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Headspace Analysis of Foams and Fixatives

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Abstract

In the process of decontaminating and decommissioning (D&D) older nuclear facilities, special precautions must be taken with removable or airborne contamination. One possible strategy utilizes foams and fixatives to affix these loose contaminants. Many foams and fixatives are already commercially available, either generically or sold specifically for D&D. However, due to a lack of revelant testing in a radioactive environment, additional verification is needed to confirm that these products not only affix contamination to their surfaces, but also will function in a D&D environment. Several significant safety factors, including flammability and worker safety, can be analyzed through the process of headspace analysis, a technique that analyzes the off gas formed before or during the curing process of the foam/fixative, usually using gas chromatography-mass spectrometry (GC-MS). This process focuses on the volatile components of a chemical, which move freely between the solid/liquid form within the sample and the gaseous form in the area above the sample (the headspace). Between possibly hot conditions in a D&D situation and heat created in a foaming reaction, the volatility of many chemicals can change, and thus different gasses can be released at different times throughout the reaction. This project focused on analysis of volatile chemicals involved in the process of using foams and fixatives to identify any potential hazardous or flammable compounds.

Introduction

When Decontaminating and Decommissioning (D&D) nuclear facilities, 3 different types of contamination must be dealt with: fixed, removable, and airborne. Fixed contamination is buried within a surface and not readily removable. This makes it the easiest to deal with because once it affixes, it will not exit the facility naturally and the affixed surface can simply be treated as radioactive. Removable contamination on a surface can be removed through surface contact. Airborne radioactive particles attach to dust and other airborne particles. Both removable and airborne pose a much larger problem as they create hazards for D&D crews and are capable of exiting the facility. In order to make D&D projects safer for workers and the surrounding environment, along with decreasing project costs, foams and fixatives can be used to partially affix contamination to their surfaces, reducing many of the dangers and problems with removable and airborne contamination. For filling odd volumes like gloveboxes, polyurethane foams are ideal products due to their variety in expansion values, rigidness, and curing conditions. Similarly, epoxy based fixatives allow for many properties to be tuned to the specific situation, allowing them to be used for coating areas that are more readily accessed to ensure better fixation. Due to the multitude of different situations these products are needed in, both foams and fixatives have been selected to be tested for their D&D capabilities.

Testing of these products is required because between the relatively new demand for this usage and the difficulties for most manufacturers to test their product in a relevant environment, commercially available foams have not been readily tested for their nuclear D&D capabilities. This project focuses on the chemicals created and off gassed during the curing process, analyzing the headspace of the foam/fixative in an attempt to find any flammable or otherwise hazardous chemicals in the air around a sample. Most liquids and even some solids have components that are volatile, meaning that small portions of them break away from the liquid/solid and into the gas area above, a process called volatilization. Because certain chemicals can become more dangerous depending on their phase and vapor pressure, these volatilizations can pose a serious risk if not dealt with, and thus we need to monitor the headspace around samples as they cure to ensure that the necessary precautions are taken.

In order to identify the compounds within the headspace of the sample, Gas Chromatography-Mass Spectrometry (GC-MS) is used. A combination of two different instruments and methods, GC-MS takes in microliter portions of samples which gas chromatography splits up into components and mass spectrometry sorts. Gas chromatography takes in small liquid or gas samples and runs them through a column (the bronze colored loop, see Figure 1) while increasing the oven temperature, changing how quickly certain components move.

Figure 1: An open GC oven

Gaseous components like air will move through the column quickly, short of an extremely low starting temperature, and will generally be the first results recorded by the instrument. Compounds whose vapor pressure increases less with temperature, generally heavier chemicals with higher boiling points, like benzyl alcohol have a much larger delay before exiting the column that depends greatly on the oven temperature. A lower initial temperature will allow more gaseous, air-like chemicals to be separated out, while a slower temperature increase will cause greater distances between peaks, helpful if multiple compounds overlap. Several precautions must be taken to ensure that these conditions to better results do not inadvertently cause problems; if the oven temperature is too low (lower than room temperature, or lower than the injector temperature can reach) then the sample will condense upon reaching the column, greatly changing the amount of time it takes the compounds to make it through the column, called response time. Additionally, if the maximum temperature of the run is too low, it is possible that not all of the sample has exited the column, and would not only fail to show up in the results for that run, but would also appear in the next run, contaminating its results.

