U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND
CHEMICAL BIOLOGICAL CENTER

ABERDEEN PROVING GROUND, MD 21010-5424

CCDC CBC-TR-1722

Reaction of QL with Li_3N+H_2O for the Tactical Disablement Project

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December 2020

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
XX-12-2020	Final	Feb 2019–Dec 2019

4. TITLE AND SUBTITLE
Reaction of QL with Li_3N+H_2O for the Tactical Disablement Project

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
McGarvey, David J. (DEVCOM CBC); Creasy, William R. (Leidos Corporation); and Kinnan, Mark K. (Sandia National Laboratories)

5d. PROJECT NUMBER
CB10412

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Director, DEVCOM CBC, ATTN: FCDD-CBR-TT, APG, MD 21010-5424
Leidos Corporation, P.O. Box 68, Gunpowder, MD 21010-0068
Sandia National Laboratories, P.O Box 5800, Albuquerque, NM 87185-0100

8. PERFORMING ORGANIZATION REPORT NUMBER
CCDC CBC-TR-1722

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Threat Reduction Agency, 8725 John J. Kingman Road, MSC 6201, Fort Belvoir, VA 22060-6201

10. SPONSOR/MONITOR'S ACRONYM(S)
DTRA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) was previously known as U.S. Army Edgewood Chemical Biological Center.

14. ABSTRACT: (Limit 200 words)
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15. SUBJECT TERMS
O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonite (QL)
Liquid chromatography/mass spectrometry (LC/MS)
Nuclear magnetic resonance (NMR)
Tactical Disablement

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Renu B. Rastogi
U	U	U	UU	58	**19b. TELEPHONE NUMBER** *(include area code)* (410) 436-7545

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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PREFACE

The work described in this report was authorized under project number CB10412. The work was started in February 2019 and completed in December 2019. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC; Aberdeen Proving Ground, MD) was known as the U.S. Army Edgewood Chemical Biological Center.

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The text of this report is published as received and was not edited by the Technical Releases Office, DEVCOM CBC.

This report has been approved for public release.

Acknowledgments

The authors acknowledge the following individuals for their hard work and assistance with the execution of this technical program:

- Mr. Kevin Morrissey (DEVCOM CBC) for his contract support of this program;
- Dr. Glenn E. Lawson (Defense Threat Reduction Agency; Fort Belvoir, VA) for program support and discussions.

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REACTION OF QL WITH Li_3N+H_2O FOR THE TACTICAL DISABLEMENT PROJECT

ABSTRACT

As part of the Tactical Disablement Project, neat weapons-grade QL was reacted with lithium nitride (Li_3N) and water in a glass reaction vessel. QL was decontaminated and solid product reaction mixture was formed. Products were analyzed. Sample analysis and kinetic results from a 2004-2006 study of QL reactions is also included.

1. INTRODUCTION

The objective of the tactical disablement project is to use a minimal amount of reagents to make bulk chemical agent (CA) unusable as a threat, through neutralization and/or solidification of the bulk agent. This can be done by performing the reactions in the CA storage container with wet chemical approaches in order to avoid transporting the storage container or transferring the CA out of the container into a reactor. The reaction should take place without mechanical mixing, excessive agitation, or external heating. It is anticipated that the container will have at least 10% of the volume as empty headspace to allow for expansion of the agent fill, so 10% was the target amount of additive reagents.

By utilizing the CA storage container as the batch reactor, the logistical resources that are needed for decontamination can be significantly reduced. Fewer personnel are required since no sophisticated equipment needs to be set up, configured, or operated. Employing the CA storage container enables the capability to add reagents to multiple containers in a short period of time, as opposed to processing one container at a time for typical flowing reactor approaches. In scenarios for which a quick response is required, the material can be added to all the CA containers and left to react on their own without intervention.

Neutralization of the CA was required to greatly reduce the toxicity as a CA. However, it was not anticipated that the toxicity will be completely eliminated as it is by an environmentally approved decontamination, such as the kind that was required for the destruction of the U.S. CA stockpile. As a result, this study didn't require a method for trace detection of residual CA in the reaction products. It also didn't require a detailed kinetic study to determine how long it would take to reach a target amount of decontamination of the CA. The reaction was done in a glass jar that simulates a storage container.

Formation of solid product was specified as a method to interfere with dispersal or nebulization of the CA, preventing its use as a weapon. Early concepts of the project involved efforts to form a solid polymer product. However, it was found that simpler reagents could be used to form solid products. The solids were characterized by several analytical chemistry methods. A study of the characterization of solid products from VX reaction has been published.[1] A study of the reaction and solidification of GB[2] and of DF[3] are in preparation.

This study demonstrates a method to perform the neutralization and solidification of bulk QL [O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonite]. QL is a precursor of VX agent that was used for synthesis or in binary weapons.

An effective reagent for the purposes of the project was found to be lithium nitride and water ($Li_3N + H_2O$). The reagent was tested for this project on other CA including VX, GB, and DF.[1-3] Preliminary surveys were done to study a few potential reagents, and then a more detailed study was done $Li_3N + H_2O$, since it was the most effective reagent.

A 100-mL scale reaction run was done and the products were analyzed. Solidification of this run was complete after the first addition of reagents. Further studies were done of the solidification process using DMMP in an attempt to make it more reproducible, reported in another publication.[2] The simulant studies provided valuable information about the limiting conditions that are required to make the products solidify. However, both VX and QL seem to solidify even more readily than DMMP and the G agents, possibly because the amine functionality can assist in the formation of ionic solid products.

QL is chemically similar to VX, but it is in a more reduced state, since the phosphorus atom is in the P(III) oxidation state rather than the P(V) oxidation state. This chemical difference affects the best strategy to use for destroying the compound or making it unsuitable for use as a binary munition. In particular, it makes the chemistry more complex, so it is difficult to completely characterize the mixture of products.

2. PRELIMINARY STUDIES

The QL that was used for all the studies was obtained from U.S. Army Chemical Transfer Facility (CTF) from lot number QL-2345-CTF-N-1 (QL24002).

2.1 Reactions with $LiAlH_4$

Preliminary studies were done using lithium aluminum hydride ($LiAlH_4$) as a reagent. $LiAlH_4$ pellets were obtained from Sigma-Aldrich, P/N 323403-100G. This reagent was chosen for study because it is a strong, reactive reducing agent that is commonly used in chemical synthesis, so it is readily commercially available. It has the capability of reducing by contributing 4 electrons, which could potentially allow a low ratio of reagent to CA to be used.

Two runs were done with QL + $LiAlH_4$. One had 10 wt.% reagent, and the other had 5 wt.%, compared to agent. Slow reaction was observed when the reagent was first added. After 24 h, there was clear pressure buildup in the vial and the mixture was becoming viscous. After a week of reaction time for the 10% vial (Sample P49A), there was a steady flame over the vial when it was opened in air. The flame was caused by spontaneous combustion of methylphosphine (CH_3PH_2). This product was observed for reaction of GB and VX with $LiAlH_4$ and identified by ^{31}P NMR.[1,2] This product is shown in the spectrum in Figure 1. Methylphosphine spontaneously burns in contact with oxygen in the air.

As the pressure released, there was foaming out of the top of the vial and formation of a dome from the dried foam. There was a gray solid residue from the $LiAlH_4$ that was too solid to pipet or pour. The vials from the reaction are shown in Figure 2.

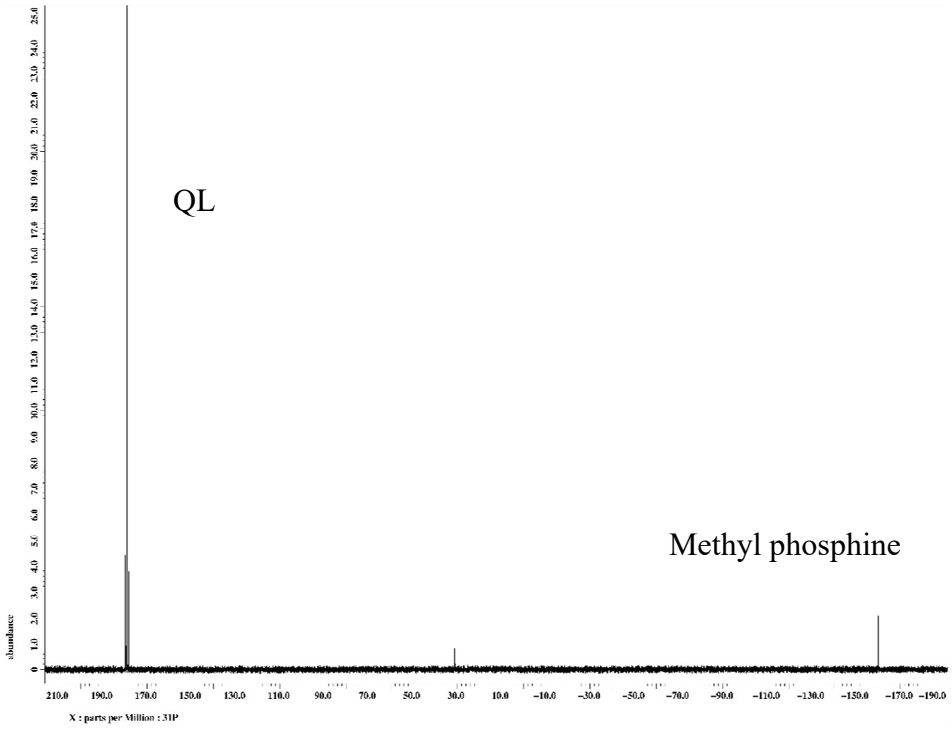

Figure 1: ^{31}P NMR spectrum of the reaction product of QL with $LiAlH_4$, Sample NB0018P49A.

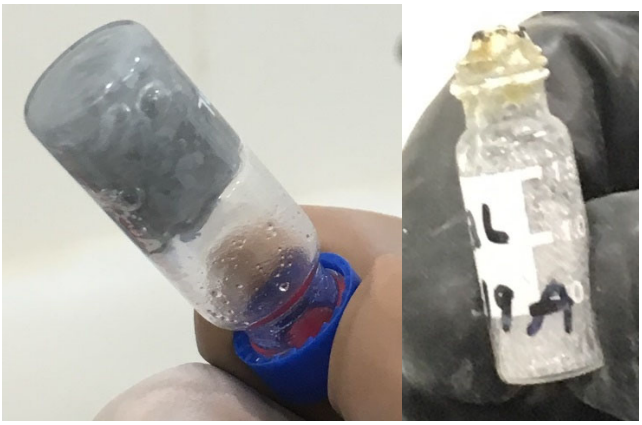

Figure 2. Reaction mixture of QL + $LiAlH_4$, sample P49A. Left photo: After one week of reaction time, with the vial tightly capped. Right photo: After 8 days reaction time, and after opening the vial so the CH_3PH_2 escaped and flared.

For the sample with 5% $LiAlH_4$ (P49B), after a week of reaction time there was a gray slurry that could be stirred and appeared wet. There wasn't an open flame over the vial, but there was some foaming.

Treatment of QL with a reducing agent has definite advantages and disadvantages. Since QL is already reduced compared to VX, it is easier to reduce it further with less consumption of the $LiAlH_4$. The final reduction reaction product that contains phosphorus is methylphosphine, as it was with VX,[1] and no intermediates are observed. The amount of CH_3PH_2 that is formed compared to VX is not accurately quantified because it is a volatile product. Determining the amount of weight loss of a volatile compound was not sufficiently accurate, and no quantitative NMR method was found for a volatile product that appears to be continuously evaporating.

The product presents a fire hazard since methylphosphine spontaneously burns in contact with air, and that could limit the applications that can use this procedure without risk to the operators. The gas is a potential explosion hazard if it collects in oxygen-depleted volume. The methylphosphine evaporates from the reaction mixture and it is a toxic vapor hazard.

Under normal storage circumstances, if QL is exposed to trace amounts of air or water, it tends to oxidize to a number of P(V) compounds. The P(V) compounds do not spontaneously react to form VX according to the usual reaction, since addition of sulfur is required. An undesirable property of the $LiAlH_4$ reaction with QL is that exposure to $LiAlH_4$ tends to reduce these natural oxidation products back to QL, which may actually increase the purity of QL following some degradation in storage. This effect would increase the amount of $LiAlH_4$ that is required to convert to methylphosphine.

2.2 Reaction with H_2O

Reaction with water alone has been used previously to decontaminate QL with a ratio of 1:5 QL:water (see Section 7),[4] showing that QL reacts with water, and this reaction can be used in decontamination.

For this project, a reaction study was done with 10% water in QL. The QL is not completely miscible with water, but it reacts at the interface. In 24 h, most of the QL reacted with only 12% remaining. When an additional 10% water was added, the amount of QL was reduced to undetectable levels (<0.05%) in 30 min. A mixture of products was observed that were not assigned, but they were not P(III) compounds according to the ^{31}P NMR chemical shifts, so they would not be suitable for CW use. ^{31}P chemical shifts in the range of 15-35 ppm indicate P(V) compounds. A ^{31}P NMR spectrum of the reaction mixture is shown in Figure 3. Multiple peaks are observed in the 15-35 ppm range.

2.3 Reactions with $Li_3N + H_2O$

Li_3N was selected as a reagent due to its strong basicity (after reacting with water to form LiOH) and low molecular weight, even though it is not widely used as an aggressive synthesis reagent.[5,6] The reaction of $Li_3N + H_2O$ forms lithium hydroxide and ammonia (or ammonium hydroxide),[7] according to the reaction:[8]

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3 \text{ (aq or gas)}$$

These products react by caustic hydrolysis with the agent. Lithium nitride was purchased from Sigma-Aldrich (MilliporeSigma, St. Louis, MO), P/N 399558-25G. Water was from an in-house distillation system.

Several small-scale studies were done for the reaction of QL with Li_3N. The first sample was a reaction of QL and Li_3N without added water, and there was no sign of reaction.

The second sample had $Li_3N + H_2O$. The mixture had bubbling and smoking after the H_2O was added. It is likely that this reaction was due to interaction between the Li_3N and water. A white precipitate was formed but there was still runny liquid. QL was present in the liquid as observed by NMR.

A study with 10 mL of QL was done for confirmation using 10 wt% Li_3N (sample P91B). Water was added incrementally. After 10 wt% of water was added, there was still 37% QL remaining. After 15 wt% water was added, the QL was undetectable. It is likely that the added Li_3N competes with QL for reaction with water, so using less Li_3N or even no Li_3N may reduce the amount of water that is needed for reaction with the QL. But the Li_3N is caustic, so it may promote the reaction by generating base. Further studies were done with this promising reagent using larger amounts of QL.

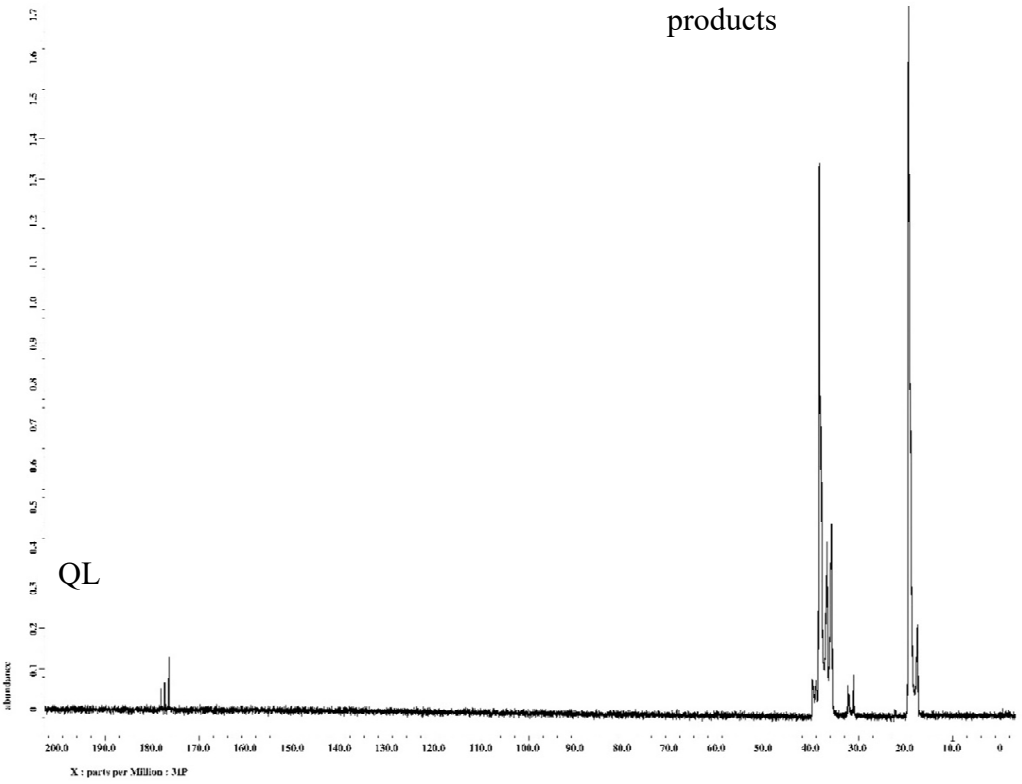

Figure 3: ^{31}P NMR spectrum of the reaction product of QL with H_2O, Sample P53A.

3. LARGER SCALE REACTION STUDY

A quantity of 100 mL QL was reacted with 5 g Li_3N as powder added first, followed by 10 mL of water. Addition of the Li_3N didn't cause any visible reaction or temperature increase. When water was added with a syringe, the mixture began to boil vigorously for about 5 min. The reaction mass began to produce solid precipitate in less than 8 min. after the water was added. Photos of the stages of the reaction are shown in Figure 4.

Previous studies have shown that Li_3N powder reacts faster and more vigorously as fine powder than as pressed tablets of Li_3N.[2] A test reaction of QL was not done with tablets, but it is anticipated that the reaction rate with tablets will be slower so there is less boiling.

