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MATERIALS COMPATIBILITY STUDY FOR THREE-DIMENSIONAL PRINTER MATERIALS

James D. Wright Jr.
Mary M. Wade

RESEARCH AND TECHNOLOGY DIRECTORATE

Bradley Ruprecht
Richard Moore

ENGINEERING DIRECTORATE

Jonathan Oyler
Kelly Smith

U.S. ARMY MEDICAL RESEARCH INSTITUTE
OF CHEMICAL DEFENSE
Aberdeen Proving Ground, MD 21010-5400

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EXECUTIVE SUMMARY

The emergence of three-dimensional (3D) print technologies brought about a modern-day industrial revolution. The 3D printers were evaluated by the U.S. Army soldiers for use in austere field environments as well as in research laboratory settings. These materials are already characterized in terms of acute toxicity and critical failure, but less is known about them in terms of safety concerns during subcritical exposure and interactions. The polymers used for 3D printing can be highly reactive, and this reactivity may be an undesired trait during experimentation and in Warfighter environments where control of all possible variables is desired. A comprehensive understanding of how 3D-printed materials behave upon exposure to chemical solvents will allow for the selection of materials that are best suited to the needs of individual assays. The experimental approach is designed to detect and identify compounds that leach from the 3D materials to prevent undesired outcomes or interferences. Using the U.S. Department of Homeland Security ASTM International (West Conshohocken, PA) guidelines, the 3D materials were printed into uniform tensile bars and exposed to the selected solvents (water, sodium hydroxide, acetone, and acetonitrile) overnight. After exposure, the solvents were examined on the appropriate mass spectrometry (MS) system (gas chromatography [GC]–MS or liquid chromatography [LC]–MS) to identify the compounds that leached from the 3D materials. The organic solvents (acetone and acetonitrile) were examined using GC–MS to optimize ionization of the nonpolar compounds, whereas the LC–MS was used to analyze the aqueous solvents (water and sodium hydroxide) for polar compounds (e.g., polyethylene glycol [PEG]). All sample combinations were examined in quintuplicate and the leachate was observed in all samples. Some of the leachates showed spectral matches to the National Institute of Standards and Technology (NIST; Gaithersburg, MD) compound library. The VeroWhitePlus composite material (Stratasys; Eden Prairie, MN) produces a demonstrated leachate that is common to organic solvents (*N*-acryloylmorpholine, which is a 2-propenoic acid derivative, and a 2-propanol derivative).

During testing, compounds that are unique to each solvent were also detected: three unknown compounds in acetone and methanone in acetonitrile. Likewise, sodiated PEG or a similar derivative was detected in water and sodium hydroxide. The PEG and its derivatives are highly ionizable in the LC–MS and could suppress the ionization of other leached compounds that may be present in the solvent. Analysis of the polycarbonate–acrylonitrile butadiene styrene material demonstrated a lower degree of leachate than that of VeroWhitePlus material; however, the spectra of those leachates did not match anything in the NIST Chemical Spectral Library. (These spectra are all documented as part of this study for identification in the future.) In this study, examination of each condition demonstrated that the selected materials actively leach multiple compounds into all four solvents, which results in a unique profile specific to the 3D material. This project demonstrated the need to characterize the chemical materials compatibility of the 3D-printed materials in the corresponding solvent conditions and to examine the different decontamination methods used to dispose of agent-exposed objects.

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PREFACE

The work described in this report was authorized under the U.S. Army Edgewood Chemical Biological Center (ECBC) Innovative Development of Employee Advanced Solutions (IDEAS) program. The work was started in March 2016 and completed in December 2016.

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MATERIALS COMPATIBILITY STUDY FOR THREE-DIMENSIONAL PRINTER MATERIALS

1. INTRODUCTION

The field of three-dimensional (3D) printing has emerged as a disruptive technology in areas of both durable and consumable plastics. Varieties of plastics to serve all conceivable uses have been adapted or created for use in this form of rapid prototyping. Possible uses for printed objects range from normal inert display and illustration objects to functional mechanical objects and, finally, to research applications.¹ Research applications are of particular interest because of the high volume of plastics used in research laboratories. A significant portion of laboratory consumables is made up of plastic tubes, racks, and containers. 3D printing could provide a highly adaptive and inexpensive method to generate these consumables “in house”, which would eliminate the tendency to purchase excessive quantities of materials in anticipation of planned work. By working with the raw materials on hand instead of using fixed forms, especially in austere environments, researchers will be able to creatively drive the research. The use of 3D printing offers more flexibility and diversity in the choice of materials without confining the work to the form of the consumables on hand. For example, a tube or vessel size could be adapted to a change in a solution volume to a nonstandard, yet optimized configuration, and the solution would not have to be scaled to the available reaction vessels.

This project was designed to characterize the noncritical interactions between 3D printer materials and routine solvents that are used in laboratory and field settings and with chemical warfare agents (CWAs). The plastics manufacturers establish baseline safety and chemical compatibility that focuses on critical failure data in written Safety Data Sheets.²⁻⁴ Previous work was conducted to determine a material’s compatibility with the specific project under consideration, without regard for other programs that might benefit from this information. These data are rarely reported in a searchable format. The objective of this project was to establish a foundation for systematically and rigorously characterizing how materials used for 3D printing will behave under typical conditions. The results will be reported to provide a reference for others to consult when they need to choose a 3D printer material that is the most appropriate for their required application.

Although 3D-printing technologies are revolutionary, concerns remain about the safety of the technology. One objective of this study was to establish the groundwork needed to develop a reference resource that would characterize the unique properties of 3D materials when exposed to solvents and military-relevant agents or compounds. This effort will be a valuable reference to incorporate 3D-printed parts into laboratory and field equipment. This reference will help to facilitate decisions, reduce trial and error, and demonstrate how to process materials for different applications. This effort will also benefit the Warfighter by informing decisions that will ensure compatibility with the intended use that is validated using a standard method, and it will provide information about how to properly decontaminate the material, should it be exposed to a hazardous chemical.

Literature⁵ has shown that the nanoparticle vapor emitted by a 3D printer can present both environmental and health concerns. A study by the Built Environment Research Group at the Illinois Institute of Technology (Chicago, IL)⁶ showed that considerable amounts of nano-sized particles were observed in aerosols emitted by 3D-printing machines. Although there has been some effort to examine the interactions between 3D materials and solvents for a number of disparate properties, such as outgassing, leaching, and corrosion, there have been few, if any, efforts to create a comprehensive reference base for all known 3D-printing materials against a functional range of chemical and biological agents.

The U.S. Army Rapid Equipping Force (REF; Fort Belvoir, VA) deployed mobile 3D-printing laboratories to Afghanistan to improve the sustainability of small forward-operating bases. Using 3D printing, the REF team was able to create a tactical light mount for handheld improvised explosive device detectors that provides illumination beneath the sensor without interfering with the detector system. This solution, along with many others, has allowed the REF to furnish immediate solutions to front-line soldiers who are facing urgent challenges in theater. With 3D technology entering into the Warfighter arena from so many divergent sources, assessing 3D materials for any unknown interactions due to contact with solvents or chemical and biological agents in the field becomes imperative.

By facilitating the quick battlefield replacement of customizable consumable components, 3D printing can be used for a variety of applications ranging from the replacement of vehicle parts to “on demand” medical tools in theater hospitals. Benefits such as lower production costs, reduced waste, rapid prototyping, and supply chain circumvention, along with continuous improvements in software and printing capabilities, make it imperative for the military to evaluate and assess how current and up-and-coming 3D manufacturing technologies can be effectively integrated into the Warfighter arena.

In this study, we examined a variety of materials, which included the following: fused deposition modeling material, selective laser sintering material, acrylonitrile butadiene styrene (ABS) material, and polylactic acid material. The compatibility of each material with a variety of solvents and chemical agents was assessed, starting with a blister agent surrogate, such as chlorodiethyl sulfide. Samples were examined for chemical differences before and after exposure using gas chromatography (GC)–mass spectrometry (MS) and liquid chromatography (LC)–MS. Exposed 3D-printed materials were examined mechanically using stress and strain tests to examine the effect of exposure on the printed objects themselves. The technical barriers and risks were low, and the impact will be high for this project due to the well-established methods for materials testing, as described in ASTM E595, E1559, and D638.⁷⁻⁹

The primary goal of this project was to reduce the time and cost associated with prototyping across all Army programs that wish to incorporate 3D printing as part of their processes. One of the key barriers to the adoption of 3D printing by the Army is the safety of introducing the new materials, and the establishment of how those materials will respond under experimental conditions, as opposed to the use of well-established materials from vendors that have undergone rigorous evaluation. It is often assumed that the 3D-printed material is defined by the dominant polymer; however, other materials are used during the production process that will persist within the final printed object.

For this project, a linear progression of steps was followed to examine the questions proposed in the Statement of Work:

- Are the VeroWhitePlus (Stratasys; Eden Prairie, MN) and polycarbonate (PC)–ABS materials inert across a variety of solvents?
- Alternate: Do the VeroWhitePlus and PC–ABS materials leach potentially reactive compounds?
- Are the VeroWhitePlus and PC–ABS materials mechanically altered by exposure to a variety of solvents?

The larger goals of this project were to characterize the contribution of the solvents in regard to analytical detection techniques, which were demonstrated by GC–MS and LC–MS. The tensile bar dimensions were based on ASTM standards (ASTM D638, D790, D256, and D648).^{9–12}

In the first year of this project, the magnitude of chemical and physical interactions between 3D-printed materials, solvents, and chemical agents (surrogates) were characterized. A matrix of two materials and four solvents, using three methodologies to examine the results of the interactions, was evaluated. The methodologies included an Instron (Norwood, MA) tensiometer, GC–MS, and LC–MS, which were used to identify chemical and mechanical changes to the 3D-printed materials. This study will also monitor samples from part generation through exposure and mechanical testing, in compliance with the ASTM standards that govern materials properties analysis. The study will be expanded in the second year to include true CWA material and complex solvent conditions (a mixture of organic and aqueous solvents) to collect actual leachate or mechanical properties changes that researchers are likely to experience. The conclusion of this project would be a valuable reference for scientists and engineers to consult during experimental design. Additionally, these results would be appropriate justification to seek out further funding through the U.S. Department of Homeland Security (DHS) or U.S. Environmental Protection Agency (EPA) program managers that are interested in this data, specifically the DHS Standards and Measures Office.

A comprehensive understanding of how 3D-printed materials behave upon exposure to chemical solvents will allow for the selection of materials that are best suited to individual assay needs.

2. MATERIALS AND METHODS

2.1 3D Materials Production

The 3D-printed materials tensile bars were produced out of VeroWhitePlus and PC–ABS Blend materials because of their relevance to current U.S. Army and U.S. Army Edgewood Chemical Biological Center rapid-prototyping standards for strength and rigidity. The tensile bars were 3D-printed to conform to the ASTM Standards D256, D638, D648, and D790^{9–12} for standard mechanical-testing conditions. The tensile bars were 3D-printed in single batches with the same lot number in the same layer of the build bed and labeled in accordance with the matrix shown in Table 1.

Table 1. Test Plan Matrix

Sample ID	Material	Solvent		Sample ID	Material	Solvent
M1001	VeroWhitePlus	H ₂ O		M2001	PC-ABS Blend	H ₂ O
M1002				M2002		
M1003				M2003		
M1004				M2004		
M1005				M2005		
M1006	VeroWhitePlus	NaOH		M2006	PC-ABS Blend	NaOH
M1007				M2007		
M1008				M2008		
M1009				M2009		
M1010				M2010		
M1011	VeroWhitePlus	Acetone		M2011	PC-ABS Blend	Acetone
M1012				M2012		
M1013				M2013		
M1014				M2014		
M1015				M2015		
M1016	VeroWhitePlus	ACN		M2016	PC-ABS Blend	ACN
M1017				M2017		
M1018				M2018		
M1019				M2019		
M1020				M2020		
M1021	VeroWhitePlus	Outgas		M2021	PC-ABS Blend	Outgas
M1022				M2022		
M1023				M2023		
M1024				M2024		
M1025				M2025		

Note: In this table, a barcode is assigned to each sample for tracking purposes, and the test conditions are documented. ACN is acetonitrile.

2.2 Material Exposure

In accordance with ASTM E595 for standard outgas analysis,¹³ the VeroWhitePlus and PC-ABS Blend tensile bars were transferred into 70 mL Pyrex glass test tubes with silicon stoppers within 1 h of print completion to capture any outgassed particles during the cooling stage. The bars were removed from the test tubes, and the tubes were rinsed with 20 mL of acetone. The acetone was collected in glass collection vials and capped for GC-MS analysis. Each of the four solvents (60 mL) were incubated with the tensile bars inside the silicon-capped test tubes overnight (24 h) in accordance with ASTM D543.¹⁴ Each solvent (20 mL) was retained in a glass collection vial for MS analysis, along with 20 mL of each solvent in a second vial as a blank. Each solvent and material permutation was run in quintuplet.