Mass Spectroscopy takes the output of the GC column and ionizes it, moving the particles through a magnetic field that makes the particles take long, curving paths to the detector. Due to their inertia, larger particles are going to curve less than lighter particles with the same charge, and similarly more charged particles are going to curve more than a more neutral particle with similar mass. Using these principles, the mass spectrometer varies the magnetic field as the particles move through, and measures how long it takes each particle to get through.

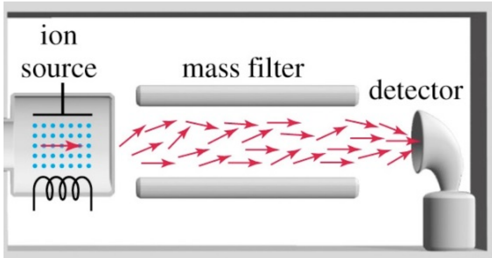


Figure 2: A basic MS setup

This time is used to calculate the mass of each particle, with respect to its charge. The number of hits on the detector is recorded, and the mass spectrometer outputs the abundance of each mass per charge (m/z) unit into a profile. These profiles are compared to profiles of known chemicals and compounds in order to determine possible matches in structures. Many of the results of the GC-MS data can be anticipated by analyzing the components of the foam or fixative being tested and understanding what causes the formation of polyurethane foam.

Polyurethane foams are created through mixing a part A, containing an isocyanate, and a part B, containing a polyol, to create a urethane polymer. Depending on the specific type of isocyanate and polyol, the resulting polymer can be made to be longer or shorter, along with massive changes in the amount of cross-linking between the individual polymers. In the creation of a foam, the more crosslinking in the product, the more rigid the foam will be. In addition to rigidity, another property that varies widely in polyurethane foams is intumescence, or fire resistant. The largest factor in determining the intumescence of polyurethane foam is the isocyanate used in its production, of which there are two main options: diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

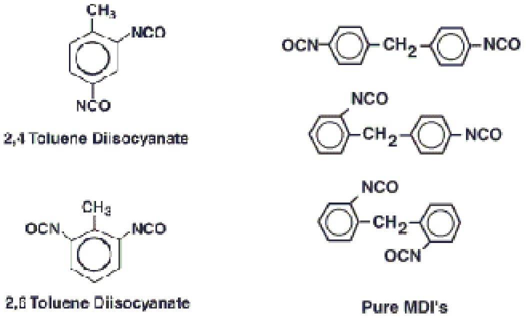


Figure 3: Basic TDI and MDI structures

MDI is more popular in the foam products due to its propensity to easily form polymer chains, and its convenient chemical composition for sparse crosslinking. The combination of these two allows the structure to expand out, creating the rising action in the foam as other reactions create carbon dioxide to fill the volume. Both MDI and TDI work for urethane foams, though, due to the options available for their formation; the cyanate (NCO chain) will react with vastly different polyols, only needing a hydroxyl group to react with to form a polymer. The variability in foam properties that polyurethane has due to different polyols is one of its greatest strengths, allowing the foams to be customized for different uses.

Experimental

This experiment was designed to primarily measure the difference in chemical abundances in the headspace of foams and fixatives over time, and thus multiple samples needed to be taken from the same main product sample. In order to achieve this, the foams and fixatives were mixed according to their specifications, and then immediately poured into a Wheaton bottle, which had a thick septum to seal off the top that was fixed in place with a metal ring. Properly done, this setup allowed a vast majority of the curing process to occur in an isolated space where off gassed chemicals could build up in the headspace to be taken at sampling times.

