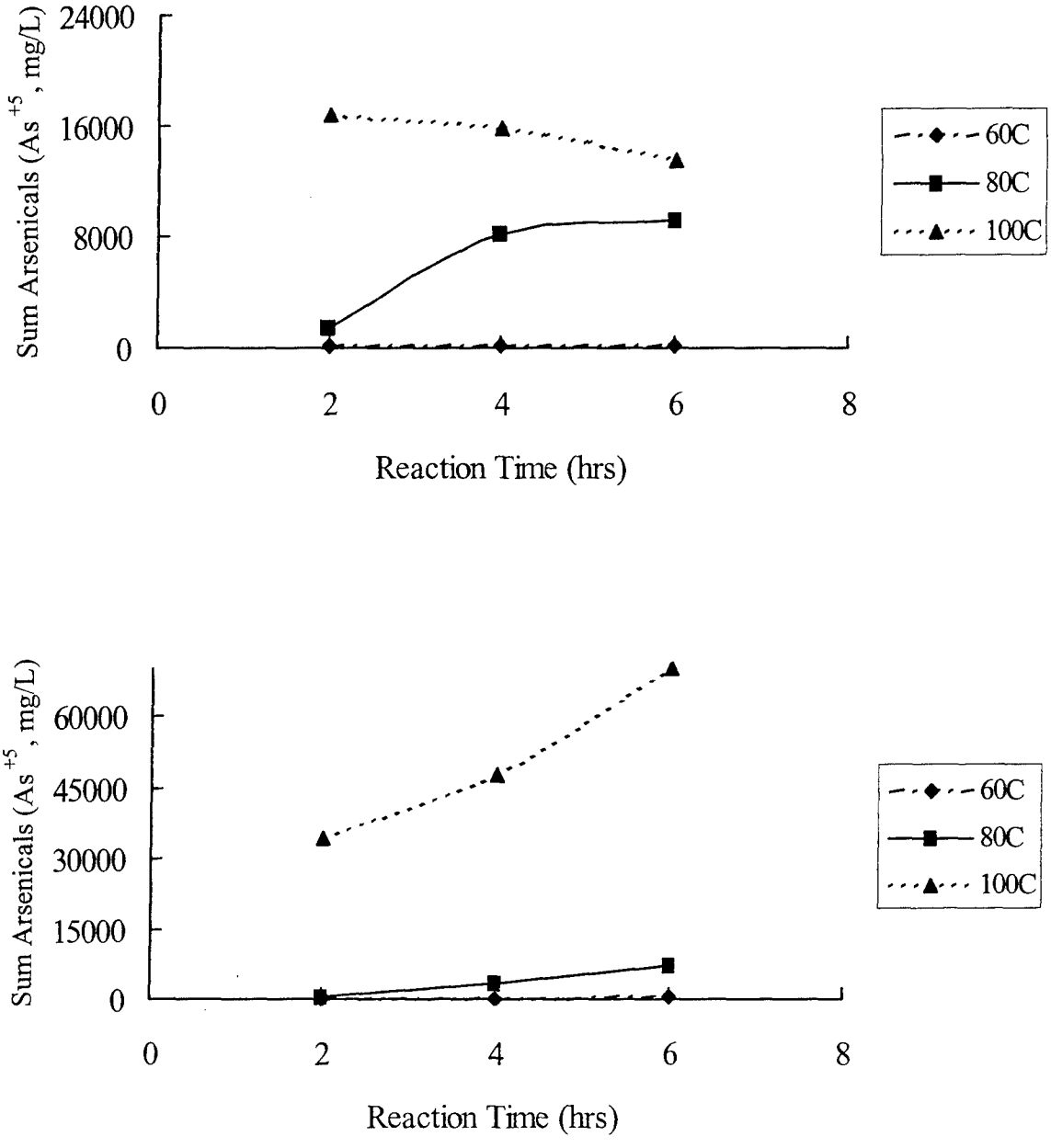


Figure 44. Sum of Dissolved Pentavalent Organo-Arsenicals as a Function of Reaction Time. The top panel is the 1:50 loading data, and the bottom panel is the 1:25 loading data. Non-detect values were plotted as 25 mg/L, and trace values were plotted as 50 mg/L.

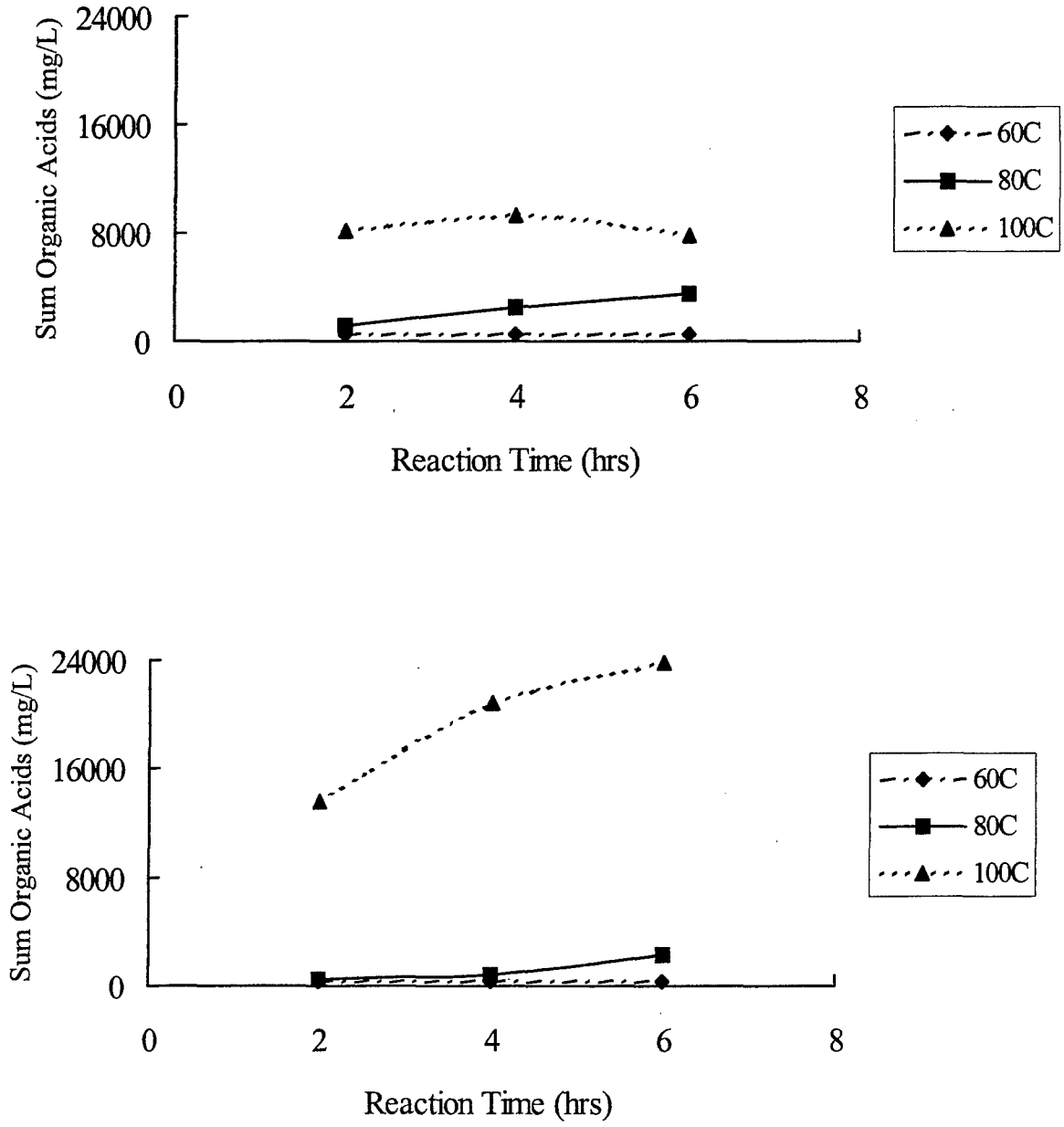


Figure 45. Sum of Dissolved Organic Acids as a Function of Reaction Time. The top panel is the 1:50 loading data, and the bottom panel is the 1:25 loading data. Non-detect values were plotted as 75 mg/L, and trace values were plotted as 150 mg/L.

3.5.5 Isolation and Characterization of Solids from Small-Scale Runs.

The solids contained in terminal neutralent samples from the reaction time/reaction temperature/arsinol loading experiment were isolated, in order to characterize the solid fraction contained in these samples. The solids were isolated by vacuum filtration through a 0.8 μm cellulose nitrate filter, after which 50 mL of 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. In addition to the solids, the filtrate (but not the deionized water wash) was also analyzed for total metals.

The isolated solids were analyzed for total metals using the digestion procedure specified in SW846, Method 3010A,[42] and some 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 EPA Method 200.8 for arsenic, iron, and manganese.[45] In addition to the isolated solids, concurrent digests of a Standard Analytical Reference Material (SARM) soil (NIST 2710, Montana Soil) were also performed. The total recovered solids and total metals data are summarized in Table 35. The average recoveries (n=2) for the SARM soil were 89.7% for arsenic, 68.3% for iron, and 83.6% for manganese. The concurrently run QC samples, such as the laboratory control spikes and sample matrix spikes (of the targeted analytes), were all within 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.

Isolated solids were analyzed for residual DA, PD, and TPA using the procedure described in Section 2.5. 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) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The residual agent data is summarized in Table 36, 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 2.6. 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 15 min. 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 37 and 38.

Table 35. Summary of Total Recovered Solids and Total Metals of Isolated Solids.

Reactor Run Conditions	Isolated Solid (g)	Total Metal (mg/kg)					
		Isolated Solid			Filtrate		
		As	Fe	Mn	As	Fe	Mn
1:50 at 60°C	6.565	81,400	1,900	268,000	670	ND[a]	58,600
1:50 at 80°C	10.256	41,200	1,150	330,000	1,820	ND[a]	36,000
1:50 at 100°C	17.935	19,700	619	360,000	3,540	ND[a]	8,530
1:25 at 60°C	10.555	100,000[b]	2,330[b]	254,000[b]	1,250	ND[a]	53,100
1:25 at 80°C	14.147	72,600	2,080	268,000	3,000[b]	ND[a,b]	35,500[b]
1:25 at 100°C	19.385	21,300	1,020	355,000	12,100	8.26	7.26

a. Not detected; detection limit approximately 7 mg/kg in the filtrate.
b. Analysis performed in duplicate; reported value is the mean.

Table 36. Summary of Residual Agents Recovered from the Isolated Solids. The reported values are the averages of duplicate determinations.

Reactor Run Conditions	Concentration (mg/kg)			Mass Recovered (mg)[a]		
	DA	PD	TPA	DA	PD	TPA
1:50 at 60°C	61.9	6.61	107	0.406	0.0434	0.702
1:50 at 80°C	48.4	4.36	32.0	0.496	0.0447	0.328
1:50 at 100°C	2.17	0.404	0.733	0.0389	0.00725	0.0131
1:25 at 60°C	735	9.06	339	7.76	0.0956	3.58
1:25 at 80°C	106	5.73	185	1.50	0.0811	2.62
1:25 at 100°C	9.26	1.46	5.76	0.179	0.0283	0.112

a. Calculated using dimensional analysis and the amount of recovered solid.

Table 37. Summary of Analytical Results for the Solids Isolated from the 1:50 Loading Experiments. The results are corrected for background of any analytes detected in the extraction blank. All data reported in the original solid, with units of mg/kg.

Target Analyte	Concentration in Solid (mg/kg)		
	60 °C	80 °C	100 °C
Arsenite (AsO_2^-)	ND[a] (625)	ND[a] (635)	ND[a] (634)
Arsenate ($HAsO_4^{-2}$)	Trace[b]	ND[a] (625)	1,570
Chloride (Cl^-)	Trace[b]	ND[a] (1,510)	Trace[b]
Fluoride (F^-)	284	ND[a] (278)	ND[a] (277)
Nitrate (NO_3^-)	ND[a] (1,960)	ND[a] (1,960)	ND[a] (1,960)
Sulfate (SO_4^{-2})	ND[a] (1,760)	ND[a] (1,790)	ND[a] (1,780)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	16,400	11,500	614
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	64,700	46,600	2,400
Phenylarsine Oxide (C_6H_5AsO)	552	Trace[b]	ND[a] (396)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	2,080	904	ND[a] (198)
Acetate ($C_2H_3O_2^-$)	ND[a] (625)	ND[a] (635)	ND[a] (634)
Formate (CHO_2^-)	ND[a] (586)	ND[a] (596)	ND[a] (594)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (782)	ND[a] (794)	ND[a] (792)
Glycolate ($C_2H_3O_3^-$)	9,400	6,690	Trace[b]
Oxalate ($C_2O_4^{-2}$)	ND[a] (1,490)	ND[a] (1,510)	ND[a] (1,510)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (782)	ND[a] (794)	ND[a] (792)

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

Table 38. Summary of Analytical Results for the Solids Isolated from the 1:25 Loading Experiments. The results are corrected for background of any analytes detected in the extraction blank. All data reported in the original solid, with units of mg/kg.

Target Analyte	Concentration in Solid (mg/kg)		
	60 °C	80 °C	100 °C
Arsenite (AsO_2^-)	ND[a] (644)	ND[a] (639)	ND[a] (643)
Arsenate ($HAsO_4^{-2}$)	1,030	326	1,540
Chloride (Cl^-)	Trace[b]	Trace[b]	Trace[b]
Fluoride (F^-)	406	Trace[b]	ND[a] (281)
Nitrate (NO_3^-)	ND[a] (1,960)	ND[a] (1,960)	ND[a] (1,960)
Sulfate (SO_4^{-2})	ND[a] (1,530)	ND[a] (1,800)	ND[a] (1,810)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	39,300	17,100	2,920
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	49,300	43,300	6,280
Phenylarsine Oxide (C_6H_5AsO)	562	Trace[b]	ND[a] (402)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	5,070	3,110	210
Acetate ($C_2H_3O_2^-$)	ND[a] (644)	ND[a] (639)	ND[a] (643)
Formate (CHO_2^-)	ND[a] (604)	ND[a] (599)	ND[a] (602)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (805)	ND[a] (798)	ND[a] (803)
Glycolate ($C_2H_3O_3^-$)	23,400	11,000	1,670
Oxalate ($C_2O_4^{-2}$)	ND[a] (1,530	ND[a] (1,540)	ND[a] (1,530)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (805)	ND[a] (798)	ND[a] (803)

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

Using dimensional analysis, and the data found in Table 35, arsenic mass recoveries were calculated for both the isolated solids, and the filtrates. The 1:50 loading experiments had 846 mg of arsenic loaded into the reactor as arsinol, and the 1:25 loading experiments had 1,690 mg of arsenic loaded into the reactor. These mass loadings of arsenic were calculated using an average feedstock density of 1.48 g/mL, and a total arsenic concentration of 286,000 mg/kg (Sections 3.23 and 3.24). The total (solid + filtrate) arsenic recoveries ranged from 71.3 to 107% across all reactions. The recoveries based on isolated solid and filtrate are illustrated in Figure 46. The arsenic recoveries for the isolated solid appear to be negatively correlated with reaction temperature, while recoveries for the filtrate appear to be positively correlated with reaction temperature. The recoveries calculated for the 1:25 loading reaction conducted at 100 °C do not fit the pattern observed for the 1:50 loading experiments, and might be due to exhaustion of the permanganate during this run. Another possible reason for the discrepancy is the solids from 1:25 loading experiment conducted at 100 °C were not isolated until 5 days after the reaction, while all other solids were isolated 1-2 days after the reactions were terminated.

The residual agents determined to be in the isolated solids are negatively correlated with reaction temperature. These relationships are illustrated in Figure 47. The residual PD concentrations appear to be independent of arsinol loading, with no significant differences in residual PD observed between loadings. There are significant differences between arsinol loadings for DA and TPA, particularly at the lower reaction temperatures. The differences are not significant at the 100 °C reaction temperature. While some of the residual agent concentrations are elevated, the total mass of agent contained in the solids is a small percentage of the agent which was loaded into the reactor. Overall, the amount of agent remaining in the solids ranged from 0.001 to 0.5% for the 1:50 loading reactions, and 0.001 to 1.3% for the 1:25 loading reactions. In both loadings, it is the TPA which makes up the largest percent of agent remaining, with TPA values ranging from 0.001 to 1.3 % for both loadings. With one exception (1:25 loading conducted at 60 °C), the residual DA and PD remaining are all less than 0.05% of the agents loaded into the reactor.

The pentavalent organo-arsenical and organic acid reaction products (Tables 37 and 38) are negatively correlated with reaction temperature, following the trend observed for the residual agents. The concentrations of inorganic arsenate were more variable, with no clear trend. This lack of a clear trend might also be due to variations in how long each neutralent was allowed to age before the solids were isolated. The chloride concentrations ranged from non-detect to trace, suggesting the chloride was not being immobilized within the solid fraction. Using the reporting limit of 1,510 mg/kg, and the total recovered solids (Table 35) this corresponds to 1.3 to 3.9% of the average mass of chloride determined to be in the bulk neutralent. The percent chloride remaining in the solids appears to be positively correlated with reaction temperature, but not arsinol loading.

3.5.6 Composition of Isolated Solids as a Function of Reaction and Storage Times.

The data collected on the solids isolated from the small-scale reactor runs (Section 3.5.5) suggested the chemical composition of the solid could vary, depending on how long the neutralent ages before being filtered. While there does appear to be a correlation, it was desired to investigate this change in more detail, under controlled conditions.

Using the micro-scale approach discussed in Section 2.1, a series of reactions using 5 mL of 20 wt% $NaMnO_4$ and 100 µL of fill materiel (1:50 loading) from GTR CA-0276 were conducted. Reaction temperatures of 60 and 80 °C at reaction times of 6, 8, 18, and 24 hr were investigated for zero day storage. Reaction temperatures of 60 and 80 °C at a reaction time of 6 hr were investigated for 5 and 12 days of storage. At each reaction time point, multiple vials were removed from the hotplate, and immersed in a water/ice bath for 10 min to inhibit the reaction. Some of the vials were stored (capped) at ambient temperature under engineering controls. Two of the vials were immediately vacuum filtered (0.45 µm), and acted as the zero storage time point. Once the neutralent liquid was pulled through,5 mL of ice cold deionized water was used to rinse the solids. The solids were then dried in a desiccator (ambient temperature and pressure) until analyses were conducted. After either five or 12 days of storage, solids in the remaining vials were also isolated as described above.

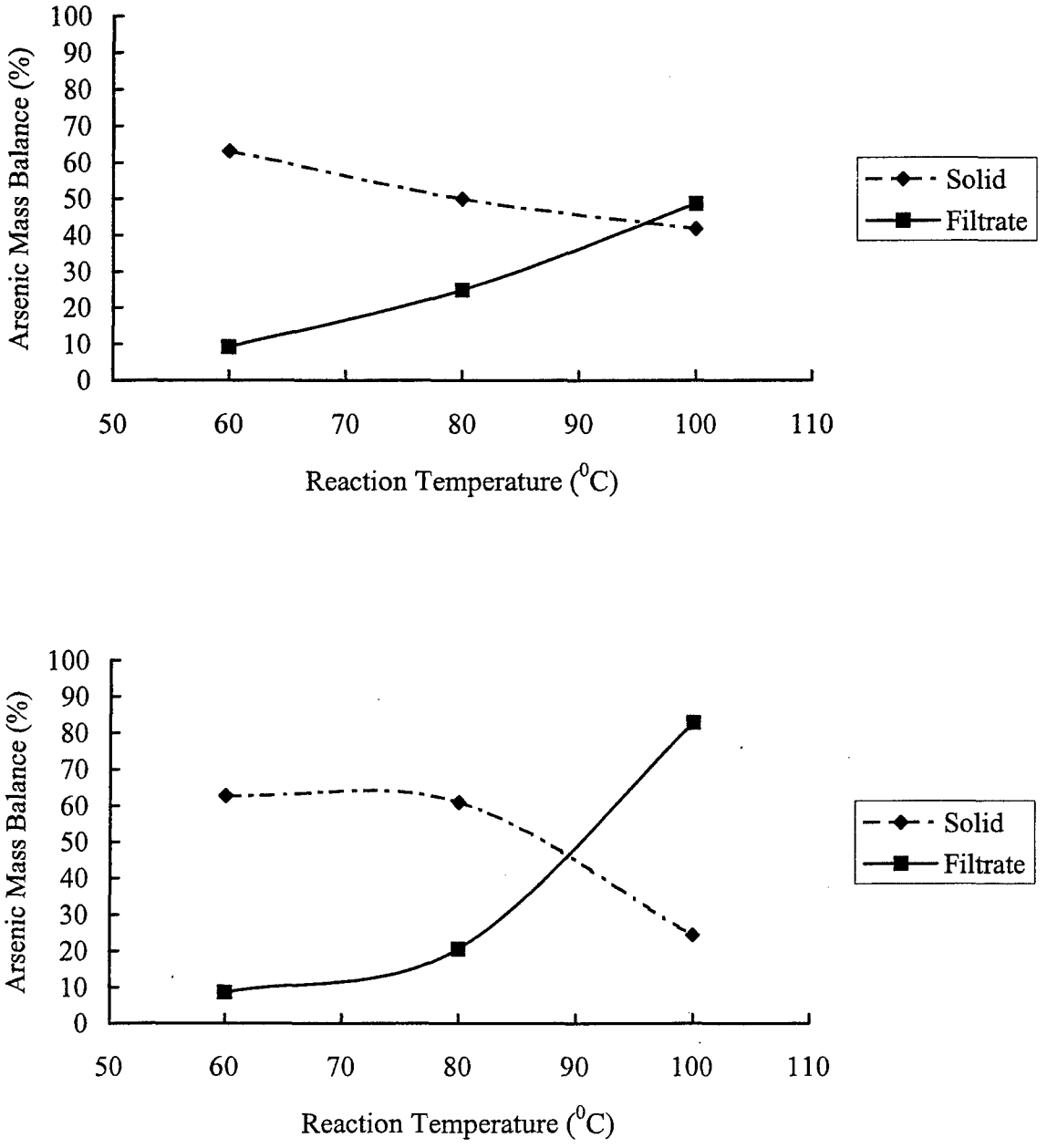


Figure 46. Arsenic Mass Balance as a Function of Reaction Temperature. The upper panel is the 1:50 loading reactions, and the bottom panel is the 1:25 loading reactions.

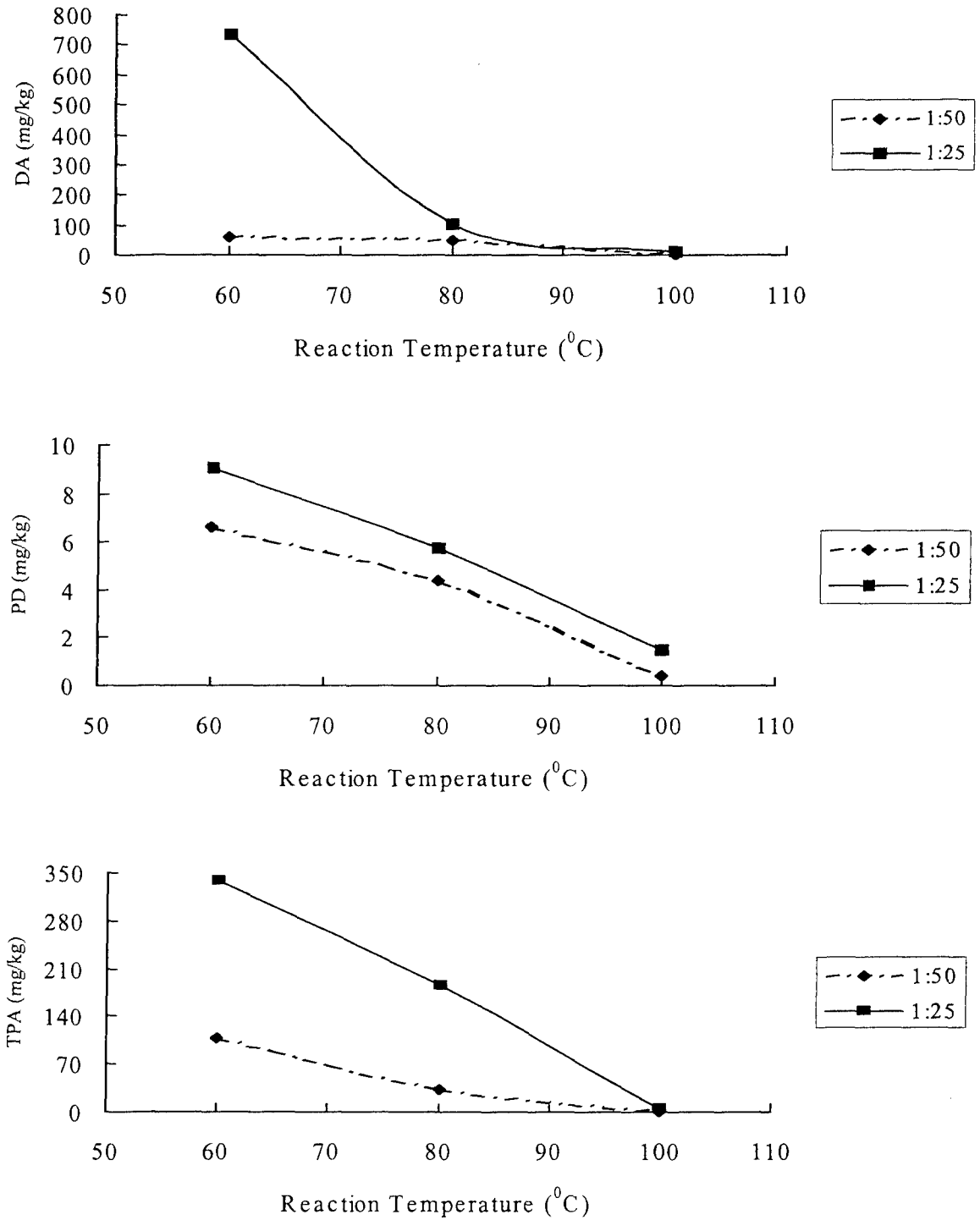


Figure 47. Residual Agents in the Isolated Solids as a Function of Reaction Temperature. The upper panel is the DA, the middle panel is the PD, and the lower panel is the TPA. All plotted values are averages of duplicate determinations.

Isolated solids were analyzed for residual DA, PD, and TPA using the procedure described in Section 2.5. 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) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The total recovered solids is illustrated in Figure 48, and the residual agent data is illustrated in Figures 49 through 52. 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 2.6. 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 15 min. 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 illustrated in Figures 53 and 54.

The isolated solids were analyzed for total metals using the digestion procedure specified in SW846, Method 3010A,[42] and some digestions were performed in duplicate. Approximately 50 mg of sample (exact weight recorded) was digested, and the final digest volume brought to 0.05 Ls. The digests were analyzed using EPA Method 200.8 for arsenic, iron, and manganese.[45] In addition to the isolated solids, concurrent digests of a SARM soil (NIST 2710, Montana Soil) were also performed. The total metals data are illustrated in Figures 55 through 58. The average recoveries (n=2) for the SARM soil were 89.5% for arsenic, 64.9% for iron, and 85.2% for manganese. The concurrently run QC samples, such as the laboratory control spikes and sample matrix spikes (of the targeted analytes), were all within 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 total mass of solids recovered during this experiment is illustrated in Figure 48. The solids recovered, as a function of reaction time, is somewhat variable, with more solids generated during the 80 °C reaction, as would be expected due to enhanced thermal degradation of the MnO_4^{-2} to the insoluble MnO_2. There is a strong positive correlation of solids generated as a function of storage time, with increases of 15 mg per day from the neutralent generated at 60 °C, and 19 mg/day from the neutralent generated at 80 °C. It does not appear these increases are statistically different from one another.

The residual agent concentrations, as a function of reaction time, are illustrated in Figures 49 and 50. The residual agent concentrations, as expected, decrease with reaction time. Using an average feedstock density of 1.48 g/mL, and the weight percent composition of the feedstock (Sections 3.21 and 3.24), 89.5 mg DA, 41.9 mg PD, and 6.07 mg TPA were loaded into each reaction vessel. While the agent concentrations are high, when calculated on a mass basis, the residual agents in the worst case are <3% of the total PD, and <7% of the total DA and TPA which was loaded into each reactor. Under the reaction conditions employed, and the apparent first-order reaction kinetics, the average reaction half-lifes were calculated to be 7 hr for DA, 7.2 hr for PD, and 13.7 hr for TPA. These half-lifes were calculated based on the 6 through 24-hr reaction times. The residual agent concentrations, as a function of storage time, are illustrated in Figures 51 and 52. The residual agent concentrations are negatively correlated with storage time, and appear to follow first-order reaction kinetics. The average half-lives of the residual agents were calculated to be 1.5 days for DA, 1.2 days for PD, and 2.4 days for TPA under the experimental conditions utilized.

