AN ABSTRACT OF THE THESIS OF

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Abstract approved: _____

Skip Rochefort

There has been much controversy in recent years over the leaching of chemicals from plastic water bottles. In this study, two of the most common plastics used in water bottles, polyethylene terphthalate (PETE) and polycarbonate (PC) were studied. The leaching of the chemical bisphenol-A (BPA) from polycarbonate (Nalgene ™, Camelback ™) water bottles was studied to examine the validity of these claims by exposing polycarbonate bottles to various conditions and analyzing how much BPA leaches into water contained in the bottles. New polycarbonate bottles were filled with water and exposed to treatment conditions ranging from 65 to 120 ⁰C. A reverse-phase solid phase extraction process was developed to extract BPA from the water and concentrate it into an organic phase. GC/MS was used to analyze the organic extract. BPA was only found to leach in detectable amounts (< 10ppb) when the bottles were exposed to 120 ⁰C water for 2 hours.

Polyethylene terephthalate bottles were also tested and were exposed to sunlight for three months during the summer. Small amounts of the plasticizer DEHP were found to leach after several months. A method for determining what chemicals would leach from BPA-Free Tritan™ copolyester was also developed but not tested due to time constraints. An analysis of internal stress due to high humidity and temperature was performed on these BPA-Free bottles.

Key Words: Plastic Leaching, Polycarbonate, Polyethylene Terephthalate, Tritan™, BPA, Dornathp@onid.orst.edu

Analysis of Chemical Leaching from Common Consumer Plastic Bottles

Under High Stress Conditions

by

Paul John Dornath

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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Paul John Dornath, Author

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I would like to dedicate this work to the wonderful teachers of ***Benson Polytechnic High School*** in Portland, Oregon. Thank you for all your years of sweat and tears to bring us an extraordinary education and inspiring us to pursue our dreams. I pray that the school closures pass you with ease and grace.

Preface

The initial inspiration for performing this research came in part from three trips to India from 2004 to 2006. While traveling abroad in countries where drinking water is questionable or unsafe, it is necessary to secure a clean potable water source. The most convenient and sometimes safest water source is from disposable water bottles. In some places these bottles are sold and stored in direct sunlight. Through personal experience one may notice that a bottle of water left in a hot car for a few hours on a hot, sunny day will produce water with a strange taste. This taste is actually caused by a chemical called acetaldehyde, which is the same substance that the body metabolizes ethanol into and causes hangovers. This chemical is formed as a result of UV photo-degradation of polyethylene terephthalate (PETE #1 plastic, used for two liter soda and disposable water bottles). Another chemical known to be in polyethylene terephthalate bottles is the plasticizer *DEHP*. Plasticizers like DEHP are chemicals that make plastic softer and are responsible for the plastic's flexibility (EPA, 2007). DEPH is also a known endocrine disrupter (EPA, 2007). DEHP was banned from toy teething rings and other products for children under three years of age in Sweden in 2000 and in the US in 2009.

Figure 1: Drink Vender in India (Chennai, India)

People in developed countries do not normally have to worry about these effects as most consumable products are transported in air-conditioned trucks and are stored in areas away from intense heat and away from direct sunlight.

A process known as *solar disinfection sterilization (SODIS)* is used in rural parts of India. In SODIS, water is put into 2 liter PETE bottles which are then put on a roof in the sun for 6 hours in an attempt to kill bacteria in the water with UV radiation from the sun. When I noticed that many of these bottles were stored in the sun and outside in the heat I thought of how this might be affecting the health of anyone who drinks from them. A small chemical exposure may be an acceptable price to pay for the easy removal of organisms that cause dysentery, but I was still concerned for those who live in areas where it is often necessary to consume water from these bottles that are stored in the sun. This concern drove me to perform my initial investigation on plastic leaching.

During my senior year of high school I attempted to develop an experiment to study the effects of water from PETE bottles exposed to UV light by growing onions. My mentor during this time was my chemistry teacher Jean Eames. I had read a similar study (Evandri, 2000) performed at the University of Rome where *Allium cepa* onions were grown with water from UV exposed PETE bottles. They observed mitotic aberrations during cell growth and they attributed this to unknown chemicals in the water.
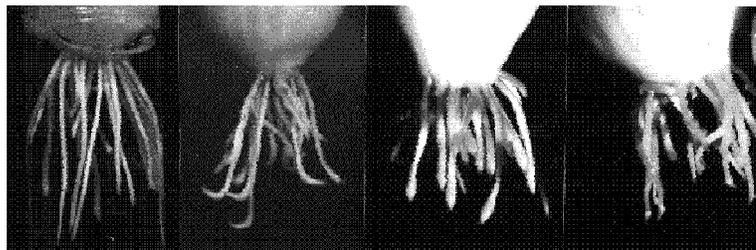
Figure 2: Onion Tumors: Tumors caused by growth in water from PETE bottles exposed to sunlight

The initial test was performed during the middle of winter so I built an incubator that could run for twelve hours a day. The incubator used a halogen lamp to mimic sunlight. The temperature in the incubator was kept between 18 and 31 $^{\circ}$C using an air conditioner, thermocouple, and two computer cooling fans.

Allium cepa onions were grown in the water from bottles that had been incubated for two weeks. I counted the number of roots, measured the length of the roots and observed pieces of root tips under the microscope every 19 hours (the length of the mitotic cycle) (Evandri, 2000). Experimental errors due to my ignorance of proper cell observation techniques nullified the results of the microscope observations. The most convincing data obtained, however, came from a Gas Chromatograph/ Mass Spectrometer (GC/MS) experiment of the water performed at Portland State University. There was no pre-concentration procedure performed so the results were very rough. Water that was exposed for 35 days and water from control bottles (bottles that were not exposed to any heat or light conditions) was run through the instrument. A signal appeared at the 105 and 91 dalton peak, the signature chemical fragments of the PETE backbone that indicates photo-degradation. These peaks only appeared when the water from the treated bottles was run through the GC/MS and were not present in any of the control samples. These results were presented at one national and two local science fairs in the spring of 2006, and served as the basis for the start of the current research.

Introduction

A number of different plastics are used to make plastic water bottles. In recent years there have been reports of chemical leaching from consumer water bottles. There is often ambiguity in the minds of consumers as it is not always clear what type of plastic one's bottle is made out of and if that plastic is considered safe. The principle resins being investigated in this study are polycarbonate (PC #7 recycling code), polyethylene terephthalate (PETE #1 recycling code) and Tritan™ copolyester. It will be important to understand some key terms before reading the rest of this study. Important nomenclature and vocabulary is presented in *Appendix I.*

Polycarbonate

Polycarbonate is the plastic that previously had been used to make Nalgene™ and Camelback™ water bottles that are designated with the recycling code #7 PC (NOTE: The current "BPA-free" bottles on the market are typically made from either Tritan™ copolyester or PETE) . It is a polymer made up of two compounds: phosgene and bisphenol-A (BPA). These two monomers, or repeating units, react via a condensation reaction to produce the polycarbonate polymer. The reaction for the formation of polycarbonate is shown in Figure 3:
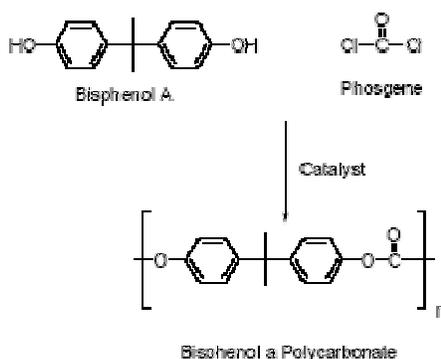
Figure 3: Polycarbonate Formation Reaction: Polycarbonate is a condensation reaction between Bisphenol-A and Phosgene to form polycarbonate. (Møller, 2003)

It is important to understand that the chemical bisphenol-A (BPA) is not an additive to the plastic. It is the monomer group from which the polymer is made and is a part of the polymer chain backbone. There may be a small amount (in the ppm range) of free BPA left unreacted in the plastic due to incomplete polymerization. This unreacted BPA will not be able to be released from the plastic matrix unless the plastic is either degraded or it is heated above its glass transition temperature (see *Appendix I* for a full description of these terms). Bisphenol-A is not only present in Nalgene water bottles. It is also present (even today) in the lining of aluminum and tin cans for food, most plastic kitchen products including hard, clear plastic glasses, bowls, blenders, dental sealants, and in a number of non-food related products such as epoxy resins, compact disks and lenses.