Samples were taken of the headspace at the 0.5, 1, 2, and 24 hour mark from mixing time, along with a few 48 hour samples for longer curing epoxy fixatives. A 250 µL gas tight syringe with a side hole needle was used to pierce the septum and take a sample after filling and emptying the syringe multiple times to minimize residual air. The gas was then locked into the syringe, transported to the GC-MS, and immediately injected as the GC-MS cycle began. For this experiment the instrument had a 2 part cycle: for the first 2 minutes the oven held at 34°C, allowing air and other very light, fluid particles to run through. Then the oven began to heat up at a rate of 9°C per minute, until it reached 150°C, at which point the run ended. This experiment was designed to find chemicals that are already volatile enough to enter the headspace in significant quantities, and thus should move through the column fast enough that further temperature increases, or a hold at the end, were not deemed necessary.

Results

Results were compiled from two fixatives and a foam: Intumax's EP-102, Instacote's CC Epoxy, and Smooth-on's Foam-iT! 8. Although these results varied significantly between products, there were small constants between them, primarily the air peaks and baseline. For the GC-MS method used, two air peaks were created at 1.50 and 1.53 minute response times that chained together See Figure X in appendix. This separation into two peaks is due to the composition of air; primarily nitrogen and oxygen, with a respectable amount of carbon dioxide as well. Oxygen on its own moves through the column far too well, even at a low starting temperature, and thus makes a large bell curve from 1.48 to 1.55 minutes. N_2 and CO_2, however, have much more clearly defined peaks and pull a lot of oxygen along with them. It is noteworthy that the minimum threshold for the mass spectrometer was set at 30 m/z in order to avoid nitrogen peaks interfering with results, and thus N_2 does not appear on any results, its peak is only distinguishable due to the oxygen pulled with it. This threshold was required due to a small air leak within the GC that was allowing an abundance of ~2000 air particulate into the results. Due to external factors this leak was not able to be resolved during the experiment time, and thus the threshold was adjusted, as excess nitrogen was found to interfere more with results than oxygen and carbon dioxide.

EP-102

Cutoff Chrom image here

EP-102 is a 2 part epoxy based fire retardant fixative with a 48 hour cure time which, when run through the GC-MS, was found to have 3 directly identifiable volatile compounds, along with 2 smaller, unidentifiable GC peaks. Peaks at 1.814, 4.71, and 9.96 minutes matched to propylene oxide, toluene, and benzyl alcohol respectively. However, the smaller peaks at 3.597 and 5.051 minute response times were too small to create a proper match, with a very high chance that these components had multiple portions fall below the mass spectrometer's 150 count threshold, and thus were not counted among the results. This is possibly due to the ratio of fixative to headspace within the sample; Wheaton bottles are about 4 inches tall, while the fixative was used at the recommended height of a quarter inch. As such, any chemical that would volatilize in small concentrations would be overwhelmed by the other gasses already present in the headspace, and would not be significantly represented in a small sample. In order to get a better match on these two peaks, a sample will have to be created in a smaller but similarly airtight container where the fixative off gas can be a more significant portion of the headspace.

Ultimately, EP-102 showed a very small amount of gas evolution over its curing time. All 3 easily matched peaks were present in one or both of EP-102's components, and showed a markedly decreased abundance in the curing product. The smaller, unidentified peaks, however, are new due to the curing process, and should be more closely examined. Beyond the headspace results found here, the other remaining concern is hydrogen creating during the curing process. Due to the GC-MS setup and column used, hydrogen content was not able to be measured, and thus remains an unknown in this analysis. This concern is caused by the likelihood of hydrogen as a product within an epoxy reaction, and is warranted on any products moving onto a second phase of testing.

CC Epoxy

Cuttof chrom image here

CC Epoxy, another 2 part epoxy based fixative, has a 12-24 hour cure time. However, unlike EP-102 this product contained no uncertain, and instead only had two non-air peaks, one at 4.71 minutes and another at 9.96 minutes. The similar GC response times are confirmed by the MS profiles created, and the peaks were shown to be the same as in EP-102: toluene and benzyl alcohol, unsurprising due to their status as common solvents. These solvents were noted, though, to have increases in peak height over the curing time. Over the 24 hour sample time, MS count number for toluene increased by 25%, while benzyl alcohol counts increased by 48%. This increase can be accounted to several things. The benzyl alcohol increase is overstated, due to the very small initial peak size, and the fact that several components were initially underneath the count threshold, then became present later, causing large jumps in difference. Additionally, it is notable that the oxygen peak did have an increase in size as well, much larger in particle number although less of an increase percentage wise. This leads to the conclusion that either larger samples were taken due to human error, the vapor pressure of the headspace was increased which causing larger samples, or a combination of the two lead to an increase in counts.

