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Characterization of Solid Reaction Products from the Reaction of VX with Li_3N+H_2O for the Tactical Disablement Project

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As part of the Tactical Disablement Project, 100 mL of neat weapons-grade *o*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX) was reacted with 8 g of lithium nitride (Li_3N) and 10 g of water in a glass reaction vessel. The addition of the water and Li_3N resulted in an approximately 16% increase in the volume of the reaction. Products were analyzed, and reaction schemes are provided to explain the products. The observed products are consistent with previous studies of VX reactions in caustic decontamination solution, forming primarily VX acid (ethyl methylphosphonic acid) and VX disulfide [bis(2-diisopropylaminoethyl) disulfide].

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PREFACE

The work described in this report was started in February 2019 and completed in December 2019.

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CHARACTERIZATION OF SOLID REACTION PRODUCTS FROM THE REACTION OF VX WITH Li_3N+H_2O FOR THE TACTICAL DISABLEMENT PROJECT

1. INTRODUCTION

The objective of this project is to eliminate and/or rendering bulk agent unusable by a threat entity via neutralization and/or polymerization of the bulk agent by using minimal quantities of additives.

This study demonstrates in situ neutralization and solidification of bulk XV (S,2-[diisopropylamino]ethyl methylphosphonotioate) chemical warfare agent (CWA). This can be done by performing reactions in the existing CWA storage container via wet chemical approaches. The minimal quantities of chemical reagents are 15-20% by weight of the amount of CWA. This approach does not require sophisticated equipment, fuel to power generators, electricity to power equipment, or large quantities of decontaminating materials. It doesn't generate a large amount of waste that must be treated.

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

As part of the Tactical Disablement Project, the decontamination reaction of a 100-mL quantity of neat weapons-grade VX was studied with the reagents lithium nitride (Li_3N) and water. Previous small scale (1-10 mL) studies indicated that the addition of 9% w/w Li_3N and 8.5% w/w DI water, compared to the amount of VX, reacted to produce a solid product. Photos of a small scale (10 mL) reaction are shown in *Figure 1*. Since there was excess Li_3N in the reaction (visible on the bottom of the vial), the amount of Li_3N was reduced from 9% w/w to 8%.

The 100-mL reaction was carried out by adding 100 mL (by volume) of weapons-grade VX (Lot No. VX-U-4205-CTF-N from Chemical Transfer Facility, CCDC CBC) to a glass reaction vessel that was positioned inside a clear acrylic plastic box, located inside a Toxic-certified fume hood. Li_3N was added as 8.0 g of tablets that were pressed in a tablet press at Sandia National Laboratories (SNL). No visible reaction occurred upon the addition of the Li_3N tablets to the VX. Next, 10 mL (by volume) of water was added using an automated syringe system. For operator safety, the plunger of the syringe was depressed using a robot arm attached to the box. The water formed visible immiscible droplets in the VX liquid but gradually dissolved in the VX. Reaction with the pellets was slow due to water being on top of the VX and diluted by the VX when the tablets were at the bottom of the reaction vessel. No temperature rise

of the reaction was detected using an IR temperature probe. A solid product slowly (over days) formed in the reaction vessel, until the liquid agent was completely converted into the solid.

The product of the 100 mL reaction is shown in Figure 2. A video was also made using time-lapse photography of the reaction over the course of 13 days. The mixture was stirred after the reaction was complete but not during the reaction. There are gray pellets of the Li3N reagent visible in the reaction vessel.

Figure 1. Reaction mixture of 10 mL VX + 0.9 g Li_3N + 0.85 g H_2O. Left: 3.5% H2O after 5 days reaction time; Right: additional 5% H_2O after additional 5 h and manual stirring.

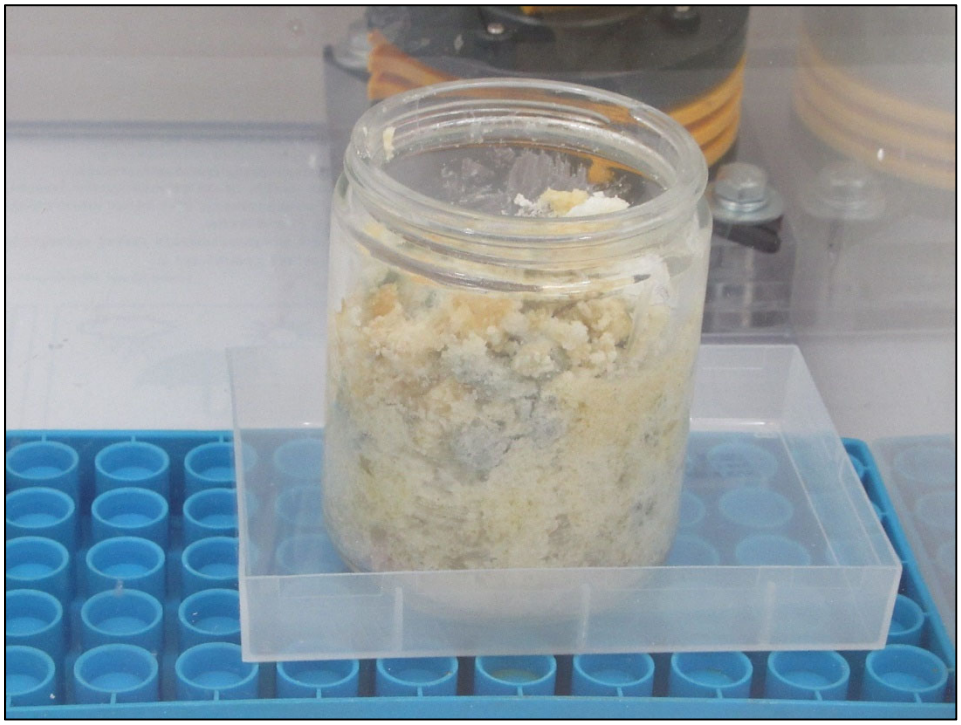


Figure 2. Solid reaction product formed from reaction of 100 mL VX with Li_3N + H_2O.

The reaction proceeds by a caustic hydrolysis process due to the reaction of Li_3N and water to form LiOH (aq) and NH_3 (aq). Caustic hydrolysis of VX has been studied in detail.[1,2] The studies are typically performed with large excess of a decontamination solution, although a previous study of decontamination of VX was done with an equimolar amount of water.[3] Nuclear magnetic resonance (NMR) spectroscopy, liquid chromatography/mass spectrometry (LC/MS), Raman spectroscopy, and wet chemistry experiments were utilized to determine the composition of the solid material of the 100 mL reaction.

2. P-31 NMR RESULTS

The best quantitative method for determining the purity of nerve agents and for determining residual agent is phosphorus (P-31 or ^{31}P) NMR due to the simplicity of distinguishing between the agent and reaction products. VX has a P-31 NMR chemical shift of 55-62 ppm, depending on solvent and pH,[4] and is well resolved from other phosphorus compounds and reaction products. An aliquot of the 100 mL VX reaction was removed and analyzed after 18 hours of reaction time. The resulting NMR spectrum, shown in ***Figure 3***, indicates the reaction mixture is mostly VX with a small amount of acid product at 31 ppm. VX is soluble in chloroform, and this solvent is used for purity determinations.

For the solid reaction product, extraction of a weighed amount (20-50 mg) of the solid in chloroform was used to determine the amount of residual VX in comparison to an internal standard, assuming 100% extraction efficiency.

Another aliquot of the 100 mL VX reaction was removed and analyzed after 7 days of reaction time. VX is still observed (Figure 4), but the signal in the chloroform extract is reduced because much of the VX has turned into products that have limited solubility in the chloroform solvent. The amount of VX remaining is 6.6 wt% determined by comparison to a known weight of internal standard. Signal from other products is not large, since the acid doesn't readily dissolve in chloroform. The peak at 95.58 ppm is an impurity in the VX.

Another aliquot was removed and analyzed after 3 months. The solid was completely dissolved in aqueous hydrochloric acid (HCl) solution. The spectrum (Figure 5) indicates that the VX is not detectable. The peak at 50 ppm is assigned to the compound EA-2192, which is a toxic hydrolysis product of VX and could still be responsible for a significant toxicity of the solid material. (The chemical shifts of EA-2192 are not as well studied as VX, but since EA-2192 is a zwitterion, it is anticipated that the chemical shifts are solvent dependent.) The large peak at 30 ppm is assigned to VX acid, the primary phosphorus-containing decontamination product.

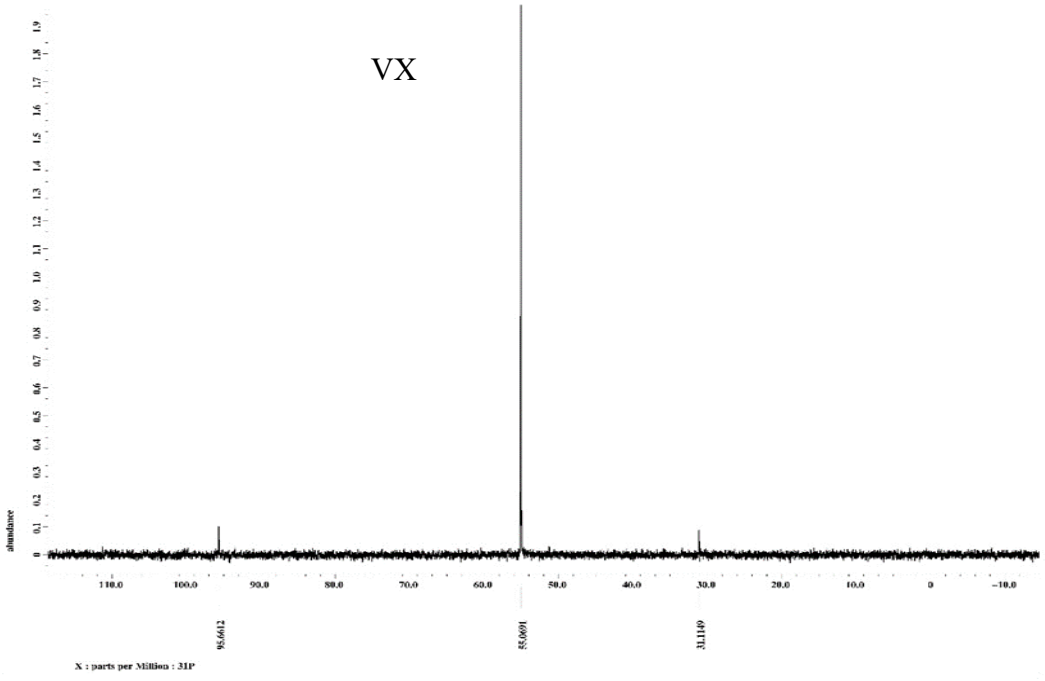


Figure 3. P-31 NMR spectrum of VX dissolved in chloroform ($CDCl_3$) after 18 hours of reaction time.

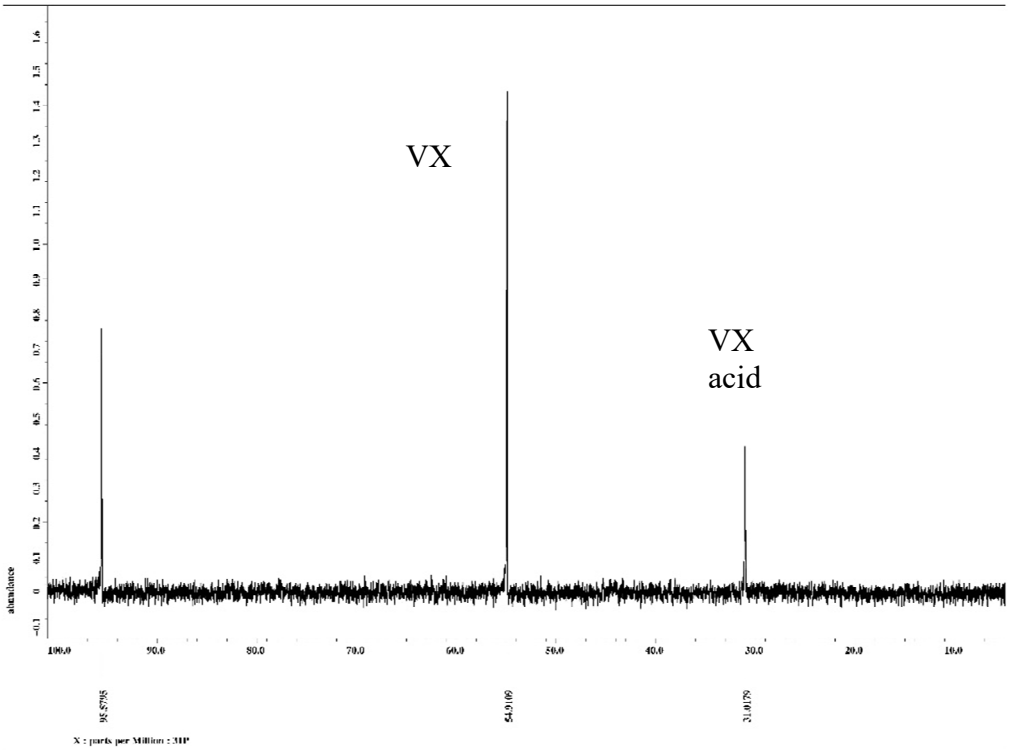


Figure 4. P-31 NMR spectrum of reaction solid extracted in chloroform after 1 week of reaction time.