In 2009 Nalgene™ and Camelback™ officially switched to a new polymer called Tritan™ copolyester, which they marketed as "BPA-free". This switch was due to the large public fear of BPA leaching from the polycarbonate bottles. In a few short years the polycarbonate bottle went from being a ubiquitous household item to a demonized product that seemingly no one wanted to use.

How did this transition happen and what was the science behind it? There were a series of experiments run in the late 1990s and early 2000s that began to show that BPA could leach from polycarbonate under certain conditions. It should be noted that the maximum reference dose of BPA as set by European Commission's Scientific Committee on Food (SCF) is 10 µg/kg/day (which is 5 times as strict as the level set by the US EPA of 50 µg/kg/day) (Opinion of the Scientific Committee on Food on Bisphenol A, 2002). A 70 kg person would have to drink 1 liter of water a day continuously with a BPA concentration of 700 parts per billion (ppb) to experience these minimal harmful effects (3500 ppb with the US standards).

There were two series of experiments, one at the University of Missouri and the other at Washington State University (Hunt, 2003 (WSU) and Howdeshell, 2003 (UM)), that showed BPA could leach from used polycarbonate animal cages. The studies tested used polycarbonate cages that had been autoclaved, washed with strong alkali detergents, and that were showing visible damage. New polycarbonate cages and glass cages were used as the negative control. All of the tests performed allowed the cages to be exposed to water for 1 week at room temperature (22 C). The results showed that the damaged cages produced water with a BPA concentration as high as 160 ppb (although most were less than 62 ppb). Further repeated testes with the same cages only yielded a BPA release of 10 ppb. This indicates that a major release of BPA would only happen once per container due to the limited amount of free BPA that exists in the matrix. The new cages released polycarbonate at a concentration of only 0.3 ppb. Further duplicate tests of these cages did not yield detectable amounts of BPA after the first trial.

The question that should arise is if the amount of BPA that leaches from a new plastic in a week is over 10,000 times lower than the US standard of maximum daily exposure how did the bottles get such a bad reputation? The main reason is that there were other tests run by many of the same researchers that BPA itself was a harmful chemical. BPA, in large enough daily doses, can produce a hormone imbalance. The effects would only show up due to a chronic daily exposure because BPA is easily excreted by the body and only remains in your body for less than a day (Opinion of the Scientific Committee on Food on Bisphenol A, 2002). Other studies have shown that BPA could cause harm but not under the levels of BPA found to leach from polycarbonate at room temperature (Hoa H. Lea, 2008).There is debate on whether or not putting boiling water in PC bottles is harmful, as some studies say that there is reason to be concerned and others do not (Hoa H. Lea, 2008, Maragou, 2008, Ehlert, 2008). Nevertheless, it was due

to these and other similar studies that polycarbonate plastic developed a reputation as a plastic to avoid. Due to the ambiguity in some of this testing, the goal of this study was to develop and perform tests to determine how much BPA leaches from polycarbonate under conditions of varying temperatures and exposure times that would be closer to common use conditions, but somewhat more severe

Polyethylene Terephthalate

Polyethylene terephthalate (PETE recycling code #1) is the resin used to make disposable soda and water bottles. Polyethylene terephthalate is a resin similar to polycarbonate. It is also made up of an aromatic ester polymerized into large chains. The chemicals that go into making the PETE backbone are ethylene glycol and terephthalic acid. The condensation polymerization reaction for PETE is shown in Figure 4.
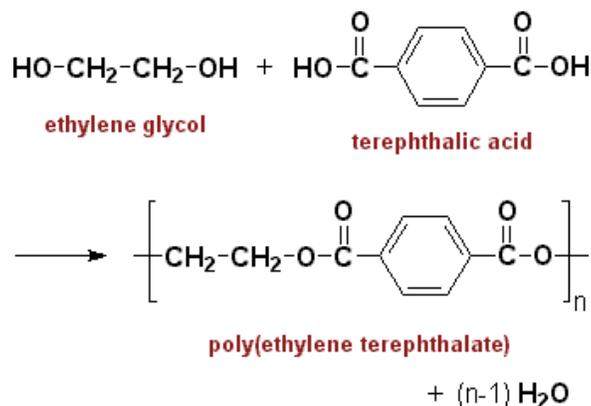
Figure 4: Polyethylene Terephthalate Formation Reaction: Condenstion reaction between ethylene glycol and terephthalic acid to form polyethylene terepthalate (Chemical Heritage Foundation, 2001)

The potential risks of using PETE plastic are considerably higher than those of using polycarbonate for several reasons. The first is that the products contained in the PETE bottles have been stored in unknown conditions for an unknown amount of time with the products one consumes touching the plastic the entire time. There are also more additives in PETE than in polycarbonate. The additive chemical of concern in PETE bottles is Bis(2-ethylhexyl)phthalate

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or DEHP. DEHP is a chemical that is added to a wide variety of ridged plastics such as PVC and PETE to make them more flexible. DEHP is one of many chemicals called *plasticizers* that are used to soften rigid plastics. The molecular weight of DEHP is low compared to that of polymers in which it is used, such that is closer to that of the free, unreacted BPA monomers left in the polycarbonate plastic. The difference between this chemical and unreacted monomer is that DEHP is added in concentrations that are much higher than those of unreacted monomer. Unreacted monomer may exist in the polymer matrix in the 1 to 10 ppm range while DEHP can be anywhere from 0.1 to 1 weight percent (1,000 to 10,000 ppm) (Hedenmark et al 2004). This chemical is therefore much more likely to leach out. PETE also has a lower glass transition temperature than polycarbonate at 85 ^{o}C compared to 150 ^{o}C. Sweden and other members of the European Union banned the use of DEHP from children's teething toys in 2000 and banned it from medical feeding tubes in 2005. The United States recently banned DEHP from children's toys in 2009 (Greenpeace 2009).

It is suspected that PETE can also undergo photo and thermal degradation. One mechanism of photo degradation is the Photo-Fries rearrangement. In this process UV light splits the ester bond leaving behind acetaldehyde and PETE backbone fragments. This process is shown in Figure 5 (Fechine, 2004).
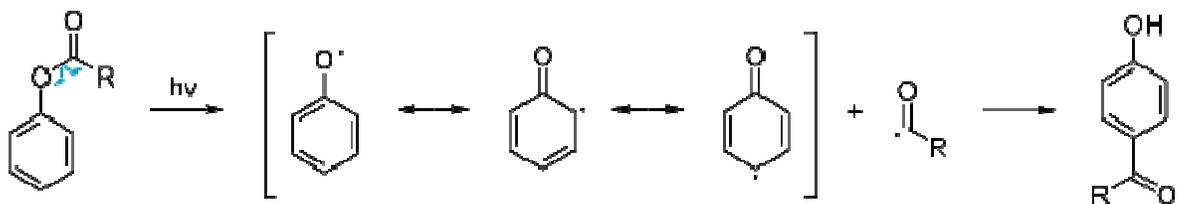

Figure 5: Photo-Fries Rearrangement of Aromatic Esters.

Photo-Fries rearrangement can happen to both PETE and polycarbonate esters (Diepens, 2007). The reason why this is more of a concern for PETE is because there is no way to tell if the products one consumes from these bottles have been left in the sun before consumption. One can notice the photo-degradation of PETE by simply leaving a water bottle in the car on a hot, sunny day. The strange taste in the water is acetaldehyde. A study from the *Journal of Water Supply: Research and Technology* performed in 2001 on the safety of solar water disinfection shows that PETE bottles will leach acetaldehyde, formaldehyde, and over eight different PETE aromatic fragments when left in the sun for several weeks (Wegelin, 2001). They did not test for the presence of DEHP.

The goal of this study will be to expose PETE water boghttles to sunlight for two months and run the samples through GC/MS to determine if any detectable amounts of DEHP, PETE monomers or degradation products were present.