2.3 GC–MS Conditions

The GC–MS samples (acetone and acetonitrile solvents) were run on an Agilent (Santa Clara, CA) 6890N/5975C mass spectrometer with a VF-5ht column (30 m, 0.25 ID, 0.1 μm film thickness) at the U.S. Army Medical Research Institute of Chemical Defense (MRICD) MS laboratory. The spectra were searched against the National Institute of Standards and Technology (NIST; Gaithersburg, MD) NIST11 and the MRICD demo1 databases, which are validated spectral libraries. Each sample was diluted 10- and 100-fold into acetonitrile and collected over 15 min. The spectral peaks were used to search the two databases. The peaks were identified by the relative percent area and the retention time, and percent confidence was reported for each peak that was assigned to a library match. The report files were reviewed manually, and the replicates were evaluated for common peaks in each sample type and used to populate a table of common peaks between replicates (Section 3).

2.4 LC–MS Conditions

The LC–MS data (water and 1N sodium hydroxide solvent samples) were collected on a Thermo Q Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Inc.; Waltham, MA) with an electrospray ionization (ESI) source for direct Hamilton (Reno, NV) syringe injection using the Thermo-supplied syringe pump. The samples were diluted 4:1 in acetonitrile and injected at 5 $\mu\text{L}/\text{min}$. Data were collected after the line was equilibrated with sample for 1 min. To eliminate carryover, the line was washed with 500 μL of 98% acetonitrile–2% H_2O between samples. The instrument was operated on the latest version of the Thermo Xcalibur software (3.0), and the instrument was set at the conditions shown in Table 2.

Table 2. LC–MS Method Parameters

Setting	Value
Full MS	N/A
Scan range	120–1800 m/z
Fragmentation	None
Resolution	70,000
Polarity	Positive
Microscans	3
Lockmass	Off
AGC target	1e6
Maximum injection time	200
Spray voltage	4
Capillary temperature	320
S-lens RF level	70
Collection time	1.00 min
Data file location	C:\Xcalibur\data\James\2016
Method file	By time

Note: Parameters were defined on Thermo Xcalibur Software, Version 3.0 on a Thermo Q Exactive Orbitrap instrument. N/A is not applicable; m/z is mass-to-charge ratio; AGC is automatic gain control; and RF is radio frequency.

3. RESULTS AND DISCUSSION

This project was designed to use two MS techniques (GC–MS and LC–MS) to assess the chemical leachate of two 3D-printed materials after they were exposed to the following solvents:

- GC–MS analysis:
 - VeroWhitePlus material exposed to
 - acetone and
 - acetonitrile solvents.
 - PC–ABS Blend material exposed to
 - acetone and
 - acetonitrile solvents.
- LC–MS analysis:
 - VeroWhitePlus material exposed to
 - water and
 - sodium hydroxide solvents.
 - PC–ABS Blend material exposed to
 - water and
 - sodium hydroxide solvents.

3.1 GC–MS Results

The overnight outgas experiments and organic solvent exposures were evaluated using GC–MS to assess the nonpolar compounds relative to the aqueous solvents, such as water. These solvents were chosen to reflect the typical experimental conditions for chemical agents¹⁵ and are usually mixtures of organic and aqueous solvents that are used to remove support material or to refine the final print object.¹⁶ For this project, the 3D-printed tensile bar was allowed to cool and sit overnight in the glass test tube to allow outgassing (Section 2.2). The glass test tube was then washed with acetone to collect any outgassed condensate. Acetone was chosen because it is used as a finishing step for processing many 3D-printed materials. These outgas condensate samples were examined by GC–MS, and unique peaks were identified (Table 3) for unique compounds from VeroWhitePlus and PC-ABS materials present on the test tube glass.

For the GC–MS analysis, the samples were diluted 1:10 and 1:100 to prevent saturation of the detector. Evaluation of the blank samples showed that the solvents contributed to the compounds detected reproducibly from acetone and displayed five major peaks (~90% of total signal area), which are identified in Tables 3 and 4 and in Figures 1–8. Acetonitrile analysis displayed 13 major peaks (~80% of the total signal area), none of which were identified in the NIST database.¹⁷ This was the baseline background that was expected in each sample.

The acetone outgas samples for the VeroWhitePlus material displayed three unique major peaks (~80% of the total peak area); two of which were identified as common industrial plastics byproducts, dodecane (~3.5%) and 2,5-dimethylheptane (~75%), and an unknown compound (~1.5%). Whereas the outgas samples for the PC–ABS Blend material contained three major peaks (~60% of total peak area) that were not identified against the NIST

database. In these instances, minor peaks were not resolved sufficiently for spectral matching (Figures 1–8).

The VeroWhitePlus material is an acrylic-based photopolymer that is composed of isobornyl acrylate, 2-propenoate, phenyl phosphine oxide derivatives, and titanium oxide, which, in total, constitutes >99% of the material as manufactured.¹⁷ The VeroWhitePlus material was used because its physical rigidity can be tuned by adjusting the ratio of the aforementioned compounds, relative to each other. Several of these compounds and further-derivatized variants were present in the GC–MS data, most notably 2-propenoic acid and *N*-acryloylmopholine, which demonstrated that the material was not chemically inert (Tables 3 and 4). These data show that the compounds were formed either during the printing process for the object or during the exposure to organic solvent. The acetone exposure had three unique unknown peaks and the acetonitrile exposure had a single unique peak that was identified as methanone by the NIST database (Tables 3 and 5). The confidence for the methanone identification was ~83%, which allowed for a significant degree of error, or it could have been a differential derivation that was a result of the different reactivity between the solvent and printer material. The samples would need to be compared to neat standards in the future.

A similar result was reflected with the PC–ABS Blend 3D-printer material. This material is used for a harder, rigid surface, and impact resistance is not required. The PC–ABS Blend material was less reactive than VeroWhitePlus material, based on the complexity of the signals observed using the GC–MS with only azacyclotridecan-2-one, which is a dodecane derivative from the solvent background. This result was identified from the spectra in both organic solvents with a few other chemical species that were not identified when compared to the NIST database (Tables 3 and 4). This reduced complexity was expected due to the relative simplicity of the PC–ABS Blend material, which was composed of a variable combination of acrylonitrile butadiene styrene. The exact chemical structures of the functionalized hydrocarbons depend on several factors that are selectable according to the application.

As shown in Table 3B, the outgas data only shows one compound, 3,5-dimethylheptane, with confidence. This was most likely due to the high solvent background signal or the poor ionization of any nanoparticles present.

The chemical stability of the 3D-printed material was examined by analyzing the leachate composition and identifying the likely source of the leachate and any potential reactivity with solvent, compounds of interest, or decontaminant solutions. Comparison of the GC–MS data (Figure 1C–1F) and LC–MS (Figures 10–13) showed that there was significant leachate present in the solvents after overnight incubation, notably the polyethylene glycol (PEG),¹⁸ which was present at the time of the filament production process as a substrate that occurred during solidification and spooling.

Table 3. GC–MS Data for PC–ABS Blend and VeroWhitePlus 3D-Printer Materials*

1A. Organic Solvent Controls				1B. Outgas Samples			
RT	Area %	Compound Identity	% Conf	RT	Area %	Compound Identity	% Conf
1.6	3	2,5-dimethylfuran	91	1.6	3	2,5-dimethylfuran	91
1.9	1.8	4-methyl-3-penten-2-one	91	1.9	1.8	4-methyl-3-penten-2-one	91
2.9	20.8	1,1,1-trichloro-2-methyl-2-propanol	91	2.9	20.8	1,1,1-trichloro-2-methyl-2-propanol	91
				2	2	3,5-dimethyl-heptane	80
1C. PC-ABS Samples in Acetone				1D. PC-ABS Ssamples in Acetonitrile			
RT	Area %	Compound Identity	% Conf	RT	Area %	Compound Identity	% Conf
5	4.3	N-Acryloylmorpholine	95	5	2.3	N-Acryloylmorpholine	94
5.7	37	1,7,7-trimethyl-bicyclo(2,2,1)hepto-2yl-2-propenoic Acid	98	5	24.7	1,7,7-trimethyl-bicyclo(2,2,1)hepto-2yl-2-propenoic Acid	91
7.7	27.6	No match	N/A	6.9	27.8	(1-hydroxycyclohexyl)-phenyl-methanone	83
7.7	26.5	(1-hydroxycyclohexyl)-phenyl-methanone	83				
9.4	5.5	1,3-diphenyl-2-propanol	99				
1E. VeroWhitePlus Samples in Acetone				1F. VeroWhitePlus Samples in Acetonitrile			
RT	Area %	Compound Identity	% Conf	RT	Area %	Compound Identity	% Conf
1.6	2.6	2,5-dimethylfuran	90	8.1	30.2	Azacyclotridecan-2-one	87
1.9	4.5	4-methyl-3-penten-2-one	90				
2	1.3	3,5-dimethyl-heptane	0				
2.1	69.7	No match	N/A				
2.9	13	1,3-diphenyl-2-propanol	87				
8.1	1.6	Azacyclotridecan-2-one	97				

*(1A) Solvent controls, (1B) Outgas solutions from acetone-washed test tubes, (1C) PC–ABS Blend/acetone, (1D) PC–ABS Blend/ACN, (1E) VeroWhitePlus/acetone, and (1F) VeroWhitePlus/ACN.

RT is retention time, ID is identification, and % Conf is percent confidence.

Table 4. GC–MS Data Highlighting Unique Peaks

Sample Type	No. of Unique Peaks	Compound Identification	Confidence (%)	%Area
Outgas control	0	N/A	N/A	N/A
VeroWhitePlus material outgas	3	Dodecane 2,5-Dimethylheptane Unknown	<10 <10 Unknown	3.30 74.60 1.37
PC–ABS material outgas	3	Unknown (3)	Unknown	73.12
Acetone control	5	2,5-Dimethylfuran 4-Methyl-3-penten-2-one 1,1,1-Trichloro-2-methyl-2-propanol Unknown (2)	91 91 91 Unknown	2.95 1.79 20.83 65.22
ACN control	13	Unknown (13)	Unknown	2–22
Acetone/ VeroWhitePlus material	6	<i>N</i> -Acryloylmorpholine 1,7,7-Trimethyl-2-propenoic acid 1,7,7-Trimethyl-bicyclo(2.2.1)hept-2-yl ester 1,3-Diphenyl-2-propanol Unknown (3)	95 98 98 Unknown	4.41 37.31 5.62 3–26
Acetone/PC–ABS material	2	Unknown (2)	Unknown	5/70
ACN/ VeroWhitePlus material	4	<i>N</i> -Acryloylmorpholine 1,7,7-Trimethyl-2-propenoic acid, 1,7,7-Trimethyl-bicyclo(2.2.1)hept-2-yl ester 1-Hydroxycyclohexyl-phenyl-methanone 1,3-Diphenyl-2-propanol	94 99 83 99	3.2 42.95 25.2 4.5
ACN/ PC–ABS material	3	Azacyclotridecan-2-one Unknown (2)	96 N/A	62 10

N/A, not applicable.

Table 5. GC-MS Peak Identity Information*

Compound Identification	MW	Formula
2,5-Dimethylfuran	96.127	C ₆ H ₈ O
4-Methyl-3-penten-2-one	98.143	C ₆ H ₁₀ O
1,1,1-Trichloro-2-methyl-2-propanol	175.5	C ₄ H ₇ Cl ₃ O
Dodecane	170.34	C ₁₂ H ₂₆
2,5-Dimethylheptane	128.255	C ₉ H ₂₀
N-Acryloylmorpholine	141.168	C ₇ H ₁₁ NO ₂
1,7,7-Trimethyl-2-propenoic acid	208.146	C ₃ H ₄ O ₂
1,3-Diphenyl-2-propanol	212.287	C ₁₅ H ₁₆ O
1-Hydroxycyclohexyl-phenyl-methanone	204.265	C ₁₃ H ₁₆ O ₂
Azacyclotridecan-2-one	197.317	C ₁₂ H ₂₃ NO

* Chemical information about peak identities based on the NIST database.

