

**Recycling and Demilitarization of Military Munitions
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List of Acronyms

ACL	Applied Chemistry Laboratory
ACS	American Chemical Society
AP	acetophenone
BA	benzaldehyde
CN	chloroacetophenone
DI	deionized
ECD	electron capture detector
EM	energetic material
GC	gas chromatograph
GPIM	green propellant infusion mission
HCE	hexachloroethane
HCl	hydrogen chloride
IC	ion chromatography
ID	industrial demilitarization
KSC	Kennedy Space Center
MS	mass spectrometer
NASA	National Aeronautics and Space Administration
OB/OD	open burning and open detonation
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
PCE	perchloroethylene
PCO	photo catalytic oxidative
PTFE	polytetrafluoroethylene
R ³	recovery, recycling, reuse
RH	relative humidity
SBA	strong base anion
SDS	safety data sheet

SEED SERDP Exploratory Project
TATP triacetone triperoxide
TCE trichloroethylene
TIC total ion chromatogram
TNT 2,4,6-trinitrotoluene
USEPA United States Environmental Protection Agency
UV ultraviolet
VLR visible light responsive
VOA volatile organic analysis
VOC volatile organic compound
ZVMg zero-valent magnesium

1. Abstract

The goal of this research was to evaluate several technologies developed at NASA Kennedy Space Center (KSC) as a means for the demilitarization of several different munitions commodities. In all, three separate and novel methods were assessed to determine their possible efficacy to demilitarize munitions including TNT, HCE, CN, and AF-M315E.

- Zero valent magnesium (ZVMg) was tested with trinitrotoluene (TNT) in an attempt to determine if a magnesium-based reaction is capable of chemically reducing the TNT to a non-hazardous byproduct. Unfortunately, it appears that the ZVMg is adsorbing the TNT rather than degrading it. While it is possible that degradation may be occurring on the surface of the metal, once it has been adsorbed, this conclusion cannot be supported at this time due to the lack of any observable daughter products. One possibility is that TNT may undergo sequential degradation while it is absorbed to surface of the ZVMg, in which case daughter products would not be observed. However, further testing is necessary to validate this supposition, although literature indicates TNT should be degraded by ZVMg.
- Ion exchange resins were tested to determine if the nitrates (oxidizer portion) of the AF-M315E explosive propellant could be easily removed, allowing for the remaining propellant to be considered “demilitarized”. Two commercial strong base anion (SBA) resins (Purolite A520E and ResinTech SIR-100-HP) were procured for this study. Static and flow-through testing showed that these resins could successfully remove the nitrates from a dilute AF-M315E solution. The flow-through testing also showed that a single batch of resin could be used and regenerated several times and still retain the ability to remove nitrate. Further testing should focus on upscaling the present flow-through system to allow for concurrent nitrate removal and resin regeneration. The ability to use these resins to allow for the long-term and safe storage of the AF-M315E until it was needed, at which point it would be reconstituted, is also proposed for further study.
- Visible light responsive (VLR) photocatalysis in conjunction with Ag-doped TiO₂ catalyst was tested for its ability to degrade hexachloroethane, HCE, (smoke generating munition) and 2-chloroacetophenone, CN, (riot control munition). Testing was performed in a static manner using 40-mL vials for both munitions components. Testing of the HCE showed near complete degradation (within 4 hours) as well identifying perchloroethylene, PCE, as a likely daughter product. Also, experimental evidence showed the production of chloride ions which would suggest that complete degradation to HCl and CO₂ may be occurring. Testing of the VLR photocatalysis for degrading CN was more difficult as the vial studies used crystals of the CN to produce gaseous CN within the headspace within the vials. As such, degradation of the CN itself was not observed since it was constantly replenished by sublimation of the neat material, however an increase in the degradation byproducts was seen (within 4 hours). Two daughter products, acetophenone and benzaldehyde, were identified during the study, both of which could be re-used in other markets.

2. Background

The goal of WP-2615 “Recycling and Demilitarization of Military Munitions” was to evaluate the feasibility of employing three novel technologies developed at NASA’s Kennedy Space Center (KSC) for the degradation of certain individual munition components. The specific technologies which were evaluated were Zero Valent Magnesium (ZVMg), ion exchange resins, and Visible Light Responsive (VLR) photocatalysis. These alternative demilitarization technologies discussed within this report represent an environmentally sound chemical treatment alternative to replace the methods currently in use. These materials are inherently hazardous and permanent stockpiling and storage is not a viable option for both safety and logistical reasons. A recent United Nations report¹ identified two major disposal options. The first, open burning and open detonation (OB/OD), is the simplest and least expensive technique, however it requires large spaces, precludes the possibility of material recycling or reuse and, due to its uncontrolled nature, may produce air, soil, and groundwater pollution. The second, industrial demilitarization (ID), consists of disassembling munitions either manually or mechanically, removal of the energetic material (EM), and physical destruction of the EM (usually via thermal processes). Because the destruction of the EM is performed in a controlled environment, pollution control systems are put in place to reduce the amount of volatile organic compounds (VOC), particulate matter (PM), and acid gasses released. ID processes can be mechanized thereby decreasing risks to workers, lowering operating costs, and can potentially be combined with recovery, recycling, and reuse (R³) processes of high-value materials to offset higher upfront costs. The major disadvantage to ID is the high cost associated with facility design and construction. The research proposed here represents an environmentally sound chemical treatment alternative to replace the thermal EM destruction techniques that are currently the foundation of most ID processes.

Four munition components were evaluated in this project: hexachloroethane (HCE), 2-chloroacetophenone (CN), 2,4,6-trinitrotoluene (TNT) and propellant AF-M315E. HCE is a component in white smoke generating munitions. It is a solid at room temperature and is used in a munition combined with aluminum and zinc oxide. CN is also a solid at room temperature and is used in riot control munitions. It does not decompose in water and is a component in the commercial product Mace. TNT is an energetic material for which various chemical treatments have been proposed and developed, but never with a focus of recovering any components as is proposed here. AF-M315E is a high-performance, low-toxicity “green” propellant (class 1.3C) developed by the Air Force Research Laboratory at Edwards Air Force Base currently scheduled to be used on Green Propellant Infusion Mission (GPIM) due to launch in 2018. OB/OD is the only accepted method for disposal of AF-M315E propellant at this time, however many facilities including Kennedy Space Center that may utilize this propellant do not possess this capability. This leads to both expensive and hazardous transport of explosive materials to a facility which is capable of performing OB/OD. Unfortunately, incomplete thermal degradation of the components in the AF-M315E mixture can produce a variety of toxic byproducts including nitrogen tetroxide. The risk of incomplete thermal degradation also limits the available chemical degradation pathways as exothermic reactions also present a danger of hazardous byproduct formation. In addition, these are destructive techniques in which all parts of the commodity in question are lost. A more economical and environmentally safe method for demilitarization

would allow for the recovery or possible reuse of the propellant in some manner while eliminating the toxic byproduct formation.

The overall system proposed for demilitarization in this project is shown in Figure 1. The green blocks were addressed in this Phase I SERDP Exploratory Development (SEED) project, while the red blocks will be integrated in a phase II project.

The objectives of Phase I were:

1. Evaluate the feasibility and kinetics of treatment of HCE, CN, and TNT with ZVMg and visible light photocatalysis and propellant AF-M315E with ion exchange resins.
2. Characterize the degradation products and identify recycling or disposal options.
3. Perform analysis to determine if these degradation methods can be integrated into a demilitarization process.

This proposed project uses chemical extraction and treatment methods that operate at lower temperatures and pressures, and utilize safer methods than the current state of the art for munitions processing such as caustic hydrolysis, solvated electron, and plasma processing. To determine if the proposed processes are feasible, the kinetics of chemical treatment must be ascertained. This will determine if the rate of munition processing is adequate for an industrial process, and will also allow for appropriate sizing of treatment equipment. Analysis of degradation products will determine if the treatment processes can in fact produce recyclable compounds or if they produce a waste stream suitable for discharge.

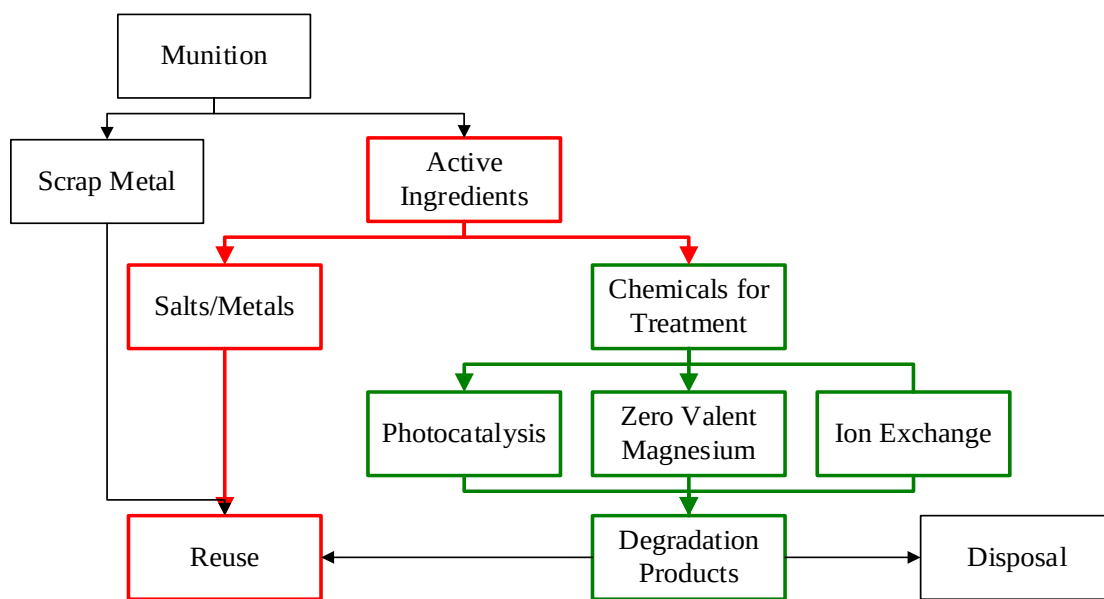


Figure 1. Recycling and Demilitarization System.

3. Degradation testing using ZVMg

3.1. Background

The purpose of the research proposed in this project was to determine if a magnesium-based reaction is capable of chemically reducing TNT. Magnesium has a very negative reduction potential (-2.37 V), a property that has been used to degrade a variety of persistent organic pollutants such as polychlorinated biphenyl (PCB)² and polybrominated diphenyl ether (PBDE)³ as well as the primary high explosive triacetone triperoxide (TATP)⁴. Values determined by Uchimiya⁵, shown in Table 1, indicate that several current and emerging explosives would be susceptible to spontaneous reduction by ZVMg (i.e. their reduction potentials are less negative than that of ZVMg).

Table 1. Experimental one-electron reduction potentials ($E_m(\text{exp})$) target explosives. All values given in volts

Compound	$E_m(\text{exp})$
TNT	-0.31
Picric acid	-0.39
CL-20	-0.39
RDX	-0.55
HMX	-0.66

While these values are only valid for reduction by the first electron, another study by Chua⁶ using cyclic voltammetry determined the reduction potentials for TNT and each of the step-wise, amine-functionalized intermediates formed during the conversion of TNT to 2,4,6-triaminotoluene and, based on these values, each is capable of spontaneous reduction by ZVMg, as shown in Figure 2.

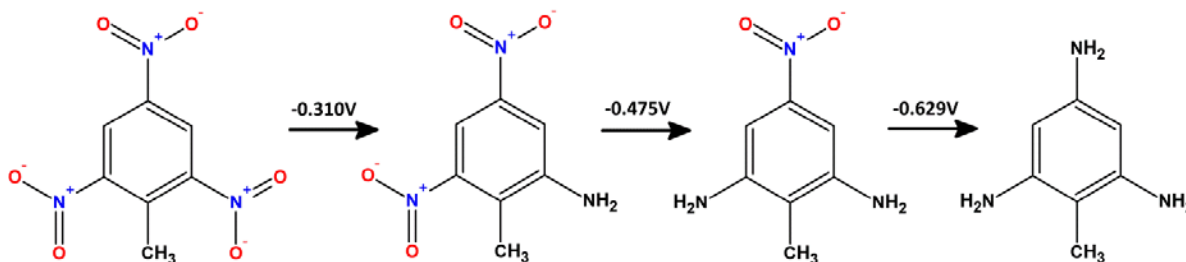
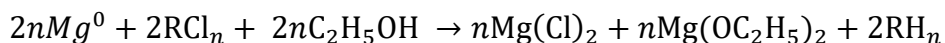
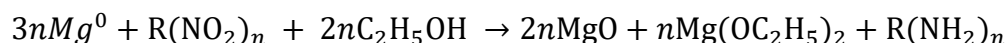


Figure 2. The reaction showing the step-wise conversion of TNT to 2,4,6-triaminotoluene and the corresponding reduction potentials (adapted from Chua 2012⁶).

Aside from ZVMg and the munition compound, the only other reactants are absolute ethanol, which acts as both a solvent and a hydrogen source, and a small amount of acetic acid which is used to remove the passivated magnesium oxide/hydroxide layer thereby exposing the reactive zero-valent magnesium metal. The following equations illustrate the overall reduction reactions where R represents the munition compound. For halogenated compounds it is a hydrodehalogenation reaction.



Or, in the case of nitro compounds, reduction to an amine



This reaction meets several of the Twelve Principles of Green Chemistry endorsed by the United States Environmental Protection Agency (USEPA)⁷ and the American Chemical Society (ACS)⁸ including:

- It prevents the generation of an uncontrolled waste stream such as those created with OB/OD disposal methods.
- Both the reactants (other than the munition compound) and the products have favorable toxicity profiles.
- The solvent, ethanol, is fairly benign and may be recovered for reuse.
- It is an energy efficient process that occurs at ambient temperature and pressure.
- The major constituent in the reaction, ethanol, is a renewable feedstock.
- It uses no derivatives.
- Its products are innocuous and do not persist in the environment.
- The process is inherently safer than either OB/OD or thermal destruction techniques.

TNT was selected as the test molecule for a number of reasons: it has three nitro groups which are the target moiety for this reaction, its analytical methods are well established and easily implemented, and analytical standards of the expected reaction products (monoamine dinitrotoluenes) are readily available. The reduction of the nitro groups on TNT to amines is expected to be applicable to other commonly used energetics with similar reduction potentials.

3.2. Testing

Pure TNT was chosen for these experiments to demonstrate the feasibility of the proposed reaction on an exemplar target molecule and to make the subsequent analysis as straightforward as possible. Given the fact that TNT in munitions is part of a formulation, it is expected that the nitro to amino reduction reaction would occur on any other energetic molecules in the formulation with similar reduction potentials.

TNT and monoamine dinitrotoluene standards were obtained from AccuStandard (New Haven, CT) and absolute ethanol, glacial acetic acid and toluene were obtained from Fisher Scientific. Stock solutions were prepared by diluting these standards to desired concentrations in absolute ethanol. Magnesium powder (4 μ m nominal diameter) was obtained from Hart Metals, Inc. (Tamaqua, PA) and was ballmilled prior to use to crack the passivated hydroxide/oxide layer and create surface defects on the metal which has been shown to increase reactivity⁹.

An initial TNT reaction experiment was performed by combining 0.25 g of Mg powder, 10.0 mL of 500 ng/mL TNT in ethanol, and 100 μ L (1% of the volume of the ethanol) of glacial acetic acid in 20-mL volatile organic analysis (VOA) vials equipped with a polytetrafluoroethylene (PTFE) lined caps. These vials were placed on a Barnstead 2309 Lab Rotator until the appropriate sampling time. Duplicate vials were sampled every 10 minutes over a 30-minute

period by withdrawing 4.0 mL of solution into a gas tight syringe fitted with a Whatman Puradisc 0.45 μm nylon syringe filter. Sample analysis was performed on a Thermo Trace 1310 gas chromatograph (GC) equipped with either an electron capture detector (ECD) or coupled with a Thermo ISQ mass spectrometer (MS). A Restek RTX-5 (30 m x 0.25 mmID, 0.25 μm film thickness) capillary column was used for chromatographic separation.

Under these reaction conditions, the TNT concentration in solution decreased very rapidly. As Figure 3 shows, the TNT parent peak has nearly disappeared in the time, $T = 0$ samples. Although the samples are nominally referred to as $T = 0$, there is approximately 20 seconds of contact between all the reactants due to the time required to seal the vial after adding the last reactant, shake for approximately 10 seconds to facilitate thorough mixing, uncup the vial, and begin collecting the sample using the filtered syringe. Also included in Figure 3 is a chromatogram from 10 minutes into the reaction showing that the TNT concentration is below the limit of quantitation.

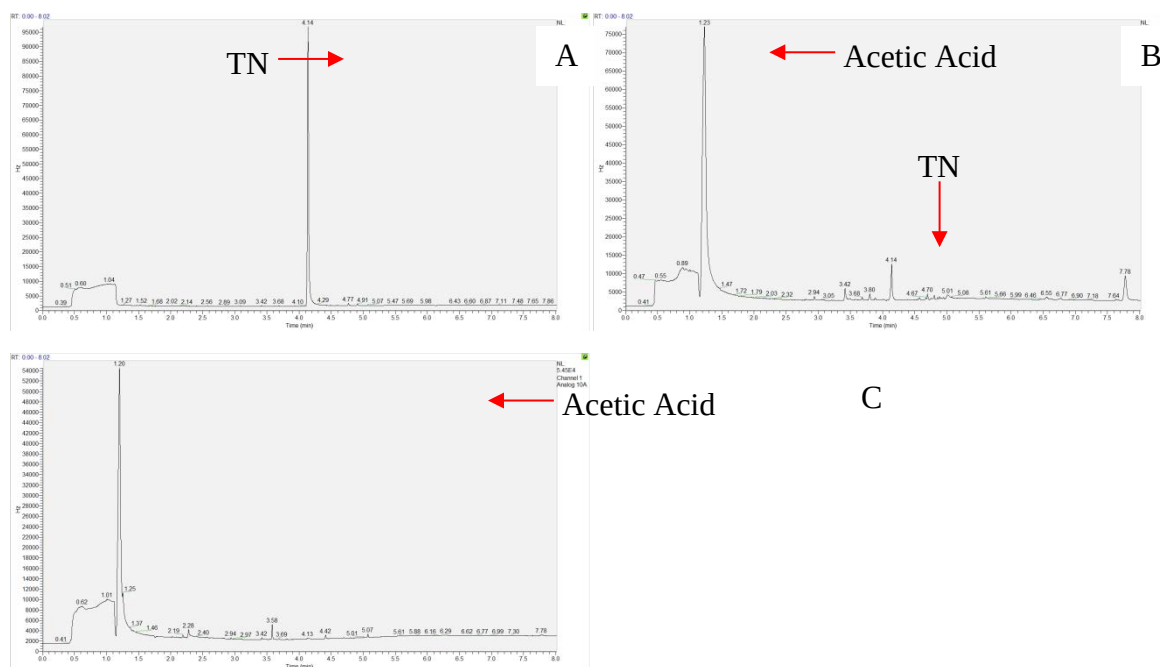


Figure 3. ECD chromatograms from a TNT degradation study using the standard reaction matrix. A) the 500 ng/mL TNT stock solution prior to being combined with the other reactants. TNT elutes with a retention time of 4.14 minutes. B) the 0 minute sample from the combined reaction matrix showing the large decrease in the original TNT concentration. C) the 10 minute sample showing the complete disappearance of TNT.

In the proposed reaction mechanism, the first step in the reduction of TNT would be conversion of the nitro groups to amines via reduction by the zero-valent Mg. This process would produce one of two possible initial reaction products; 2-amino-4,6-dinitrotoluene or 4-amino-2,6-dinitrotoluene. Standards of these chemicals were purchased and instrumental methods were developed to allow for positive identification of these compounds should they be produced

during the reaction. The ECD chromatograms of these compounds (Figure 4) show that both compounds are readily detected by GC/ECD and that their signal response is similar to that of TNT.

The stoichiometry of the conversion of TNT to a monoamine dinitrotoluene product in the proposed reaction is 1:1. It is clear by their absence in chromatograms B and C of Figure 3 that neither of the monoamine dinitrotoluene compounds were produced in the quantities predicted by the proposed reaction scheme. Furthermore, neither was observed in any of the chromatograms up to the final sampling time of 60 minutes.

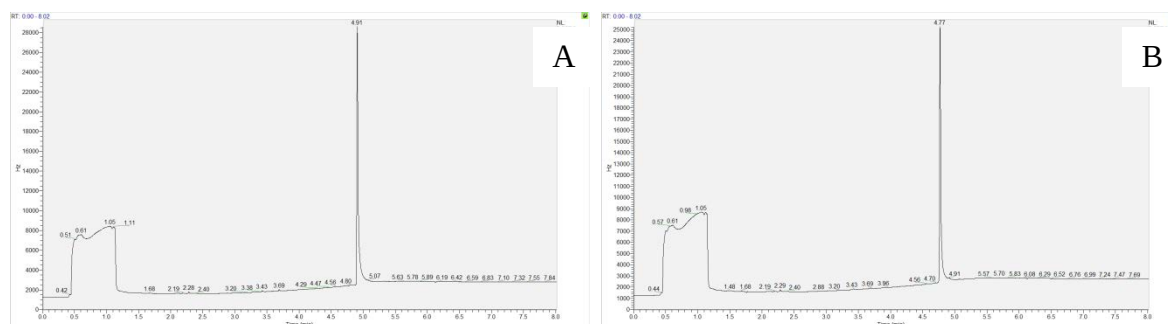


Figure 4. ECD chromatograms of 100 ng/mL solutions of the two possible monoamine dinitrotoluene reaction products. A) 2-amino-4,6-dinitrotoluene which elutes at 4.91 minutes. B) 4-amino- 2,6-dinitrotoluene which elutes at 4.77 minutes

Efforts were made to detect and identify reaction products other than the two monoamine dinitrotoluenes in the event that the reaction was proceeding via a different mechanistic pathway. Several different GC/ECD methods were developed with increased chromatographic durations and varied zone temperatures to detect any possible late-eluting, high boiling point, or thermally labile products. No such products were detected by any of these instrumental methods. Additional analyses were conducted on a GC/MS in order to detect possible product molecules with little to no electron affinity that would be undetectable by GC/ECD. Eleven different GC/MS instrument methods were used in an attempt to detect these other possible products however none were found.