Tritan[TM] BPA-free Copolyester

The "BPA-free" plastic that Nalgene™ has chosen to use to replace polycarbonate in their water bottles is called Tritan ™ copolyester made by Eastman Chemical Company. Chemical structure information on this plastic is difficult to find. The monomers used to make the plastic are known, but the actual structure of the plastic and the monomer arrangement in the repeating unit are unknown. The monomers used to make Tritan™ are currently not known endocrine disrupters. It is likely that these monomers could leach in the same way that unreacted BPA leaches from polycarbonate. The unreacted monomers could leach if the plastic is brought close to its glass transition temperature. The chemical structures of the known Tritan ™ monomers are shown in Figure 6.
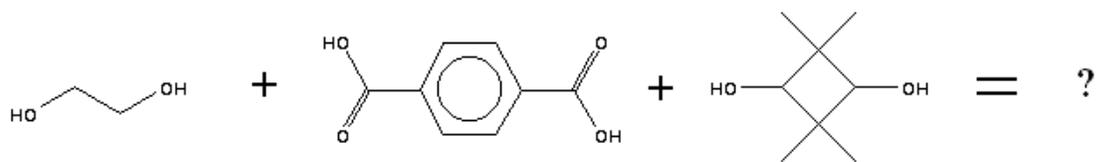
Figure 6: Tritan™ Copolyester Monomers: The known monomers used to make Tritan ™ copolyester (Morris, 1998 (Tritan Patent)). From left to right they are ethylene glycol, terephthalic acid and 2,2,4,4-tetramethyl- 1,3-cyclobutanediol.

The monomers to make Tritan are very similar to those used to make PETE only with a cyclobutanediol, which is likely added for extra strength. It is likely that there are two terephthalic acid monomers for every one monomer each of ethylene glycol and cyclobutanediol because the condensation polymerization reaction requires there to be one acid for every alcohol group.

Materials and Methods

The testing of each material had four phases. The first phase was background research. The discussion thus far has been based on this massive literature search. The second step was developing exposure, extraction and detection techniques for each resin. The third step was performing the plastic leaching studies, and fourth step was analysis of the data.

Polycarbonate Exposure Techniques

Literature results indicated it was very difficult to produce detectable amounts of bisphenol-A in water from polycarbonate bottles treated with room temperature (20 ^{o}C) or even dishwasher (55 to 65 ^{o}C) conditions (Chang, 2005, Hoa H. Lea, 2008, Yamamoto, 1999). The first experiment is therefore to determine if leaching occurs in any amount under high stress conditions such as in an autoclave at 121 ^{o}C. New 500 mL polycarbonate bottles were purchased from Dicountmugs.com. The bottlers were confirmed to be polycarbonate using differential scanning calorimetry (DSC). The DSC shows thermal transition data such as glass transition temperature, melting point, crystallization, and the relief of residual stress from the manufacturing process. The DSC does this by comparing the heat flow between an empty pan and a pan that has a plastic sample. The DSC ramps the temperature of both pans at the same time and tries to keep the temperature of both pans equal. The DSC must provide additional heat to pans with sample that undergo melting (endothermic process) or a glass transition and less heat to samples undergoing crystallization (exothermic process) (Höhne, 2003) . See Figure 13 in the *Results and Discussion* section.

An autoclave was used to heat the bottles and bring them closer their glass transition temperature (150 ^{o}C). This heating could cause the polymer structure to partially relax, and increase the mobility of lower molecular weight molecules (BPA monomer) through the matrix.

Bottles were raised to 121 ^{o}C at 2 bar pressure for two hours. Figure 7 shows the autoclave bottles exposure set up.

Figure 7: Autoclaving Polycarbonate Bottles

Two bottles were used with every test so that a total volume of 1000 mL could be used in the solid phase extraction process. The bottles were not modified in any way before they were treated. The water that was used was filtered via reverse osmosis before testing. Powdered 99.9 % pure bisphenol – A was purchased from Fisher Scientific to be used in standard solutions. Standard solutions of 1000, 100 and 10 ppb BPA were made for GC/MS calibration.

Polyethylene Terephthalate Techniques

The treatment to the polyethylene terephthalate bottles varies greatly from that for the polycarbonate bottles. The study of PETE bottles focused on the effect ultraviolet light in the degradation on the polymer backbone. New bottles were purchased in sets of 24 that all had the same bottling data. The bottles were proven to be PETE using differential scanning calorimetry. The bottles were placed on the south-facing roof of the Oregon State University Kelley Engineering Center during the summer months (from June to September). There was no shade in this area of the roof. The bottles were placed on corrugated PVC plastic roofing material coated in aluminum foil to simulate the placement of PETE bottles on tin roofs in SODIS. One set of

bottles was placed on the roof for 3 months and another for 2 months. Temperature (measured using a thermocouple several times per day) and the daily UV index (internet data) was recorded during this time. Temperature was measured at 9:00 AM, 12:00 PM and 5:00 PM. Temperatures were recorded inside and underneath three of the bottles (using the same three bottles for each measurement to avoid opening new ones) as well as in the ambient air. Hourly air temperatures and UV indices for the Corvallis Oregon area were also recorded from intellicast.com. There were no stock chemicals available to make a GC/MS standard solution, so there was therefore no way of determining an exact concentration of DEHP and other leachants from the PETE bottles. Figure 8 shows the PETE exposure arrangement on the roof of Kelley Engineering Center.

Figure 8: Solar Exposure of PETE Bottles: Bottles were exposed to sunlight on the roof of Kelley Engineering Center for 3 months. The bottles were place on corrugated PVC material wrapped in aluminum foil.

Tritan ™ *Techniques*

There was not sufficient time to develop a GC/MS extraction technique for this polymer. The work done on the Tritan ™ bottles was mainly focused on determining thermal transition data using differential scanning calorimetry.

The Tritan™ bottles were autoclaved at 102 and 121 ^{o}C to test the polymer matrix stress and relaxation of bottles that have been heated close to their glass transition temperature. The bottles were also heated slowly from 25 to 125 ^{o}C in an oven to test the effects of heating without the being exposed to the humid conditions of the autoclave.

Extraction Technique

The exposure conditions for each plastic were slightly different but the extraction method was the same regardless of plastic type. The flow sheet for this extraction technique is shown in Figure 10. A reverse-phase solid phase extraction process was used because the extraction is removing non-polar molecules from an aqueous phase. In this process 1000 mL of treated water is pushed through a filter using a syringe. A C8 Silica filter from Fisher Scientific in a nylon filter holder was used. The filter has a high affinity for organic non-polar compounds and will extract the organic leachants from the treated water (Bulletin 910: Guide to Solid Phase Extraction, 1998). The atomic structure of the filter is shown in Figure 9.
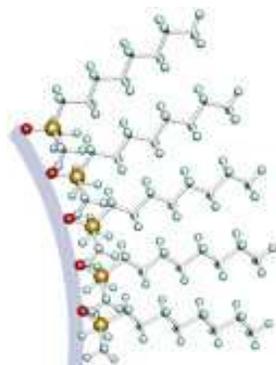

Figure 9: SPE C8 Silica Filter Wall. This filter can capture organic compounds (2009 by MACHEREY-NAGEL)

The filter holders are then connected to a vacuum tube. The vacuum sucks the remaining

water out of the filter for 20 minutes. Dichloromethane (DCM), a strong organic solvent is then

pushed through the filter to capture the organic compounds. A small amount of sodium sulfate

salt is then added to the DCM to remove any residual water. The top layer of this solution is then

removed and placed into a separate container. The volume of this solution is measured. The

solution is then evaporated using a nitrogen stream. The DCM is much more volatile than the

extracted compounds. The DCM evaporates and the organic compounds become more

concentrated. This entire process effectively concentrates the compounds by a factor of 5000