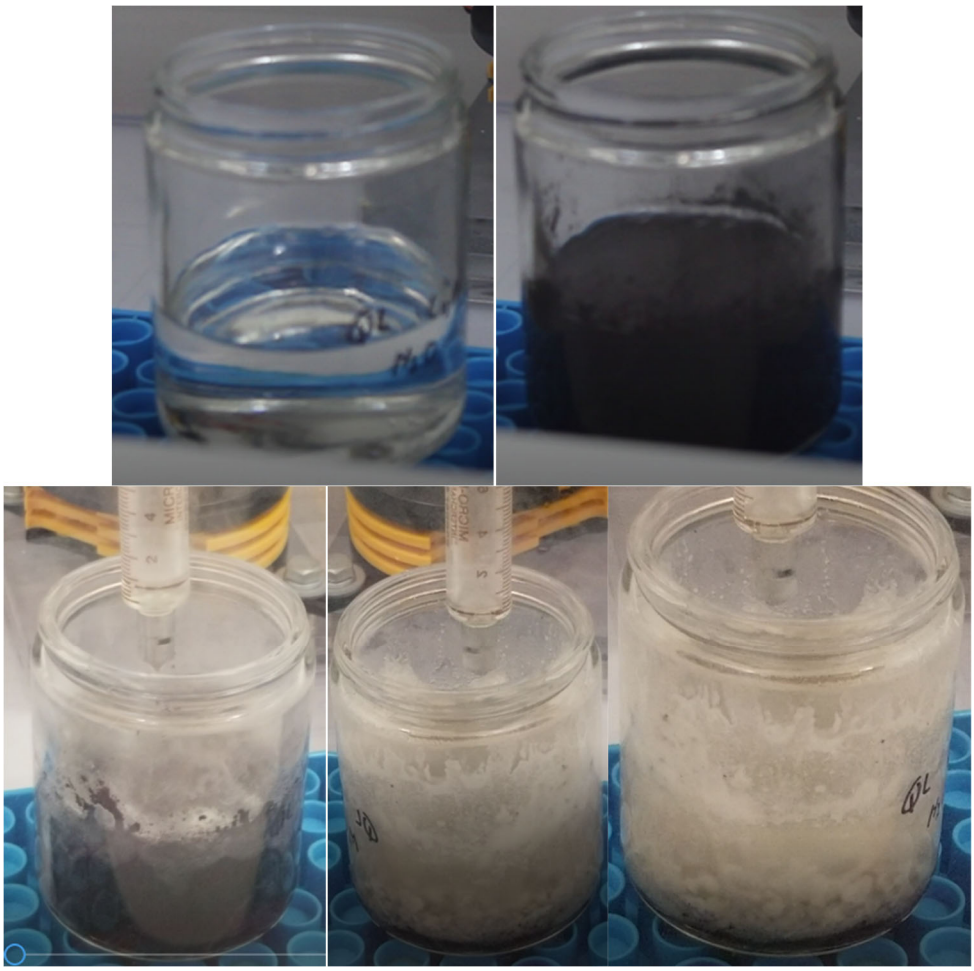

Figure 4: Stages in the reaction of 100 mL QL with 5 g Li_3N + 10 mL H_2O. Top left, starting QL liquid; Top right, after addition of Li_3N powder; Bottom left, addition of water with a syringe with liquid beginning to boil; Bottom center, reaction after 5 min. showing boiling slowing down; Bottom right, reaction after 8 min. showing no boiling and solid formation.

The products didn't completely solidify in 10 days. An additional 3 mL of water was added and no visible reaction was observed. The reaction products were a thick slurry by 14 days after the start (an additional 4 days). NMR analysis showed that 7.7 wt% QL remained in the product. Photos of the reaction product are shown in Figure 5. Photos and videos of the reaction were used to produce a video.

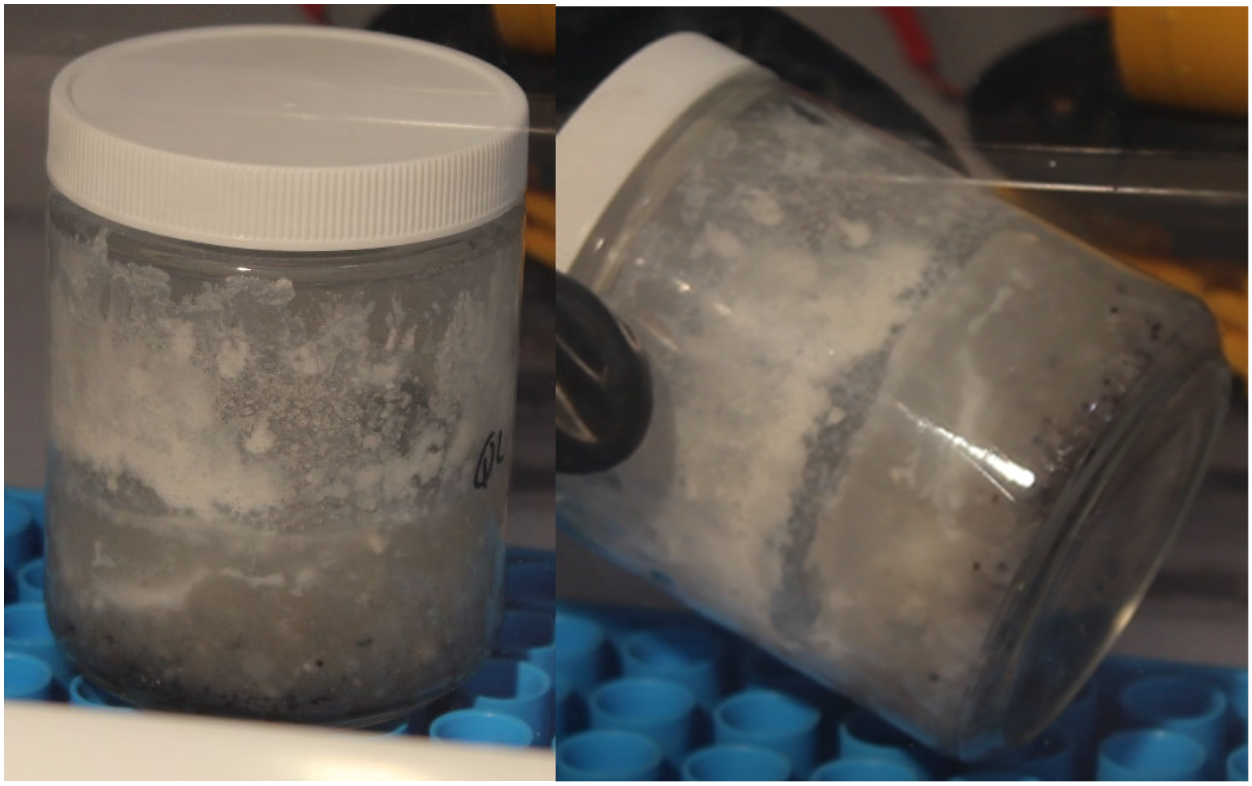

Figure 5: Completely solidified product from 100 mL reaction of QL with 10 mL water and 5 g Li_3N (Sample P03A) and with additional 3 mL of water added at 10 d, and allowing a total of 14 d of reaction time.

4. ^{31}P NMR RESULTS

The best quantitative method for determining the purity of nerve agents and for determining residual agent is phosphorus (^{31}P) NMR due to the simplicity of distinguishing between the agent and reaction products, and because the compounds can be detected without complex separation and derivatization steps. QL has a ^{31}P NMR chemical shift of 170 ppm, depending on solvent, and is well resolved from other phosphorus compounds and reaction products (except for O,O'- diethyl methylphosphonite, referred to as TR, and O,O'- bis-(diisopropylaminoethyl) methylphosphonite, referred to as LT, that are related byproducts).

NMR spectra from the 100 mL reaction run are shown in Figure 6 and

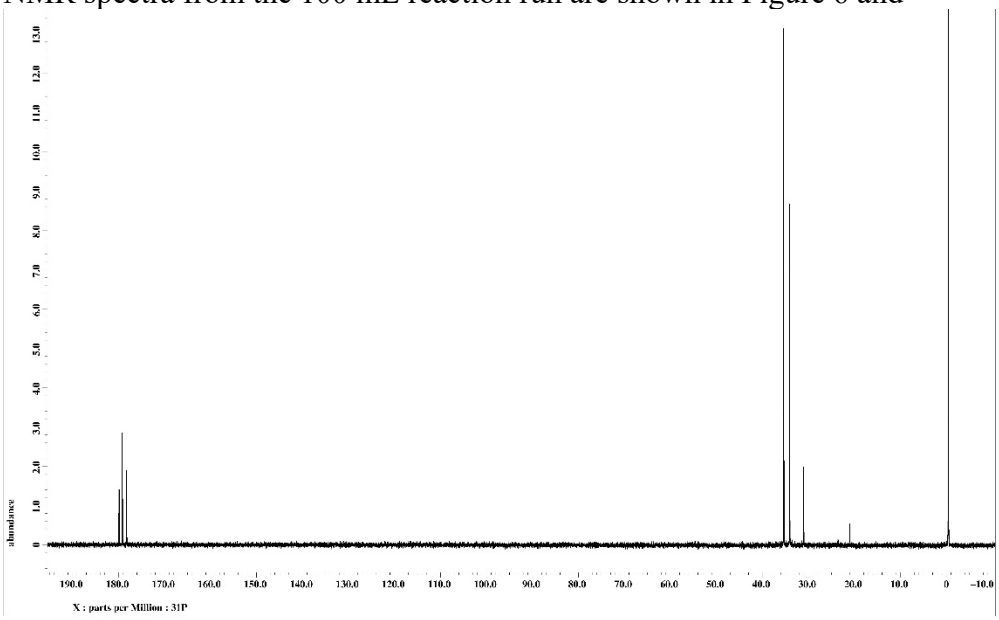

Figure 7.

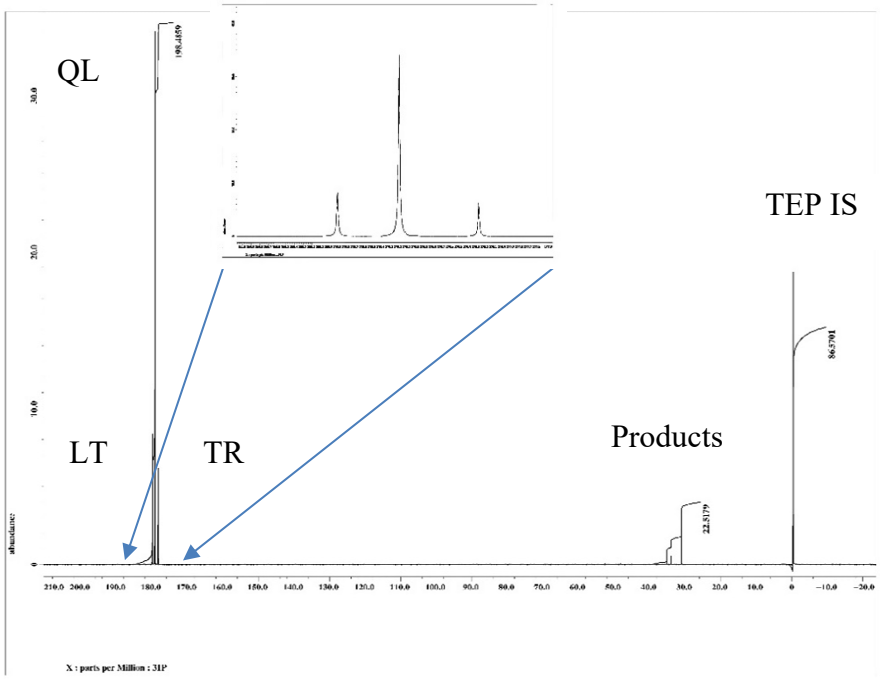

Figure 6: ^{31}P NMR spectrum of reaction of 100 mL QL with Li3N + H_2O early in the run showing QL, byproducts LT and TR, and reaction products, with internal standard of triethyl phosphate (TEP), in Sample P03A. The solvent is chloroform ($CDCl_3$).

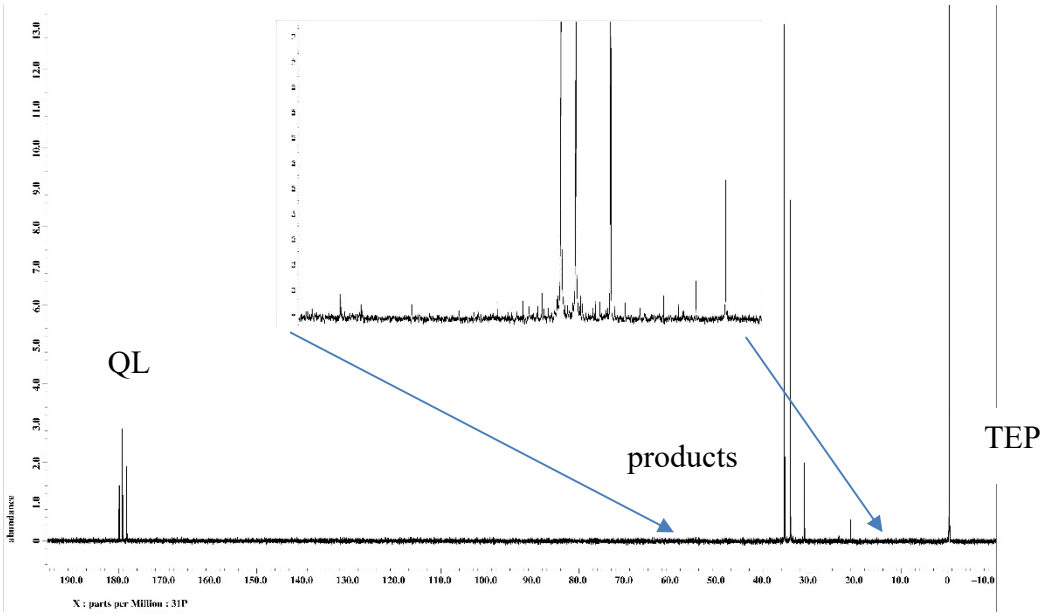

Figure 7: ^{31}P NMR spectrum of reaction of 100 mL QL with Li3N + H_2O after 5 weeks of reaction showing QL and the reaction products, with internal standard of triethyl phosphate (TEP), in Sample P03A. The scale is of the inset is expanded to show three major peaks from P(V) compounds and multiple minor peaks. The solvent is chloroform ($CDCl_3$).

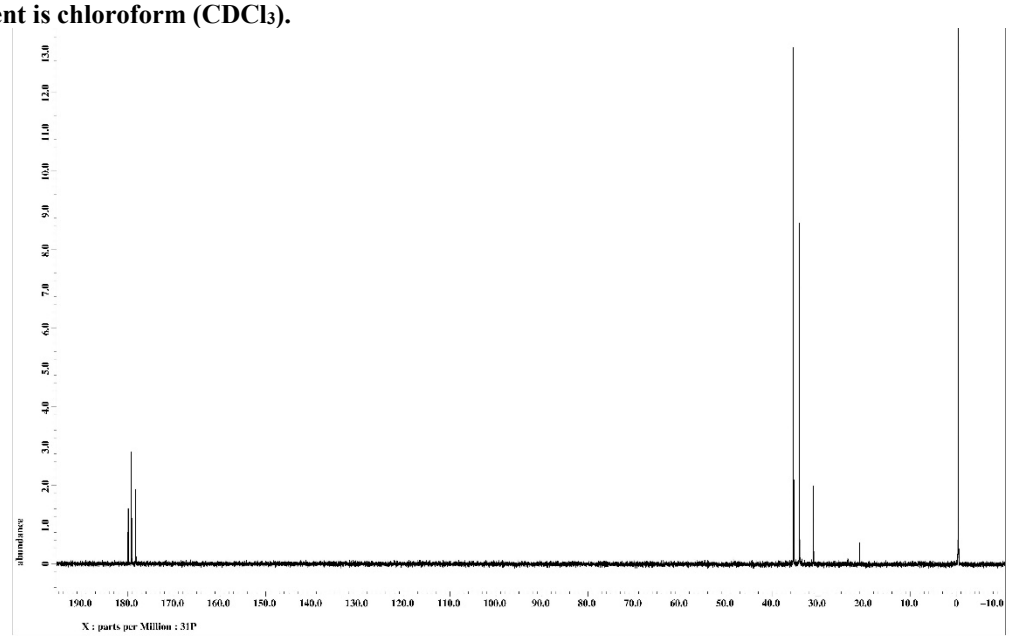

Figure 7Figure 6 shows a significant amount of QL and small amount of products, along with the internal standard TEP that is added for quantitation of the amount of QL that is in an extract in chloroform ($CDCl_3$). The QL stock solution contained small amounts of the expected disproportionation byproducts TR and LT, which are made during the QL synthesis. They form an apparent triplet with peaks on either side of the main QL peak. Figure 7 shows the reaction mixture after 5 weeks of reaction extracted in chloroform ($CDCl_3$). There are three major peaks from P(V) compounds and multiple minor peaks, although some peaks are quite

small. There is some QL left, and the calculation of the amounts using weights of the sample and internal standard indicate that 7.7 wt% QL remained in the product.

The extract in chloroform ($CDCl_3$) was used to determine the residual QL in the solid and liquid product mixture. All the vials or jars from reaction runs were periodically sampled to determine residual QL. This was done by using the following preparation procedure: 1) remove a quantity (10-100 mg) of the solid and/or liquid reaction product and transfer to a sample vial, 2) weigh it, 3) add and weigh an amount of internal standard triethyl phosphate (TEP), 4) dissolve or extract with chloroform ($CDCl_3$) for 0.5-1 min. with vortexing, and 5) transfer the solution to doubly contained NMR tubes using an inner Teflon insert and outer glass 5 mm NMR tube. Samples were analyzed by standard ^{31}P NMR parameters on a JEOL ECS-400 NMR Spectrometer with a relaxation delay time of 90 sec. Quantitation was calculated based on the signal of QL compared to triethyl phosphate internal standard (Sigma-Aldrich P/N 538728-100ML). Double containment of solutions is required for safety reasons for CA solutions and to prevent reactions with glass tubes. Using doubly contained tubes decreased the sensitivity to some extent. For QL samples, paramagnetic impurities were not a major problem, unlike reactions that were studied previously for GB[2] and DF.[3]

In some cases, some of the solid was not dissolved in this solvent. In those cases, the extraction efficiency of QL from the solid wasn't measured. Kinetic time points were not systematically measured for the samples to get rate constant information.

Solid final reaction product was also dissolved in deuterated water (D_2O) to look for major reaction products. After about 2 months of reaction time, an aqueous solution (in D_2O) of the reaction product has one major product in the ^{31}P NMR spectrum, although there are a few smaller abundance products. The ^{31}P NMR spectrum of this solution is shown in Figure 8.

The most likely assignment of the single ^{31}P NMR peak is to methylphosphinic acid, $CH_3PH(O)OH$, a P(V) compound. (It was not determined whether other reaction products that are observed in the $CDCl_3$ extract can react with water to form this product.) This compound was previously identified in aqueous solution in a study that is discussed in Section 7. A definitive measurement to identify this compound class is to use ^{31}P NMR without proton decoupling. This method shows that without ^{1}H decoupling the ^{31}P singlet correlates to a widely-spaced doublet of quartets, which is assigned to the P-H bond with a coupling constant of 510 Hz and a P-CH_3 group. The spectrum is shown in Figure 9. The results don't definitively exclude a product that is an ester of methylphosphinic acid, $CH_3PH(O)OR$, although results from additional ^{1}H and ^{13}C spectra in the next section indicate that the product is not an ester.