Selected reaction product concentrations, as a function of reaction time, are illustrated in Figure 53. The inorganic arsenate and glycolate are negatively correlated with reaction time, while the DPAOA is somewhat variable, with no clear trends observed. The decrease in arsenate concentration over time is somewhat surprising, and suggests a desorption is taking place during the reaction. This is supported by the dissolved arsenate concentrations, which increased over time during similar reactions (Section 3.5.4, Figure 43). Selected reaction product concentrations, as a function of storage time, are illustrated in Figure 54. The inorganic arsenate is positively correlated with storage time, while the glycolate is negatively correlated with storage time. The DPAOA is somewhat variable, with no clear trends observed. The increase in arsenate concentrations suggest arsenate is being sorbed onto the solids during storage, which took place at ambient temperature. This observation is supported by another ambient storage study (Section 3.6.4), where the dissolved arsenate decreased to non-detect levels during storage of the bulk neutralent.

Total metal concentrations, as a function of reaction time are illustrated in Figure 55, and the corresponding absolute mass values are illustrated in Figure 56. While concentration of total arsenic tends decreases with reaction time, the total mass of arsenic contained in the solid stays fairly constant over the reaction times evaluated. The same general pattern holds for total iron. The total manganese concentration and total mass tend to increase with reaction time, as is expected from decomposition of MnO_4^{-2} to insoluble MnO_2. The apparent decrease in total arsenic and iron concentrations might be attribute to simple dilution by the formation of MnO_2. Total metal concentrations and mass, as a function of storage time, are illustrated in Figures 57 and 58. The masses of total arsenic and iron initially increase, then tend to level off during storage. The mass of total manganese increases in a linear fashion, with the 60 °C neutralent gaining 4.8 mg manganese per day of storage, and the 80 °C neutralent gaining 7.1 mg of manganese per day of storage. If the linear relationship holds until all the MnO_4^{-2} is decomposed to MnO_2, it would take 83 or 54 days of storage for all of the soluble MnO_4^{-2} to be converted to insoluble MnO_2.

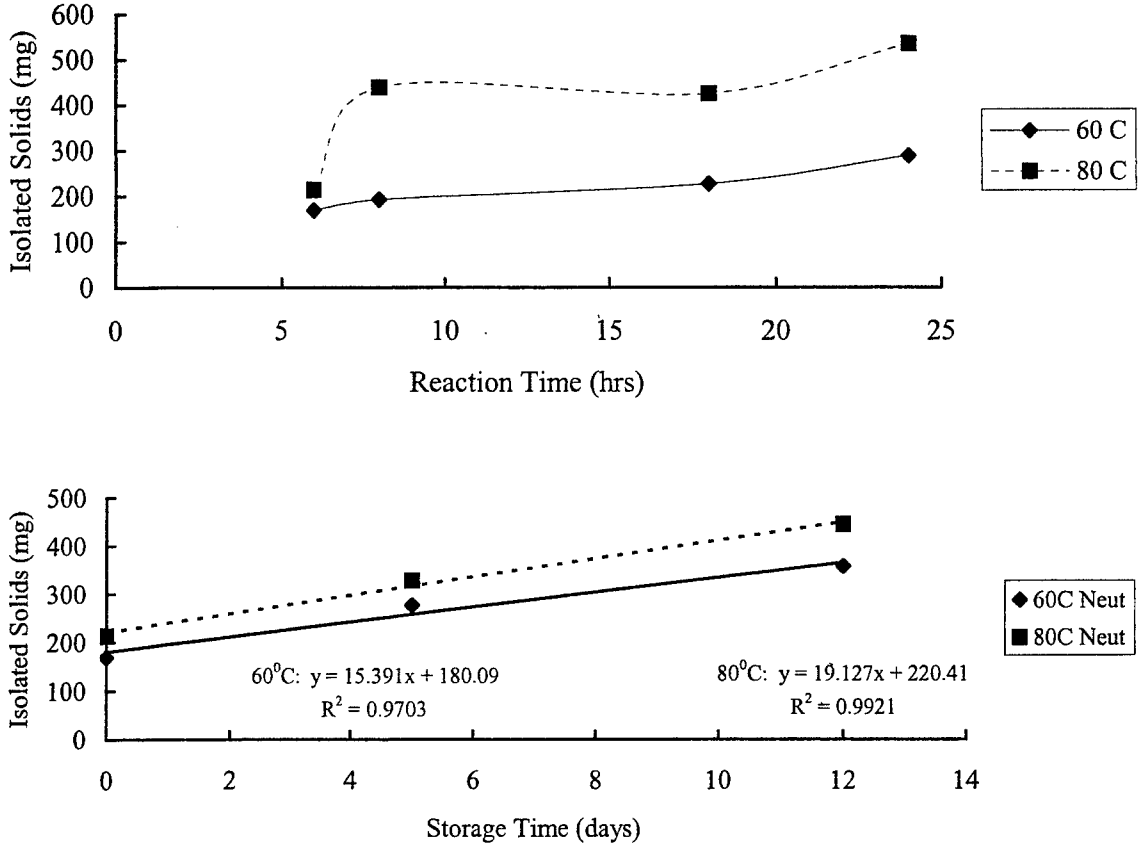


Figure 48. Total Mass of Isolated Solids Recovered. The upper panel is the amount of solids recovered as a function of reaction time (zero days of storage), and the bottom panel is the amount of solids recovered as a function of storage time (6-hr reaction time).

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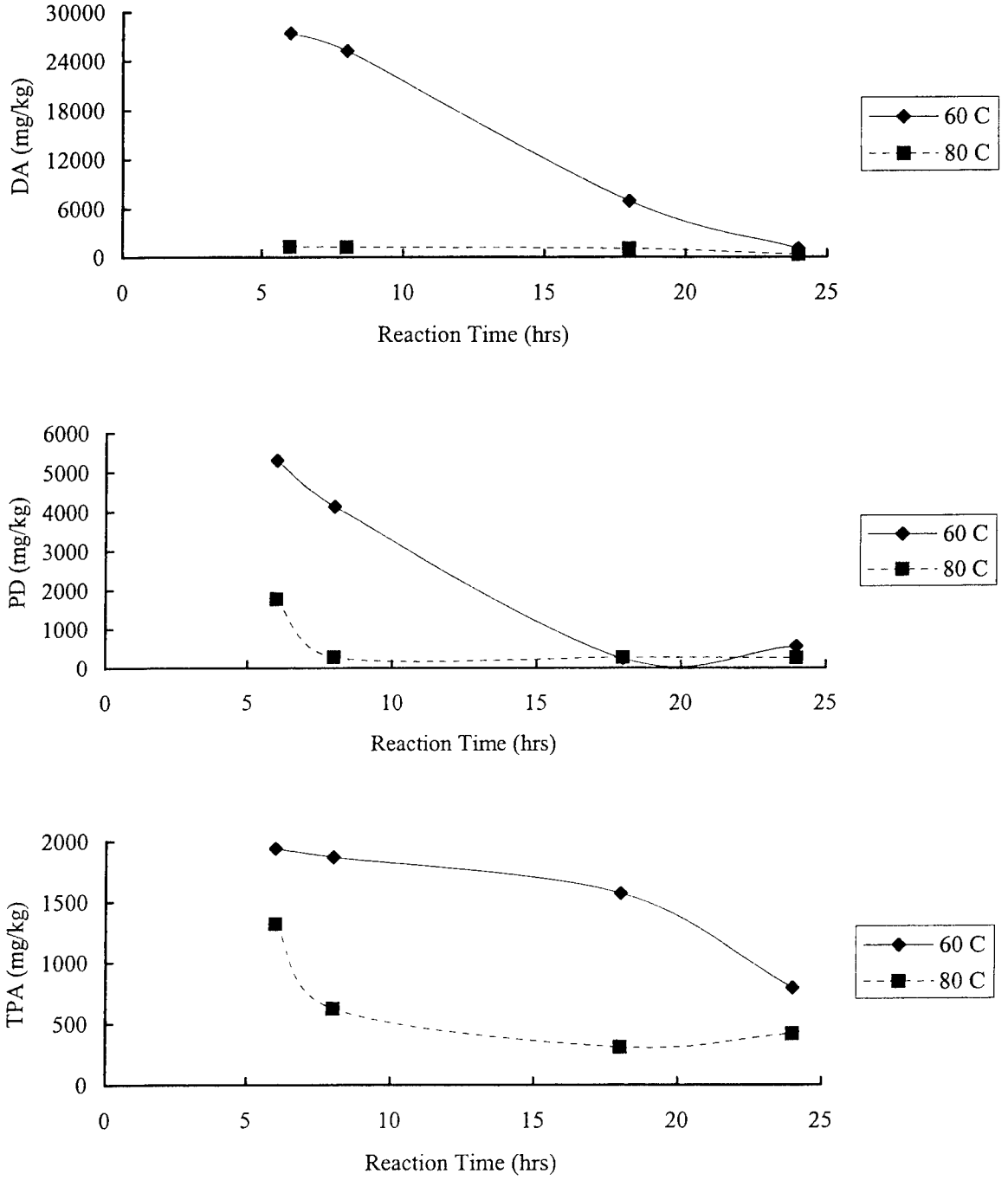


Figure 49. Agent Concentration in the Isolated Solid as a Function of Reaction Time when the Solids are Immediately Isolated (Day 0). The top panel is DA, the middle panel is PD, and the bottom panel is TPA.

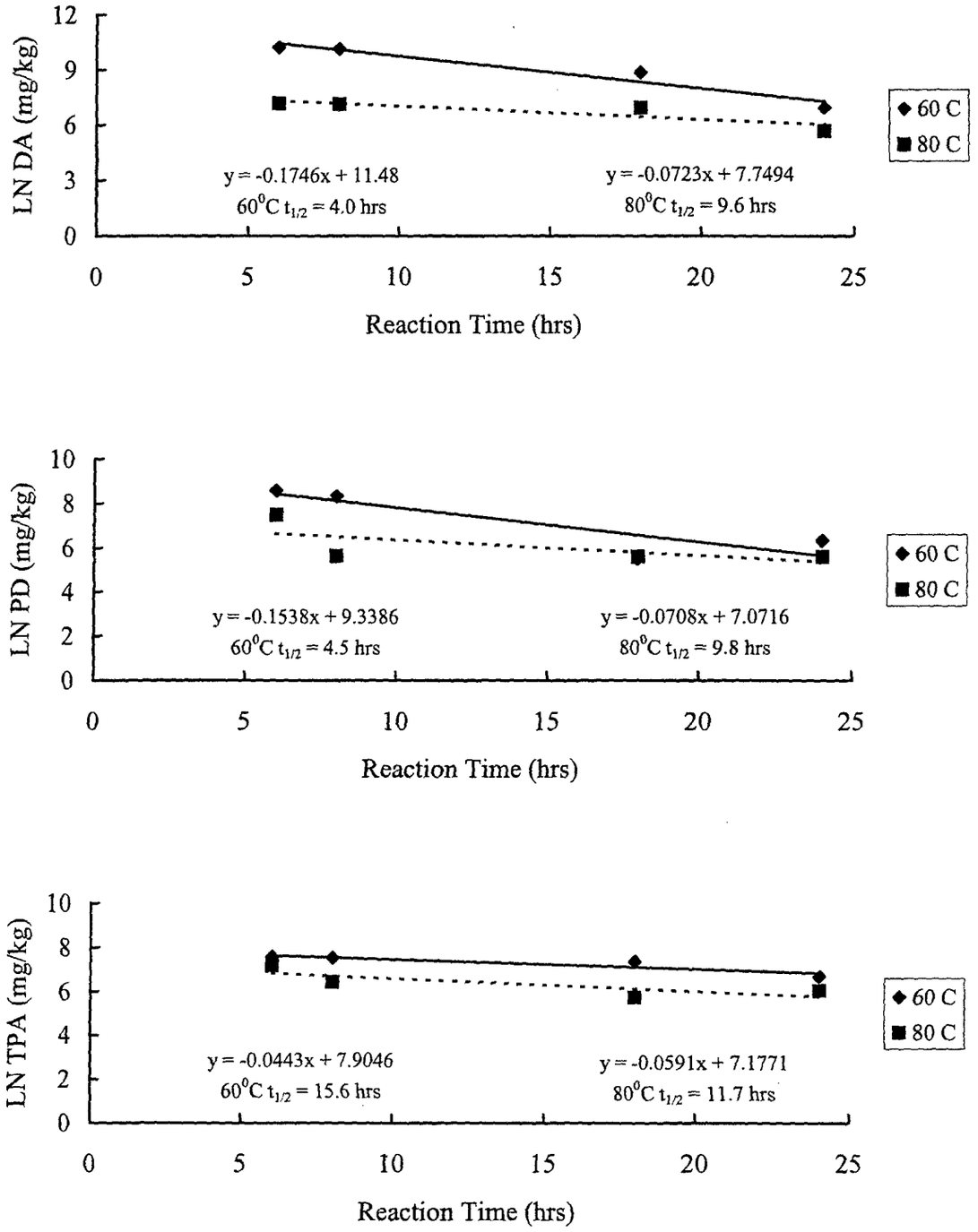


Figure 50. Natural Log Agent Concentration in the Isolated Solid as a Function of Reaction Time when the Solids are Immediately Isolated (Day 0). The top panel is DA, the middle panel is PD, and the bottom panel is TPA.

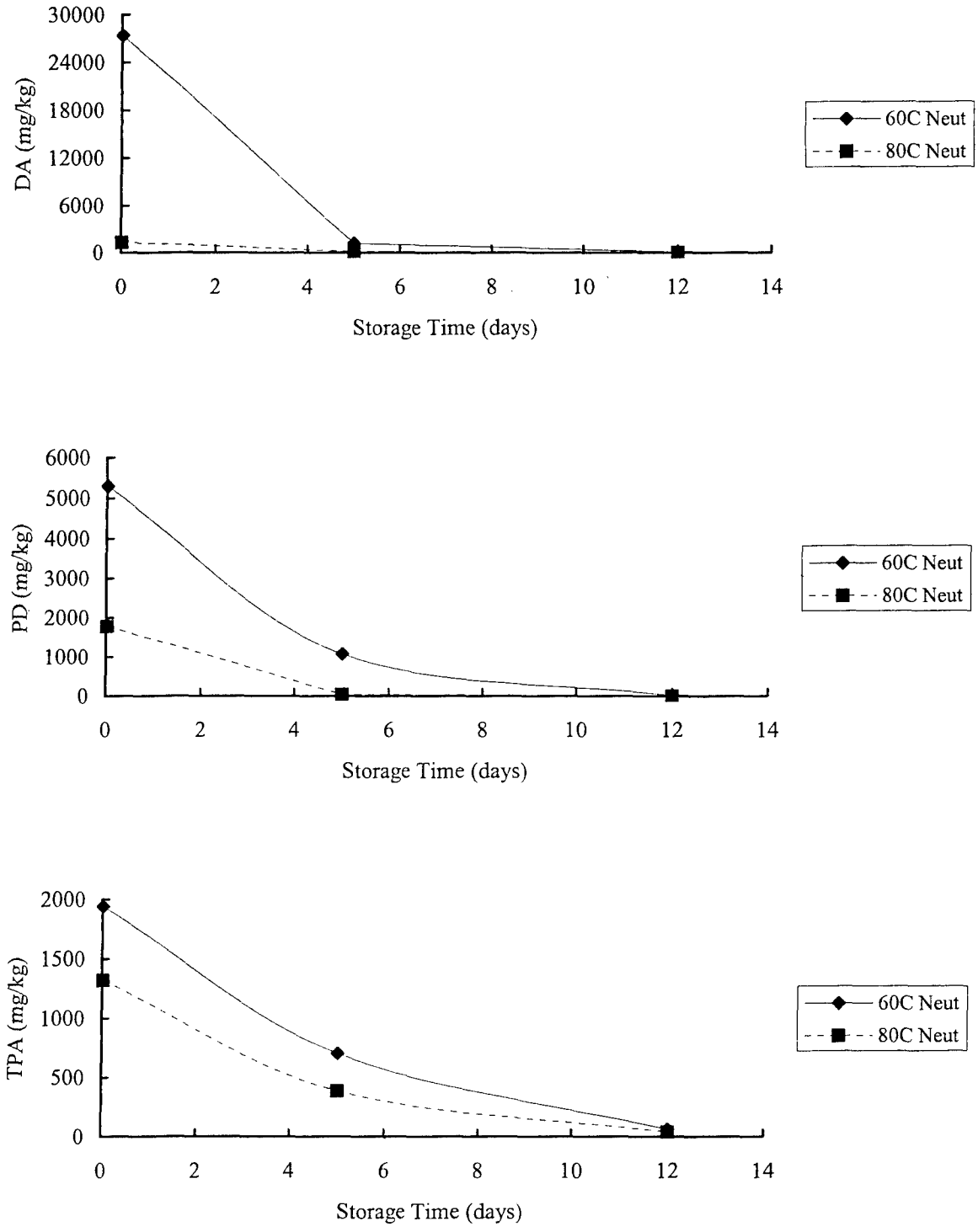


Figure 51. Agent Concentration in the Isolated Solid as a Function of Storage Time when the Solids are Isolated from 6-hr Neutralent. The top panel is DA, the middle panel is PD, and the bottom panel is TPA.

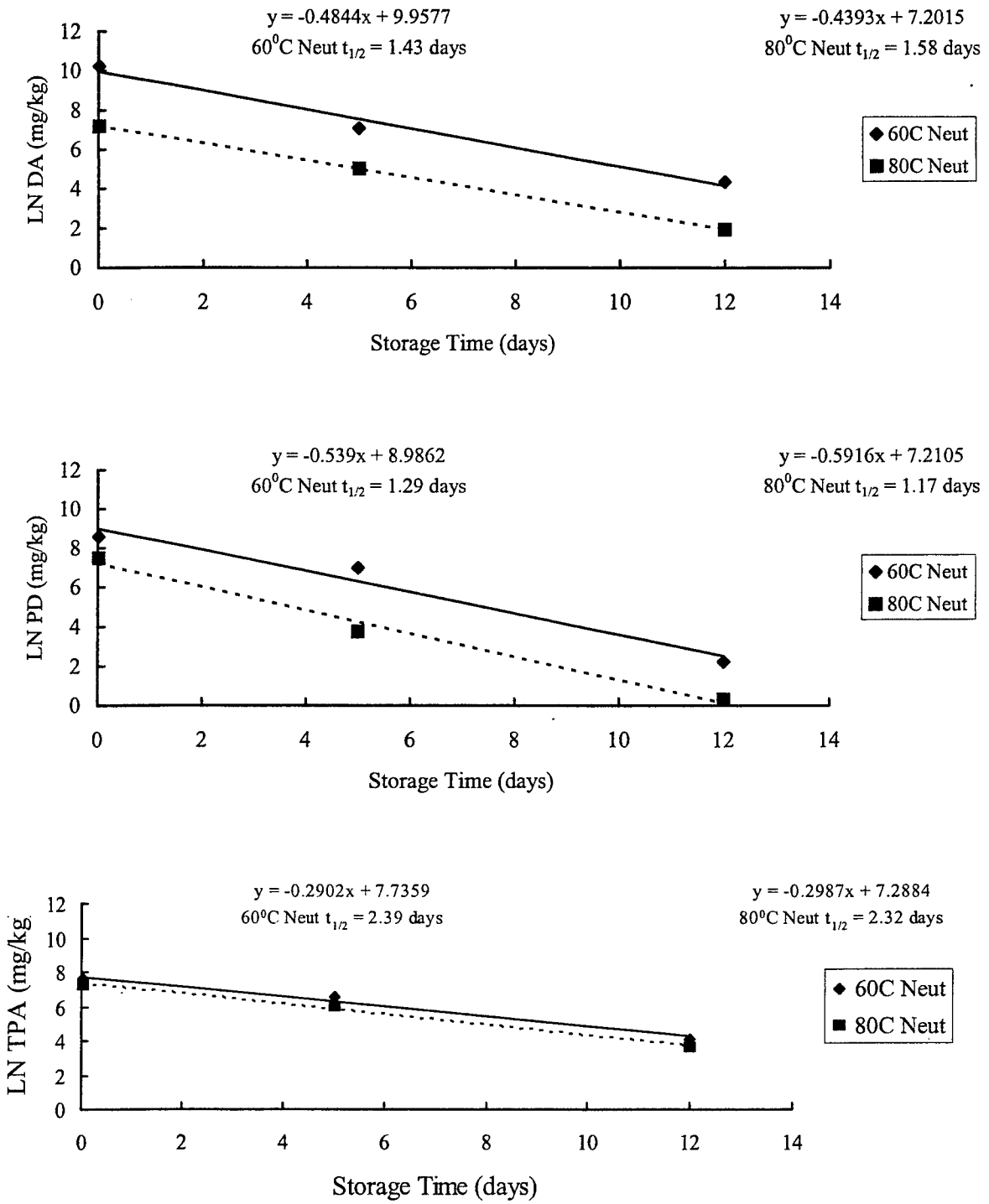


Figure 52. Natural Log Agent Concentration in the Isolated Solid as a Function of Storage Time when the Solids are Isolated from 6-hr Neutralent. The top panel is DA, the middle panel is PD, and the bottom panel is TPA.

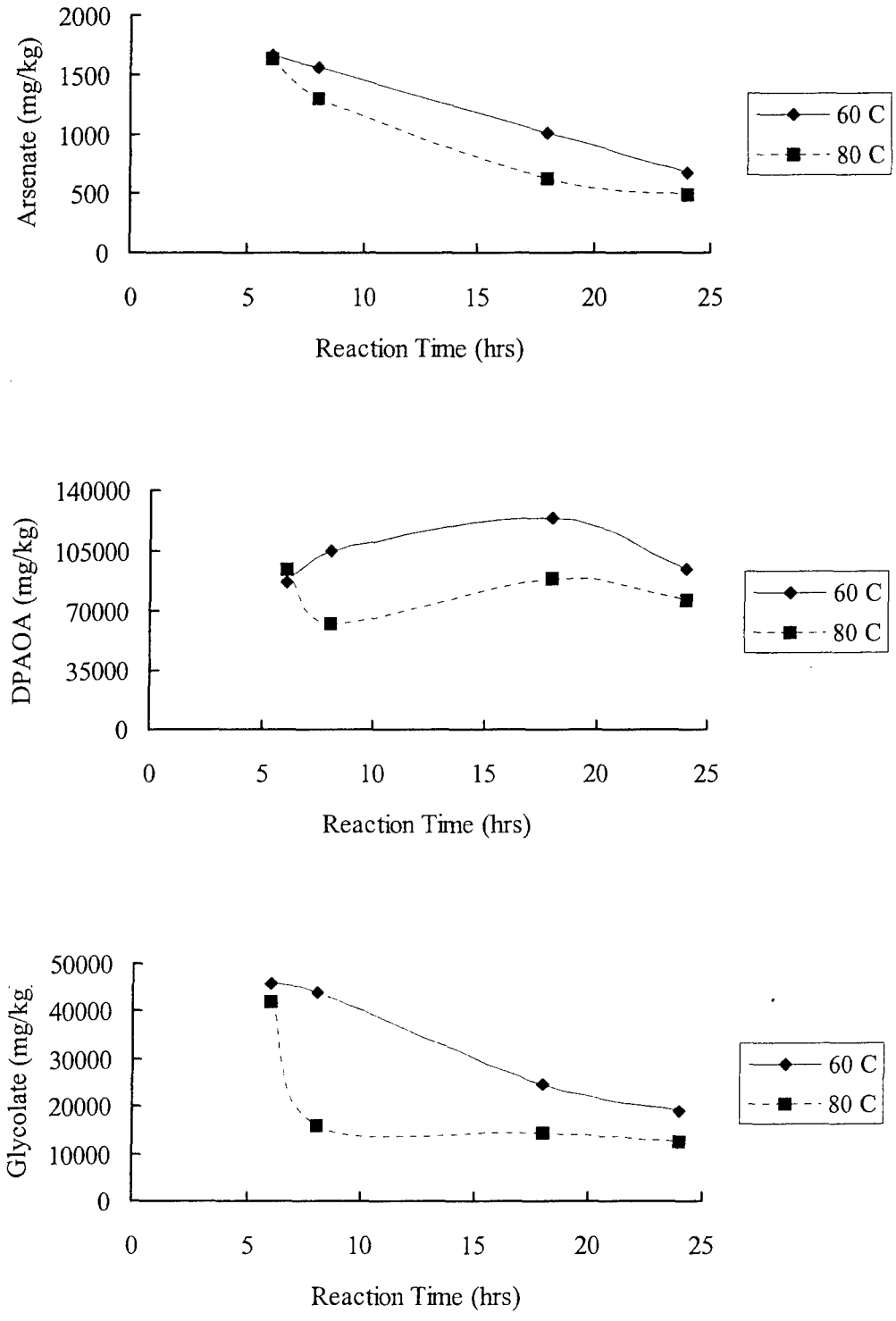


Figure 53. Reaction Product Concentration in the Isolated Solid as a Function of Reaction Time when the Solids are Immediately Isolated (Day 0). The top panel is arsenate, the middle panel is DPAOA, and the bottom panel is glycolate.

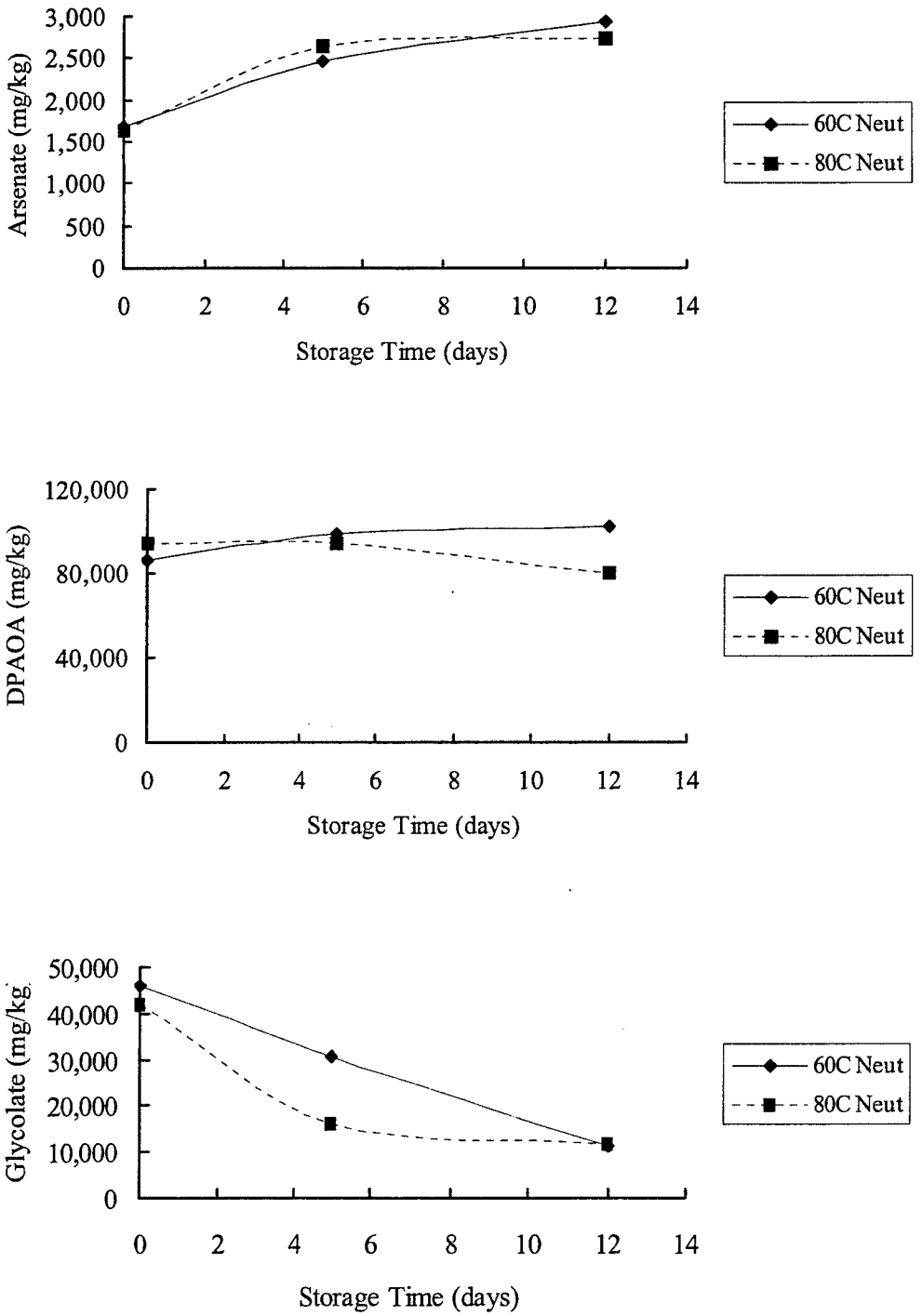


Figure 54. Reaction Product Concentration in the Isolated Solid as a Function of Storage Time when the Solids are Isolated from 6-hr Neutralent. The top panel is arsenate, the middle panel is DPAOA, and the bottom panel is glycolate.