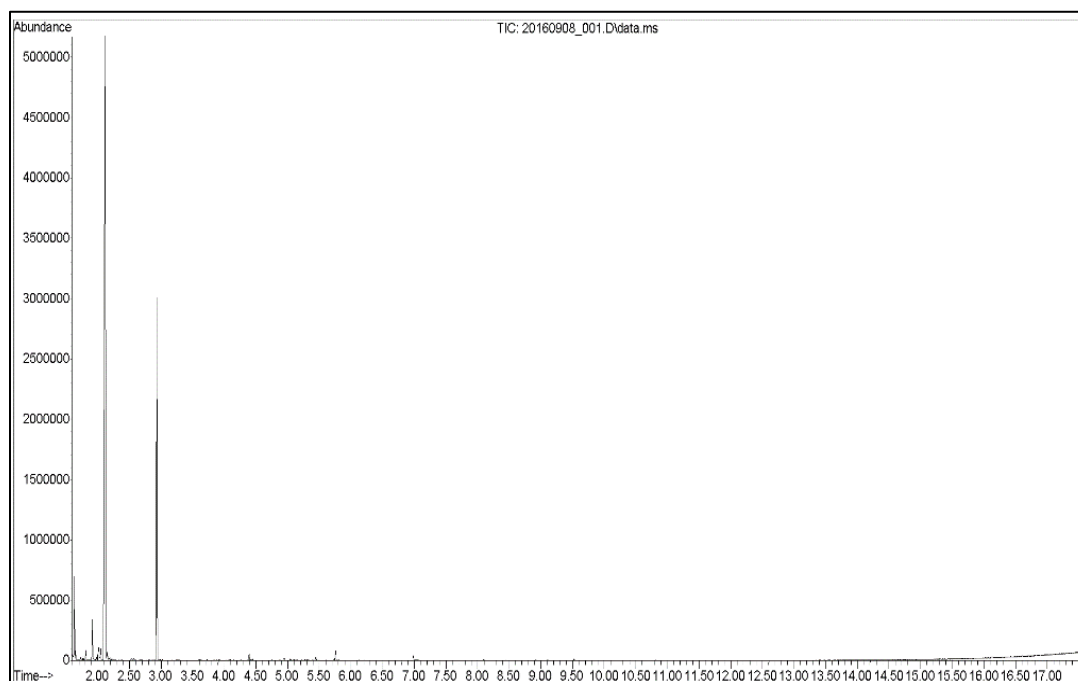


Figure 1. GC-MS spectrum for acetone control sample.

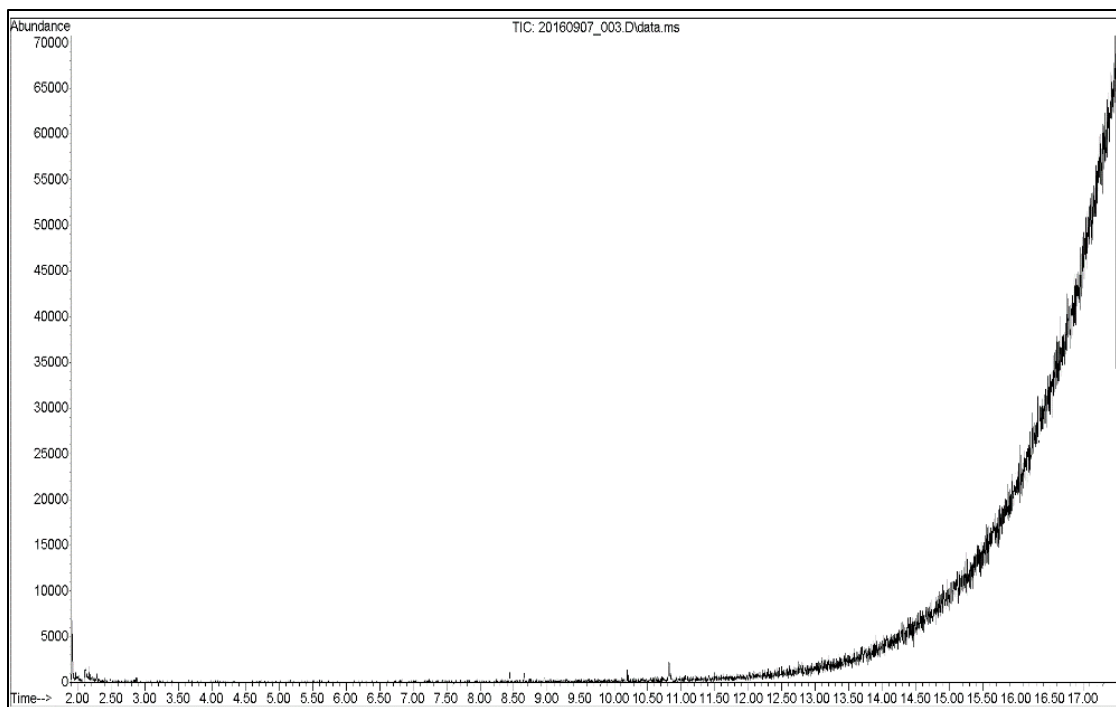


Figure 2. GC-MS spectrum for acetonitrile control.

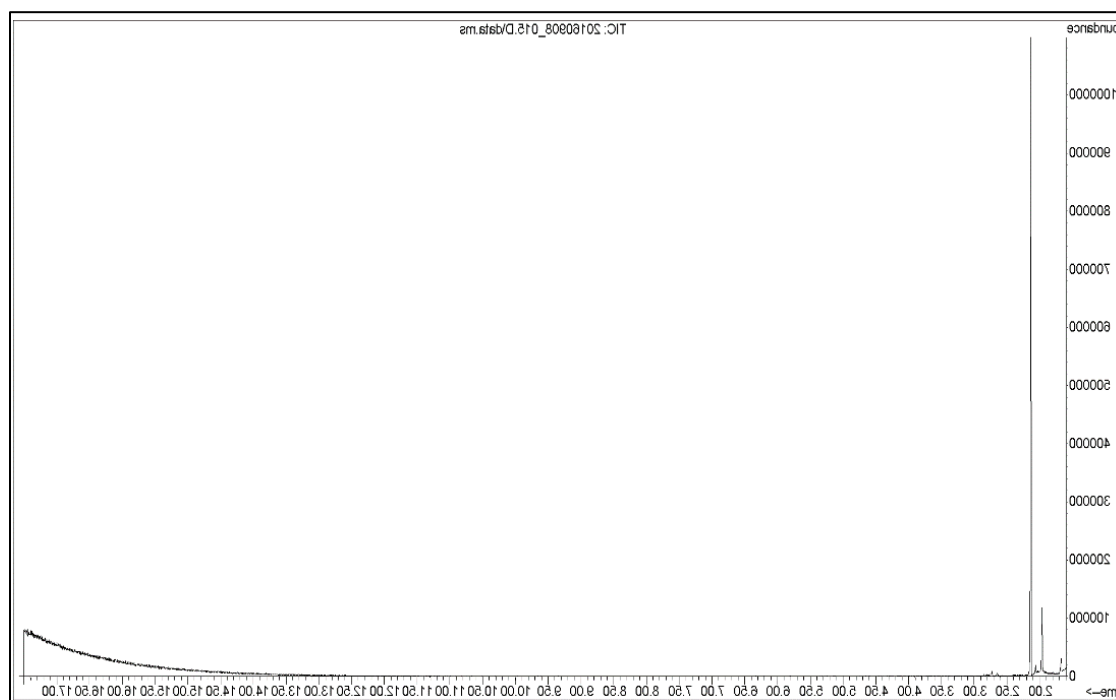


Figure 3. GC-MS spectrum for VeroWhitePlus material in acetone (M2011).

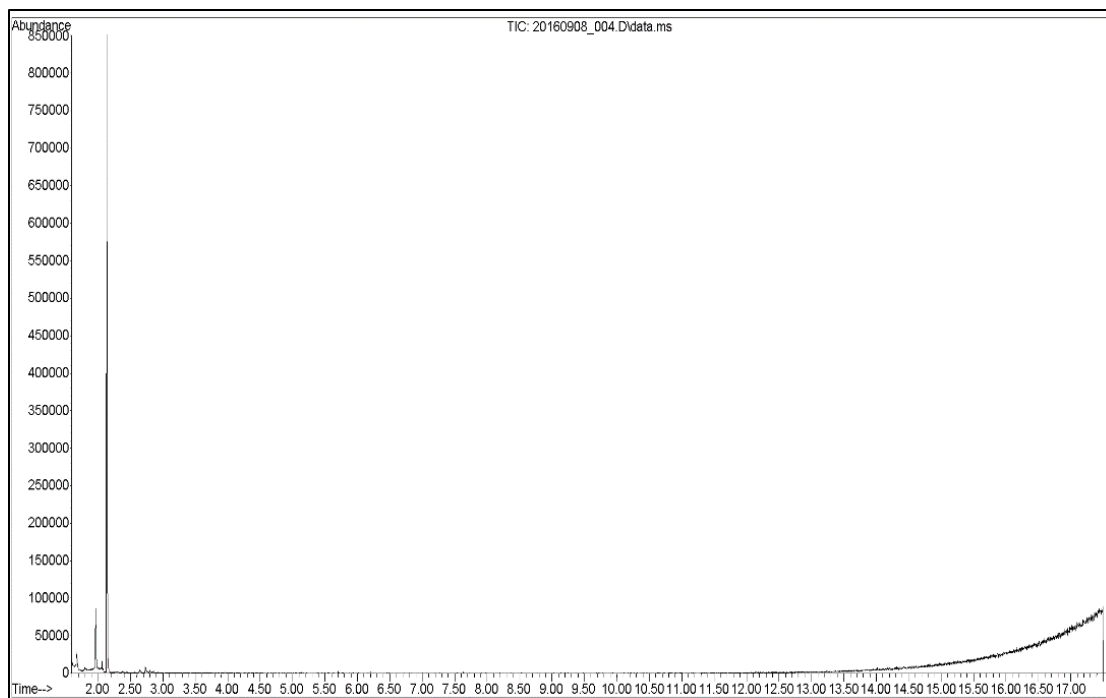


Figure 4. GC-MS spectrum for PC-ABS Blend material outgas sample (M2021).

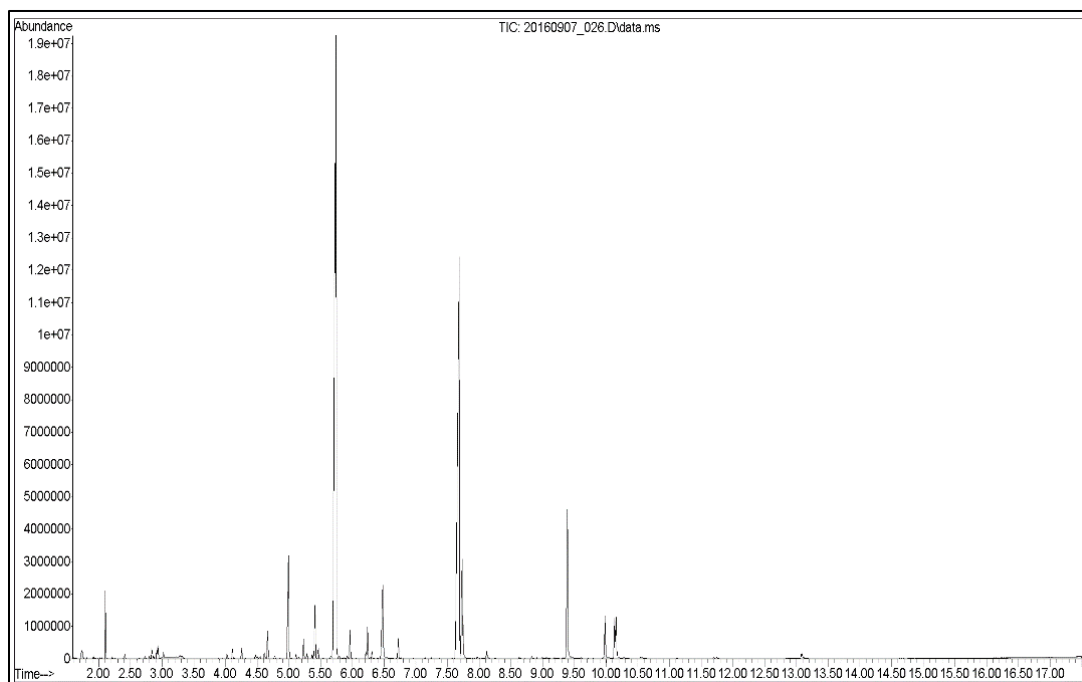


Figure 5. GC-MS spectrum for VeroWhitePlus material in acetone (M1011).

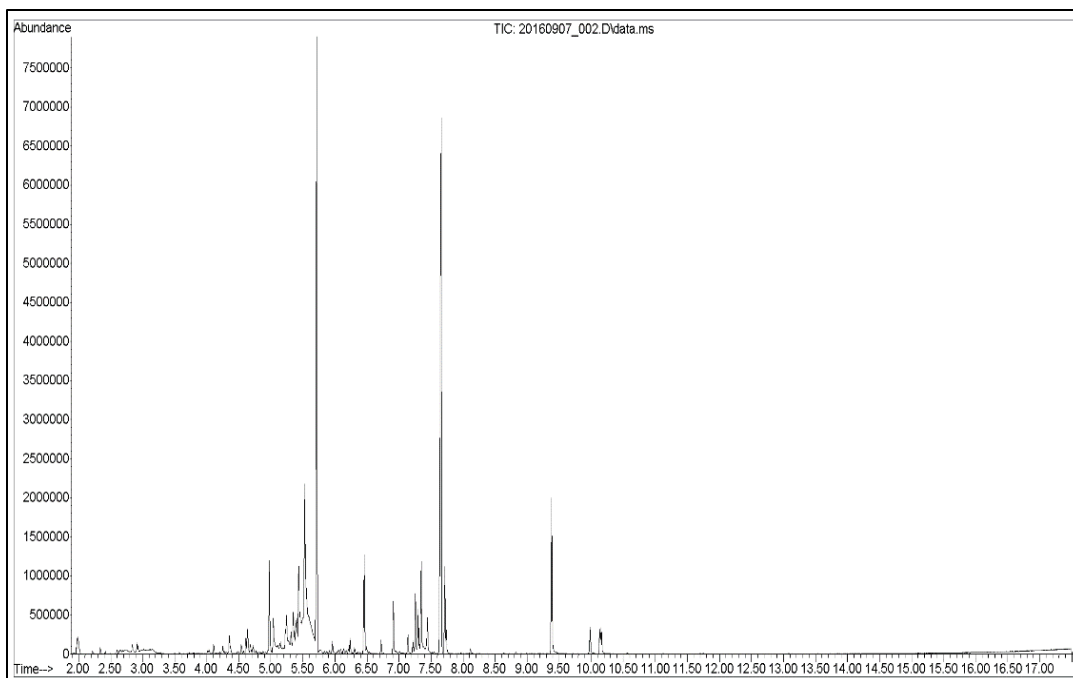


Figure 6. GC-MS spectrum for PC-ABS Blend material in acetone (M2011).