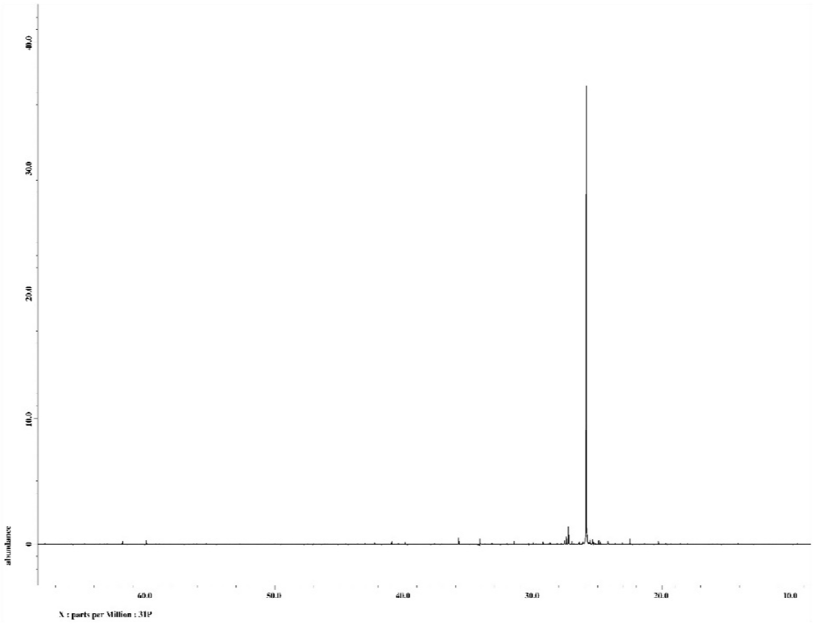

Figure 8: ^{31}P NMR spectrum with proton decoupling of reaction of 100 mL QL with Li_3N + H_2O after 2 months reaction time, solid dissolved in aqueous solution. The spectrum shows one major phosphorus-containing product.

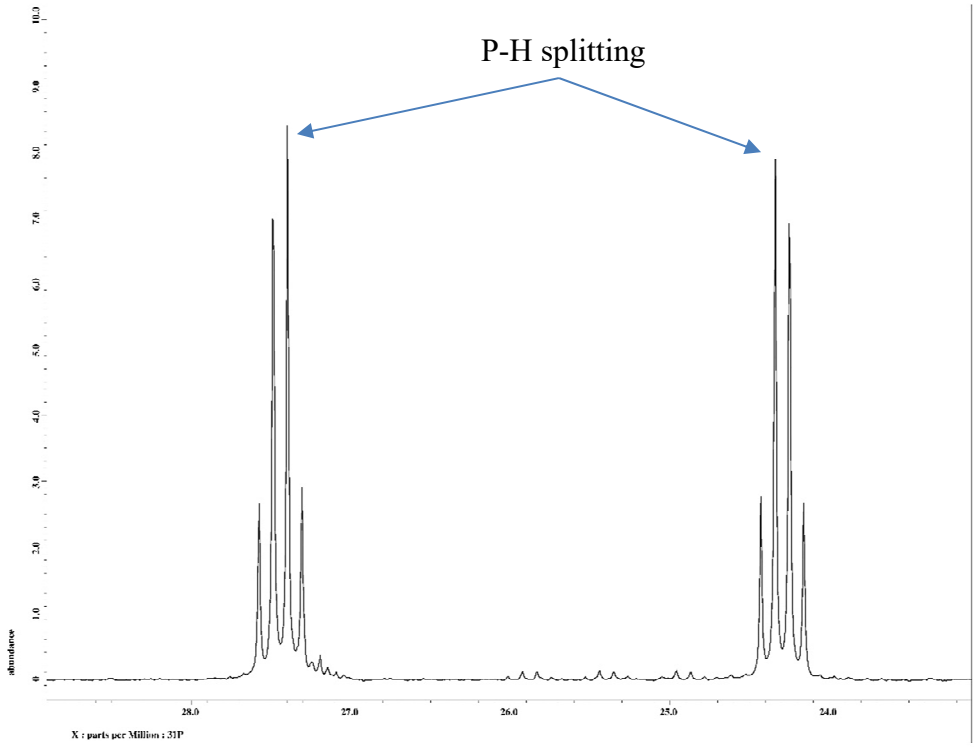

Figure 9: ^{31}P NMR spectrum without proton decoupling of reaction of 100 mL QL with Li3N + H_2O after 2 months reaction time, solid dissolved in aqueous solution.

5. ^{13}C AND ^{1}H NMR RESULTS

Although ^{31}P NMR is useful for determining residual QL and phosphorus-containing products, it is not helpful for products without phosphorus. There are several amine-group-containing products that are generated from oxidation of the P atom and loss of the amine side-chain. Many product peaks are at similar chemical shift positions due to the chemical similarity of the products. This can make it difficult to distinguish between the products using these NMR signals. This problem was also discussed in connection with the analysis of products from reactions of VX.[1]

The aqueous solution used to collect the spectra in Figures 8 and 9 was also used to acquire the proton (^{1}H) spectum in Figure 10. The peaks for the P-H proton of methylphosphinic acid, $CH_3PH(O)OH$, are at chemical shifts of 7.48 and 6.18 ppm, which have splitting that is the same as the splitting for the ^{31}P peaks without proton decoupling in Figure 9. Peaks at 3.96 and 1.14 ppm correspond to the two types of protons in TEP, the internal standard. Other peak groups may be combinations of the multiple amine-containing products.

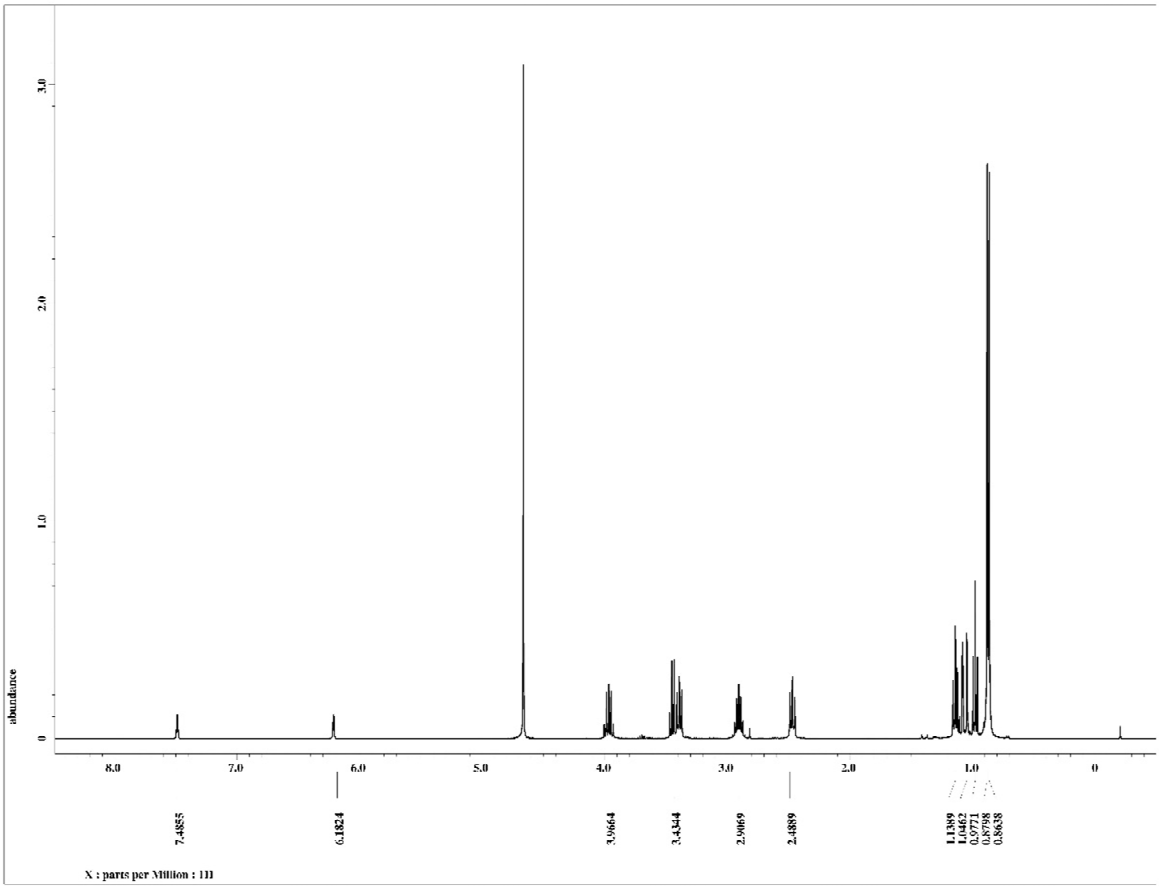

Figure 10: Proton NMR spectrum of reaction of 100 mL QL with $Li_3N + H_2O$ after 2 months reaction time, solid dissolved in aqueous solution, which is same sample that was used for Figure 8.

Figure 11 shows a type of two dimensional spectrum called HMBC (heteronuclear multiple-bond correlation) that shows the coupling between the P-H proton at chemical shifts of 7.48 and 6.18 ppm with the ^{31}P atom in methylphosphinic acid, and the coupling of the P-CH_3 protons at a chemical shift of 1.0 ppm with the same phosphorus. This spectrum confirms the previous assignment of the main component in the spectrum. No other protons are coupled to the phosphorus in the major component, indicating that the compound likely isn't an ester of the acid.

The ^{13}C NMR spectra are less sensitive than proton spectra since ^{13}C atoms are only 1.1% natural abundance compared to ^{12}C atoms, but the spectra usually have better resolution than proton spectra. Figure 12 shows a ^{13}C NMR spectrum of reaction of 100 mL QL with Li_3N + H_2O at the beginning and end of the run, showing QL and the reaction products, with internal standard triethyl phosphate (TEP) in $CDCl_3$ solvent extracts.

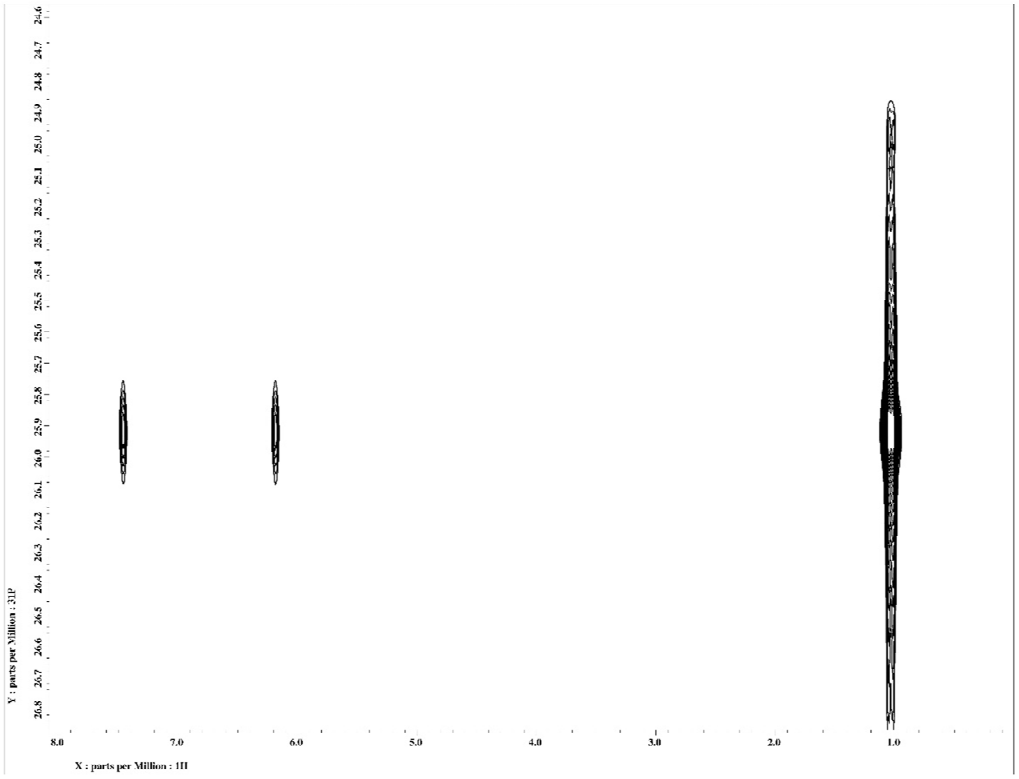

Figure 11: Proton-phosphorus (^{31}P) HMBC spectrum showing the coupling between the P-H proton at chemical shifts of 7.48 and 6.18 ppm with the 31P atom in methylphosphinic acid, and the coupling of the P-CH3 protons at a chemical shift of 1.0 ppm with the same phosphorus. No other coupled protons are observed.

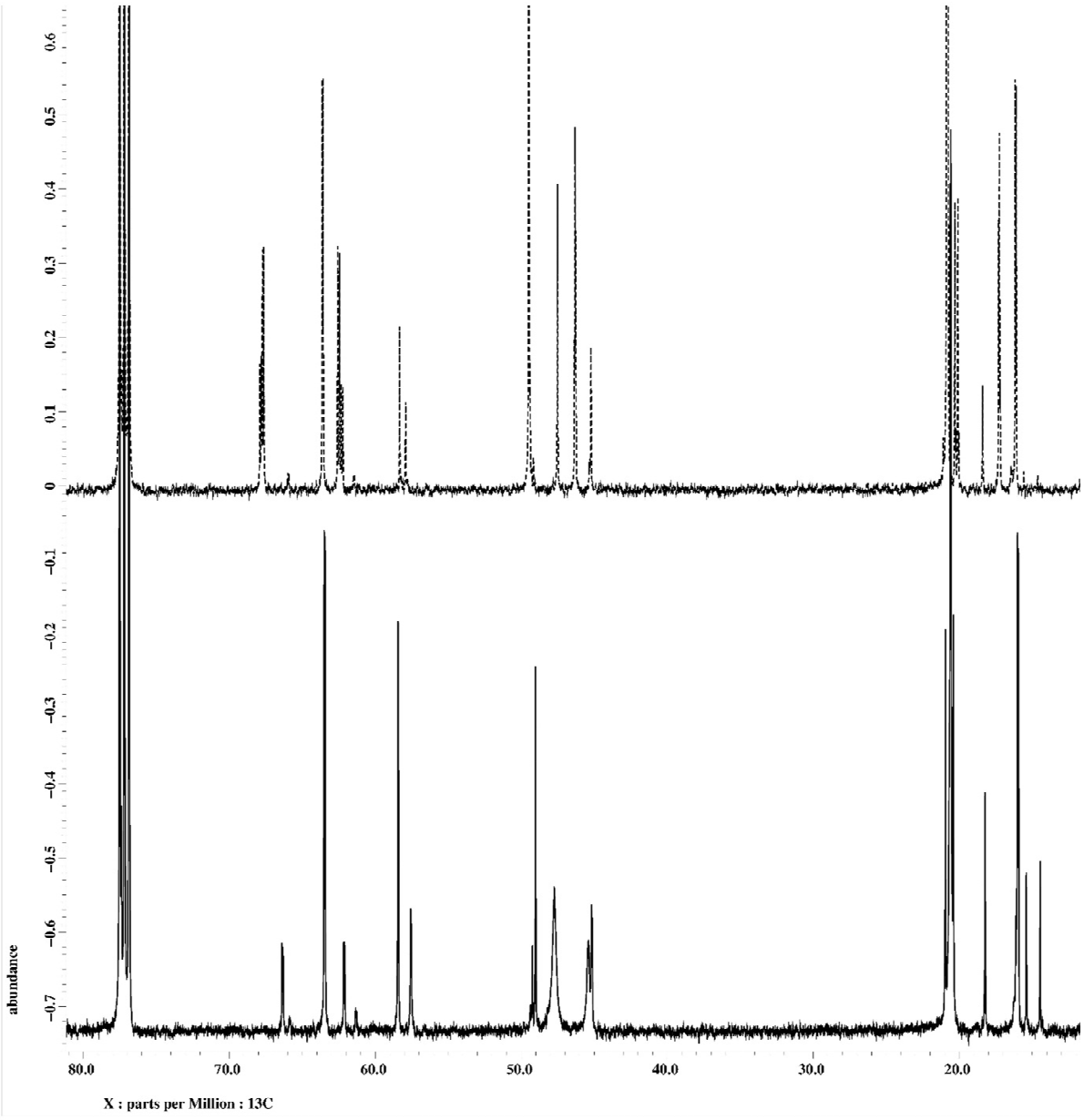

Figure 12: ^{13}C NMR spectrum of reaction of 100 mL QL with Li3N + H_2O; Top, beginning of run with mostly QL; Bottom, end of the run, showing the hydrophobic reaction products, with internal standard triethyl phosphate (TEP), Sample P03A. Both samples are $CDCl_3$ solvent extracts (which give a multiplet at 77 ppm).

Figure 13 shows the ^{13}C NMR spectrum corresponding to Figure 8. Four of the NMR lines can be assigned to diisopropylaminoethanol. The calculated spectrum of this compound is shown in Figure 14. It appears that this compound is the major non-phosphorus containing product. Two peaks are assigned to TEP internal standard, and a doublet is assigned to methylphosphinic acid. These peaks don't correspond to the peaks in Figure 12, but there could be shifts due to the solvent difference.

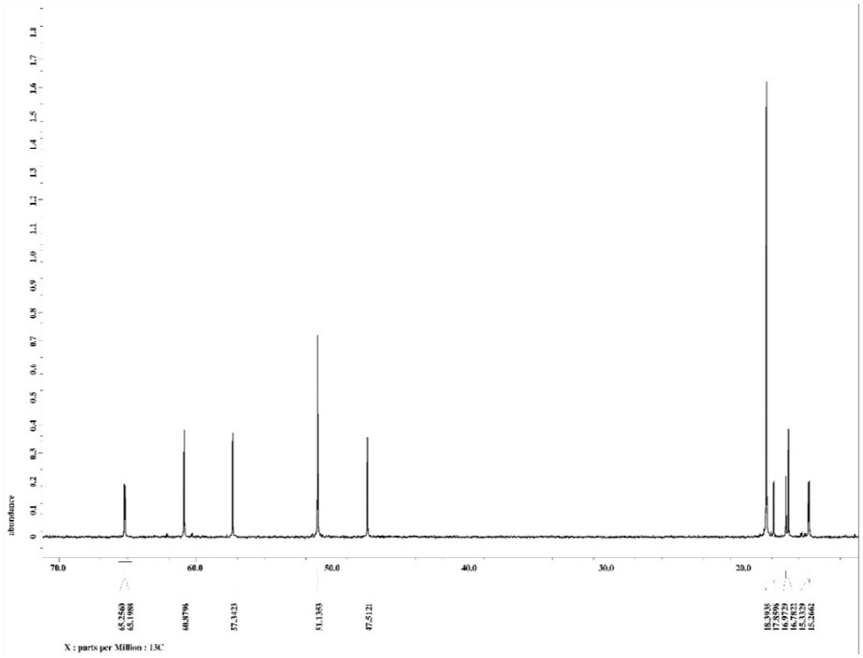

Figure 13: ^{13}C NMR spectrum of reaction of 100 mL QL with Li3N + H_2O showing the reaction products, with internal standard triethyl phosphate (TEP) after 2 months reaction time, solid dissolved in aqueous solution, the same sample as Figure 8.