from their initial state. The extraction process flow diagram is shown in Figure 10.
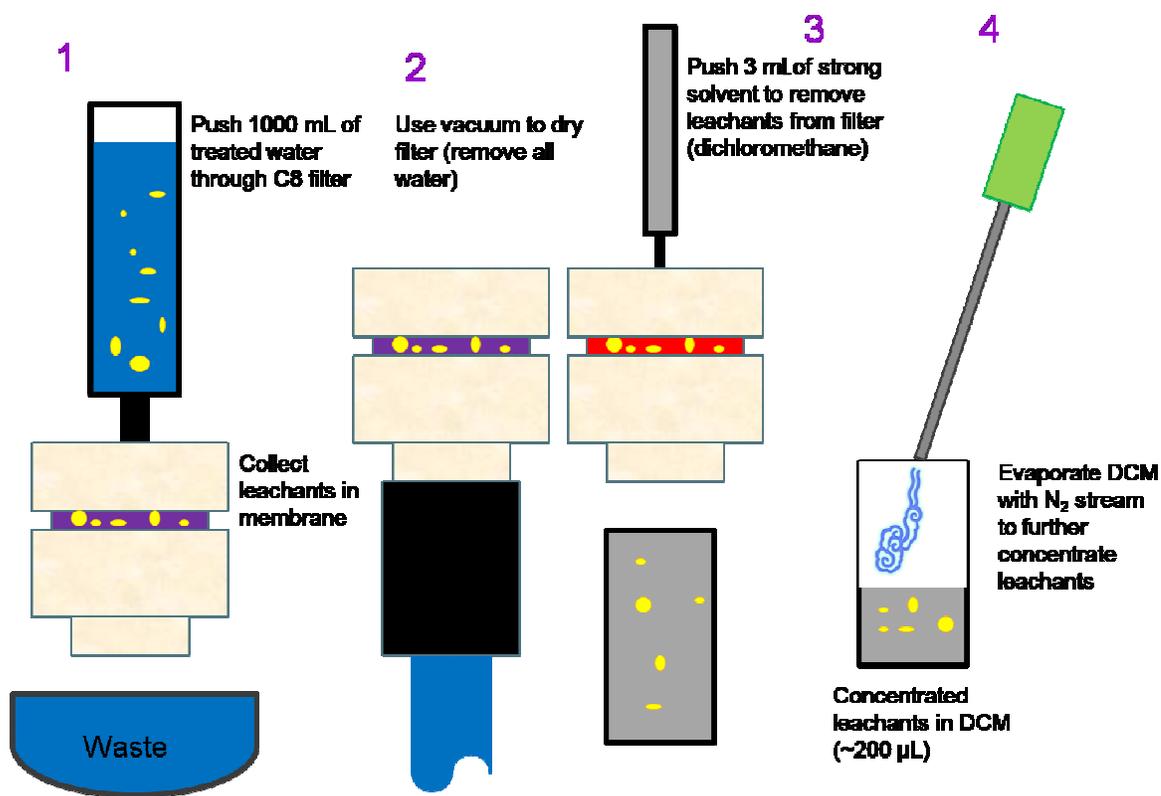
Figure 10: Solid Phase Extraction Process. **1:** 1000 mL of solution is pushed through the C8 filter. **2:** The filter is vacuum dried. **3:** 3 mL of dichloromethane is pushed through the filter and the organic compounds are extracted. **4:** Nitrogen is purged through the headspace of the vile, evaporating away most of DCM and thus further concentrating the organic compounds.

There was no way of knowing if the extraction process actually removed all the organic compounds contained in the filter. While techniques do exist, it was not possible to perform them at the time. Standard solutions of known concentration were instead run through the same solid phase extraction processes and run through the GC/MS. The signals of these solutions were used to compare the treated water from the bottles to a solution of known concentration so the approximate organic compound concentration in the treated water could be determined.

Detection Technique

A gas chromatograph in tandem with a mass spectrometer (GC/MS) was used to detect the organic compounds. The gas chromatograph is a HP 6890 GC and the mass spectrometer uses a 5973 Mass Selective Detector. The GC uses a C-18 reverse phase column with an elecrospray ionizer.

Results and Discussion

Polycarbonate Results:

      The results for the polycarbonate tests are still somewhat qualitative. Due to time constraints on the instrument only several runs were performed. There was enough time to run 3 bisphenol-A standards (at 1 ppm, 100 ppb, and 10 ppb). Three successful 1 L volume trials were also successfully run through the instrument (two were new bottles and one was a repeat of bottles that had already been run through). The amount of BPA that was detected fell below the level of 10 ppb. The GC/MS figures can be seen in *Appendix II: GC/MS Data*. Qualitatively the amount of BPA is most likely between 1 and 5 ppb given the size of the peak seen relative to the background and the 10 ppb peak. The second runs through the machine yielded a higher BPA concentration than the first run for that particular bottle. The difference, however, was very small and they are not likely statistically different.

      The most conservative estimate of the toxicity based on this study can be taken using the EU Food Commission's lower chronic exposure limit of 10 µg/kg/day with a BPA concentration of 4 ppb (4 µg/ L) in the water. The average 70 kg person would have to drink 175 liters of this autoclaved water daily to experience these effects (875 L/day with the US EPA standards). This would be considered the upper limit, the amount detected in the leached bottles was likely less than 4 ppb. Many previous studies have shown that BPA does not leach above 1 ppb in less than a week under normal conditions (Maragou, 2008, Ehlert, 2008). According to a study from *Food Additives and Containments* (Goodson et. al. 2002), the amount of BPA in canned food is usually between 10 and 350 ppb (ranging from sliced carrots in salt water to canned ham respectively). This level of BPA is considerably higher than the amount of BPA found in autoclaved polycarbonate water bottles but is still not enough to cause harm under chronic exposure.

The leachants from the polycarbonate tests are shown in Figure 11. Many of the chemicals detected in the GC/MS samples were fragments from the filtration process. The filter is silicate based with large carbon chains sticking off the ends that capture the organic fragments. It is possible that too much force was used to tighten the filters in the filter holder. This would cause some fragments to break off and become dissolved in the DCM. The two largest peaks in all GC plots appear to be fragments that look to be the silicate-alkane chains (Hexanoic acid, trimethylsilyl ester and 1-hexacosanol). There were also a number of aromatic silicate molecules that were likely fragments from the filtration. Any molecule that contains silicon is not likely leaching from the bottles but from the filter. These chemicals appear in both PETE and PC trials.

There were, however, other BPA-like fragments in the solution. These species include the trimethyl benzene molecules and Phenol, 4-(1-methyl-1-phenylethyl).

Name	Shape
Benzene, 1,2,3-trimethyl- (BPA Fragment)	
Benzene, 1,2,4-trimethyl- (BPA Fragment)	
17-Pentatriacontene	
Phenol, 4,4'-(1-methylethylidene)bis- (Bisphenol-A)	HO— —OH
Phenol, 4-(1-methyl-1-phenylethyl) (BPA fragment)	HO—
3-isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5- tris(trimethylsiloxy)tetrasiloxane	(chemdrug Database.com)
Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester	
Morphinan, 7,8-didehydro-4,5-epoxy-17-methyl- 3,6-bis[(trimethylsilyl)oxy]-, (5α,6α)-	
Heptadecene	
Octadecanol	OH
Hexanoic acid, trimethylsilyl ester (large peak 1)	
1-hexacosanol (large peak 2)	H₃
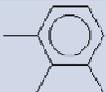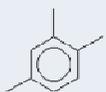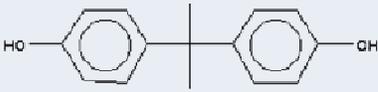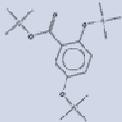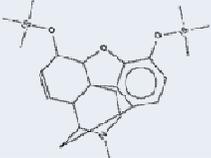
Figure 11: PC Release Chart. It is likely that most of these species are a result of filtration. Structures were obtained from webbook.nist.gov.

Polyethylene Terephthalate Results

Two successful PETE samples were prepared and run through the GC/MS. Both of the PETE samples were from bottles that were on the roof for 3 months (June through September). There were 14 identifiable compounds in the PETE GC/MS results. It is likely that 12 of these are from the filtration process. The complete table of compounds can be seen in Figure 12 on page 33. Most of the compounds were either long carbon chains indicative of C8 filter fragments or aromatic compounds containing silicon that were identical to the compounds seen in the PC GC/MS also from the filter. The glycine ester could have come from the nylon filter holder interacting with DCM.

The main chemical that most certainly came from the plastic was DEHP. The DEHP was not quantified because there was no standard solution available. It is believed that the amount of DEHP leaching was low (most likely < 10 ppb) because the sample was still concentrated 5000 times and the DEHP peak was relatively small. The lower toxicity limit for DEHP is 20 µg/kg/day (EPA, 2007). The dosage of DEHP received from 1 L of water would have to be 1400 ppb for a 70 kg person to receive this harmful effect. The bottles themselves, however, did become more brittle which is an indication that the DEHP either evaporated into air or leached into the water.