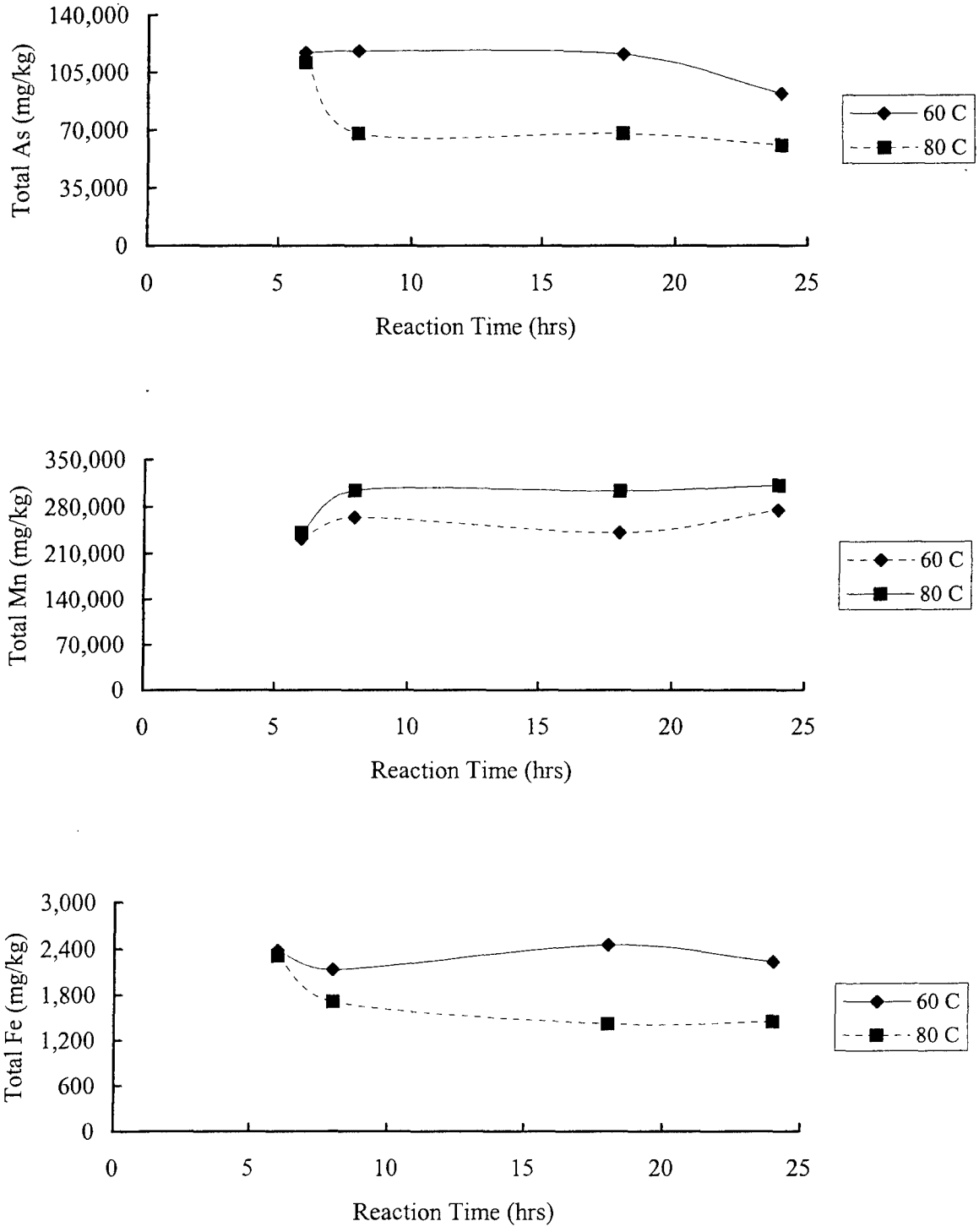


Figure 55. Total Metal Concentration (mg/kg) in the Isolated Solid as a Function of Reaction Time when the Solids are Isolated Immediately (Day 0). The top panel is arsenic, the middle panel is manganese, and the bottom panel is iron.

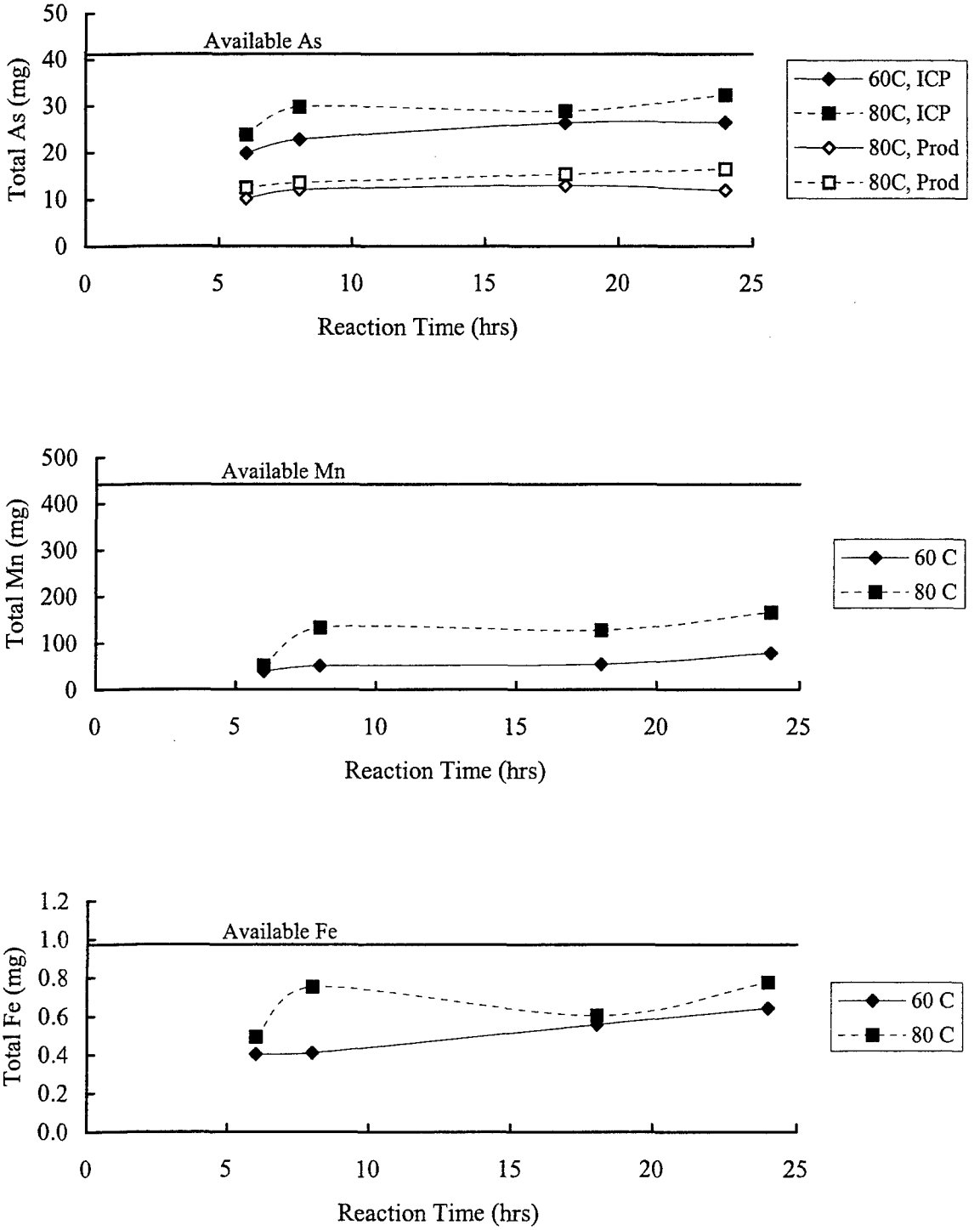


Figure 56. Total Metal (mg) in the Isolated Solid as a Function of Reaction Time when the Solids are Isolated Immediately (Day 0). The top panel is arsenic (open symbols are arsenic from dimensional analysis of products), the middle panel is manganese, and the bottom panel is iron.

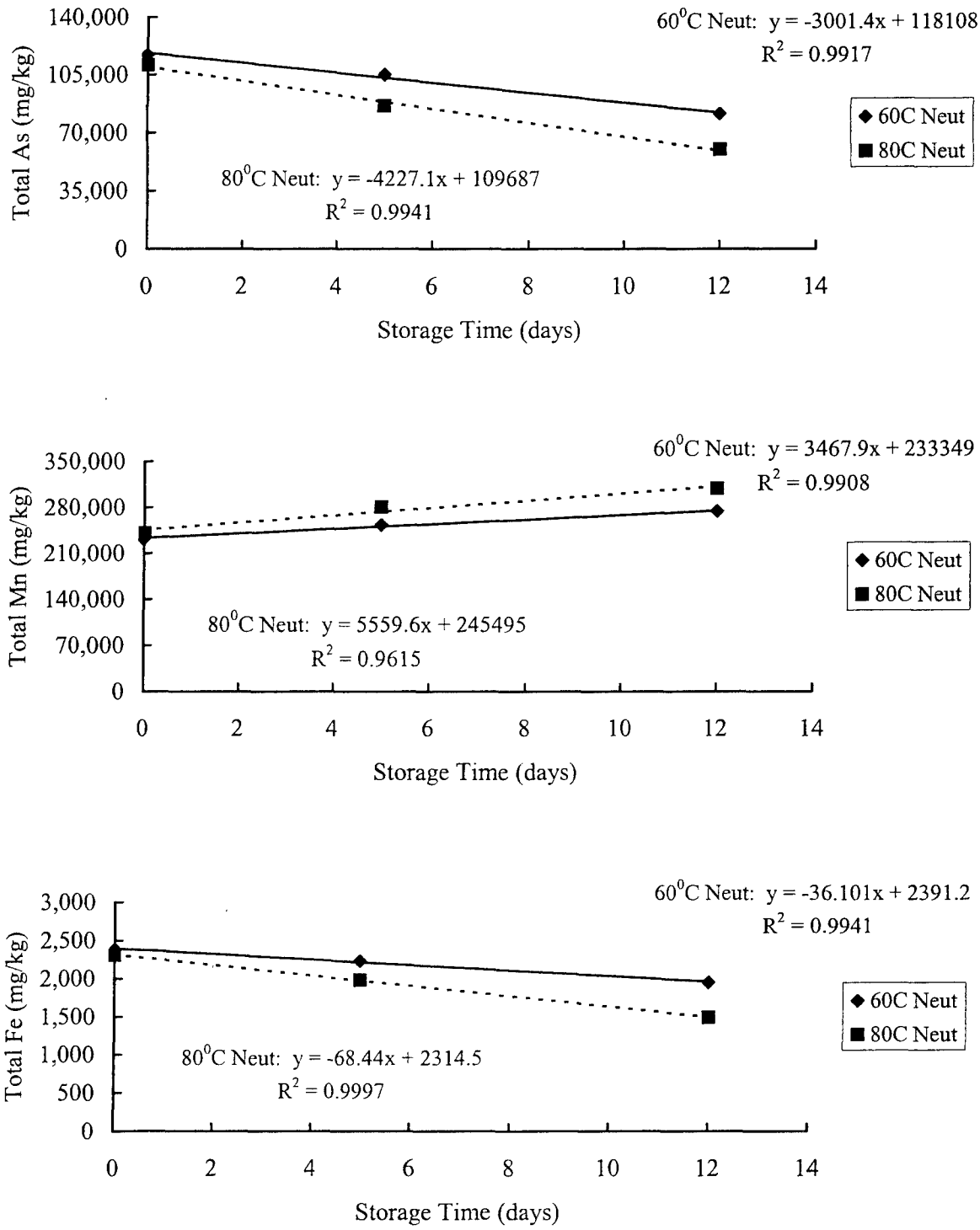


Figure 57. Total Metal Concentration (mg/kg) in the Isolated Solid as a Function of Storage Time when the Solids are Isolated from 6-hr Neutralent. The top panel is arsenic, the middle panel is manganese, and the bottom panel is iron.

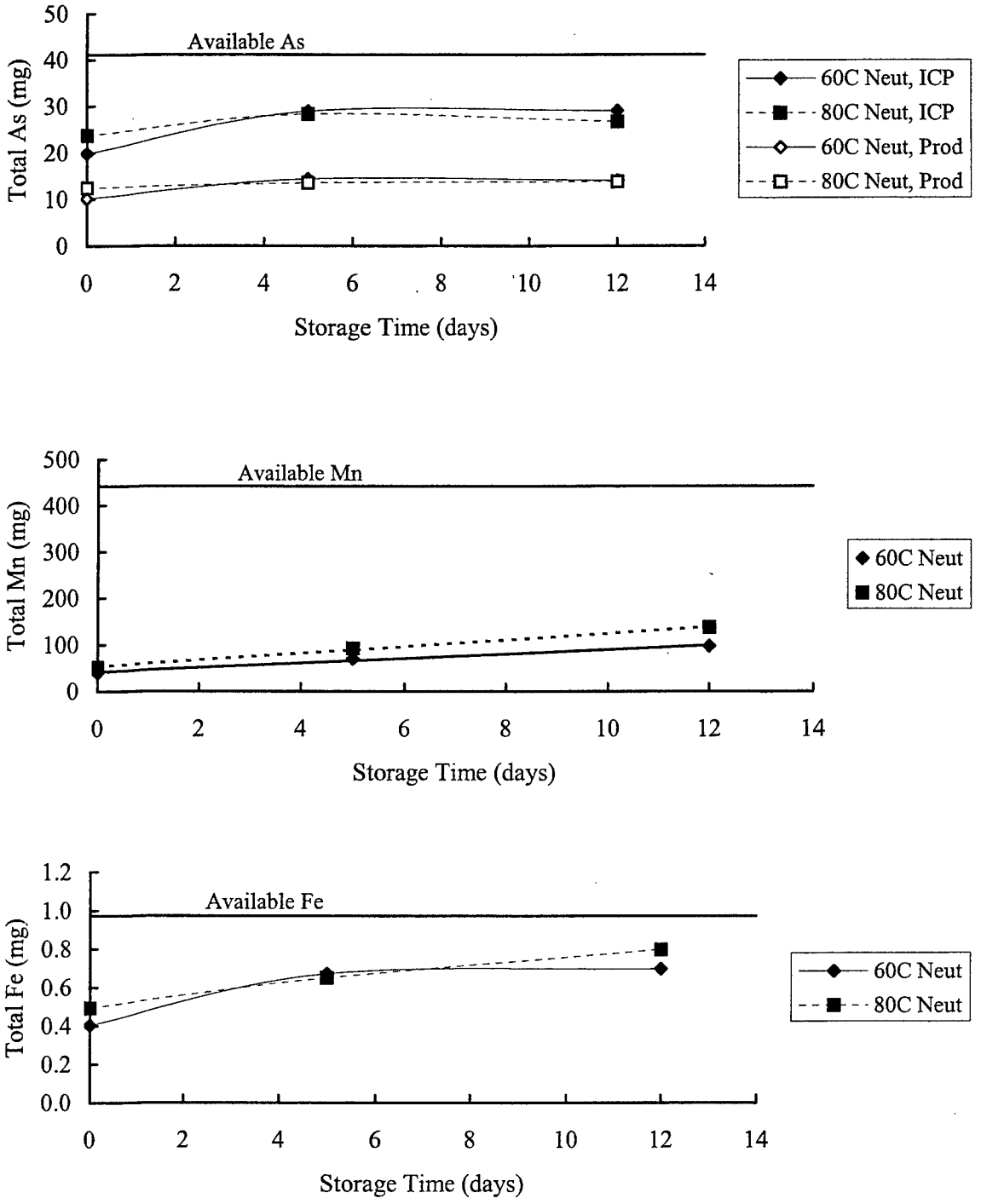


Figure 58. Total Metal (mg) in the Isolated Solid as a Function of Storage Time when the Solids are Isolated from 6-hr Neutralent. The top panel is arsenic (open symbols are arsenic from dimensional analysis of products), the middle panel is manganese, and the bottom panel is iron.

3.6 Large-Scale Demonstration of Permanganate Reagent.

A series of large-scale (500 and 1,000 mL) reactions were conducted to generate samples for a neutralent storage study, RCRA waste characterization, and material compatibility testing. These reactions were all conducted at an arsinol to reagent loading of 1:50, at reaction temperatures of 60 and 80 °C. These reactions were conducted using a composite feedstock of arsinol from all the GTRs.

3.6.1 Reaction Conditions.

The composite feedstock was prepared by mixing together fill materiel from the following GTRs: 123.6 g from CA-0175, 75.1 g from CA-0178 (liquid fraction), 46.7 g from CA-0276, and 134.0 g from CA-0280. The agent concentrations in the composite feedstock were calculated, using dimensional analysis, and the weight percent compositions of the individual feedstocks (Section 3.2.1). The composite feedstock was calculated to contain 594,000 mg/kg of DA; 284,000 mg/kg of PD; and 36,500 mg/kg of TPA.

Samples for the neutralent storage study were prepared using the stainless steel reactor system described in Section 2.3. In these runs, a piece of copper (1/8 inch copper tubing, approximately 2.5 g) and common steel (wire, approximately 15 g) were suspended in the reaction vessel by means of a Teflon string, and then 10 mL of composite arsinol was added. The reactor was then sealed, and charged to 5-8 psi with nitrogen. Five hundred milliliters of pre-warmed reagent (approximately 40 °C) was added through the pressure pipet, using a 25-30 psi nitrogen push. Once all the reagent was added, stirring was started, and the reaction temperature set-point raised to either 60 or 80 °C. Once the desired reaction temperature was reached, neutralent samples were removed from the reactor at various time points via a sampling valve. Neutralent samples (approximately 5 mL per sample) were removed from the reactor at 1.25, 3.5, and 5.5 hr after the desired reaction temperature was achieved. In both cases, the runs were terminated after 5.5 hr.

Samples for the RCRA waste characterization and material compatibility studies were prepared using the glass reactor system described in Section 2.3. The glass reaction flasks were 2 L Erlenmeyer type flasks, equipped with air cooled condensers. Stirring was accomplished by use of a TFE coated stir bar, and a combination magnetic stir plate/hot plate, with the reaction stirred at moderate speed throughout the reaction. Prior to any runs being conducted, hot plate settings were calibrated to desired temperatures by using 1,000 mL of deionized water in the flask. In these runs, a piece of copper (1/8 inch copper tubing, approximately 5 g) and common steel (wire, approximately 30 g) were suspended in the reaction vessel by means of a Teflon string, and then 1,000 mL of reagent was added, and the temperature adjusted to 40 °C. Once the temperature stabilized, 20 mL of arsinol was quickly added as a single bolus. Approximately 15 min after the arsinol was added to the reactor, the temperature was adjusted to 60 or 80 °C, and the reaction was allowed to proceed for 5.5 to 6.0 hr. No time point samples were collected during these runs.

3.6.2 Temperature Profiles and Observations.

The reactions conducted in the stainless steel reactor were all well behaved, with no significant exotherm or pressure build-up observed when the 20% $NaMnO_4$ was added to the arsinol, or at anytime during the reaction. It was difficult to track any exotherms, because of the order of additions; the 40 °C reagent being added to room temperature arsinol. Example temperature profiles are illustrated in Figures 59 and 60. While not continuously monitored during the runs, pressure was measured using a pressure gauge installed on the reactor. In both cases, pressures rose 5-10 psi during the course of the reaction. The terminal pH values were 7.53 for the 60 °C reaction, and 7.72 for the 80 °C reaction. For reference, the pH of the starting 20 wt% $NaMnO_4$ reagent was determined to be 7.85. In all runs the terminal neutralent was dark purple in color, indicating there was still MnO_4^- available in the neutralent.

3.6.3 Residual Agents.

Time-point samples were removed from the reactor, and analyzed for residual DA, PD, and TPA using the method described in Section 2.5. The five mL samples were removed from the reactor using a sampling valve, with sample being taken from approximately 1 in. from the bottom of the reactor. Once removed from the reactor, samples were placed into a 15 mL glass vial, and immediately placed into a water/ice bath to inhibit further reaction. 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 (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 from laboratory control spikes were: DA 89.7%, PD 88.3%, and TPA 79.3%. The neutralent time point data is illustrated in Figure 61. The reaction of DA, PD, and TPA with 20 wt% $NaMnO_4$ proceeds very quickly, and appears to be independent of temperature. The residual agent results obtained during these large-scale runs correlates well with data obtained during the small-scale reactions (Section 3.5.3).

The reaction appears to approximate first-order kinetics, and half-life estimates were calculated using the data illustrated in Figure 61. The half-life for DA at 60 °C was calculated to be 0.38 hr, while it was calculated to be 0.33 hr at a reaction temperature of 80 °C. The half-life for PD at 60 °C was calculated to be 0.55 hr, while it was calculated to be 0.34 hr at a reaction temperature of 80 °C. The half-life for TPA at 60 °C was calculated to be 0.67 hr, while it was calculated to be 0.62 hr at a reaction temperature of 80 °C. The half-lives calculated for the small-scale reactions (Section 3.5.3) ranged from 0.13 to 0.18 hr. The difference in half-lives is, most likely, due to the differences in loading the arsinol. In the small-scale reactions, the arsinol was added to the reagent, while in the large-scale reactions, the reagent was added to the arsinol. The somewhat longer half-lives calculated for the large-scale reactions appears to be related to mixing, with the arsinol in the small-scale reactions being more quickly dispersed, due to how the arsinol was loaded.

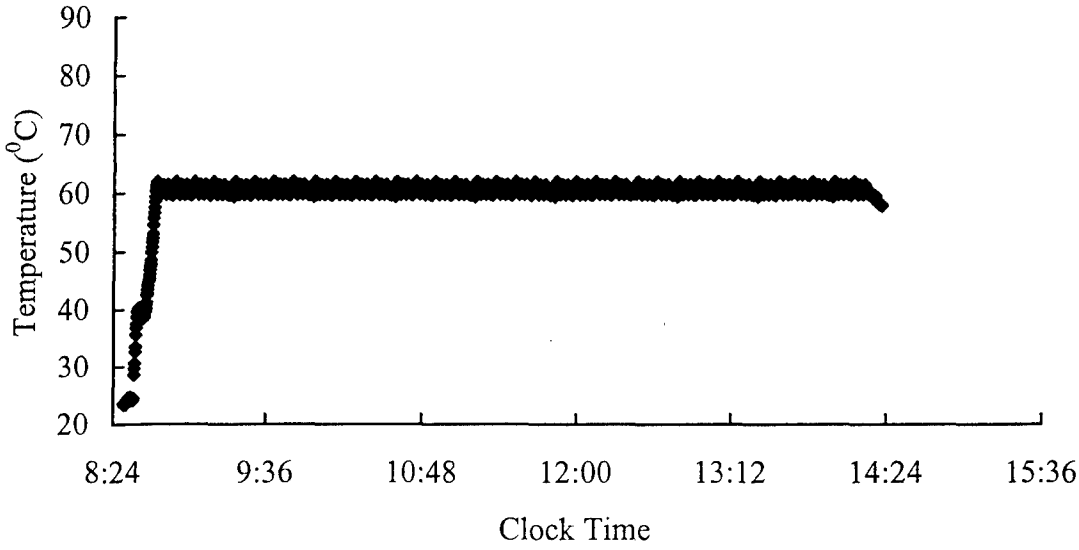


Figure 59. Temperature Profile for the 60 °C Large-Scale Reaction

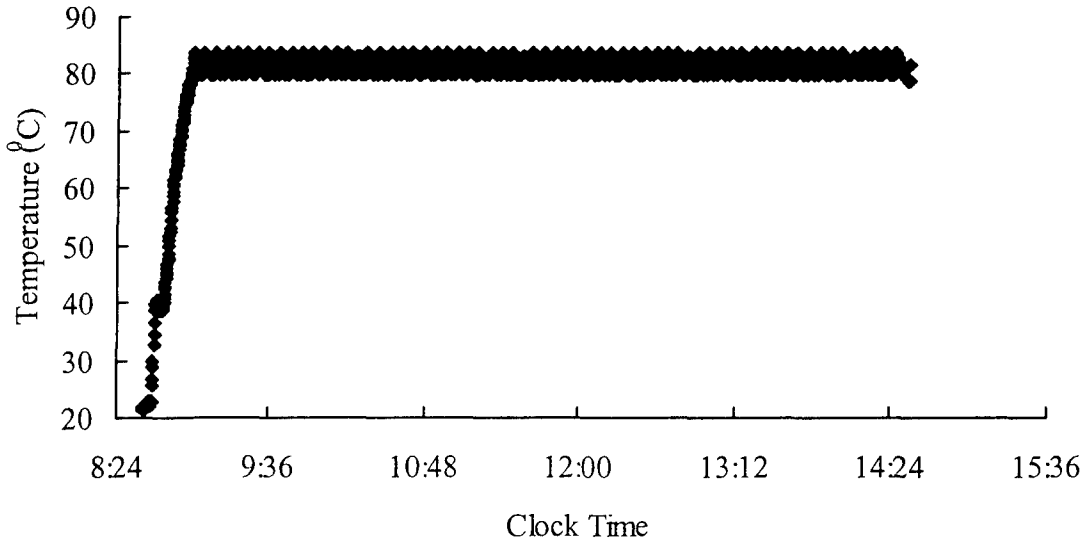


Figure 60. Temperature Profile for the 80 °C Large-Scale Reaction

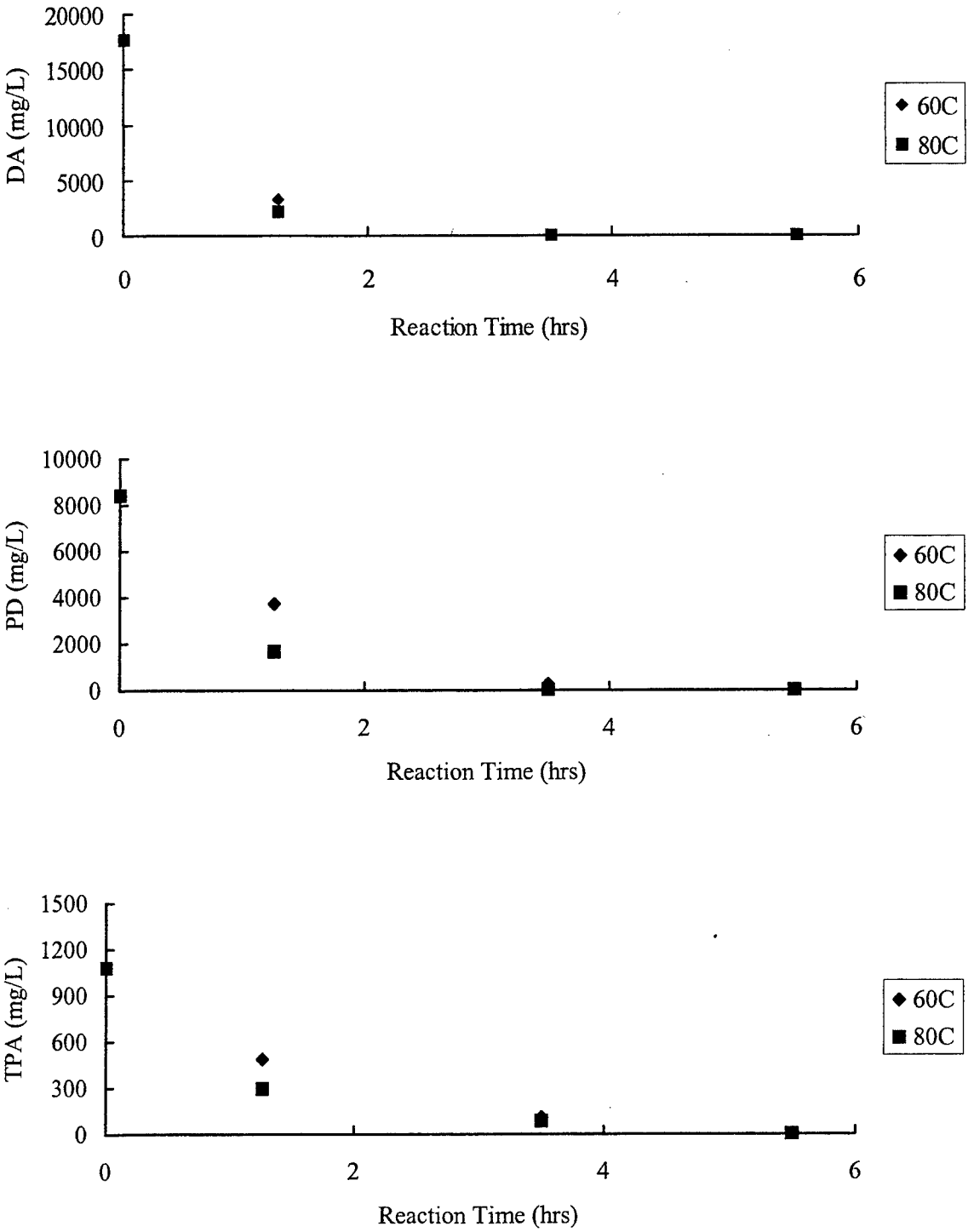


Figure 61. Residual Agent in Whole Neutralent Collected During the Large-Scale Reactor Runs. The plotted data are averages of duplicate derivatization/extractions. The top panel is DA data, the middle panel is PD data, and the bottom panel is TPA data.