The lack of extra peaks and unknowns is a significant positive for CC Epoxy, but its significant quantity of toluene is not. Even if toluene quantities do not increase as significantly over time in legitimate use, CC Epoxy's headspace contained significantly more toluene than any other product, and at the correct vapor pressure toluene is flammable. Due to the constraints of this sampling method, however, the actual amount of toluene produced per inch of fixative covering was not able to be derived, and further testing will be needed to assess whether this concentration creates a legitimate flammable hazard.

Foam-iT! 8

Cut off top chrom to show 4 peaks

Foam-iT! 8 is a 2 part polyurethane foam designed to expand to 4 times its procuring size and become rigid. It had 4 significant non-air peaks, two of which accurately matched a library value, and two of which had enough components near or under the threshold that they were unable to be matched. The first matching peak, at 1.814 minutes, had a fair amount of contamination due to its proximity to the air peak, adding significant amounts of 32, 44, and 45 m/z. When these amounts are accounted for, along with the minimum MS threshold of 30 m/z, a near perfect match is found with acetone, as seen in Figure X in appendix. This peak had a significantly higher abundance than other solvents found, but this is partially due to the contamination from the air peak's downslope. This peak decayed significantly throughout the 24 hour sample time, and was outweighed by the excess air by the end. The second peak was free of contamination, and had both a high quality MS match, and a perfect GC response time match of 4.710 minutes, the same as the other toluene peaks. While this peak also decreased in size over time, its reduction was far less than the acetone's, and the MS was still able to create the match at 24 hours. Of the two unidentifiable peaks, the one at 8.987 minutes had more significant markers. Outside of the 3 air identifiers (32, 40, and 44 m/z), only 3 additional masses were found, 281, 282, and 283. Several matches were found with proper concentrations of these elements, however they all had other abundances that should have easily exceeded the count threshold, and thus are not reliable matches. A test with a greater foam to headspace ratio may yield better results for this peak. At 2.671 minutes however, very little can be found in the way of legitimate results, due to very low abundances that decayed even further, such that none exceeded the count threshold by the 24 hour mark. When testing with a higher foam amount it may be worthwhile to lower the m/z threshold and count threshold in order to find the components responsible for the peak on the GC.

The most significant result of this foam, however, is the air peaks, which are significantly different than the other products. While all of the products off gassed some amount of carbon dioxide, Foam-iT! 8 created enough to massively shift the molecular ratio of the air peaks. By the 30 minute mark into the curing time, carbon dioxide abundance levels had already exceeded oxygen amounts. Despite the foam listing as foam formation finishing in 30 minutes and curing finishing in 4 hours, carbon dioxide production continued well beyond that, evening out by the 24 hour mark, while oxygen levels continually decreased over the same time period. Normal air has abundances of about 550 parts O_2 to 1 part CO_2[1], and most mass spectrometry results showed abundances of 4-10 parts O_2 to each part CO_2. When the values for both air peaks are totaled at the 24 hour mark, the headspace contains 5 parts

CO_2 to 1 part O_2. The calculated lethal dose of CO_2 levels is 6% air concentration[2], equivalent to 10 parts O_2 to 3 parts CO_2, a point that this foam well exceeded with a foam taking up slightly less than half the Wheaton bottle's volume. In an airtight environment, or even one without significant airflow/ventilation, this foam would create safety concerns about the breathability of air.

Future Work

There are multiple different experiments to be done that expand on the information found in this experiment, primarily testing the foams/fixatives in a heated environment, running possible match compounds through the GC-MS in order to compare response times, and devising tests for non-standard foams. The heated test would mix the foams and fixatives and allow them to cure at a temperature at or above 40°C by keeping their Wheaton bottle in an oven or furnace. This environment would simulate the more extreme end of D&D environment options, and would serves two different functions: to ensure that the foams properly expand/fixatives properly harden, and to find any additional volatilizations that may occur.