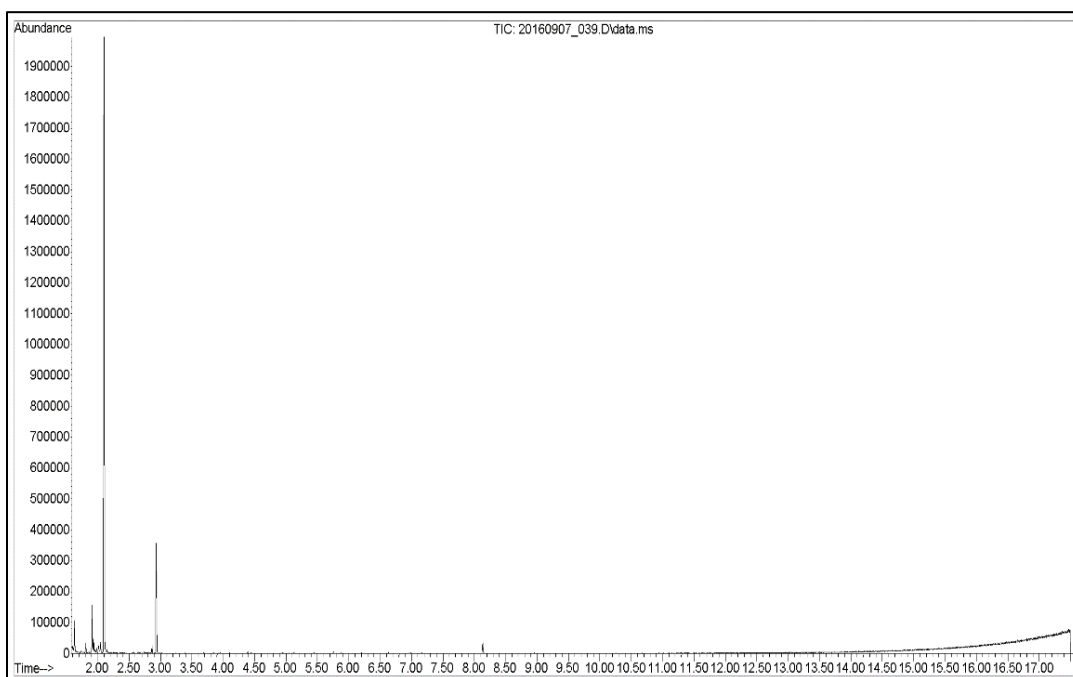


Figure 7. GC-MS spectrum for VeroWhitePlus material in acetonitrile (M1016).

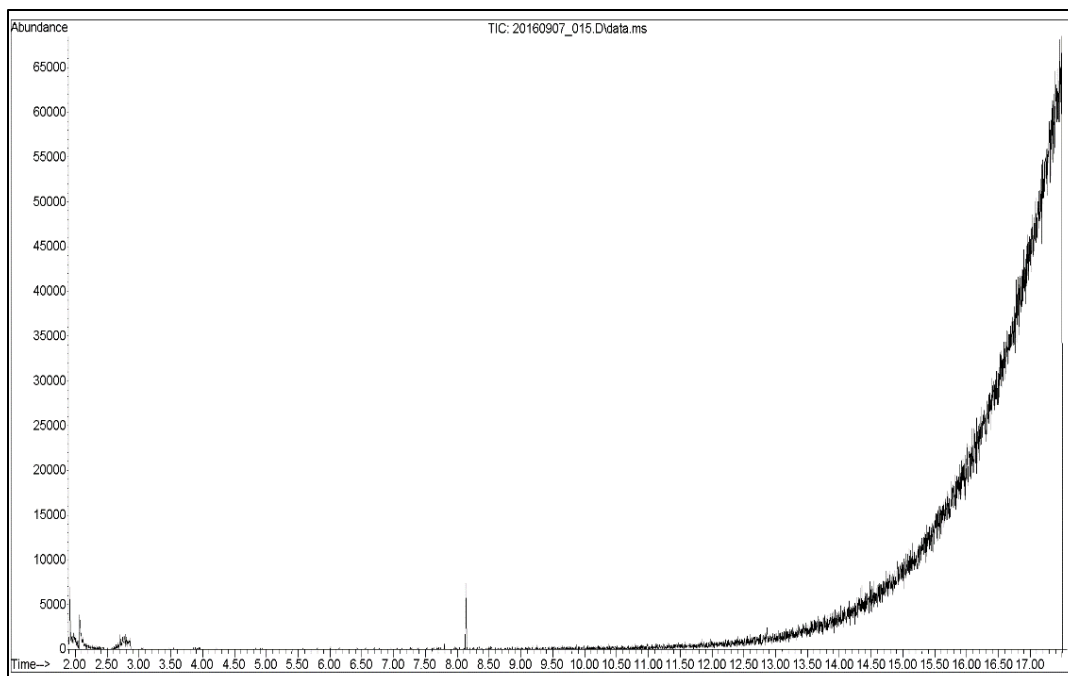


Figure 8. GC-MS spectrum for PC-ABS Blend material in acetonitrile (M2016).

3.2 LC-MS Results

The aqueous samples were run on an LC-MS (Thermo Q Exactive Orbitrap) with an ESI source. The results showed a major set of peaks that corresponded to sodiated PEG, which has a monomeric molecular weight of 85 Da. The formula for sodiated PEG is

$$\text{PEG polymer weight} = 41 + 44x, \text{ where } x \text{ is the number of subunits.}$$

Analysis of PEG shows characteristic peaks that are centered at approximately 437 Da and successively smaller peaks that are distributed approximately 44 Da apart for at least 10 resolvable peaks in both directions of molecular weight (Table 6, Figures 9-18). This dominant signal is a concern because it can be a source of ion suppression for other compounds that do not ionize as readily under these conditions. The samples were applied by direct injection through the ESI source and examined for mass peaks that are distinct from PEG (Table 6). The water and sodium hydroxide controls did not show any signals above background.

The VeroWhitePlus material displayed the most resistance with no peaks that were comparable to the PEG peaks (>75% of total peak area). However, a few peaks were present that warrant further interrogation, such as 1082 m/z and over a dozen poorly resolved peaks between 250 and 650 m/z for the water-exposed samples. The sodium hydroxide solvent samples had peaks at 993, 1075, and 269 m/z , some of which may also be polymers, but the signal was washed out as compared with PEG.

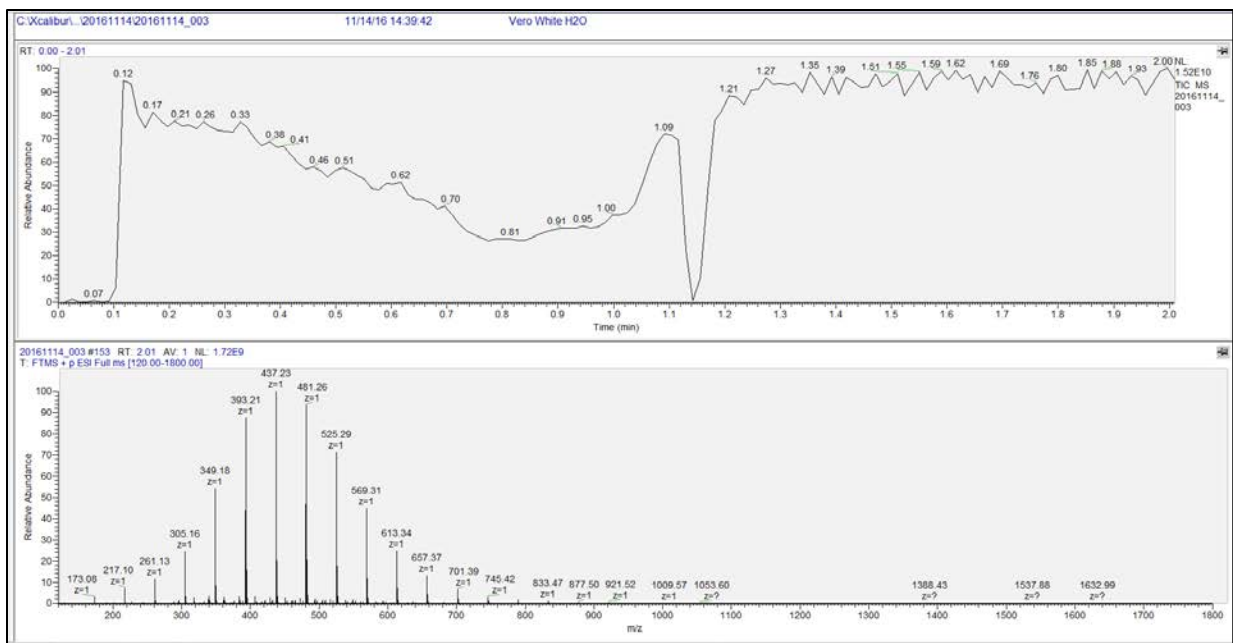


Figure 9. LC-MS spectrum for Sample ID M1003, VeroWhitePlus material exposed to water overnight.

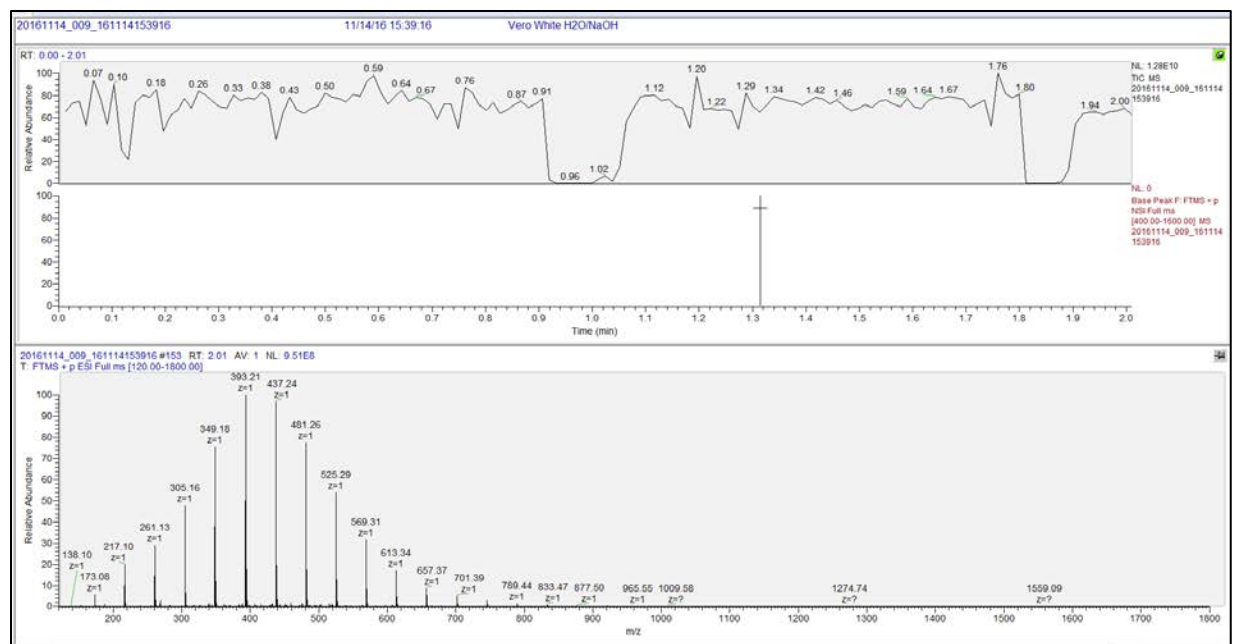


Figure 10. LC-MS spectrum for Sample ID M1009, VeroWhitePlus material exposed to 1N sodium hydroxide overnight.