In addition to altering the instrumental methods, different extraction techniques were employed in an attempt to recover potential reaction products. In the normal extraction procedure, the ethanol reaction solution is filtered (to remove the Mg powder) and analyzed directly. In order to determine if unanticipated reaction products, that are insoluble in ethanol, were being formed, the volume of ethanol in the reaction was reduced from 10 mL to 5mL and instead of withdrawing the ethanol at the predetermined time, 5.0 mL of toluene was added to the reaction matrix. The vials were then shaken by hand for 2 minutes to facilitate thorough mixing and contact with the magnesium surface before the solution was withdrawn via filtered syringe as in the normal experimental procedure. The 4.0 mL of filtered ethanol/toluene solution were then deposited into a second 20 mL VOA vial to which an additional 2.0 mL of deionized water was added. The addition of the water causes a phase separation into polar (ethanol and water) and

nonpolar (toluene) layers. This technique has been used previously to simplify the analysis of complex matrices by separating analytes by their respective polarities. It was employed in this case to determine if there any nonpolar analytes that were not being extracted in the ethanol alone. GC/ECD and GC/MS analysis of both layers failed to reveal any previously undetected reaction products.

Subsequent tests were performed using the original reaction conditions with the exception that the initial TNT concentration was increased from 500 ng/mL to 100,000 ng/mL. The purpose of this study was to determine if an increase in the starting concentration of TNT would produce detectable quantities of any products that would have been below detection levels at the 500 ng/mL starting concentration. The chromatograms from these studies are virtually identical to those with the lower starting concentration seen in Figure 3. Even at 100,000 ng/mL the TNT concentration decreased significantly in the 0 minute samples and is below quantitation limits in the 10 minute samples.

Following the unsuccessful efforts described above to detect and identify reaction products researchers began to consider the possibility that the decrease in observed TNT levels was not due to conversion by a chemical reaction but by some other process. In other similar ZVMg-based experiments, there is a delay of approximately 10 minutes before organic reactants begin to be converted to products³. This has been attributed to the time required for the acetic acid to react with the MgOH₂/MgO passive layer and expose the zero-valent magnesium. The 0-minute chromatogram (B) in Figure 3 shows that the TNT concentration is decreasing virtually immediately even though it is unlikely the acetic acid has had sufficient time to remove the passive layer from the Mg. The immediate decrease in the TNT concentration, coupled with the lack of observed reaction products may indicate that the TNT is being adsorbed on the surface of the Mg powder rather than undergoing a chemical reaction with the ZVMg. To test this possibility, an experiment was setup identical to the experiment described above with the exception that acetic acid was not added to the reaction matrix. The chromatograms from this experiment were nearly identical to the previous experiments in which the acetic acid was included which makes it highly unlikely that the loss of TNT is due to a chemical reaction.

4. Selective Ion Exchange Resins for Demilitarization of AF-M315E

4.1. Background

AF-M315E is a high-performance, low-toxicity “green” propellant (classified as a 1.3C explosive commodity) developed by the Air Force Research Laboratory at Edwards Air Force Base. It is currently scheduled to be used on the Green Propellant Infusion Mission (GPIM) due to launch in 2018. OB/OD is the only accepted method for disposal of AF-M315E propellant at this time, however many facilities (including KSC) that may utilize this propellant do not possess this capability. This leads to both expensive and hazardous transport of explosive materials to a facility which is capable of performing OB/OD. Unfortunately, incomplete thermal degradation of the components in the AF-M315E mixture can produce a variety of toxic byproducts including nitrogen tetroxide. The risk of incomplete thermal degradation also limits the available chemical degradation pathways as exothermic reactions also present a danger of hazardous byproduct formation. In addition, these are destructive techniques in which all parts of the commodity in

question are lost. A more economical and environmentally safe method for demilitarization would allow for the recovery or possible reuse of the propellant in some manner while eliminating the toxic byproduct formation.

The object for this portion of WP-2615 “Recycling and Demilitarization of Military Munitions” was to demonstrate and validate the feasibility of using selective ion exchange resins to facilitate a flow-through demilitarization process for AF-M315E. In the proposed system, an ion-exchange resin was used to physically separate the oxidizer component (nitrate anion) from the AF-M315E commodity. The use of ion exchange resins for the removal of nitrates from waste water is prevalent in literature and has been used for demineralization for decades¹⁰. In this process, the nitrate displaces a chloride ion on an active site of the resin, leaving the effluent stream free of the oxidizer component of the propellant. This would allow the fuel components to be recycled or reused. A two-stage ion exchange bed operated in parallel mode would allow for continuous operation, with one reactor bed acting as the sorption stage and the second as the regeneration stage, as shown in a proposed reactor schematic in Figure 5.

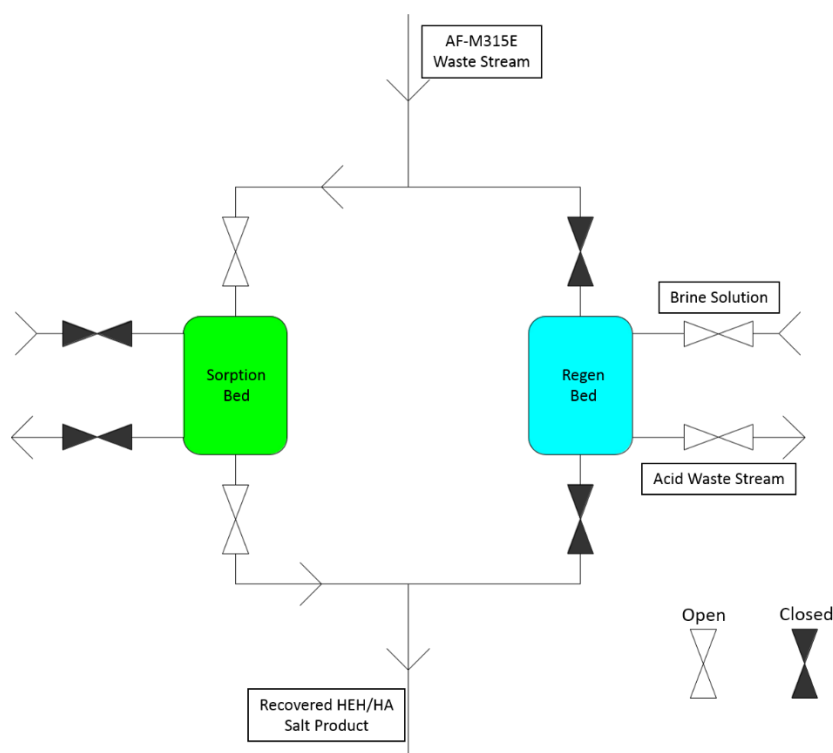


Figure 5. A two-stage ion exchange bed for processing AF-M315E.

4.2. Testing/Results

Two types of nitrate specific strong base anion (SBA) resins were obtained for initial evaluation during this testing. These were Purolite A520E and ResinTech SIR-100-HP. Both of these resins arrived in the chloride form, so a regeneration solution that was 10% NaCl (by weight) was prepared and suitable for both resins. All resins were activated/regenerated prior to use using this 10% NaCl solution. Additionally, calculations for the maximum removal capacity of

the resins, based upon the nitrate component of the AF-M315E, were performed to determine the required amount of resin needed for testing. The chemical components for AF-M315E are given in Table 2.

Table 2. Analysis of AF-M315E to determine nitrate concentration.

Constituent	%wt in AF-M315E	%wt NO ₃ in constituent	%wt NO ₃ in AF-M315E	[NO ₃] (mg/L)
HEHN	44.5%	44.4%	19.7%	
HAN	41.83%	64.3%	26.9%	
H ₂ O	11.0%	0%	0%	
AN	2.225%	76.8%	1.7%	
2,2-Bipyridyl	0.445%	0%	0%	
Total	100%	--	48.3%	483431

These values were utilized to determine the theoretical concentration of nitrate ions in pure AF-M315E from all possible sources within the propellant. The “wet” capacity of both tested resins was 0.9 mEq/mL. Based on these calculations, and guidance from the SBA resin manufacturer for nitrate removal, it was decided that testing would be performed using a 1:500 diluted solution of AF-M315E in water. This would theoretically generate a 966 mg/L NO₃⁻ nitrate solution to be used for testing, however the diluted solutions of AF-M315E actually used had nitrate concentrations of ~1250 mg/L NO₃⁻. This difference could be explained by the age of the AF-M315E, which was well over 1 year old and had not been stored in climate controlled conditions. The concentration of each batch of dilute AF-M315E solution prepared was tested prior to use in order to allow for an effective evaluation of the resin’s removal capability.

4.3. Static Testing

Initial laboratory scale studies were conducted in 40-mL vials to verify the ability of the selected ion exchange resins to remove nitrate from dilute solutions of AF-M315E. Approximately 35 mL of a dilute AF-M315E aqueous solution was added to 5 g (wetted/activated) of the selected ion exchange resins. The test vials were agitated for 5 minutes prior to the initial sampling event to ensure sufficient contact between the dilute AF-M315E solution and the SBA resins (Figure 6).

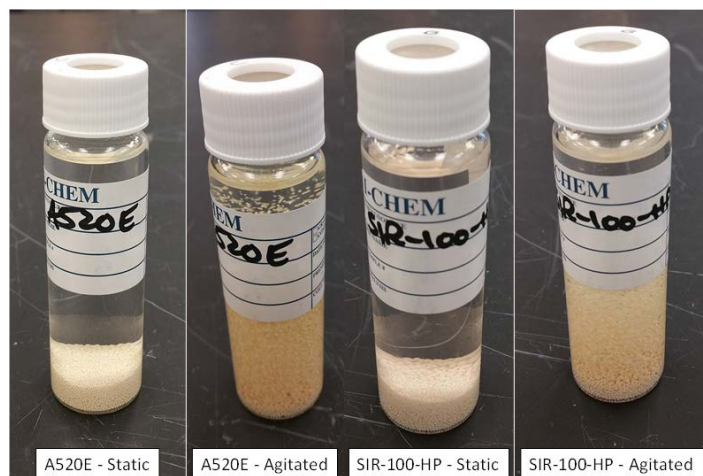


Figure 6. Initial vial studies using nitrate-specific resins Purolite A520E and ResinTech SIR-100-HP (static and agitated).

At various pre-determined times throughout the experiment, the resins were allowed to settle so that a near real-time analysis of the nitrate concentration could be obtained through the use of a calibrated RQFlex plus 10 system (Figure 7) combined with Reflectoquant Nitrate Test Strips (5 - 225 mg/L). The test strips are placed in the liquid and change color based on the amount of nitrate present. The RQFlex plus 10 instrument functions based upon the principle of reflectometry where reflected light from the test strips are measured. The difference in the intensity of the emitted and reflected light allows for a rapid, quantitative determination of the concentration of specific analytes in this case, nitrate. In addition, the use of the Reflectoquant Plus Test Strips allow for a specific barcode calibrated analysis.



Figure 7. RQFlex Plus 10 reflectometer

The results from this initial vial study are given in Table 3.

Table 3. RQFlex 10 Plus results from static vial study.

Sample ID	Concentration (mg/L)	Reaction Time (min)	% Removal
Blank (DI H ₂ O)	Low (BDL)	N/A	N/A
1:500 AF-M315E	High	N/A	N/A
1:5000 AF-M315E	125	N/A	N/A
100 mg/L IC Standard	98	N/A	N/A
Purolite A520E	52	4:42	95.8%
	32	12:00	97.4%
	29	63:39	97.7%
	27	74:11	97.8%
ResinTech SIR-100-HP	40	6:39	96.8%
	28	10:03	97.8%
	26	65:25	97.9%
	26	75:59	97.9%

Results from this study show that more than 95% of the nitrate is removed by both resins within 5 minutes using only manual agitation in a non-flow through system. The "Low" reading from the DI water indicates that the analysis was below detectable limits (as would be expected) and the "High" reading from the 1:500 diluted solution of AF-M315 indicates a concentration above 226 mg/L NO₃⁻ (also as expected). A further 1:10 dilution (total dilution of 1:5000) of this stock resulted in concentration of 125 mg/L NO₃⁻, which back-calculates to the previously mentioned ~1250 mg/L NO₃⁻ of the diluted stock solution.

Additionally, ion chromatography (IC) was run on one of the samples (A520E) from the vial study above to confirm these preliminary results. Specifically, we were looking for a sharp rise in the chloride concentration (as nitrate was removed and chloride was released) and a nitrate concentration of ~30 mg/L. The chromatogram displayed in Figure 8 shows the 5-minute sample from the A520E resin test, in which the chloride peak is nearly off scale (~980 mg/L) while the nitrate peak is at ~36.53 mg/L which is in good agreement with the reflectometer data.

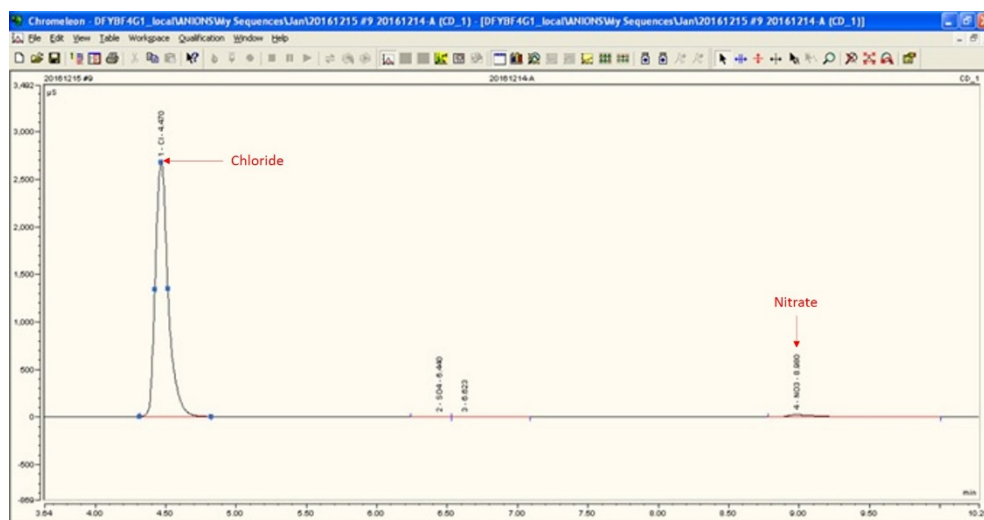


Figure 8. IC analysis of A520E resin effluent (5 minute sample).

4.4. Flow-Through Testing

The next phase of testing was performed to determine the ability to regenerate and re-use the SBA resins. Based upon the results from the initial static vial studies, it was decided that these tests would focus on only a single resin, Puralite A520 (as the previous testing results are nearly identical). A single-bed reactor design was used for the flow-through tests and is shown in Figure 9 and Figure 10.

This system was designed with a 12" long x 1" diameter reactor bed (Figure 10) which contained 153 g of resin. Using the previous resin capacity calculations, it was determined that ~153 g (wet weight) of the Purolite A520E resin would be added to the bed. A series of four tests were performed on the same batch of resin to determine if A520E was being effectively regenerated and re-used after initially demilitarizing a diluted solution of A520E. Additionally, these tests also allow for the determination of the removal capacity of the resin, as testing was conducted until breakthrough/saturation was observed. The theoretical capacity of the bed used in this test can supposedly demilitarize 12.4 mL of pure AF-M315E. However, breakthrough will likely occur at a lower volume due to flow dynamics within the resin itself (path of least resistance, resin packing, etc...). A total of four tests were run on a single batch of A520E resin. Test #1 was performed to determine the capacity of the resin to remove nitrate from a dilute solution (as well as determine the initial breakthrough/saturations points), while Test #2 – Test #4 were performed to evaluate the resin regeneration process and determine if any removal capacity was lost. These tests were conducted over the period of a month.

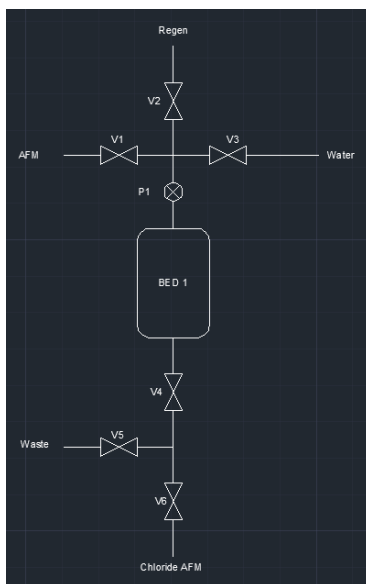


Figure 9. Single-bed reactor design.

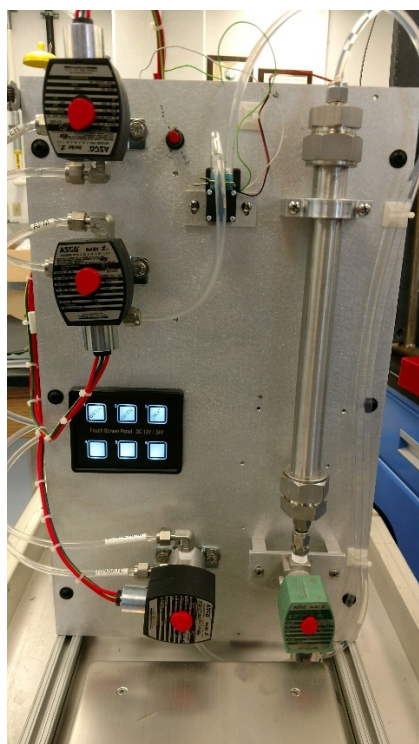


Figure 10. Single-bed flow through reactor setup.

The general procedure for these tests was to initially flush the system with deionized (DI) water to remove any excess chloride ions from the resin. This also allowed for the determination (and adjustment, if necessary) of the systems flow rate. Based upon the manufacturer's specifications, a minimum of 1 L of DI water was necessary to flush the bed volume used in these experiments, however at least 2 L of DI water were used to ensure that all excess chloride was removed prior

to each tests and samples of the flush water were collected prior to switching to the dilute AF-M315E solution to verify this. During testing, ~5 mL (minimum) samples were collected in duplicate every three minutes until breakthrough/saturation was detected. Near-real time analysis during the test was performed using a calibrated RQFlex 10 Plus reflectometer, and samples were set aside for later verification with IC analysis. Once breakthrough/saturation was detected and the test was terminated, at least 1 L of DI water was pumped through the reactor bed to flush the system. In addition, the concentration of the dilute AF-M315E solution that was used during testing was determined as this concentration varies slightly per batch due to the dilution itself. Results of these tests are combined into a single breakthrough plot which was normalized for flow rate (Figure 11).

Test #1 – As stated previously, the objective of the Test #1 was to initially determine the breakthrough/saturation time for Puralite A520E resin when exposed to a dilute solution of AF-M315E as well as demonstrating the ability of a flow-reactor to successfully demilitarize AF-M315E. As this resin had already been previously activated using a 10% NaCl solution, regeneration of the resin was not necessary for this experiment. 3 L of DI water were used to flush the reactor bed prior to the initiation of testing. The flow rate for this test was 77 mL/min. Analysis of the dilute AF-M315E solution used in Test #1 showed a concentration of 1305 mg/L NO_3^- .

Testing shows that the Puralite A520E resin was effective in completely removing the nitrate from the dilute AF-M315E solution for a total of 33 minutes prior to any breakthrough of the resin bed. At that point, breakthrough of the resin is observed and the nitrate concentration rises to saturation levels (~1100 mg/L NO_3^-). A normalized (for flow rate) breakthrough plot is presented in Figure 11. One interesting fact was that the effluent generated during the demilitarization process was pink in color as opposed to the clear dilute AF-M315E solution. Additionally, it was noticed that the pink color disappeared after the testing was completed during flushing of the resin with DI water. However, if the system was allowed to remain static for a period of time, the pink color would return upon the application of a fresh flush rinse. Examination of the resin bed after all testing was completed showed a slight discoloration along the filter material used in the construction of the reactor bed. Since this pink discoloration was noticed within the resin itself, it is suspected that some component of the dilute solution may be chelating upon this surface, although this has not been confirmed.

Test #2 - To evaluate the ability to regenerate and re-use previously exposed A520E resin, Test #2 was run using the same resin from Test #1. Regeneration of the resin was accomplished by pumping ~1 L of a 10% NaCl solution through the reactor bed. Once the resin had been regenerated ~3 L of DI water was used to flush any residual excess chloride from the bed prior to the beginning of testing. Flow tests prior to the introduction of the dilute AF-M315E solution show that the flow rate for this test was 82 mL/min. Analysis of the dilute AF-M315E solution used in Test #2 showed a concentration of 1317 mg/L NO_3^- .

Again, the pink color returned upon the introduction of the dilute AF-M315E solution. As before the pink color disappeared after the testing was completed (during flushing of the resin with DI water). A normalized (for flow) breakthrough plot is shown in Figure 11. One major

difference in the results of Test #2 (as compared to Test #1) was nitrate was detected immediately at levels of ~20 mg/L. However, rather than rising immediately as was seen during the previous breakthrough tests, the concentration remained constant for ~2.1 L of the solution before increasing concentrations indicated breakthrough. This test showed the lowest removal capacity of all testing, however this is likely due to incomplete regeneration of resin (discussed in more detail in Test #4). Testing was halted once breakthrough of the resin bed was detected.

Test #3 - Upon reviewing the specifications of the A520E resin in conjunction with the above test results, it was determined that the initial NaCl regeneration may not have been sufficient to fully regenerate the resin due to high flow rate used during the test). In order to correct this, the flow rate used during the regeneration cycle was reduced to ~12 mL/min. The documentation indicated that a 20 - 60 minute regeneration cycle at these flows would be sufficient, however to ensure complete regeneration the 10% NaCl solution was pumped through the bed for ~120 minutes. ~3 L of DI water were used to flush any residual excess chloride from the bed prior to the beginning of testing. In addition, the flow rate during the previous test may have been too high for the length of the reactor bed used, so Test #3 (and Test #4) were conducted at approximately half of the previous flow rates used, 38.75 mL/min. Analysis of the dilute AF-M315E solution used in Test #3 showed a concentration of 1413 mg/L NO_3^- .

As before, the effluent solution turned pink upon initiation of testing and disappeared during the post-test DI water flush. A normalized (for flow) breakthrough plot for Test #3 is shown in Figure 11. Unlike Test #2, the effluent reading prior to breakthrough showed 0 mg/mL of nitrate ions indicating that the resin was again completely removing all nitrate. Also, the normalized breakthrough curve is nearly identical to the results in Test #1, indicating full recovery of the system. Testing was halted once breakthrough of the resin bed was detected.

Test #4 - The objective of Test #4 to test the re-use of the A520E resin using the new regeneration parameters (first used in Test #3). As was done in Test #3, the regeneration cycle was performed using a 10% NaCl solution that was pumped through the bed for ~120 minutes (~12 mL/min flow rate). ~3 L of DI water was used to flush any residual excess chloride from the bed prior to the beginning of testing. Flow tests prior to the introduction of the dilute AF-M315E solution show that the flow rate for this test was 40.5 mL/min. Analysis of the dilute AF-M315E solution used in Test #4 showed a concentration of 1413 mg/L NO_3^- .