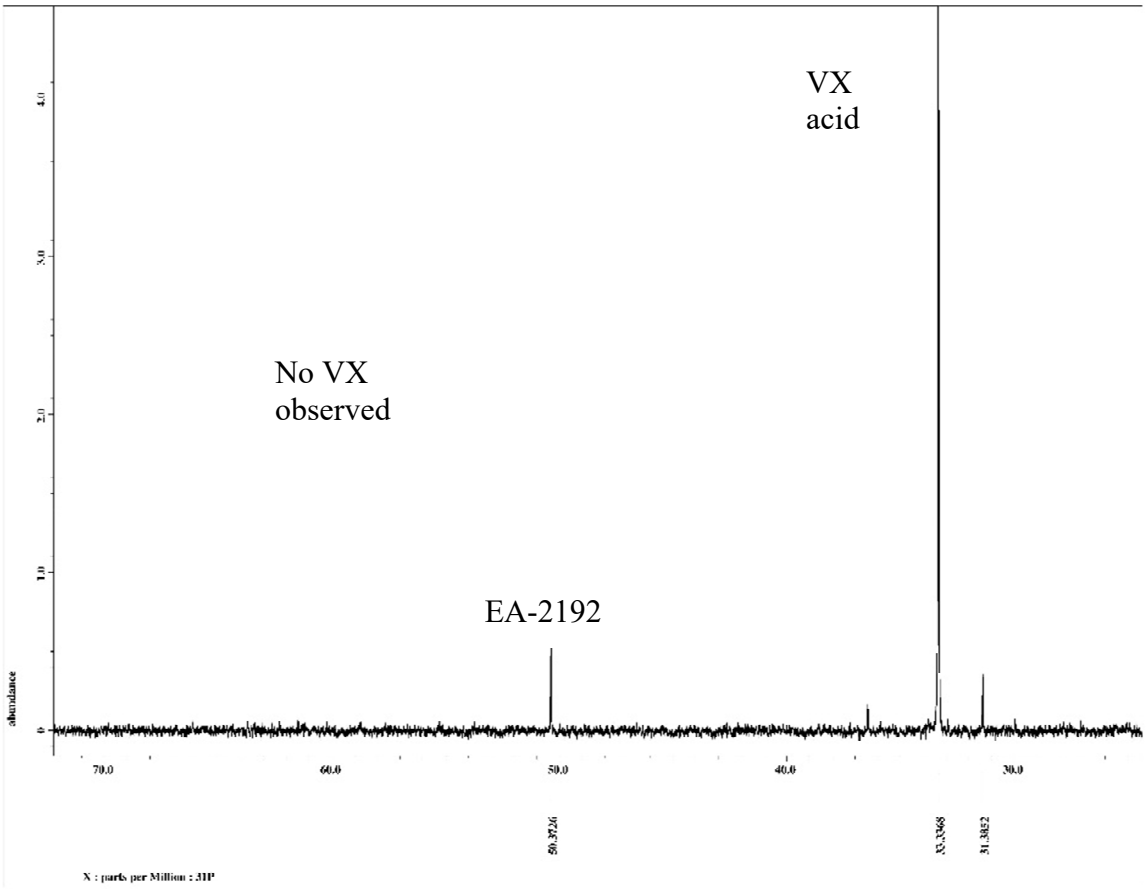


Figure 5. P-31 NMR spectrum of reaction solid dissolved in aqueous HCl after 3 months reaction time.

3. C-13 NMR RESULTS

Although P-31 NMR is useful for determining residual VX and phosphorus products, it is not helpful for products that have lost phosphorus. There are several likely candidate products that are generated from loss of the P-S bond. NMR spectrum modeling software[5] can be used to calculate the expected C-13 NMR spectra for these products. Calculated spectra are shown in Appendix A. The calculated C-13 chemical shifts for the compounds are listed in Table 1. Some of the peaks are at similar positions for many of the products due to the chemical similarity of the products. This can make it difficult to distinguish between the products using these NMR signals. Several of the peaks shift slightly depending on changes of the nearby groups, but the shifts can also be somewhat solvent dependent (especially for protonation of the amine group), and the software predictions are not perfectly accurate.

A C-13 NMR spectrum of the VX reaction solid product dissolved in aqueous HCl is shown in Figure 6. The peaks from the experimental spectrum are also included in Table 1 for comparison to the calculated chemical shifts.

A helpful feature of C-13 NMR spectra is that the peaks have small splittings that correspond to C-13 atoms that are coupled to P-31 atoms. For VX, all the C-13 lines are split.[4] From the experimental spectrum, the peaks at 62.29 and 15.46 ppm are split because they are from the VX acid, which contains phosphorus. Figure 7 shows that the 62.29 ppm peak is split into two peaks of the same height. The peaks at 55.7 ppm and 46.5 have multiple peaks but do not appear to be split, since the two nearby peaks have different intensities. It is more likely that the two peaks originate from two different, similar compounds. The peaks could also arise from different solvation states of one compound. There are also additional smaller peaks near 55 ppm that are probably from different compounds, such as EA-2192.

The results in Table 1 indicate that the NMR signals for the major products are consistent with VX disulfide and VX acid, the products that are expected based on review of the literature. There may also be smaller amounts of related compounds.

However, there is one large, separate peak at 16.3 ppm that is is not accounted for by these two major products. It may be accounted for as diisopropylamine. This is not a primary reaction product of VX, but it is a secondary reaction product. The source of this compound is discussed in Section 5.

Table 1. Calculated and observed C-13 NMR chemical shifts (in PPM).

C-13 Group	VX	VX thiol	VX disulfide	VX acid	Diisopropyl-amine	Observed in solid
iPr CH_3	19.39	19.32	19.61		22.07	18.3, 16.3
iPr CH	49.17	49.41	48.88		47.02	55.7
N-CH_2*-CH_2-S	46.27	47.08	45.44			46.5
N-CH_2-CH_2*-S	29.03	22.86	37.20			33.2
P-CH_3	18.13			18.57		11.3 (doublet)
P-O-CH_2	63.47			64.68		60.8
P-O-CH_2-CH_3*	17.4			13.14		16.0

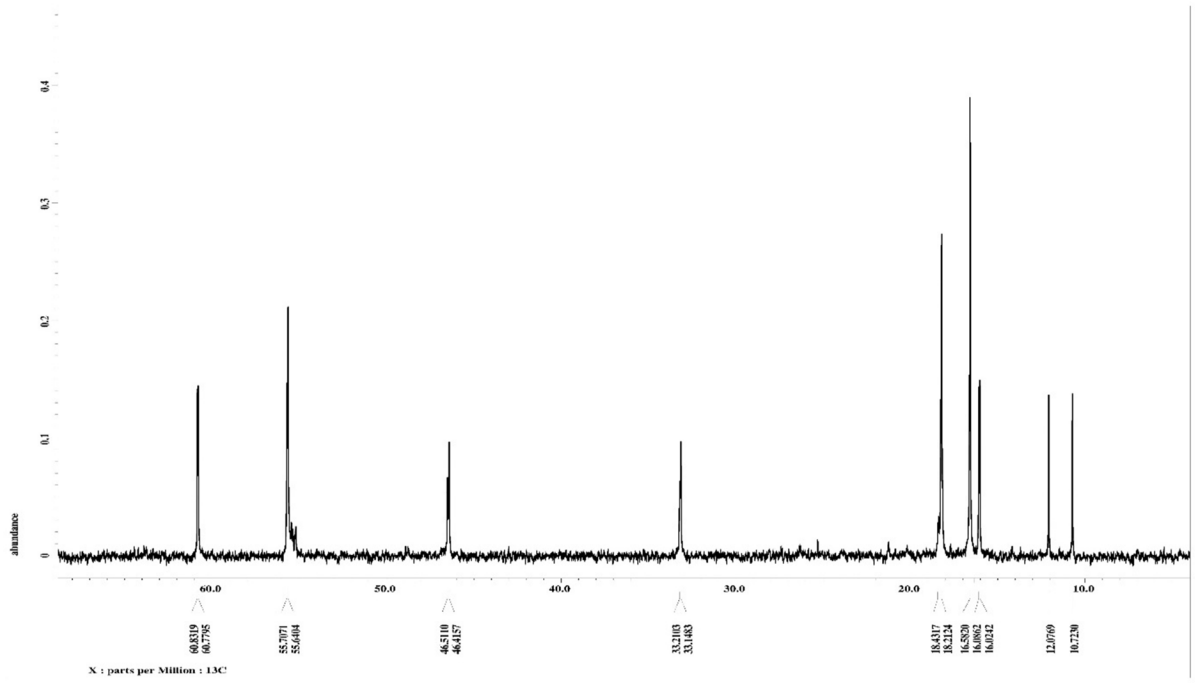


Figure 6. C-13 NMR spectrum of VX reaction product solid dissolved in dilute aqueous HCl.

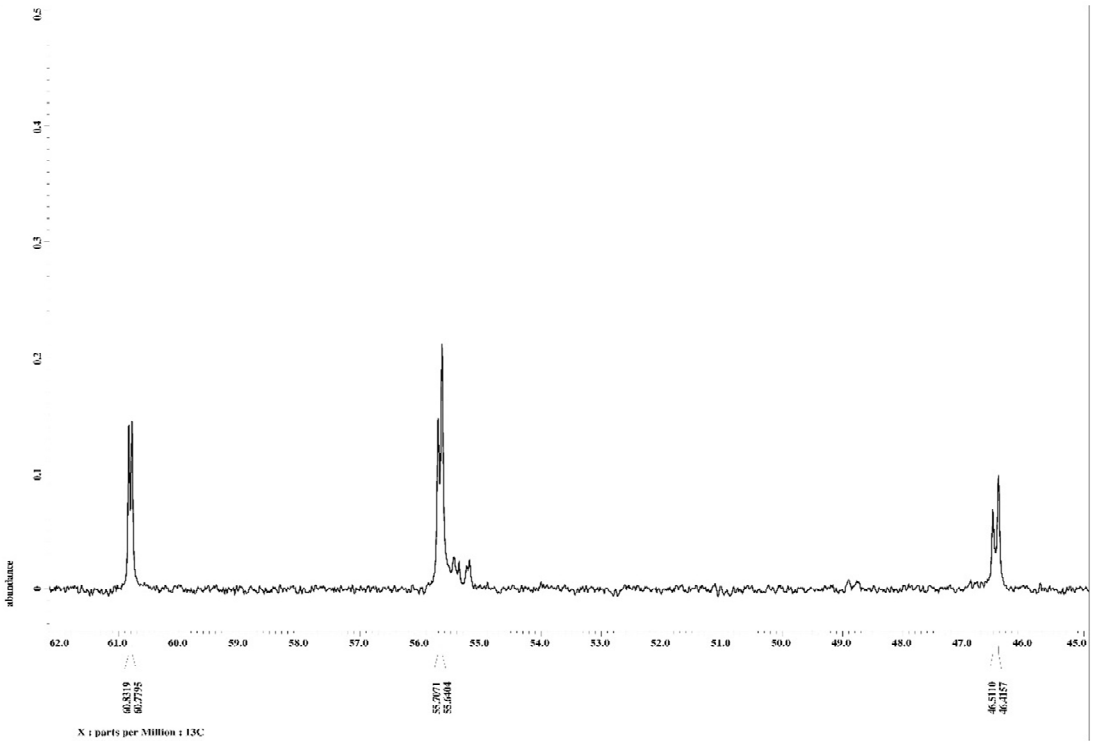


Figure 7. Expanded region of the spectrum in Figure 6 showing splitting from P-31 for the peak at 60.8 ppm.