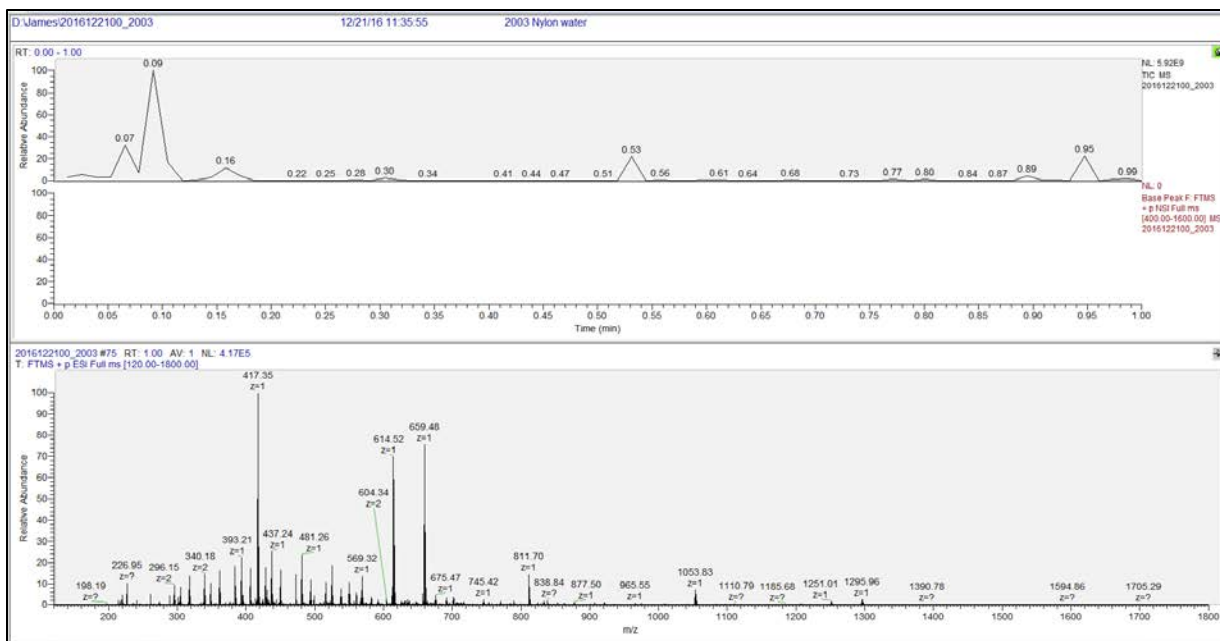


Figure 11. LC-MS spectrum for Sample ID M2003, PC-ABS Blend material exposed to water overnight.

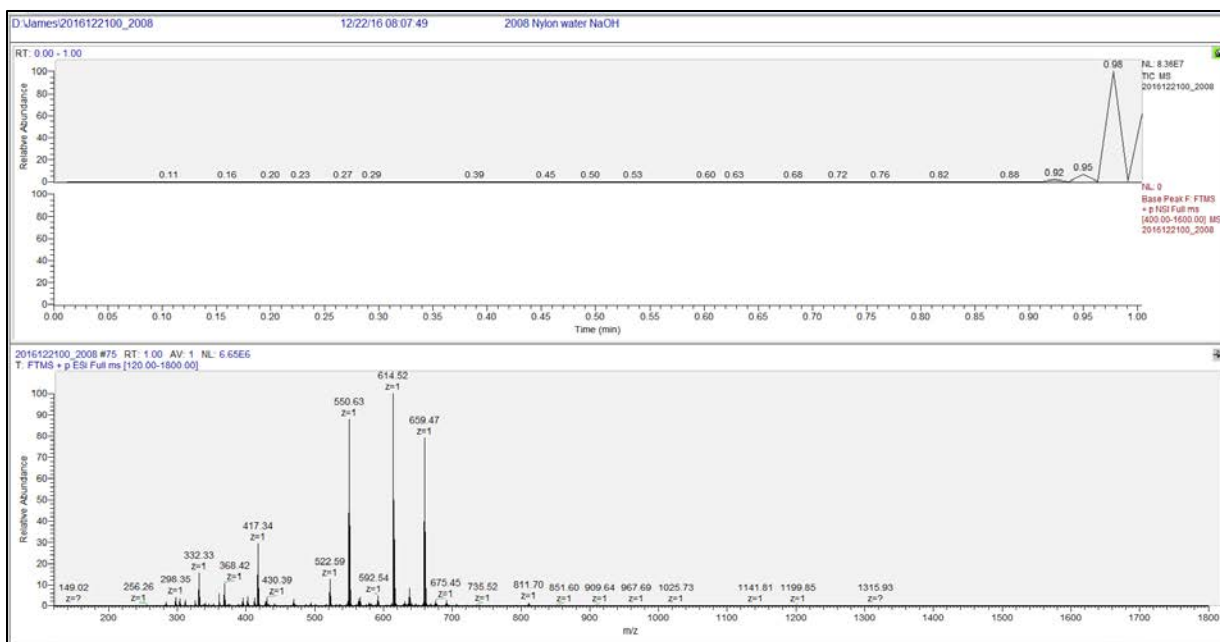


Figure 12. LC-MS spectrum, Sample ID M2008, PC-ABS Blend material exposed to 1N sodium hydroxide overnight.

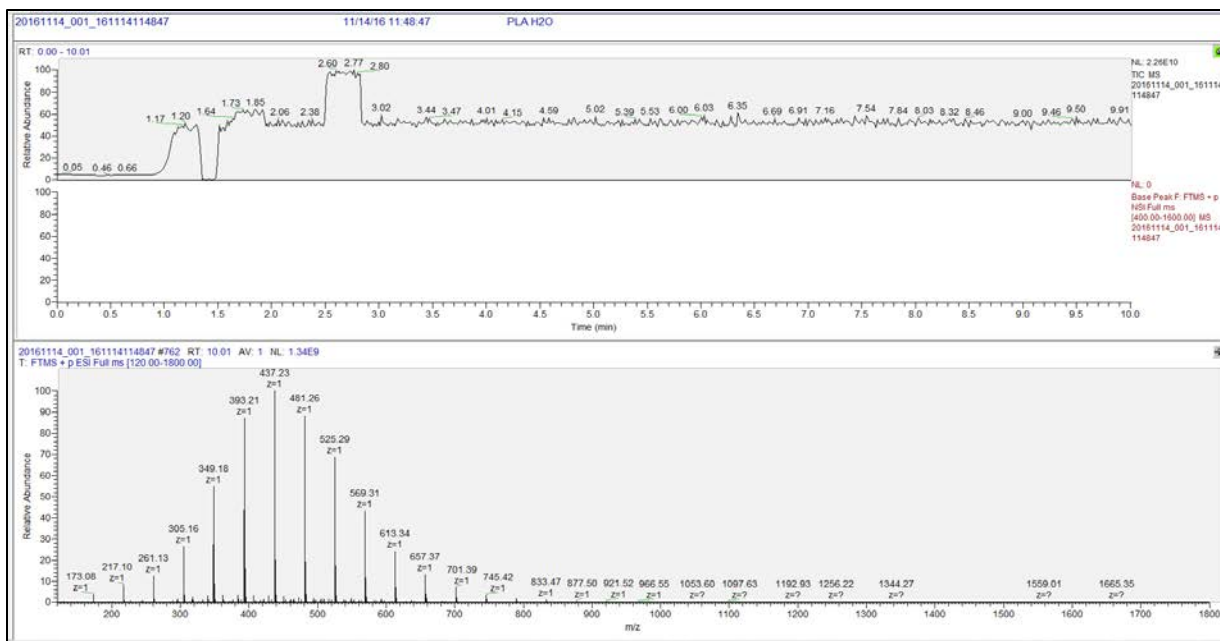


Figure 13. LC-MS spectrum for Sample ID M1001, VeroWhitePlus material exposed to water overnight.

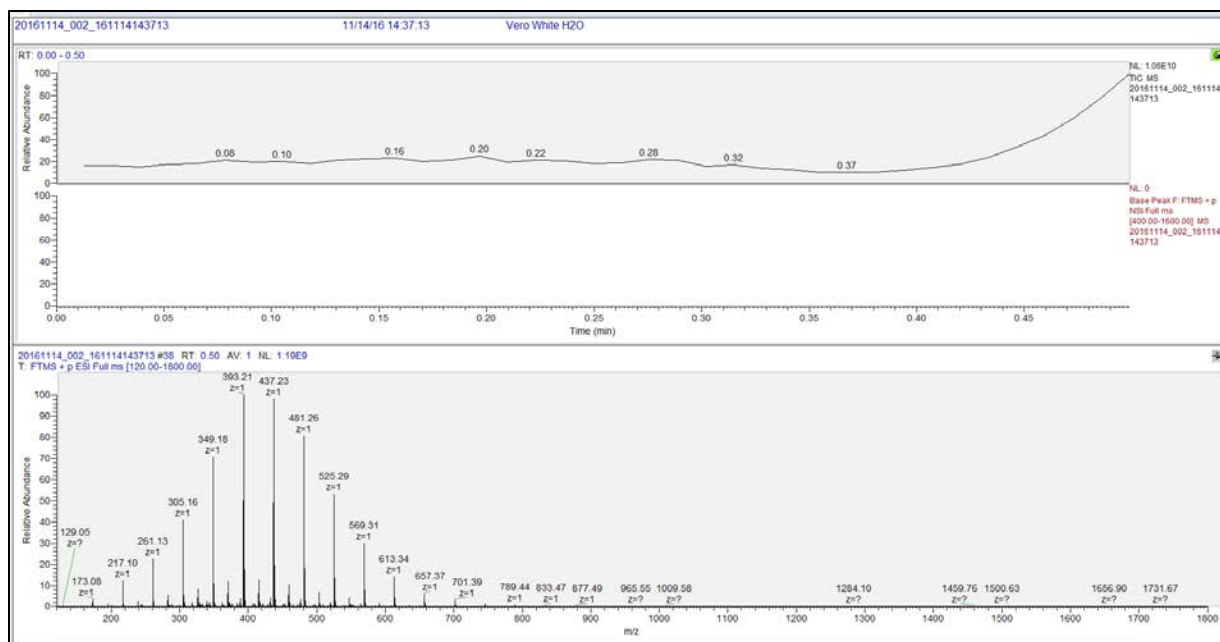


Figure 14. LC-MS spectrum for Sample ID M1002, VeroWhitePlus material exposed to water overnight.

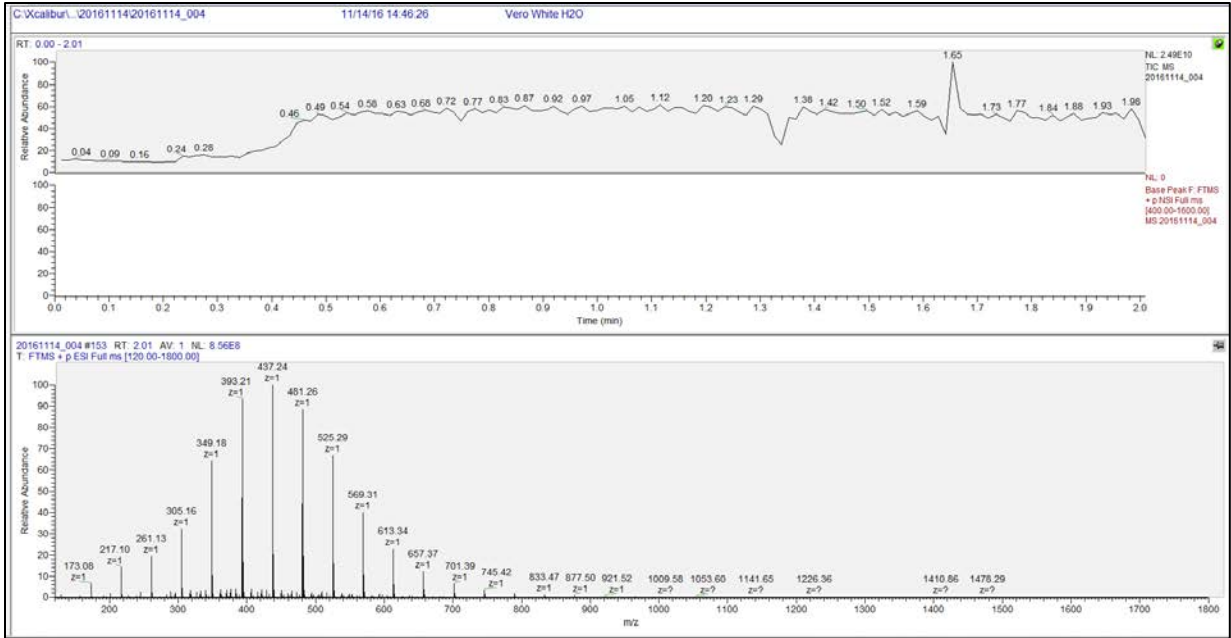


Figure 15. LC-MS spectrum for Sample ID M1004, VeroWhitePlus material exposed to water overnight.