As expected (from prior results) the effluent solution turned pink upon initiation of testing and disappeared during the post-test DI water flush. A normalized (for flow) breakthrough plot for Test #4 is shown in Figure 11. The results for Test #4 were very similar to Test #2 in that a small amount nitrate ion was detectable throughout the run in the effluent. Again, this nitrate concentration was stable until true breakthrough was detected, and nearly matched the treatment capacity results from Test #1 and Test #3. Testing was halted once breakthrough of the resin bed was detected.

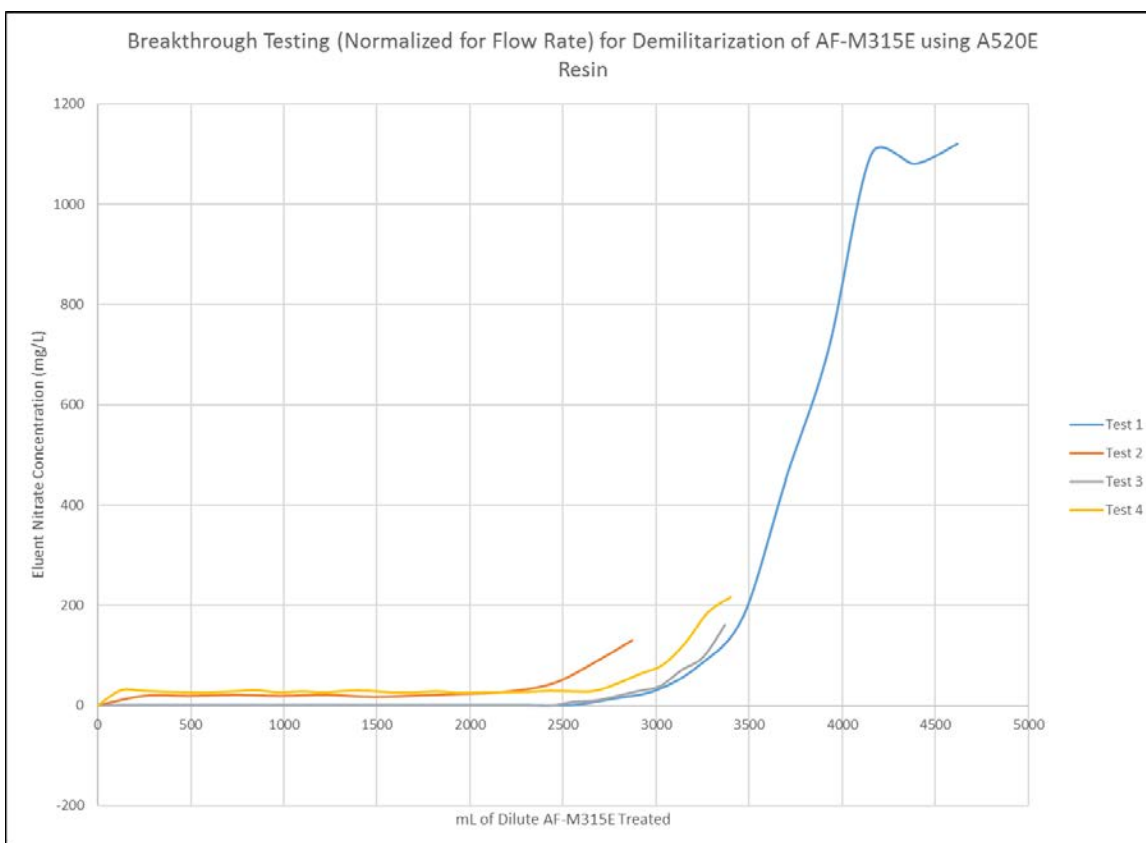


Figure 11. Normalized (flow rate) breakthrough plots of all flow-through testing.

The normalized breakthrough plots do show that regeneration of the resin is successful. In fact, Test #3 nearly mirrors the breakthrough curve of Test #1, indicating that full recovery is possible with a single batch of Puralite A520E resin. Test #2 shows some loss of total capacity, however this is most likely due to the incorrect flow rates used in both the regeneration and testing cycles for a reactor bed of this length. This conclusion is supported by the fact Test #3/#4 both show increased removal capacity using the correct flow rates. Test #2 and Test #4 both show initial breakthrough from the onset of testing, however the effluent concentration levels remain stable until true breakthrough is seen. This low-level residual nitrate reading may be due to incomplete flushing of the system, however further testing is necessary to confirm this. Even for these two tests, the system is removing greater than 95% of the nitrate ions from the dilute AF-M315E solution indicating the resin is still functioning as expected. Later testing of the collected effluent showed high chloride levels. This is consistent with the idea that the nitrate is being removed from the dilute AF-M315E solution through the ion exchange process, releasing free chlorides into the effluent stream.

The resin itself was examined for signs of physical deterioration after testing (Figure 12) but none were detected.

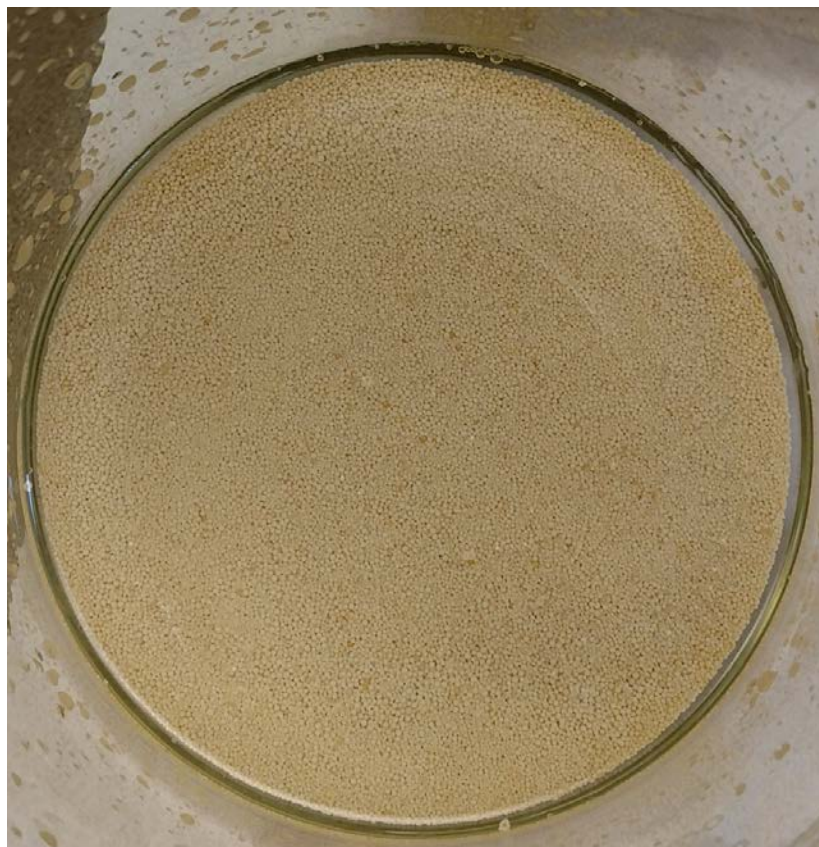


Figure 12. Puralite A520E resin post-test examination.

4.5. Resulting Waste Streams

The Puralite A520E resin acts in an ion-exchange capacity, allowing for the removal of the oxidizer component (nitrate ion) from the dilute AF-M315E solution and exchanging it with an innocuous chloride ion in its place. The resulting waste stream contains a mixture of hydroxyethylhydrazinium chloride, hydroxyl ammonium chloride, ammonium chloride and 2-2 bipyridyl. While there is currently no long-term data on the stability of this chlorinated waste stream, it does provide the benefit of having separated the oxidizer component from the AF-M315E solution thereby neutralizing the possibility of it acting as monopropellant. Further testing and analysis of this waste stream is discussed further in Section 7.2.

5. Degradation Testing using Visible Light Photocatalysis

5.1. Background

The use of titanium dioxide as a photocatalyst has dominated the field of photocatalysis for several decades. Applications, both realized and forecasted, encompass a broad range of processes including hydrogen production via photocatalytic water splitting, chemical and biological purification of water and air, and synthesis of organic compounds. The most commonly used titanium dioxide, Degussa P25, is a simple mixture of anatase (70-85%), rutile, and amorphous (minor) titania¹¹ and has demonstrated high photocatalytic activity in numerous studies¹²⁻¹⁶. The anatase phase, known for its superior activity relative to the rutile phase¹⁷, has a

band gap energy of 3.2 eV; thus, photons with a wavelength of 388 nm or less (i.e., ultraviolet (UV) radiation) are required to activate anatase TiO₂¹⁸. These high photonic energy requirements disallow effective use of indoor lighting or solar radiation, which only consists of ~4-6% UV radiation at the Earth's surface¹⁹, as energy sources. A solution for overcoming these limitations is to enable the TiO₂ photocatalyst to be activated by visible light. Developing a TiO₂-based catalyst that is responsive to visible region wavelengths, will allow the use of visible band solar radiation (~45% of the solar spectrum lies in the visible region¹⁹), or highly efficient blue or white LEDs in photocatalytic systems; thereby making photocatalysis approaches more efficient, economical, and safe. The past decade has witnessed a shift in catalyst development towards VLR. Efforts have included sensitization of TiO₂ with absorbed dye molecules, metal cation²⁰⁻²⁴ or anion²⁵⁻²⁷ doping, narrow band gap semiconductor and TiO₂ coupling²⁸⁻³⁰, to name a few. Within the past two years, researchers at Kennedy Space Center created a library of VLR-enabled TiO₂ catalysts that were screened for both gaseous and aqueous phase activity³¹; several of these catalysts out-performed commercially available VLR catalyst systems in both media. The top-performing catalyst was used to examine the ability to photocatalytically degrade CN and HCE.

Little to no research has been cited on the destruction of CN by photocatalysis or any other method. Tayade et al.³² included acetophenone, the parent compound of CN, as a test contaminant in their photocatalytic experiments showing destruction of the molecule, but did not discuss product formation. Similarly, Amereh and Afshar³³ demonstrate the destruction of acetophenone without any discussion of intermediates or products of the photocatalytic reaction. Limited information on an initiative to breakdown even this parent product is not surprising, as acetophenone (AP) a major organic building block for several industries. As such, Kohtani et al.³⁴ focuses on a novel application of photocatalysis to hydrogenate AP derivatives using TiO₂ to produce desired alcohols for further organic synthesis procedures. While CN was not one of the tested derivatives, the successful transformation with the use of ethanol, or other alcohol, as a hole scavenger shows promise for a photocatalytic process to demilitarize CN to its alcohol derivative, 2-chloro-1-phenylethanol, which is considered non-hazardous by most regulatory authorities (see Safety Data Sheet (SDS)). The addition of the alcohol as a hole scavenger in this reaction is also beneficial in the treatment of riot control munitions since the composition within a canister is the agent dissolved in an organic solvent.

Similarly to CN, research directed at the destruction of HCE is not prevalent in the field of photocatalysis. However, it has appeared as an intermediate in the photocatalytic degradation of similar chlorinated compounds such as trichloroethylene^{35,36} that is subsequently degraded further through undiscussed mechanisms. Several studies have also shown successful destruction of other closely related chlorinated compounds such as carbon tetrachloride in the gas phase³⁶ using base titanium dioxide and in the liquid phase using a dye-sensitized TiO₂ VLR photocatalyst. Based on the existing technologies for remediation of the myriad of closely-related compounds, there exists a strong likelihood that VLR photocatalysts will successfully degrade hexachloroethane. Furthermore, studies have also demonstrated the ability of HCE to sublime from pyrotechnic matrices at 41°C within 24 hours, making it easy to separate from the matrix and treat photocatalytically in the gas phase³⁷.

5.2. Methods

A gas phase screening methodology previously developed in our lab for ethanol degradation was adapted for HCE and CN degradation tests. The general procedure is as follows and further details are provided in later sections. The catalyst is synthesized and then applied onto small aluminum coupons in three spots. The coupons are placed in 40-ml vials sealed with a cap that allows for gas sampling. The catalyst panel and vial are shown in Figure 13. The gas species being subjected to the test is introduced into the vial through the syringe port, and then the head space is sampled at the desired interval. Only one sample is acquired from each vial meaning that measuring degradation at different times requires completely different vials.

Marine-Glo Fluorescent T5 HO 24-Watts bulbs were used in the photodegradation tests. Figure 14 shows the spectral emission for this bulb which is centered in the blue region of the visible spectrum. Six of these bulbs were arranged in a light bank for testing. The complete degradation setup is shown in Figure 15. The vials were placed on a rack which allowed multiple samples to be evaluated at one time. The rack was placed such that the vials were one inch from the light bank. During testing, the entire setup was covered in dark fabric acting as a light curtain.

HCE is a solid at room temperature and was introduced into the vials using the following procedure. A quantity of HCE crystals was placed in a 1-L Tedlar bag with humid air (~50% relative humidity (RH)). The HCE crystals within the bag were allowed to sublime at ambient temperature for approximately 12 hours to ensure sufficient vapor generation. According to PubChem Open Chemistry Database (PubChem CID: 6214) the vapor pressure for HCE at 20°C is 0.4 mmHg. Applying the ideal gas law this should result in 540 mg/L of HCE vapor in the 1-L bag, however, the concentration was slightly lower than that. This bag was used as the working source of HCE vapor for degradation studies. 0.75 ml of HCE vapor from the source bag was injected into each vial before testing, while also removing 0.75 ml of air from the vial. This resulted in an HCE concentration of about 3 ppm. In some tests, a chloride ion analysis was conducted to determine if any hydrochloric acid was produced. This was accomplished by introducing water into the vial and then performing a chloride analysis on the water with ion chromatography.

The vapor pressure for CN at 20°C is 0.0054 mmHg, obtained from PubChem Open Chemistry Database (PubChem CID: 10757), which is considerably lower than for HCE. Applying the ideal gas law indicates that there should be 6.71 mg/L of CN vapor at room temperature. This vapor pressure is much lower than for HCE, so a different strategy was employed. About 0.1 mg of solid CN was added to each vial before testing. This resulted in a steady concentration of CN being present for the duration of the test. CN degradation was determined by monitoring the increase in two daughter products, acetophenone (AP) and benzaldehyde (BA).

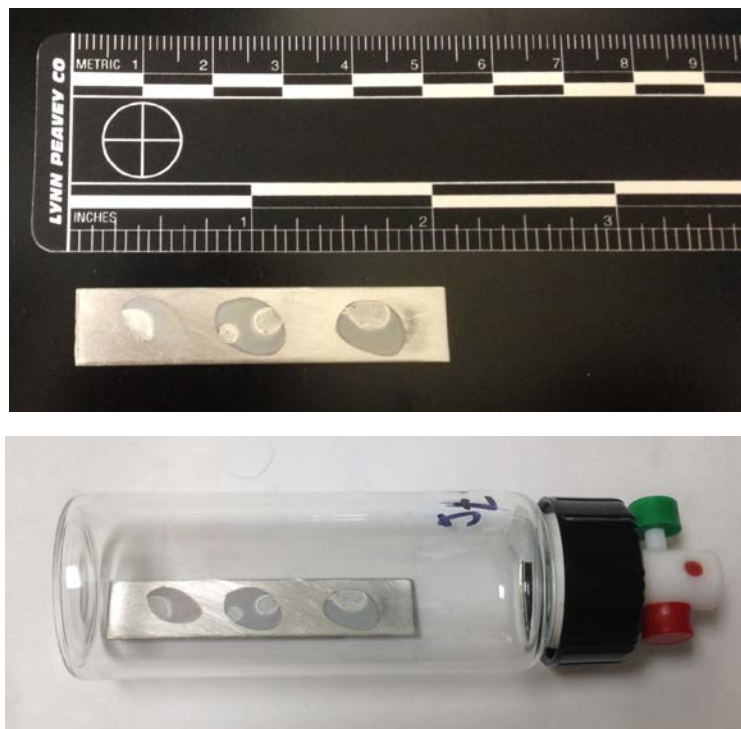


Figure 13. Top: Catalyst applied in three spots on an aluminum panel; Bottom: Catalyst panel in sealed vial.

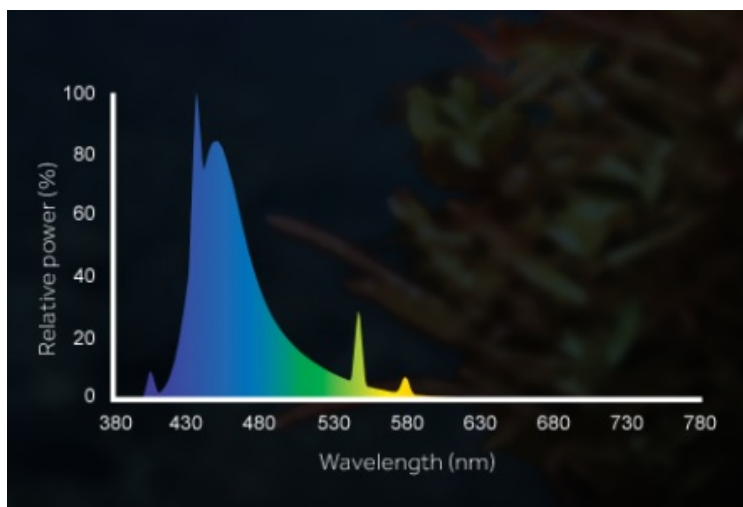


Figure 14. Spectral Working range for Marine-Glo Fluorescent Bulb T5 HO Used during Testing

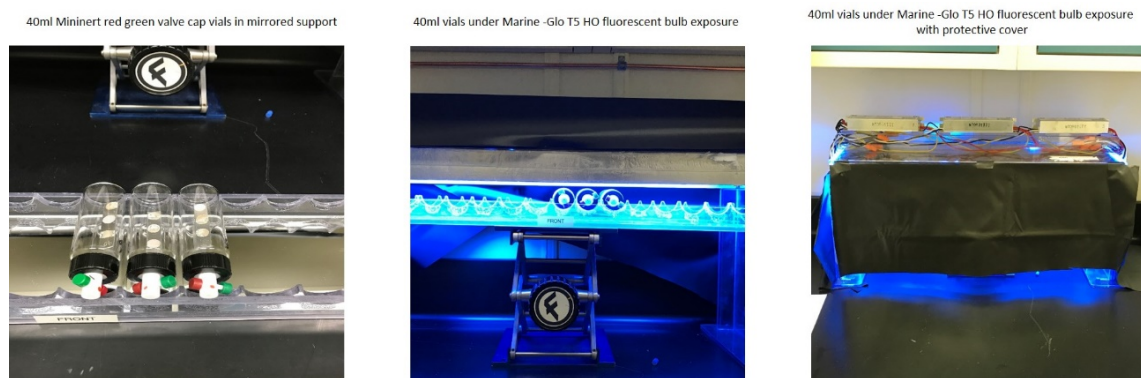


Figure 15. PCO Static Test Setup for HCE and CN Vapor Exposure. Left: Vials placed on rack; Center: Vials and rack placed below light bank; Right: Complete setup with light curtains.

5.3. Preparation and Application of Photocatalyst

Previous work³¹ had shown that 3%-silver-doped titanium dioxide powder was an effective visible light catalyst for photocatalytic oxidation. The catalyst was synthesized using the procedure described here. 0.25 g Degussa P25 titanium dioxide powder and 939 μl 0.1 M AgNO_3 were added to a de-aerated 5% aqueous ethanol solution. This mixture was placed on a stir plate and exposed to UV-A radiation from two fluorescent bulbs for 30 minutes. During this time, the UV activated titanium dioxide reduces silver ions causing silver to deposit on the titanium dioxide particles. After silver deposition, the resulting mixture was transferred into centrifuge tubes and centrifuged at 4000 rpm for 10 minutes. The supernatant was discarded and the solids re-suspended in a minimal quantity of Nanopure water and centrifuged again for 10 minutes at 4000 rpm. A second and final rinsing was performed and the tube plus resulting solids dried in an oven at 70°C. This method would generate a ~70% yield of the 3% Ag/TiO₂ powdered catalyst. Previous work with this catalyst had shown a shift in the band gap to 2.72 eV; this energy correlates to activation of the catalyst by light at a wavelength of 457 nm or lower³⁸.

The catalyst was prepared for testing by drying small amounts on aluminum coupons. A 5 mg/ml aqueous mixture of 3% Ag/TiO₂ catalyst powder was made. The catalyst powder was suspended by sonication and then 100 μl quantities of the mixture were applied to 3 locations on the surface of a pre-weighed aluminum coupons. The coupons were allowed to dry overnight. The coupons were then reweighed to determine the mass of 3% Ag/TiO₂ catalyst powder applied.

5.4. Analysis Systems & Conditions

HCE and CN degradation analysis was done with gas chromatography/mass spectrometry. Calibration standards for the target compound and suspected daughter products were acquired and used in the analysis. In the case of HCE degradation, tests were performed after light exposure to determine if the compound had been fully mineralized to hydrochloric acid. This

was done by introducing an amount of water into the vial and then performing ion chromatography on the water to look for the presence of chloride ions. The details of the instrumentation is given here.

Cal standards: Hexachloroethane from AccuStandard, M-8120-08, 2000 µg/ml in Hexane,
Lot: 215111039

Tetrachloroethylene from AccuStandard, AS-E0083, 5000 µg/ml in Methanol
Lot: 216031049

2-Chloroacetophenone from AccuStandard, IRT-001S, 100 µg/ml in Hexane,
Lot: 214041091-02

GC System: Thermo Scientific Trace 1310 (4732 125335)

MS System: Thermo Scientific ISQ LT (4732 125335)

Column: Restek Rxi-5ms, 30 m x 0.25 mm x 0.25 µm df (S/N: 918646) for HCE
Analysis

Restek RTX-5ms, 30 m x 0.25 mm x 0.25 µm df (S/N: 1470776) for CN
Analysis

Oven Program: Initial temperature of 40°C, held for 7 minutes then ramped to 250°C at a rate of 25°C/min, and held at the final temperature for 1 minute. Total run time of 16.4 minutes.

Inlet: HCE Analysis: Splitless injection with Programmable Temperature Vaporization mode (PTV) Initial temperature of 60°C, ramped to 250°C at a rate of 10°C/sec, 2-minute transfer time followed by a split flow of 50 mL/min with constant septum purge.

CN Analysis: PTV Splitless injection in constant temperature mode at 200°C; splitless time of 1 minute followed by a split flow of 50 ml/min with constant septum purge.

Carrier: Helium, Constant Flow Setting, 1.5 mL/min

Detector: Mass spectrometer (MS): Ionization mode is EI, Transfer line temperature of 260°C, Ion source temperature of 290°C, Solvent delay of 6 minutes with a solvent delay of 4.5 minutes for HCE PCO exposed samples, Mass Range of 35-250amu, Dwell time of 0.2s for a total scan time of 0.204s.