A small amount of benzophenone was also detected in the PETE bottles. Benzophenone is a chemical added as a UV inhibiter to protect against photo-degradation. The GC peak for benzophenone was extremely faint and it is likely that there is very little present in the water. The UV protection gained by the benzophenone may explain why no photo-degradation products were detected

None of the PETE monomer groups were detected. Temperature measurements were taken three times a day in three different bottles that had been placed on the Kelley Engineering Center roof. Temperatures were taken inside and underneath the bottles as well as from the ambient air. The air temperatures typically ranged from 15 to 20 ^{o}C at 9:00 AM (average 18 ^{o}C) and 23 to 32 ^{o}C at 5:00 PM (average 28 ^{o}C). The average 5:00 PM temperature inside the bottles was 34 ^{o}C and the average 5:00 PM temperature underneath the bottles was 39 ^{o}C. This temperature is far below the glass transition temperature of PETE of 85 ^{o}C. This could explain the absence of PETE monomers in the GC/MS results, as the polymer matrix would still be fairly rigid.

It would have been beneficial to develop at test that quantified the amount of acetaldehyde in the water. This was not possible with the extraction and detection method used in this study for two reasons. The first was that the acetaldehyde molecule partitions through the column faster than the DCM solvent. In order to detect any acetaldehyde one would have to allow all of the solvent to pass through the GC column. The GC normally burns off all of the solvent for 3.5 minutes because that amount of material flowing through the instrument at once would damage the detector. It would therefore be impossible to detect using this system. The second reason why acetaldehyde cannot be detected using this technique is because acetaldehyde will not partition into the C8 filter. Acetaldehyde is more easily dissolved in the aqueous phase than the filter. Thus a completely different method would be needed to detect acetaldehyde in the UV treated PETE bottles.

Name	Shape
2-chlorocyclohexanol	
Glycine, methyl ester	
Caprolactam	
3-isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	(chemdrug Database.com)
Benzophenone (UV inhibiter)	
Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester	
Morphinan, 7,8-didehydro-4,5-epoxy-17-methyl-3,6-bis[(trimethylsilyl)oxy]-, (5α,6α)-	
Hexanoic acid, trimethylsilyl ester (large peak 1)	
1-Nonadecanol	
Benzeneacetic acid, α,3,4-tris[(trimethylsilyl)oxy]-, trimethylsilyl ester	
1-Hexadecene	
Bis(2-ethylhexyl)phthalate (DEHP)	
1,2-bis(trimethylsilyl) benzene	(Cole-parmer.com)
1-hexacosanol (large peak 2)	
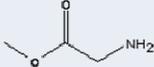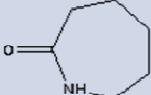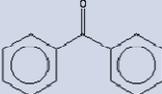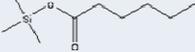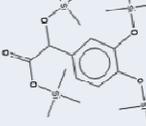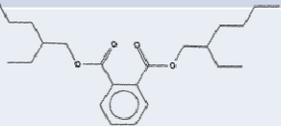
Figure 12: PETE Release Chart. It is likely that most of these species are a result of filtration. Structures were obtained from webbook.nist.gov

Tritan™ Copolyester Results

Thermal stress and transition data for Tritan™ was obtained using differential scanning calorimetry (DSC). DSC charts were obtained for every plastic to verify the resin type was correct. Figure 13 shows the DSC of all three bottle types used in the experiment.
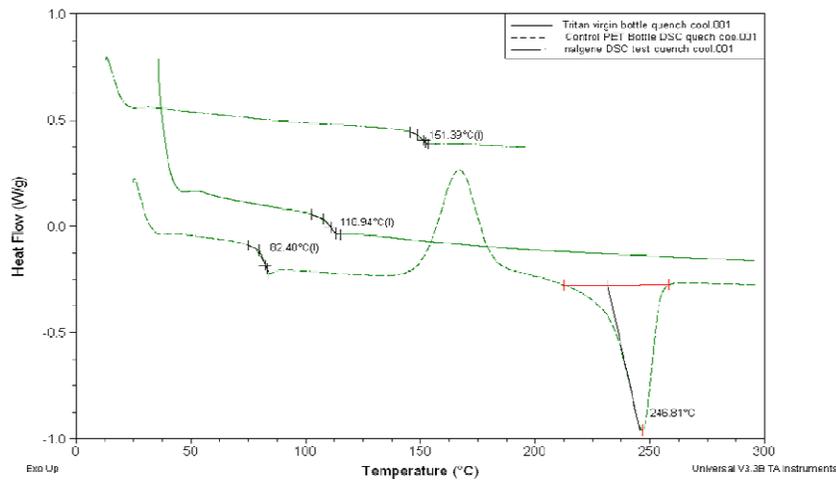

Figure 13: DCS of PC, PETE and Tritan™. The samples were run through once and quench cooled prior to this measurement to remove any initial stress in the bottles from the manufactuing process

The PETE and PC graphs are the known fingerprint for each plastic. The thermal transition properties for Tritan™ were not known beforehand but it was assumed that these were the correct plastic. It has therefore been shown through this experiment that the glass transition temperature of Tritan™ is 110 °C.

The other data obtained for the Tritan™ polymer comes from analyzing the stress patterns after the bottles have been heated to various temperatures. Figure 14 shows the DCS graph of a virgin bottle compared to a sample that quench cooled. The samples are quench cooled so that the plastic does not have time to crystallize or form a more relaxed structure. The quench cooled DCS lines look very smooth because they are essentially stress free. There is

residual stress left over from the manufacturing process in the virgin bottles. The Tritan™ bottles may begin to leach if they are heated to a temperature that shows a DCS with no stress. The reason for this is that the plastic has relaxed and the polymer matrix would have literally shifted. Figure 15 shows the DSC of plastic that was heated to 102 ^{o}C (8 degrees below glass transition) for two hours. The bottle physically shrank during this test.
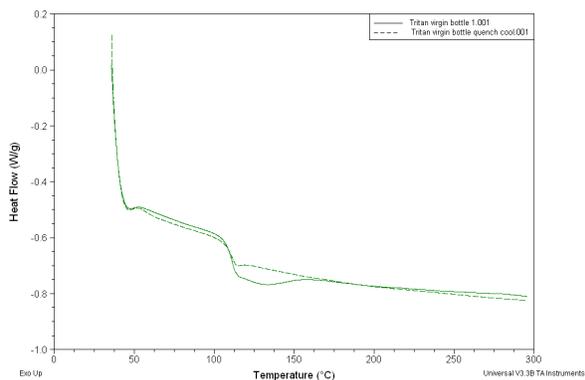

**Figure 14:** DSC of New Tritan™ Copolyester Bottle. There is stress from manufacturing.
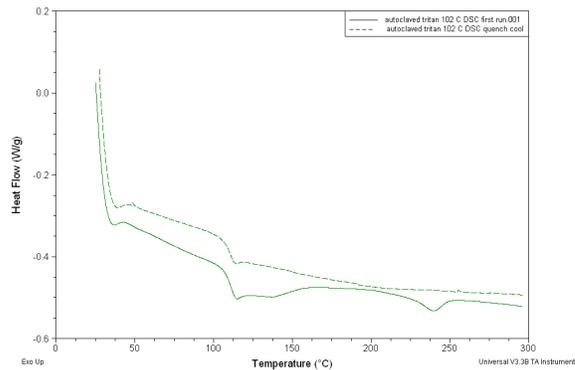
Figure 15: DSC of Tritan™ Copolyester Bottle Heated to 102 ^{o}C. A slight melting point appears in the initial test that is not in the quench cool. Bottles heated in an autoclave for 2 hours.

The bottles begin to show signs of a melting point after being heated in the oven and autoclave. This melting point appears to be at 237 ^{o}C. This implies the samples that are heated in the DSC do not exhibit this behavior even after they are quench cooled. This only happens after the *bottles* have been heated in the oven or autoclave and not when the small DSC sample is heated in the machine. This effect is even more dramatic after the bottles are heated to 121 ^{o}C as shown in Figure 16. The melting point is much sharper than the melting point shown in the bottles that were heated to 102 ^{o}C. All of the stresses due to manufacturing have been dissipated in this sample. The polymer has clearly had time to relax. It is unclear, however, how the plastic began to produce crystallites and why they do not appear in the virgin plastic samples. Figure 17 shows several bottles heated in different ways.
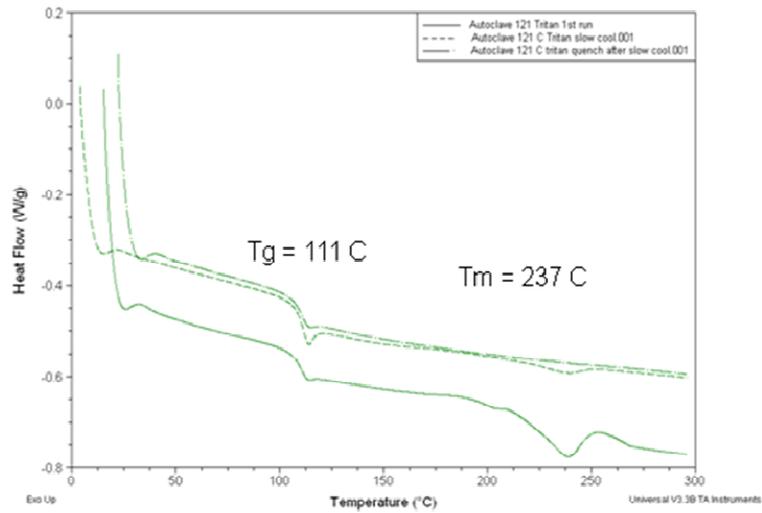
Figure 16: DSC of Tritan™ bottle heated to 121 °C. A definite melting point has been produced that is not seen in quench cooled or virgin bottle samples. Bottles were heated in an autoclave for 2 hours.