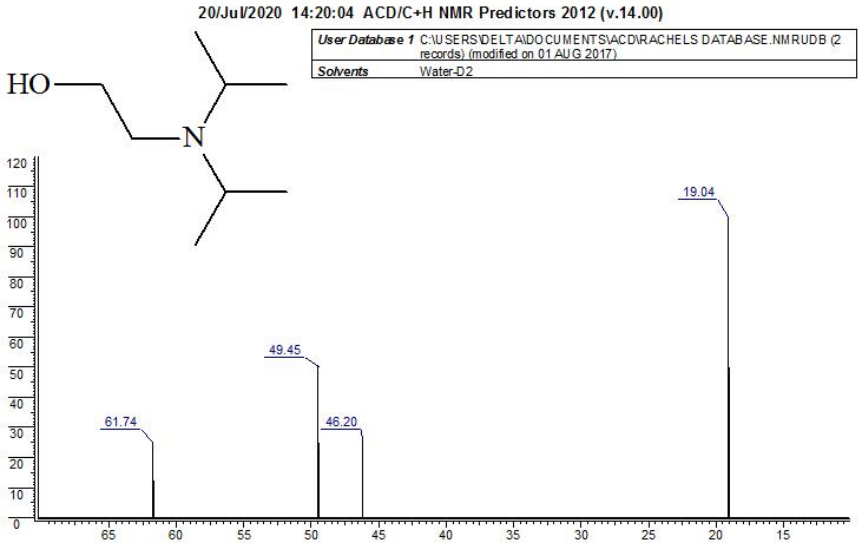

Figure 14: Calculated 13C spectrum of diisopropylaminoethanol, structure shown in the figure. This compound accounts for four of the peaks in the spectrum in Figure 13.

6. MASS SPECTROMETRY RESULTS

6.1 Analysis of volatile product compounds in reaction products

The QL reaction product contains numerous compounds. One issue of interest is the volatile compounds in the product that could produce a vapor hazard. A method to analyze for volatile products is by placing solid reaction product in a 20 mL headspace vial and sampling the vapor in the vial, and then analyzing the vapor composition using gas chromatography/mass spectrometry (GC/MS). A general method for this kind of analysis has been published.[9]

The chromatograph and sample mass spectra from headspace sampling are included in Appendix 1. Mass spectra are assigned based on matches to the NIST 05 mass spectral library. Some of the mass spectral matches are not conclusive and are excluded, but some compounds that have good matches are tabulated in Table 1. Compounds were not quantified, since that depends on both MS detection sensitivity and volatility of the compounds.

6.2 LC/MS Method and analysis

Another method to analyze a range of products is by using Liquid Chromatography/Mass Spectrometry (LC/MS). In this method, compounds are separated by flowing through a liquid chromatography column. Then a solution in a polar solvent is sprayed through a needle with a high charge in order to ionize polar compounds, which are detected with a mass spectrometer. The reaction solid was dissolved in aqueous HCl to completely dissolve all the solid and was diluted by approximately 1:100. The solution was analyzed using LC/MS using an Agilent 6410 Triple Quadrupole LC/MS/MS. Sample preparation methods and LC/MS instrument conditions were not optimized for sensitivity but to obtain qualitative mass spectra to identify compounds. Compounds were tentatively identified based on molecular weight and any reasonable fragments, but there wasn't a library or exact mass measurement for the LC/MS data and some isomers could be difficult to distinguish.

Compounds that were observed for both the LC/MS and the headspace methods are listed in Table 1. There are several amine-containing products. Assignments with only one method may be considered tentative. Methylphosphinic acid is not observed by LC/MS or GC/MS, possibly because it has low volatility or low ionization efficiency.

The reaction mechanism by which the products are formed is not known. A complete reaction mechanism scheme has not been developed. Some products may be from basic hydrolysis. Some products may involve oxidation, but the reagent Li_3N is not be capable of oxidation reactions. This suggests that reaction with oxygen or water may be involved.

In the LC/MS spectra, there was no evidence of Li^+ adducts with the analytes of interest. That is notable since the solid reaction product contains a significant amount of Li^+ or LiOH. Li^+ adduct masses are not indicated in the table.

Table 1: Compounds identified in the QL neutralent waste solution by NMR, Headspace GC/MS (HS) with EI mass spectral search, or LC/MS identification of the corresponding $M+H^+$ peak.

Compound name	**MW (Da)**	**$(M+H)^+$**	**Detection Method**
Methylphosphinic acid (MP)	80	81	Major P product identified by NMR but not either HS or LC/MS
Diisopropylaminoethanol (DIPAE)	145	146	Major non-P product by HS, LC/MS, and ^{13}C NMR.
Diethyl methylphosphonate	152	153	HS, LC/MS
R ethyl ether	173	174	HS, LC/MS
3-diisopropylamino-1,2-propanediol	175	176	HS
1,2-Bis(2-diisopropylamino) ethane	228	229	HS
Diisopropylformamide	129	130	HS, LC/MS
O-ethyl O-R methylphosphonate	251	252	LC/MS
O-R methylphosphonic acid	223	224	LC/MS
O-R methylphosphinic acid	207	208	LC/MS (or another isomer of the same mass)
Bis(R) ether	272	273	LC/MS
O-ethyl R-methylphosphinate (QC)	235	236	LC/MS, impurity in QL, not a reaction product[10]

R=diisopropylaminoethyl

7. REPORT ON THE NMR SUPPORT FOR THE PILOT PLANT REACTOR RUNS FOR QL DECONTAMINATION: SAMPLE ANALYSIS AND KINETIC STUDIES

QL is not a commonly studied CA, and there is little published information about analytical chemistry methods for QL. However, it is a fairly reactive compound, so analysis can be challenging. In 2004-2006, some methods were developed as part of a decontamination effort to destroy containers of QL and DF. The QL methods were not published so they are included for reference. Studies of reaction kinetics are also included.

7.1 Method of analysis of QL neutralent samples for residual QL

A Pilot Plant Reactor was tested in 2004-2006 with reaction runs to decontaminate methylphosphonodifluoridate (DF) and O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonite (QL), two precursors to binary chemical warfare agent systems of GB and VX, respectively. Containers of DF and QL were destroyed at Pine Bluff Arsenal, AR. This was part of the effort to destroy the U.S. chemical weapons stockpile under the Chemical Weapons Convention (CWC). In order to meet the requirements for the Organization for the Prohibition of Chemical Weapons (OPCW) Treaty Inspection of the destruction process, the neutralent solutions were screened for DF and QL to a concentration of less than 0.1 wt% to demonstrate that the chemicals were destroyed.

The analysis of QL, a reactive compound, in low concentrations has significant difficulties as a quantitative method. A method is described that uses GC/MS with electron impact (EI) ionization which includes mass spectral library searches and GC retention indices to confirm the identification of compounds of interest. This analysis method was not validated on the reaction products in the current Tactical Disablement study since it was not required by the project but it may be necessary for further development work.

The analytical method was validated in order to screen the neutralent solution made from a mixture of 1 part QL to 4 parts water in a liquid matrix. To validate an analytical method, the typical procedure involved spiking the sample matrix with a low concentration of the analyte and processing it through the sample preparation procedure, in order to demonstrate that the method was effective in detecting the analyte. Quality control and validation procedures are important for this analysis, since standards of QL can degrade which could produce a false negative result.

QL was spiked into the aqueous solution and recovered by solvent extraction. QL reacted slowly enough in the aqueous solution that it could be recovered, at least if the solution has a neutral or weakly basic pH. The detection of QL was compared to VX when it was spiked in the same solution. VX is a related compound for which extensive detection method development work has been documented.[11] In addition, an alternate method was developed to convert QL to VX via addition of sulfur, which provided better recovery efficiency.

7.1.1 Experimental approach

Aqueous samples are extracted with hexane and the organic phase is analyzed for extractable compounds.

Hexane extraction procedure

a) Transfer 10 mL of the aqueous sample to a 25 mL vial. (Smaller quantities of sample can be used if the rest of the method steps are reduced proportionately.)

b) Measure the pH of the sample and neutralize with 0.1 M ammonium hydroxide or 0.1 M hydrochloric acid if necessary

c) Add 5 mL of hexane and tightly cap the vial.

d) Shake the vial for approximately 3 minutes and then allow the phases to separate. If needed, centrifuge for 5 minutes in a 15 mL centrifuge.

e) Transfer the hexane phase (top layer) to another 25 mL vial with a transfer pipet. Add anhydrous sodium sulfate as necessary, cap, shake, let dry for 30 minutes. (This is an optional step to prevent water from being injected into the GC/MS.)

f) Filter about 1 mL of the dried extract into a GC vial using a filter tipped transfer pipet and perform GC/MS analysis.

QL Neutralent Sample Preparation: It was possible to detect the QL directly by GC/MS, but it appears that QL is very sensitive to specific instrument conditions. The QL may react or adsorb to the GC injection port or GC column. As a result, two approaches are suggested for detecting the QL. One approach extracts and detects the QL directly. The experiments indicate that some of the QL may be detected, but it may not be detected with high efficiency. The detection efficiency should be sufficient to meet the requirement of 0.1%.

The other approach converts the QL to the VX isomer, called CV [O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonothioate]. The conversion is done by extracting QL from solution with a hexane solution of sulfur, S_8. Reaction of QL with sulfur produces CV. Under normal conditions of VX synthesis, the CV is heated to isomerize it to VX. In dilute solution of a volatile solvent, it was not possible to completely convert the CV to VX. Some VX was observed, probably due to isomerization in the hot GC injection port. It will be necessary to identify both CV and VX in the GC chromatogram in order to identify the original QL. These compounds have significantly different retention times but similar mass spectra.

Effectiveness of each method can be validated by spiking a sample of neutralent with QL so that it is 0.1 wt% or less in concentration, and then following the extraction and analysis procedure to verify the detection of QL, either directly or by conversion to CV+VX.

If the validation of the method is successful, actual samples can be analyzed by using VX (or another compound) as a spiking compound rather than QL for quality control purposes. Alternately, QL can be spiked for the sample analysis, if the QL solution is regularly tested to show that it doesn't degrade.

The following procedure was used. Five preparations will be used to include validation purposes:

1) Sample of QL neutralent, extracted with hexane: this sample is prepared to extract residual QL. Hexane improves the extraction efficiency of QL relative to other amines and reaction products that will be present in the neutralent.
2) Sample of QL neutralent, extracted with sulfur solution in hexane: this sample will extract residual QL and convert it to CV and VX. This preparation is optional, if good results are observed with Step 1.
3) Sample of QL neutralent spiked with VX, extracted with hexane: this is a QC sample to demonstrate that VX (as a simulant for QL) would have been detected in Step 1 if it were present.
4) Standard of VX (or QL) in hexane.
5) Solvent blank (hexane or sulfur solution in hexane).

The following chemicals and reagents were used:

- QL neutralent solution: Neutralent made with a ratio of QL to water of 1:4 by volume, or a comparable decontamination reaction product can be tested. If the product is a solid, it can be dissolved in water or dilute acid solution. If recovery is not successful, the pH can be adjusted.
- QL feedstock: Feedstock from the neutralent reaction is used for spiking. The purity of the QL should be determined.
- VX standard: Solution of <1 mg/mL in IPA can be prepared from stock VX or obtained from CASARM.
- Hexanes, 95% n-hexane, reagent grade (J.T.Baker Ultra Resi-Analyzed or equivalent)
- Sulfur, 99.998%, CAS 7704-34-9 (Aldrich part no. 21,329-2 or equivalent)
- Sulfur solution in hexane: add excess sulfur to hexane, and allow sulfur to dissolve at room temperature for at least an hour.

- Standard of mixed normal hydrocarbons for retention time calibration. Any hydrocarbon standard that includes the range of C_{12} to C_{18} will be acceptable.

7.1.2 Results

VX Spike results: The spike and recovery measurements showed that the VX spiked into the QL neutralent could be successfully recovered, detected by GC/MS, and matched to a MS library spectrum. The retention index for VX was determined as 1707 in the neutralent extract, compared to the retention index of 1708 determined from the VX standard in methylene chloride. The percent recovery of VX from the neutralent is close to 100%, showing that there is little degradation of the VX in the neutralent solution that was used.

The reference hydrocarbon retention times, which are used for calculating the retention index, are given in Table 2. A sample total ion chromatogram and extracted ion chromatogram from the GC/MS run of the extract is shown in Figure 15. The VX peak is found at a retention time of 16.15 min., slightly longer than the C_{17} straight-chain hydrocarbon.

Table 2: Retention times for the straight chain hydrocarbon standards for retention index determination, using a ZB-5 GC column and the GC program: 40 C (hold 1 min.) ramped at 10 C/min to 250 C (hold 1 min.) with 1 mL/min. constant flow of He.

Straight chain hydrocarbon	retention time (min.)
C12	9.79
C14	12.51
C15	13.75
C16	14.96
C17	16.07
C18	17.12

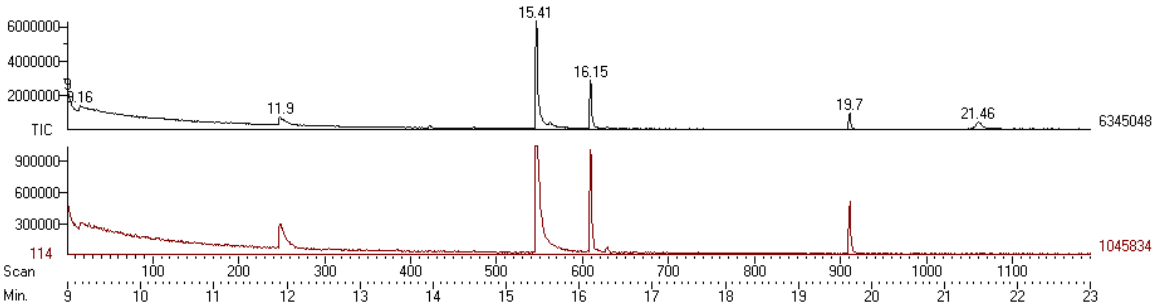

Figure 15: Total ion chromatogram and extracted ion chromatogram of *m/z* 114 for the first spiked sample at 78 µg. The VX peak is at 16.15 min.

QL Spike Results, recovered as QL: A study was done to determine that QL could be recovered from a spike. A QL standard with a concentration of <0.1% was run. (The concentration was 0.1% assuming 100% pure standard, but the standard had lower purity.) Figure 16 shows the chromatogram from this analysis. QL was positively identified as the peak at 11.82 min. from the EI mass spectrum search, shown in Figure 17, and the retention index of the peak was 1351.

Some preliminary extractions of QL from spiked neutralent were attempted. It was observed that hexane was a better solvent than dichloromethane for the extraction. Dichloromethane extracted an interfering compound that tailed significantly into the QL retention time region.

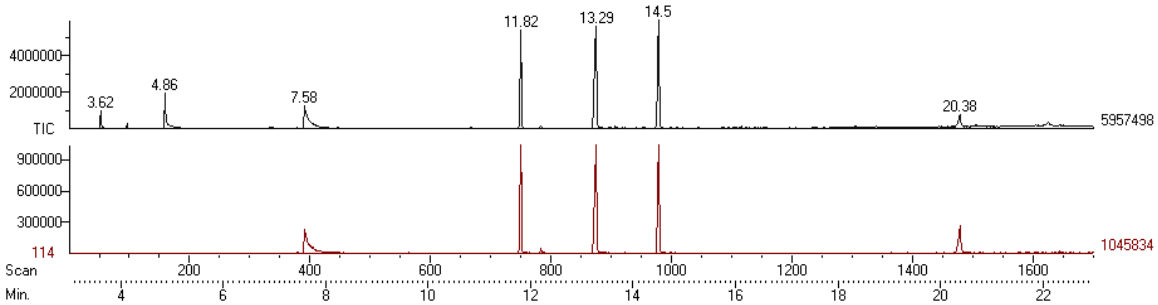

Figure 16: **Total ion chromatogram and extracted ion chromatogram (114 Da) of a QL standard with concentration <0.1%. The QL peak was identified at 11.82 min. The peaks at 13.29 and 14.5 min. are probably degradation products of QL.**

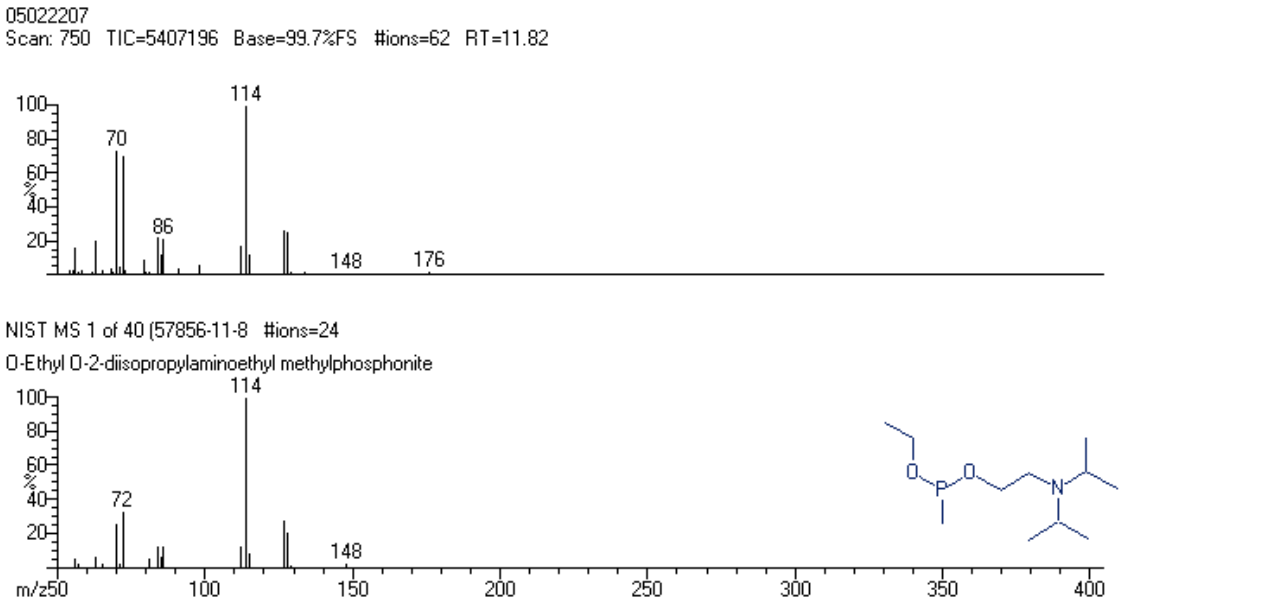

Figure 17: **Mass spectrum and library search result for the peak at 11.82 min. The best NIST02 MS library match is for QL, structure shown on the figure.**

Using hexane, three repetitions of extractions of the QL neutralent were done. The neutralent was spiked at 200 ppm, or 20% of the standard shown in Figure 16. A table of the results is shown in Table 3. The signal for the VX standard is used as the reference for quantitation of the recoveries. The QL peaks are definitely present, as shown in Figure 18. However, recoveries are only 3.7% relative to VX. Notably, the signal for the QL standard, made from the same stock solution as in Figure 16, also gives a low signal. An NMR analysis of the stock solution showed that it contains a significant fraction of QL, so the low % recovery may reflect the difficulty in analyzing QL by GC/MS.