Injection Vol. 100 µL for HCE and CN headspace samples (100-µL Hamilton 1710 SL syringe); 1 µL for HCE and CN standards (Thermo scientific 10-µL autosampler syringe, with TriPlus RSH Autosampler)

Chloride Analysis

Cal Standard: Chloride from Inorganic Ventures, DYNCO-ICAL-1, 1000 µg/ml in water,
lot: J2-MEB615041

IC System: Thermo Scientific ICS3000 (ECN 2229819)

Thermo Scientific ICS2100 (ECN 2237816)

Column: Dionex IonPac AS18 4mm x 250mm (S/N: 060549) used in the ICS3000

Dionex IonPac AS18 4mm x 250mm (S/N: 014301) used in the ICS2100

Mobile phase: 32mM KOH from an eluent generator

Flow: 1.0 ml/min

Detector: Conductivity detector with an applied suppression current of 80mA

Injection Volume: 25 µl for ICS3000; 5 ml for the ICS2100

Calibration curves were prepared from pre-prepared stock standards and analysis of the headspace samples, aqueous samples and standards was performed using the methods above. The calibration curves for HCE, perchloroethylene (possible byproduct (PCE)), and CN together with the quantitation routine is presented in Appendix C.

5.5. Results

5.5.1. Hexachloroethane PCO Degradation Results

Each HCE degradation test involved the use of two controls. The first was a vial with HCE vapor but with no catalyst, called the ‘control’, and the second was a vial with HCE vapor and catalyst that was placed in the dark, called the ‘dark’ sample. The control was used to determine the initial amount of HCE present, and varied slightly from day to day. The reported percent loss of HCE are in reference to the amount of HCE determined in the control. The dark sample was used to evaluate loss of HCE due to adsorption onto the catalyst or other losses. Controls and dark samples were always done in triplicate. Results from timed degradation tests were done with at least triplicate samples. Once the experimental methods had been validated, there were a series of four tests. Each test was conducted on the same day. Tests 1 – 3 were used to initially evaluate photocatalytic degradation of HCE and Test 4 was performed to confirm the degradation over time in one test on a single day.

- Test 1 – Control, dark, and 30 minute degradation test.
- Test 2 - Control, dark, and 2 hour degradation test.
- Test 3 - Control, dark, 4, and 6 hour degradation test.
- Test 4 - Control, dark, 2, 4, and 6 hour degradation test.

Table 4 shows the results from all the tests. There is a loss of HCE after 30 minutes exposure to lights, but complete loss is not observed until at least 4 hours. Figure 16 shows the average percent loss over time combining all the tests. There is about 10% loss in the dark samples due to either adsorption or other mechanisms. The samples that were exposed to light always show increased loss as compared to the dark samples, indicating that photocatalytic degradation is occurring. There is high variability in the amount of degradation in the 0.5 and 2 hour tests, but beginning at 4 hours almost all of the HCE is completely removed.

Table 4. HCE percent loss over time for each test.

	Test 1		Test 2		Test 3		Test 4	
	Percent Loss	Standard Deviation	Percent Loss	Standard Deviation	Percent Loss	Standard Deviation	Percent Loss	Standard Deviation
Dark	20.9%	11.3%	-6.1%	5.9%	6.2%	2.0%	20.3%	2.7%
0.5 hour	43.8%	25.2%						
2 hour			68.9%	36.3%			86.7%	0.3%
4 hour					98.4%	1.6%	97.0%	2.5%
6 hour					99.7%	0.2%	100.3%	0.1%

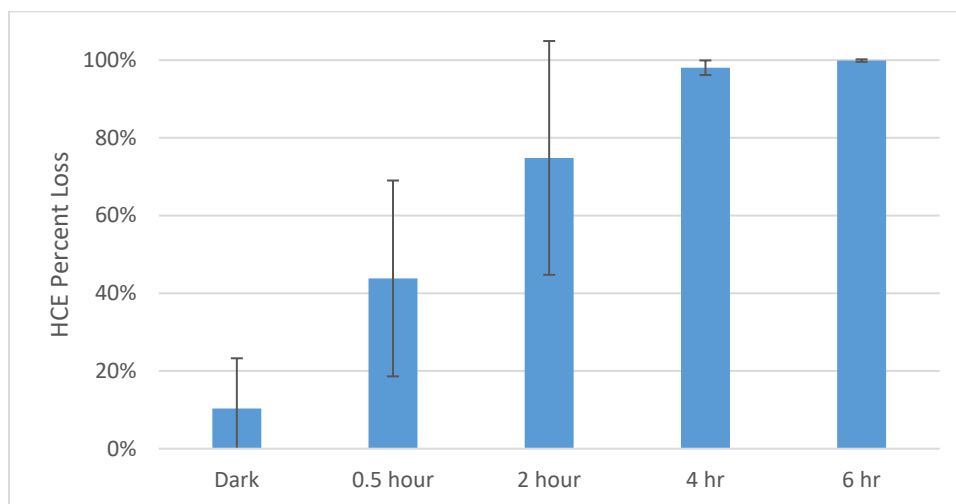


Figure 16. Average HCE percent loss over time from all testing.

Some daughter products were identified during testing. During test 1, all three HCE samples exposed to catalyst and visible light showed a component of degradation at 6.49 – 6.68 minutes into the chromatogram run. The NIST library search indicated the presence of Tetrachloroethylene (perchloroethylene or PCE) in the headspace (Figure 17). During test 2, none of the samples showed the presence of PCE or other degradation products. All samples of tests 3 and 4 again showed the presence of PCE. PCE was never detected in the dark or control samples. The average concentration of PCE over time is given in Table 5. The concentrations

Figure 1 displays the GC-MS analysis of the sample. The top left panel shows the total ion chromatogram (TIC) with peaks labeled by retention time. The top right panel shows the mass spectrum of the peak at 1.12 minutes, with a base peak at m/z 43. The bottom left panel shows the mass spectrum of the peak at 1.12 minutes, with a base peak at m/z 43. The bottom right panel shows the mass spectrum of the peak at 1.12 minutes, with a base peak at m/z 43.

Experiments	Average
1	0.0000
2	0.0000
3	0.0000
4	0.0000
5	0.0000
6	0.0000
7	0.0000
8	0.0000
9	0.0000
10	0.0000
11	0.0000
12	0.0000
13	0.0000
14	0.0000
15	0.0000
16	0.0000
17	0.0000
18	0.0000
19	0.0000
20	0.0000
21	0.0000
22	0.0000
23	0.0000
24	0.0000
25	0.0000
26	0.0000
27	0.0000
28	0.0000
29	0.0000
30	0.0000
31	0.0000
32	0.0000
33	0.0000
34	0.0000
35	0.0000
36	0.0000
37	0.0000
38	0.0000
39	0.0000
40	0.0000
41	0.0000
42	0.0000
43	0.0000
44	0.0000
45	0.0000
46	0.0000
47	0.0000
48	0.0000
49	0.0000
50	0.0000
51	0.0000
52	0.0000
53	0.0000
54	0.0000
55	0.0000
56	0.0000
57	0.0000
58	0.0000
59	0.0000
60	0.0000
61	0.0000
62	0.0000
63	0.0000
64	0.0000
65	0.0000
66	0.0000
67	0.0000
68	0.0000
69	0.0000
70	0.0000
71	0.0000
72	0.0000
73	0.0000
74	0.0000
75	0.0000
76	0.0000
77	0.0000
78	0.0000
79	0.0000
80	0.0000
81	0.0000
82	0.0000
83	0.0000
84	0.0000
85	0.0000
86	0.0000
87	0.0000
88	0.0000
89	0.0000
90	0.0000
91	0.0000
92	0.0000
93	0.0000
94	0.0000
95	0.0000
96	0.0000
97	0.0000
98	0.0000
99	0.0000
100	0.0000

Identify hydrochloric acid, a potential daughter product, and 3, 10 ml of Nanopure water was added (2-hour, 4-hour and 6-hour). These were vortexed to improve mixing and to stand in the dark for approximately 1 hour and filtered through a 0.45 μm filter. 25 μl of Nanopure water in a 5-ml Autosampler Vial for IC analysis (IC). The resulting solutions were analyzed for chloride ions. During Test 4 a separate set of samples (2-hour, 4-hour and 6-hour) to minimize the IC analysis.

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Chloride ions were identified in each of the vials where HCE was exposed to light and catalyst. The control and dark samples also had chloride ions, but in concentrations less than in the light + catalyst vials. There was no observable trend in the chloride ion concentration as would be expected from the HCE loss results. It was expected that the chloride ion concentration would increase from two to four hours and then be similar at four and six hours. However, this was not observed and thus the chloride ion measurements cannot be used to validate the HCE loss results or indicate that HCE is being fully mineralized.

5.5.2. 2-Chloroacetophenone PCO Degradation Results

As described in section 5.2 Methods, CN degradation testing was done by placing a small amount of solid CN in the vials and looking for the appearance of degradation products. After an initial degradation test, a NIST library search of the breakdown products identified in the chromatogram at retention times of 10.5 and 11.6 minutes give a reasonable probability for the presence of benzaldehyde (BA) (89.73%) and acetophenone (AP) (77.88%) respectively (Figure 18).

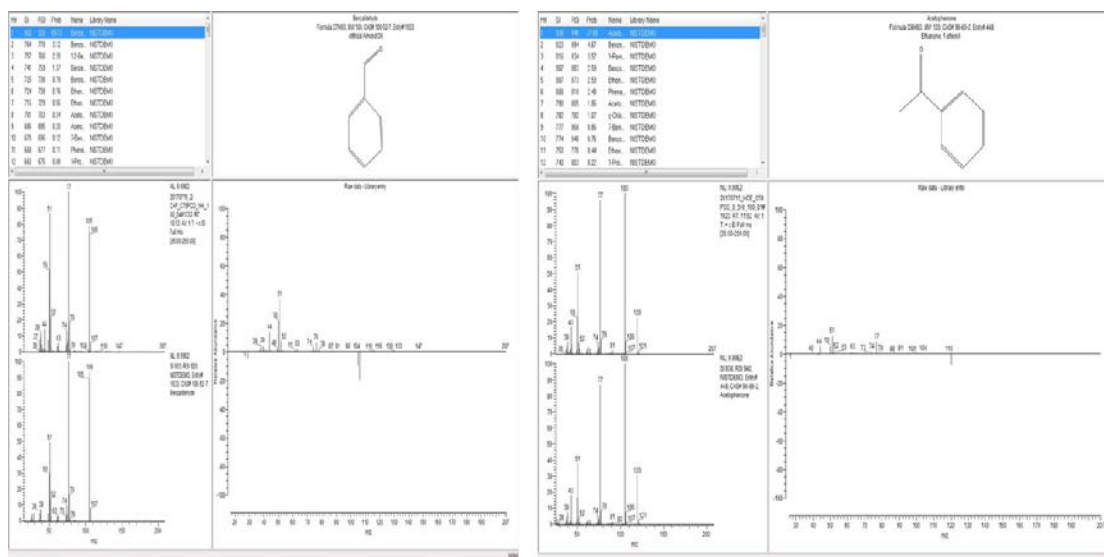


Figure 18. NIST library search of breakdown product BA observed at 10.5 minutes and AP observed at 11.6 minutes by GC-MS in the TIC

All fifteen samples containing Ag-doped Titania spotted coupons and exposed to visible light from 0.5 to 6 hours and the three dark samples showed the presence of AP as a degradation product. Relative quantitation of these peaks was performed and is shown in Figure 19. The concentration of degradation products could be seen to increase up to the 4 hour interval. A comparison between the 4- to 6-hour exposure periods showed no significant increase in the AP or BA concentration by this point. AP is observed in the dark samples indicating a non-light catalyzed source. It is not clear why the amount of BA plateaus at 4 hours, considering there is still CN in the system. If it were an intermediate, it is possible it would reach a steady state concentration where it was being produced and removed at the same rate. However, no other daughter products were identified to support this theory.

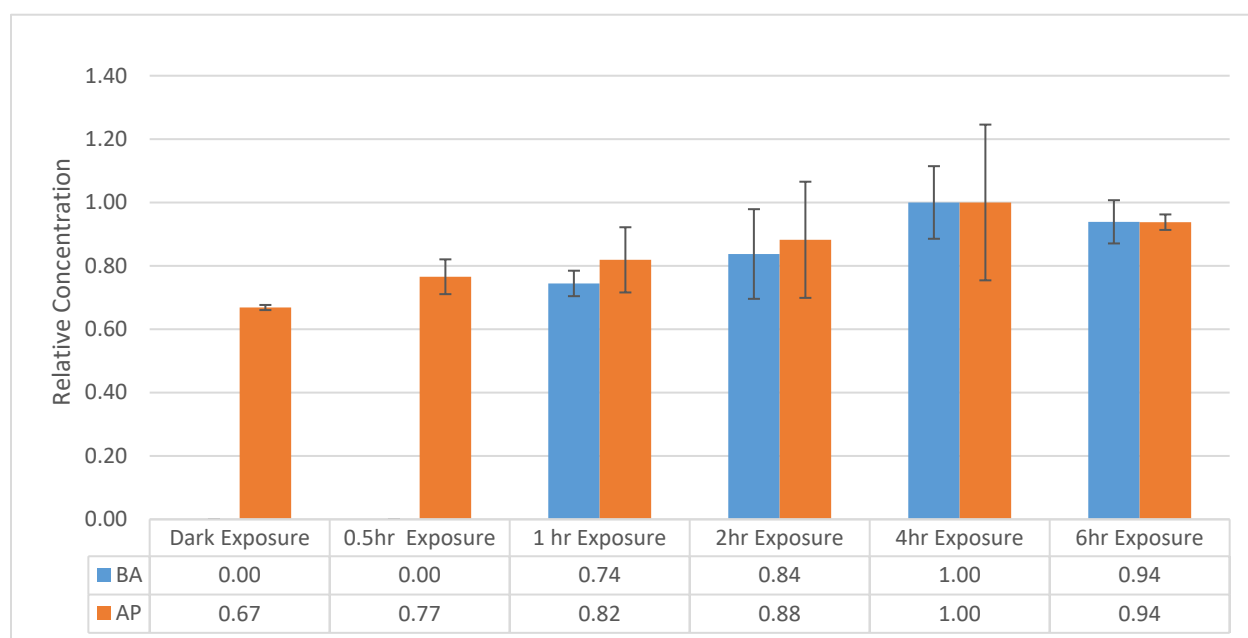


Figure 19. BA and AP degradation products showing an increase with Ag-Doped Titania under visible light exposure for 0.5-, 2-, 4- and 6- hours including Dark Exposure for 0.5 hours.

6. Analysis of Daughter Compounds

6.1. ZVMg degradation of TNT

No daughter products were detected during TNT degradation tests using ZVMg.

6.2. Selective Ion Exchange Resins for Demilitarization of AF-M315E

Ion chromatography showed that chloride ion had replaced the nitrate ion in AF-M315E indicating the product of this process is a chloride substituted dilute aqueous solution of AF-M315E. The other product is an ion exchange resin which tests showed could be regenerated and reused, while liberating the nitrate ion which can also be reused.

6.3. Visible light photocatalysis

6.4. Hexachloroethane

HCE photodegradation resulted in the formation of the observed degradation products PCE and HCl. The presence of HCl was inferred from the increased concentration of chloride ions present in the Nanopure water used to dissolve any HCl vapor present in the headspace following visible light exposure.

A possible reaction pathway could be with formation of a hydroxyl free radical on the catalyst surface from the moist air which could then remove chlorine atoms from HCE:

1. $\text{C}_2\text{Cl}_6 + 2\text{HO}\cdot \rightarrow \text{C}_2\text{Cl}_4 + 2\text{HCl} + \text{O}_2$ followed by
2. $\text{C}_2\text{Cl}_4 + 4\text{HO}\cdot \rightarrow 4\text{HCl} + 2\text{CO}_2$

Step 2 of the proposed pathway refers to the work by Yamazaki-Nishida in which they observed complete mineralization of trichloroethylene (TCE) to CO₂ and HCl at 64°C³⁹. However, this reaction was not observed in our testing.

PCE is mainly used as a cleaning solvent in dry cleaning and textile processing and in the manufacture of fluorocarbons. Exposure to this substance irritates the upper respiratory tract and eyes and causes neurological effects as well as kidney and liver damage. PCE is reasonably anticipated to be a human carcinogen as referenced in the PubChem Open chemistry Database (PubChem CID: 31373). This degradation product would have be treated with extreme caution.

6.5. 2-Chloroacetophenone

Acetophenone and benzaldehyde were identified by GC-MS as two degradation products formed during degradation testing of CN.

A possible reaction pathway would again be the formation of a hydroxyl free radical from the moist air which could then remove the chlorine atom to yield AP followed by the removal of the methyl group to form BA:

1. $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl} + 2\text{HO}\cdot \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl} + \text{O}_2$
2. $\text{C}_6\text{H}_5\text{COCH}_3 + 2\text{HO}\cdot \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{CH}_2\text{O} + \text{H}_2\text{O}$

AP is the simplest aromatic ketone and this colorless, viscous liquid is a precursor to useful resins and fragrances. Commercially significant resins are produced from treatment of AP with formaldehyde. The EPA has classified AP as a Group D, not classifiable as to human carcinogenicity as described in the PubChem (PubChem CID: 7410).

BA is an aromatic aldehyde used in cosmetics as a denaturant, a flavoring agent, and as a fragrance. It is a generally regarded as a safe (Generally Recognized as Safe) food additive in the United States and is accepted as a flavoring substance in the European Union as described in the PubChem (PubChem CID: 240).

The two degradation products observed in the photocatalytic degradation of CN would in this case be more benign and still useful.

7. Implementation Analysis

7.1. ZVMg

At this time, it is not clear if the TNT is being degraded by ZVMg or adsorbed onto a surface so there is no proposed implementation plans.

7.2. Demilitarization of AF-M315E

One of the issues with any commodity is that storage conditions must be maintained as specified by the manufacturer to guarantee quality control. This is especially true for any commodity used in aerospace applications, and the possible use of AF-M315E has introduced issues that were not issues with more traditional propellants. Specifically, AF-M315E must be stored in a climate-

controlled area, but due to its classification as a 1.3C explosive this can be difficult to maintain (depending upon the facility where it is to be stored). A NASA New Technology Report (NTR) was submitted for a possible further use of the ion exchange resins in conjunction with AF-M315E in an attempt to address this issue. NTR KSC-14115, “Method for Long-Term Storage of Explosive AF-M315E Green Propellant” postulates that the oxidizer (nitrate) component of the propellant can be removed prior to storage (removing the 1.3C explosive designation). The nitrate ion could be re-introduced when the propellant is ready for use. This could help to reduce both storage and transport costs of AF-M315E, as well as serving to increase safety of the stored “demilitarized” propellant. This concept is simply an outgrowth of the current “demilitarization and re-use” research, although testing will be necessary to confirm its viability. One possible issue is that the regeneration process will increase the amount of sodium ions in the propellant, however none of the current Acceptance/Qualification testing or the proposed Mil-Spec Performance Specifications for AF-M315E require testing for sodium. Figure 20 shows a schematic of a 2 bed continuous flow system. This system allows for continuous operation by having one bed regenerate while the other bed is operating. Future work in this area should include scaling to a two bed system that allows continuous nitrate extraction and bed regeneration, and attempting to reintroduce the nitrate ion thus reconstituting the propellant.

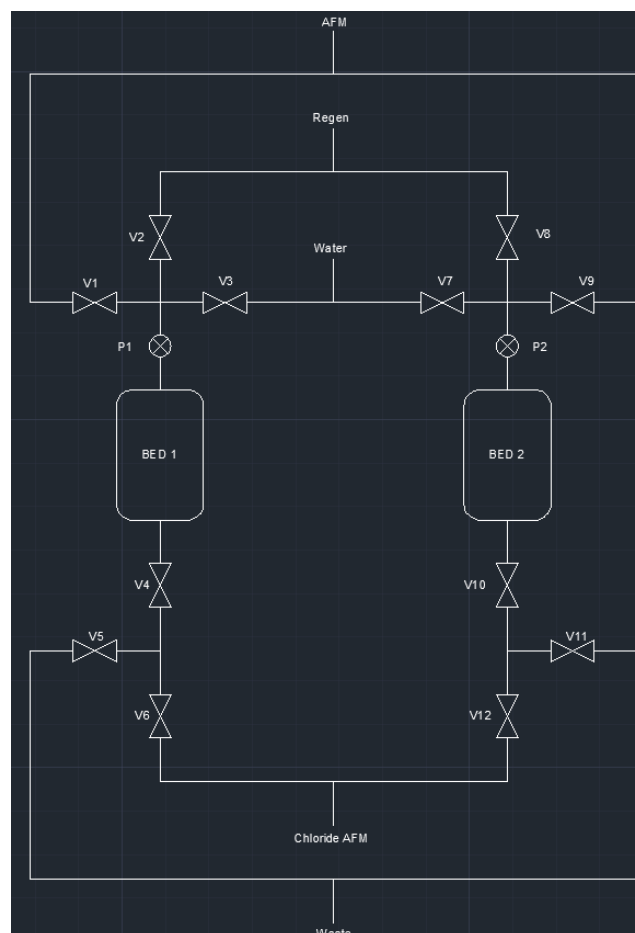
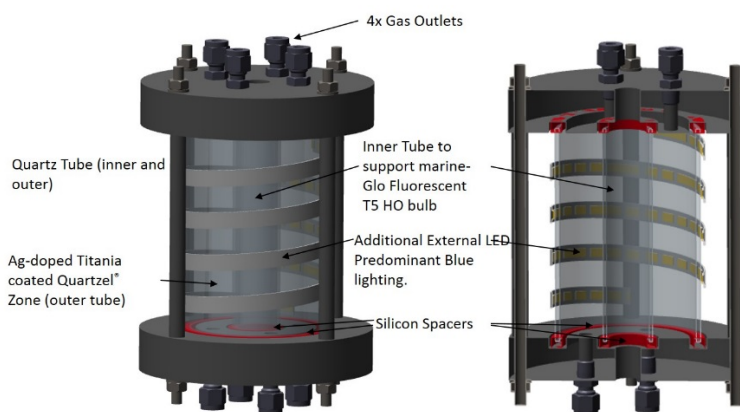


Figure 20. Updated 2-bed continuous flow-through reactor system.

7.3. Visible light photocatalysis

A higher loading of the Ag-doped catalyst on a matrix such as Quartzel® wool placed within a flow through annular style reactor would improve the processing rate. Figure 21 shows the design of a reactor that has been built at Kennedy Space Center. The HCE and CN vapor would be allowed to diffuse through the Quartzel® resulting in potentially improved reaction times due to increased catalyst surface area and light exposure.