4. RECRYSTALLIZATION STUDY

Although it is possible to do NMR on solid material, there are complications from peak broadening that make it difficult to obtain a narrow line width and assign the spectrum. As a result, the NMR studies were performed using liquid solutions. It is reasonable to expect that VX will be extracted into chloroform, but it is possible that the other solid material will be modified by the solvent, or that some material will not dissolve. As a result of this problem, some effort was taken to dissolve all the solid, and then recrystallize the solid from the solution to show that it was unchanged. This experiment indicates that the NMR spectra of the liquid solution is representative of the solid material.

For the recrystallization experiment, 0.5 g of the solid reaction product was dissolved in 0.41 mL of dilute HCl. After the solid dissolved, 0.10 mL of 7.4 M NaOH was slowly added until solid precipitated. The solid was filtered using a syringe filter, rinsed with two 0.3 mL volumes of chloroform, and then redissolved again using 0.37% HCl solution. The NMR spectra are very similar to before, indicating that the major components of the solid are VX disulfide and VX acid, the expected hydrolysis products. The C-13 NMR spectrum after redissolving the solid is shown in *Figure 8*.

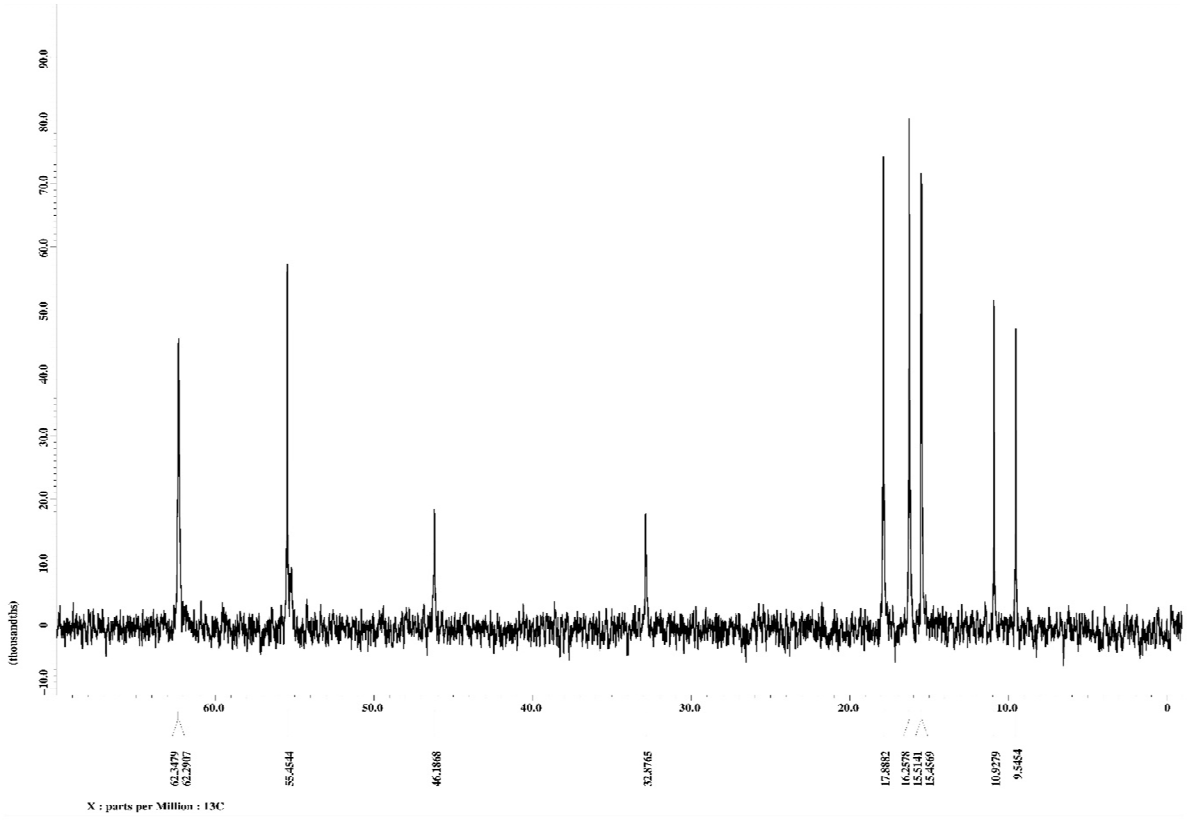


Figure 8. VX solid sample following solution in aqueous HCl, recrystallization using NaOH solution, and redissolving in aqueous HCl.

5. LC/MS RESULTS

The reaction solid, after dissolution in aqueous HCl, was diluted by approximately 1:100 and analyzed using Liquid Chromatography/Mass Spectrometry using an Agilent 6410 Triple Quadrupole LC/MS/MS. Results showing the Total Ion Chromatogram (TIC) and selected mass spectra are shown in Appendix B. Sample preparation methods and LC/MS instrument conditions were not optimized for sensitivity, but simply to obtain qualitative mass spectra to identify compounds.

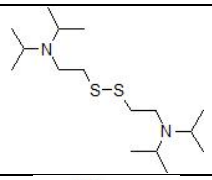
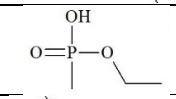
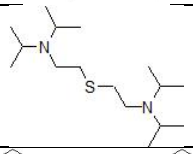
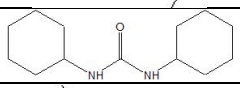
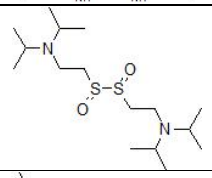
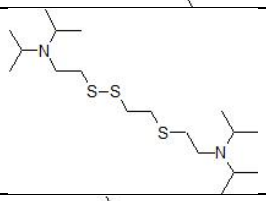
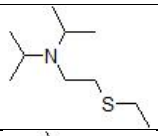
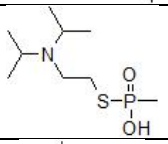
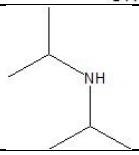
The peak with the largest signal in the TIC is at 6.2 min. corresponding to m/z 321 D (with a fragment at 161 D) that corresponds to VX disulfide, which is also consistent with the C-13 NMR spectrum. The major peak at 3.7 min. corresponds to VX acid, with m/z for $M+H^+$ at 125 D, with $[2M+H]^+$ of m/z 249 D. An m/z 535 D peak can be assigned to $K[VX\ acid)_4^+$, although it isn't clear why this peak is significant (it may have unusual stability in the LC/MS ion source).

Other components have significantly less signal. It isn't possible to obtain quantitative information about their concentration from the spectrum without standards of the compounds. Some compounds are listed in Table 2 with probable assignments.

The toxic hydrolysis product EA-2192 was observed with m/z 240 D at a retention time of 6.29 min. An extracted ion chromatogram (EIC) of this ion signal is shown in Appendix B that shows a single peak for this ion mass.

Several peaks were observed with m/z 268 D, which is the same mass as VX. This peak is not likely to be VX, since the fragment peaks are different; VX has a large fragment ion at 128 D. This component could complicate the use of LC/MS for screening the reaction product for low residual amount of VX. The development of an analytical chemistry method for trace detection of VX in a decontamination matrix requires a significant effort to validate and optimize the sample preparation method.[6,7]

Table 2. Compounds from LC/MS results

$M+H^+$ ion mass	Secondary ions	Common name	Structure
321	161	VX disulfide	
125	249	VX acid	
289		VX sulfide	
224	447	Product of dicyclohexyl carbodiimide stabilizer	
353	161,177	VX disulfoxide or VX sulfone	
381	162, 191		
190		Ethyl diisopropylaminoethylsulfide	
240	161, 479	EA-2192	
102		Diisopropylamine	

6. MECHANISM OF REACTION

With these analytical chemistry results, we propose the mechanism shown in Figure 9. It appears that VX degrades much like it has been reported in previous studies. Since the VX is present as >80% of the liquid in the reaction solution, the unreacted VX acts as a solvent for the reaction products. As the products build up, they become insoluble in the VX and precipitate out

as an ionic solid. In a previous study of the autocatalytic reaction of VX with equimolar water,[3] the reaction products remained a viscous liquid. This may be due to the lack of a strong base to form ionic solids.

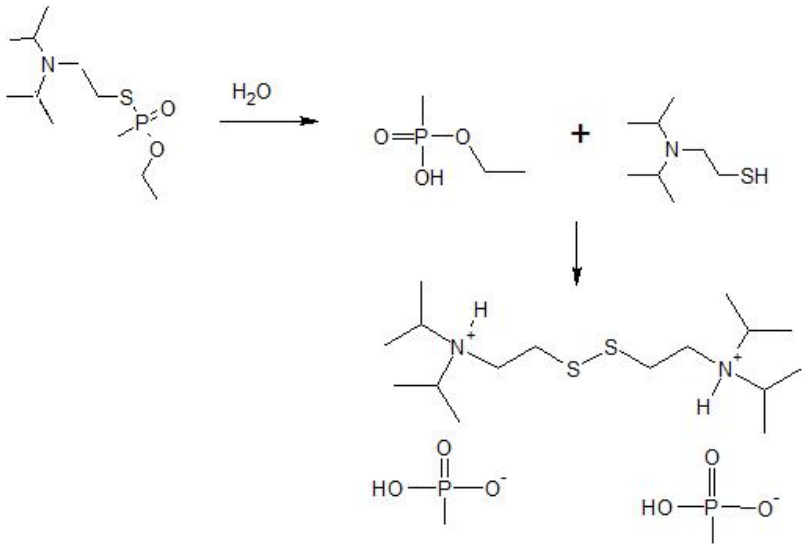


Figure 9. Reaction scheme for reaction of VX to form an ionic solid product.

The VX acid is unreactive, but the other primary reaction product, VX thiol, is quite reactive and forms most of the other products by secondary reactions, especially in concentrated, alkaline solutions. VX disulfide is a secondary product of oxidation of VX thiol to form a dimer. VX disulfide can further oxidize at the sulfur to form a disulfoxide or sulfone (L/MS peak at 353 D). It can also polymerize by loss of diisopropylamine to form m/z 381 D. Larger n-mers can also be formed, but these n-mers don't seem to be a large component of the solid. The product at m/z 190 D also indicates loss of a diisopropylamine.

Because of these reactions, the extra C-13 NMR peak was tentatively assigned to diisopropylamine, although there could be contribution from a number of other products. A peak for diisopropylamine was observed in the LC/MS chromatogram with m/z 102 D at retention time 5.78 min.

Further reaction of the VX disulfide to be partially polymerized is indicated in a reaction scheme in Figure 10. This mechanism accounts for the observation of the product with 381 D. This product was also observed by Yang and co-workers.[3] They proposed that the reaction proceeded by the formation of an ethanesulfide three-member ring rather than via a direct reaction. In either case, the reaction produces diisopropylamine, also previously reported,[3] consistent with the peak in the C-13 NMR spectrum. However, in order to confirm this assignment, a standard of diisopropylamine should be obtained to spike in the sample.