Other bottles were heated slowly in an oven and watched as temperature increased from 25 to 125 °C. The melting point also appeared on the DSC of these bottles.

Figure 17: Heat Treated Tritan™ Copolyester Bottles. **1:** New Tritan ™ copolyester bottle. **2:** After 1 hour ramping from 25 to 125 °C. **3:** 2 hours in autoclave at 102 °C. **4:** 2 hours in autoclave at 121°C. This sample has turned opaque which is an indication that crystallites have formed.

Conclusion

The results from this study have indicated that polycarbonate and polyethylene terephthalate are benign in terms of the health risks related the leaching low molecular weight migrant molecules. Polycarbonate was shown to only leach around 1 to 4 ppb of bisphenol-A when exposed to an autoclave at 121 ^{o}C for 2 hours. These tests were analyzing using GC/MS and concentrated using reverse phase solid phase extraction. A 70 kg person would have to consume 175 L of this water a day consistently to experience any of these harmful effects (based off of the EU's minimum daily tolerance of 10 µg / kg bodyweight / day). The lining of canned food is also made out of BPA and is much softer. A can of carrots leaches about 10 ppb BPA, a can of spaghetti sauce about 40 ppb BPA and a can of ham about 350 ppb BPA (Goodson et. al 2001). These are orders of magnitude higher than the BPA coming from autoclaved polycarbonate bottles. Polycarbonate is therefore not a significant source of BPA intake.

Polyethylene terephthalate (PETE) was only shown to leach a small amount of DEHP after being left in the sun during the summer months of June through September. The DEHP was not quantifiable due to the lack of a standard. A trace of Benzophenone was also detected with no standard to compare with. No PETE monomers were detected. This is likely because the temperature of the plastic did not come close the glass transition temperature while being outside. The DEHP contained in sample is a much higher weight percent than unreacted monomers (perhaps 1 wt % vs. 10^{-4} wt %) and would therefore be expected to have much higher mobility. No monomer fragments were observed but other studies have shown that it is possible to extract and detect PETE chain fragments when it is exposed to UV light (Wegelin M. et al, 2001).

The other fragments shown in both the PC and PETE GC/MS came from the extraction process. It will be recommended for future groups to centrifuge their samples before using them to make sure there is no sodium sulfate salt in the GC/MS sample. It was difficult to obtain samples that were not contaminated with particles of sodium sulfate (which was used to remove excess water from the samples). As a result over half the samples prepared were unsuited for running through the sensitive GC/MS equipment. It will also be recommended to use a metal sample holder rather than a nylon one. C18 filters may also be used instead of C8 because they will increase the retention of migrant molecules.

The Tritan™ copolyester tests showed few significant results because instrument time was not available by the time an experiment was designed that could test for possible monomer leaching. Thermal transition data was obtained for the Tritan™ bottles heated to various temperatures. The glass transition temperature of Tritan™ was found to be 110 ^{o}C. The plastic appears to be an amorphous polymer when the DSC of a virgin, untreated bottle is observed as there is no detectable melting point. When the bottles are heated in an autoclave at 102 ^{o}C and 121 ^{o}C there is an apparent crystallization. This crystallization is seen as a slight melting point in bottles that have been heated that is not present in the DSC of virgin bottles. There is no explanation at this time as to why this crystallization occurs.

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Appendix I: Important Terms

- Polymer structure terms

  o **Polymer:** A polymer is a large macromolecule (molecular weight usually 40,000 grams/ mole and higher) composed of one or several repeating units. Examples of polymers include all plastics (such as polyethylene, polycarbonate and Nylon), cellulose, gelatin and DNA.

  o **Monomer:** Monomers are chemicals that make up the repeating units of polymer. Monomers differ from polymers in that they are much smaller, usually on the order of 100 grams/mol. Single monomers are not normally present in the finished polymer product, although it is possible to have extremely small traces of unreacted monomers existing in the polymer matrix. Examples of monomers are styrene in polymer poly*styrene* and ethylene in the polymer poly*ethylene*. Sometimes polymers are made up of more than one repeating unit. These are called copolymers. All of the plastics investigated in this study are copolymers.

  o **Chemical Leaching:** In the context of this project it is when low molecular weight particles (such as broken chain fragments or unreacted monomers) come out of the polymer matrix and seep into their surroundings. The leaching can also occur when the surface of the plastic degrades and migrates into the contents of the container.

  o **Polymer matrix:** Polymer molecules are large molecular strands. These strands entangle together to form large interwoven molecular matrices. Many polymer strands are connected in these matrices. It is this matrix that gives plastics their solid structure.

Appendix I: Important Terms

- **Plasticizer:** A small compound with a relatively low molecular weight (100 – 500 g/mol) that is added to the polymer matrix to allow it to be more flexible or that changes the tensile properties of the substance. One of the most common plasticizers is DEHP.

- **Thermophysical properties**

  - **Glass Transition Temperature (T_g):** Plastics do not necessarily have a melting temperature as "melting" refers to the dissociation and ordered crystal structures into amorphous or liquid like arrangement. The transition from liquid to solid of a plastic is not straightforward because there are many different chain lengths and variations between crystalline and amorphous regions in the matrix. It is important to know when the polymer matrix can begin to relax. The point of total polymer relaxation is called the glass transition temperature (T_g). The T_g is the point at which the molecular chains can begin to move within the matrix. Low molecular weight substances such as plasticizers, unreacted monomers and other additives can begin to move at when the plastic becomes close to this temperature. This is the temperature of interest when investigating leaching.

Appendix II: GC/MS Data: Figure 2: Polyethylene Terephthalate GC 3 month UV exposure (2)

```
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Operator    : Paul
Acquired    : 29 Aug 2008  15:14     using AcqMethod PMB_082608.M
Instrument  :    Instrument #1
Sample Name: PETE#3
Misc Info   :
Vial Number: 1
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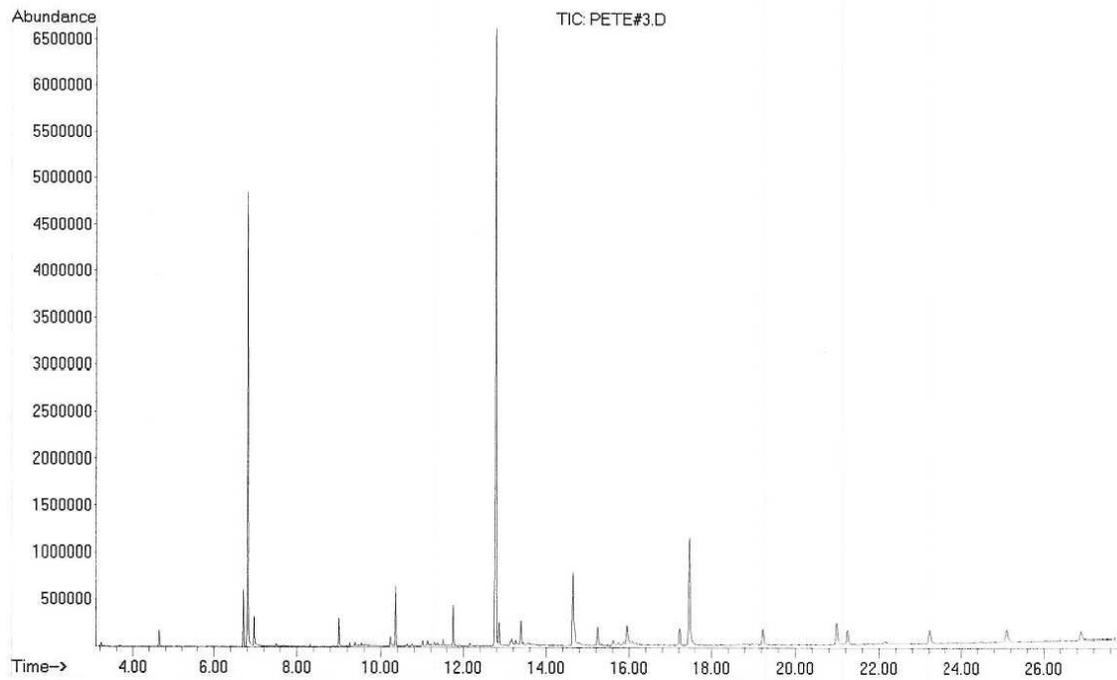
Appendix II: GC/MS Data: Figure 3: Polycarbonate GC Autoclaved Once (1)

Appendix II: GC/MS Data: Figure 4: Polycarbonate GC Autoclaved Once (2)

Appendix II: GC/MS Data: Figure 5: Polycarbonate GC Autoclaved twice