Courtesy of Annie Meier

Figure 21. PCO Flow-through reactor design.

8. Performance Analysis

Table 6 shows metrics for each technology as included in the project proposal.

Table 6. Performance objectives that will be used to downselect technologies for future development.

Technology	Metric	Data Required	Measurement Technique	Target Success Criteria
Quantitative Performance Objectives				
ZVMg	Destruction of target compound	Compound concentrations before and after treatment	Analytical measurement	Destroy 99% of target compound
	Daughter products	Identification of daughter products Quantification of daughter products if standards are available	Analytical measurement	Daughter products are recoverable and reusable, or disposable in a waste stream less hazardous than the parent compound.
Ion Exchange Resins	Nitrate concentration in AF-M315E	Nitrate concentration before and after ion exchange	Analytical measurement	Remove 99% of nitrate anion
	Reuse of ion exchange resin	Multiple exchange resin tests.	Analytical measurement	Meet 99% removal of nitrate anion with resin that has been regenerated
Visible Light Photocatalysis	Destruction of target compound	Compound concentrations before and after treatment	Analytical measurement	Destroy 99% of target compound
	Daughter products	Identification of daughter products Quantification of daughter products if standards are available	Analytical measurement	Daughter products are recoverable and reusable, or disposable in a waste stream less hazardous than the parent compound.

Technology	Metric	Data Required	Measurement Technique	Target Success Criteria
Qualitative Performance Objectives				
All	Scale up potential	Processing rate	Analytical measurement and calculation	Compare processing rate determined in this study with other processes that have been successfully scaled up
	Safety	Safety review and process observations	Observation	Process can be carried out safely

8.1. ZVMg Technology

Although the target compound was removed, no daughter products were identified leaving uncertainty as to the fate of the TNT. Therefore, the ZVMg technology did not meet the metrics and no future work is proposed.

8.2. Demilitarization of AF-M315E

Tests 1 and 3 both showed that nitrates could be removed to levels below detection limits. Test 1 used a fresh resin and test 3 used a regenerated resin. This technology met all metrics, although the regeneration process needs improvement so it is more consistent.

8.3. Visible Light Photocatalysis

Greater than 99% destruction of HCE was observed. However, the observed daughter product perchloroethylene, C_2Cl_4 , is a probable human carcinogen is potentially more hazardous than the parent compound (HCE). CN degradation tests showed degradation was possible and the observed daughter products are not harmful. In neither case was full mineralization confirmed. This technology met some but not all metrics and therefore no future work is proposed.

8.4. Qualitative Performance Objectives

Processing rate: Tests 1 and 3 were both fully successful so they can be used to calculate the processing rate. Test 1 used a flow rate of 77 ml/min and test 3 was about half, 38.8 ml/min. Accounting for the 1:500 dilution of AF-M315E in water before processing, this corresponds to a maximum processing rate of 9 ml/hr of pure AF-M315E using a resin bed of 154 ml, containing 153 g. Using a simple linear scaling of 100 to get to 1 l/hr, the bed would be 15 liters. Theoretically, the 154 ml bed should have been able to process 12.4 ml of pure AF-M315E, but in these tests only the equivalent of 5 ml of pure propellant was processed before breakthrough. Further optimization should lead to faster processing rates and/or smaller bed volumes. If implemented in a continuous as described in section 7.2, then the time of regeneration is actually the slow step. In these tests, AF-M315E processing took 30 – 60 minutes while bed regeneration took 120 minutes.

Safety: No safety issues occurred or would be anticipated in future work. Before starting laboratory work for this project, the proposed process went through a full safety review.

8.5. Future work

The following tasks are proposed to further advance this technology.

- Design and build a scaled up system with multiple beds for continuous processing of AF-M315E and ion exchange resin bed regeneration. Within this task, optimization of the AF-M315E processing rate and the bed regeneration time would be performed.
- Evaluate stability of chloride containing daughter products.
- Attempt to reconstitute the propellant by exchanging chloride for nitrate. Then, the water must be removed from reconstituted propellant. The reconstituted propellant would need to be evaluated by the Air Force Research Lab that makes it to determine if it has the same performance as the fresh material.

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10. Appendix: PCO GC-MS Data

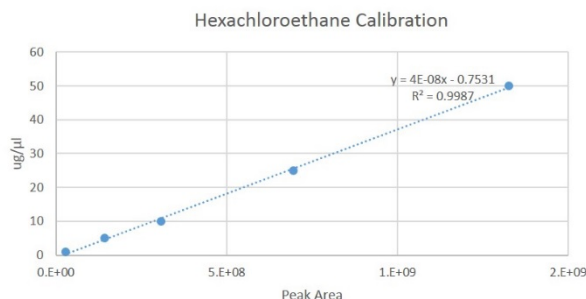
HCE PCO Test Data

TEST 1 – Initial half-hour interval PCO exposure test.

Table 7. Table of HCE Analysis with Calibration Data for 0.5 hour Visible light exposure Test.

ID	RT	Area	ng/ul	nanomoles HCE, assuming 1 ul injection
HCE_1ppm_01	11.02	27889722.00	1	0.00
HCE_5ppm_02	11.02	141961309.00	5	0.02
HCE_10ppm_03	11.02	307817047.00	10	0.04
HCE_25ppm_04	11.02	695536722.00	25	0.11
HCE_50ppm_05	11.02	1324962226.00	50	0.21
HCE_100ppm_06	11.03	1930639622.00	100	0.42

3.793E-08 slope
-0.753 intercept



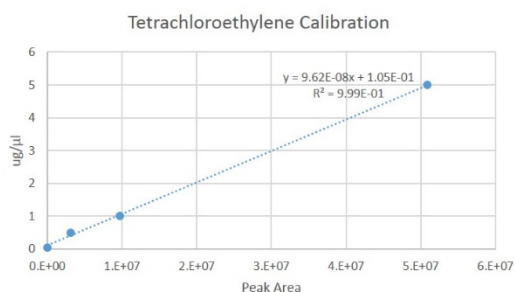
Analysis of Vapor phase HCE in 40ml VOA Vials:

Filename	Date	Time	inj vol (mL)	Component	RT	HCE Area	ng on column	ppm	Comment
HCE_10ppm_100_01	2/23/2017	15:05:00	0.001	HCE	11.03	276791498.0	11.3	---	Check Standard
Hdsp_10ppm_100_01	2/23/2017	15:36:00	0.1	HCE	11.80	74640038.0	3.6	3.7	HCE Vapor only
Hdsp_10ppm_100_02	2/23/2017	15:57:00	0.1	HCE	11.71	79063720.0	3.8	3.8	HCE Vapor only
Hdsp_10ppm_100_03	2/23/2017	16:22:00	0.1	HCE	11.28	69808358.0	3.4	3.5	HCE Vapor only
HCE_C127_DRK_10ppm_100_04	2/23/2017	16:43:00	0.1	HCE	11.37	65663387.0	3.2	3.3	HCE + Ag Doped Titania Coupon
HCE_C36_DRK_10ppm_100_05	2/23/2017	17:34:00	0.1	HCE	11.31	44345828.0	2.4	2.5	HCE + Ag Doped Titania Coupon
HCE_C90_DRK_10ppm_100_06	2/23/2017	18:27:00	0.1	HCE	11.49	54241712.0	2.8	2.9	HCE + Ag Doped Titania Coupon
HCE_C16_PCO_10ppm_100_01	2/23/2017	17:09:00	0.1	HCE	11.36	60085058.0	3.0	3.1	HCE + Ag Doped Titania Coupon Exposed to Visible light
HCE_C142_PCO_10ppm_100_02	2/23/2017	18:00:00	0.1	HCE	11.23	15013477.0	1.3	1.3	HCE + Ag Doped Titania Coupon Exposed to Visible light
HCE_C21_PCO_10ppm_100_03	2/23/2017	18:55:00	0.1	HCE	11.33	24393203.0	1.7	1.7	HCE + Ag Doped Titania Coupon Exposed to Visible light

Table 8. Table of PCE degradation product Analysis with Calibration data for 0.5 hour visible light exposure Test.

ID	RT	Area	ng/ul	nanomoles HCE, assuming 1 ul injection
TCE_0.05ppm_01	5.87	34301	0.05	0.00
TCE_0.5ppm_02	5.88	3074652.0	0.5	0.00
TCE_1ppm_03	5.87	9746804.0	1	0.01
TCE_5ppm_04	5.86	50877353.0	5	0.03
TCE_10ppm_05	5.86	181214953.0	10	0.06

9.616E-08 slope
0.10533 intercept



					Breakdown Product				
					Component	RT	Area	ng on column	ppm
HCE_C16_PCO_10ppm_100_01	2/23/2017	17:09:00	0.1	TCE	11.36	1962771.0	0.3	0.4	HCE + Ag Doped Titania Coupon Exposed to Visible light
HCE_C142_PCO_10ppm_100_02	2/23/2017	18:00:00	0.1	TCE	11.23	11647644.0	1.2	1.8	HCE + Ag Doped Titania Coupon Exposed to Visible light
HCE_C21_PCO_10ppm_100_03	2/23/2017	18:55:00	0.1	TCE	11.33	9193697.0	1.0	1.4	HCE + Ag Doped Titania Coupon Exposed to Visible light

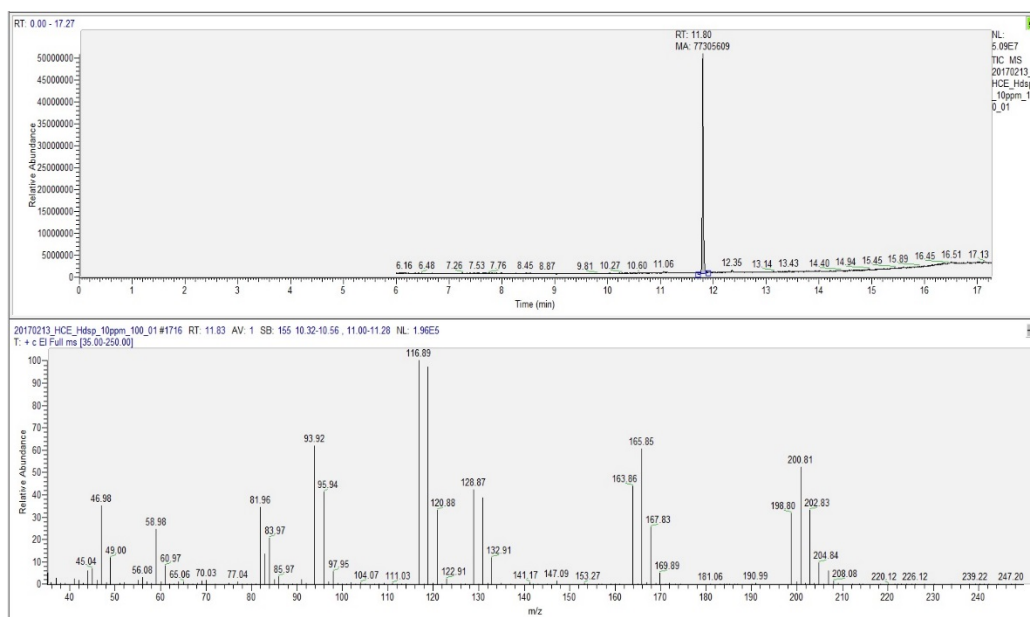


Figure 22. HCE vapor in 40-ml vial TIC + Mass Spectrum.

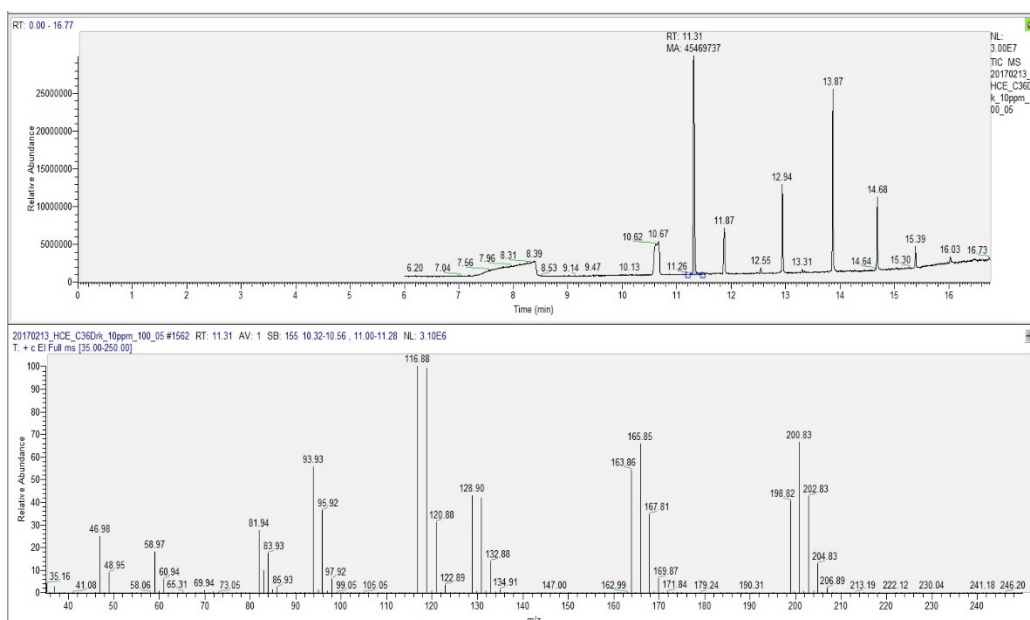


Figure 23. HCE vapor in 40-ml vial w/ Ag-doped TiO₂ coupon held in the Dark TIC + Mass Spectrum.

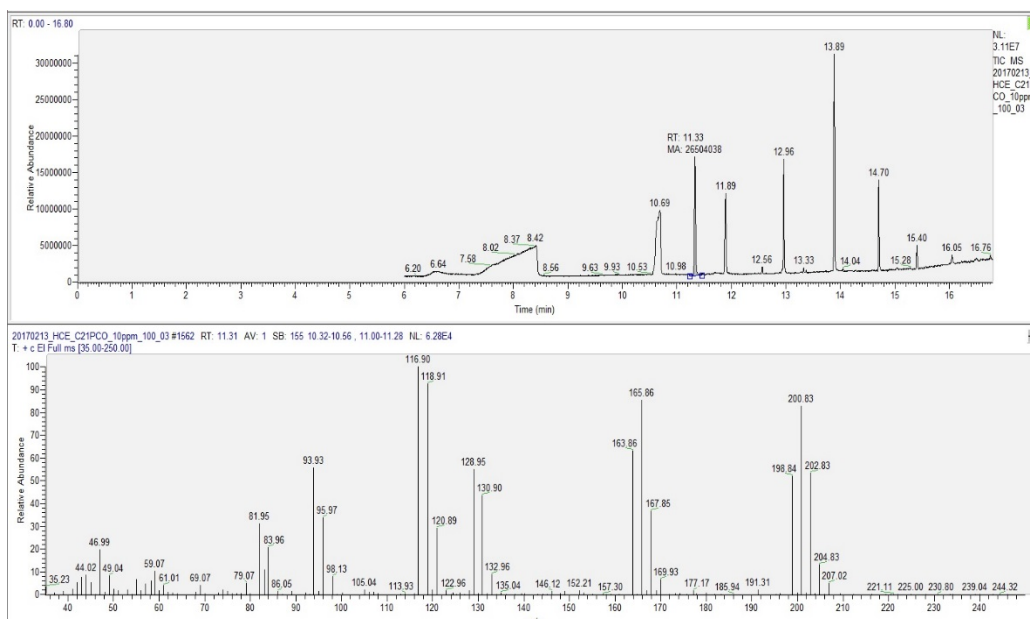


Figure 24. HCE vapor in 40-ml vial w/ Ag-doped TiO₂ coupon exposed to visible light TIC + Mass Spectrum.

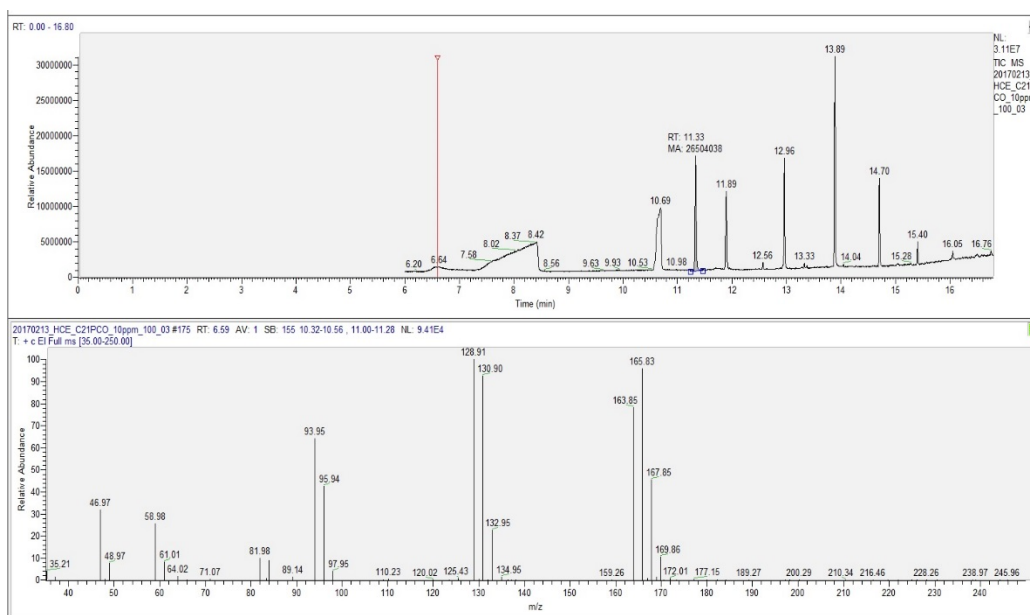


Figure 25. HCE vapor in 40-ml vial w/ Ag-doped TiO₂ coupon exposed to visible light showing breakdown product TIC + Mass Spectrum.

TEST 2 – Two-hour interval PCO exposure test.

Table 9. Table of HCE Analysis with Calibration Data for 2 hour Visible light exposure Test.

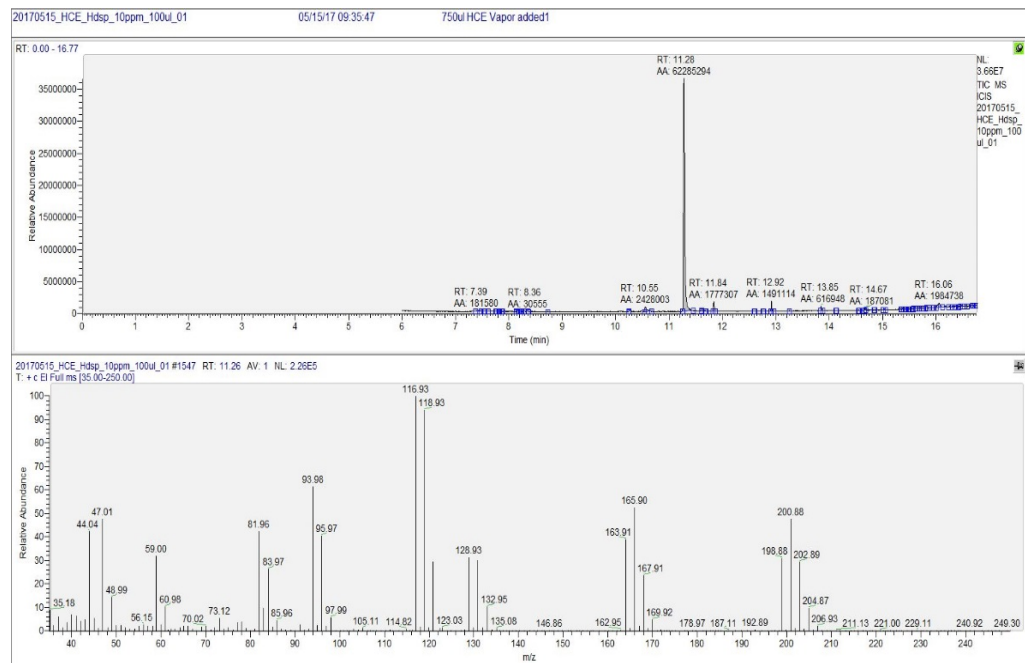
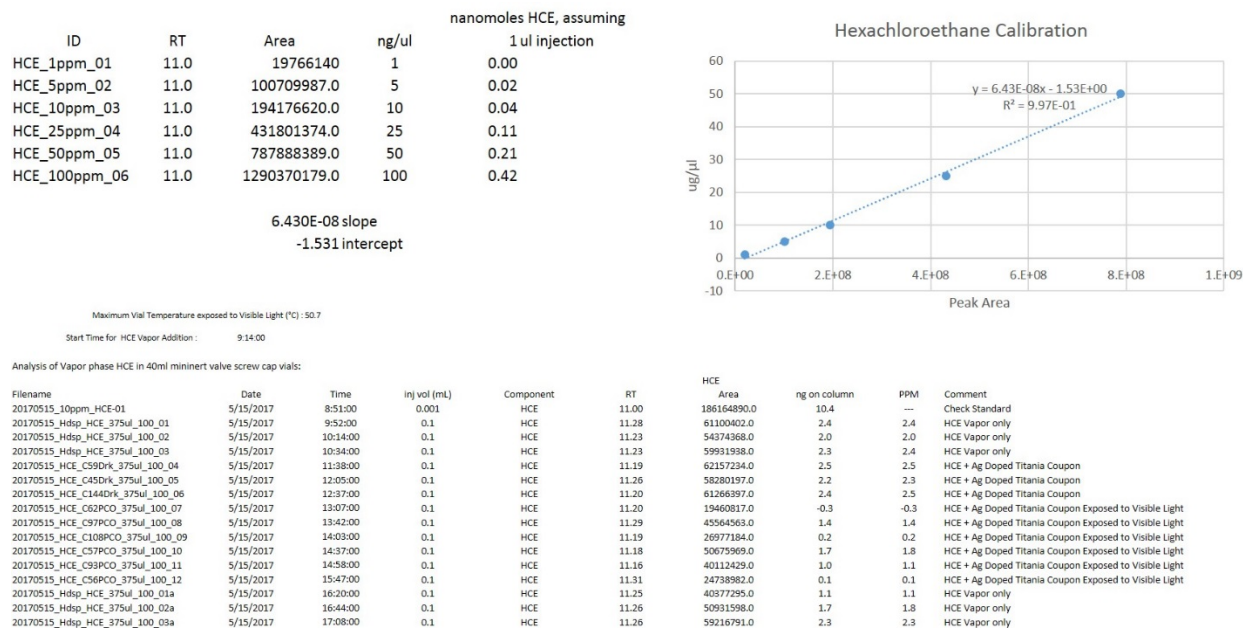


Figure 26. HCE vapor in 40-ml Mininert Valve vial TIC + Mass Spectrum.