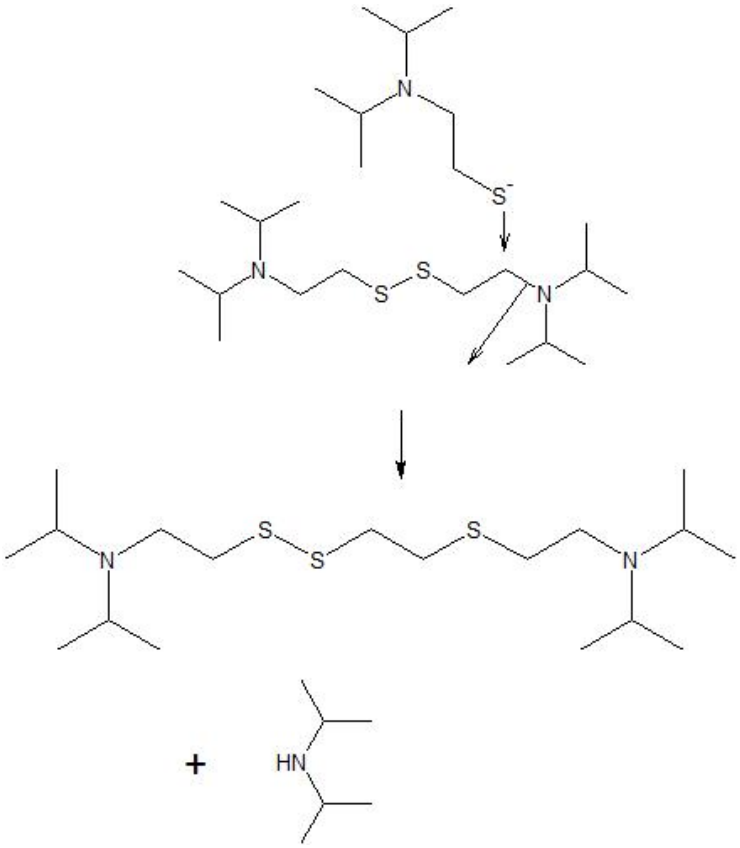


Figure 10. Secondary reaction mechanism.

7. RAMAN SPECTROSCOPY RESULTS

Raman spectroscopy can provide fingerprint vibrational spectra of liquids. For some solid or colored materials, the fluorescence background overwhelms the fingerprint spectra. Spectra for this study were taken using a FirstDefender RMX RX2232 portable Raman spectrometer,[8] made by Thermo Scientific, that was borrowed from Phillip Wilcox, Spectroscopy Branch, R&T Directorate, CCDC CBC.

Several attempts to obtain spectra of the solid material gave a spectrum with weak molecular signals. A sample spectrum of the solid material in the glass reaction vessel is shown in *Figure 11*. There are small peaks between 500-1000 cm^{-1}, but they are not strong enough to provide a library match, or else there wasn't a similar compound in the library.

A better spectrum was obtained by dissolving the solid in aqueous HCl. The spectrum is shown in *Figure 12*. This spectrum has molecular features, but it didn't give a library match. The lack of a match may have only been because there was no suitable entry in the library for VX disulfide or the other reaction product. The instrument has the option for adding spectra to the library, so the spectrum of the reaction products could be used as a library reference in the future.

Other studies have indicated that disulfide bonds have Raman features near 500 cm^{-1}.[9,10] The spectrum in *Figure 12* has features at 481 and 509 cm^{-1}, so these features may confirm the presence of a disulfide in the product.

In comparison, a Raman spectrum was taken of the VX starting material in a sealed glass vial. The spectrum gave a good library match. The spectrum and the library match is shown in Figure 13. The library search for this instrument is based on the frequency of the peak, not the intensity, so it can tolerate some fluorescent background like the amount in Figure 13 and still find the peak match.

Bruker Instruments advertises a patented system on their BRAVO Handheld Raman System to mitigate fluorescence signal.[11] This is done by using two laser wavelengths to identify peaks, rather than only one laser wavelength. This instrument was not available for testing on the VX reaction product.

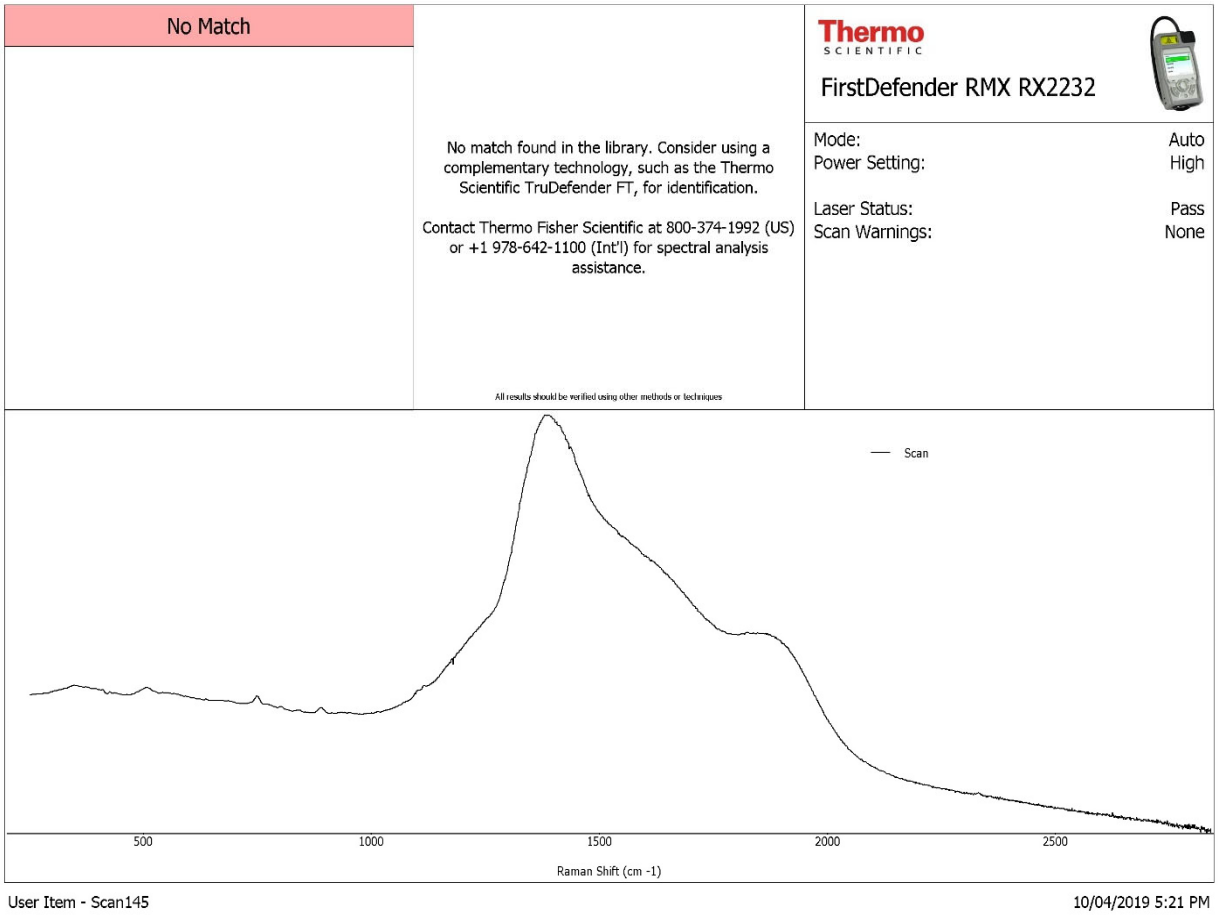


Figure 11. Raman spectra of solid VX reaction product in a glass reaction vessel.

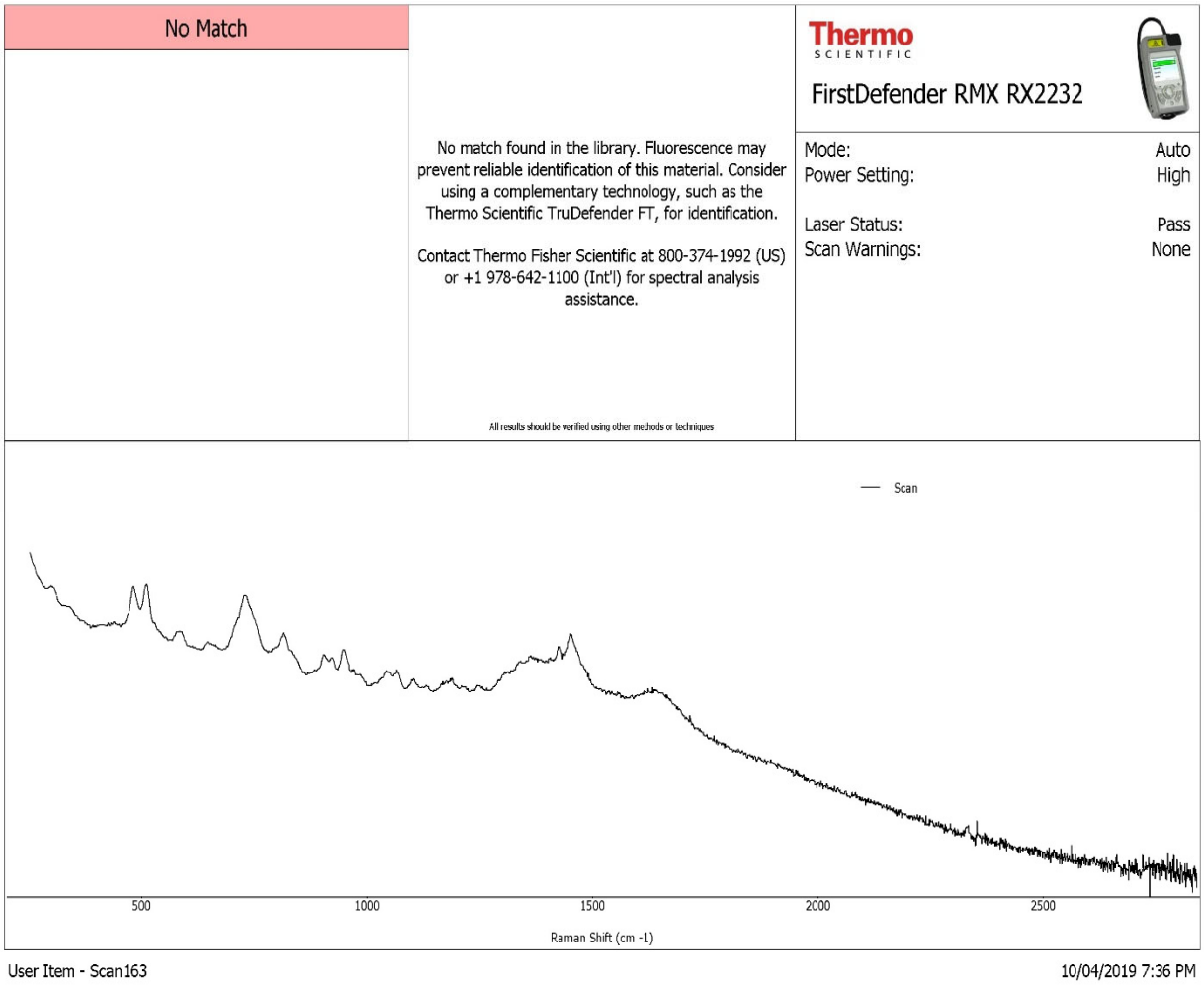


Figure 12. Raman spectrum of solid dissolved in aqueous HCl.