3.6.4 Neutralent Storage Study.

In previous studies examining the neutralization of chemical warfare agents, the formation of parent materiel during storage was either documented, or speculated to be occurring. In a study examining the caustic neutralization of G-class nerve agents, it was determined formation of the parent G-agent would occur during storage if the pH of the neutralent was adjusted from basic (pH 10-11), to acidic (pH 4-5).[94] A study examining the oxidative neutralization of lewisite found increasing lewisite concentrations over time, both during the neutralization process, and during storage of the neutralent.[95] These results were speculated to be from formation of the lewisite, but a later report suggested an analytical artifact as the source of elevated lewisite levels.[96] This experiment was performed to evaluate the potential formation of parent materiels during storage of the unmodified neutralent.

Approximately 30 min after each of the reactions were completed, the neutralent samples were split between two, 250 mL high density polyethylene (HDPE) storage bottles. One bottle had been modified to accept a 0-30 psi pressure gauge through the cap. After placing approximately 225 mL of neutralent into the modified bottle, the cap was screwed on, and the cap further sealed by wrapping Parafilm™ around the cap. This modified bottle was used to monitor pressure build-up during storage of the neutralent, and was not opened during the experiment. In addition to the neutralent samples, pressure in the headspace above controls of unused 20 wt% $NaMnO_4$ reagent and HPO_2™ reagent was also monitored. A second 225 mL aliquot of each neutralent was also transferred to an unmodified 250 mL HDPE storage bottle. Time point samples were collected from each neutralent stored in this unmodified storage bottle, and were analyzed for $NaMnO_4$, residual agents, and select reaction products. The temperature during the storage experiment ranged from 4 to 15 °C for all the samples and controls. The low temperatures for the storage experiment were not planned, but the result of mechanical issues with the heating system in the laboratory. The study extended over approximately 23 days (547 hr), and pressures above the stored neutralents and unused reagent never exceeded 2 psi. The pressure above the HPO_2™ reagent rose to approximately 5 psi, and stayed at that pressure throughout the study.

Time-point samples were removed from the HDPE storage bottle, and analyzed for residual DA, PD, and TPA using a modification to method described in Section 2.5. The 3 mL samples were removed from the HDPE storage bottle using a modified glass Pasteur pipet, with the tip of the pipet being approximately 3/4-in. below the surface of the neutralent. The samples were removed from the storage bottle after the bottle was shaken for approximately 30 sec to re-suspend solids. Once removed from the storage bottle, samples were placed into a 4 mL glass vial. Duplicate aliquots were removed from this 4 mL vial, and prepared as described in Section 2.5. In addition, the neutralent sample was also filtered (0.45 μm PTFE Acrodisc™) prior to being analyzed. The derivitization/extraction process was started within 5 min of the sample being removed from the storage bottle. Quantitation was accomplished using an external calibration model, with a check standards analyzed at the start, and at the end of each sequence analyzing sample extracts. Concurrently with analysis of these samples, extraction blanks (n=14) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks.

The residual agent data is illustrated in Figures 62 through 64. There were no anomalies during the preparation or analysis of these samples. While there is some scatter in the data, there are no clear trends suggesting agent concentrations will increase during storage. The residual agent data from the whole neutralent samples is consistently higher than the filtered neutralent, suggesting the residual agents predominantly exist as sorbed species. The scatter observed in the data might be due to sample heterogeneity issues, with some samples having more solids, and thus more agent.

The filtered samples generated during the analyses for residual agents were also analyzed for select reaction products using one of the capillary electrophoresis methods described in Section 2.6. 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 samples. 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 illustrated in Figures 65 and 66. Two of the products, chloride and fluoride (the fluoride is in the starting reagent) show no trends over time, with only a small amount of scatter in the data. The arsenate concentrations decrease over time, reaching non-detect levels after approximately 5 days of storage. This suggests the arsenate is being sorbed by particulates in the sample, and no longer detectable in the filtrate. This observation is supported by micro-scale studies examining the composition of isolated solids over time (Section 3.5.6), which showed increasing levels of arsenate when neutralent was stored at room temperature.

The whole neutralent samples and unused $NaMnO_4$ reagent were also analyzed for residual $NaMnO_4$ using the method described in Section 2.7, with each sample prepared and analyzed in triplicate. 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 $NaMnO_4$ data are illustrated in Figure 67, and show no significant trending with storage time. The $NaMnO_4$ concentrations were obtained using a standard spectroscopic method, and are reported on a mass/volume basis (milligrams/liter). The initial reagent concentration was determined to be 311,000 mg/L, which translates to 26.8 wt% if a density of 1.16 kg/L is used. While not listed as an interferent (Section 2.7), it is believed the high levels of arsenic may have interfered with the assay. Another possible source of the error is the large dilutions (10,000 – 15,000 times) required to analyze these concentrated samples. Small errors in the measurement will be magnified by the large dilution factor required to use this assay. Note the zero-time-point permanganate concentrations for the neutralent samples are less than the starting reagent concentration, with the neutralent from the 60 °C reaction being 89% of the original $NaMnO_4$ concentration. The neutralent permanganate concentration generated from the 80 °C reaction is 80% of the original $NaMnO_4$ concentration. These results suggest the $NaMnO_4$ concentration in the neutralent will remain stable during storage in HDPE in the temperature range (4-15 °C) evaluated. The apparent stability of $NaMnO_4$ is also supported by the lack of pressure build-up in the storage vessels.

Test continues on page 121.

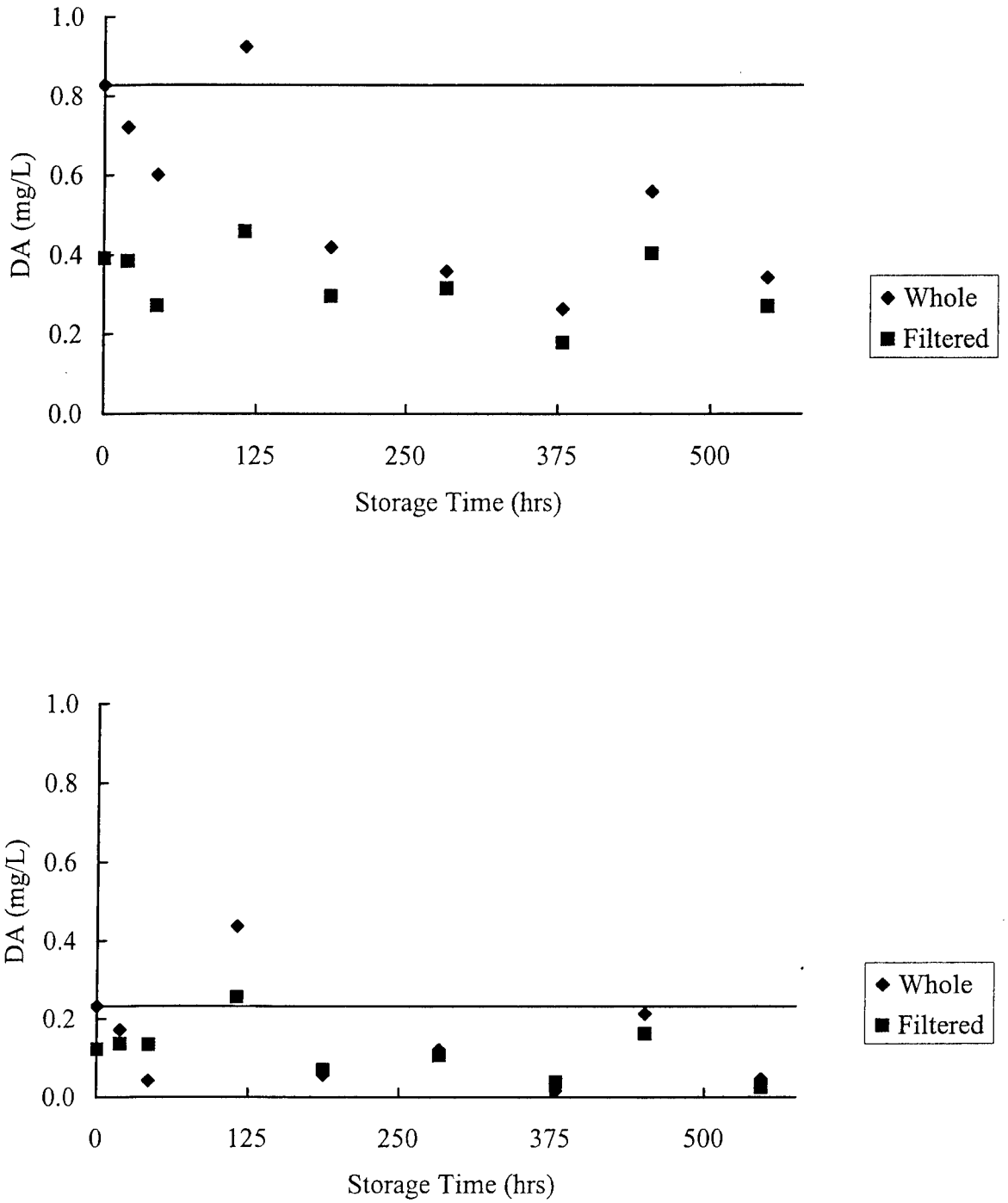


Figure 62. Concentration of DA in Neutralent as a Function of Storage Time. The upper panel is storage of neutralent produced at 60 °C, and the lower panel is storage of neutralent produced at 80 °C. The horizontal line is the average concentration of the whole neutralent at the zero time point.

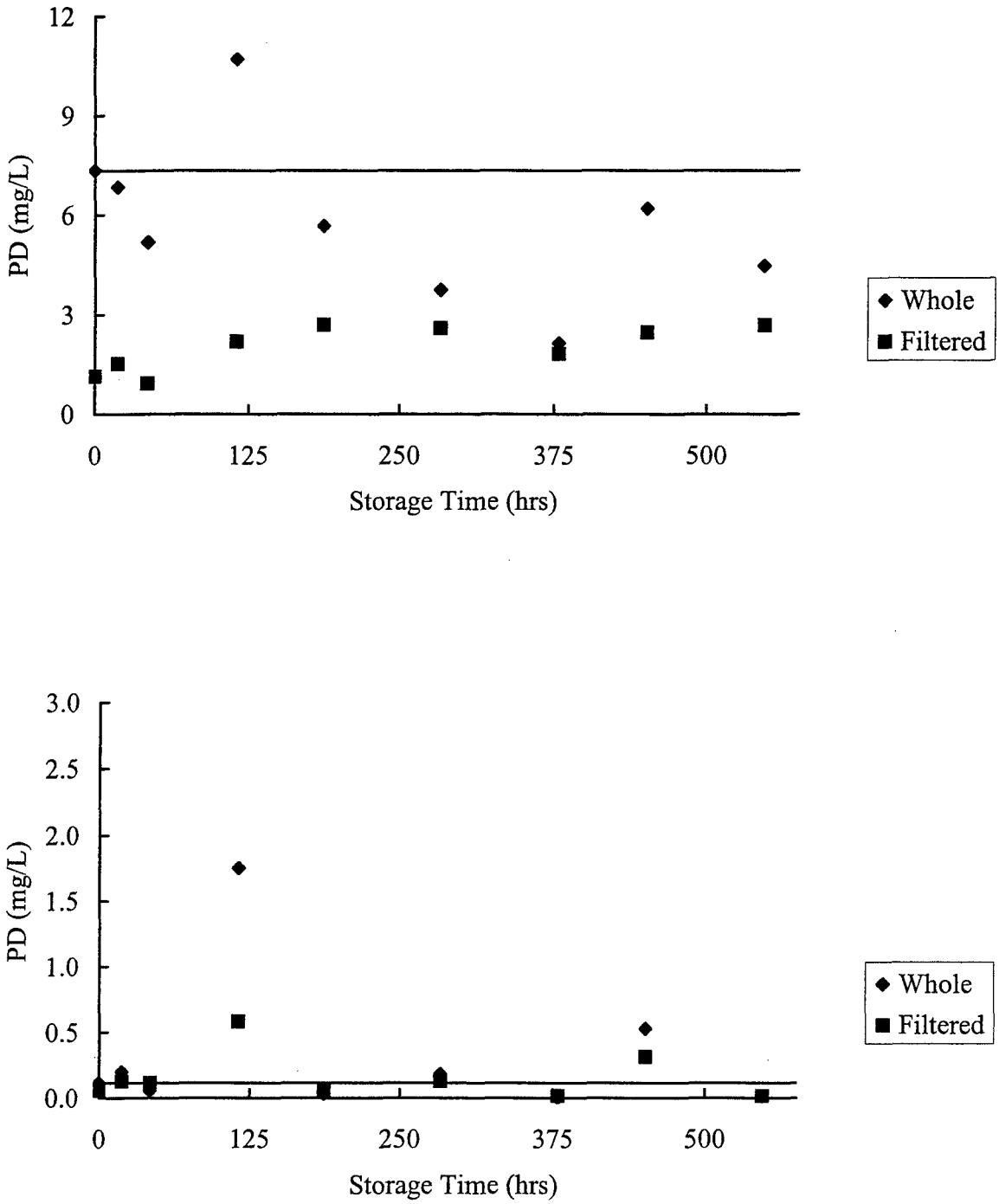


Figure 63. Concentration of PD in Neutralent as a Function of Storage Time. The upper panel is storage of neutralent produced at 60 °C, and the lower panel is storage of neutralent produced at 80 °C. The horizontal line is the average concentration of the whole neutralent at the zero time point.

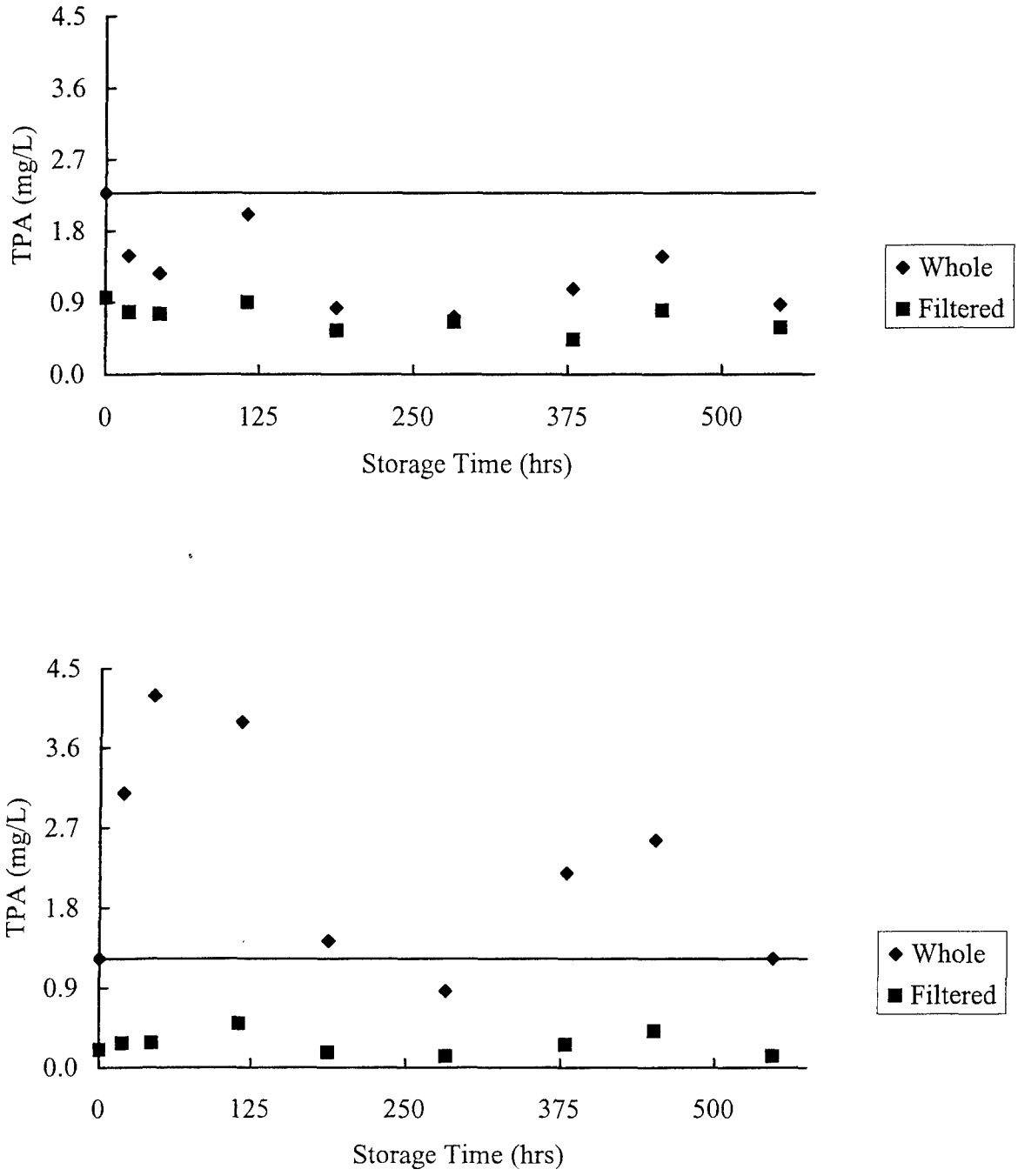


Figure 64. Concentration of TPA in Neutralent as a Function of StorageTime. The upper panel is storage of neutralent produced at 60 °C, and the lower panel is storage of neutralent produced at 80 °C. The horizontal line is the average concentration of the whole neutralent at the zero time point.

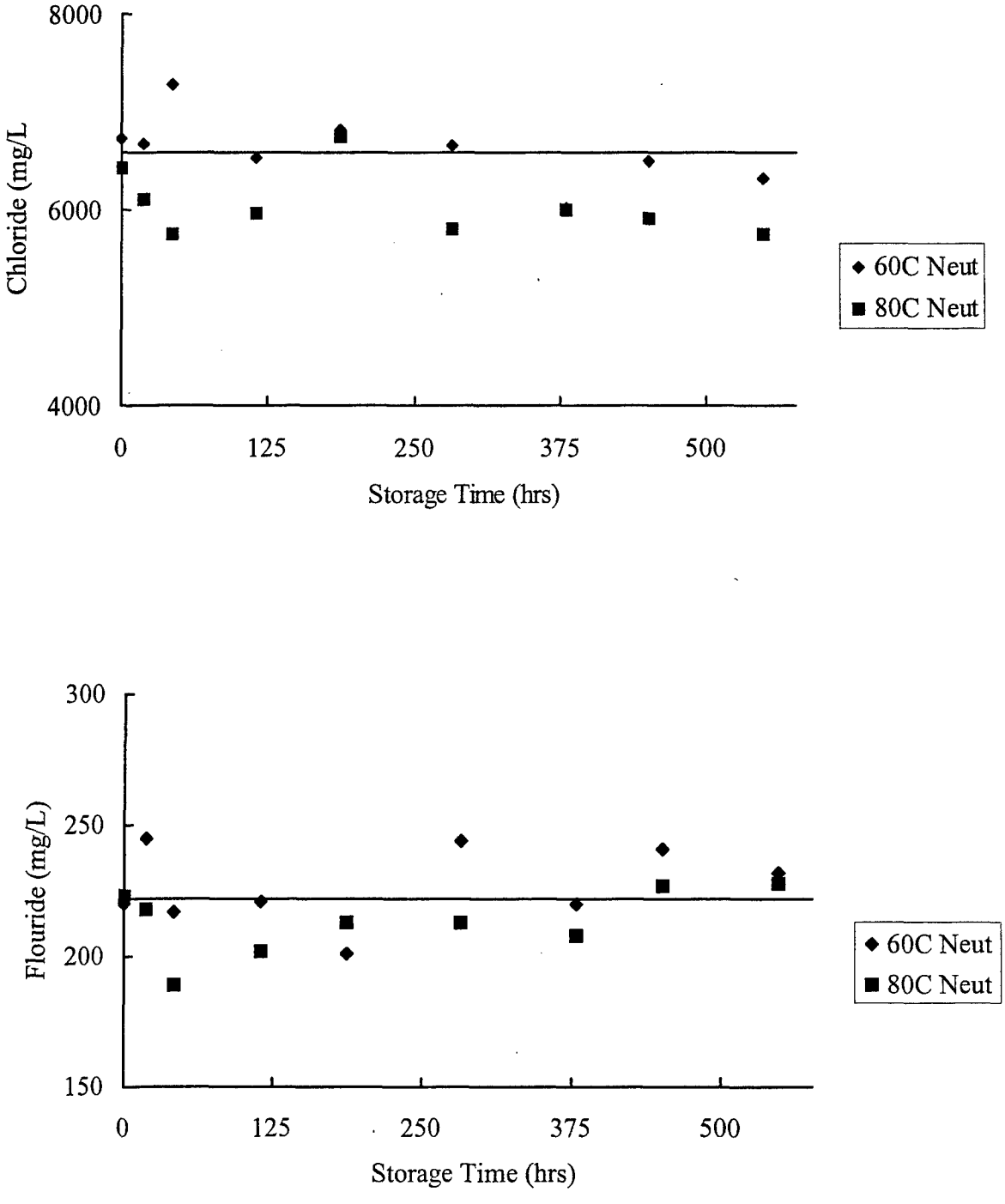


Figure 65. Concentration of Reaction Products in Filtered (0.45 μm) Neutralent as a Function of Storage Time. The upper panel is chloride, and the bottom panel is fluoride. The horizontal line is the average analyte concentration in the 60 and 80 °C time zero neutralents.

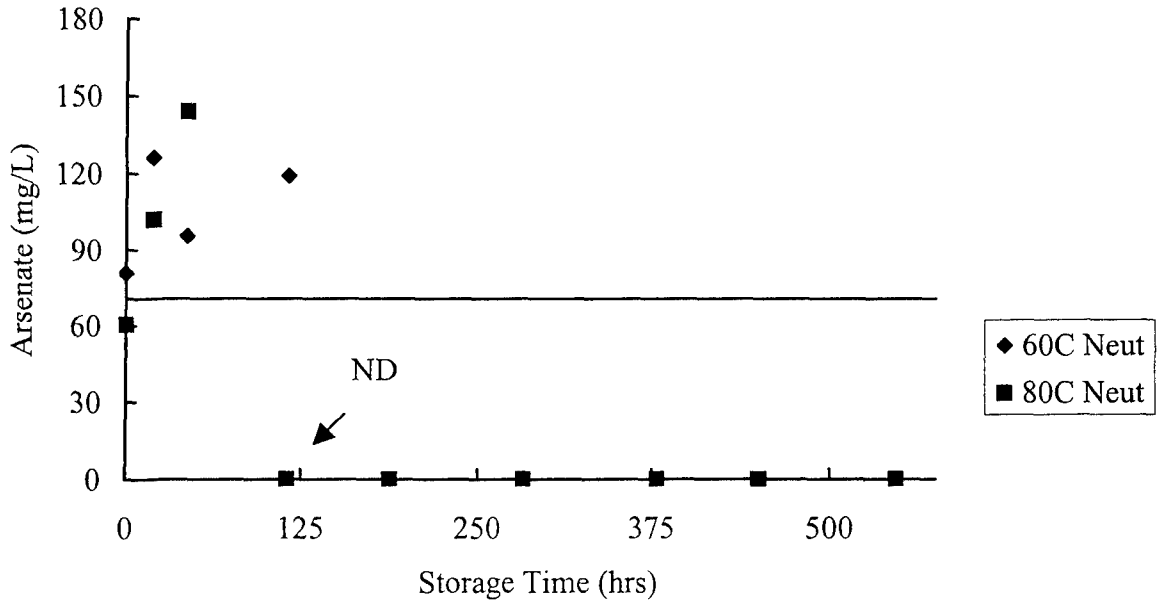


Figure 66. Concentration of Arsenate in Filtered (0.45 μm) Neutralent as a Function of Storage Time. The horizontal line is the average arsenate concentration in the 60 and 80 °C time zero neutralents.

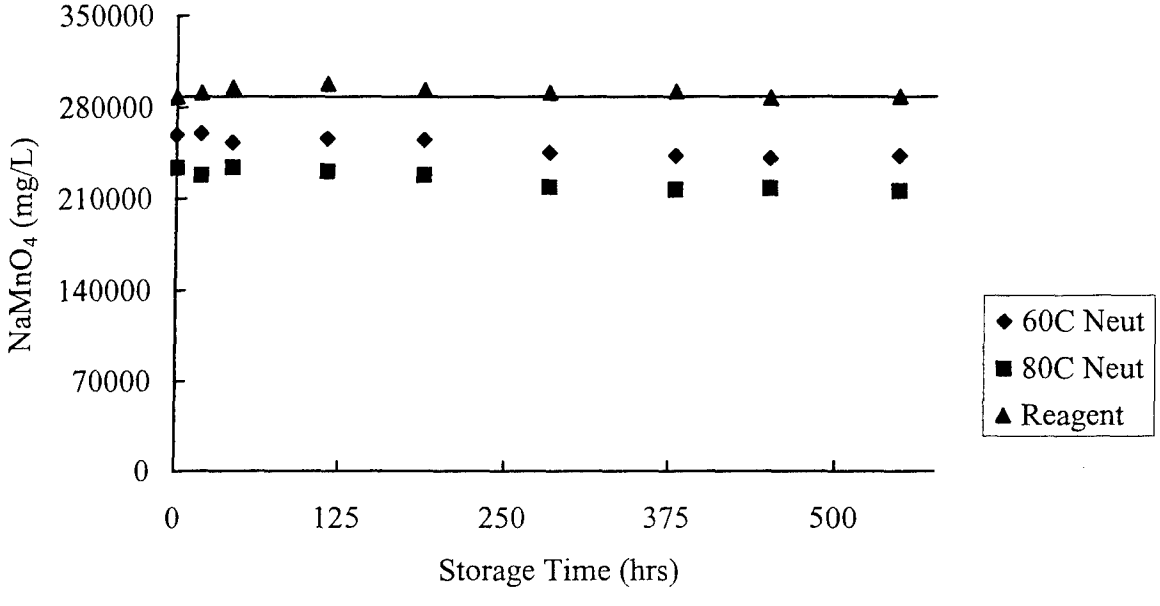


Figure 67. Concentration of $NaMnO_4$ in Neutralent as a Function of Storage Time. The horizontal line is the average $NaMnO_4$ concentration in the time zero reagent.

3.6.5 RCRA Waste Characterization.

The Resource Conservation and Recovery Act mandates waste be classified as hazardous if it possesses certain characteristics (such as ignitability, corrosively, reactivity, or toxicity), or it is derived from a process or waste stream that EPA has determined to contain hazardous components.[97] The neutralent produced by the detoxification of arsinol with permanganate reagent will need to be disposed of, so a preliminary waste characterization of the neutralent was conducted. There are no Federal EPA hazardous waste "listings" applicable to the waste neutralent;[98] however, some states may be more stringent than the Federal EPA.

The standard tests used to characterize waste typically require large volumes of sample, and these volumes were not available from each of the individual reactor runs performed during this study. In order to obtain a preliminary evaluation of the hazard characteristics of the neutralents, composite samples were prepared. The composite samples were prepared by mixing neutralent from multiple reactor runs (60 °C for 6 hr), to generate a composite sample. After compositing, the neutralents were aliquoted into appropriate sample containers. The samples were sent to an independent laboratory certified to perform RCRA waste characterization. The samples were prepared and analyzed in accordance with standard EPA and ASTM test methods.[99,100]

Waste characteristics testing includes analysis for pH, ignitability (as flashpoint), sulfide reactivity, cyanide reactivity, and an evaluation of corrosivity and overall reactivity. The pH test was performed on a 1:1 mixture of neutralent and deionized water after being tumbled for 30 min. The ignitability characteristic was evaluated by measuring flash point in a Pensky Martens closed cup apparatus. Reactivity is based on the production of either hydrogen cyanide or hydrogen sulfide by the sample. The reactivity test involved extracting the sample by the interim method described in SW846, Chapter 7.3,[101] and analyzing the extract for cyanide and sulfide. Waste is considered reactive or hazardous if it generates a quantity of hydrogen cyanide exceeding 250 mg/kg, or hydrogen sulfide exceeding 500 mg/kg. These interim threshold limits were established by the Solid Waste Branch of EPA, July, 1992.[102] Waste is corrosive if it exhibits a pH ≤ 2, or ≥ 12.5. The results are summarized in Table 39, and indicate the arsinol/permanganate neutralent did not fail for any of these waste characteristics.