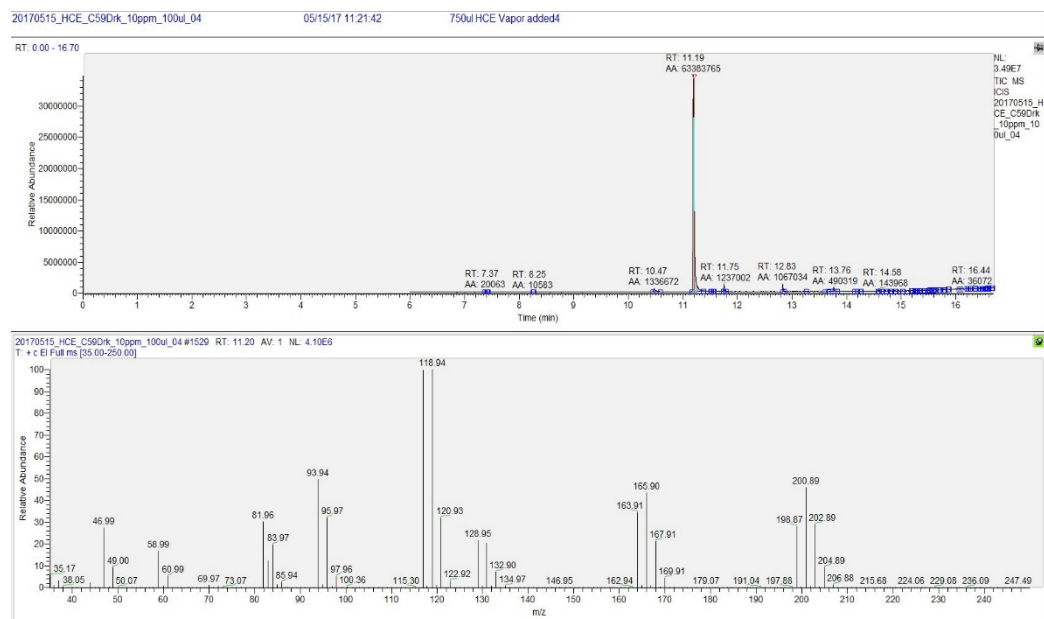


Figure 27. HCE vapor in 40-ml Mininert valve vial w/ Ag-doped TiO₂ coupon held in the Dark TIC + Mass Spectrum.

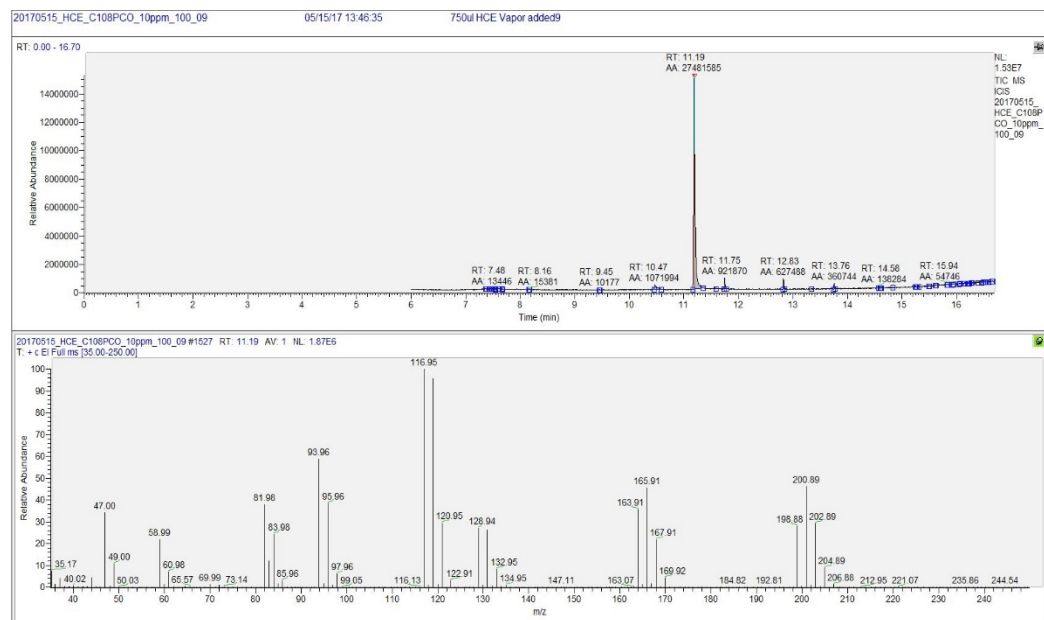


Figure 28. Reduction of HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light showing a reduction in the HCE response TIC + Mass Spectrum.

TEST 3 – Four- and Six-hour interval PCO exposure test.

Table 10. Table of HCE Analysis with Calibration Data for 4 and 6 hour Visible light exposure Test.

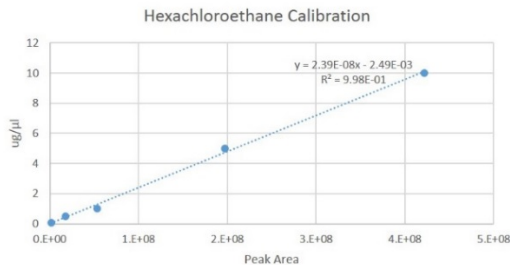
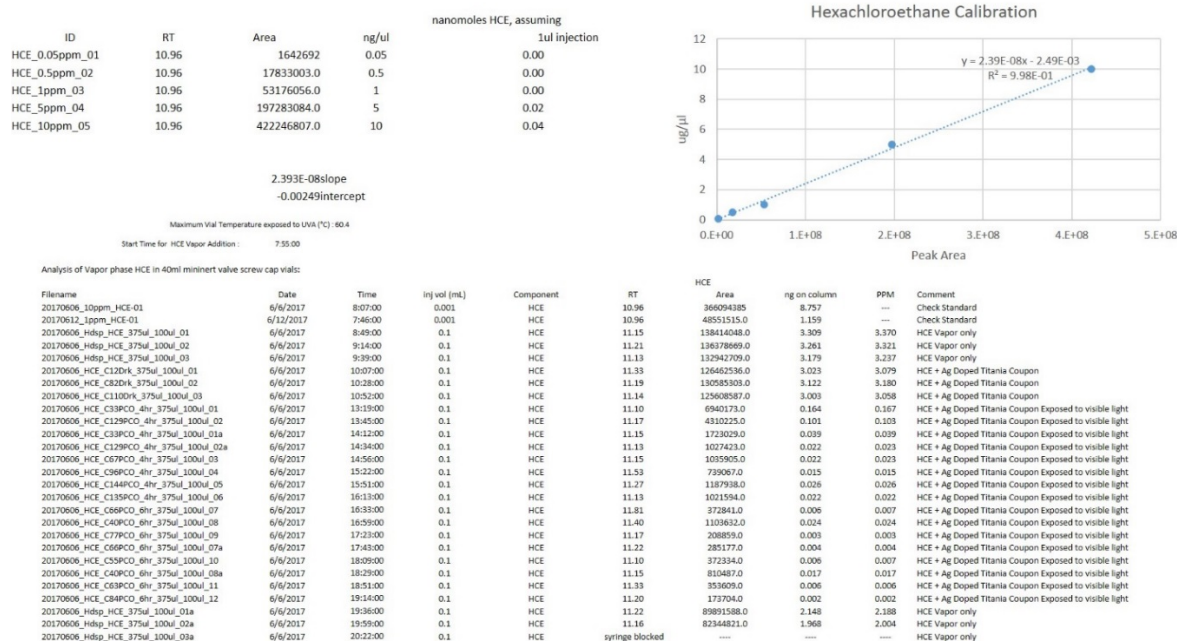
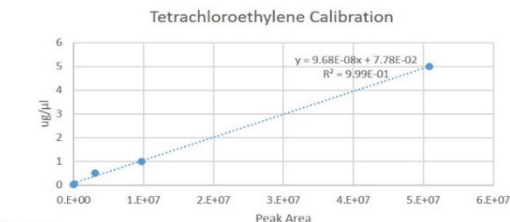
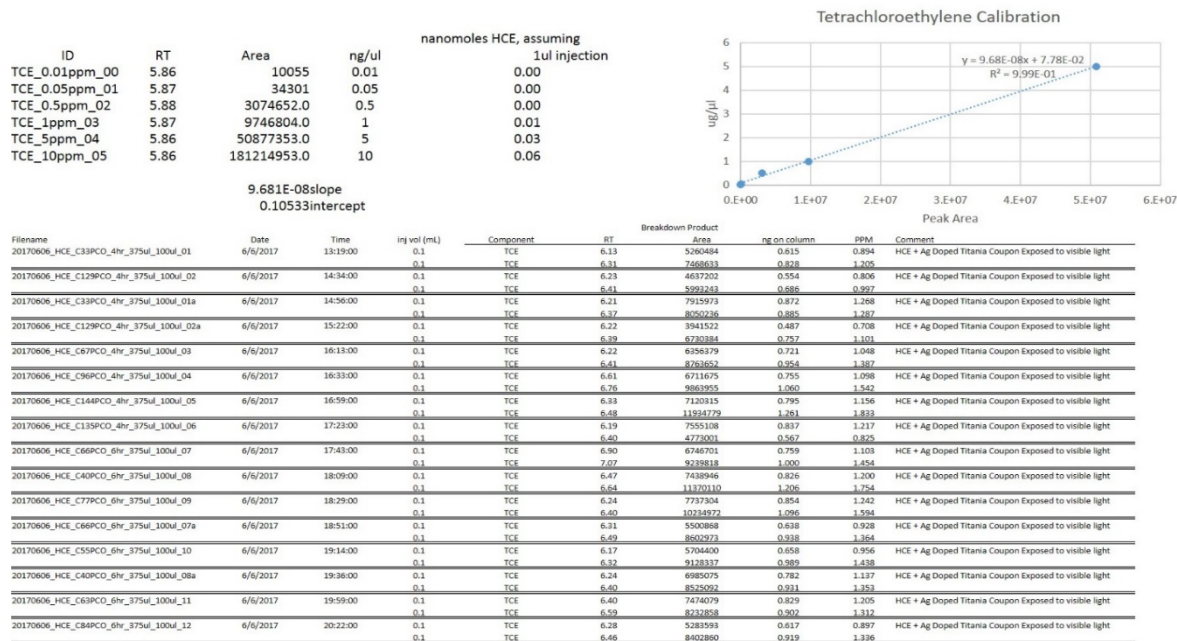


Table 11. Table of PCE Analysis with Calibration Data for 4 and 6 hour Visible light exposure Test.



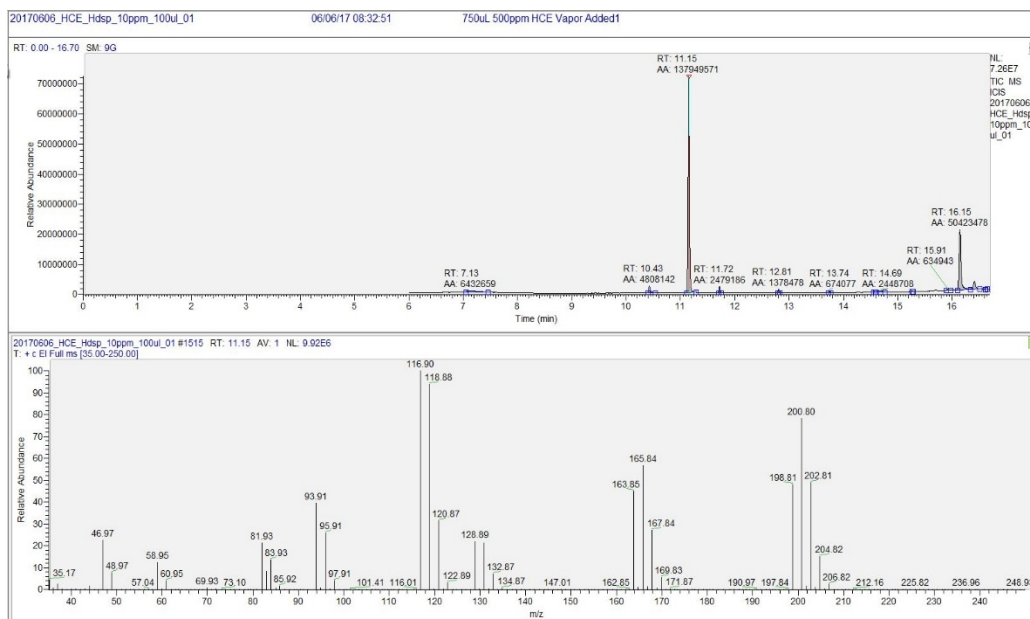


Figure 29. HCE vapor in 40-ml Mininert Valve vial TIC + Mass Spectrum.

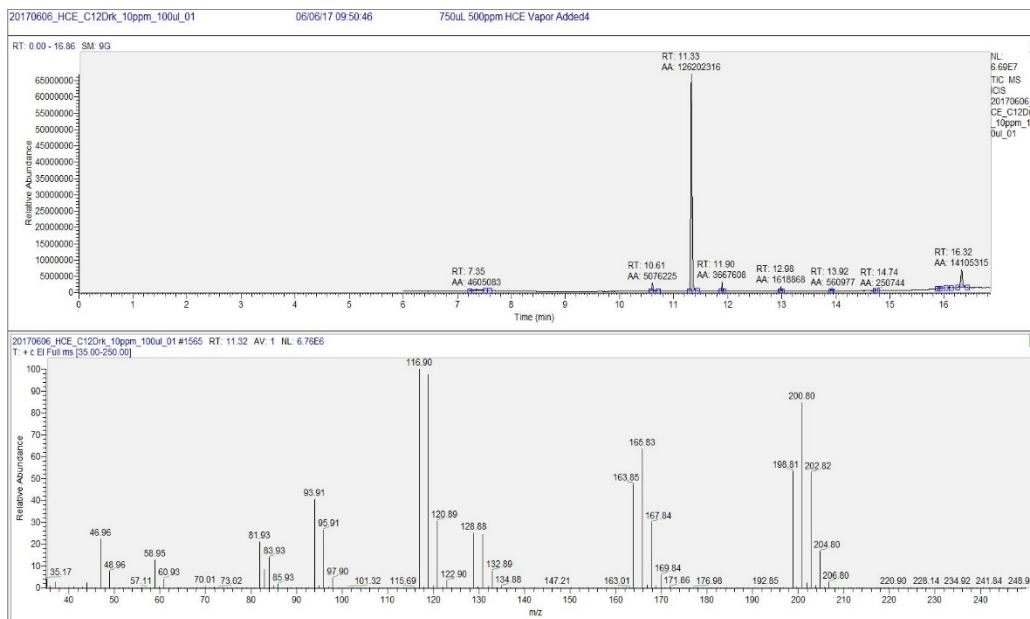


Figure 30. HCE vapor in 40-ml Mininert valve vial w/ Ag-doped TiO₂ coupon held in the Dark TIC + Mass Spectrum.

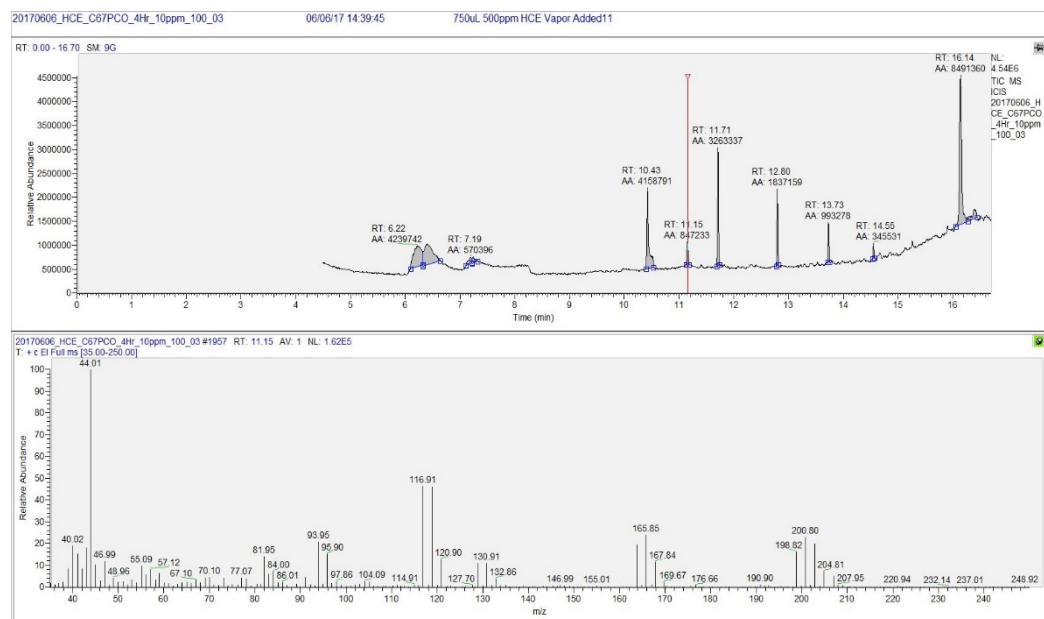


Figure 31. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO_2 coupon exposed to visible light for 4 hours showing a reduction in the HCE response TIC + Mass Spectrum.

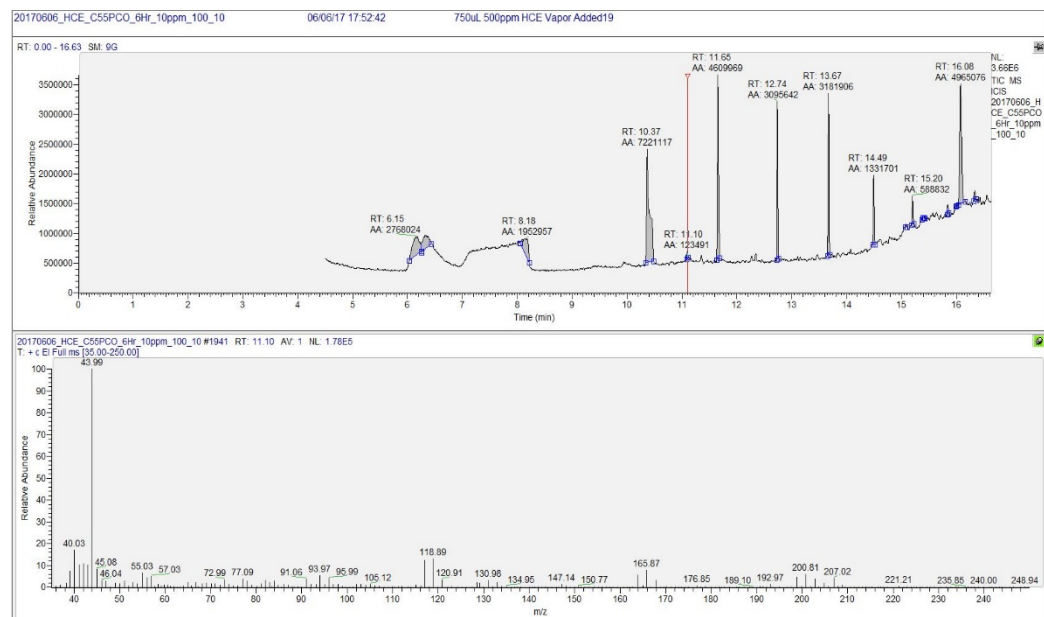


Figure 32. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO_2 coupon exposed to visible light for 6 hours showing a further reduction in the HCE response TIC + Mass Spectrum.

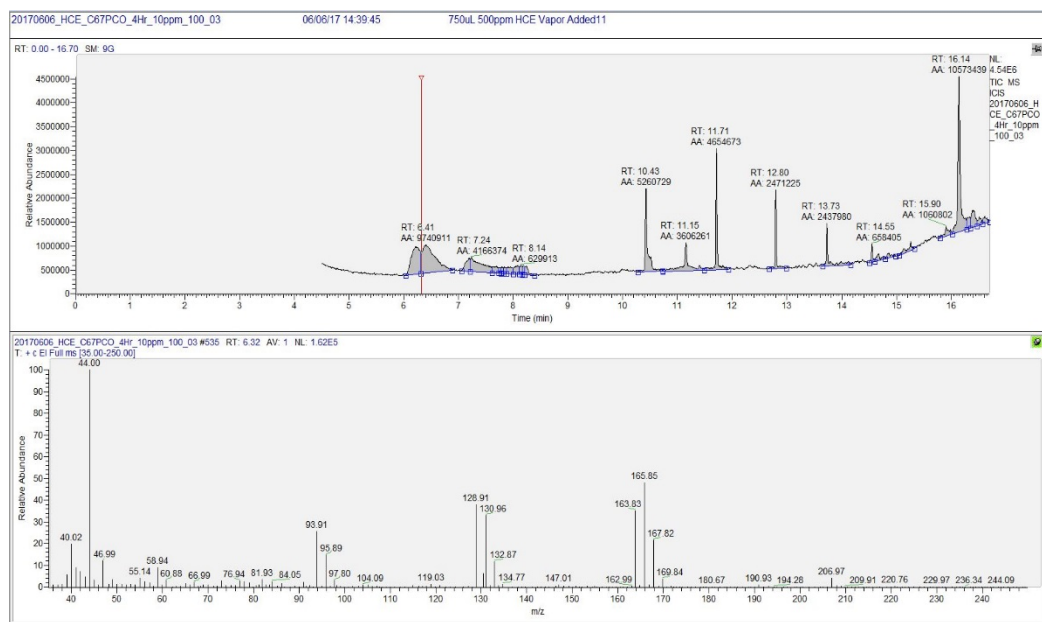


Figure 33. PCE vapor present following exposure of HCE to visible light for 4 hours TIC + Mass Spectrum.