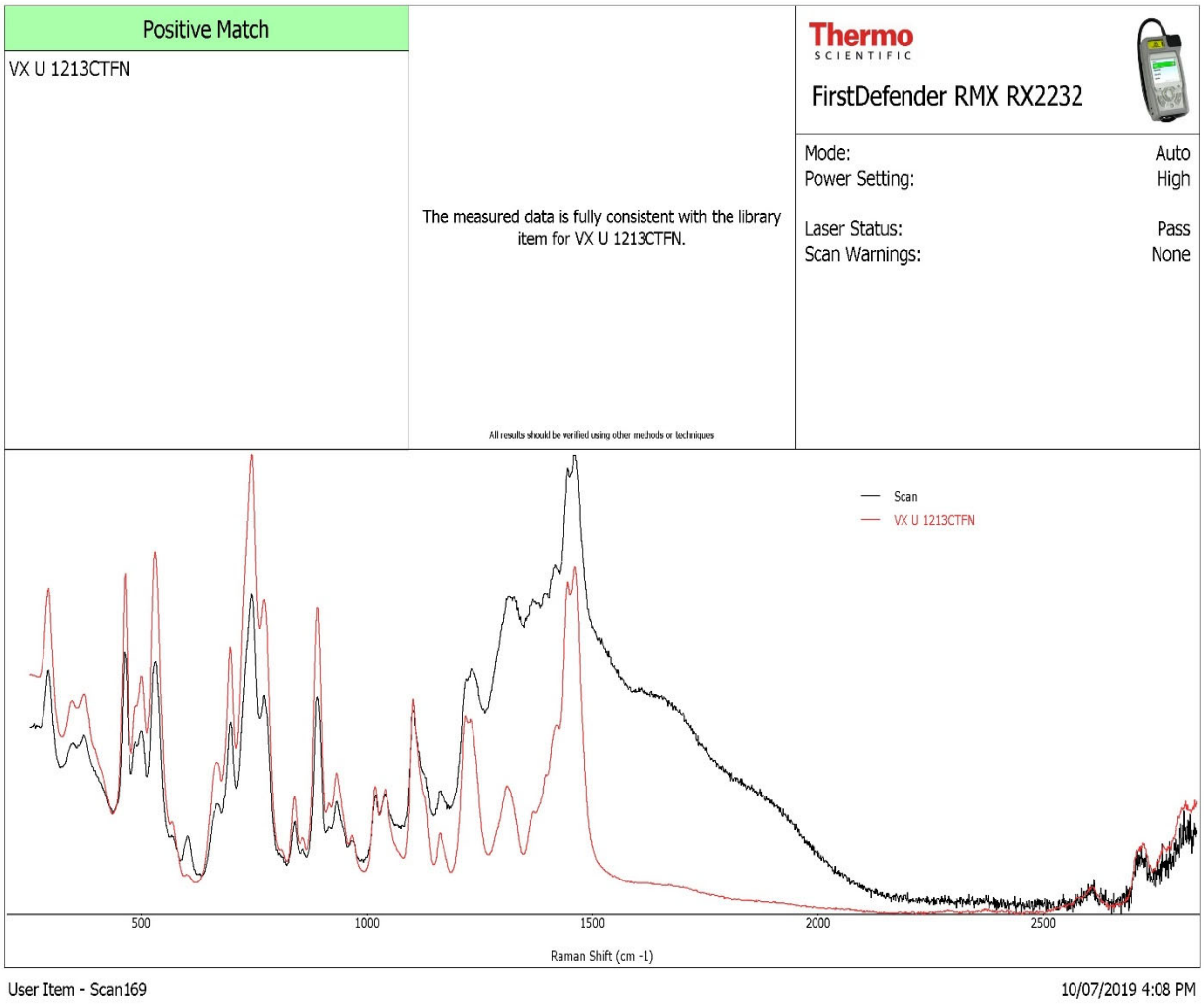


Figure 13. Raman spectrum of VX starting material (black trace) and library match (red trace).

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ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
ACN	Acetonitrile
CA	chemical agent
CTF	chemical transfer facility
CW	chemical warfare
CWA	chemical warfare agent
EA-2192	S-[2-(diisopropylamino)] methylphosphonothioic acid
EIC	Extracted ion chromatogram
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromagraph/tandem mass spectrometer
NMR	Nuclear magnetic resonance
TIC	Total ion chromatogram
VX	S-[2-(disopropylamino)]ethyl methylphosphonothiolate
VX acid	Ethyl methylphosphonic acid
VX disulfide	Bis[2-(diisopropylamino)ethyl] disulfide
VX sulfide	Bis[2-(diisopropylamino)ethyl] sulfide

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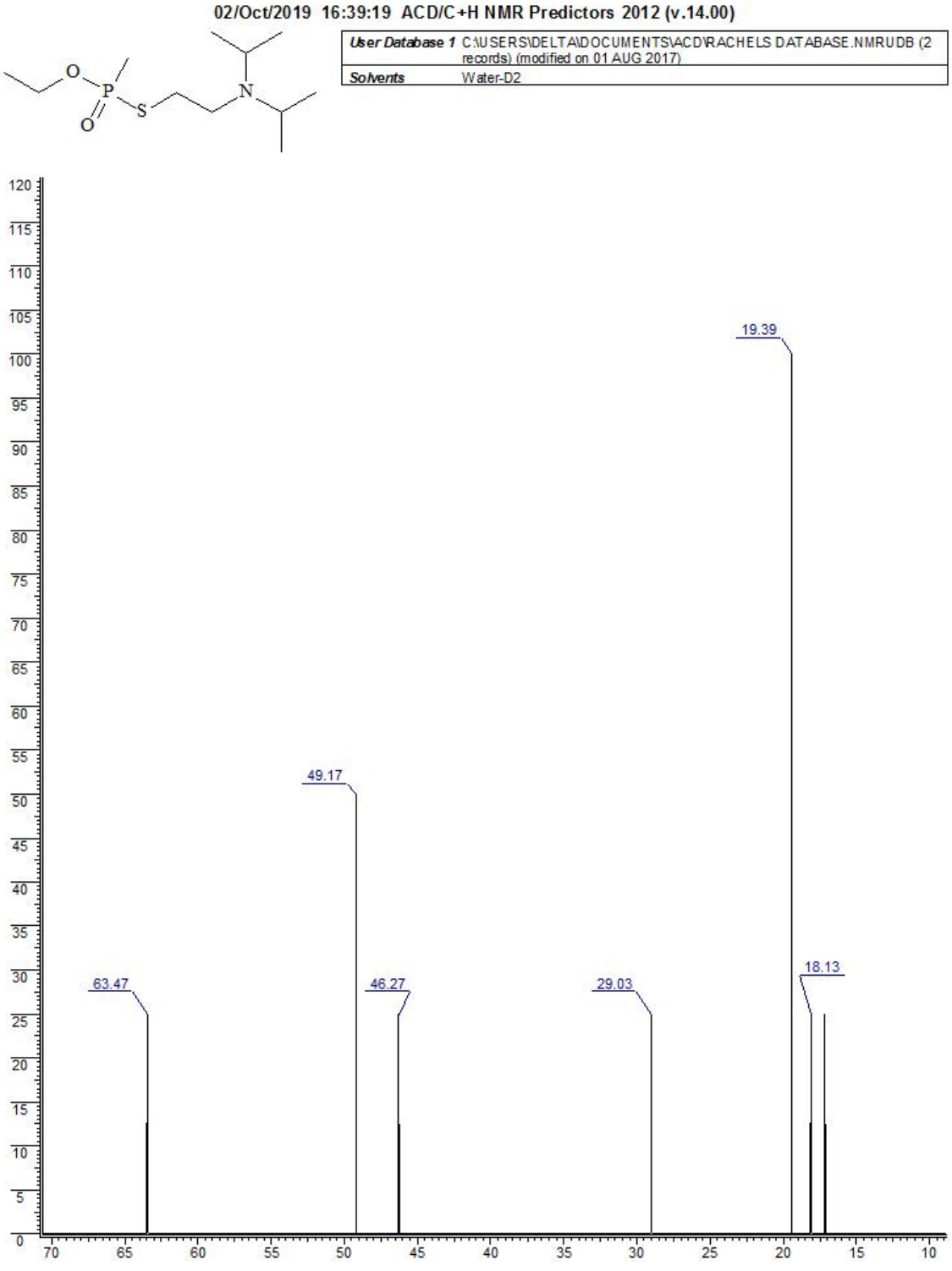
APPENDIX A
CALCULATED C-13 SPECTRA FOR VX AND EXPECTED THIOL-DERIVED PRODUCTS



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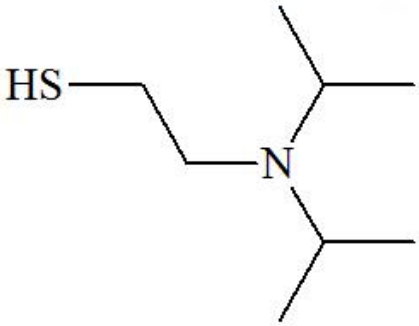

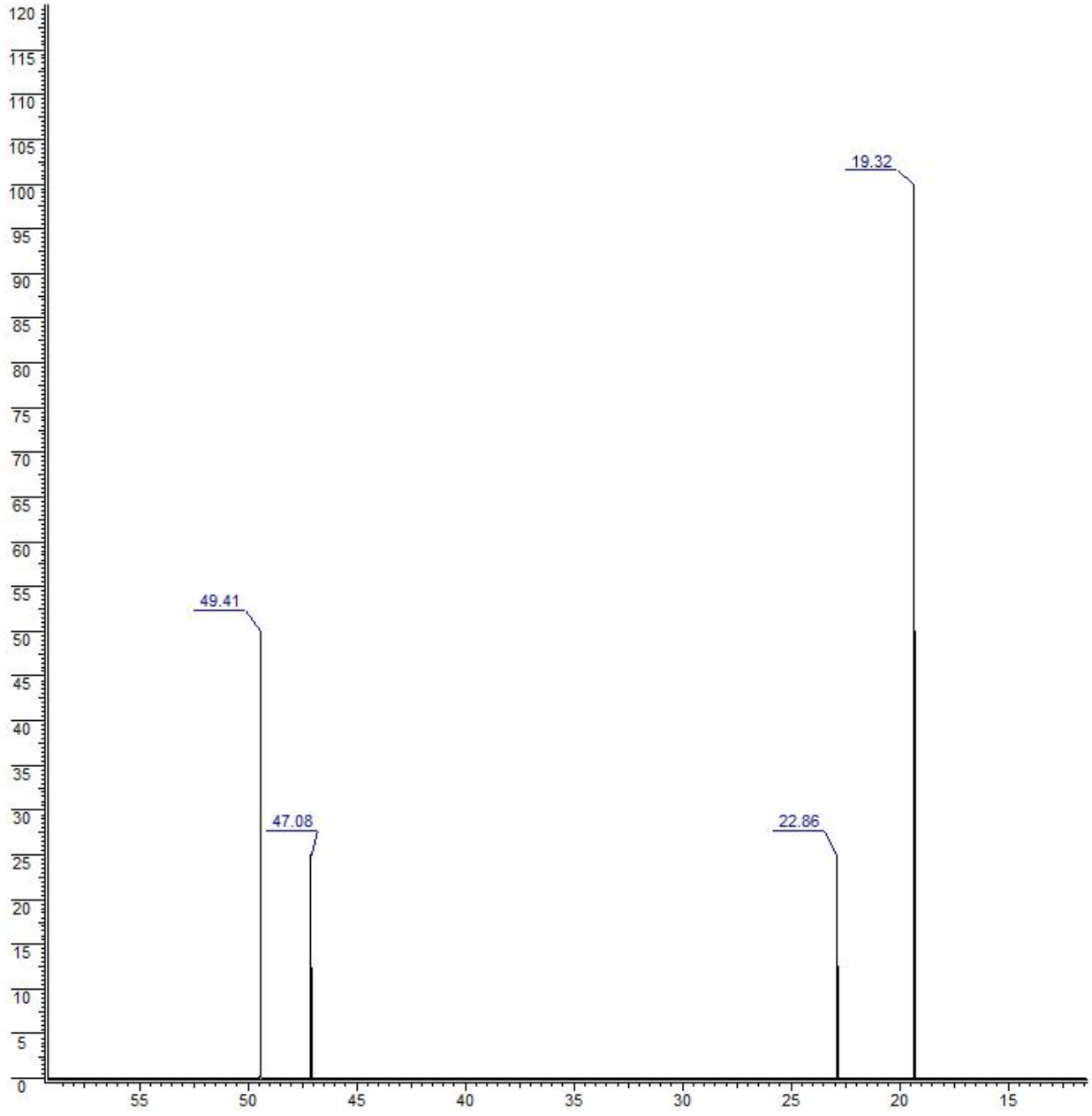

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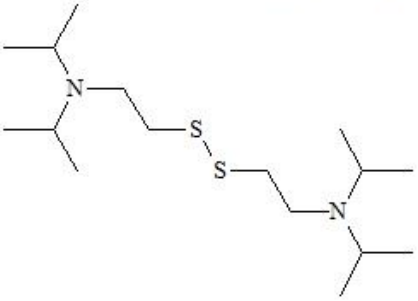