Table 3: QL recovery results for QL spiked into neutralent matrix

Description	m/z 114 signal (K)	spike level	%recovery	r.t. (min.)	retention index	delta RI
39 ppm VX std.	381	39	100.00%	16.1	1707.55	
<200 ppm QL	37	200	1.89%	11.82	1352.59	0.00
spike, <200 ug	111	400	2.84%	11.83	1353.33	0.74
spike, <200 ug	72	400	1.84%	11.82	1352.59	0.00
spike, <200 ug	322	400	8.24%	11.82	1352.59	0.00
Unspiked interference	887			11.76	1348.15	-4.44
VX spike	380	39	99.74%	16.1	1707.55	
blank	ND	0				
	QL Ave.		3.70%	11.82	1352.78	0.19
	Std. Dev.		3.06%	0.005	0.37	

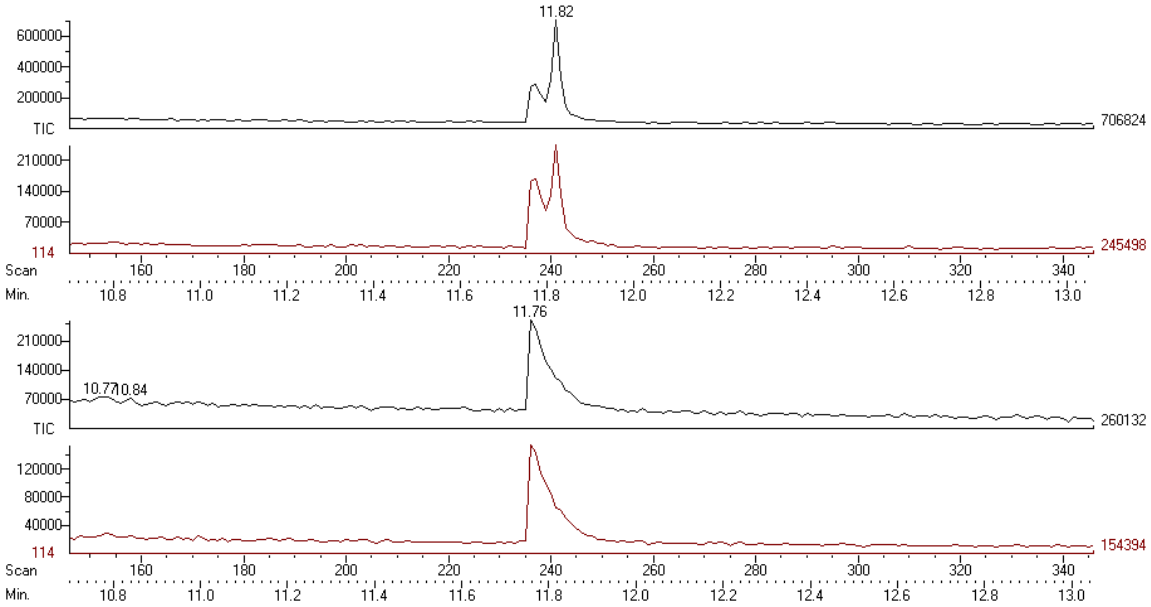

Figure 18: Top panel: Total ion and extracted ion chromatograms of QL spiked neutralent extract. Bottom panel: Corresponding traces of unspiked neutralent extract showing the interference at 11.76 min.

Since the QL peak is relatively small, a peak from the compound in the neutralent that elutes at 11.76 min. is a significant interference. This peak is not baseline resolved from the QL peak, so the signal in the unspiked run had to be subtracted from the integrated signal to give the QL signal that is listed in the table. The peaks for the QL spiked sample and unspiked sample extracts are shown in Figure 18. The QL peak has good agreement to the expected retention index. The mass spectrum alone is not definitive for identification because mass spectral peaks other than the 114 Da peak have low signal intensity. The additional peaks can be used for confirmation if they were observed in the mass spectrum. For this reason, it is helpful to identify the retention index for confirmation.

QL Spike Results, recovered as CV and VX: Using a hexane saturated with sulfur, three repetitions of extractions of the QL neutralent were done. The neutralent was spiked at 200 ppm, or 20% of the standard shown in Figure 16. Unlike the previous method, the extraction was done with a saturated solution of sulfur in hexane, and the sulfur reacted with the QL to form a mixture of CV and VX. The results are shown in Table 4 for both the integrated areas of CV and VX. The signal for the VX standard is used as the reference for quantitation of the recoveries of both CV and VX.

The QL peaks are efficiently converted to CV and VX. The average recovery from the data was 44%, but this number includes a factor from the purity of the QL standard. Clearly the recovery is much better than the recovery of QL as QL under the same conditions. The disadvantage is that there are two peaks instead of one. Figure 19 shows the chromatogram with both the CV peak, at 15.07 min., and the VX peak at 16.12 min. An interfering peak at 15.39 min. is between these two peaks of interest. The broad peak at 18.79 min. is from the elution of the sulfur compound.

Table 4: QL recovery results for QL spiked into neutralent matrix, with QL converted and recovered as CV and VX.

Description	m/z 114 signal for VX	m/z 114 signal for CV	spike level	%recovery, total of CV and VX	r.t. (min.)	retention index of CV
39 ppm VX std.	381		39	100.00%	16.1	
spike, <200 ug	361	1267	400	41.66%	15.07	1614.41
spike, <200 ug	560	1627	400	55.97%	15.07	1614.41
spike, <200 ug	331	1011	400	34.34%	15.07	1614.41
unspiked	ND		0			
VX spike	380		39	99.74%	16.1	
blank	ND		0			
	QL Ave			43.99%	15.07	1614.41
	Std. Dev.			11.00%		

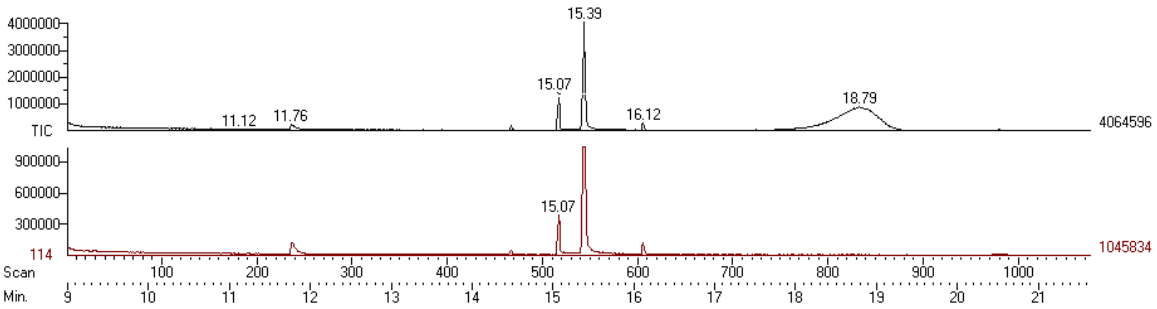

Figure 19: **Total ion and extracted ion chromatogram of the QL neutralent, spiked with QL to 200 ppm, and extracted with sulfur in hexane. The peak at 15.07 min. corresponds to CV, and the peak at 16.12 min. corresponds to VX. No unreacted QL is observed.**

7.1.3 Discussion

Several technical issues were observed with regard to the detection of QL.

Passivation of the GC: In order to detect QL at all, the GC injection port and column need to be passivated. Several steps can be taken to improve the detection of QL and related compounds, including VX:

- Replace injection port liner and septum with new ones. Restek Siltek single gooseneck splitless inlet liners without glass wool (Restek part number 20798-214, 4 mm ID) or comparable products from other vendors can be used.
- Inject a very high concentration of QL or VX standard (0.1-1% concentration), and run using the normal GC conditions. The MS does not have to be running for data collection. The high concentration should passivate the active sites on the inlet and column, so that subsequent lower concentration standards can be analyzed with better signal.
- It may be helpful to replace the entire GC column with a new column reserved for the QL neutralent samples. It may be less reproducible to passivate a used column than a new column.
- It may help to use the technique of cool on-column injection. This method requires a different type of injection port that has to be installed on the GC. The method has the advantage of avoiding possible thermal degradation or surface reaction in a hot injection port.

Stability of the QL standard: A standard solution of 2% QL in dichloromethane was prepared from neat QL. The solvent was not dried. The standard was stored in an unsealed plastic bottle. Purity was tested over time using NMR. The concentration gradually decreased, but the standard contained a significant concentration of QL for 2 weeks of testing. It will not be possible to certify a QL dilute standard on a particular day to the same accuracy as a CASARM VX standard.

Stability of QL and VX in the extract: It was observed that the VX is stable overnight in the hexane extract. The analysis of the samples for VX is not time critical. The QL is less persistent, and it can disappear faster, so it should be analyzed as soon as possible after preparation.

7.2 NMR analysis and kinetic studies

NMR was used to test the decontamination reactions of QL. QL is the binary precursor to VX, in the mechanism that is shown in

Figure 20. One possible decontamination reaction is shown in Figure 21. NMR was used for 1) sample analysis of the reactor runs in pilot plant runs in 2004, 2) purity determinations of the initial starting materials, and 3) bench scale studies of the kinetics of the QL decontamination.

For the analysis of samples from the pilot-scale reactor runs, no residual QL was observed in any samples, to a detection limit of approximately 0.1%. The final reaction product that contains phosphorus was observed to be methylphosphinic acid. Purity determinations were performed and reported to the project. Feedstock was analyzed before and after the reactor runs.

A number of studies of the reaction kinetics were done. It was found that QL is immiscible in caustic aqueous solution that was used for the decontamination. Mixing the sample disperses the QL and affects the kinetics. The products of the reaction are water soluble. As a result, the mixed reaction solution is cloudy as the QL is added, but it becomes a clear solution after the QL is consumed. If the solution is allowed to sit at room temperature without mixing, a detectable amount of QL remains after 24 hours. At elevated temperatures (38 °C or higher), the QL is consumed much more quickly. QL is expected to undergo hydrolysis in water, and one potential mechanism is shown in

Figure 21.

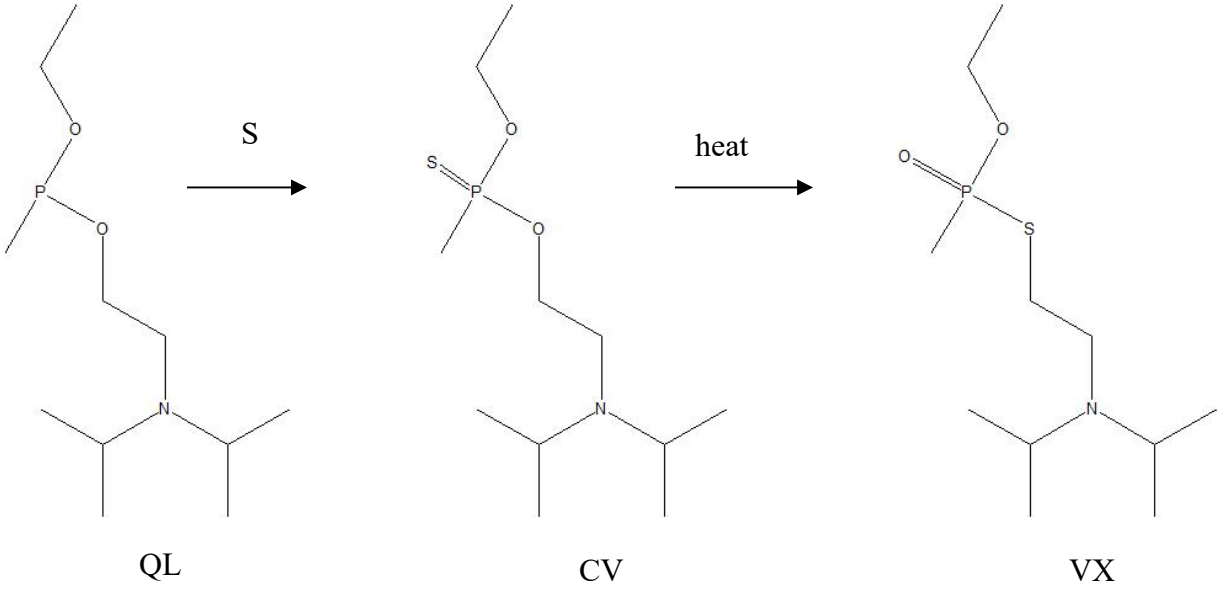

Figure 20: QL reaction that produces VX.

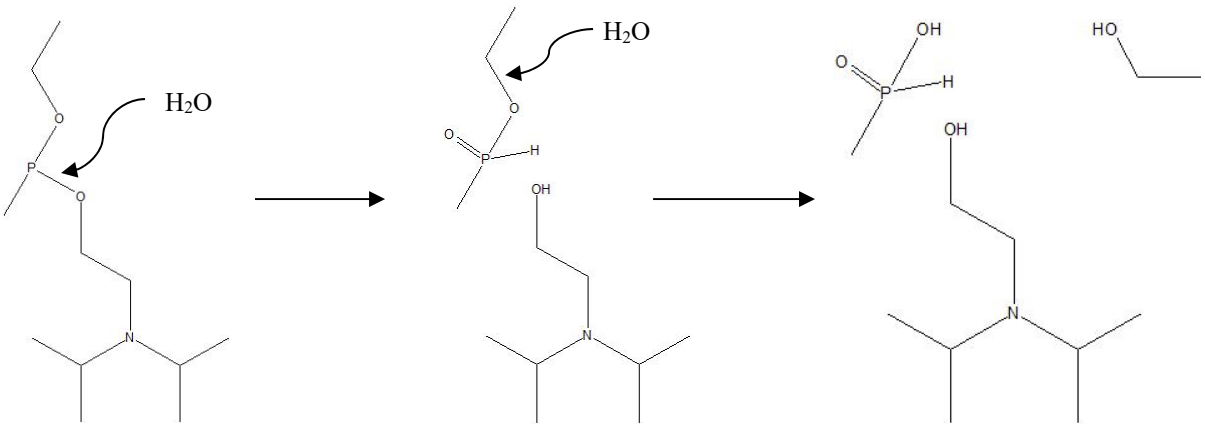

Figure 21: One possible QL hydrolysis reaction.

7.2.1 Experimental methods

For the NMR analysis, a Bruker Avance 300 NMR was used. Sample preparation was minimal, since the sample was transferred to a 5 mm NMR tube and added to a deuterated lock solvent. The instrumental analysis was done using ^{31}P with ^{1}H decoupling.

For the feedstock purity determinations, samples were prepared for analysis using the procedure described in a Technical Report.[12] Samples were handled according to safety procedures as toxic CA samples. In brief, about 100 µL of the material was transferred to a vial and weighed. An internal standard of 100 µL of triethyl phosphate (TEP) was added and weighed. TEP was unreactive with QL. Deuterated lock solvent $CDCl_3$ was added. The solution was mixed and transferred to a 4 mm diameter PTFE tube insert and capped with a PTFE cap. The insert was placed in a glass 5 mm NMR tube for secondary containment of a CA sample, and the glass tube was flame sealed. The doubly-contained sample was placed in the NMR and analyzed using ^{31}P with ^{1}H decoupling using a long recovery delay of 96 s for accurate quantitation. The total collection time was 25 min./repetition, with 3 to 7 repetitions.

For the kinetic determinations, ^{31}P NMR experiments were carried out with a shorter recovery delay setting to allow faster repetition rates.

Reaction conditions were provided that were used for pilot-scale reactors, and the conditions were reproduced in NMR tubes. NMR tube reactions at various temperatures were performed by mixing the component with solvent in a 1:5 ratio. Reactions were carried out with tap water (from the process site) as the solvent. An aliquot from the reaction was placed in an NMR tube, with ~50 µL D_2O added as a lock solvent. NMR experiments were run on each sample at periodic time intervals.

A second set of reactions were carried out in 0.3% aqueous NaOH. The reactions were inhomogeneous and had 2 liquid phases. Therefore, a stirred benchtop experiment was carried out in addition to the NMR tube reactions in a glass vial using Teflon-coated magnetic stir bars and magnetic stirrer. Aliquots were withdrawn from the organic and aqueous layers at time intervals. Prior to each sampling, stirring was stopped and the reaction phases were allowed to separate for 1 minute and the layers were sampled separately. Stirring was resumed after

sampling. Products were assigned based on chemical shift. The stirred reaction and NMR experiments were temperature controlled at 38 ºC (100 °F). Additional NMR experiments were done in NMR tubes at 21, 38, and 50 °C.

In addition to the NMR determinations, liquid chromatography/mass spectrometry (LC/MS) and tandem mass spectrometry (MS/MS) were done on select samples after the reaction was complete. LC/MS was done using an Agilent 1100 LC/MSD with electrospray ionization. MS/MS was done using a ThermoFinnigan TSQQuantum triple quadrupole mass spectrometer with electrospray ionization.

7.2.2 Result for analysis of reactor samples

The major final reaction product that contains phosphorus was observed to be methylphosphinic acid (MP) for reactions in the pilot-scale reactor. Samples were not cloudy and did not have a visible organic layer on top. A sample spectrum of a QL neutralent solution is given in Figure 22. The identity of the methylphosphinic acid was confirmed by running a ^{31}P NMR analysis without proton decoupling that shows a widely spaced doublet characteristic of a P-H bond, also shown in Figure 22.

Products identified in QL neutralent: The ^{31}P spectra for the QL reaction solution indicate the major phosphorus containing compound. Some samples were run by LC/MS and MS/MS to identify products. No standards of the compounds were available, so the results are not quantitative. Table 5 shows the list of compounds that are identified in the QL neutralent. A sample LC/MS extracted ion chromatogram is shown in Figure 23.

Samples were rerun after sitting at room temperature for two months by NMR and LC/MS. There is no indication that the sample changed, and the methylphosphinic acid was not converted to methylphosphonic acid or other secondary products to a noticeable amount.

Table 5: Compounds identified in the QL neutralent reaction solution.