```
File      :C:\MSDChem\1\DATA\PMB.D\ACRUN2.D
Operator  : Paul
Acquired  : 29 Aug 2008  15:55    using AcqMethod PMB_082608.M
Instrument :   Instrument #1
Sample Name: ACRun2
Misc Info  :
Vial Number: 1
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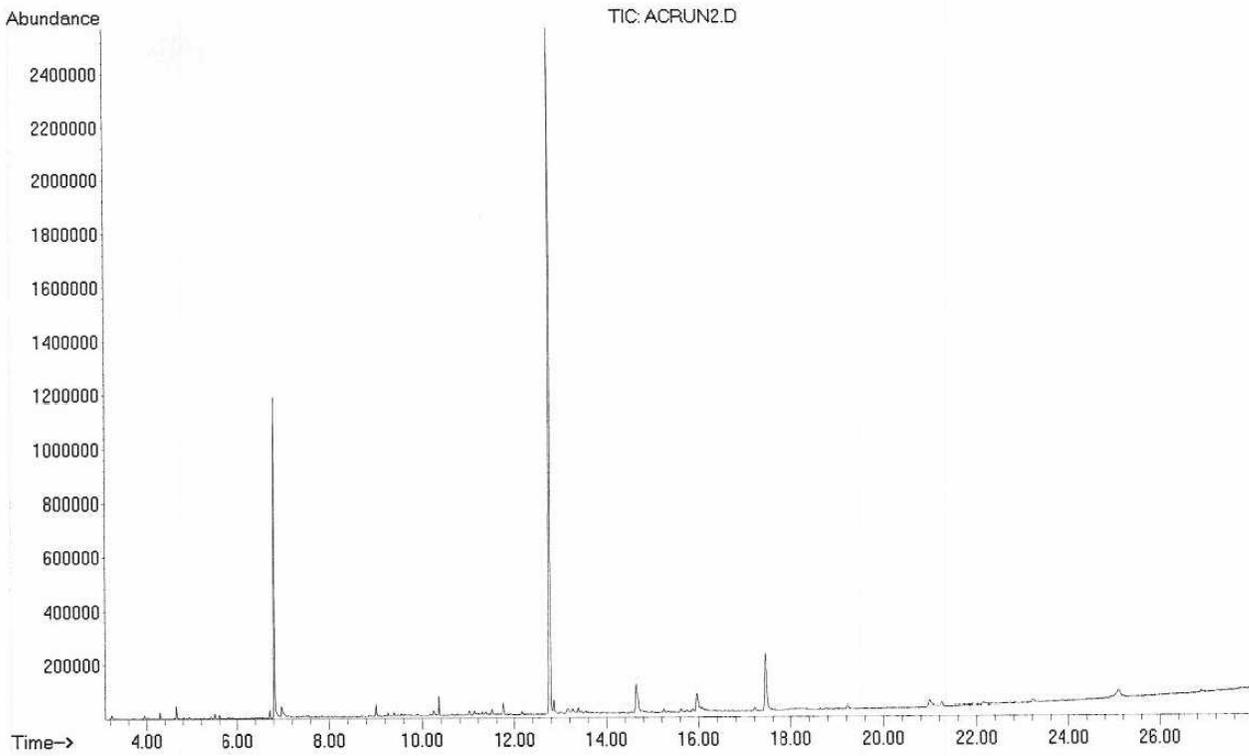
Appendix II: GC/MS Data: Figure 6: Bisphenol-A Control Test 1 ppm