The volatile organic analyses were performed on a zero headspace toxicity characteristic leachate of the combined neutralent sample. The leachate was prepared according to the procedure specified in SW-846, Chapter 7.4 (Revision 3, 12/94).[101] The results are summarized in Table 40. While benzene and chlorobenzene were detected, they were both below the regulatory limit.

The pesticide/herbicide analyses were performed on a non-volatile toxicity characteristic leachate of the combined neutralent sample. The leachate was prepared according to the procedures specified in the March 29 and June 29, 1990 Federal Registers.[103,104] The results are summarized in Table 41, and indicate the arsinol/permanganate neutralent did not fail for any of these chemicals.

The semi-volatile organic analyses were performed on a non-volatile toxicity characteristic leachate of the combined neutralent sample. The leachate was prepared according to the procedure specified in SW-846, Chapter 7.4 (Revision 3, 12/94).[101] The results are summarized in Table 42, and indicate the arsinol/permanganate neutralent did not fail for any of these chemicals.

The metal analyses were performed on a non-volatile toxicity characteristic leachate of the combined neutralent sample. The leachate was prepared according to the procedure specified in SW-846, Chapter 7.4 (Revision 3, 12/94).[101] The results are summarized in Table 43, and indicate the arsinol/permanganate neutralent failed for arsenic.

Table 39. Results of the Waste Characteristics Testing. Values exceeding the toxicity characteristic limits are in bold font.

Waste Characteristic	Reported Value	Reporting Limit	Method Used
pH	7.8 @ 16°C	NA[a]	EPA 9040B
Flash Point	>201°F[b]	NA[a]	EPA 1010
Sulfide Reactivity	ND[c]	10.0 mg/kg	SW-846 7.3.4.2
Cyanide Reactivity	ND[c]	1.0 mg/kg	SW-846 7.3.3.2
Reactivity	Non-Reactive	NA[a]	SW-846
Corrosion to Steel	ND[c]	6 mm/year	EPA 1110

a. Not applicable.
b. No flash observed; test flame extinguished.
c. Not detected above reporting limit.

Table 40. Summary of the TCLP Volatiles Analyses. All reported values are inmillgrams/liter. Values exceeding the toxicity characteristic limits are in bold font.

Target Analyte	Reported Value (mg/L)	Reporting Limit (mg/L)[a]
Benzene	0.0266	0.0200
Carbon Tetrachloride	ND[b]	0.0200
Chlorobenzene	0.202	0.0200
Chloroform	ND[b]	0.0200
1,2-Dichloroethane	ND[b]	0.0200
1,1-Dichloroethene	ND[b]	0.0200
Methyl Ethyl Ketone	ND[b]	0.0200
Tetrachloroethene	ND[b]	0.0200
Trichloroethene	ND[b]	0.0200
Vinyl Chloride	ND[b]	0.0200

a. Reporting limit is in the original neutralent sample.
b. Not detected above reporting limit.

Table 41. Summary of the TCLP Pesticide and Herbicide Analyses. All reported values are in millgrams/liter. Values exceeding the toxicity characteristic limits are in bold font.

Target Analyte	Reported Value (mg/L)	Reporting Limit (mg/L)[a]
Chlordane	ND[b]	0.000750
Endrin	ND[b]	0.000125
Heptachlor	ND[b]	0.000125
Heptachlor Epoxide	ND[b]	0.000125
Lindane	ND[b]	0.000125
Methoxychlor	ND[b]	0.000125
Toxaphene	ND[b]	0.000125
2,4-D[c]	ND[b]	0.500
2,4,5-TP[c]	ND[b]	0.500

a. Reporting limit is in the original neutralent sample.
b. Not detected above reporting limit.
c. Used EPA Method 8151.

Table 42. Summary of the TCLP Semi-Volatile Analyses. All reported values are inmillgrams/liter. Values exceeding the toxicity characteristic limits are in bold font.

Target Analyte	Reported Value (mg/L)	Reporting Limit (mg/L)[a]
2-Methylphenol	ND[b]	10.0
4-Methylphenol[c]	ND[b]	10.0
1,4-Dichlorobenzene	ND[b]	10.0
2,4-Dinitrotoluene	ND[b]	10.0
Hexachlorobenzene	ND[b]	10.0
Hexachlorobutadiene	ND[b]	10.0
Hexachloroethane	ND[b]	10.0
Nitrobenzene	ND[b]	10.0
Pentachlorophenol	ND[b]	10.0
Pyridine	ND[b]	10.0
2,4,5-Trichlorophenol	ND[b]	10.0
2,4,6-Trichlorophenol	ND[b]	10.0

a. Reporting limit is in the original neutralent sample.
b. Not detected above reporting limit.
c. The reported result is the sum of 3-methylphenol and 4-methylphenol, which are not chromatographically resolved.

Table 43. Summary of the Metal Analyses. All reported values are in milligrams/liter. Values exceeding the toxicity characteristic limits are in bold font.

Target Metal	Total Metal		TCLP Metal	
	Reported Value (mg/L)	Reporting Limit (mg/L)[a]	Reported Value (mg/L)	Reporting Limit (mg/L)[a]
Arsenic	378	0.050	**108**	1.00
Barium	ND[b]	0.050	ND[b]	0.50
Cadmium	ND[b]	0.01	ND[b]	0.50
Chromium	1.40	0.050	ND[b]	1.00
Lead	ND[b]	0.025	ND[b]	1.00
Mercury	0.0308	0.000750	ND[b]	0.0015
Selenium	ND[b]	0.150	ND[b]	0.500
Silver	ND[b]	0.050	ND[b]	0.500

a. Reporting limit is in the original neutralent sample.
b. Not detected above reporting limit.

3.6.6 Materials Compatibility.

The neutralent produced by the detoxification of arsinol with permanganate reagent will come into contact with various materials during the processing and handling steps,[74] so a preliminary evaluation of the materials compatibility of the neutralent was conducted. In order to obtain a preliminary evaluation of corrosivity of the neutralents, composite samples were prepared. The composite samples were prepared by mixing neutralent from multiple reactor runs (80 °C for 6 hr), to generate a composite sample. This preliminary evaluation focused on EPDM, 316 stainless steel, and Inconel 718. The stainless steel and Inconel alloys were chosen because some pitting was observed in the initial EDS runs neutralizing lewisite with permanganate reagent.[105] The pitting was only observed in the 316 stainless beneath the Inconel 718 door seal material. The materials compatibility studies were conducted in accordance with standard NACE and ASTM test methods.[77,78]

The preliminary compatibility of neutralent with EPDM was conducted at two temperatures: 60 and 80°C. The EPDM coupons were approximately 1" X 1" X 0.125 ", and the average initial weight was 3.168 g. In each test, a sample of EPDM was fully immersed in the neutralent, with each treatment being conducted in duplicate. Care was taken that none of the sample coupons were touching each other during the test. After 120 hr of immersion, test specimens were removed, and after cleaning the specimens, measurements were made on mass, dimensions, and hardness. The data are summarized in Table 44, and photographs of the test specimens are illustrated in Figure 68. There were no significant changes to mass, volume, or hardness of the EPDM exposed to neutralent, which are the same results obtained when EPDM was exposed to 20 wt% $NaMnO_4$ reagent (Section 3.4.2).

The preliminary compatibility of neutralent with 316 stainless steel and Inconel 718 was conducted using a modification of ASTM Method G48.[106] In the original method, which is designed to evaluate pitting and crevice corrosion, the test solution is an aqueous solution of ferric chloride, and the recommended temperatures are 22 and 50 °C. In this evaluation, arsinol/permanagnate neutralent was used as the test solution, and the temperatures were 60 and 80 °C. The modifications were made to more closely match conditions expected during actual EDS operations. In each test, the materials were either fully immersed in the neutralent, or only partially immersed, with each treatment conducted in duplicate. In all cases, the specimens were removed from the neutralent after 120 hr of immersion. There were three scenarios investigated during this baseline evaluation:

- Type 316 stainless steel crevice test specimens were assembled with PTFE multiple crevice assemblies on both faces. Duplicate specimens were assembled on a single length of threaded rod. Each test specimen, as well as the mounting hardware, were electrically isolated from each other with PTFE insulators.

- Inconel 718 crevice test specimens were assembled with PTFE multiple crevice assemblies on both faces. Duplicate specimens were assembled on a single length of threaded rod. Each test specimen, as well as the mounting hardware, was electrically isolated from each other with PTFE insulators.

- Type 316 stainless test specimens were assembled with Inconel 718 washers in direct contact (galvanically coupled) on one side, and a PTFE multiple crevice washer on the other. Duplicate specimens were assembled on a single length of threaded rod. Each test specimen, as well as the mounting hardware, were electrically isolated from each other with PTFE insulators.

The metals data are summarized in Tables 45 and 46, and photographs of the test specimens are illustrated in Figures 69 through 73. One of the 316 test specimens experienced pitting up to 19 mils deep; this was also the only specimen with a corrosion rate greater than 0.1 mpy. This specimen was galvanically coupled to Inconel 718, and was partially immersed at 80 °C. The pitting was observed in an area associated with the liquid/vapor interface.

The partial immersion Inconel 718 specimens experienced superficial crevice corrosion as evidenced by dulling of the surface location of the crevice washers. The total immersion Inconel specimens experienced shallow crevice attack up to 0.25 mils deep. No crevice attack was observed on the Inconel 718 washers that were galvanically attached to the 316 stainless steel specimens.

Accelerated corrosion in the form of pitting occurred on one galvanically coupled 316 stainless steel specimen. This results confirms that 316 SS is susceptible to accelerated corrosion due to galvanic coupling with Inconel 718. It is not uncommon for materials to be individually resistant to corrosion, but galvanic corrosion does occur when they are coupled together. In this case, accelerated corrosion of the 316SS only occurs when the 316SS transitions

Text continues on page 133.

from the passive state to the active state. Once in the active state, the galvanic coupling to a more noble metal (Inconel 718) will keep the 316SS in an active state, accelerating corrosion. Additional data concerning the galvanic corrosion of 316SS and Inconel 718 in this environment could be obtained through electrochemical measurements and/or longer exposure times.

Table 44. Results from the Testing of EPDM with Arsinol/Permanganate Neutralent

Test Condition	Replicate Number	Percent Change After Exposure for 120 Hr					Change in Hardness[a]
		Mass	Length	Width	Thickness	Volume	
60°C	1	+0.3	NC[b]	-0.1	+1.7	+1.5	+0.8
	2	+0.3	+0.6	+0.4	-0.6	+0.4	+0.8
80°C	1	+0.6	NC[b]	+0.2	-1.1	-0.8	+0.4
	2	+0.6	+0.1	+0.9	NC[b]	+1.0	+0.6

a. Hardness is in Shore A units; original hardness was 79. Values are averages of five readings taken on each specimen.
b. No change, or change within error of measurement.

Table 45. Results from the Testing of Metals with Arsinol/Permanganate Neutralent. The study was conducted at 60 °C for 120 hr.

Corrosion Evaluation	Metal	Immersion Treatment	Replicate Number	Corrosion Rate (mpy)[a]	Comments
Crevice Corrosion Test	316 SS	Partial[b]	1	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
		Full	1	<0.1	Uniform corrosion
			2	0.1	Uniform corrosion
Crevice Corrosion Test	Inconel 718	Partial[b]	1	0.1	Superficial crevice corrosion
			2	0.1	Superficial crevice corrosion
		Full	1	0.1	Superficial crevice corrosion
			2	0.1	Superficial crevice corrosion
Galvanic Crevice Corrosion Test	316 SS Coupled with Inconel 718 Washer	Partial	1	<0.1	Uniform corrosion
			1	0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
			2	0.1	Uniform corrosion
		Full	1	<0.1	Uniform corrosion
			1	0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
			2	0.1	Uniform corrosion

a. Mils per year; a mil is 0.001 in..
b. Specimens became fully immersed on day 3 when line broke.

Table 46. Results from the Testing of Mtals with Arsinol/Permanganate Neutralent. The study was conducted at 80 °C for 120 hr.

Corrosion Evaluation	Metal	Immersion Treatment	Replicate Number	Corrosion Rate (mpy)*	Comments
Crevice Corrosion Test	316 SS	Partial	1	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
		Full	1	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
Crevice Corrosion Test	Inconel 718	Partial	1	0.1	Superficial crevice corrosion
			2	<0.1	Superficial crevice corrosion
		Full	1	<0.1	Superficial crevice corrosion
			2	<0.1	Superficial crevice corrosion
Galvanic Crevice Corrosion Test	316 SS Coupled with Inconel 718 Washer	Partial	1	3.18	Pits to 19 mils deep
			1	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
		Full	1	<0.1	Uniform corrosion
			1	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion
			2	<0.1	Uniform corrosion

* Mils per year; a mil is 0.001 in..

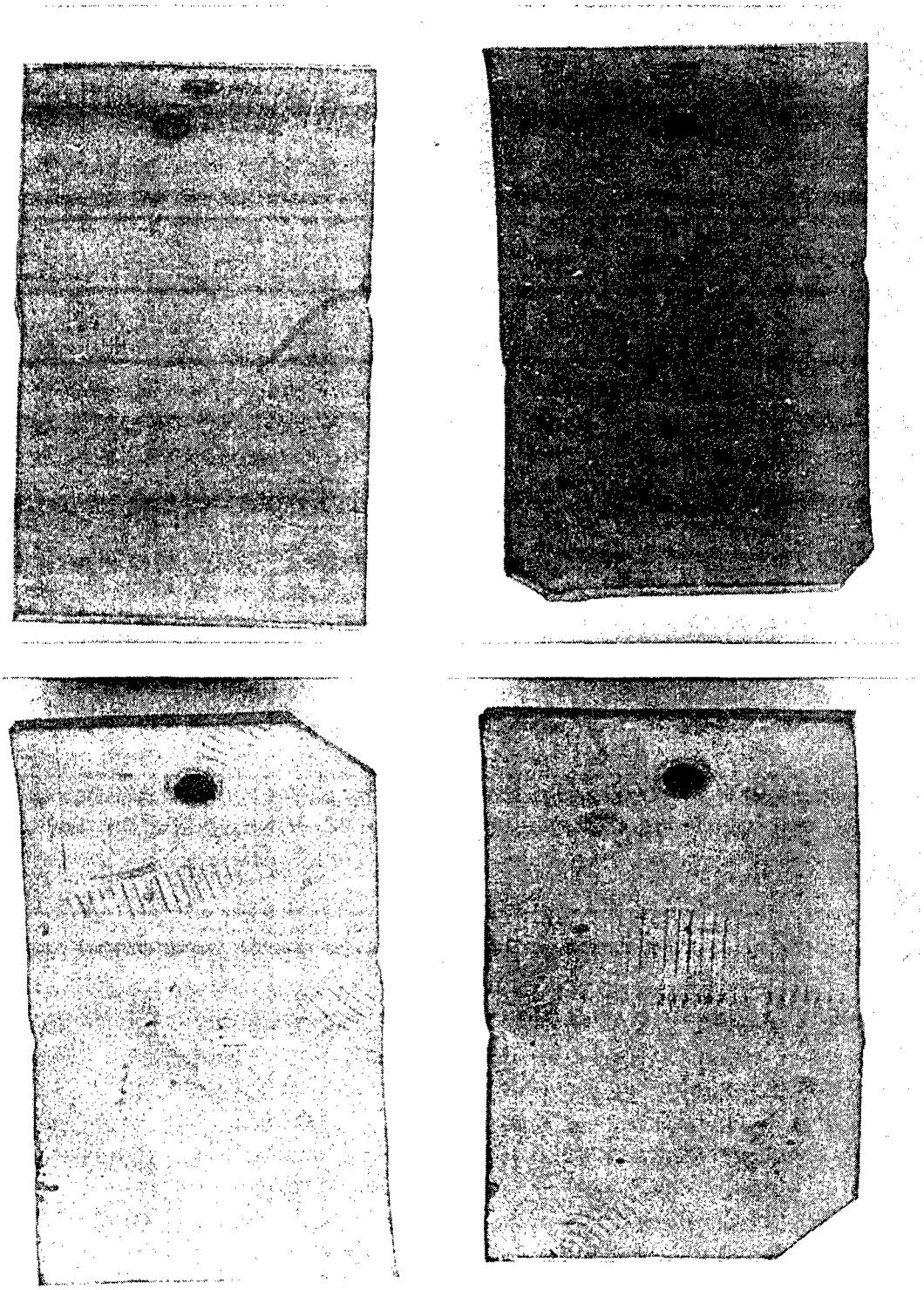


Figure 68. EPDM Specimens Exposed to Arsinol/Permanganate Neutralent for 120 hr while Fully Immersed. The top panel is the 60 °C exposure, and the bottom panel is the 80 °C exposure.

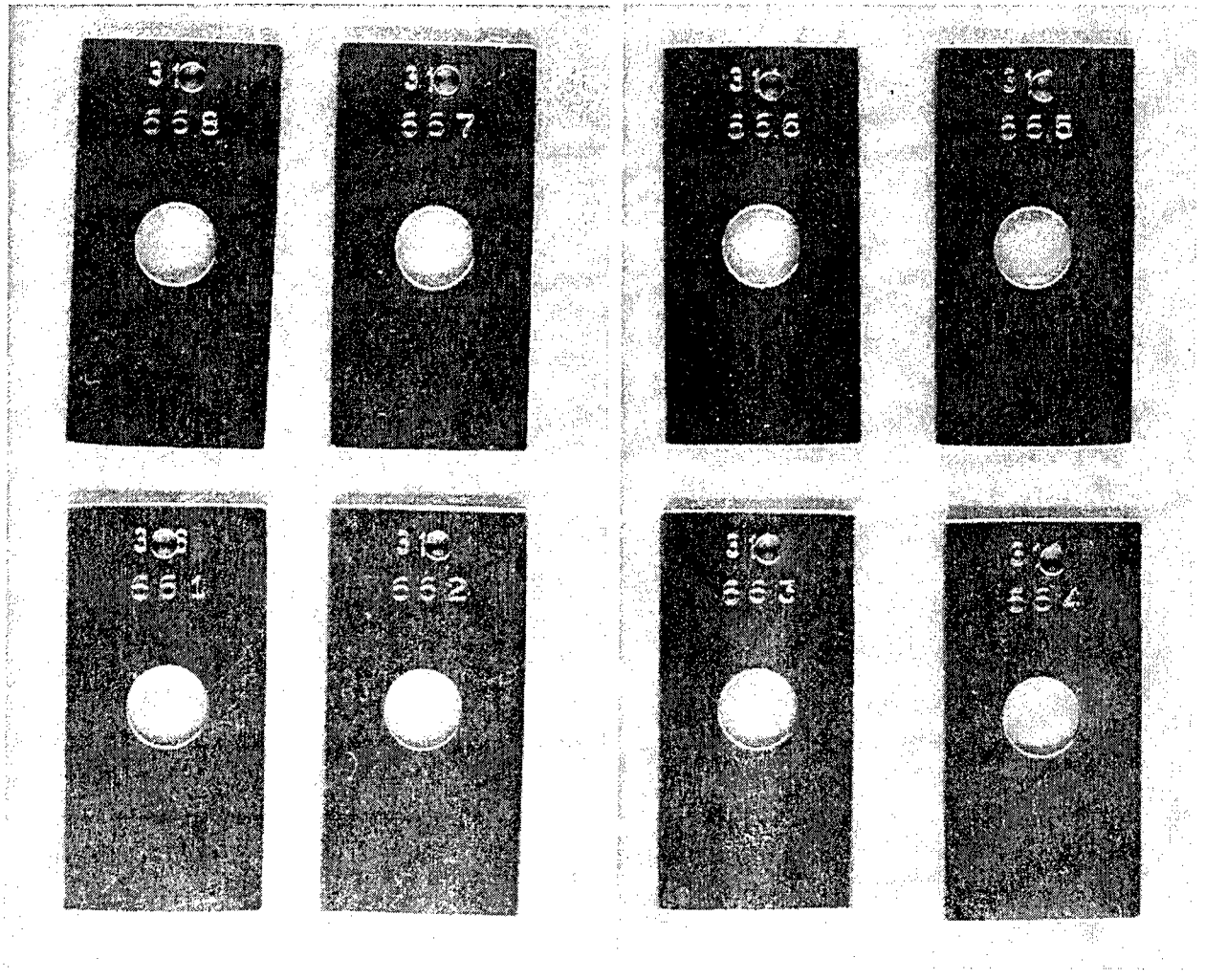


Figure 69. Metal Specimens (316 SS) with Multi-Crevice Assemblies Exposed to Arsinol/Permanganate Neutralent for 120 hr. The left panel is the 60 °C exposure, and the right panel is the 80 °C exposure. In each panel, the left specimens were partially immersed, and the right specimens were fully immersed.

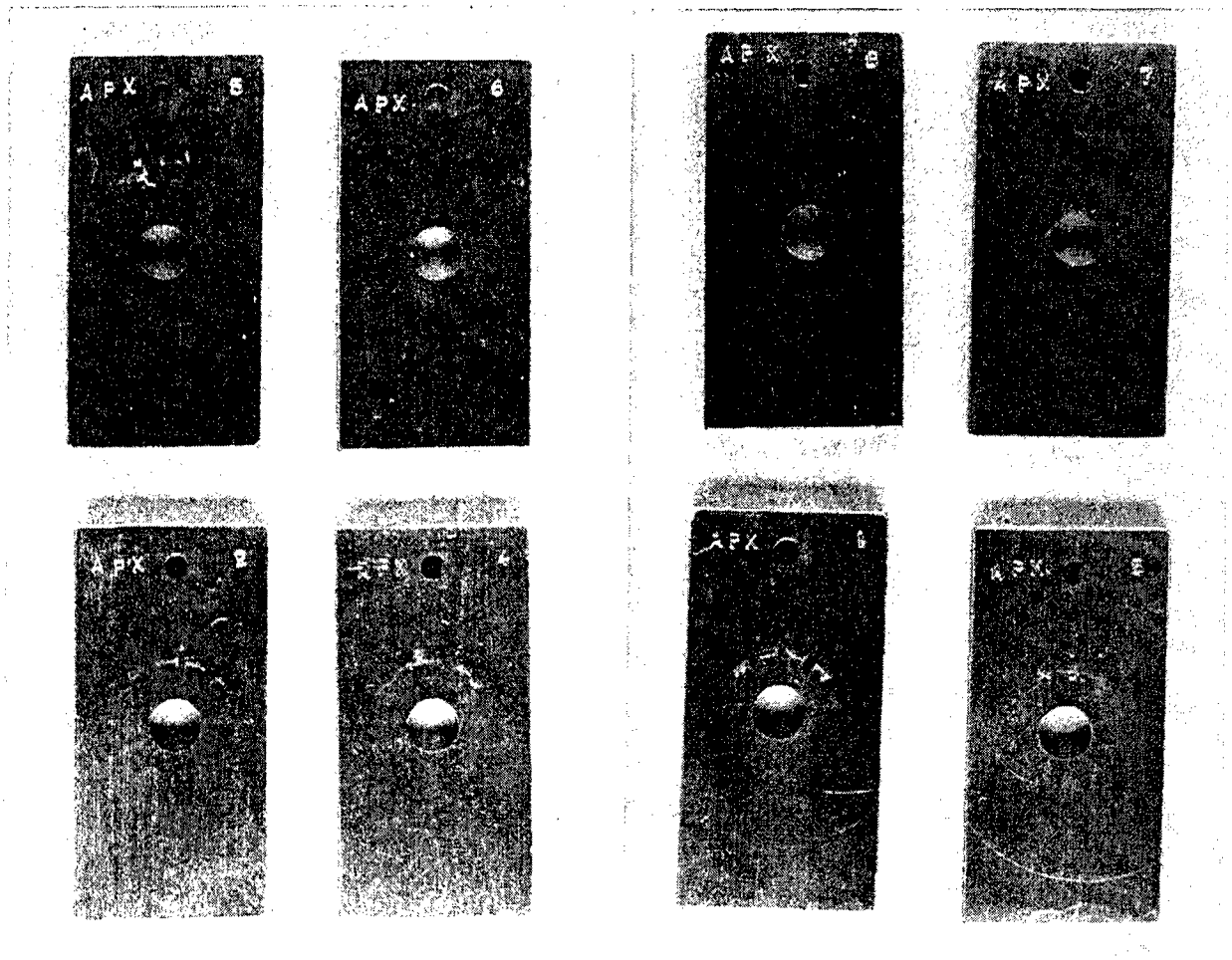


Figure 70. Metal Specimens (Inconel 718) with Multi-Crevice Assemblies Exposed to Arsinol/Permanganate Neutralent for 120 hr. The left panel is the 60 °C exposure, and the right panel is the 80 °C exposure. In each panel, the left specimens were partially immersed, and the right specimens were fully immersed.

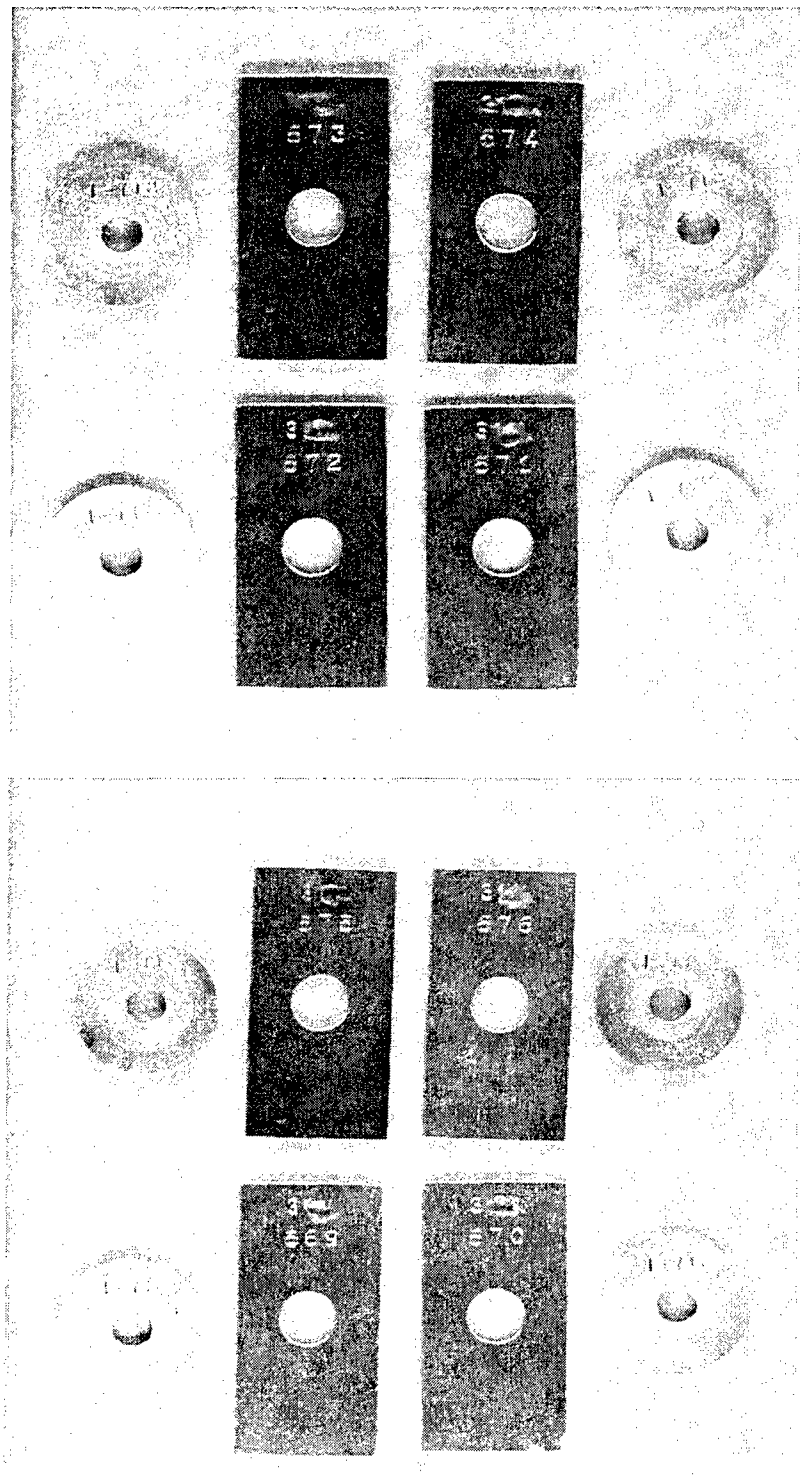


Figure 71. Metal Specimens with Galvanic-Crevice Assemblies Exposed to Arsinol/Permanganate Neutralent for 120 hr. The top panel is the 60 °C exposure, and the bottom panel is the 80 °C exposure. In each panel, the top specimens were partially immersed, and the bottom specimens were fully immersed.