Compound name	**$(M+H)^+ \rightarrow$ fragment ions**	**Comments**
Methylphosphinic acid (MP)	81	Major ^{31}P product
Diisopropylaminoethanol (DIPAE)	146 → 104, 86, 62, 44	Major non-^{31}P product, confirmed by ^{13}C NMR
Ethyl methylphosphonic acid	125 → 95	
O-R methylphosphonic acid	224 → 128, 86	
O-R methylphosphinic acid	208 → 166, 128, 114, 86	
R ether	273 → 172, 128, 86	
O-ethyl R-methylphosphinate	236	Impurity in QL[10]

R=diisopropylaminoethyl

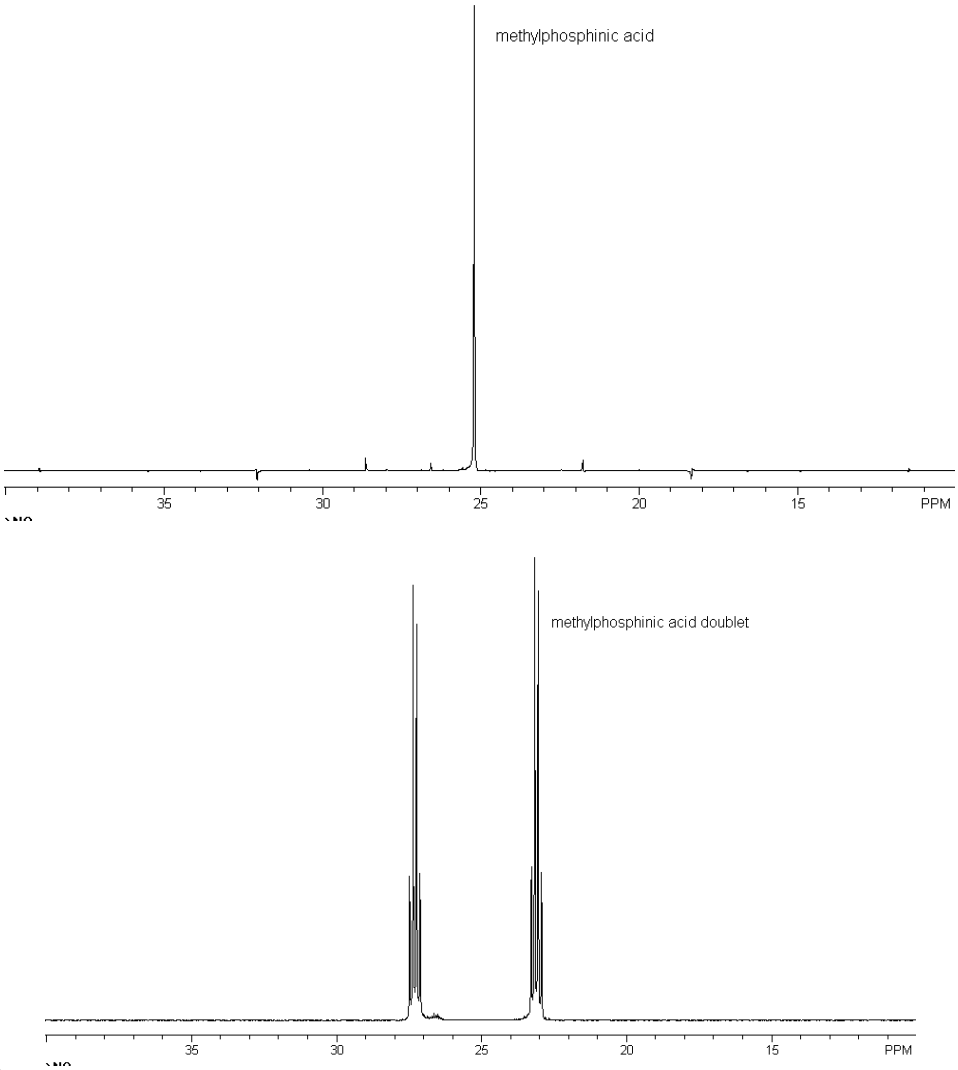

Figure 22: **^{31}P NMR spectra of QL reactor samples showing the product spectrum. Top panel: spectrum with proton decoupling; Bottom panel: same sample, with undecoupled ^{31}P detection to show the widely spaced doublet of multiplets that are characteristic of a P-H bond in methylphosphinic acid. The spectra strongly resemble those in Figure 8 and Figure 9.**

7.2.3 Results for feedstock purity analysis

The lot number of QL that was received, QL-7115-CTF-N, was found not to contain any QL. The sample had degraded to a large number of degradation products that were not all identified. The different lot number of QL designated QL-2345-CTF-N-1 had a purity of 80.11 wt.% QL. The purity is calculated by comparison to the weight and integrated signal of the internal standard. A sample NMR spectrum is shown in Figure 24. The QL stock solution contained traces of small amounts of its expected disproportionation products: O,O'- diethyl methylphosphonite (TR) and O,O'-bis(2-diisopropylaminoethyl) methylphosphonite (LT). (See

also Figure 6.) These peaks were integrated with the QL peak for the purity determination, since they are chemically similar to QL and can be considered to be hazardous.

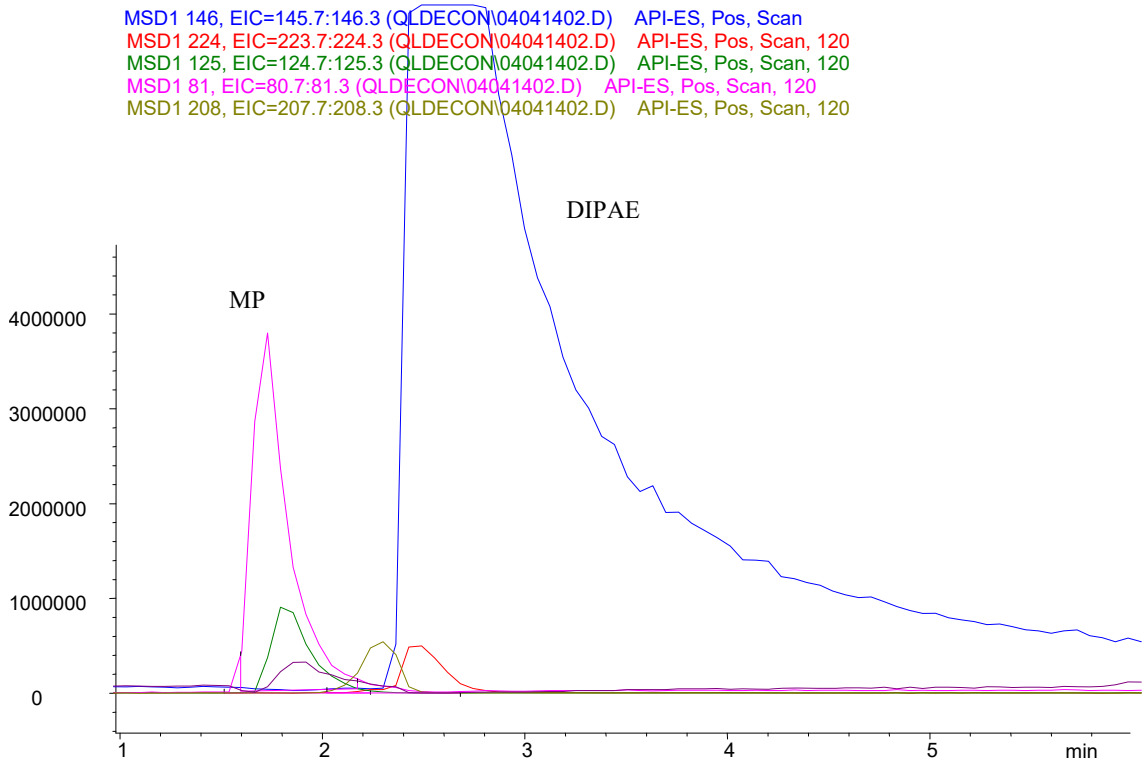

Figure 23: **Extracted ion chromatogram of an LC/MS run of the QL reactor sample with extracted $(M+H)^+$ ions that are identified in Table 5. The instrument sensitivity for DIPAE is much higher than it is for MP, even though these two compounds have approximately the same concentration.**

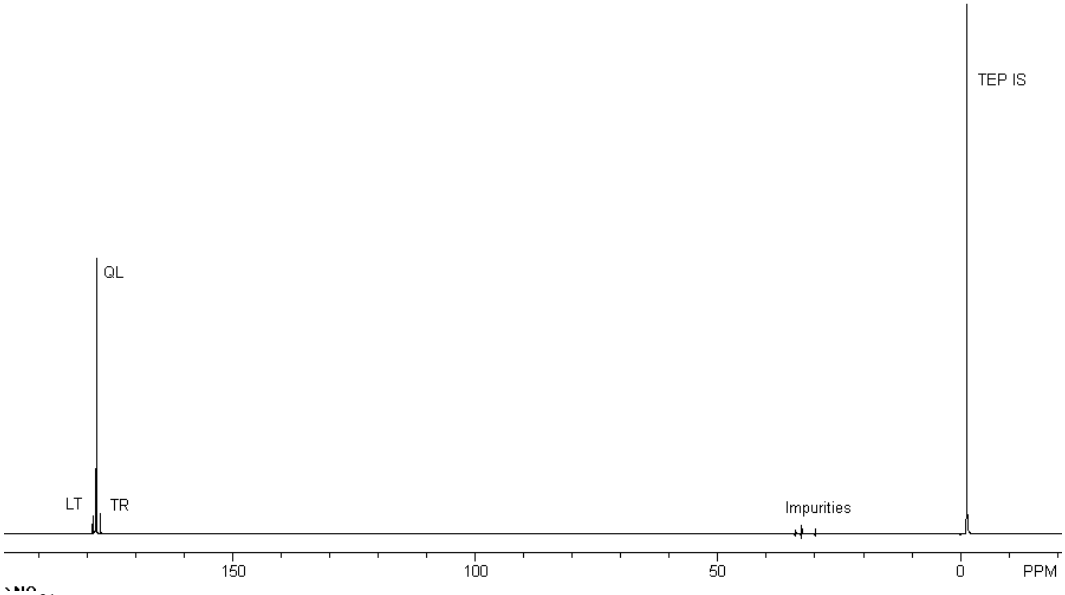

Figure 24: **^{31}P NMR spectrum of the QL feedstock sample, which has a purity of 80.11 wt.% QL.**

7.2.4 Results for kinetic studies

QL was added in a ratio of 1:5 by volume of QL to reaction solution that was an aqueous solution of 0.3% NaOH. This solution was determined by the pilot plant testing and wasn't ideal for kinetic studies. QL was not soluble in caustic, so it formed a separate organic layer on the surface of the aqueous solution. The QL reaction products include both weak acid and base, and the solution was not buffered sufficiently to maintain a constant pH. The final pH of the reaction was nearly neutral to slightly basic (pH 7-8). As the reaction proceeded, the QL did not appear to dissolve but rather reacted at the interface with the water. The reaction products dissolved in water. Stirring of the reaction matrix affected the reaction rate by increasing the area of the interface between the phases. At the beginning of the reaction, the stirred solution was visibly cloudy, and it became clear as the QL was consumed.

In order to simulate the reactor runs, the reaction was studied in a heated, stirred vial in a hood. A total volume of 5.0 mL of aqueous solution and 1.0 mL of QL were used. Samples were periodically removed from both the aqueous phase (sample size of 25 μL) and the organic phase (sample size of 5 μL), with sample sizes chosen to maintain the ratio of the phases. Each sample was diluted in 5-mm NMR tubes in D_2O or $CDCl_3$, respectively, to a total volume of 250 μL. In order to obtain accurate quantitation of the two phases relative to each other, it was necessary to use an internal standard in each phase. For the aqueous phase, phosphate was used as the internal standard. For the organic phase, tributylphosphate was used. The internal standards were determined to be insoluble in the other phase, so interference in the quantitation was not a problem.

The reaction was run at 38 °C (100 °F) in a glass vial in an aluminum block on a hot plate/magnetic stirrer. The solution was stirred with a Teflon stirbar sufficiently to form a vortex to the bottom, and the solution appeared to be cloudy. The solution was removed from the block and allowed to separate for a minute before sampling the organic and aqueous layers.

Sample spectra for the organic and aqueous layers are shown in Figure 255. The results of the kinetic data are shown in Figure 266. The data in Figure 266 are shown for the QL in the organic layer and the MP (methylphosphinic acid, the major product) in the aqueous layer, determined relative to their respective internal standards, and normalized to be on the same relative scale. The plot is in linear units, not log units. The measurements of reactants and products are independent of each other since they are in separate phases, but they track each other well. The total of the relative amounts is shown as a solid line.

The kinetics are not logarithmic and don't follow a simple kinetic rate law. Instead, there appears to be a relatively flat induction period, followed by a linear decrease in QL amount and increase in MP, and then a final flat region after the QL is consumed.

All three related species (QL, TR, LT) react to form methylphosphinic acid (MP) as the major final product. The relative kinetics of these three compounds could be observed, shown in the plot in Figure 277. TR reacts much faster, QL is intermediate, and LT is slowest. These compounds were not detected by NMR in the aqueous phase, only in the organic phase.

The reaction was also studied by putting the reaction solution in NMR tubes, still consisting of two separated phases. The conditions for the reaction that were done in NMR tubes, rather than on a hot plate, are not completely comparable to the pilot scale reactor run. The collection of kinetic data using the NMR was complicated by the two separated phases. The sample mixing was different since it is not possible to use a stir bar in the NMR magnet. However, the advantages were the capability to take an unlimited number of data points, since the reaction mixture is not sampled and consumed; less QL consumption; easier thermostatting, since the NMR probe should have good temperature control; and the samples could be doubly contained during analysis. The studies were also less labor intensive and hazardous. Because of these advantages, the kinetics in the NMR tubes were compared to the in-vial measurements.

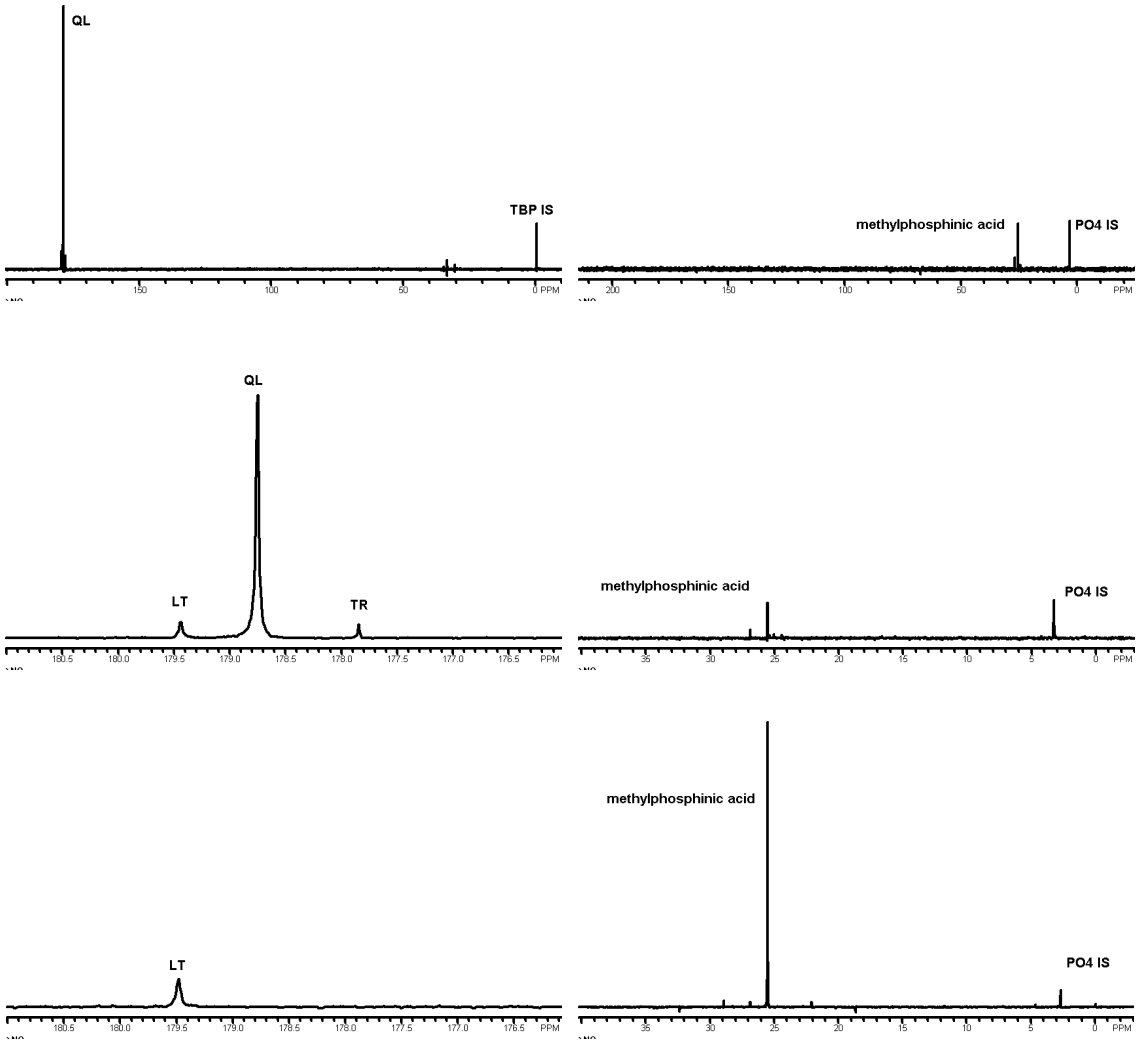

Figure 255: **Spectra for reaction mixture organic and aqueous layers. Reaction temp. is 38 °C, using NMR parameters of 10 s relaxation delay, 16 scans, 121 MHz, using the Bruker Avance 300 MHz NMR. Top spectra: full spectra for organic (left) and aqueous (right) layers at time = 6 min. Middle spectra: expanded regions for organic and aqueous layers at time = 12 min. Bottom spectra: expanded regions at time = 213 min., with the QL completely consumed but LT remaining.**

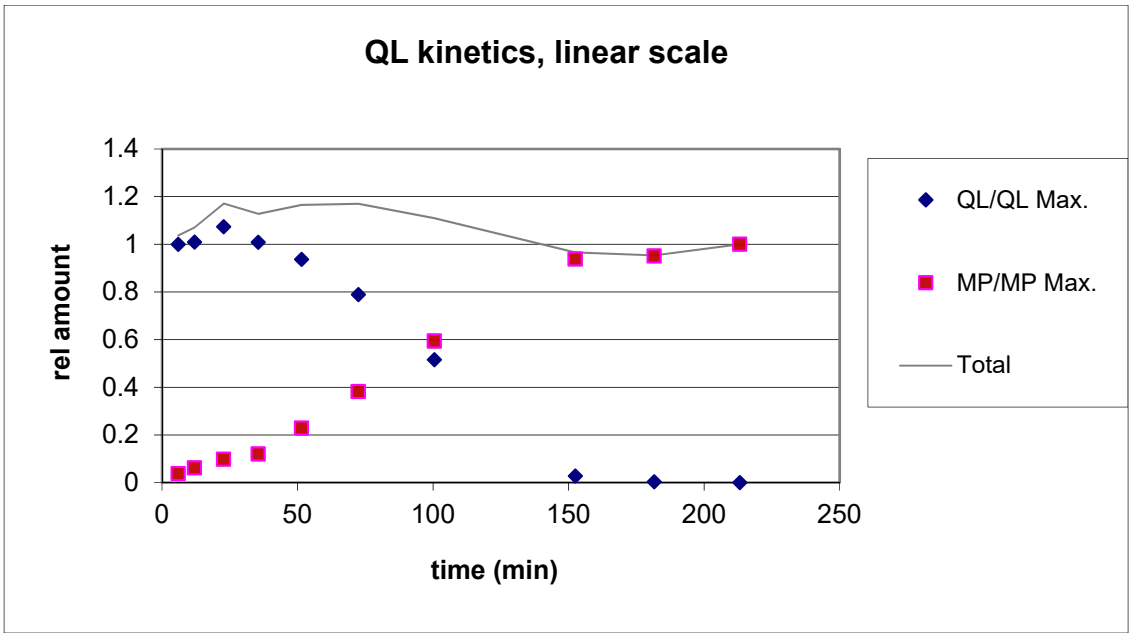

Figure 266: **Kinetics of QL in a stirred vial at 38 °C. QL and MP are each measured independently in two separated phases. The solid line is the sum of the normalized amount of reactant and product during the course of the reaction.**