In order to confirm the accuracy of both the test results found here and the results of this high temperature test, possible match compounds will need to have their response time in the GC-MS recorded individually. While the mass spectrometer is a very accurate instrument, many factors such as low concentration numbers or an air leak can lead to incorrect library matches. The gas chromatography, however, is fairly indifferent to these conditions, and will still create a proper peak at the correct time. As such, the mass spectrometry data should be used as a baseline for future testing, and the possible library matches should be run through the instrument individually to confirm these matches.

Finally, certain products exist that will require individual testing formats and extra testing on their own to determine viability. The most prominent of these being GrafGuard, an expanding graphite flake that relies on chemicals trapped between layers to achieve the desired expansion and flame retardant properties. GrafGuard begins its curing process through the product reaching a desired temperature rather than the chemical combination of a standard 2 part foam, thus instead of a cool run and a hot run, GrafGuard will have to be run once just hitting the curing temperature and once held there. Additionally, the composition of this product has other concerns that are not present in other foams, like degradation temperature, where the carbon structure begins to break down. While unlikely that the product would reach curing temperature on its own while in use, much less exceed it significantly, these products are being tested as long term solutions and must be tested for many different eventualities.

Acknowledgements

This research project was funded by the DOE through the SULI program in which Natalie Ferguson organizes at SRNL.

Resources

1: http://www.arl.noaa.gov/faq_ac14.php

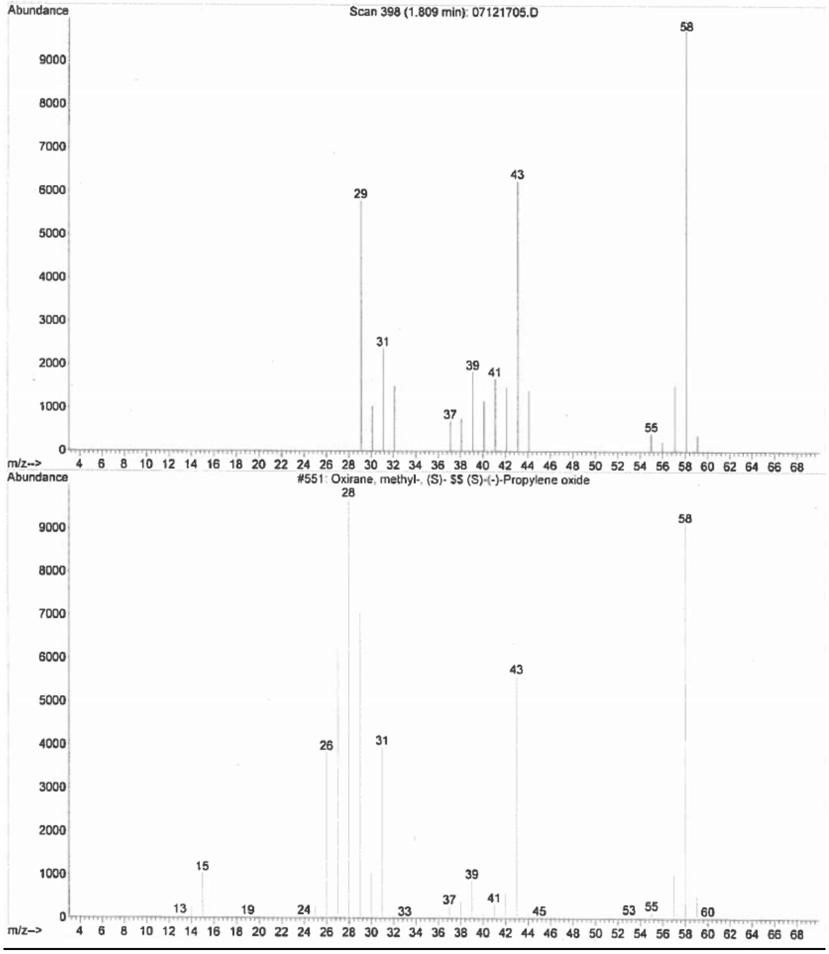
2: http://principia-scientific.org/at-what-concentration-does-co2-becomes-toxic-to-humans/