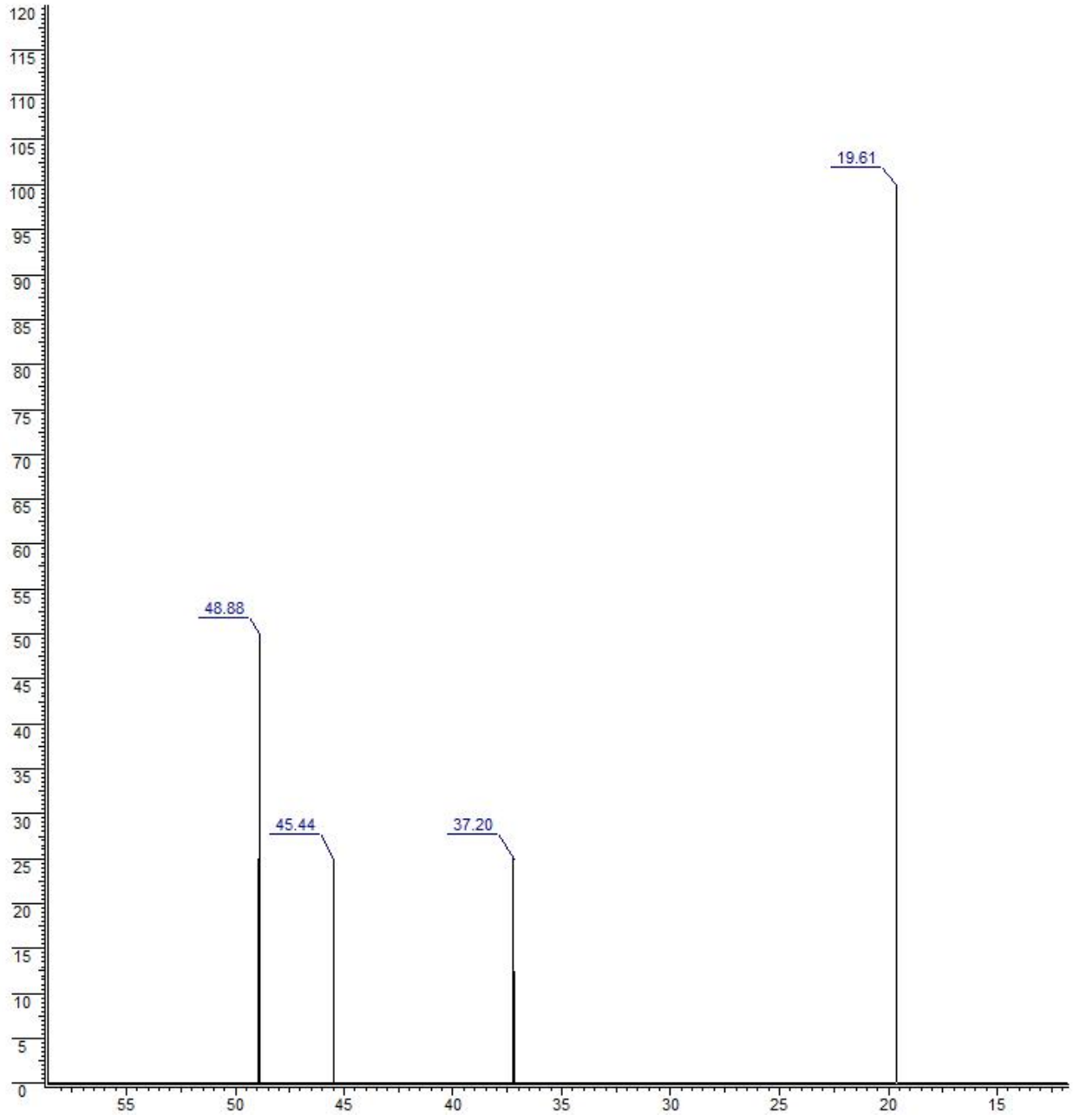

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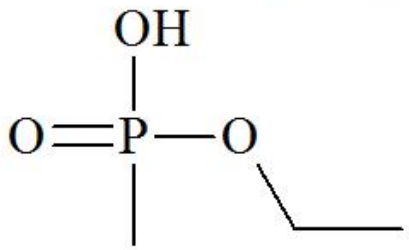

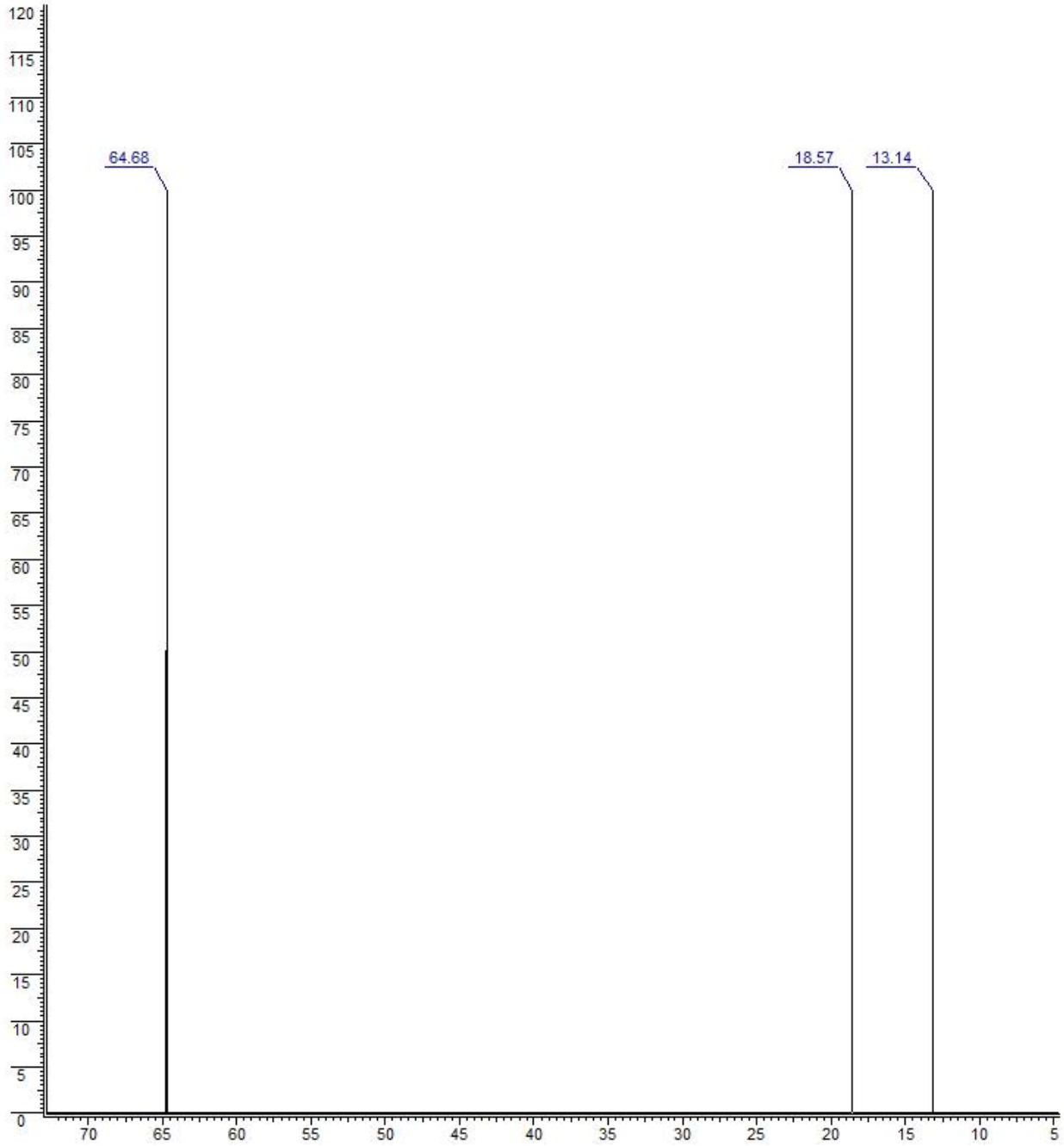

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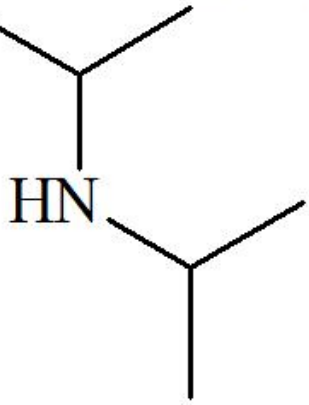