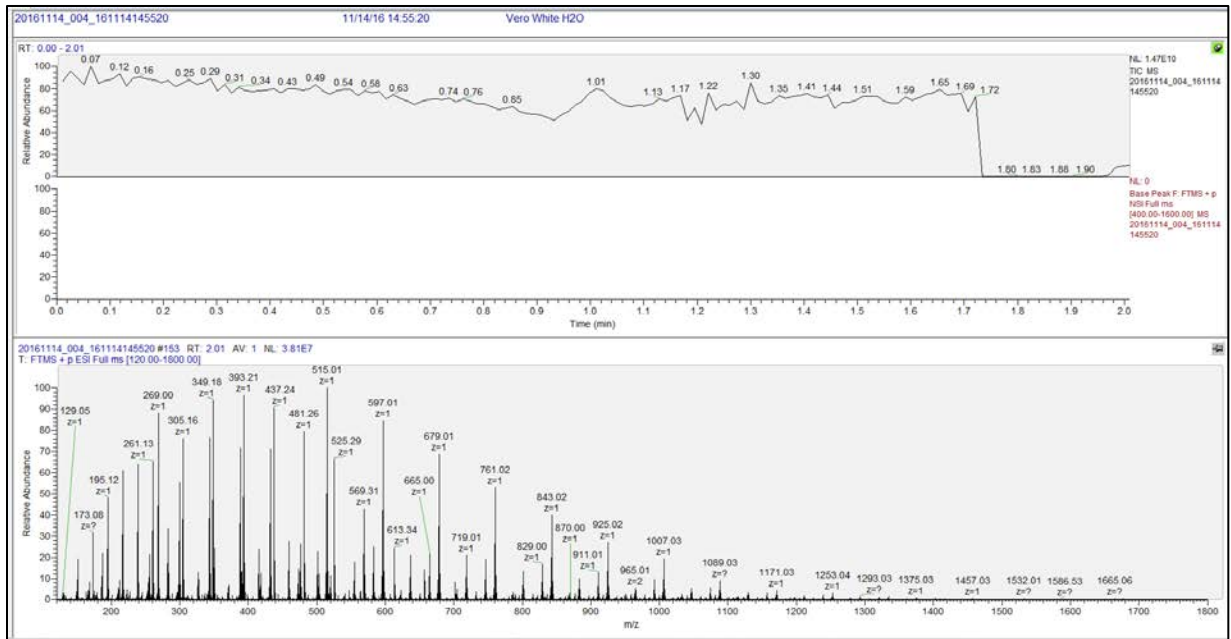
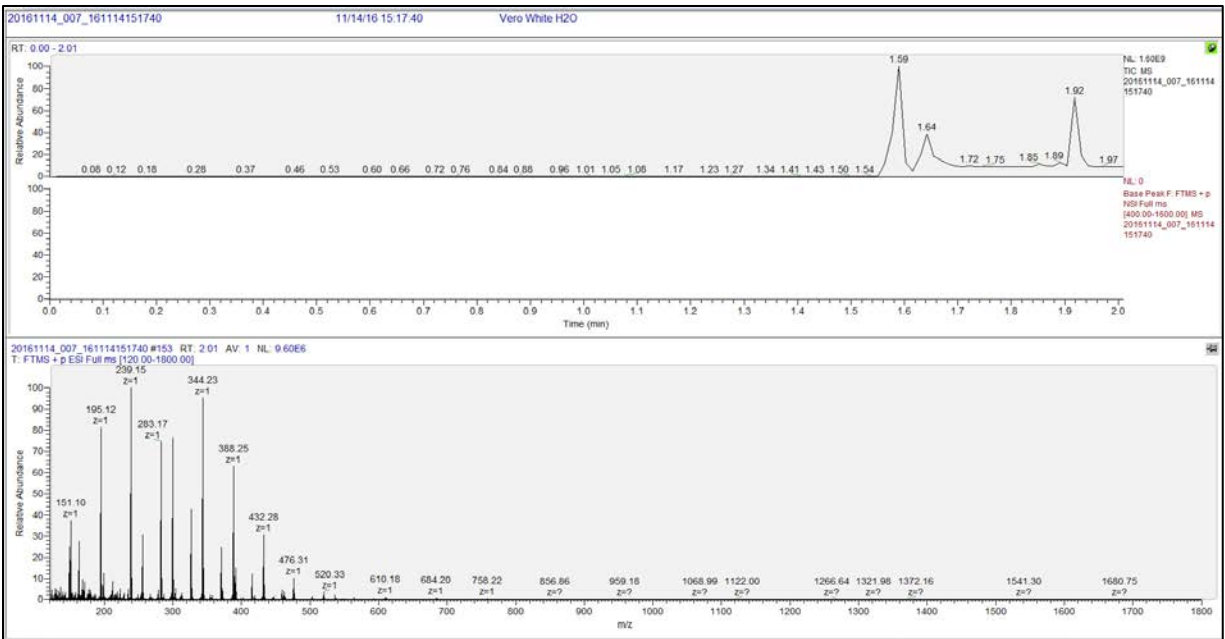
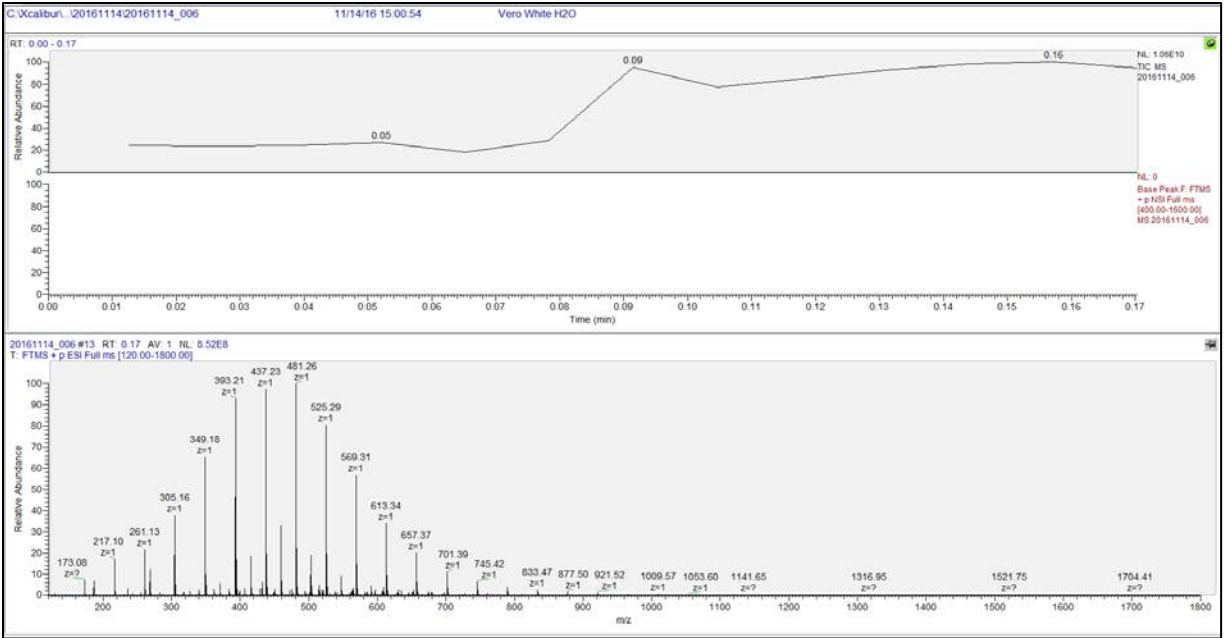


Figure 16. LC-MS spectrum for Sample ID M1005, VeroWhitePlus material exposed to water overnight.



The spectral data for the PC–ABS Blend material have very different profiles from those of the VeroWhitePlus material. For the PC–ABS Blend material, there were distinct and clear peaks over the PEG signal by 2 orders of magnitude. In water, the PC–ABS Blend material had four major peaks at 187.00, 269.00, 433.01, and 515.01 m/z (Figures 19–23). In 1N sodium hydroxide, the PC–ABS Blend material had peaks at 417.34, 614.52, and 659.48 m/z (Figures 24–28). The four peaks observed in water were likely sodium acetate (515 m/z) and the dissociated product ions of sodium acetate (187, 269, and 433 m/z). The peaks in the sodium hydroxide were not present on any contaminant list or conclusively identified previously with these methods.

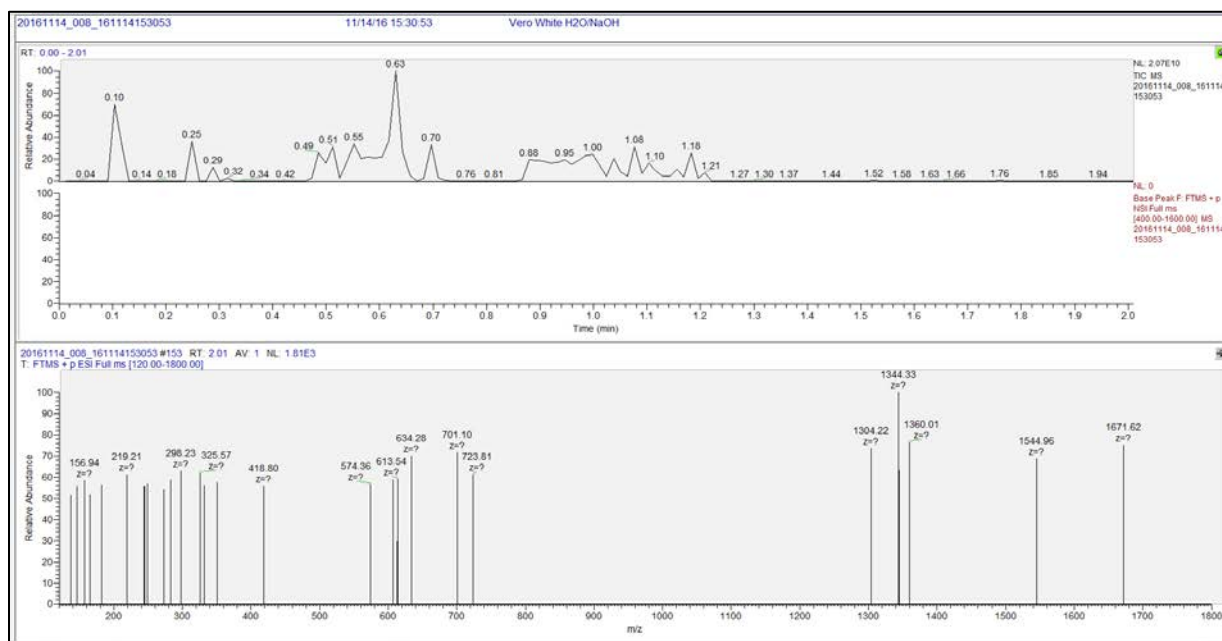


Figure 19. LC–MS spectrum for Sample ID M1008, VeroWhitePlus material exposed to 1N sodium hydroxide overnight.

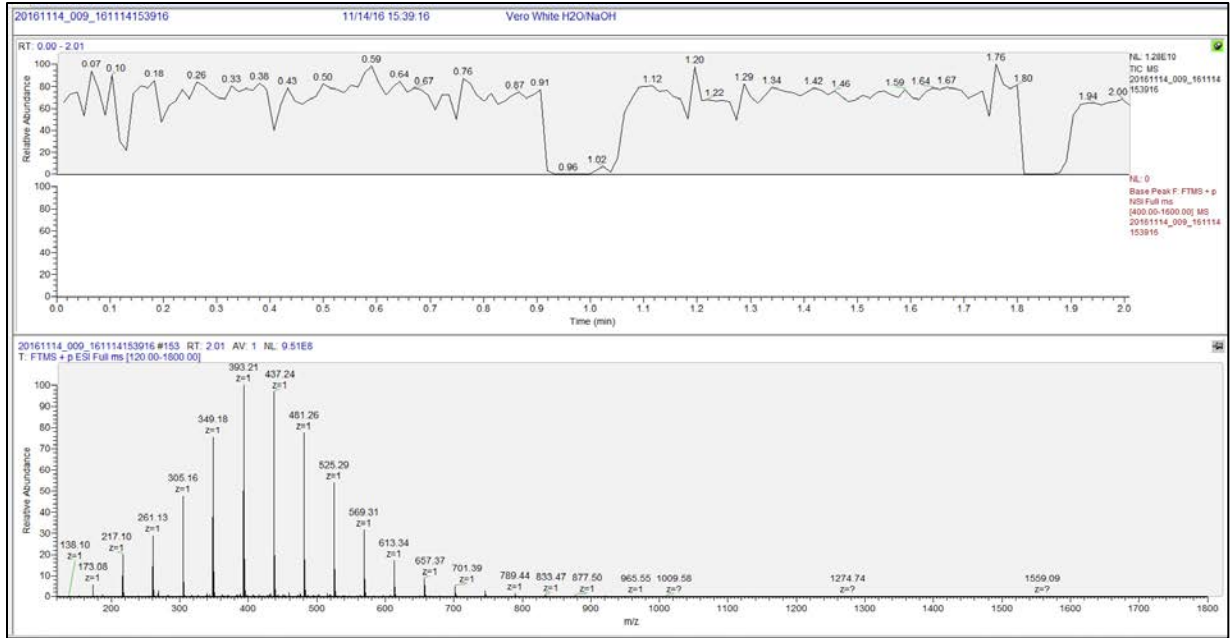


Figure 20. LC-MS spectrum for Sample ID M1010, VeroWhitePlus material exposed to 1N sodium hydroxide overnight.