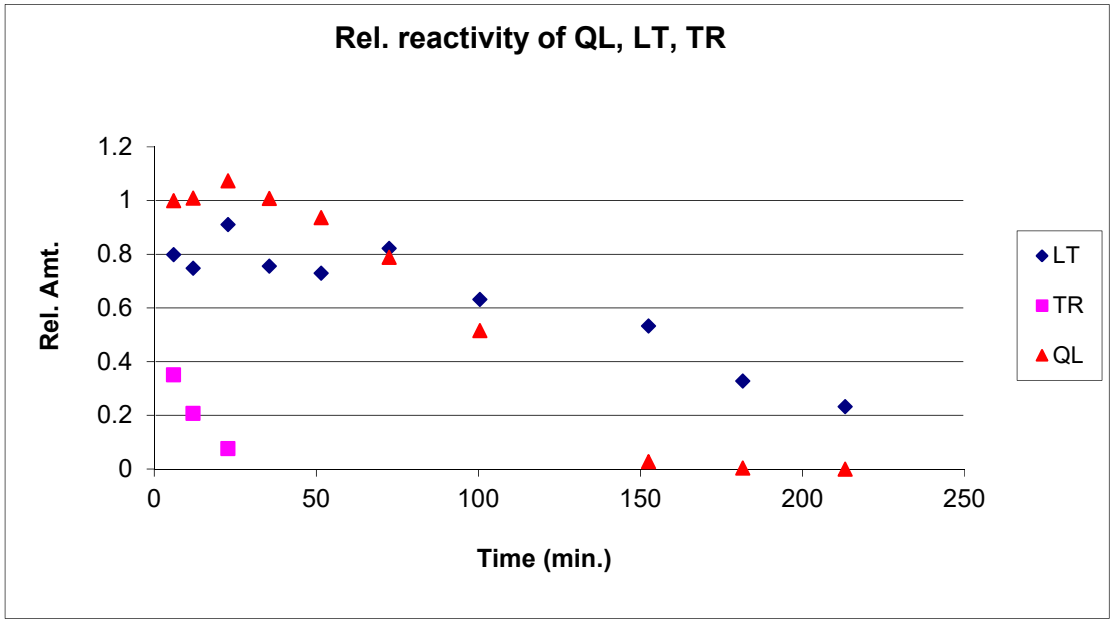

Figure 277: **Plot showing the relative reactivities of LT, QL, and TR.**

The NMR approach was to use a small total volume of solution so that the entire amount of solution including both phases was positioned within the NMR detection coil. The total volume was 120 µL. It was possible to detect both phases with the QL and the reaction products. The QL peak was very broad, and attempts to narrow the peak by adjusting the magnet

shimming were not successful. QL is very well separated in chemical shift from the other compounds except the TR and LT, so these three starting compounds were integrated together. Since the QL chemical shift is at 178 ppm, the peak is easily resolved from the product peaks. A sample spectrum is shown in Figure 288. Another effort by monitoring only the aqueous phase with the NMR by adjusting the NMR tube so the aqueous phase was in the detection coil produced erratic results.

Kinetics plots were obtained by this method at 38 °C for two reaction runs, shown in Figure 29. The runs were nominally identical, but the half-lives of the runs varied from 11.7 to 55.9 min. The range of the half-lives indicates that there is a significant amount of sensitivity to the sample preparation or mixing. The temperature may have not been reproducible, since the temperature was not independently calibrated for the runs. The kinetic plots are linear on a logarithmic plot, with correlation coefficients of 0.97, indicating that the kinetics can fit a pseudo-first-order kinetic model. Since the sample has two phases, there is not necessarily a physical reason that the reaction should fit an exponential rate law.

These results are unlike the plot from the run in the vial that was vigorously stirred, shown in Figure 266, for which the reaction is half completed in about 100 min. It is unexpected that the stirred reaction is slower, since the mixture should have a higher surface area for the two phases to be in contact than the NMR tube experiments, which would imply that the reaction should be faster for the stirred sample.

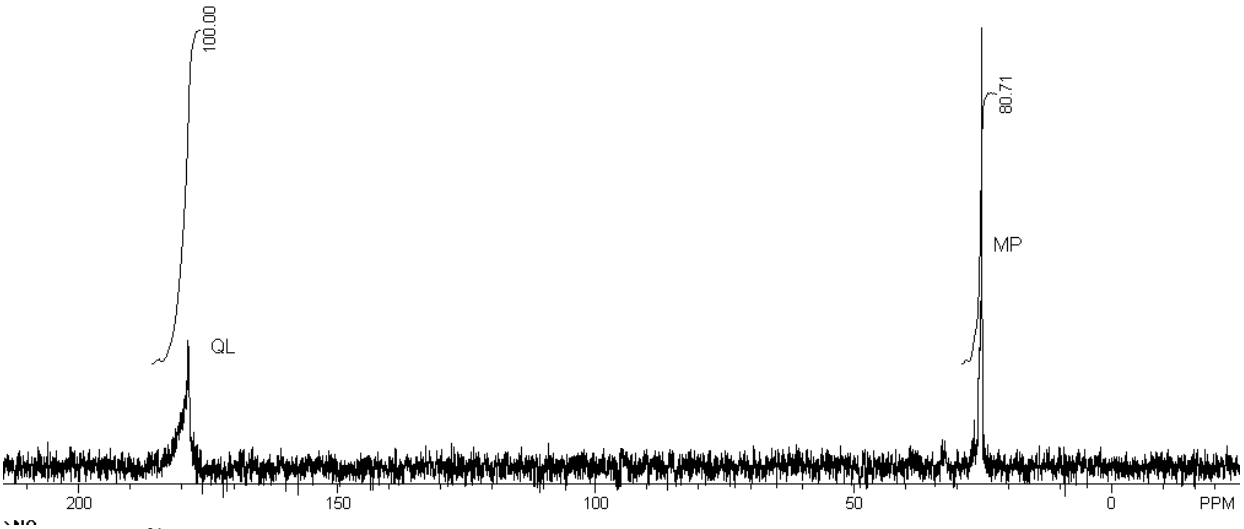

Figure 288: **^{31}P NMR spectrum from kinetics study of QL. The broad QL peak has a higher integrated signal than the narrow MP peak.**

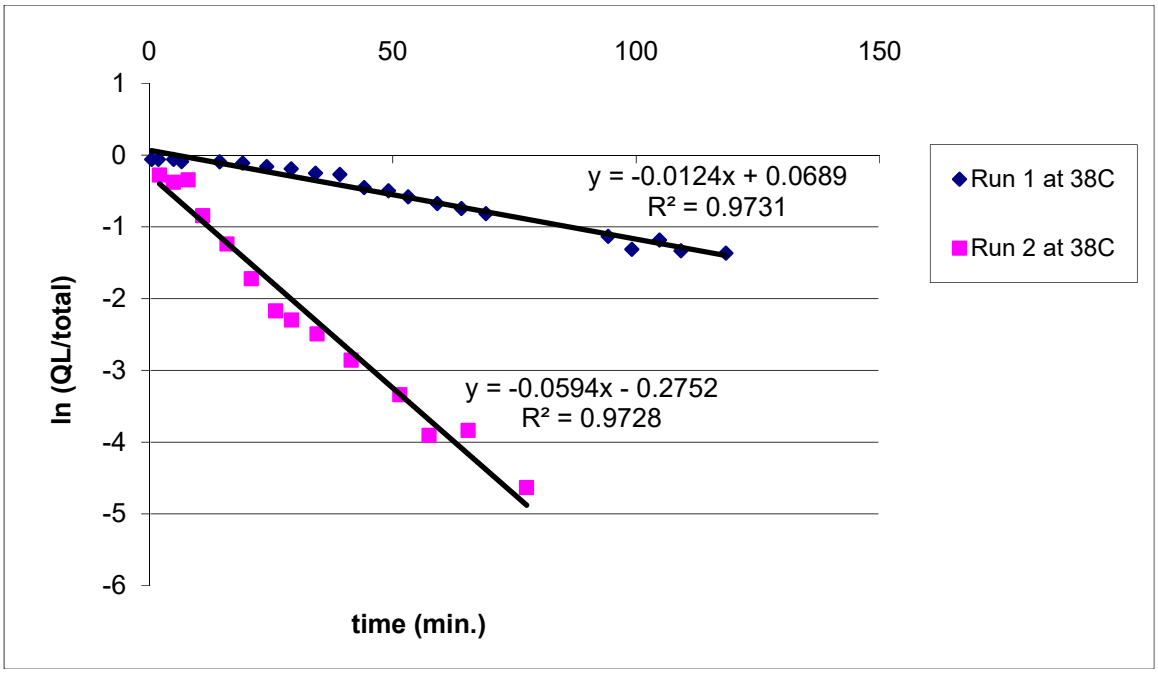

Figure 29: Kinetic runs of QL with 0.3 wt% aqueous NaOH at 38 °C. The runs are nominally identical, but the half-lives of the runs vary from 11.7 to 55.9 min.

Additional kinetics runs were performed at room temperature (22 °C) and at 60 °C, shown in Figure 30 and Figure 31, respectively. The sample was not agitated except for the 20 Hz tube spinning in the NMR. Even though the QL peak was broad, it could be detected in 24 hours after the beginning of the reaction in the 22 °C run. The log plot also appears to be linear. The half-life from the plot is 4.7 h at 22 °C.

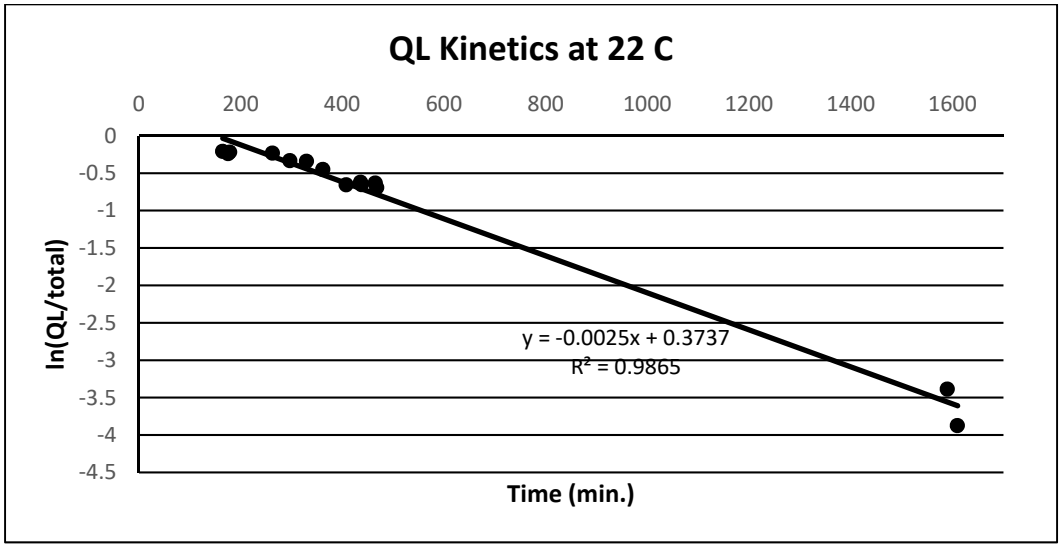

Figure 30: Plot of the kinetics of QL in 0.3 wt% aqueous NaOH at room temperature. The half-life from the plot is 4.7 h. Although the log plot appears linear, the reaction mixture has two phases.

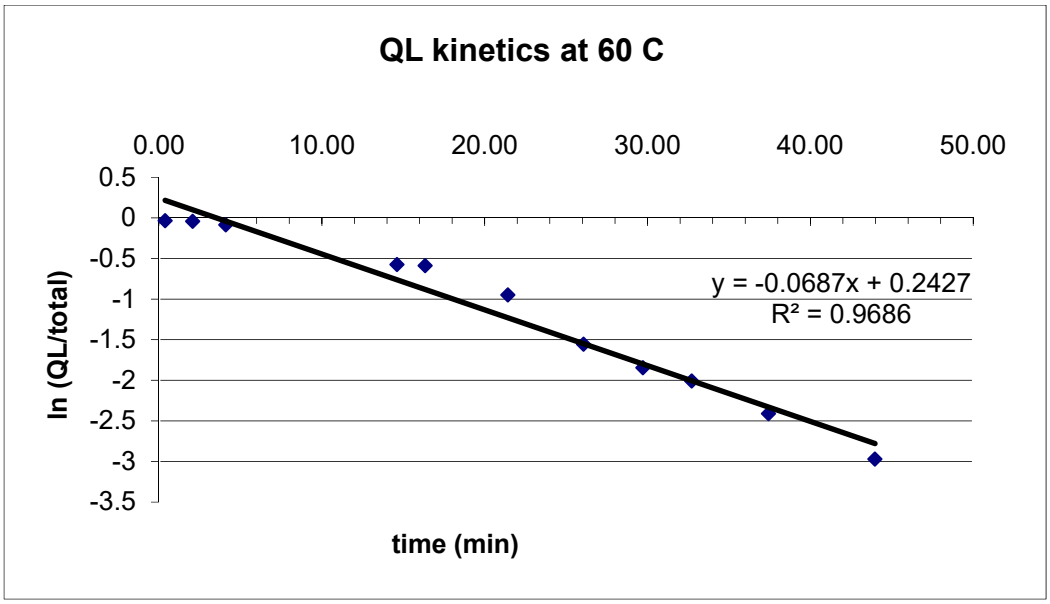

Figure 31: **Kinetics of QL in 0.3 wt% aqueous NaOH at 60 °C. The half-life from the plot is 10 min. Although the log plot appears linear, the reaction mixture has two phases.**

The results for the kinetics run at 60 °C is faster, and the QL is undetectable in less than an hour. The log plot is linear with a half-life of 10.0 min. Both plots have a positive y-intercept, which indicates that there may be an induction period with little reaction, similar to the behavior for the stirred vial in Figure 266.

QL dissolves immediately in an acidic aqueous solution. The kinetics with acidic aqueous solutions were not studied, but they have been reported previously by Verwiej and co-workers.[13] It was found that in acidic media, the QL dissolves and reacts too fast to detect by NMR. However, intermediate decontamination products were formed that were slower to convert to methylphosphinic acid.

8. CONCLUSIONS

As part of the Tactical Disablement Project, neat weapons-grade QL was reacted with 5% lithium nitride (Li_3N) powder and 10% water in a glass reaction vessel, compared to the amount of QL by weight. In a 100 mL reaction, addition of water produced boiling of the QL and water mixture. The product solidified after an extra 3% water was added. Possibly the extra water was needed because of the boiling or secondary reactions that could be taking place. Products were analyzed, and the primary phosphorus product was methylphosphinic acid. The observed products with amine groups were a more complex mixture that wasn't quantified.

In the 2004-2006 studies of QL chemistry, decontamination reactions in a 1:5 ratio of QL to water were studied. In each case, QL was present as oily layer formed above the aqueous layer. The heterogeneity of the reaction mixture may have affected the accuracy of the half-life determinations for NMR tube reactions. Nevertheless, the bench-top reaction shows

that QL degraded to ~0.10% of its initial concentration in less than 150 minutes at 38 ºC or higher.

The results indicated that in order to provide a sufficient reaction rate for destruction of QL (and its disproportionation products TR and LT) in less than a day under neutral to basic conditions, the reaction must be vigorously stirred and maintained at 38 ºC or higher. At room temperature, the QL can persist at least a day, and in the case of the Li_3N+H_2O reaction, it can persist for at least 10 days, unless sufficient excess water is added.