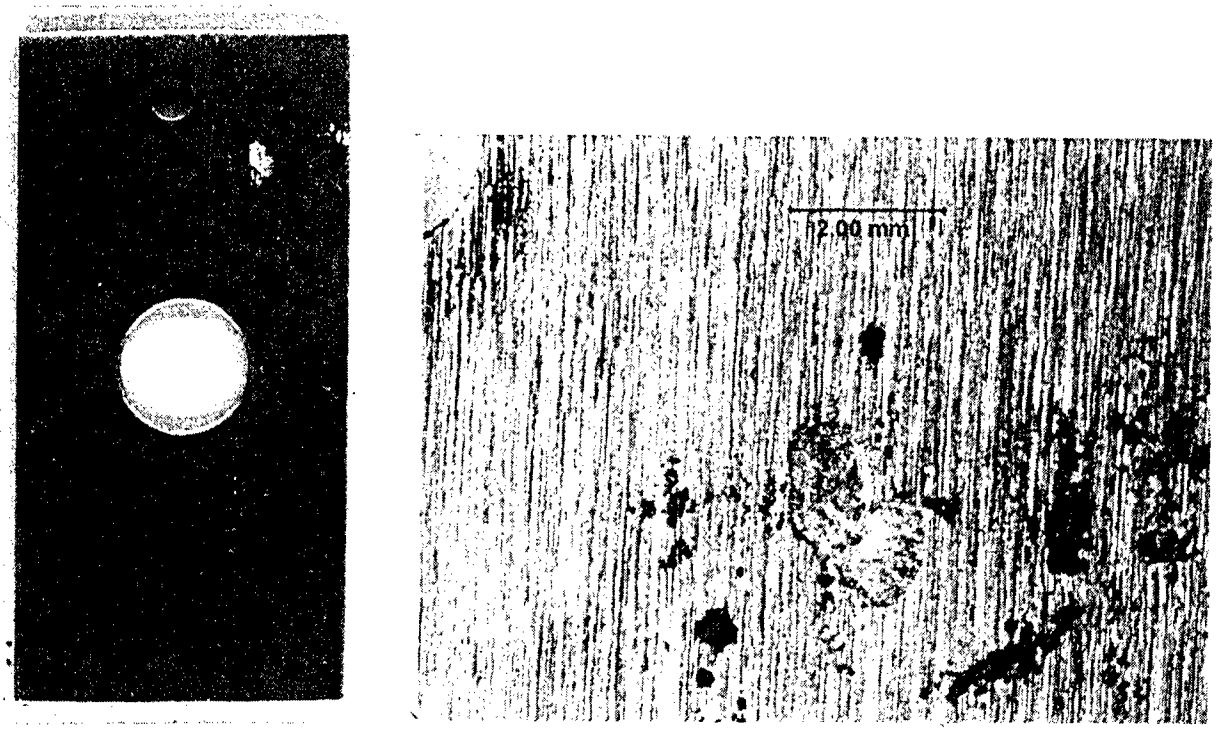


Figure 72. Metal Specimen of 316 SS with Pitting. This specimen was partially immersed in arsinol/permanganate neutralent for 120 hr at 80 °C. This test specimen was galvanically coupled to an Inconel 718 washer.

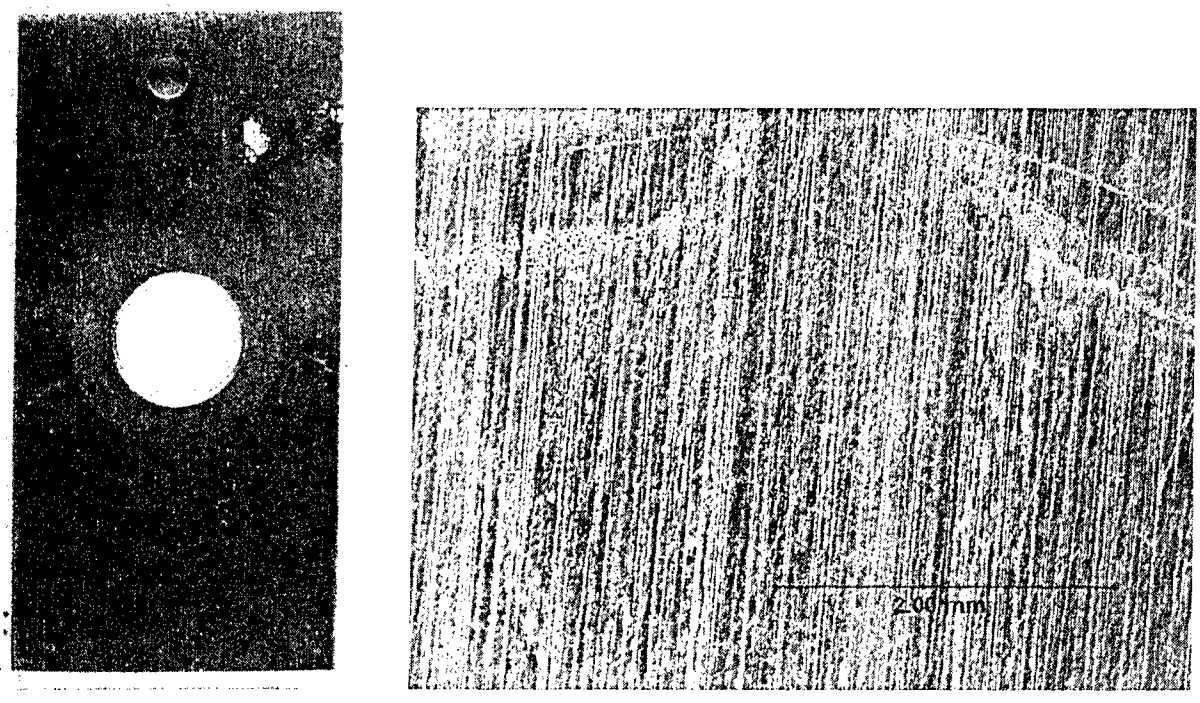


Figure 73. Metal Specimen of Inconel 718 with Crevice Attack. This specimen was fully immersed in arsinol/permanganate neutralent for 120 hr at 80 °C. This test specimen was evaluated with a PTFE multiple crevice assembly.

3.7 Full-Scale Validation of Permanganate Reagent.

The Explosive Destruction System, is a trailer-mounted system designed to safely neutralize a variety of chemical munitions.[107,108] 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.[109]

3.7.1 Reaction Conditions.

The reaction conditions are summarized in Table 47, and were obtained from a separate report describing operational effectiveness of the reagent.[109] Procedural details can also be found in the same report.[109] In summary, a Department of Transportation (DOT) bottle containing arsinol was placed into the EDS vessel, and explosive charges attached to the bottle. 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 tapwater was pumped into the reactor to rinse the vessel. On average, 83 L of tapwater 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, 68 L was used for the second rinse, and it was also conducted at ambient temperature. During the reactor campaign, multiple samples were collected at various times during the experiment. The identity and description of the samples are summarized below:

- *One-Hour Neutralent:* Sample of neutralent removed from the reactor after 1 hr of reaction.

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

- *Four-Hour Neutralent:* Sample of neutralent removed from the reactor after 4 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.

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

- *Waste Two:* Sample collected from the second waste drum. This drum contains the combined rinses drained from the reactor.

Table 47. Summary of Reaction Conditions. Data is taken from reference 109.

EDS Run Number	GTR Fill Materiel		Reagent Added (L)	Reaction Temperature (°C)
	Amount (L)[a]	Composition (wt%)[b]		
One	1.01	DA = 60.5 PD = 28.3 TPA = 4.1	49.8	60[c]
Two	1.99	DA = 57.9 PD = 31.1 TPA = 4.5	100	60
Three	2.23	DA = 57.1 PD = 29.9 TPA = 4.2	120	60
Four	2.22	DA = 58.1 PD = 29.7 TPA = 3.8	120	65[d]

a. Used average density of 1.48 to convert weight to volume. See section 3.2.5 for details.
b. Mixtures of multiple rocket fills (except run one). Composition calculated from composition of individual rocket, and amount of individual fill materiel.
c. Temperature set to 60 °C, but problem with temperature. One hour sample taken at 33 °C, three hour sample taken at 46 °C, and four hour sample taken at 74 °C.
d. Power outage during test; only reached 60 °C. Only a 1-hr sample collected.

3.7.2 Residual Agents.

Samples were received after being screened by another laboratory,[110] and then analyzed for residual DA, PD, and TPA using the method described in Section 2.5. In all cases, the samples were not extracted/derivatized for several days after the reactions were completed. The delay in processing ranged from two to seven 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=8) and laboratory control spikes (5 mg/L spike level, n=8) 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: DA 92.7% (RSD = 6.75%), PD 86.3% (RSD = 11.9%), and TPA 76.9% (RSD = 10.4%). The neutralent time point data is summarized

in Table 48, and the rinse, waste, and sludge data is summarized in Table 49. Example chromatograms are illustrated in Figure 74. There were no anomalies during the preparation or analysis of these samples.

The residual agent concentrations obtained on the day the reactions were performed (Day 0) are higher than the results obtained during this study,[110] but this difference was expected given the continued reactivity of the reagent (See Section 3.5.6). A comparison of the neutralent data for EDS Run One is illustrated in Figure 75. In this run, the samples were re-extracted/analyzed 7 days after the reaction was completed. The PD data obtained on Day 0 shows increasing concentration with time, while the data obtained during this study shows a decreasing trend. The other two analytes both show decreasing concentrations with time, for both sets of analyses. There is no obvious answer why the PD concentrations would increase with time, though it should be noted the magnitude of the increase is small. Data entry errors were ruled out by tracking the reported PD values back to the original chromatograms.

The data was used to estimate half-life during the reaction, and the estimates were based on a first-order reaction. The half-life determinations during the reaction are illustrated in Figure 76. The initial reaction (0-1 hr) is very fast, with average $t_{1/2}$ values of <0.1 hr for DA and PD, and 0.2 hr for TPA. After 1 hr, the rate slows down considerably, with an overall average $t_{1/2}$ of 2.7 hr for all three agents. The $t_{1/2}$ values calculated for the full-scale EDS runs compares quite well with the small-scale (Section 3.5.3) laboratory runs, where initial $t_{1/2}$ values were calculated to be 0.13 hr for DA and PD, and 0.18 hr for TPA under conditions similar to those used in the EDS runs. The fast reaction of arsinol fills with permanganate reagent is also supported by another study,[92] which demonstrated 95% of the trivalent arsenic would be oxidized to the pentavalent form in< 1 min, under a variety of conditions.

3.7.3 Quantitation of Reaction Products.

The samples were analyzed for reaction products using the capillary electrophoresis methods described in Section 2.6. 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 waste 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 waste and sludge samples were prepared using this second approach. There was not enough sample from the neutralent and rinse samples to perform the caustic extraction. The reaction product data is summarized in Tables 50 through 61. 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.

Text continues on page 141.

Table 48. Residual Agents in Neutralent Time Point Samples. All data reported in the original neutralent, with units of milligrams/liter. These reported results are the averages of duplicate analyses.

Target Analyze	Concentration in Neutralent (mg/L)[a]		
	@ 1 hr	@ 3 hr	@ 4 hr
	EDS Run One		
DA	0.672	0.237	0.261
PD	1.49	0.285	0.926
TPA	27.6	18.6	9.39
	EDS Run Two		
DA	Trace[b]	0.402	0.227
PD	Trace[b]	1.93	1.20
TPA	4.18	2.76	1.05
	EDS Run Three		
DA	0.193	0.114	0.237
PD	0.654	0.661	0.868
TPA	3.31	0.535	0.446
	EDS Run Four		
DA	0.317	NA[c]	NA[c]
PD	1.08	NA[c]	NA[c]
TPA	5.50	NA[c]	NA[c]

a. Reported values are the averages of two derivatization/extraction duplicates.
b. Peak detected, but below reporting limit of 0.1 mg/L.
c. Samples were not collected at these time points.

Table 49. Residual Agents in Rinse, Waste, and Sludge Samples. All data reported in the original sample, with units of milligrams/liter for liquids, and mg/kg for the sludges. These reported results are the averages of duplicate analyses.

Target Analyte	Concentration in Sample (mg/L)[a]			
	Rinse	Waste 1	Waste 2	Sludge[b]
	EDS Run One			
DA	11.4	0.126	2.88	68.8
PD	1.35	0.482	0.265	4.40
TPA	8.17	0.113	2.34	38.4
	EDS Run Two			
DA	4.06	Trace[c]	2.68	109
PD	0.598	0.610	0.299	4.33
TPA	6.01	0.237	3.06	83.4
	EDS Run Three			
DA	2.55	Trace[c]	Trace[c]	6.14
PD	0.678	0.517	0.670	0.473
TPA	1.32	Trace[c]	Trace[c]	6.03
	EDS Run Four			
DA	0.294	0.131	1.78	11.5
PD	Trace[c]	0.811	0.246	1.68
TPA	0.963	0.374	8.66	27.3

a. Reported values are the averages of two derivatization/extraction duplicates.
b. Units are mg/kg.
c. Peak detected, but below reporting limit of 0.1 mg/L.

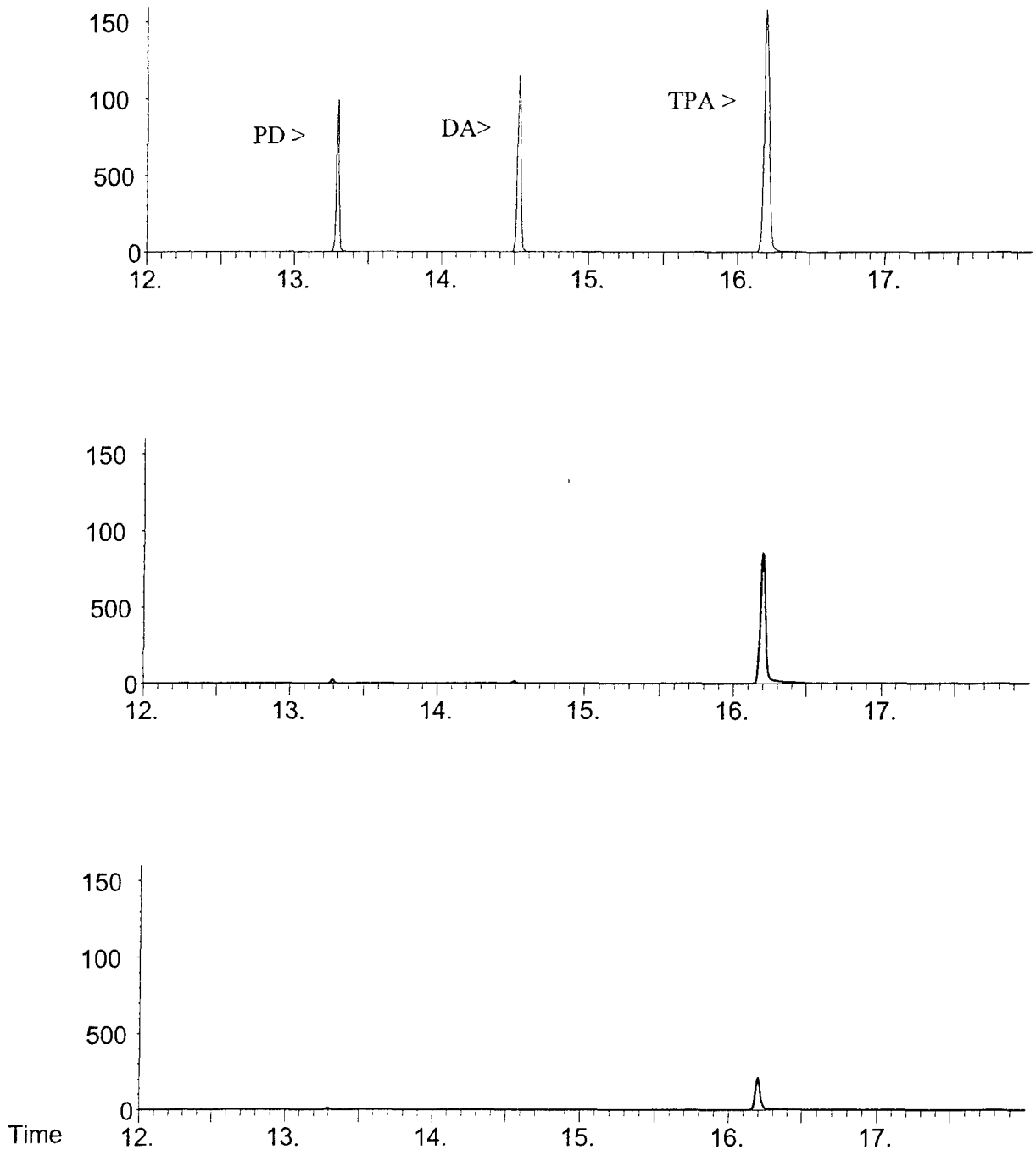


Figure 74. Example Chromatograms for Samples from EDS Run Number One. The upper panel is a 10 mg/L mixed standard, the middle panel is a 1 hr neutralent sample, and the bottom panel is a 4-hr neutralent sample. Data was acquired by GC/MSD-EI, in SIM mode.

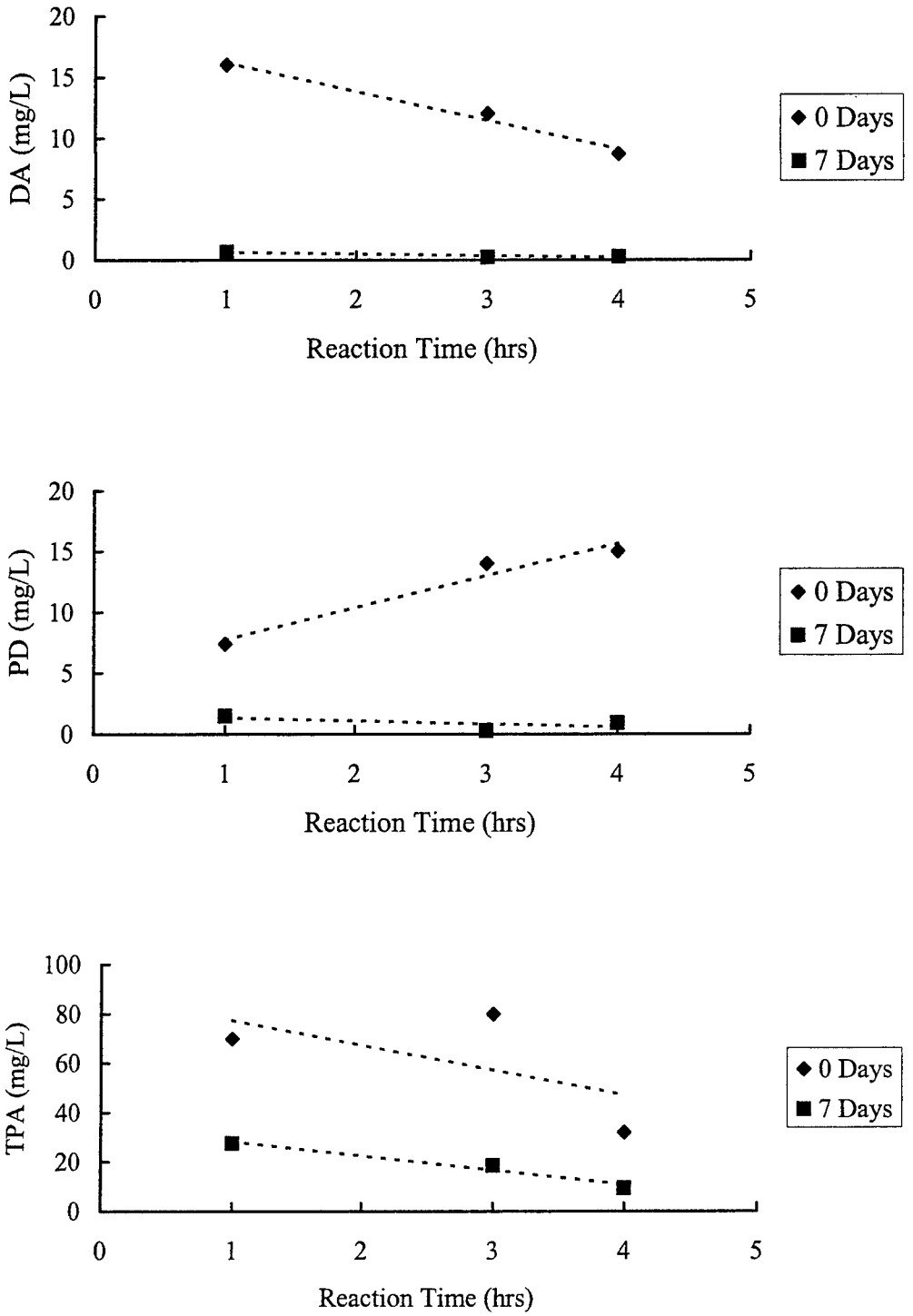


Figure 75. Comparison of Residual Agent Data Obtained on Day 0 and Day 7 for EDS Run Number One. The upper panel is DA, the middle panel is PD, and the bottom panel is TPA.

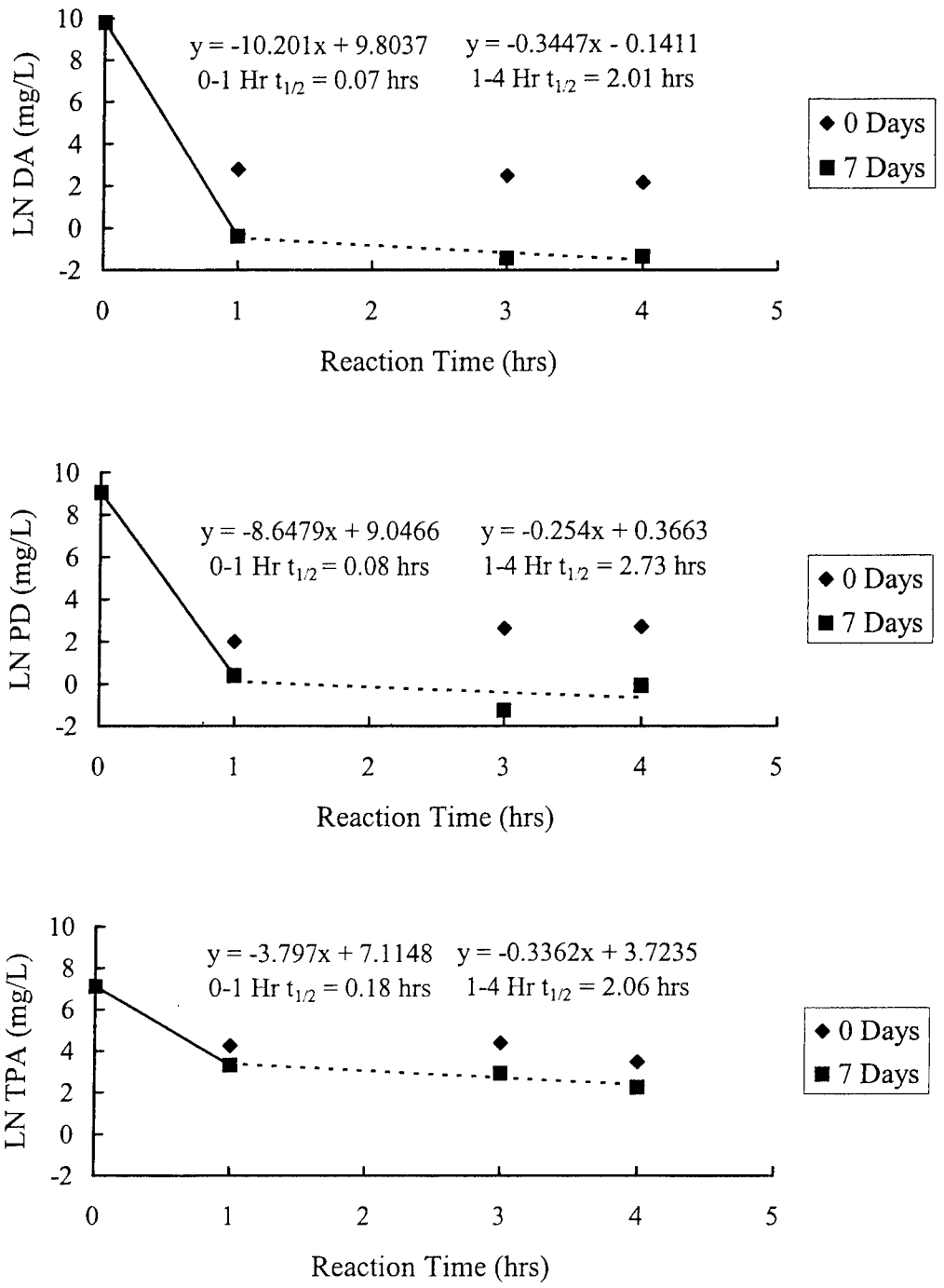


Figure 76. Comparison of Half-Life Data from Residual Agent Concentrations Obtained on Day 0 and Day 7 for EDS Run Number One. The upper panel is DA, the middle panel is PD, and the bottom panel is TPA. For clarity, only regression data for day 7 is shown.

The reaction products determined to be in the filtered neutralents generated during the full-scale EDS runs were similar to those found during analysis of neutralents generated during small-scale laboratory runs conducted at 60 and 80 °C with a 1:50 loading (Section 3.5.4). The F^- and SO_4^{-2} concentrations in the filtered neutralents generated during EDS testing were somewhat elevated relative to the small-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 lab-scale testing. These two differences could easily account for the observed differences. The filtered neutralents generated during EDS testing also had elevated levels of NO_3^- relative to the small-scale laboratory testing. The most likely explanation for this is explosives were used in the EDS runs, but were not used in the laboratory testing.

Table 50. Summary of Neutralent Results for EDS Run One. All data reported in the original neutralent, with units ofmilligrams/liter. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 1 hr	@ 3 hr	@ 4 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	5,420	4,590	4,280
Fluoride (F^-)	344	346	365
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	531	Trace[b] (450)	Trace[b] (450)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	378	303	537
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	1,610	1,120	2,340
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	97.6	89.4	82.6
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	Trace[b] (200)	Trace[b] (200)	285
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 indicated reporting limit.

Text continues on page 152.

Table 51. Reaction Products in Rinse and Waste Samples from EDS Run One. All data reported in the original sample, with units of milligrams/liter. These results are on the filtered (0.45 μm) sample. The values in parentheses are reporting limits.

Target Analyte	Concentration in Sample (mg/L)		
	Rinse	Waste 1	Waste 2
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	Trace[b] (380)	4,230	Trace[b] (380)
Fluoride (F^-)	Trace[b] (70.0)	377	Trace[b] (70.0)
Nitrate (NO_3^-)	ND[a] (490)	Trace[b] (490)	Trace[b] (490)
Sulfate (SO_4^{-2})	ND[a] (450)	488	Trace[b] (450)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	110	1,810	116
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	438	1,220	696
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	57.9	Trace[b] (50.0)	66.1
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	Trace[b] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	ND[a] (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)	1,100	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	Trace[b] (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 52. Reaction Products in Waste and Sludge Samples from EDS Run One. All data reported in the original sample, with units of mg/kg. 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 of 509.5 mg.

Target Analyte	Concentration in Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (130)	ND[a] (130)	ND[a] (130)
Arsenate ($HAsO_4^{-2}$)	308	150	84.5
Chloride (Cl^-)	2,920	115	156
Fluoride (F^-)	250	37.1	58.3
Nitrate (NO_3^-)	Trace[b] (192)	ND[a] (192)	ND[a] (192)
Sulfate (SO_4^{-2})	329	Trace[b] (177)	Trace[b] (177)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	1,560	1,250	2,410
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	916	2,970	8,710
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.2)	ND[a] (39.2)	ND[a] (39.2)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	Trace[b] (19.6)	117	270
Acetate ($C_2H_3O_2^-$)	Trace[b] (62.8)	Trace[b] (62.8)	ND[a] (62.8)
Formate (CHO_2^-)	Trace[b] (58.9)	ND[a] (58.9)	Trace[b] (58.9)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)
Glycolate ($C_2H_3O_3^-$)	1,090	1,020	1,700
Oxalate ($C_2O_4^{-2}$)	Trace[b] (149)	219	ND[a] (149)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)

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

Table 53. Summary of Neutralent Results for EDS Run Two. All data reported in the original neutralent, with units of milligrams/liter. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are reporting limits

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 1 hr	@ 3 hr	@ 4 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	9,630	6,920	4,900
Fluoride (F^-)	385	374	366
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	659	Trace[b] (450)	Trace[b] (450)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	546	619	669
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	1,990	2,230	2,230
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	141	112	91.7
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
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 ($C_2H_3O_3^-$)	330	395	439
Oxalate ($C_2O_4^{-2}$)	Trace[b] (380)	ND[a] (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 indicated reporting limit.

Table 54. Reaction Products in Rinse and Waste Samples from EDS Run Two. All data reported in the original sample, with units of milligrams/liter. These results are on the filtered (0.45 μm) sample. The values in parentheses are reporting limits.