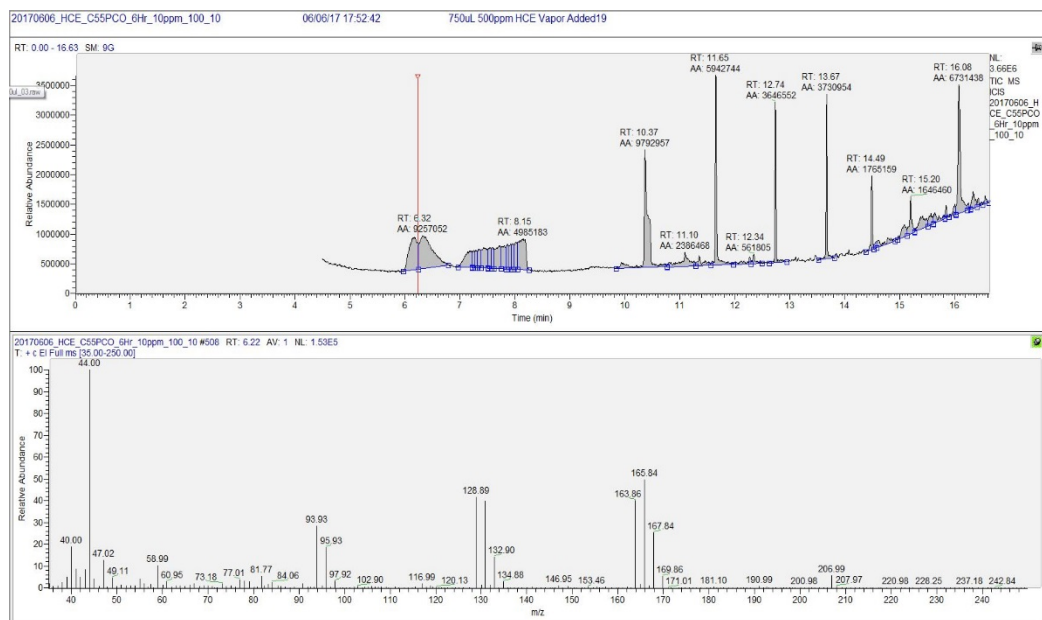


Figure 34. PCE showing no significant increase in response after exposure of HCE to visible light for 6 hours TIC + Mass Spectrum.

TEST 4 – Two-, Four- and Six-hour interval PCO exposure test.

Table 12. Table of HCE Analysis with Calibration Data for 2, 4 and 6 hour Visible light exposure Test.

ID	RT	Area	ng/ul	nanomoles HCE, assuming 1ul injection
HCE_0.05ppm_01	10.95	629652	0.05	0.00
HCE_0.5ppm_02	10.95	7096402.0	0.5	0.00
HCE_1ppm_03	10.94	20199517.0	1	0.00
HCE_5ppm_04	10.94	103468603.0	5	0.02
HCE_10ppm_05	10.94	187403032.0	10	0.04

5.239E-08slope
-0.03033intercept

Maximum Vial Temperature exposed to UVA (°C): 45.9

Start Time for HCE Vapor Addition : 8:02:00

Analysis of Vapor phase HCE in 40ml mininert valve screw cap vials:

Filename	Date	Time	inj vol (mL)	Component	RT	Area	ng on column	PPM	Comment
20170630_1ppm_HCE-02	6/30/2017	8:17:00	0.001	HCE	10.94	19945195.0	1.015	---	Check Standard-Prep'd 6/19/17
20170630_1ppm_HCE-03	6/30/2017	8:38:00	0.001	HCE	10.94	18033846.0	0.914	---	Check Standard prep'd 6/12/17
20170630_1ppm_TCE-04	6/30/2017	8:59:00	0.001	HCE	5.87	9866090.0	1.054	---	Check Standard prep'd 6/26/17
20170630_HdSp_HCE_1ml_100ul_01	6/30/2017	9:28:00	0.1	HCE	11.12	150968728.0	7.879	8.024	HCE Vapor only
20170630_HdSp_HCE_1ml_100ul_02	6/30/2017	9:51:00	0.1	HCE	11.10	123818792.0	6.456	6.575	HCE Vapor only
20170630_HdSp_HCE_1ml_100ul_03a	6/30/2017	10:35:00	0.1	HCE	11.09	110388423.0	5.753	5.859	HCE Vapor only
20170630_HCE_C55Drk_1ml_100ul_01	6/30/2017	10:57:00	0.1	HCE	11.09	104468029.0	5.443	5.543	HCE + Ag Doped Titania Coupon
20170630_HCE_C63Drk_1ml_100ul_02	6/30/2017	11:26:00	0.1	HCE	11.11	98510395.0	5.131	5.225	HCE + Ag Doped Titania Coupon
20170630_HCE_C40Drk_1ml_100ul_03	6/30/2017	11:55:00	0.1	HCE	11.12	104308969.0	5.434	5.534	HCE + Ag Doped Titania Coupon
20170630_HCE_C118PCO_2hr_1ml_100ul_01	6/30/2017	12:21:00	0.1	HCE	11.11	17867566.0	0.906	0.922	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C81PCO_2hr_1ml_100ul_02	6/30/2017	13:06:00	0.1	HCE	11.10	17742897.0	0.899	0.916	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C56PCO_2hr_1ml_100ul_03	6/30/2017	13:31:00	0.1	HCE	11.08	17059746.0	0.863	0.879	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C95PCO_2hr_1ml_100ul_06	6/30/2017	13:53:00	0.1	HCE	11.17	3613947.0	0.159	0.162	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C96PCO_4hr_1ml_100ul_07	6/30/2017	14:19:00	0.1	HCE	11.09	1616075.0	0.054	0.055	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C121PCO_4hr_1ml_100ul_08	6/30/2017	14:45:00	0.1	HCE	11.10	7899241.0	0.384	0.391	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C45PCO_6hr_1ml_100ul_11	6/30/2017	15:28:00	0.1	HCE	11.13	355197.0	-0.012	-0.012	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C76PCO_6hr_1ml_100ul_12	6/30/2017	16:11:00	0.1	HCE	11.16	232535.0	-0.018	-0.018	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C97PCO_6hr_1ml_100ul_13	6/30/2017	16:36:00	0.1	HCE	11.11	113960.0	-0.024	-0.025	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HdSp_HCE_1ml_100ul_01a	6/30/2017	16:58:00	0.1	HCE	11.10	90044871.0	4.687	4.773	HCE Vapor only
20170630_HdSp_HCE_1ml_100ul_02a	6/30/2017	17:24:00	0.1	HCE	11.09	68831469.0	3.576	3.642	HCE Vapor only
20170630_HdSp_HCE_1ml_100ul_03a	6/30/2017	17:46:00	0.1	HCE	11.25	66810324.0	3.470	3.534	HCE Vapor only

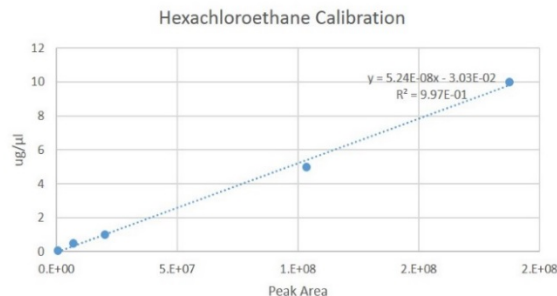
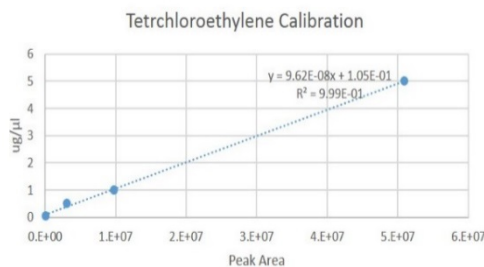


Table 13. Table of PCE Analysis with Calibration Data for 2, 4 and 6 hour Visible light exposure Test.

ID	RT	Area	ng/ul	nanomoles HCE, assuming 1ul injection
TCE_0.05ppm_01	5.87	34301	0.05	0.00
TCE_0.5ppm_02	5.88	3074652.0	0.5	0.00
TCE_1ppm_03	5.87	9746804.0	1	0.00
TCE_5ppm_04	5.86	50877353.0	5	0.02
TCE_10ppm_05	5.86	181214953.0	10	0.04

9.616E-08slope
0.10533intercept



Breakdown Product

Filename	Date	Time	inj vol (mL)	Component	RT	Area	ng on column	PPM	Comment
20170630_HCE_C118PCO_2hr_1ml_100ul_01	6/30/2017	12:21:00	0.1	TCE	6.45	1450729	0.245	0.356	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C81PCO_2hr_1ml_100ul_02	6/30/2017	13:06:00	0.1	TCE	6.20	1468003	0.246	0.358	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C56PCO_2hr_1ml_100ul_03	6/30/2017	13:31:00	0.1	TCE	6.41	8177509	0.892	1.296	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C95PCO_2hr_1ml_100ul_06	6/30/2017	13:53:00	0.1	TCE	6.41	5531701	0.637	0.927	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C96PCO_4hr_1ml_100ul_07	6/30/2017	14:19:00	0.1	TCE	6.32	6386859	0.719	1.046	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C121PCO_4hr_1ml_100ul_08	6/30/2017	14:45:00	0.1	TCE	6.17	4871165	0.574	0.834	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C45PCO_6hr_1ml_100ul_11	6/30/2017	15:28:00	0.1	TCE	6.33	6319012	0.713	1.037	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C76PCO_6hr_1ml_100ul_12	6/30/2017	16:11:00	0.1	TCE	6.14	7624085	0.838	1.219	HCE + Ag Doped Titania Coupon Exposed to visible light
20170630_HCE_C97PCO_6hr_1ml_100ul_13	6/30/2017	16:36:00	0.1	TCE	6.34	5591242	0.643	0.935	HCE + Ag Doped Titania Coupon Exposed to visible light

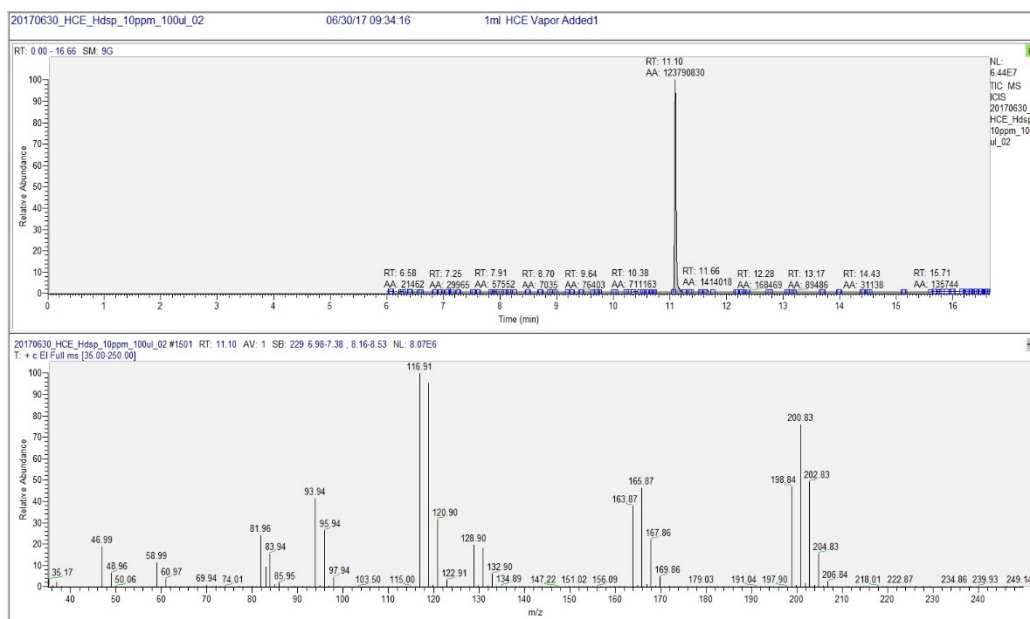


Figure 35. HCE vapor in 40-ml Mininert Valve vial TIC + Mass Spectrum.

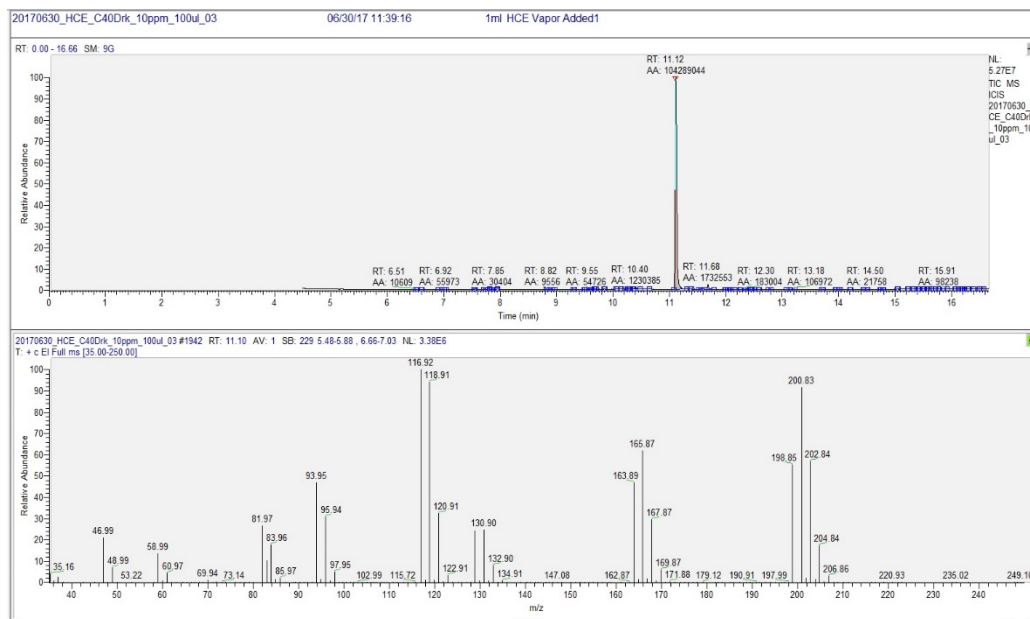


Figure 36. HCE vapor in 40-ml Mininert valve vial w/ Ag-doped TiO₂ coupon held in the Dark TIC + Mass Spectrum.

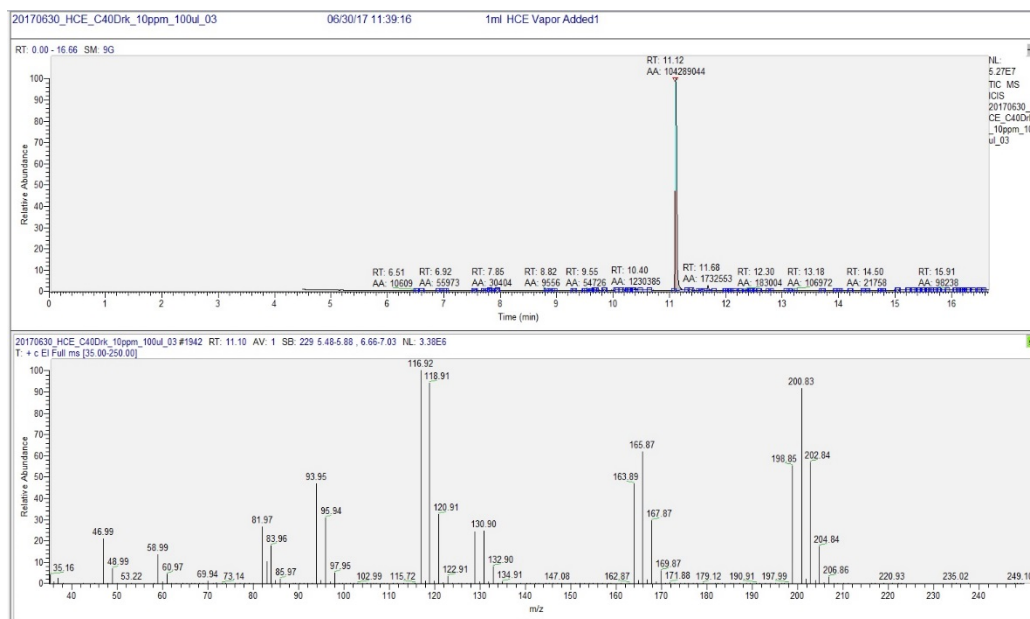


Figure 37. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO_2 coupon exposed to UVA for 2 hours light showing a reduction in the HCE response TIC + Mass Spectrum.

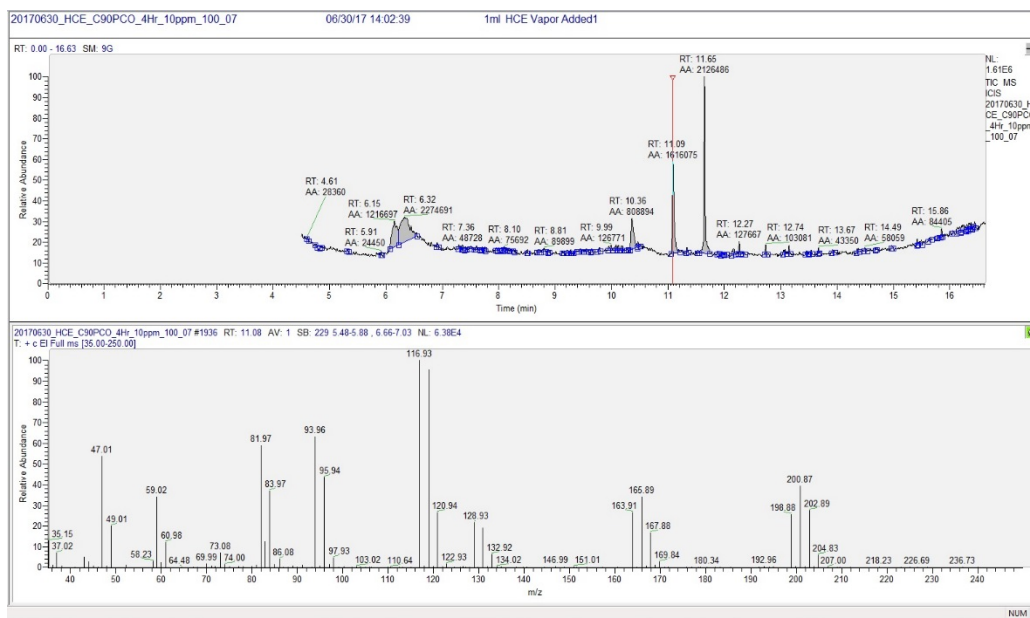


Figure 38. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO_2 coupon exposed to visible light for 4 hours showing a further reduction in the HCE response TIC + Mass Spectrum.

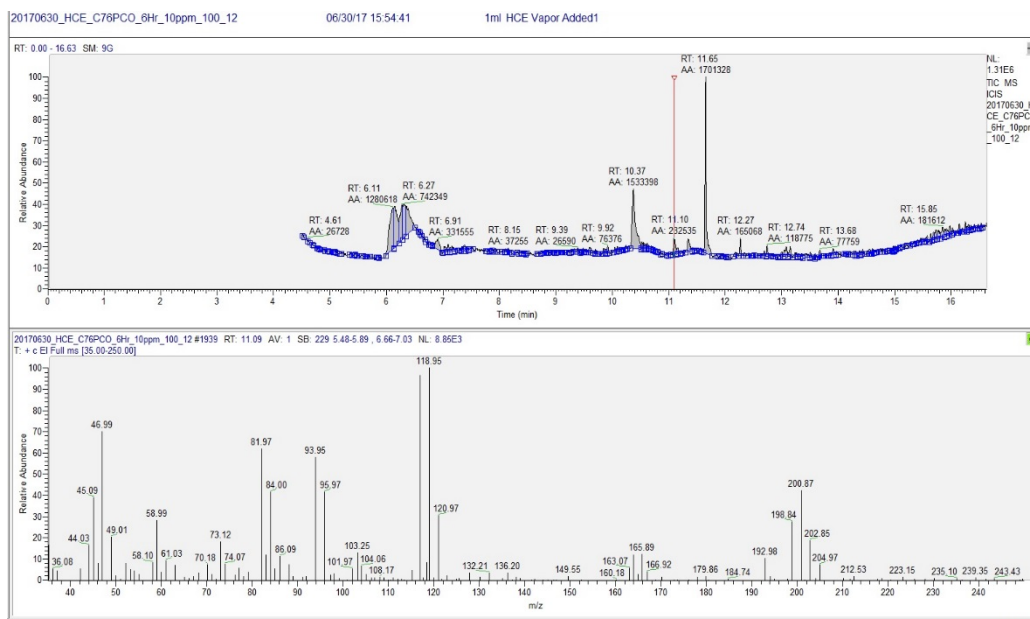


Figure 39. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 6 hours light showing a further reduction in the HCE response TIC + Mass Spectrum.

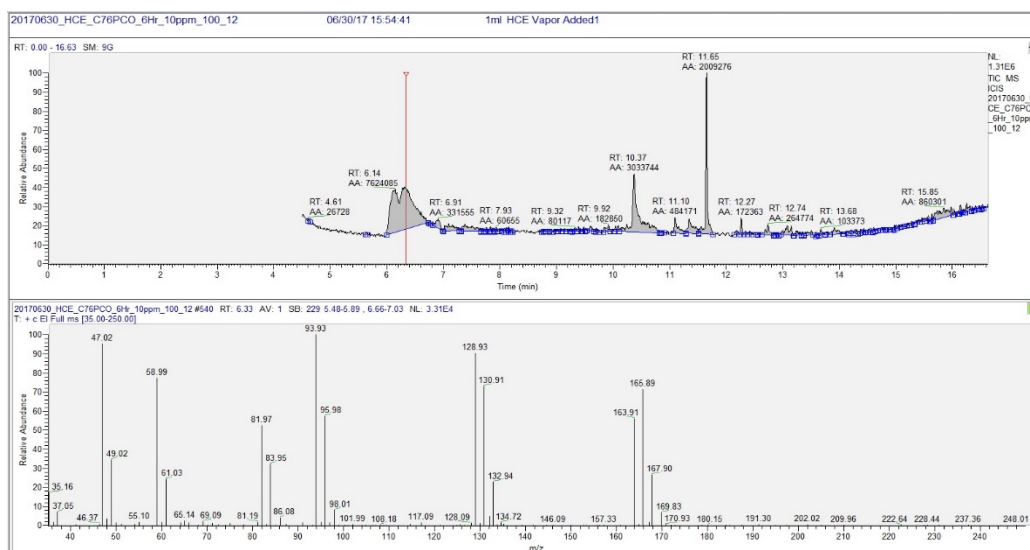


Figure 40. HCE vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 6 hours light showing the intermediate degradation product PCE response TIC + Mass Spectrum.

CN PCO Test Data

2-Chloroacetophenone 0.5-, 1-, 2-, 4-, 6-hour PCO exposure test.

Table 22. Table of CN Analysis with Calibration Data for 0.5, 1, 2, 4 and 6 hour Visible light exposure Test.