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ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
ACN	Acetonitrile
CA	chemical agent
CTF	chemical transfer facility
CV	O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonothioate
CW	chemical warfare or chemical weapon
CWA	chemical warfare agent
DF	Methylphosphonodifluoridate
EIC	Extracted ion chromatogram
GB	Isopropyl methylphosphonofluoridate
GC/MS	Gas chromatography/mass spectrometry
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromagraph/tandem mass spectrometer
LT	O,O'- bis-(diisopropylaminoethyl) methylphosphonite
NMR	Nuclear magnetic resonance
QL	O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonite
TIC	Total ion chromatogram
TR	O,O'- diethyl methylphosphonite
VX	O-ethyl-S-[2-(disopropylamino)]ethyl methylphosphonothiolate

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APPENDIX 1: Headspace GC/MS Analysis of QL reaction product

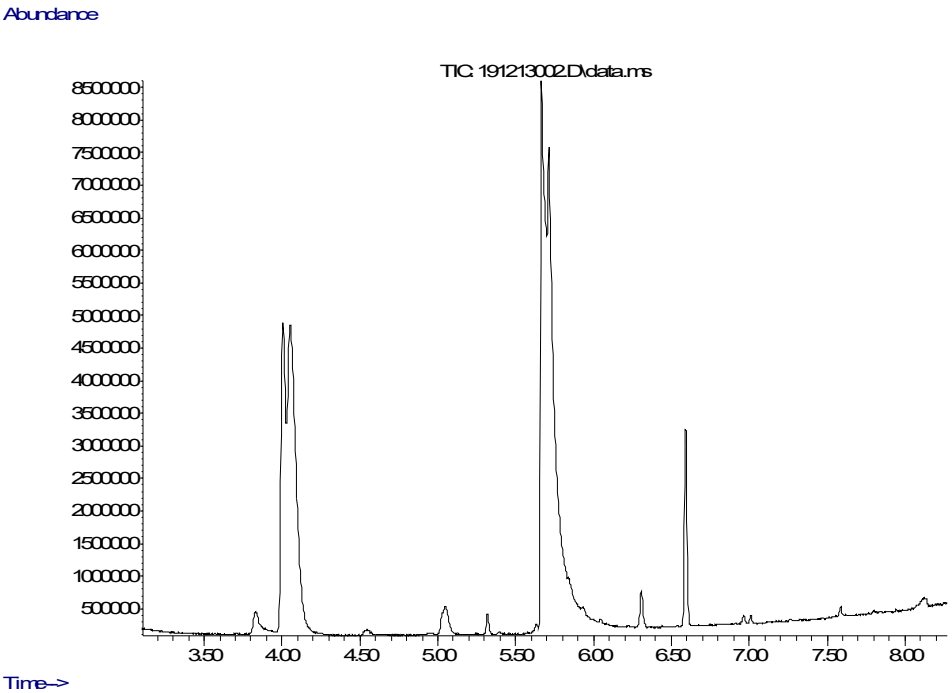

Figure A 1: Headspace TIC for QL 100 mL sample, NB0049P03A4

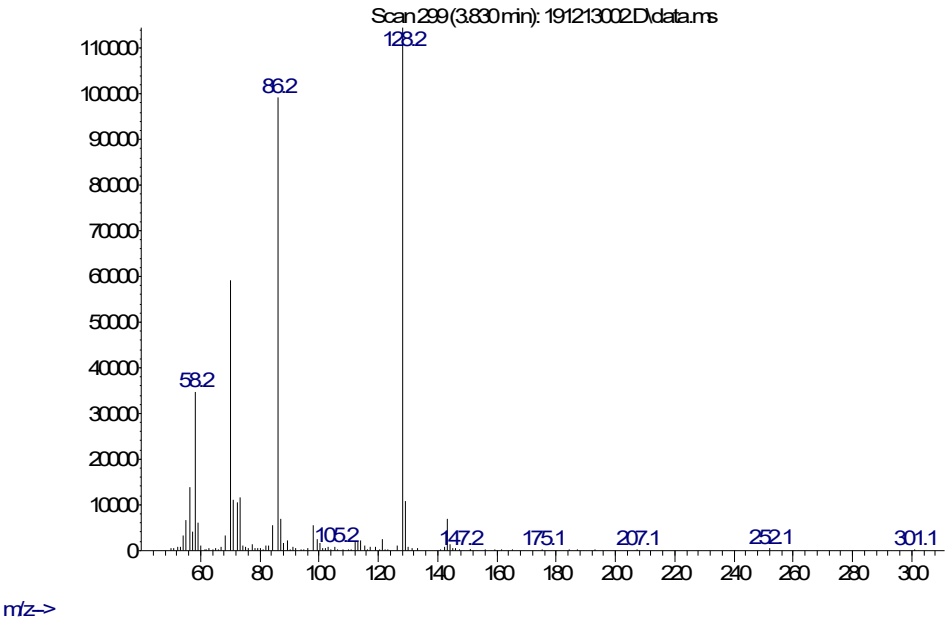

Figure A 2: MS at 3.83 min. MS library search is inconclusive but the spectrum indicates an amine

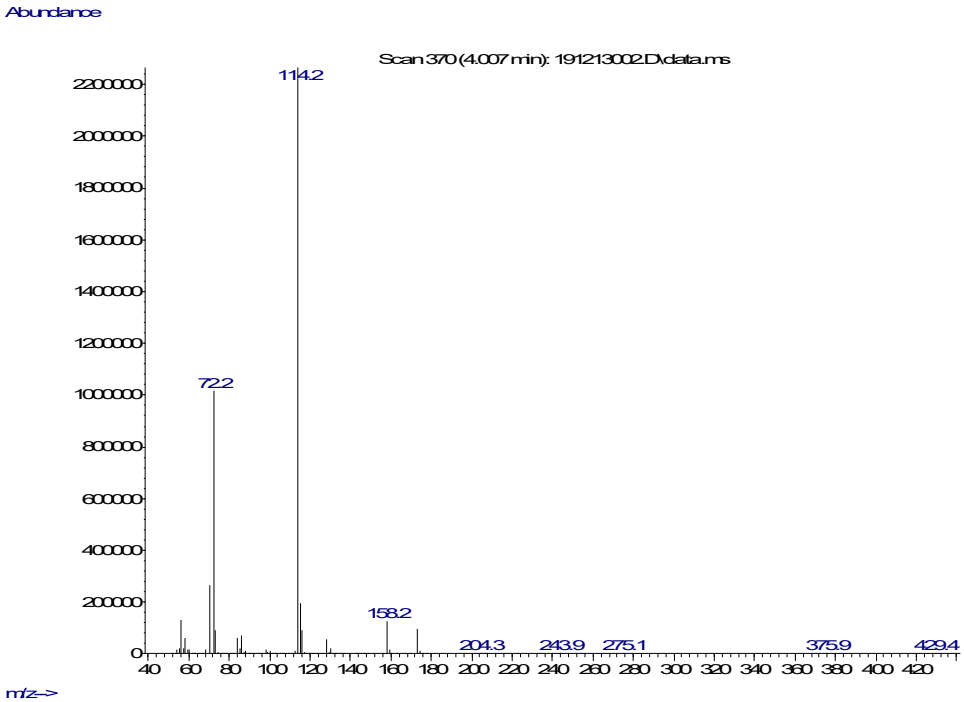

Figure A 3: MS at 4.00-4.059 min. Best MS library match is 2-diisopropylaminoethyl ethyl ether, MW 173 Da.

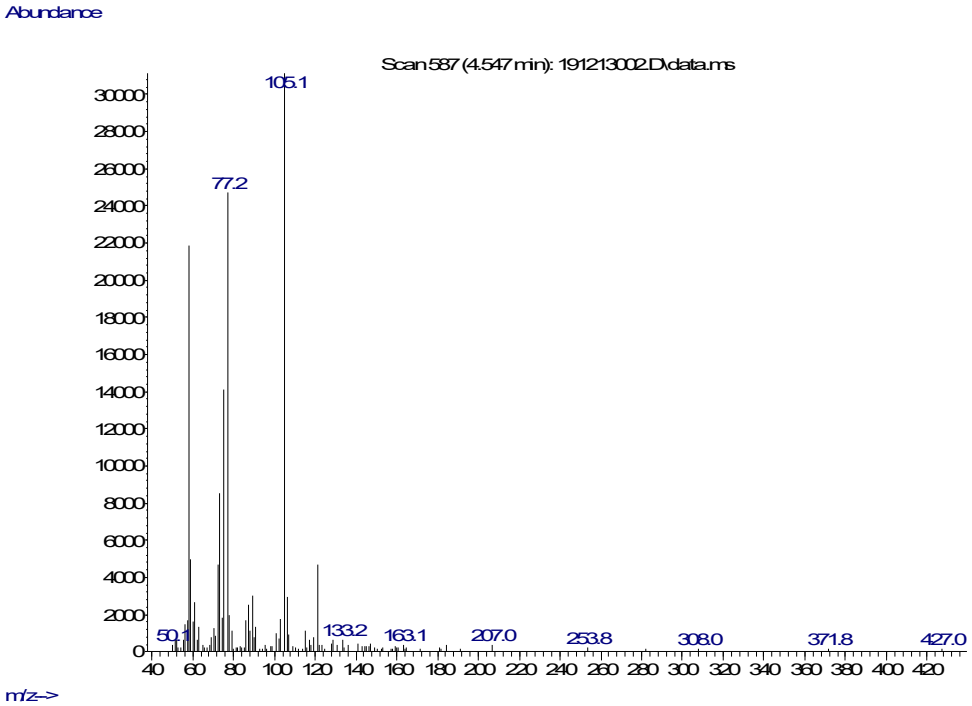

Figure A 4: MS at 4.547 min. MS library search is inconclusive.

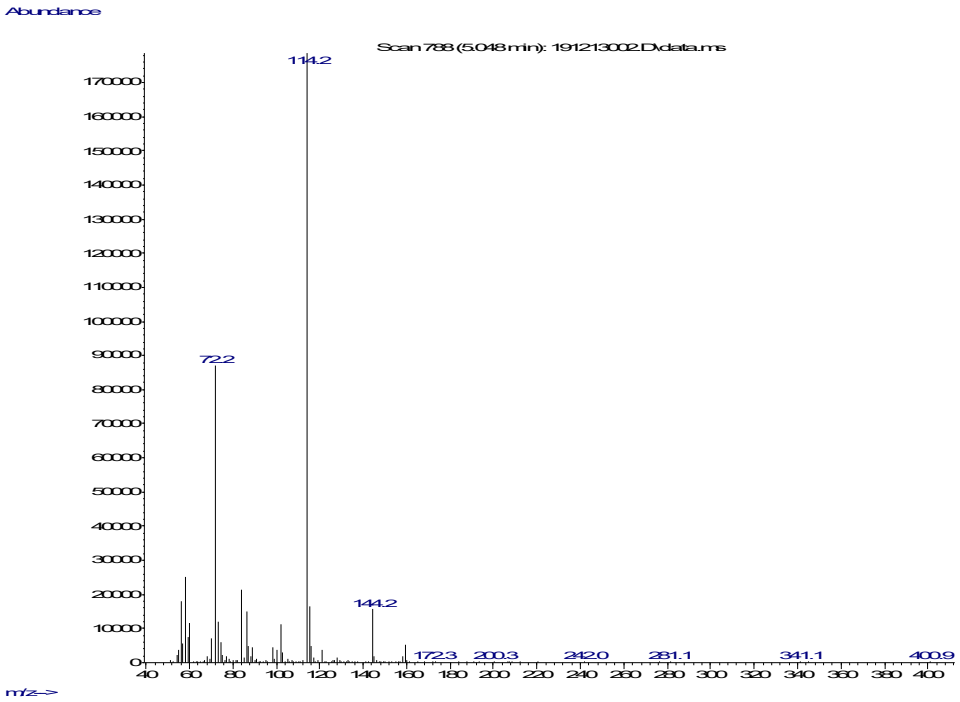

Figure A 5: MS at 5.048 min. The best MS library match is for 3-diisopropylamino-1,2-propanediol, MW 175 Da

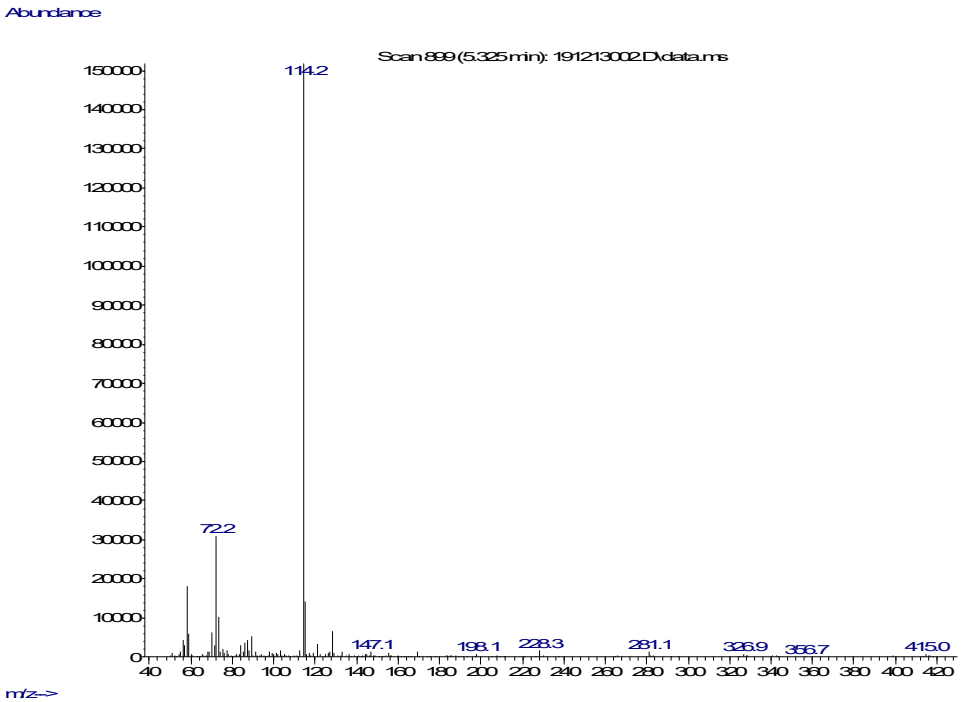

Figure A 6: MS at 5.325 min. Best MS lib match is for 1,2-Bis(2-diisopropylamino) ethane.

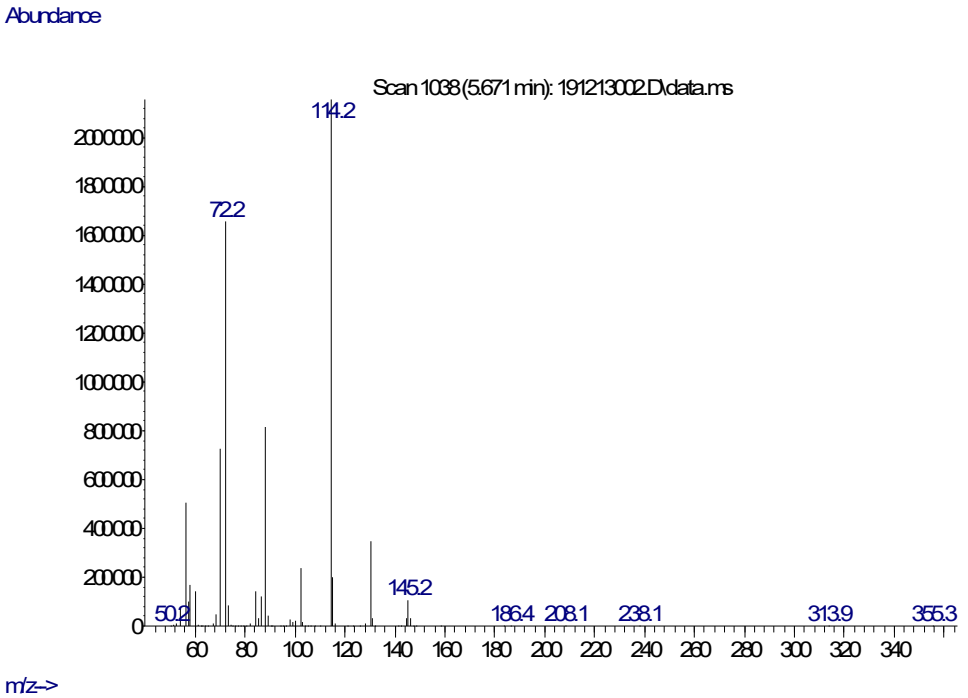

Figure A 7: MS at 5.671-5.716 min. Best MS lib match is for diisopropylaminoethanol, MW 145 Da. This peak has the highest area in the chromatogram.

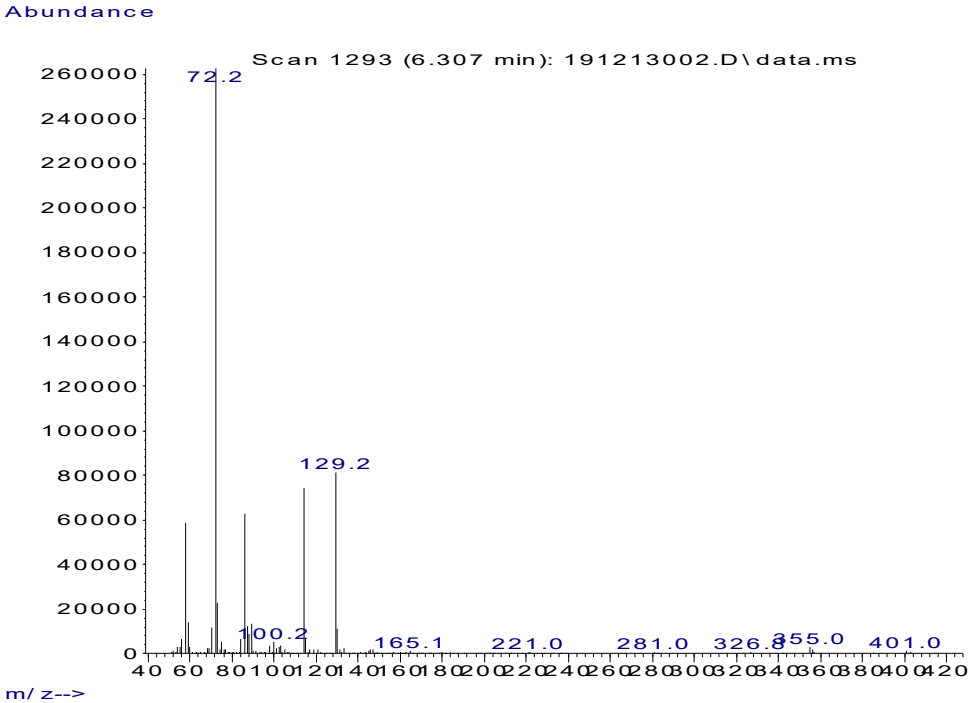

Figure A 8: MS at 6.307 min. Best MS match for diisopropylformamide.

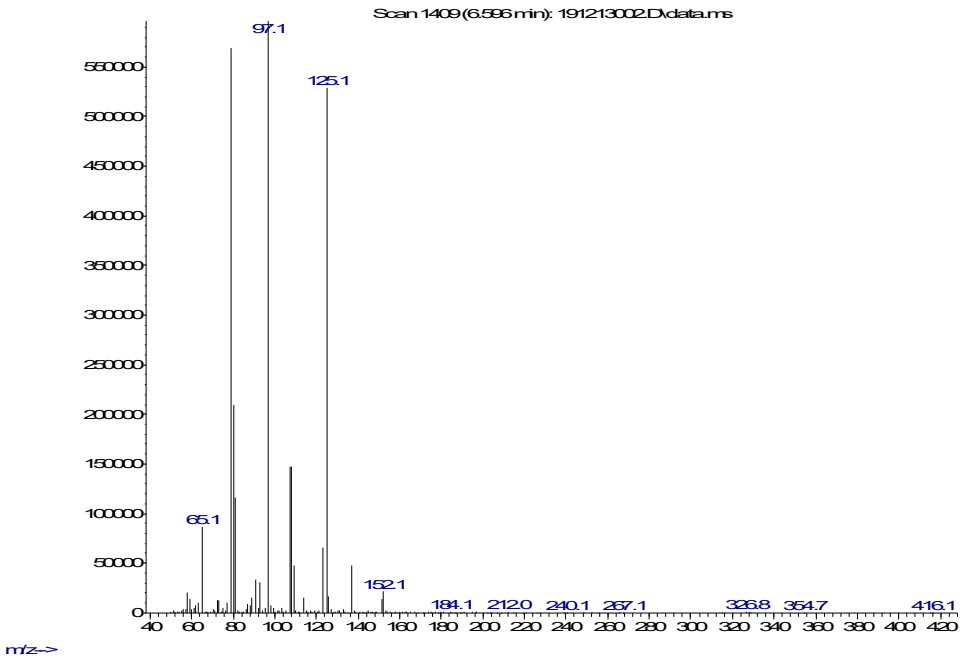

Figure A 9: MS at 6.596. MS match for diethyl methylphosphonate.

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