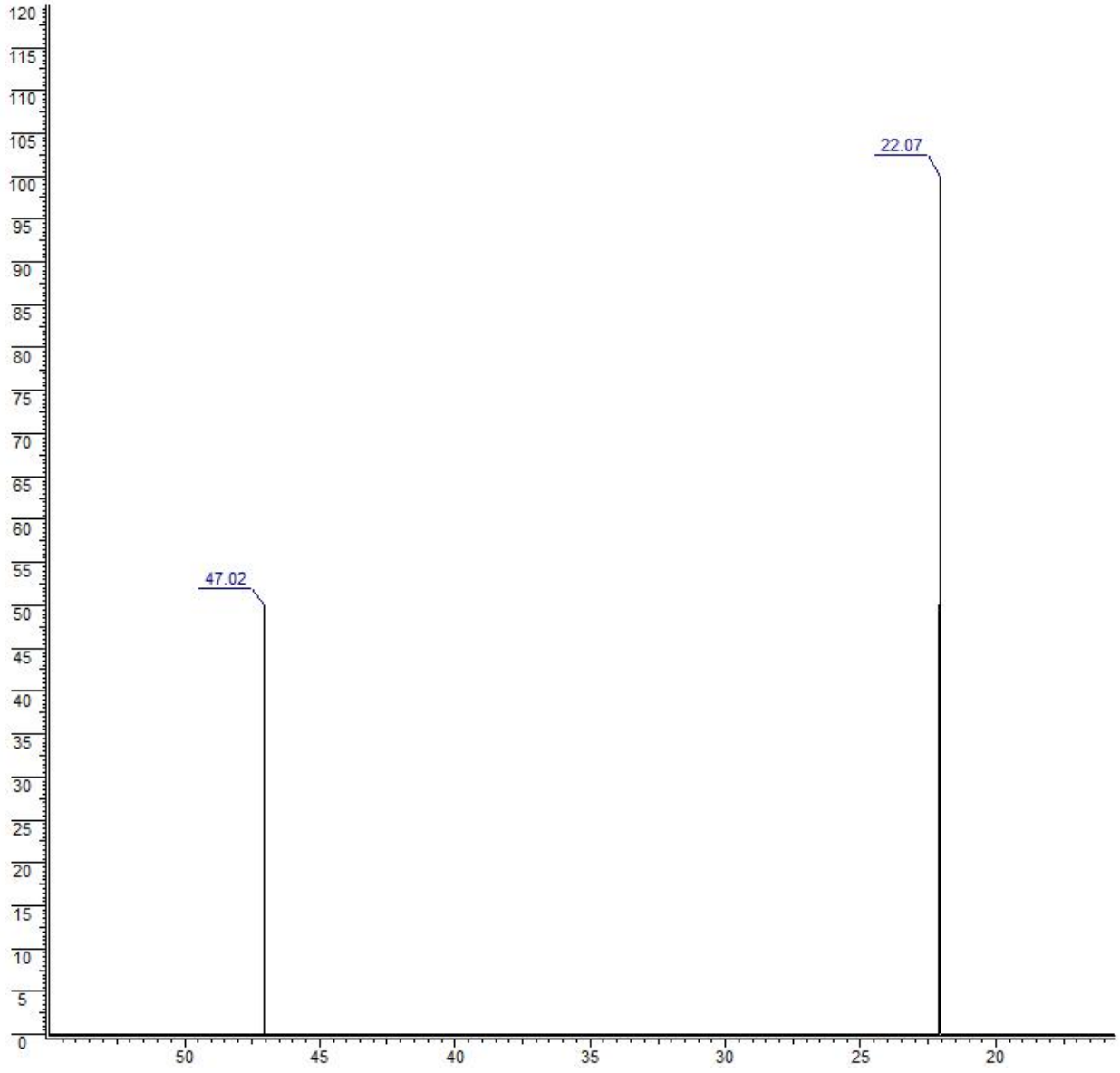

APPENDIX B
RESULTS FROM LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY SAMPLE ANALYSIS

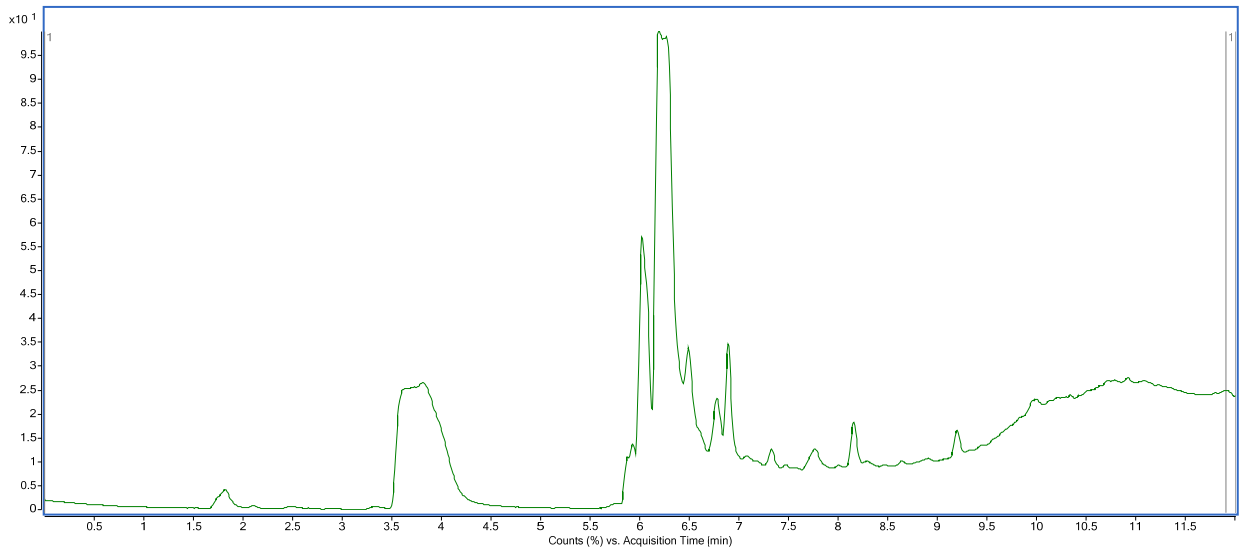

Figure B-1. Total Ion Chromatogram from 190819-VXsolid1.d on Agilent 6410 Triple Quadrupole LC/MS/MS. The LC column was an Agilent Eclipse XDB-C18, 4.6X150 mm, 50 µm particles, gradient from 0.1% formic acid/water to 0.1% formic acid/acetonitrile.

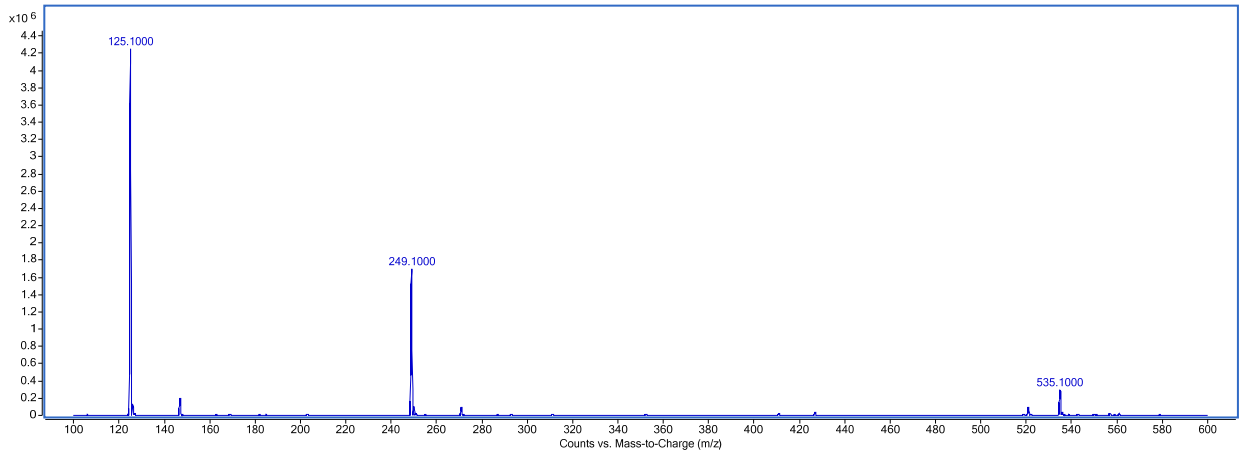

Figure B-2. Mass spectrum at 3.678 min.

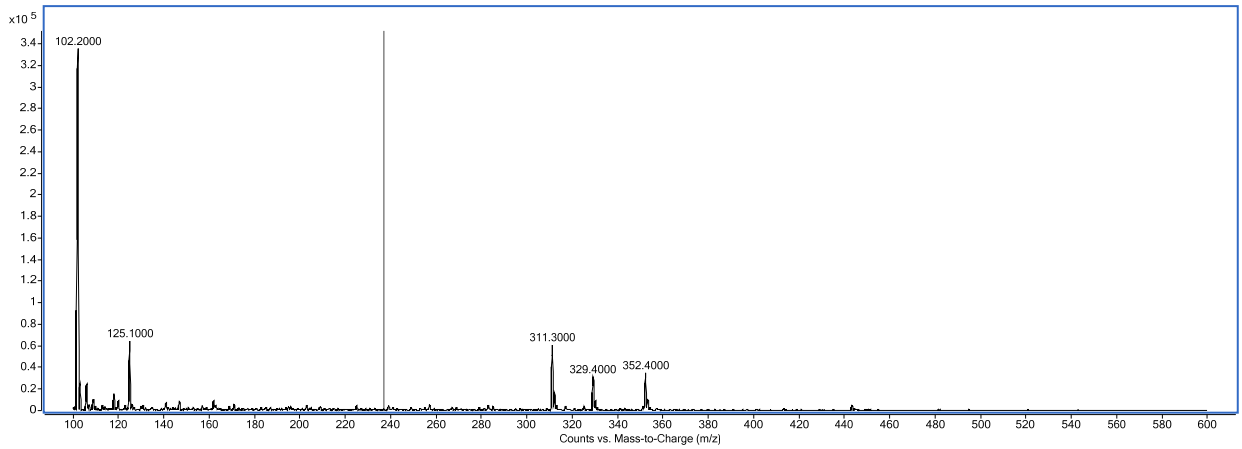

Figure B-3. Mass spectrum at 5.777 min.

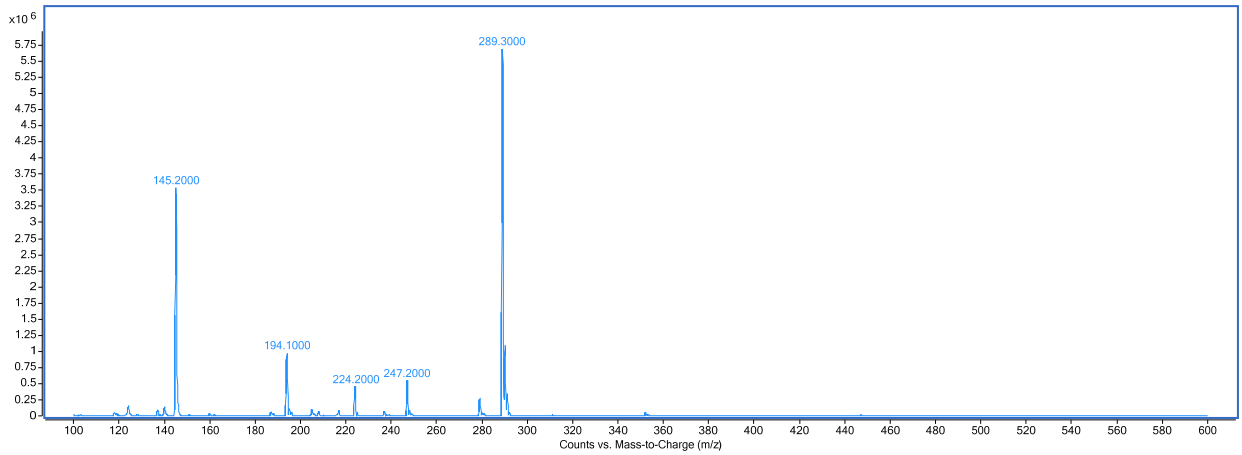

Figure B-4. Mass spectrum at 6.029 min

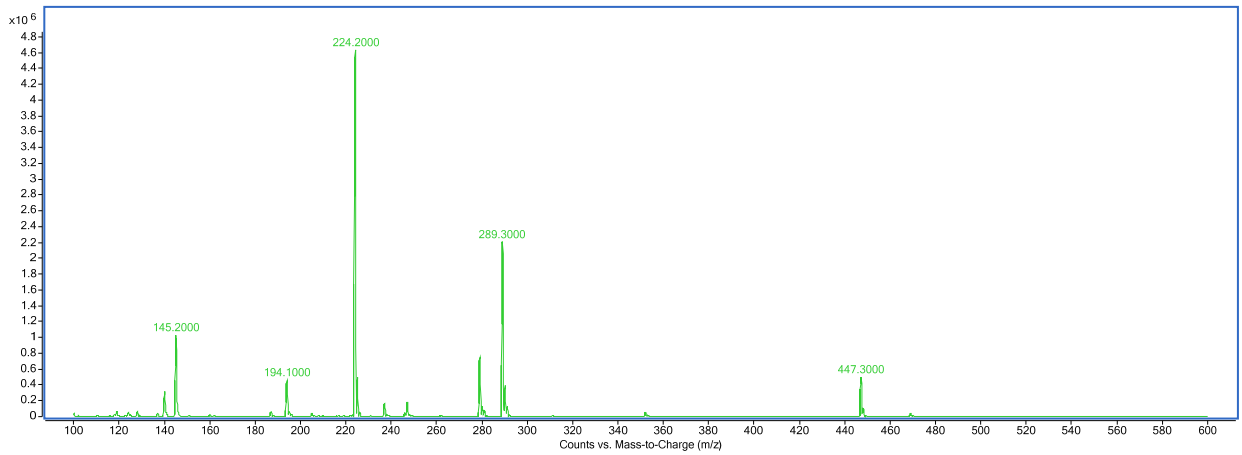

Figure B-5. Mass spectrum at 6.062 min.

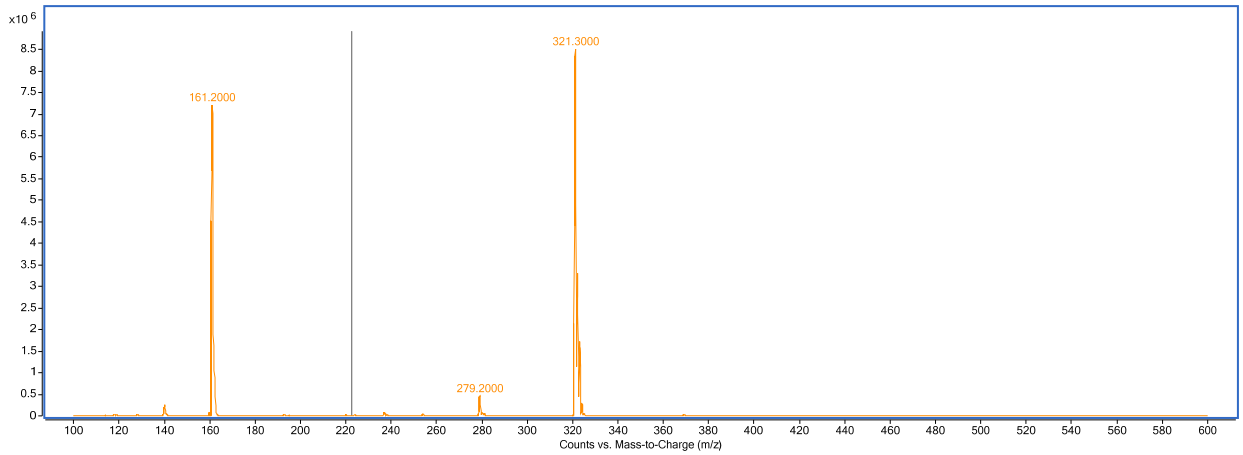

Figure B-6. Mass spectrum at 6.216 min.