ID	RT	Area	ng/ul	nanomoles HCE, assuming 1ul injection
CN_0.5ppm_02	12.94	1871466.0	0.5	0.00
CN_1ppm_03	12.94	3435572.0	1	0.01
CN_5ppm_04	12.94	43357477.0	5	0.03
CN_10ppm_05	12.94	81352759.0	10	0.06
CN_25ppm_06	12.94	322483655.0	25	0.16

7.464E-08slope
1.54513intercept

Maximum Vial Temperature exposed to UVA (°C) : 53.2
Start Time for CN Vapor Addition : 1:55:00 PM 7/14/2017

Analysis of Vapor phase CN in 40ml mininert valve screw cap vials:

Filename	Date	Time	inj vol (mL)	Component	RT	Area	ng on column	PPM	Comment
20170703_CN_1_25ppm_100-01	7/3/2017		0.001	CN	12.69	3522781.0	1.808	---	cal standard prep/d 7/10/17
20170715_Hdip_CN_100ul_01	7/15/2017	8:54:00	0.1	CN	13.06	13329282.0	11.494	17.926	HCE Vapor only
20170715_Hdip_CN_100ul_02	7/15/2017	9:27:00	0.1	CN	13.14	155335102.0	13.139	20.492	HCE Vapor only
20170715_Hdip_CN_100ul_03	7/15/2017	9:49:00	0.1	CN	13.07	144914015.0	12.361	19.279	HCE Vapor only
20170715_CN_C55Drk_100ul_01	7/15/2017	10:16:00	0.1	CN	11.09	8942501.0	2.183	3.404	HCE + Ag Doped Titania Coupon
20170715_CN_C56Drk_100ul_02	7/15/2017	11:00:00	0.1	CN	11.11	20655235.0	3.087	4.814	HCE + Ag Doped Titania Coupon
20170715_CN_C57Drk_100ul_03	7/15/2017	11:26:00	0.1	CN	11.12	32501464.0	3.971	6.193	HCE + Ag Doped Titania Coupon
20170715_CN_C59PCO_0_5hr_100ul_01	7/15/2017	11:49:00	0.1	CN	11.09	117568788.0	10.320	16.095	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C63PCO_0_5hr_100ul_02	7/15/2017	12:16:00	0.1	CN	11.11	33035358.0	4.011	6.255	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C68PCO_0_5hr_100ul_03	7/15/2017	12:42:00	0.1	CN	11.12	72539051.0	6.959	10.854	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C75PCO_1hr_100ul_04	7/15/2017	13:09:00	0.1	CN	11.11	147966194.0	12.589	19.634	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C76PCO_1hr_100ul_05	7/15/2017	13:52:00	0.1	CN	11.10	15274892.0	2.685	4.188	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C78PCO_1hr_100ul_06	7/15/2017	14:15:00	0.1	CN	11.08	107706712.0	9.584	14.947	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C80PCO_2hr_100ul_07	7/15/2017	14:41:00	0.1	CN	11.11	9995139.0	1.843	2.875	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C81PCO_2hr_100ul_08	7/15/2017	15:06:00	0.1	CN	11.10	174297476.0	14.555	22.699	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C90PCO_2hr_100ul_09	7/15/2017	15:30:00	0.1	CN	11.08	90785010.0	8.321	12.978	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C94PCO_4hr_100ul_10	7/15/2017	15:54:00	0.1	CN	11.17	99829738.0	8.996	14.031	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C95PCO_4hr_100ul_11	7/15/2017	16:17:00	0.1	CN	11.09	172767496.0	14.440	22.521	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C97PCO_4hr_100ul_12	7/15/2017	16:40:00	0.1	CN	11.10	19242899.0	2.981	4.650	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C107PCO_6hr_100ul_13	7/15/2017	17:13:00	0.1	CN	11.13	21664004.0	3.162	4.932	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C111PCO_6hr_100ul_14	7/15/2017	17:38:00	0.1	CN	11.16	118647829.0	10.401	16.221	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C115PCO_6hr_100ul_15	7/15/2017	18:00:00	0.1	CN	11.11	35555060.0	4.199	6.549	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_Hdip_CN_100ul_01a	7/15/2017	18:23:00	0.1	CN	11.10	126967281.0	11.022	17.189	HCE Vapor only
20170715_Hdip_CN_100ul_02a	7/15/2017	18:48:00	0.1	CN	11.09	144237476.0	12.311	19.200	HCE Vapor only
20170715_Hdip_CN_100ul_03b	7/15/2017	19:08:00	0.1	CN	11.25	148939465.0	12.662	19.747	HCE Vapor only

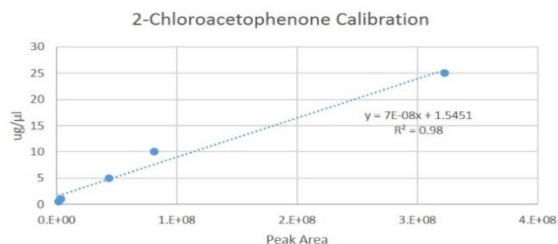


Table 23. Table of Degradation Product (AP and BA) Analysis for 0.5, 1, 2, 4 and 6 hour Visible light exposure Test.

Filename	Date	Time	inj vol (mL)	Component	RT	Area	ng on column	PPM	Comment
20170715_CN_C55Drk_100ul_01	7/15/2017	10:16:00	0.1	AP	11.05	139357	1.556	2.262	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C56Drk_100ul_02	7/15/2017	11:00:00	0.1	AP	11.55	428614	1.577	2.293	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C57Drk_100ul_03	7/15/2017	11:26:00	0.1	AP	11.59	649124	1.594	2.317	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C59PCO_0_5hr_100ul_01	7/15/2017	11:49:00	0.1	AP	11.52	5117445	1.927	2.802	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C63PCO_0_5hr_100ul_02	7/15/2017	12:16:00	0.1	AP	11.52	1662304	1.669	2.427	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C68PCO_0_5hr_100ul_03	7/15/2017	12:42:00	0.1	AP	11.64	3635181	1.816	2.641	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C75PCO_1hr_100ul_04	7/15/2017	13:09:00	0.1	AP	11.6	8408116	2.173	3.159	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C76PCO_1hr_100ul_05	7/15/2017	13:52:00	0.1	AP	11.55	1910323	1.688	2.454	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C78PCO_1hr_100ul_06	7/15/2017	14:15:00	0.1	AP	11.62	5147073	1.929	2.805	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C80PCO_2hr_100ul_07	7/15/2017	14:41:00	0.1	AP	11.05	886420	1.611	2.343	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C81PCO_2hr_100ul_08	7/15/2017	15:06:00	0.1	AP	11.56	12294765	2.463	3.581	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C90PCO_2hr_100ul_09	7/15/2017	15:30:00	0.1	AP	11.51	8282120	2.163	3.145	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C94PCO_4hr_100ul_10	7/15/2017	15:54:00	0.1	AP	11.72	8745594	2.198	3.196	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C95PCO_4hr_100ul_11	7/15/2017	16:17:00	0.1	AP	11.68	19473968	2.999	4.360	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C97PCO_4hr_100ul_12	7/15/2017	16:40:00	0.1	AP	11.5	4398522	1.873	2.724	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C107PCO_6hr_100ul_13	7/15/2017	17:13:00	0.1	AP	11.6	8129960	2.152	3.129	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C111PCO_6hr_100ul_14	7/15/2017	17:38:00	0.1	AP	11.76	9674643	2.267	3.296	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C115PCO_6hr_100ul_15	7/15/2017	18:00:00	0.1	AP	11.64	8922290	2.211	3.215	HCE + Ag Doped Titania Coupon Exposed to visible light

Filename	Date	Time	inj vol (mL)	Component	RT	Area	ng on column	PPM	Comment
20170715_CN_C55Drk_100ul_01	7/15/17	10:16:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C56Drk_100ul_02	7/15/17	11:00:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C57Drk_100ul_03	7/15/17	11:26:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C59PCO_0_5hr_100ul_01	7/15/17	11:49:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C63PCO_0_5hr_100ul_02	7/15/17	12:16:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C68PCO_0_5hr_100ul_03	7/15/17	12:42:00	0.1	BA	BDL	BDL	BDL	BDL	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C75PCO_1hr_100ul_04	7/15/17	13:09:00	0.1	BA	BDL	3626671	1.816	4.125	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C76PCO_1hr_100ul_05	7/15/17	13:52:00	0.1	BA	10.47	1146741	1.631	3.705	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C78PCO_1hr_100ul_06	7/15/17	14:15:00	0.1	BA	10.54	2683464	1.745	3.966	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C80PCO_2hr_100ul_07	7/15/17	14:41:00	0.1	BA	10.57	571051	1.588	3.607	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C81PCO_2hr_100ul_08	7/15/17	15:06:00	0.1	BA	10.49	9224378	2.234	5.075	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C90PCO_2hr_100ul_09	7/15/17	15:30:00	0.1	BA	10.44	6339467	2.018	4.585	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C94PCO_4hr_100ul_10	7/15/17	15:54:00	0.1	BA	10.64	10402301	2.322	5.274	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C95PCO_4hr_100ul_11	7/15/17	16:17:00	0.1	BA	10.6	14031395	2.592	5.890	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C97PCO_4hr_100ul_12	7/15/17	16:40:00	0.1	BA	10.42	6896338	2.060	4.680	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C107PCO_6hr_100ul_13	7/15/17	17:13:00	0.1	BA	10.52	8884434	2.208	5.017	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C111PCO_6hr_100ul_14	7/15/17	17:38:00	0.1	BA	10.68	10472843	2.327	5.286	HCE + Ag Doped Titania Coupon Exposed to visible light
20170715_CN_C115PCO_6hr_100ul_15	7/15/17	18:00:00	0.1	BA	10.56	6265679	2.013	4.573	HCE + Ag Doped Titania Coupon Exposed to visible light

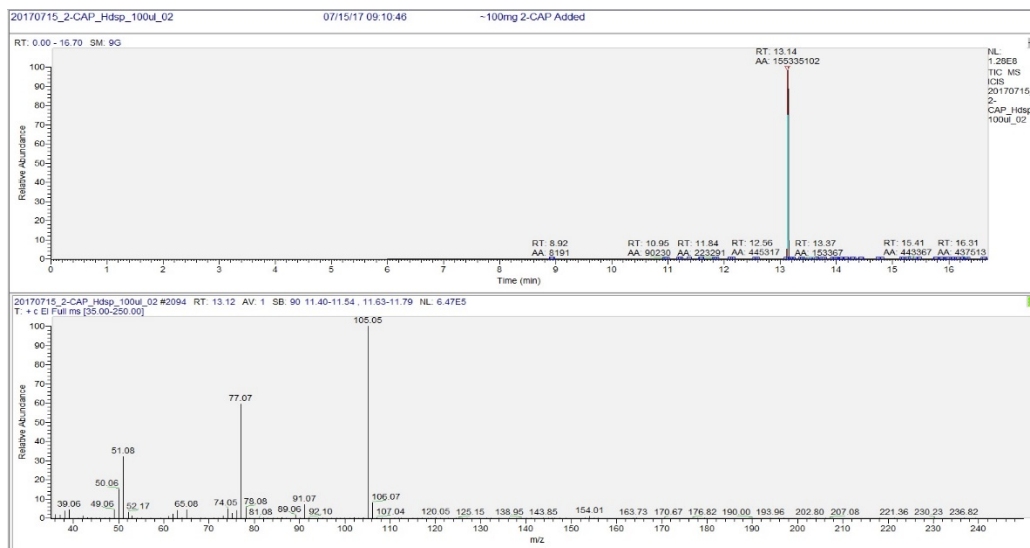


Figure 41. CN vapor in 40-ml Mininert Valve vial TIC + Mass Spectrum.

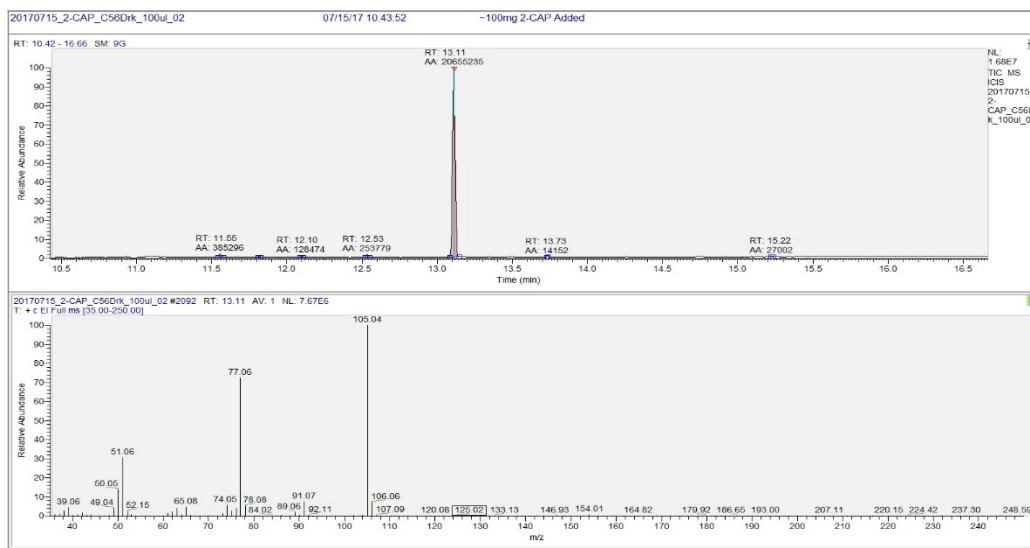


Figure 42. CN vapor in 40-ml Mininert valve vial w/ Ag-doped TiO₂ coupon held in the Dark TIC + Mass Spectrum.

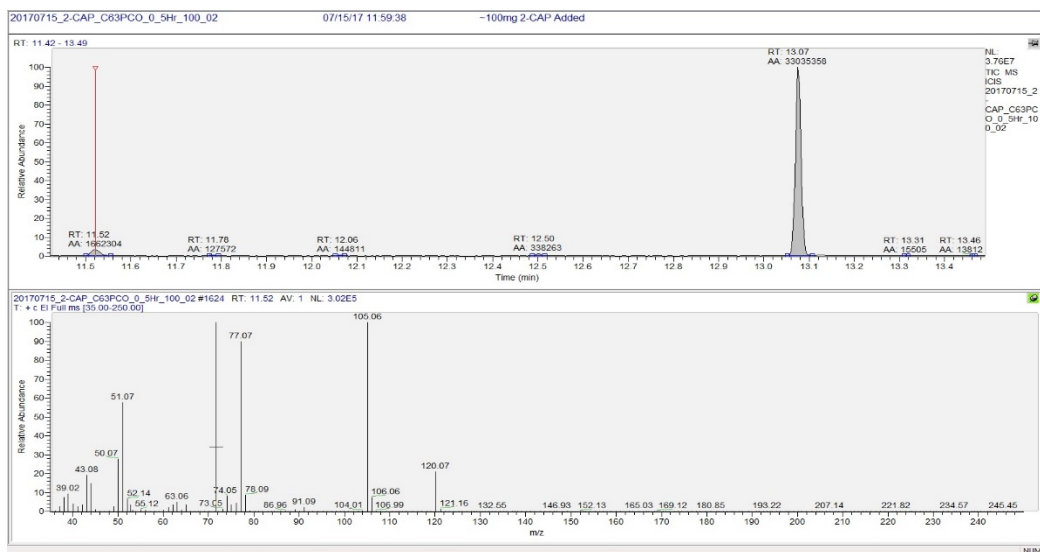


Figure 43. CN vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 0.5 hours showing the presence of AP TIC + Mass Spectrum.

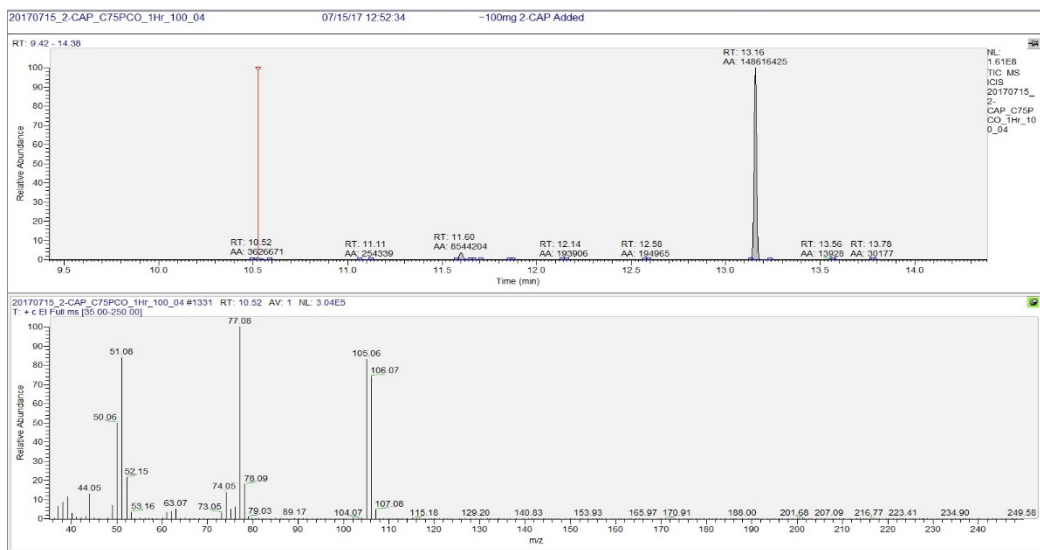


Figure 44. CN vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 1 hour showing the presence of BA TIC + Mass Spectrum.

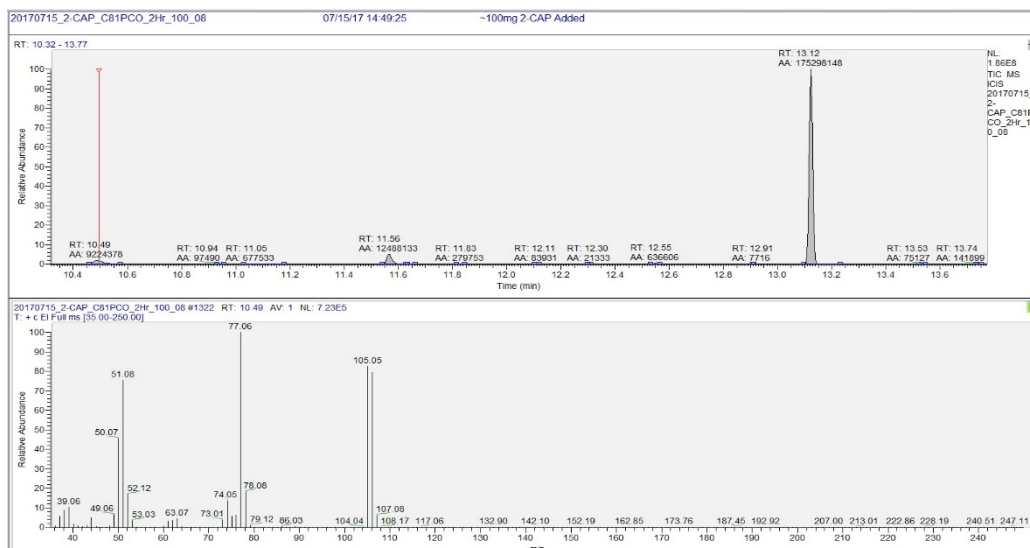


Figure 45. CN vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 2 hours showing an increase in the BA response TIC + Mass Spectrum.

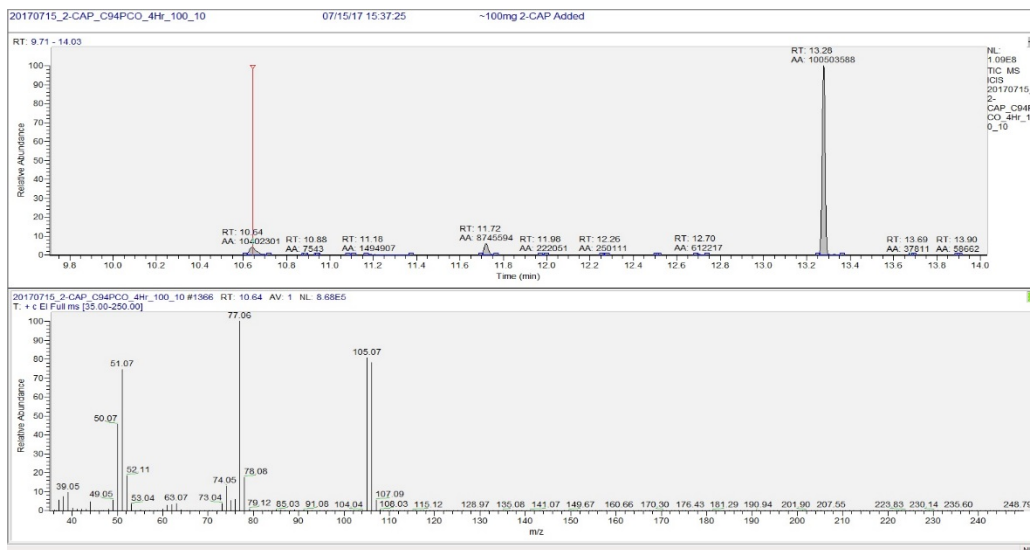


Figure 46. CN vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 4 hours showing a further increase in the AP TIC + Mass Spectrum.

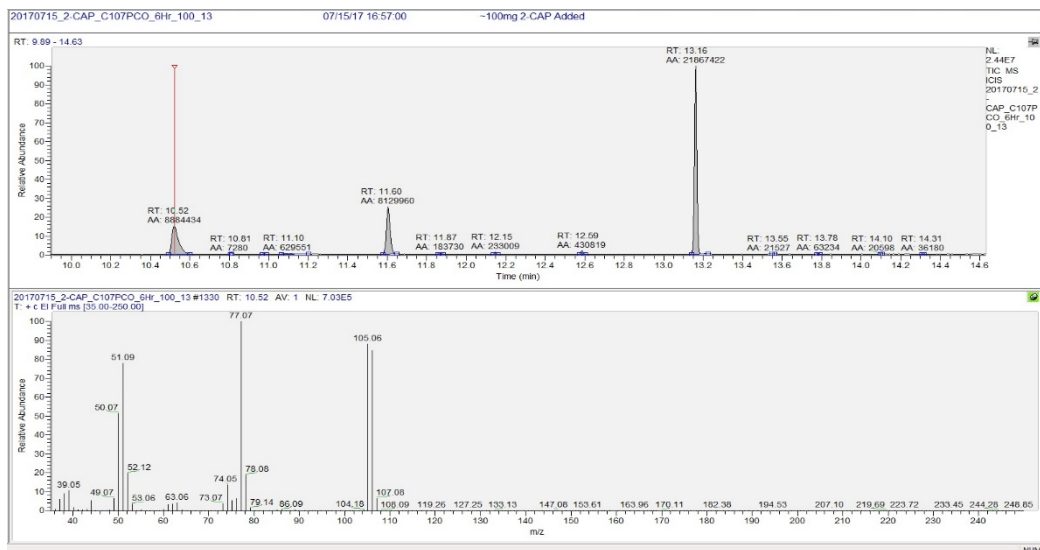


Figure 47. CN vapor in 40-ml Mininert Valve vial w/ Ag-doped TiO₂ coupon exposed to visible light for 6 hours showing a plateau in AP and BA response TIC + Mass Spectrum.