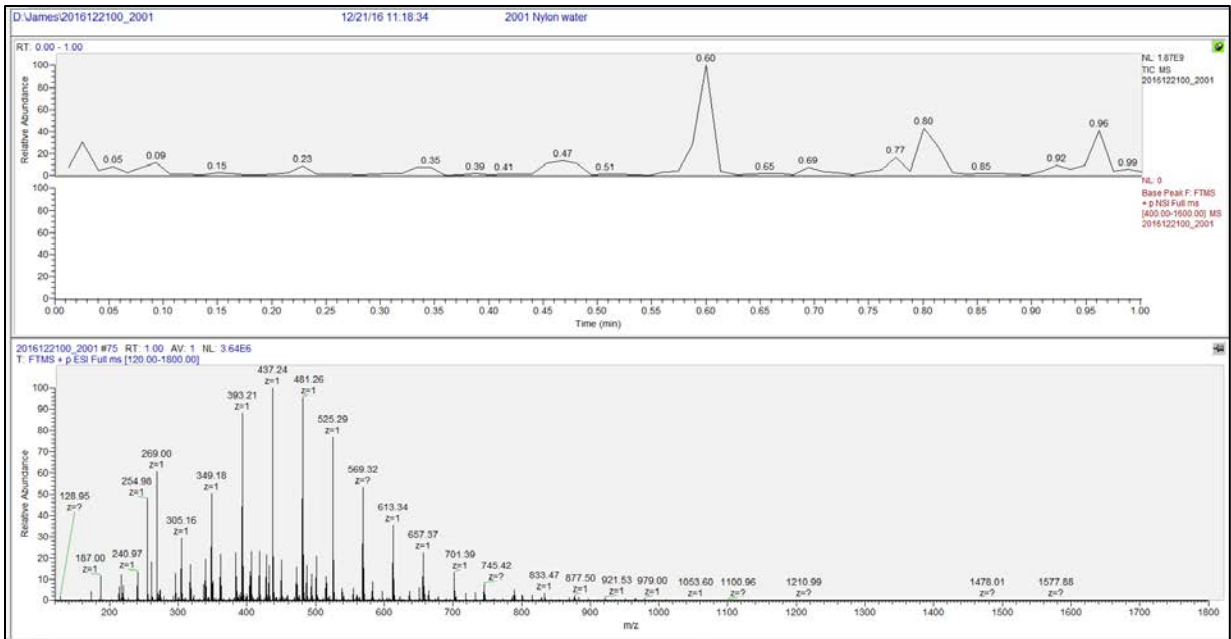


Figure 21. LC-MS spectrum for Sample ID M2001, PC-ABS Blend material exposed to water overnight.

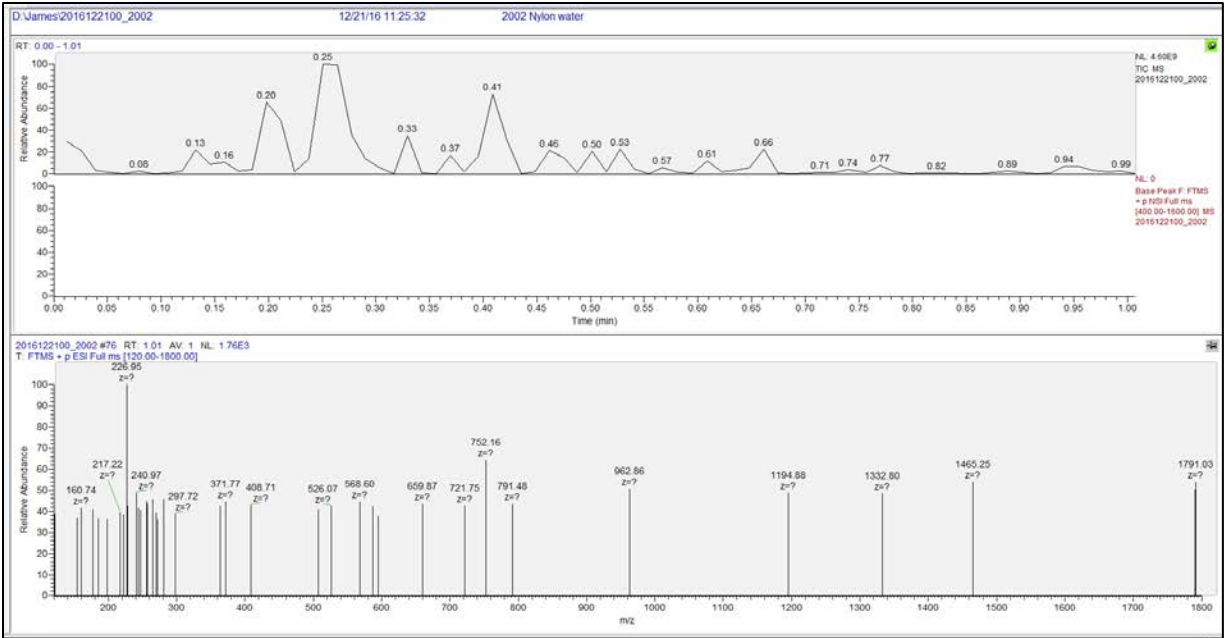


Figure 22. LC-MS spectrum for Sample ID M2002, PC-ABS Blend material exposed to water overnight.

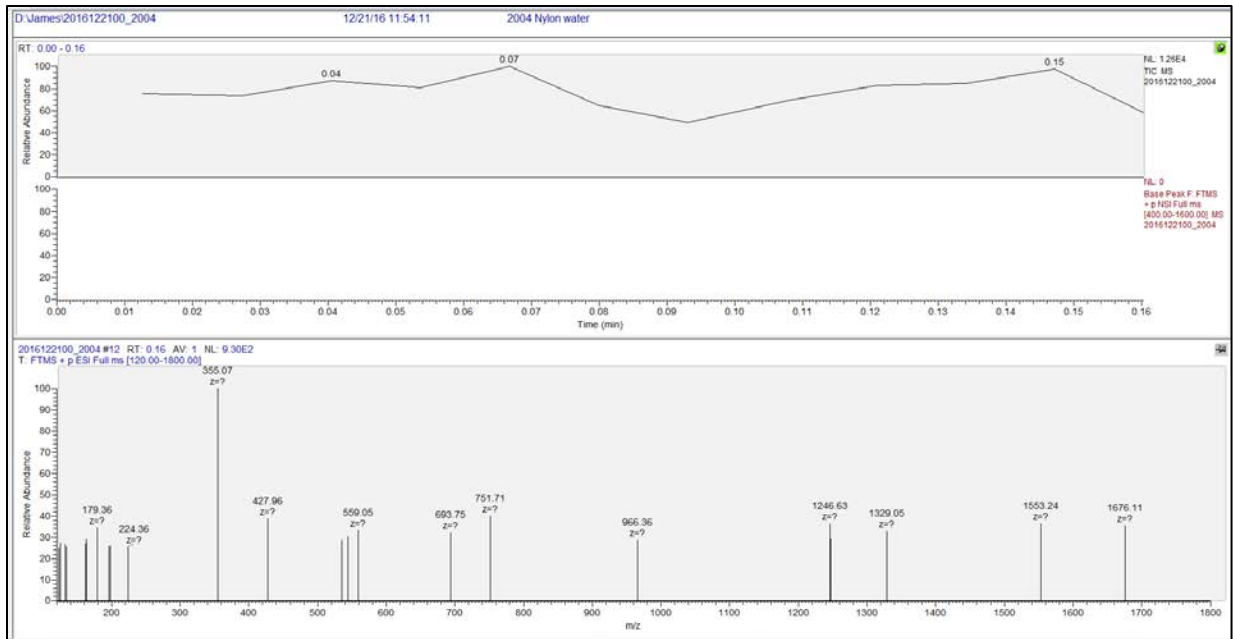


Figure 23. LC-MS spectrum for Sample ID M2004, PC-ABS Blend material exposed to water overnight.

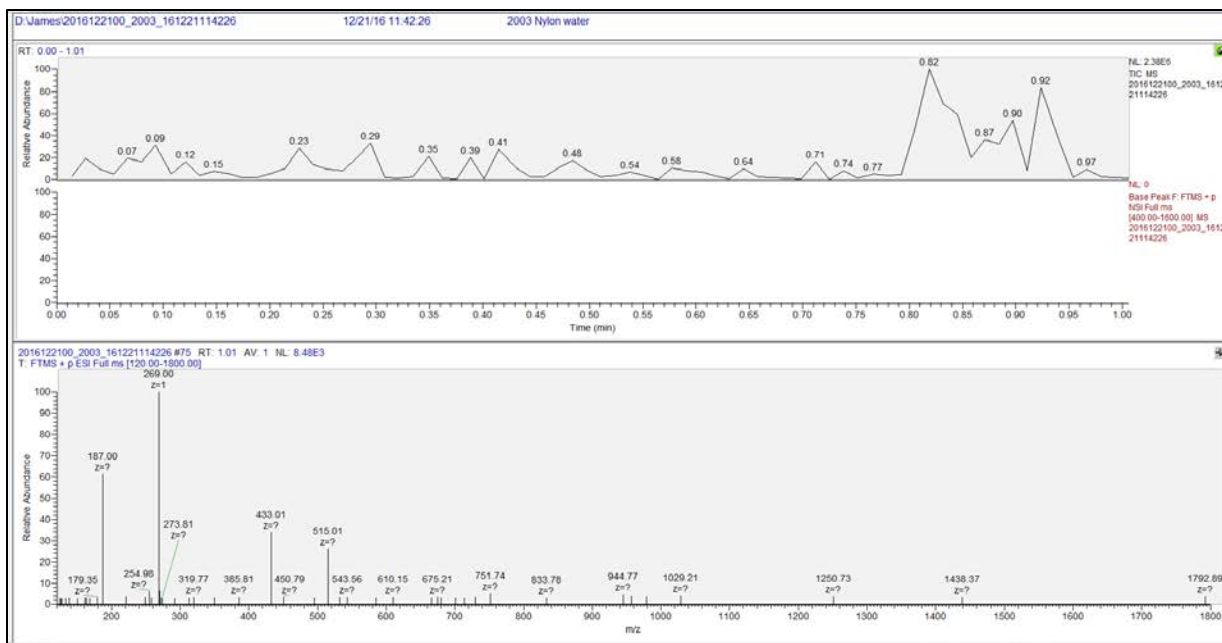


Figure 24. LC-MS spectrum for Sample ID M2005, PC-ABS Blend material exposed to water overnight.

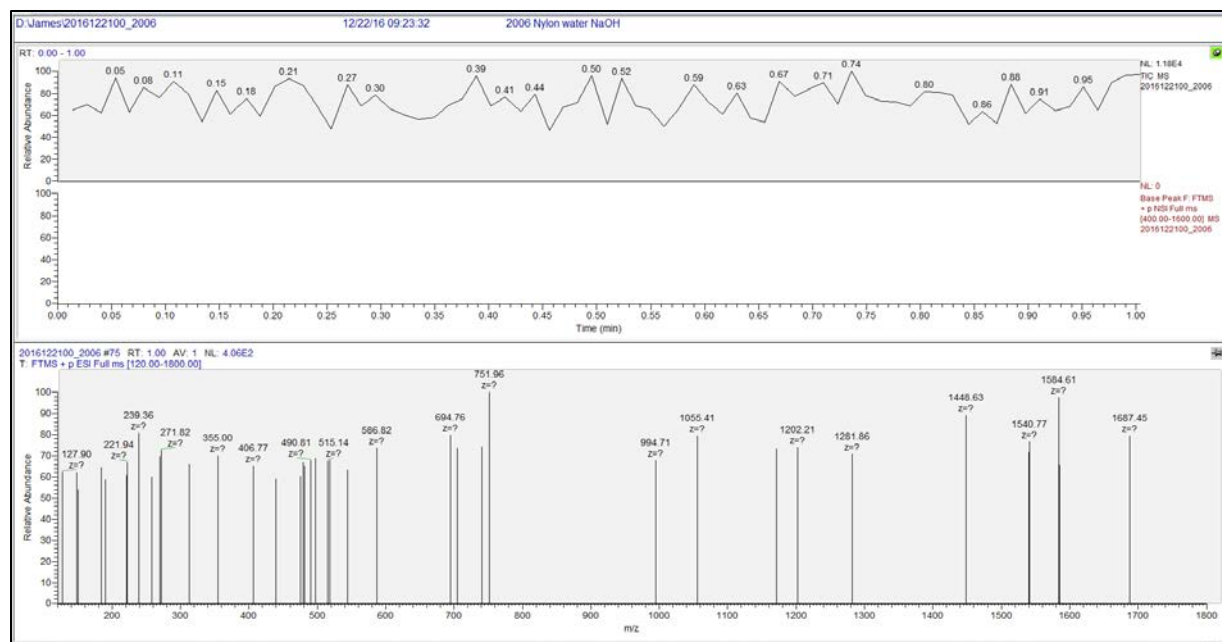


Figure 25. LC-MS spectrum for Sample ID M2006, PC-ABS Blend material exposed to 1N sodium hydroxide overnight.