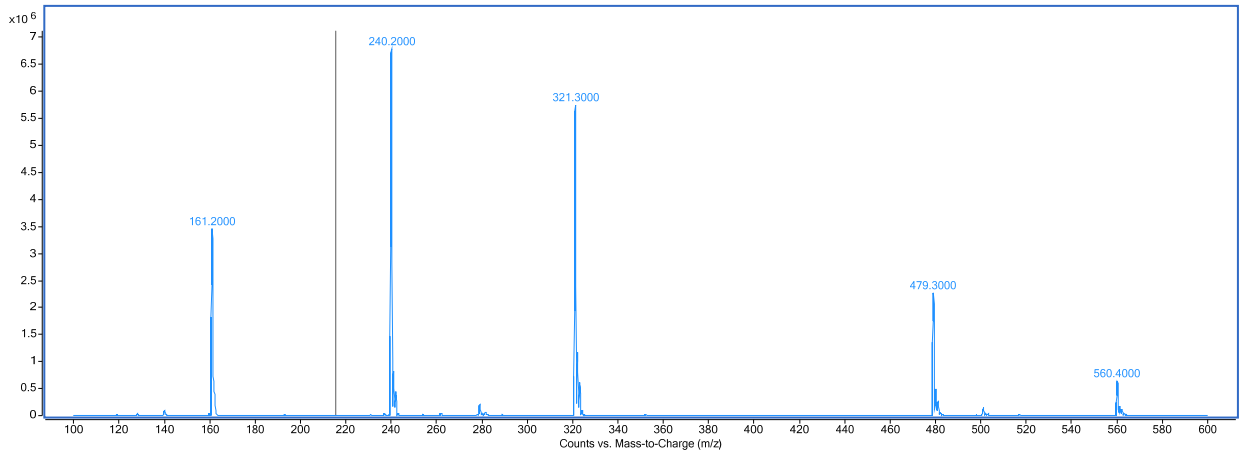

Figure B-7. Mass spectrum at 6.289, peak for 240 D signal for EA-2192.

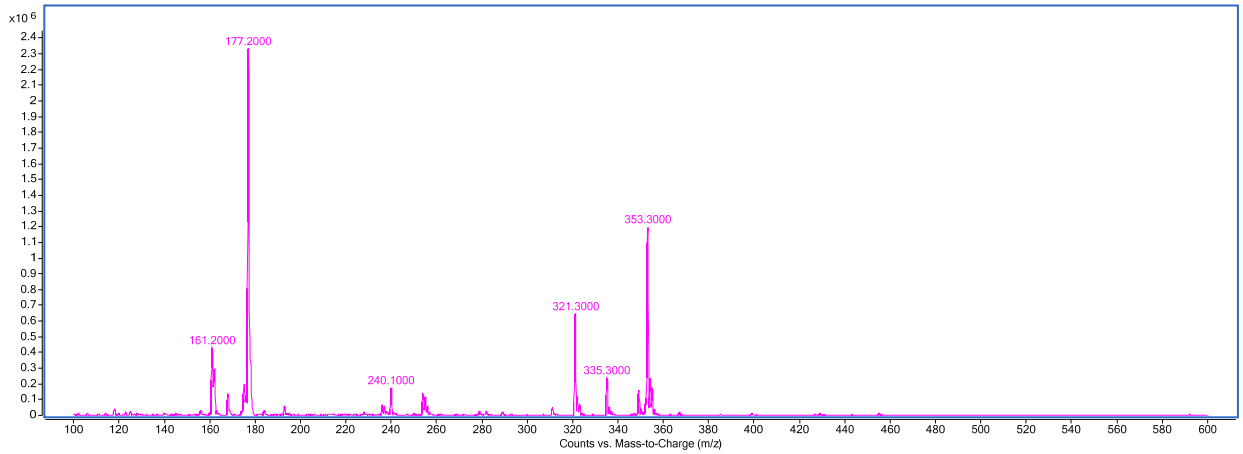

Figure B-8. Mass spectrum at 6.493 min.

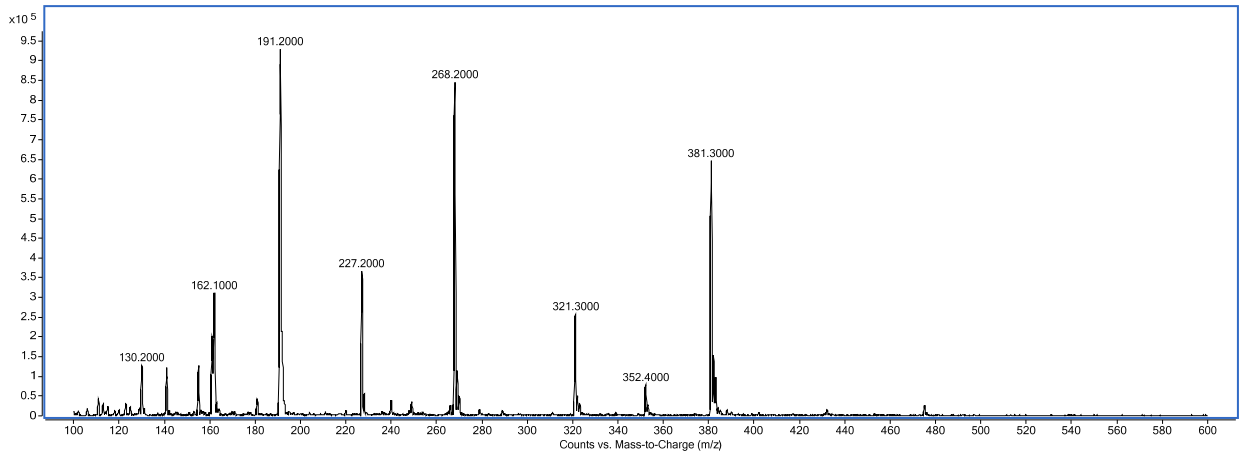

Figure B-9. Mass spectrum at 6.778 min.

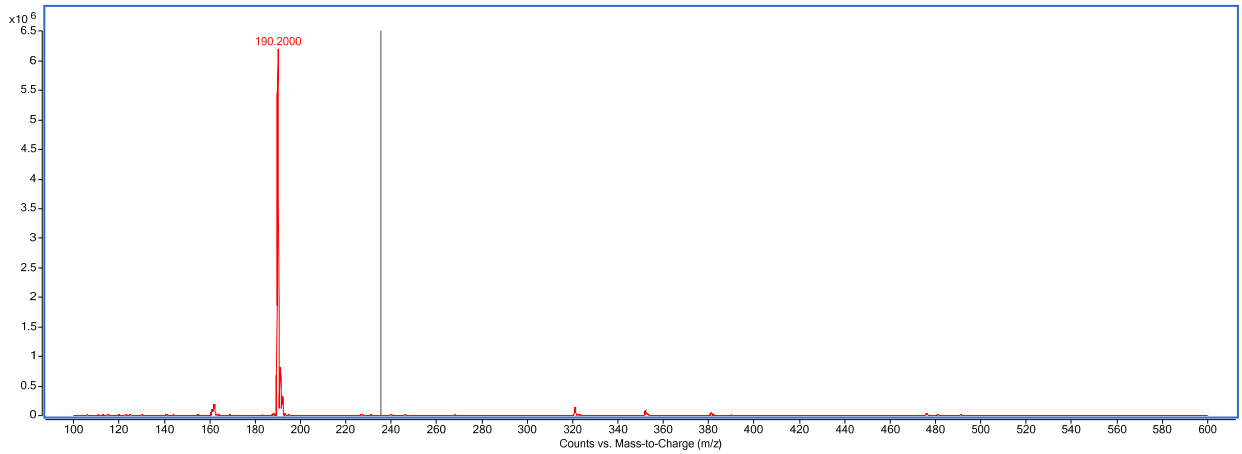

Figure B-10. Mass spectrum at 6.89 min.

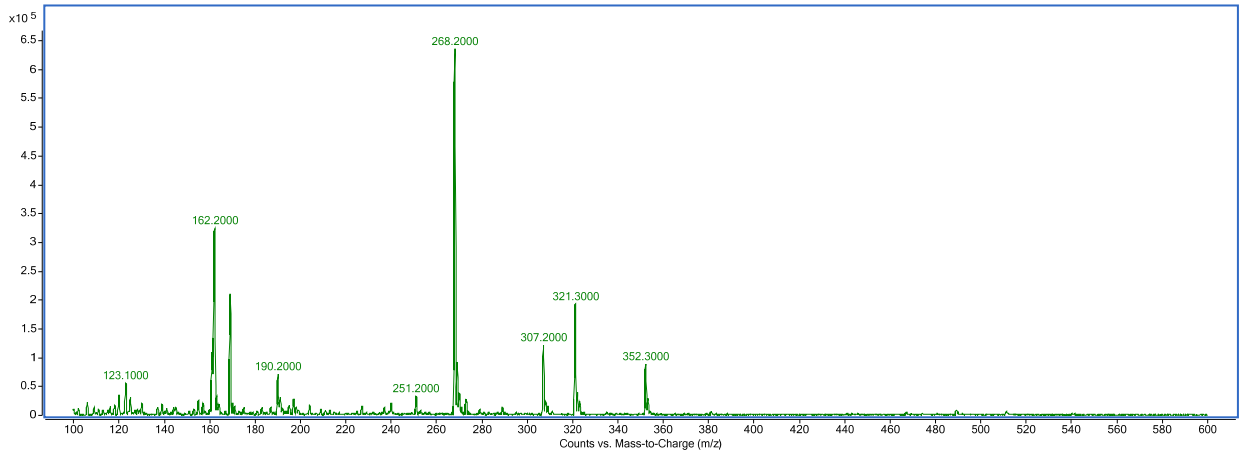

Figure B-11. Mass spectrum at 7.33 min.

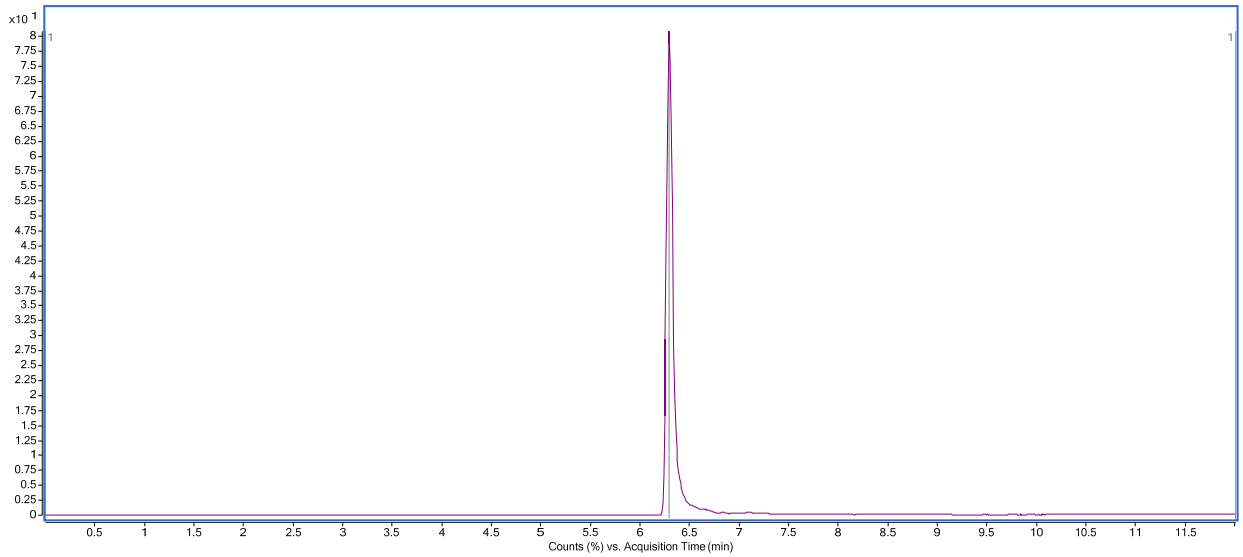

Figure B-12. EIC for m/z 240 D, corresponding to EA2192.

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