Target Analyte	Concentration in Sample (mg/L)		
	Rinse	Waste 1	Waste 2
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Chloride (Cl^-)	470	5,400	376
Fluoride (F^-)	77.8	387	76.0
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	Trace[b] (450)	411	ND[a] (450)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	154	655	125
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	554	2,920	2,030
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	64.9	78.2	87.5
Acetate ($C_2H_3O_2^-$)	ND[a] (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)	614	ND[a] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	Trace	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 55. Reaction Products Waste and Sludge Samples from EDS Run Two. All data reported in the original sample, with units of mg/kg. 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 of 509.5 mg.

Target Analyte	Concentration in Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (130)	ND[a] (130)	ND[a] (130)
Arsenate ($HAsO_4^{-2}$)	130	153	Trace[b] (62.8)
Chloride (Cl^-)	4,130	327	78.7
Fluoride (F^-)	254	49.7	65.4
Nitrate (NO_3^-)	Trace[b] (192)	ND[a] (192)	ND[a] (192)
Sulfate (SO_4^{-2})	311	Trace[b] (177)	Trace[b] (177)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	1,380	821	1,820
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	5,090	3,730	17,600
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.2)	ND[a] (39.2)	ND[a] (39.2)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	213	122	448
Acetate ($C_2H_3O_2^-$)	Trace[b] (62.8)	Trace[b] (62.8)	ND[a] (62.8)
Formate (CHO_2^-)	Trace[b] (58.9)	ND[a] (58.9)	Trace[b] (58.9)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)
Glycolate ($C_2H_3O_3^-$)	1,320	972	1,570
Oxalate ($C_2O_4^{-2}$)	193	245	Trace[b] (149)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)

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

Table 56. Summary of Neutralent Results for EDS Run Three. All data reported in the original neutralent, with units of milligrams/liter. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 1 hr	@ 3 hr	@ 4 hr
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	Trace[b] (160)	Trace[b] (160)
Chloride (Cl^-)	7,950	6,570	5,270
Fluoride (F^-)	429	446	400
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	525	454	489
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	734	713	755
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	2,040	1,860	1,690
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	118	102	74.6
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	Trace[b] (150)	Trace[b] (150)	ND[a] (150)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	ND[a] (200)	ND[a] (200)
Glycolate ($C_2H_3O_3^-$)	362	399	382
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 indicated reporting limit.

Table 57. Reaction Products in Rinse and Waste Samples from EDS Run Three. All data reported in the original sample, with units of milligrams/liter. These results are on the filtered (0.45 μm) sample. The values in parentheses are reporting limits.

Target Analyte	Concentration in Sample (mg/L)		
	Rinse	Waste 1	Waste 2
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND[a] (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	Trace[b] (160)	Trace[b] (160)
Chloride (Cl^-)	336	5,690	3,280
Fluoride (F^-)	81.6	467	460
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND[a] (490)
Sulfate (SO_4^{-2})	ND[a] (450)	466	461
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	85.0	1,450	1,450
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	370	1,610	1,840
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	54.6	50.0	55.3
Acetate ($C_2H_3O_2^-$)	ND[a] (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)	821	734
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	666	676
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 58. Reaction Products in Waste and Sludge Samples from EDS Run Three. All data reported in the original sample, with units of mg/kg. 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 of 509.5 mg.

Target Analyte	Concentration in Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (130)	ND[a] (130)	ND[a] (130)
Arsenate ($HAsO_4^{-2}$)	348	324	131
Chloride (Cl^-)	3,090	2,960	109
Fluoride (F^-)	275	276	67.5
Nitrate (NO_3^-)	Trace[b] (192)	Trace[b] (192)	ND[a] 9192)
Sulfate (SO_4^{-2})	290	294	Trace[b] (177)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	1,040	1,020	699
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	2,290	2,530	10,700
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.2)	ND[a] (39.2)	ND[a] (39.2)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	35.8	34.7	208
Acetate ($C_2H_3O_2^-$)	ND[a] (62.8)	ND[a] (62.8)	ND[a] (62.8)
Formate (CHO_2^-)	Trace[b] (58.9)	Trace[b] (58.9)	ND[a] (58.9)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)
Glycolate ($C_2H_3O_3^-$)	1,080	1,160	675
Oxalate ($C_2O_4^{-2}$)	Trace[b] (149)	Trace[b] (149)	197
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)

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

Table 59. Summary of Neutralent Results for EDS Run Four. All data reported in the original neutralent, with units of milligrams/liter. These results are on the filtered (0.45 μm) neutralent. The values in parentheses are reporting limits.

Target Analyte	Concentration in Neutralent (mg/L)		
	@ 1 hr	@ 3 hr	@ 4 hr
Arsenite (AsO_2^-)	ND[a] (330)	NA[c]	NA[c]
Arsenate ($HAsO_4^{-2}$)	Trace[b] (160)	NA[c]	NA[c]
Chloride (Cl^-)	9,170	NA[c]	NA[c]
Fluoride (F^-)	462	NA[c]	NA[c]
Nitrate (NO_3^-)	ND[a] (490)	NA[c]	NA[c]
Sulfate (SO_4^{-2})	536	NA[c]	NA[c]
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	581	NA[c]	NA[c]
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	2,640	NA[c]	NA[c]
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	NA[c]	NA[c]
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	145	NA[c]	NA[c]
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	NA[c]	NA[c]
Formate (CHO_2^-)	ND[a] (150)	NA[c]	NA[c]
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (200)	NA[c]	NA[c]
Glycolate ($C_2H_3O_3^-$)	492	NA[c]	NA[c]
Oxalate ($C_2O_4^{-2}$)	Trace[b] (380)	NA[c]	NA[c]
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (200)	NA[c]	NA[c]

a. No peak was detected in the electropherogram.
b. A peak was detected, but below the indicated reporting limit.
c. No samples collected at these time points during this run.

Table 60. Reaction Products in Rinse and Waste Samples from EDS Run Four. All data reported in the original sample, with units of milligrams/liter. These results are on the filtered (0.45 μm) sample. The values in parentheses are reporting limits.

Target Analyte	Concentration in Sample (mg/L)		
	Rinse	Waste 1	Waste 2
Arsenite (AsO_2^-)	ND[a] (330)	ND[a] (330)	ND (330)
Arsenate ($HAsO_4^{-2}$)	ND[a] (160)	Trace[b] (160)	ND (160)
Chloride (Cl^-)	ND[a] (380)	7,780	389
Fluoride (F^-)	ND[a] (70.0)	477	86.2
Nitrate (NO_3^-)	ND[a] (490)	ND[a] (490)	ND (490)
Sulfate (SO_4^{-2})	ND[a] (450)	Trace[b] (450)	Trace[b] (450)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	ND[a] (5.0)	918	113
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	20.1	3,070	520
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (100)	ND[a] (100)	ND[a] (100)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	ND[a] (50.0)	116	67.3
Acetate ($C_2H_3O_2^-$)	ND[a] (160)	ND[a] (160)	ND[a] (160)
Formate (CHO_2^-)	ND[a] (150)	ND[a] (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)	611	Trace[b] (200)
Oxalate ($C_2O_4^{-2}$)	ND[a] (380)	Trace[b] (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 61. Reaction Products in Waste and Sludge Samples from EDS Run Four. All data reported in the original sample, with units of mg/kg. 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 of 509.5 mg.

Target Analyte	Concentration in Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (130)	ND[a] (130)	ND[a] (130)
Arsenate ($HAsO_4^{-2}$)	255	219	190
Chloride (Cl^-)	4,300	334	126
Fluoride (F^-)	298	57.5	85.6
Nitrate (NO_3^-)	Trace[b] (192)	ND[a] (192)	ND[a] (192)
Sulfate (SO_4^{-2})	307	Trace[b] (177)	Trace[b] (177)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	1,720	1,260	3,620
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	5,230	5,210	19,700
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.2)	ND[a] (39.2)	ND[a] (39.2)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	166	208	831
Acetate ($C_2H_3O_2^-$)	Trace[b] (62.8)	ND[a] (62.8)	ND[a] (62.8)
Formate (CHO_2^-)	Trace[b] (58.9)	Trace[b] (58.9)	Trace[b] (58.9)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)
Glycolate ($C_2H_3O_3^-$)	1,610	1,380	2,930
Oxalate ($C_2O_4^{-2}$)	Trace[b] (149)	175	ND[a] (149)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (78.5)	ND[a] (78.5)	ND[a] (78.5)

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

3.7.4 Total Metals.

The total metal analyses were performed on duplicate digests of the waste and sludge samples. There was not enough material in the neutralent or rinse samples to perform the total metals analyses. The digests were prepared according to the procedure specified in SW846, Method 3010A.[42] The digests were analyzed using two different methods; EPA 200.7 for iron, sodium, and sulfur;[44] and EPA 200.8 for arsenic, copper, and manganese.[45] The EPA 200.7 method uses ICP, with optical detection, and EPA 200.8 uses ICP, with mass detection. In addition to the waste and sludge 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 62 through 66. 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 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: 9.00 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 62. 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 eight 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 177.1 mg.

Total Metal	Mean Value (mg/kg)	Percent Recovery		
		Mean	SD	Percent RSD
Arsenic	573	91.5	6.09	6.66
Copper	2,840	96.1	5.48	5.70
Iron	22,300	65.9	1.11	1.68
Manganese	8,260	81.8	7.86	9.61
Sodium	ND[a] (141)	NA[b]	NA[b]	NA[b]
Sulfur	2,200	91.6	2.41	2.63

a. Not detected in digest.
b. Not applicable.

Table 63. Total Metals in Waste and Sludge Samples from EDS Run One. 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 54.6 mg.

Total Metal	Concentration in Original Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	4,160	1,010	16,300
Copper	412	88.0	2,030
Iron	1,110	1,480	16,300
Manganese	87,100	6,980	56,600
Sodium	33,200	1,870	7,370
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 64. Total Metals in Waste 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 54.6 mg.

Total Metal	Concentration in Original Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	6,410	1,340	28,900
Copper	346	69.1	2,380
Iron	1,620	1,300	22,300
Manganese	66,200	8,660	100,000
Sodium	29,200	3,630	14,900
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 65. Total Metals in Waste and Sludge Samples from EDS Run Three. All data reported in the original sample, with units of mg/kg. 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 of 54.6 mg.

Total Metal	Concentration in Original Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	10,700	8,260	20,300
Copper	624	628	2,010
Iron	1,870	1,320	13,400
Manganese	144,000	127,000	108,000
Sodium	42,300	41,600	17,700
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 66. Total Metals in Waste and Sludge Samples from EDS Run Four. 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 values in parentheses are the estimated reporting limits, based on the average sample weight of 54.6 mg.

Total Metal	Concentration in Original Sample (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	6,140	2,240	17,600
Copper	460	162	764
Iron	1,220	611	3,400
Manganese	91,200	16,900	50,100
Sodium	36,300	4,670	6,440
Sulfur	ND (910)	ND (910)	ND (910)

a. Not detected in digest.

3.7.5 Qualitative Analyses by NMR and LC/MS.

The neutralent, rinse, and waste samples were qualitatively analyzed for bulk reaction products using the NMR and LC/MS methods described and referenced in Section 3.1. The reaction products were determined after samples were prepared using two different extraction approaches. Approximately 500 mg (exact weight recorded) of sample was weighed into a 4 mL glass vial, then either 2 mL of $CDCl_3$ (for NMR analyses) or 2 mL of 2-propanol (for LC/MS analyses) 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. The results are summarized in Table 67, and example spectra and chromatograms are illustrated in Figures 77 and 78.

The NMR and LC/MS analyses support the peak assignments made during the quantitative analysis of these samples for reaction products (Section 3.7.3). The NMR and LC/MS could not provide quantitative data, due to the nature of the sample matrices. The samples contained large backgrounds of metals, which affected both analyses. In addition, the background of oxygen (a paramagnetic species) from the decomposition of MnO_4^{-2} prevented the NMR from being able to acquire data with sufficient precision and sensitivity to provide quantitative results.

3.7.6 Residual Sodium Permanganate.

The samples were analyzed for residual $NaMnO_4$ using the method described in Section 2.7. The neutralent, rinse, and waste samples were all analyzed, with each sample prepared and analyzed in triplicate. The residual $NaMnO_4$ data is summarized in Table 67. 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 67 are higher than expected, based on dimensional analysis of the initial 20 wt% $NaMnO_4$ reagent. 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. The positive controls were elevated, with an average (n= 15) concentration of 305,000 mg/L (RSD = 11.4%). While not listed as an interferent (Section 2.7), it is believed the high levels of arsenic may have interfered with the assay. Another possible source of the error are the large dilutions (10,000–15,000 times) required to analyze these concentrated samples. Small errors in the measurement will be magnified by the large dilution factor required to use this assay.

3.7.7 Isolation and Characterization of Solids from Waste and Sludge Samples.

The solids contained in the waste and sludge samples were isolated, in order to characterize the solid fraction contained in these samples. There was not enough sample of the neutralent or rinse 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 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 Section 3.5.6. The time between start of reaction, and isolation of solids, is summarized in Table 68.

Table 67. Summary of NMR and LC/MS Data for the Neutralent, Rinse, and Waste Samples.

Sample Description	Peaks Detected in Phenyl Shift Region of Spectrum		Peaks Detected by LC/MS	
	^{1}H-NMR	^{13}C-NMR	DPAOA	TPAO
	EDS Run One			
1 Hr Neutralent	Yes	Yes	Yes- Large[a]	Yes- Small[b]
3 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
4 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
Rinse	Yes	No	Yes- Small	Yes- Small
Waste 1	Yes	Yes (2)	Yes- Large	No
Waste 2	Yes	No	Yes- Small	Yes- Small
	EDS Run Two			
1 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
3 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
4 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
Rinse	Yes	No	Yes- Small	Yes- Small
Waste 1	Yes	Yes (2)	Yes- Large	Yes- Small
Waste 2	Yes	Yes	Yes- Large	Yes- Small
	EDS Run Three			
1 Hr Neutralent	Yes	Yes	Yes- Small	Yes- Small
3 Hr Neutralent	Yes	Yes	Yes- Small	Yes- Small
4 Hr Neutralent	Yes	Yes	Yes- Small	Yes- Small
Rinse	Yes	No	Yes- Small	No
Waste 1	Yes	Yes (2)	Yes- Small	No
Waste 2	Yes	Yes	Yes- Small	No
	EDS Run Four			
1 Hr Neutralent	Yes	Yes	Yes- Large	Yes- Small
Rinse	No	No	No	No
Waste 1	Yes	Yes	Yes- Large	Yes- Small
Waste 2	Yes	No	Yes- Small	No

a. Large is a peak area response ≥ 1,000,000 area counts.
b. Small is a peak area response < 1,000,000 area counts.

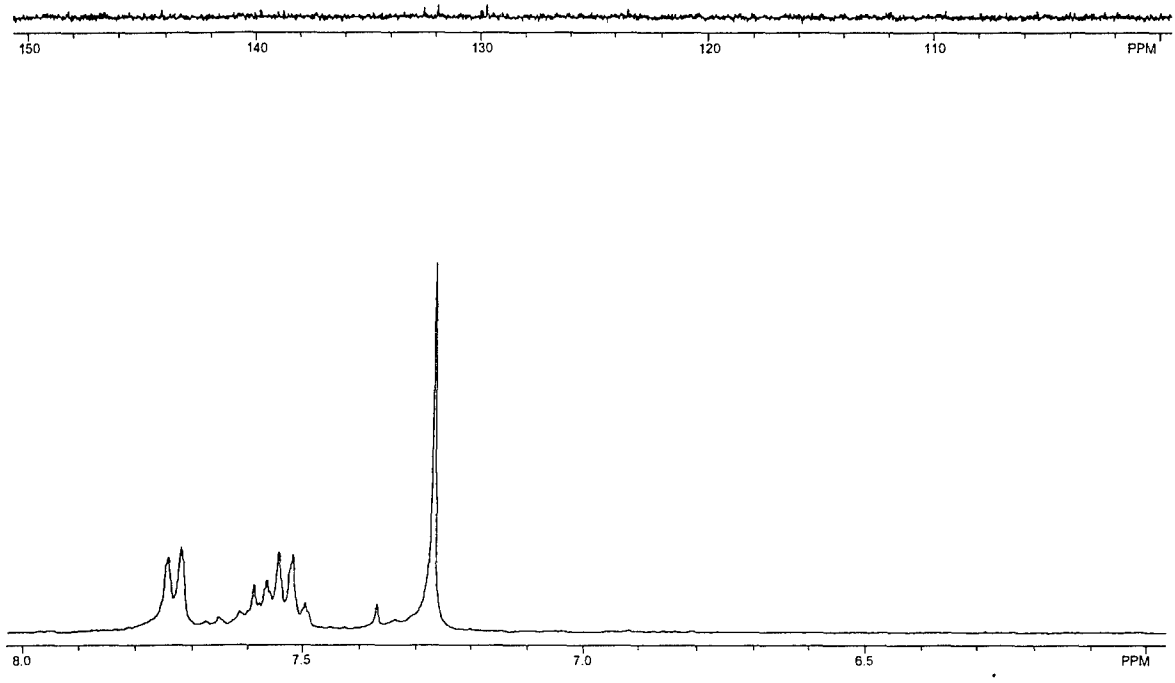
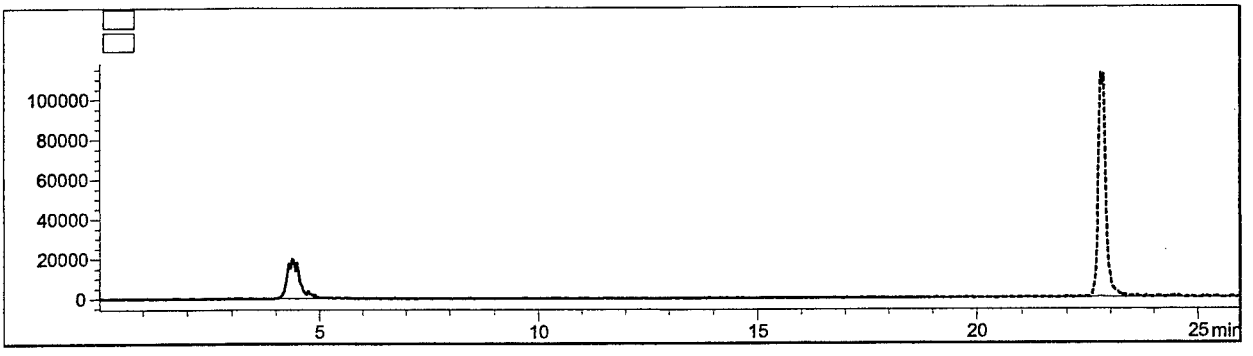
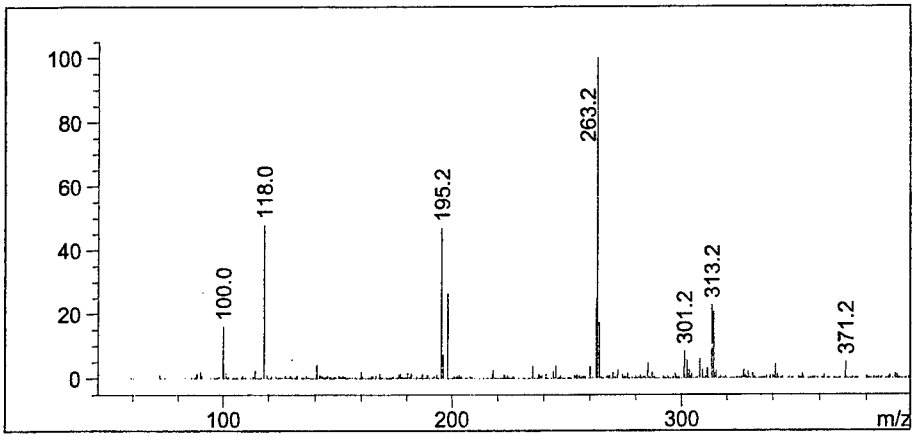


Figure 77. Example NMR Spectra Obtained from the Analysis of the Waste 2 Sample Generated During EDS Run Two. The upper panel is the ^{13}C-NMR spectrum, and the lower panel is the ^{1}H-NMR spectrum. In both cases, the spectra have been zoomed into the phenyl-shift region.





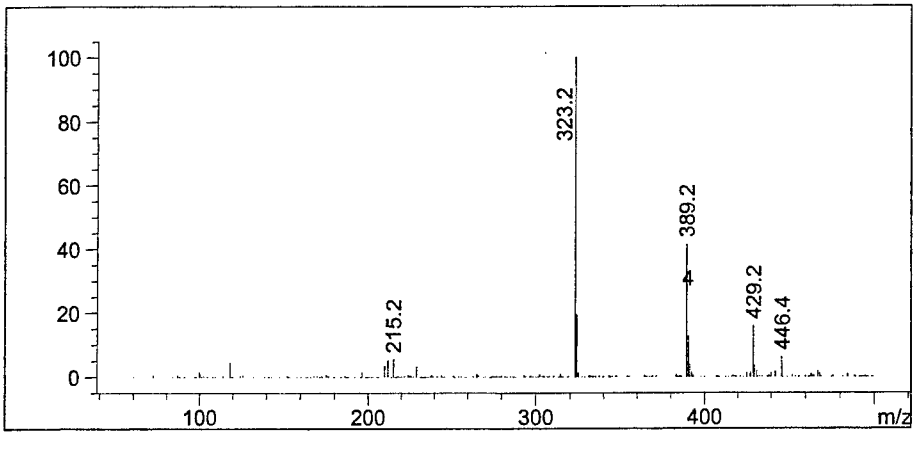


Figure 78. Example LC/MS Data Obtained from the Analysis of the Waste 2 Sample Generated During EDS Run Two. The upper panel is the chromatographic trace, the middle panel is the MS spectrum of DPAOA, and the bottom panel is the MS spectrum of TPAO.

Table 68. Residual Sodium Permanganate Data from the Analysis of Neutralent, Rinse, and Waste Samples.

Sample Description	$NaMnO_4$ in Sample (mg/L)		
	Low	High	Mean
	EDS Run One		
1 Hr Neutralent	249,000	318,000	**281,000**
3 Hr Neutralent	227,000	263,000	**246,000**
4 Hr Neutralent	241,000	254,000	**247,000**
Rinse	19,700	20,900	**20,400**
Waste 1	191,000	199,000	**196,000**
Waste 2	8,190	11,100	**9,160**
	EDS Run Two		
1 Hr Neutralent	254,000	263,000	**259,000**
3 Hr Neutralent	208,000	227,000	**220,000**
4 Hr Neutralent	194,000	198,000	**203,000**
Rinse	17,700	19,000	**18,400**
Waste 1	174,000	190,000	**183,000**
Waste 2	23,500	26,600	**24,600**
	EDS Run Three		
1 Hr Neutralent	249,000	257,000	**253,000**
3 Hr Neutralent	221,000	222,000	**222,000**
4 Hr Neutralent	190,000	199,000	**194,000**
Rinse	15,600	16,300	**16,000**
Waste 1	191,000	217,000	**202,000**
Waste 2	192,000	195,000	**194,000**
	EDS Run Four		
1 Hr Neutralent	241,000	247,000	**245,000**
Rinse	5,490	5,630	**5,550**
Waste 1	255,000	269,000	**262,000**
Waste 2	38,000	38,000	**38,000**

Isolated solids were analyzed for residual DA, PD, and TPA using the method described in Section 2.5. 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=4) and laboratory control spikes (5 mg/L spike level, n=4) were also prepared and analyzed. In all cases, there were no analytes detected in any of the extraction blanks. The average recoveries were: DA 88.7% (RSD = 5.83%), PD 88.1% (RSD = 13.1%), and TPA 81.6% (RSD = 9.86%). The residual agent data is summarized in Table 69, and there were no anomalies during the preparation or analysis of these samples.

The solids isolated from the sludge sample from EDS Run Two was re-extracted after approximately two weeks of storage at room temperature, using a modification to the method described in Section 2.5. These analyses were performed to demonstrate extraction efficiency of residual agents from the isolated solids. Approximately 50 mg (exact weight recorded) of solid was used for each derivatization/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: DA 79.7% (RSD = 7.34%), PD 92.7% (RSD = 10.9%), and TPA 76.3% (RSD = 11.2%). In these analyses, the solids were extracted a total of three times, with each extract being analyzed individually. The residual agent data is summarized in Table 70, and demonstrates the analysis procedure utilized in this study is a valid approach to analyzing these types of solids. Additionally, these results suggest the residual agent composition of the **isolated** solids is stable, at least over a two week time period.

The isolated solids were analyzed for reaction products using the capillary electrophoresis methods described in Section 2.6. 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 15 min. 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 71 through 74.

Table 69. Days Elapsed from First Day of Reaction until the Solids were Isolated.

Sample Identification	Days Elapsed From Reaction to Isolation
EDS Run One	
Waste 1	20
Waste 2	21
Sludge	15
EDS Run Two	
Waste 1	10
Waste 2	10
Sludge	14
EDS Run Three	
Waste 1	4
Waste 2	9
Sludge	7
EDS Run Four	
Waste 1	6
Waste 2	6
Sludge	7

The isolated solids were analyzed for total metals using the digestion procedure specified in SW846, Method 3010A,[42] 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 two different methods; EPA 200.7 for iron, sodium, and sulfur;[44] and EPA 200.8 for arsenic, copper, and manganese.[45] The EPA 200.7 method uses ICP, with optical detection, and EPA 200.8 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 75 through 79. 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.

Table 70. Residual Agents in Solids Isolated from Waste and 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)[a]		
	Waste 1	Waste 2	Sludge
	EDS Run One		
DA	1.80	180	104
PD	Trace[b]	10.2	7.14
TPA	Trace[b]	53.5	38.0
	EDS Run Two		
DA	108	34.5	205
PD	9.18	4.84	10.5
TPA	38.9	30.0	116
	EDS Run Three		
DA	30.4	17.8	72.8
PD	2.84	3.03	7.43
TPA	5.13	8.74	32.7
	EDS Run Four		
DA	10.3	143	169
PD	1.33	9.89	9.03
TPA	10.3	290	144

a. Reported values are the averages of two derivatization/extraction duplicates.
b. Peak detected, but less than estimated reporting limit of 1 mg/kg.

Table 71. Residual Agents in Solids Isolated from EDS Run Two Sludge Sample. All data reported in the isolated solid, with units of milligrams/kilograms. These reported results are the averages of duplicate analyses. These extractions were performed approximately two weeks after the data summarized in Table 69.

Target Analyte	Concentration in Isolated Solids (mg/kg)[a]		
	1st Extraction	2nd Extraction	3rd Extraction
DA	187	3.47	Trace[b]
PD	12.4	Trace[b]	ND
TPA	98.4	8.28	Trace[b]

a. Reported values are the averages of two derivatization/extraction duplicates.
b. Peak detected, but less than estimated reporting limit of 1 mg/kg.

The isolated solids were qualitatively analyzed for bulk reaction products using the NMR and LC/MS methods described and referenced in Section 3.1. The reaction products were determined after samples were prepared using two different extraction approaches. Approximately 500 mg (exact weight recorded) of sample was weighed into a 4 mL glass vial, then either 2 mL of $CDCl_3$ (for NMR analyses) or 2 mL of 2-propanol (for LC/MS analyses) 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. The results are summarized in Table 80, and example spectra and chromatograms are illustrated in Figures 79 and 80. The NMR and LC/MS analyses support the peak assignments made during the quantitative analysis of these samples for reaction products.

Table 72. Residual Reaction Products in Solids Isolated from Waste and Sludge Samples from EDS Run One. All data reported in the original sample, with units of mg/kg. 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 of 501.7 mg.

Target Analyte	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (132)	ND[a] (132)	ND[a] (132)
Arsenate ($HAsO_4^{-2}$)	525	176	236
Chloride (Cl^-)	1,470	193	246
Fluoride (F^-)	216	55.5	46.0
Nitrate (NO_3^-)	320	ND[a] (195)	ND[a] (195)
Sulfate (SO_4^{-2})	294	ND[a] (179)	Trace[b] (179)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	2,660	2,530	3,890
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	836	25,100	20,900
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.9)	ND[a] (39.9)	ND[a] (39.9)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	Trace[b] (19.9)	696	608
Acetate ($C_2H_3O_2^-$)	ND[a] (63.8)	ND[a] (63.8)	ND[a] (63.8)
Formate (CHO_2^-)	ND[a] (59.8)	Trace[b] (59.8)	Trace[b] (59.8)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)
Glycolate ($C_2H_3O_3^-$)	1,730	1,800	2,620
Oxalate ($C_2O_4^{-2}$)	ND[a] (151)	ND[a] (151)	ND[a] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	NDa (79.7)

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

Text continues on page 170.

Table 73. Residual Reaction Products in Solids Isolated from Waste and Sludge Samples from EDS Run Two. All data reported in the original sample, with units of mg/kg. 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 of 501.7 mg.