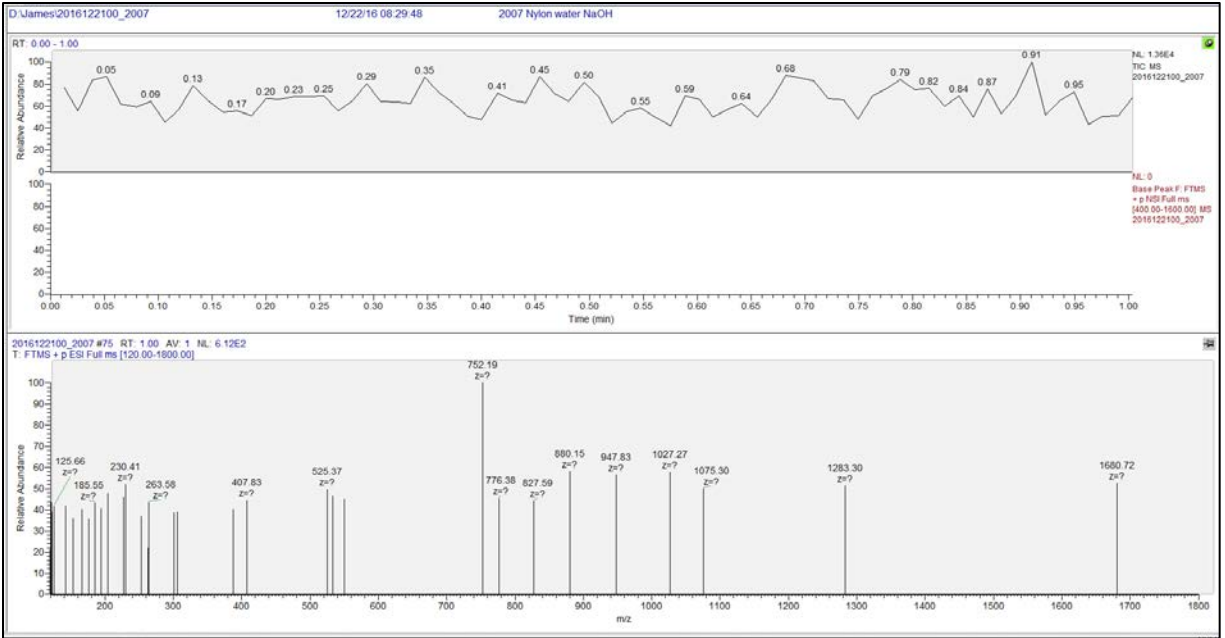


Figure 26. LC-MS spectrum for Sample ID M2007, PC-ABS Blend material exposed to 1N sodium hydroxide overnight.

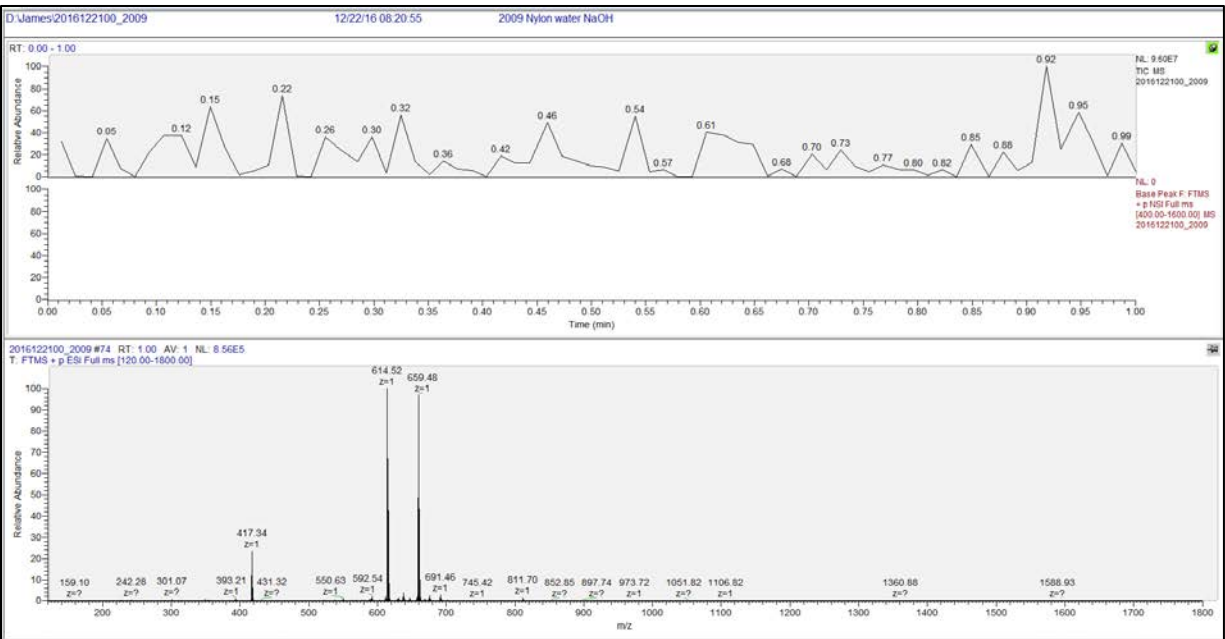


Figure 27. LC-MS spectrum for Sample ID M2009, PC-ABS Blend material exposed to 1N sodium hydroxide overnight.

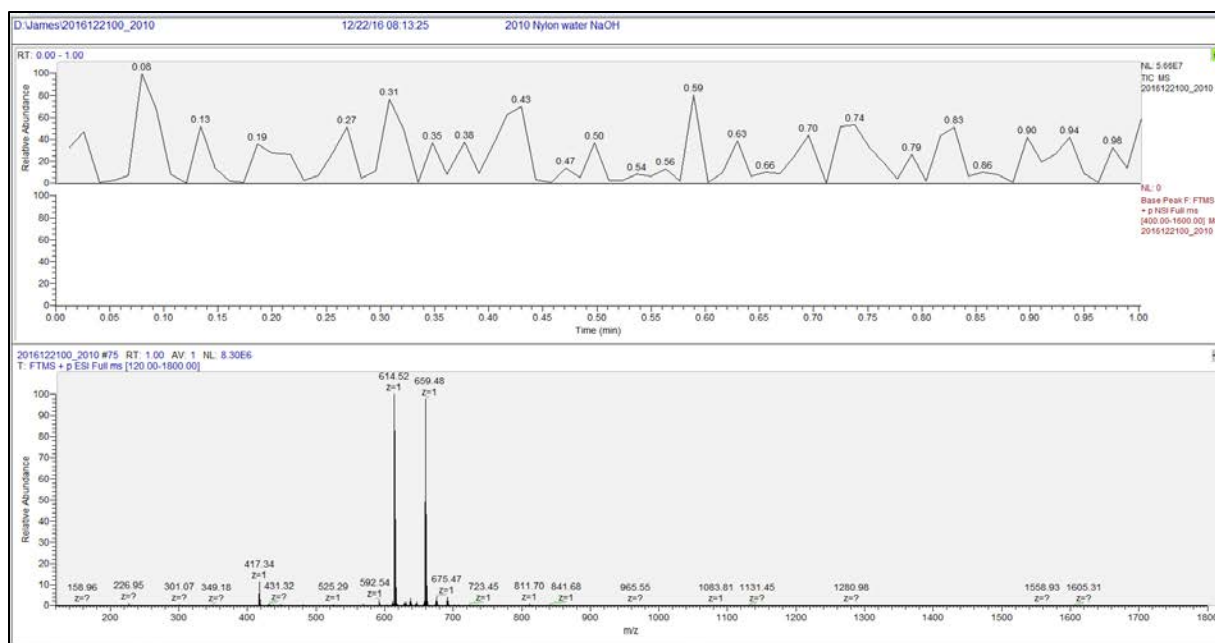


Figure 28. LC–MS spectrum for Sample ID M2010, PC–ABS Blend exposed to 1N sodium hydroxide overnight.

Table 6. LC–MS Peaks Summary

VeroWhitePlus in Water		VeroWhitePlus in 1N NaOH		PC–ABS in Water		PC–ABS in 1N NaOH	
Peak (m/z)	Identity	Peak (m/z)	Identity	Peak (m/z)	Identity	Peak (m/z)	Identity
187.00	Product ion	417.34	Possibly PEG	1082	Unknown	993	Unknown
269.00	Product ion	614.52	Possibly PEG	250–650	Unknown	1075	Unknown
433.01	Product ion	659.48	Possibly PEG			269	Unknown
515.01	Sodium acetate						

Blank cells indicate no data available.

4. CONCLUSIONS

The GC–MS data illustrate the direct interactions between the two 3D-printed materials, VeroWhitePlus and PC–ABS Blend, with the organic solvents acetone and acetonitrile. The common detection leachates from the VeroWhitePlus material were *N*-acryloylmorpholine, 2-propenoic acid, and 2-propanol (Tables 3 and 4), which were found in both organic solvents. These are likely passive leachate derivatives from the 3D-print material fabrication process. The unique compounds that were found in each solvent, three unknowns in

acetone and methanone in acetonitrile, were likely the product of direct reactions between the solvents and the VeroWhitePlus material. To a lesser extent, it is possible that the differential detection was because of solubility differences in the two solvents. However, the inability to identify the compounds in acetone in the NIST database is an indication of a novel product, because the constituents of the polymer are well-characterized and present in the NIST database. The GC–MS data suggested that the VeroWhitePlus material is highly susceptible to acetone (Tables 3 and 4), whereas the PC–ABS Blend material is much more resilient. Both of these materials are resistant to acetonitrile; however, there was a small amount of leachate present (Table 6, Figures 12 and 13). The identity of the leachate was determined using the NIST chemical database and verified against an independent database generated by MRICD staff.

The spectra of the PC–ABS Blend material was much simpler in profile (Figures 11 and 13); therefore, its analysis was less conclusive because the compounds in the controls and the experimental samples were not identified. It is clear that the unknowns are different in the experimental and control samples because of the different retention times and spectral features (Figures 10–13). In addition, azacyclotridecan-2-one (62% confidence level for identification) was identified in acetonitrile (Table 6) and is likely to be unique to the interaction of the solvent and PC–ABS Blend material. The azacyclotridecan-2-one was possibly a derivative of the dodecane that was observed in the outgas experiment.

The LC–MS data were more complex and challenging to interpret without the ability to search the spectral libraries. The ionization method using the ESI source is biased towards sodiated compounds and PEG oligomers, as shown in Table 6 and the spectra (Figures 10–13). However, there are signs that these solvents also interact with the materials to produce byproducts that are nontrivial (minor, poorly resolved peaks in Figures 10–13). A thorough and detailed method can be developed to separate the PEG from the rest of the compounds to enhance the ionization. It is possible that in addition to applying a column, other types of sources can be used, such as matrix-assisted laser desorption and ionization or capillary electrophoresis inlet techniques. Filtering the solutions was considered; however, the potential for contamination from the filter and for adherence of the polymers to the filters was sufficient motivation to find alternate methods for removing the sodiated compounds and PEG. The simplest solution was to find an LC method that effectively isolates the PEG and allows resolution of the lesser peaks.

The next phase of this work is to examine CWAs (2–4 compounds composed of CWAs), toxic industrial chemicals, toxic industrial materials, and drugs of abuse. In addition, work will be done to examine the behavior of the 3D-printed materials in the common decontamination solutions (two to four solutions composed of bleach, 1N sodium hydroxide, and a corresponding decontamination for the compounds chosen). The results from this study indicated that consideration of the decontamination conditions will affect the compatibility with 3D-printed materials. Opportunities for funding through DHS Standards and Measures and the appropriate EPA office will be pursued as Phase 2 proceeds to identify the requirements for the funding partners to become involved programmatically.

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ACRONYMS AND ABBREVIATIONS

3D	three-dimensional
ABS	acrylonitrile butadiene styrene
ACN	acetonitrile
AGC	automatic gain control
ARL	Army Research Lab
CWA	chemical warfare agent
DHS	U.S. Department of Homeland Security
EPA	U.S. Environmental Protection Agency
ESI	electrospray ionization
GC	gas chromatography
LC	liquid chromatography
MRICD	U.S. Army Medical Research Institute of Chemical Defense
MS	mass spectrometry
<i>m/z</i>	mass-to-charge ratio
NIST	National Institute of Standards and Technology
PC	polycarbonate
PEG	polyethylene glycol
REF	U.S. Army Rapid Equipping Force
RF	radio frequency

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