File   :C:\MSDCHEM\1\DATA\Snapshot\PMB 1MMP.D
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Acquired : 25 Aug 2008 15:57   using AcqMethod CHE_080708.M
Instrument :   Instrument #1
Sample Name: 1 mmp bpa
Misc Info :
Vial Number: 1
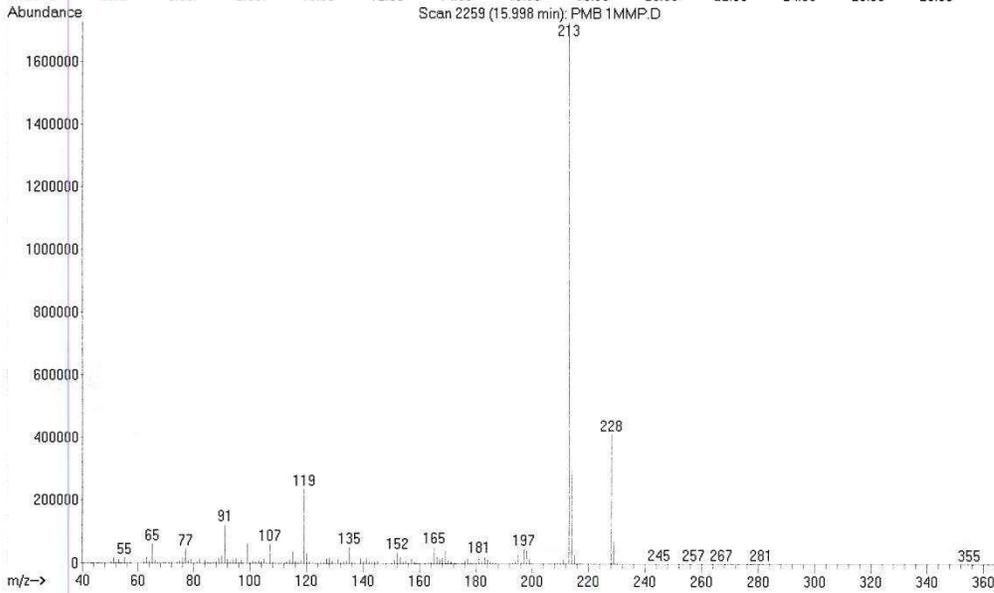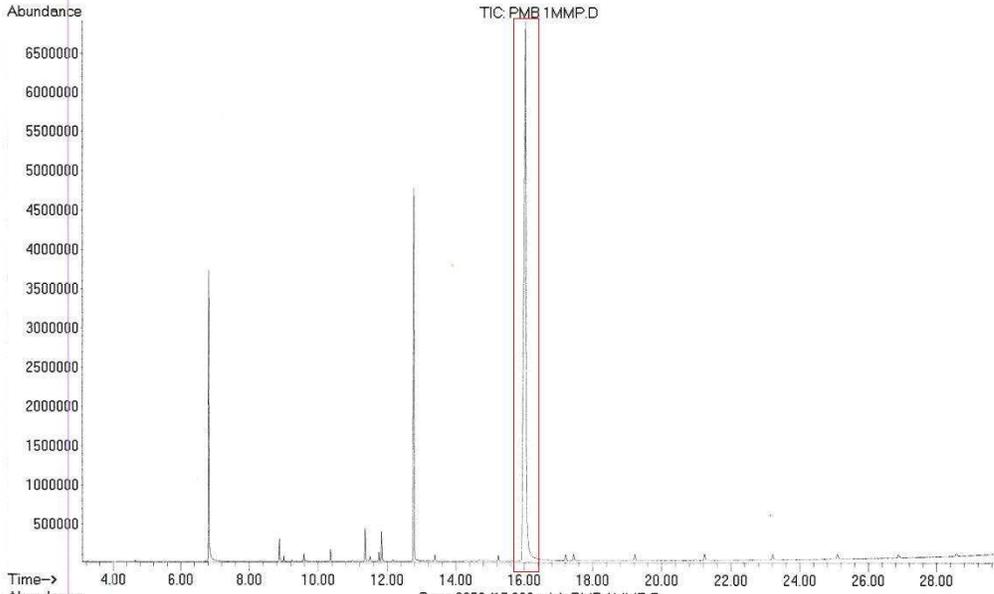
Appendix II: GC/MS Data: Figure 7: Bisphenol-A Control Test 100 ppb


```
File      :C:\MSDCHEM\1\DATA\PMB.D\Snapshot\100MMP BPA2.D
Operator  : Brian
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Sample Name: 100ppm BPA2
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Vial Number: 1
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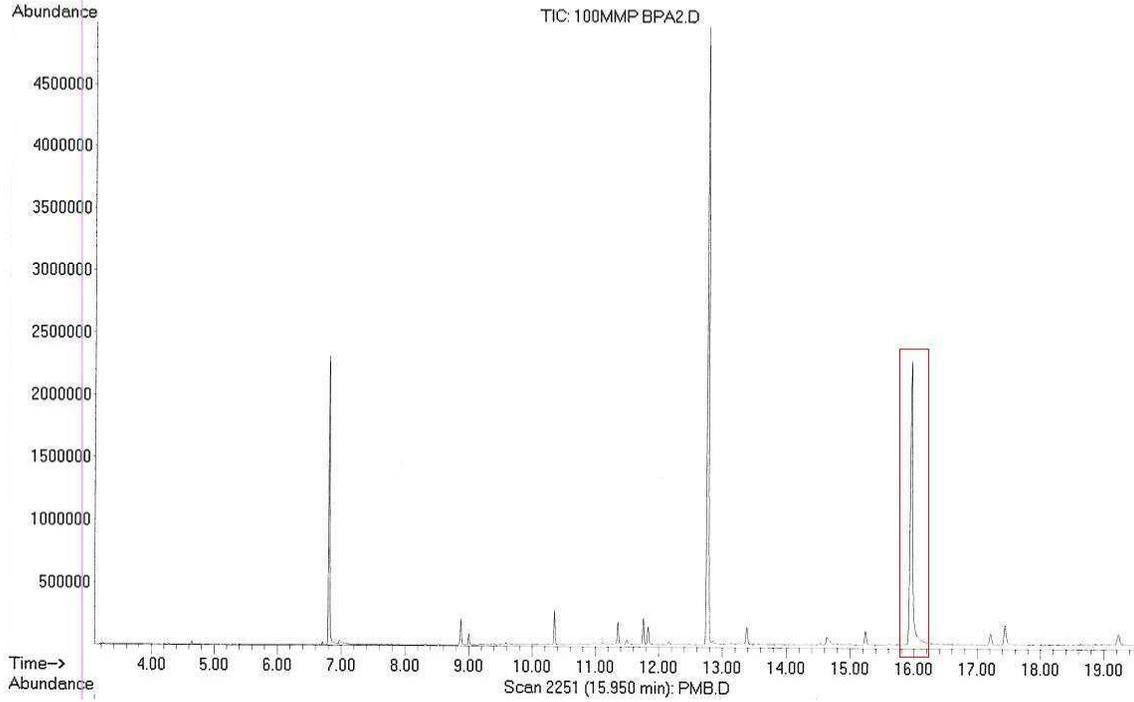
Appendix II: GC/MS Data: Figure 8: Bisphenol-A Control Test 10 ppb
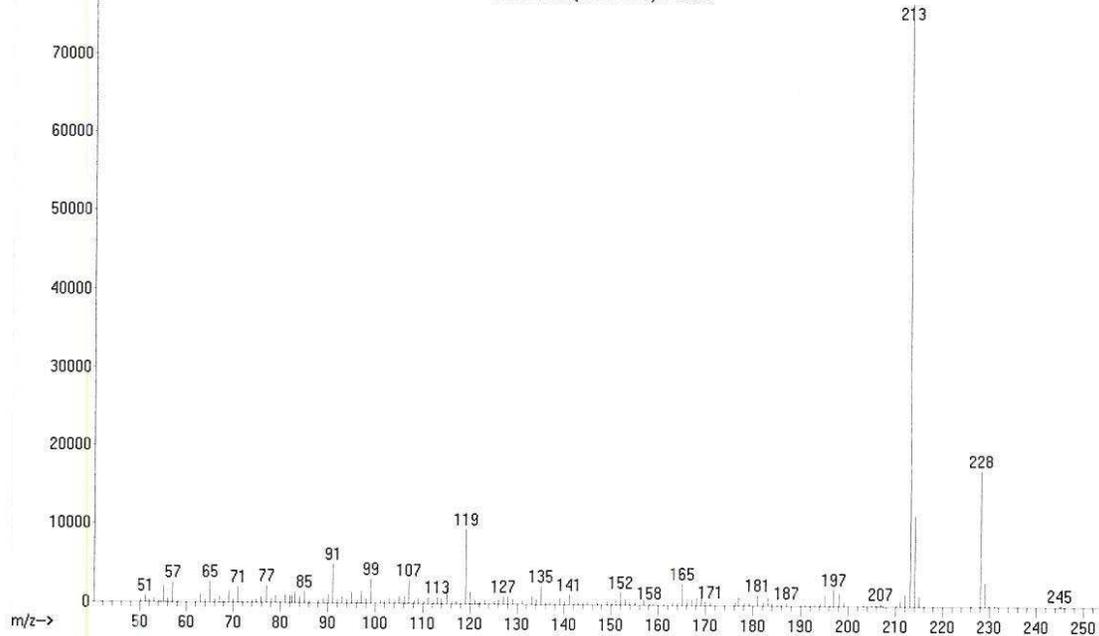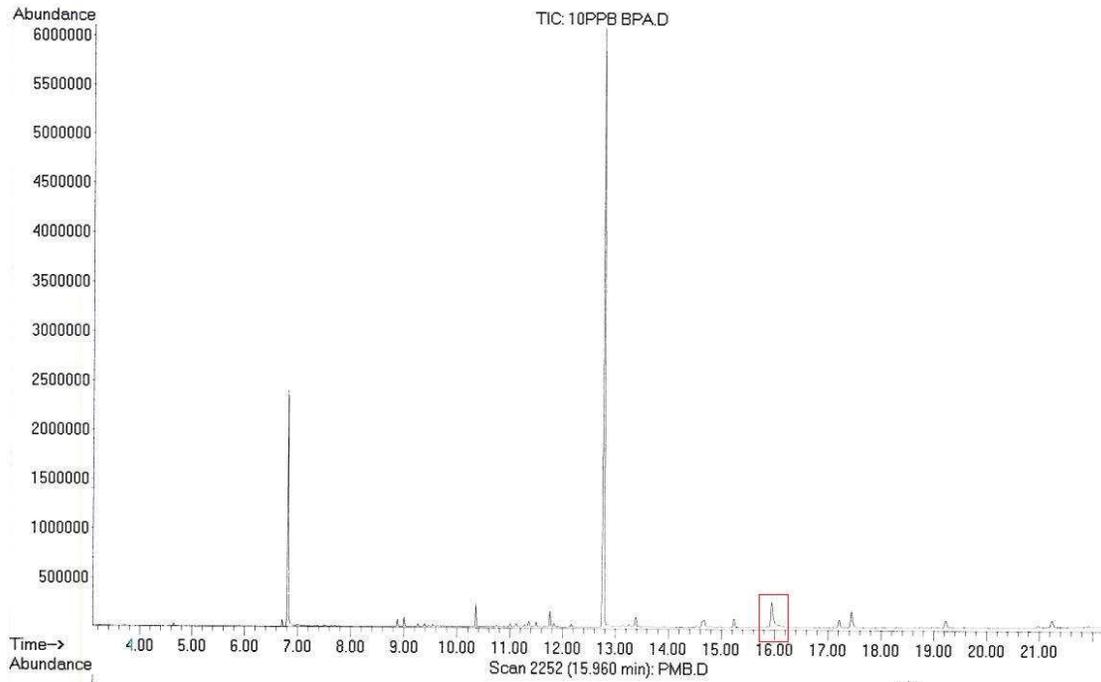
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