Target Analyte	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (132)	ND[a] (132)	ND[a] (132)
Arsenate ($HAsO_4^{-2}$)	431	173	212
Chloride (Cl^-)	200	220	220
Fluoride (F^-)	278	73.5	43.0
Nitrate (NO_3^-)	ND[a] (195)	ND[a] (195)	ND[a] (195)
Sulfate (SO_4^{-2})	Trace[b] (179)	Trace[b] (179)	Trace[b] (179)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	9,370	5,110	5,250
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	37,800	44,900	31,400
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.9)	ND[a] (39.9)	ND[a] (39.9)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	1,080	1,280	856
Acetate ($C_2H_3O_2^-$)	ND[a] (63.8)	ND[a] (63.8)	ND[a] (63.8)
Formate (CHO_2^-)	Trace[b] (59.8)	Trace[b] (59.8)	Trace[b] (59.8)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)
Glycolate ($C_2H_3O_3^-$)	6,070	2,570	2,700
Oxalate ($C_2O_4^{-2}$)	ND[a] (151)	ND[a] (151)	ND[a] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)

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

Table 74. Residual Reaction Products in Solids Isolated from Waste and Sludge 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 reporting limits based on the average sample weight of 501.7 mg.

Target Analyte	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (132)	ND[a] (132)	ND[a] (132)
Arsenate ($HAsO_4^{-2}$)	1,250	686	217
Chloride (Cl^-)	1,180	1,780	207
Fluoride (F^-)	360	327	88.0
Nitrate (NO_3^-)	ND[a] (195)	458	ND[a] (195)
Sulfate (SO_4^{-2})	213	235	Trace[b] (179)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	23,000	6,080	3,620
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	18,500	13,000	33,300
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.9)	ND[a] (39.9)	ND[a] (39.9)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	262	190	726
Acetate ($C_2H_3O_2^-$)	ND[a] (63.8)	Trace[b] (63.8)	Trace[b] (63.8)
Formate (CHO_2^-)	Trace[b] (59.8)	ND[a] (59.8)	Trace[b] (59.8)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)
Glycolate ($C_2H_3O_3^-$)	15,900	3,740	2,020
Oxalate ($C_2O_4^{-2}$)	2,150	336	Trace[b] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)

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

Table 75. Residual Reaction Products in Solids Isolated from Waste and Sludge Samples from EDS Run Four. 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 of 501.7 mg.

Target Analyte	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenite (AsO_2^-)	ND[a] (132)	ND[a] (132)	ND[a] (132)
Arsenate ($HAsO_4^{-2}$)	525	347	585
Chloride (Cl^-)	3,040	Trace[b] (151)	195
Fluoride (F^-)	451	102	83.5
Nitrate (NO_3^-)	Trace[b] (195)	ND[a] (195)	ND[a] (195)
Sulfate (SO_4^{-2})	313	Trace[b] (179)	Trace[b] (179)
Phenylarsonic Acid ($C_6H_5AsO_3^{-2}$)	8,670	6,440	11,500
Diphenylarsinic Acid ($C_{12}H_{10}AsO_2^-$)	14,800	28,600	31,700
Phenylarsine Oxide (C_6H_5AsO)	ND[a] (39.9)	ND[a] (39.9)	ND[a] (39.9)
Triphenylarsine Oxide ($C_{18}H_{15}AsO$)	333	948	1,610
Acetate ($C_2H_3O_2^-$)	Trace[b] (63.8)	Trace[b] (63.8)	Trace[b] (63.8)
Formate (CHO_2^-)	ND[a] (59.8)	Trace[b] (59.8)	Trace[b] (59.8)
Fumarate ($C_4H_2O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)
Glycolate ($C_2H_3O_3^-$)	5,530	4,090	7,770
Oxalate ($C_2O_4^{-2}$)	522	ND[a] (151)	ND[a] (151)
Succinate ($C_4H_4O_4^{-2}$)	ND[a] (79.7)	ND[a] (79.7)	ND[a] (79.7)

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

Table 76. 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 eight 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 177.1 mg.

Total Metal	Mean Value (mg/kg)	Percent Recovery		
		Mean	SD	Percent RSD
Arsenic	573	91.5	6.09	6.66
Copper	2,840	96.1	5.48	5.70
Iron	22,300	65.9	1.11	1.68
Manganese	8,260	81.8	7.86	9.61
Sodium	ND[a] (141)	NA[b]	NA[b]	NA[b]
Sulfur	2,200	91.6	2.41	2.63

a. Not detected in digest.
b. Not applicable.

Table 77. Total Metals in Solids Isolated from Waste and Sludge Samples from EDS Run One. 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 of 54.6 mg.

Total Metal	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	13,700	59,100	51,200
Copper	1,670	7,660	6,130
Iron	4,130	42,100	77,300
Manganese	216,000	322,000	261,000
Sodium	46,900	29,400	14,300
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 78. Total Metals in Solids Isolated from Waste and Sludge Samples from EDS Run Two. 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 of 54.6 mg.

Total Metal	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	46,800	40,900	57,200
Copper	3,690	2,430	4,040
Iron	9,880	20,600	33,100
Manganese	318,000	182,000	206,000
Sodium	49,200	26,200	23,900
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 79. Total Metals in Solids Isolated from Waste and Sludge Samples from EDS Run Three. 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 of 54.6 mg.

Total Metal	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	34,000	27,100	48,800
Copper	2,070	1,630	4,100
Iron	6,460	4,670	27,300
Manganese	370,000	270,000	243,000
Sodium	76,100	68,600	38,600
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

Table 80. Total Metals in Solids Isolated from Waste and Sludge Samples from EDS Run Four. 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 of 54.6 mg.

Total Metal	Concentration in Isolated Solids (mg/kg)		
	Waste 1	Waste 2	Sludge
Arsenic	26,600	68,800	64,800
Copper	2,140	4,760	3,090
Iron	6,870	19,200	16,100
Manganese	229,000	330,000	167,000
Sodium	67,600	47,000	21,700
Sulfur	ND[a] (910)	ND[a] (910)	ND[a] (910)

a. Not detected in digest.

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. A correlation of arsenic (total and extracted) to total iron is made in Figure 81. The comparison of total arsenic to total iron suggests good correlation, but there appears to be two groupings of samples. The reason for this grouping is not clear, but is not grouped by sample type or digestion group. There is not a strong correlation of total extracted arsenic to total iron, but if the arsenic is speciated, correlations become apparent. The speciation of extracted arsenic is presented in Figure 82. The concentration of arsenate is strongly negatively correlated with total iron concentration, suggesting higher levels of iron are reducing extraction efficiency. This decrease in extraction efficiency has been demonstrated in other studies, which examined the binding affinity of arsenicals to soils and various metal oxides.[93,111,112] There does not appear to be a correlation of extracted arsenic (as DPAOA) to total iron, but the extracted arsenic (as PAOA) does correlate well with total iron concentration.

Text continues on page 176.

Table 81. Summary of the Qualitative NMR and LC/MS Data on Isolated Solids.

Sample Description	Peaks Detected in Phenyl Shift Region of Spectrum		Peaks Detected by LC/MS	
	^{1}H-NMR	^{13}C-NMR	DPAOA	TPAO
	EDS Run One			
Sludge	Yes	NA[a]	No	Yes- Small[b]
Waste 1	Yes	NA	No	No
Waste 2	Yes	Yes	No	Yes- Small
	EDS Run Two			
Sludge	Yes	Yes	Yes- Small	Yes- Large[c]
Waste 1	Yes	NA	Yes- Small	Yes- Small
Waste 2	Yes	Yes	Yes- Small	Yes- Large
	EDS Run Three			
Sludge	Yes	Yes	Yes- Small	Yes- Small
Waste 1	Yes	NA	No	Yes- Small
Waste 2	Yes	NA	Yes- Small	Yes- Small
	EDS Run Four			
Sludge	Yes	Yes (2)	Yes- Small	Yes- Large
Waste 1	Yes	No	Yes- Small	Yes- Small
Waste 2	Yes	Yes	Yes- Small	Yes- Small

a. Sample not analyzed by ^{13}C-NMR.
b. Small is a peak area response < 1,000,000 area counts.
c. Large is a peak area response ≥ 1,000,000 area counts.

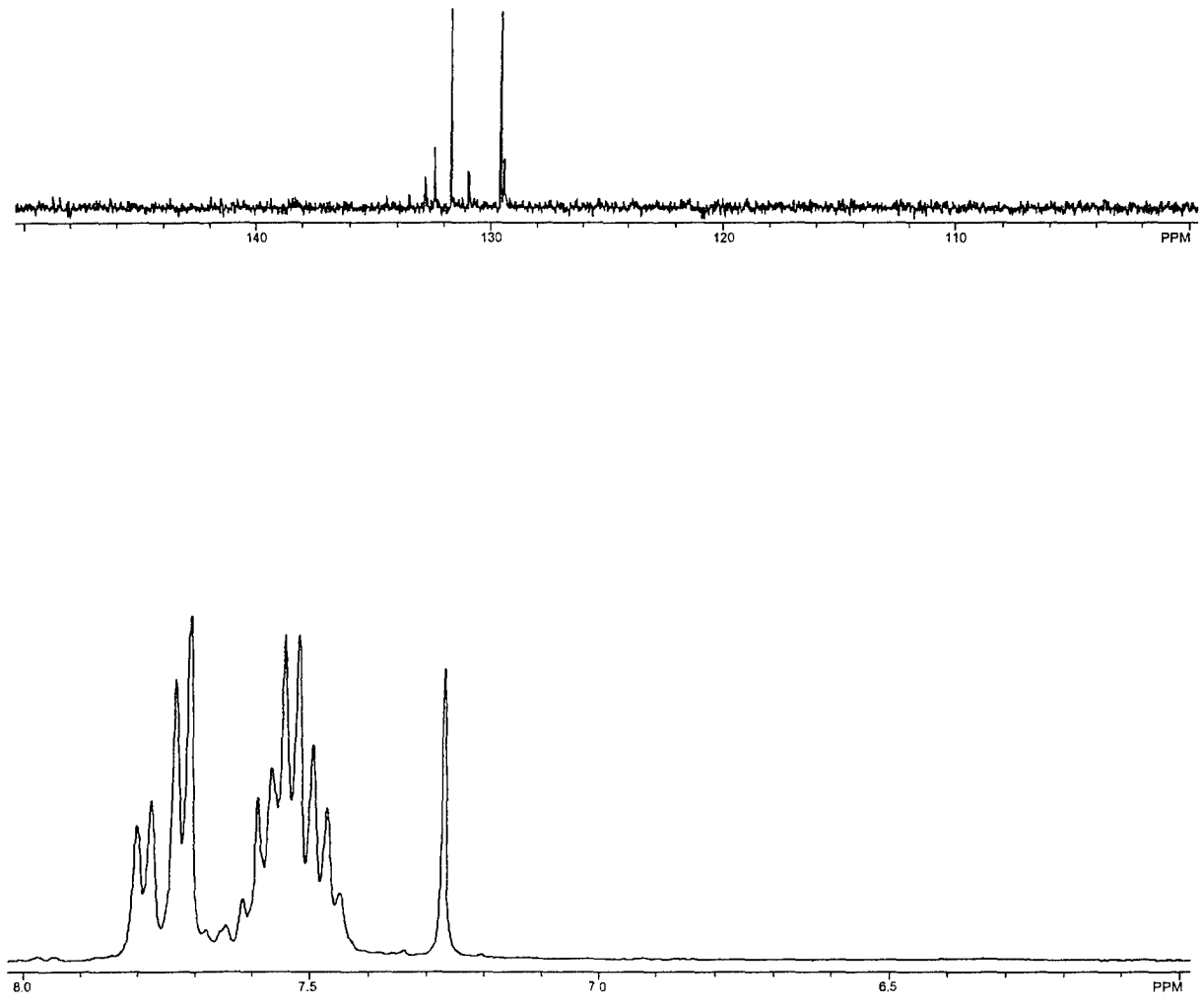


Figure 79. Example NMR Spectra Obtained from the Analysis of Solids Isolated from the Waste 2 Sample Generated During EDS Run Two. The upper panel is the ^{13}C-NMR spectrum, and the lower panel is the ^{1}H-NMR spectrum. In both cases, the spectra have been zoomed into the phenyl-shift region.

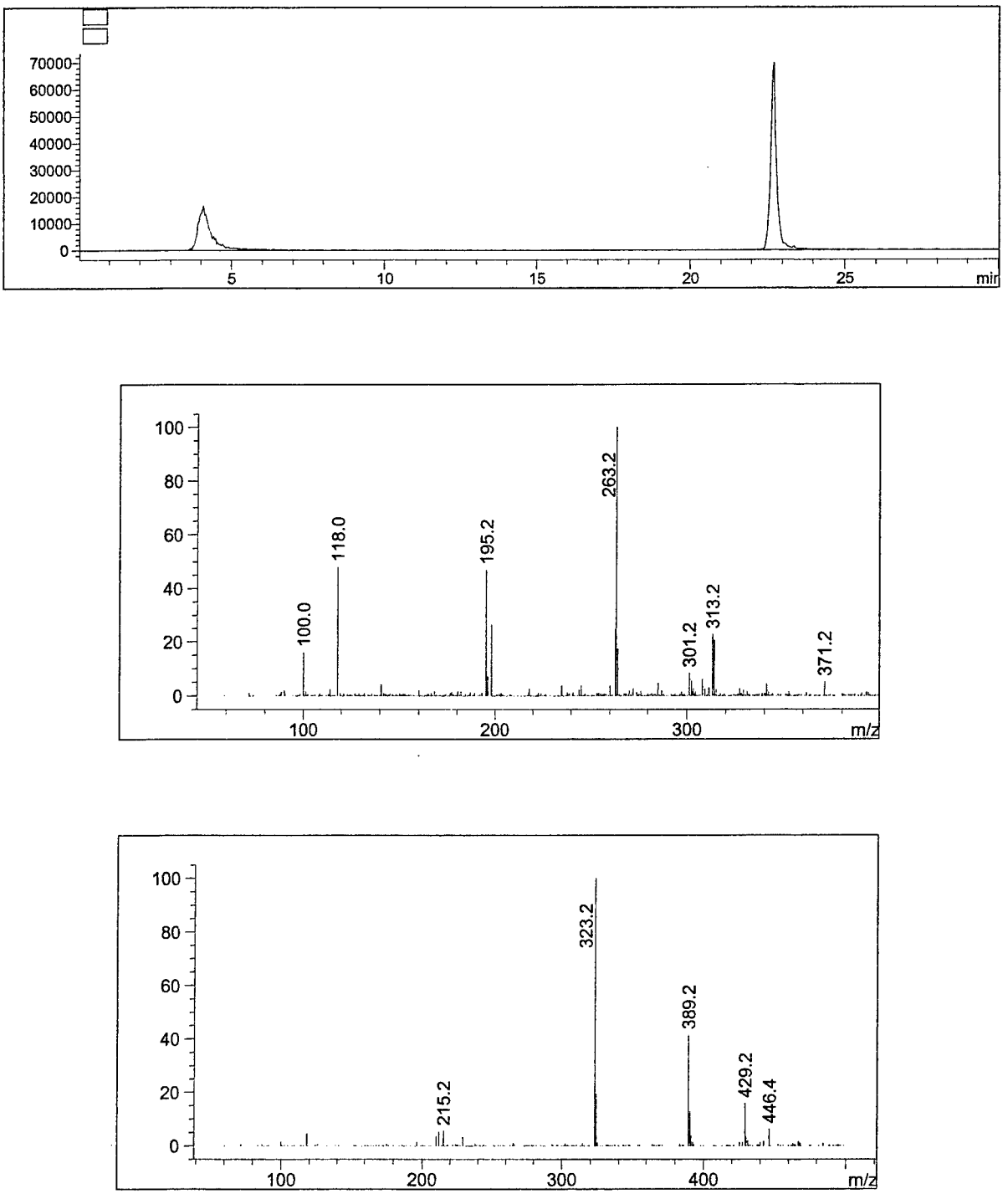


Figure 80. Example LC/MS Data Obtained from the Analysis of Solids Isolated from the Waste 2 Sample Generated during EDS Run Two. The upper panel is the chromatographic trace, the middle panel is the MS spectrum of DPAOA, and the bottom panel is the MS spectrum of TPAO.

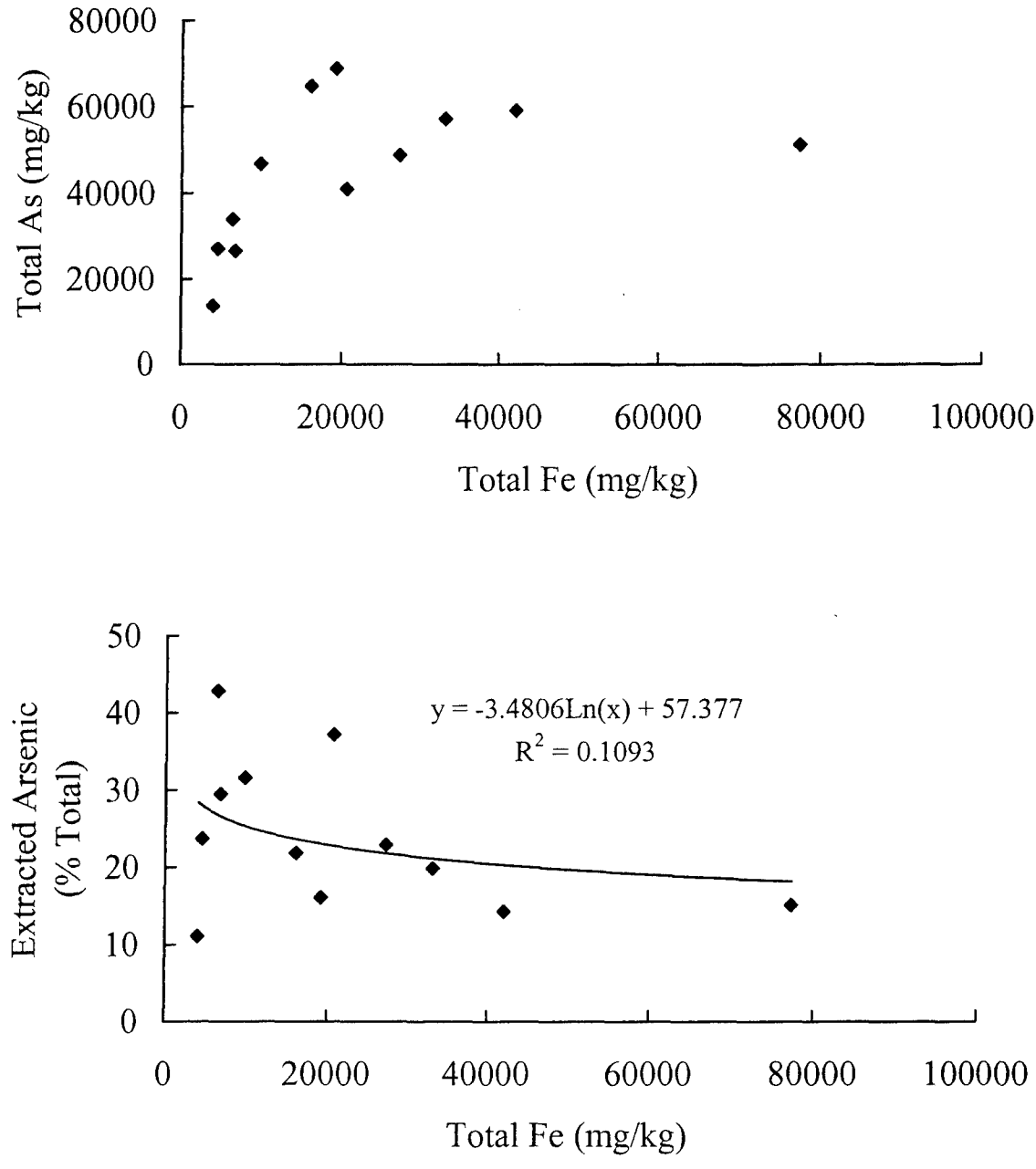


Figure 81. Correlation of Arsenic Concentrations with Total Iron Concentrations of the Isolated Solids. The upper panel is total arsenic as determined by ICP, and the lower panel is extracted arsenic as determined by dimensional analysis calculations.

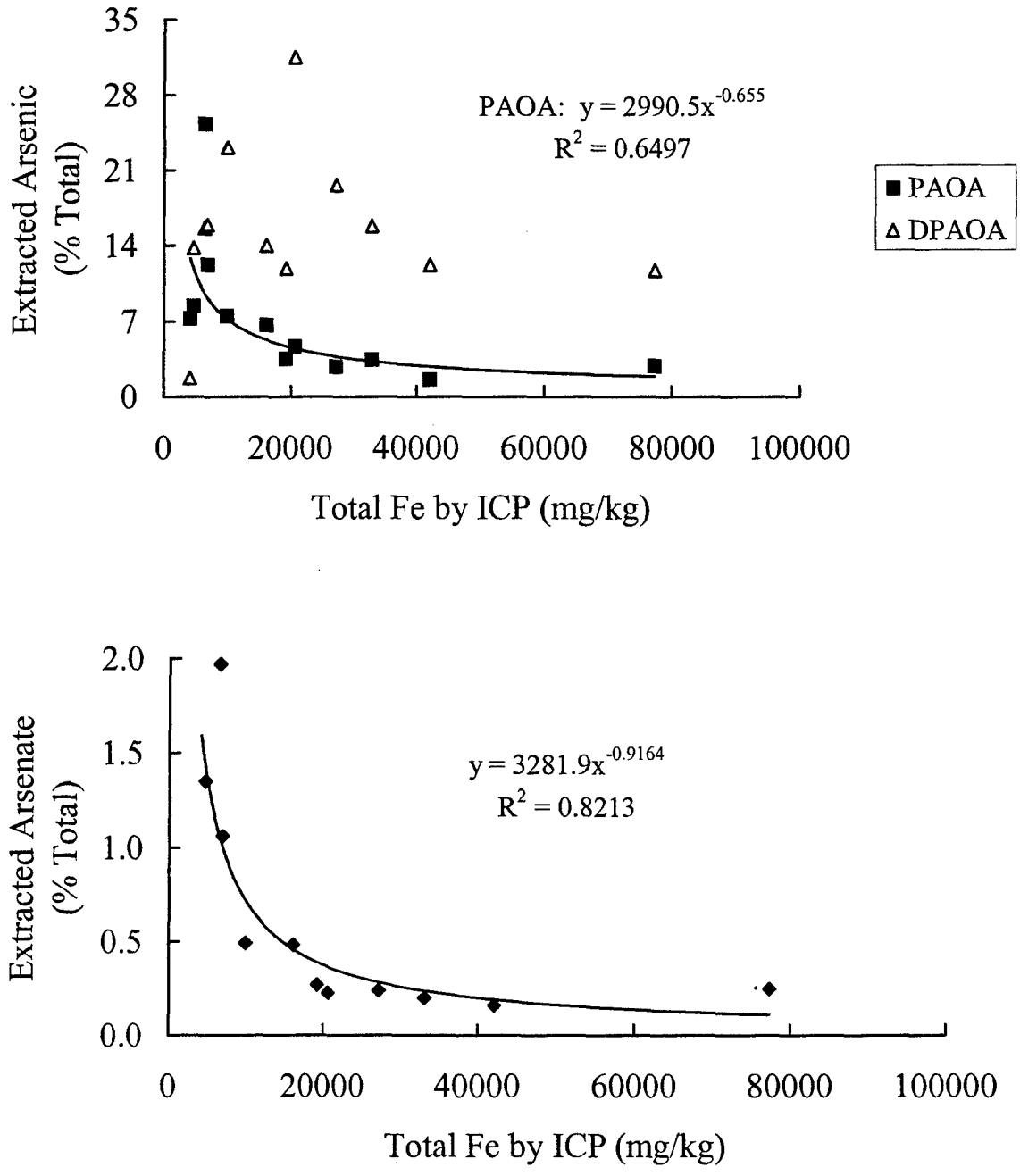


Figure 82. Correlation of Extracted Arsenic Concentrations with Total Iron Concentrations of the Isolated Solids. The upper panel is extracted arsenic in the form of PAOA and DPAOA, and the bottom panel is extracted arsenic in the form of arsenate.

4. CONCLUSIONS

The selected neutralization reagent, aqueous 20% sodium permanganate, was found to be effective in destroying the arsenical fills found in German Traktor Rockets 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 agent levels below the treatment goal of 50 mg/L (ppm). The reaction products included inorganic pentavalent arsenate and various pentavalent organo-arsenicals, with inorganic arsenate concentration positively correlated with reaction temperature. 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% 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% sodium permanganate, was found to be stable, and have an estimated shelf-life of 18 months.

The selected neutralization reagent, aqueous 20% 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.

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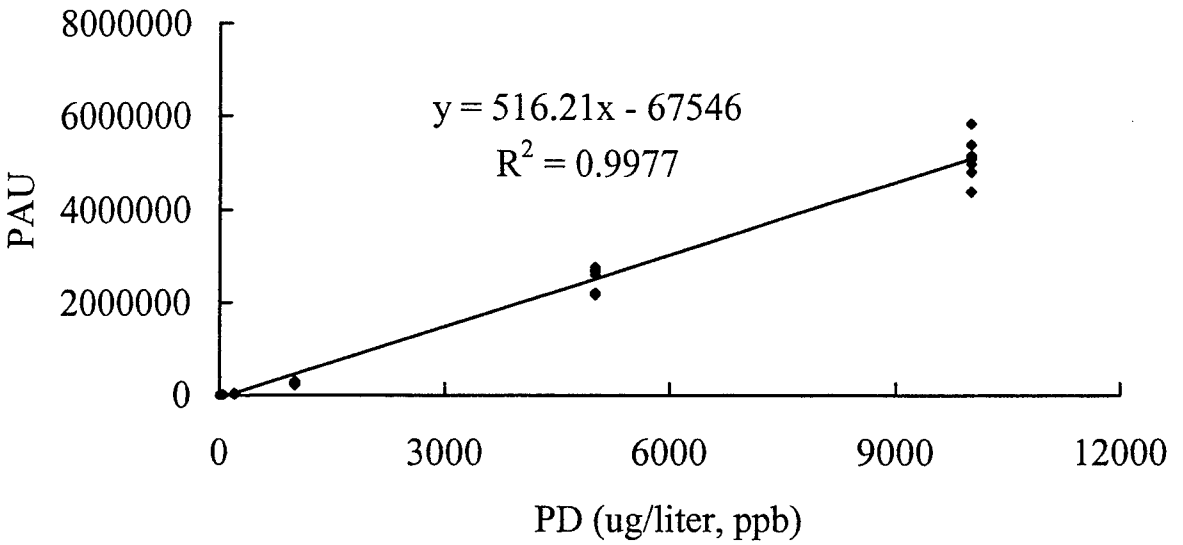
6. PURPOSE AND APPLICATION

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



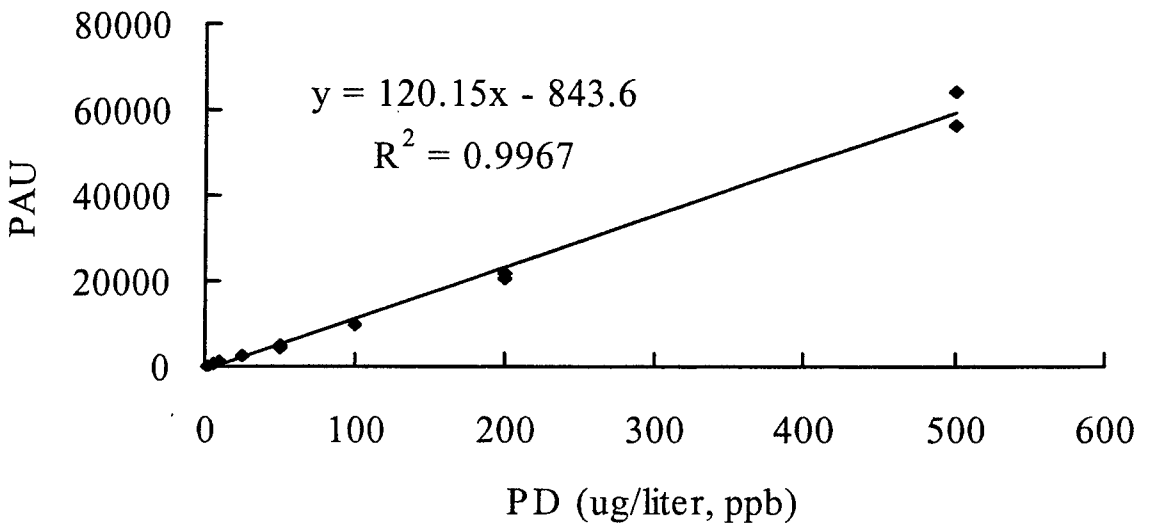


Figure. Example external calibration curves for PD. The upper panel is the entire range evaluated during the validation process, and the lower panel is the typical working calibration range used during the spike recovery and MDL experiments. The data is based on the extracted m/z ion 274.

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 oc — 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 laboratories.

APPENDIX