Appendix:

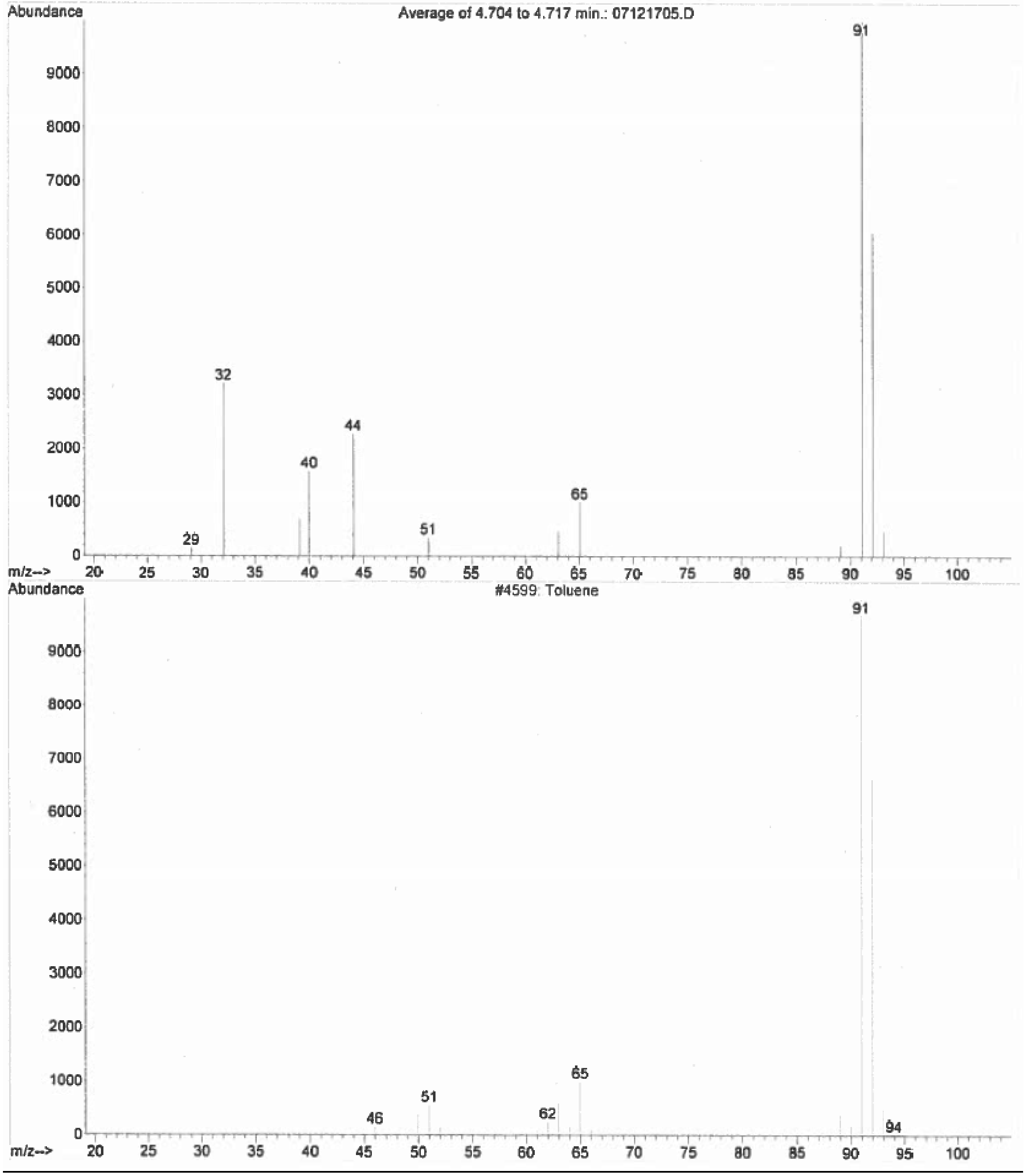
EP-102 Part A GC-MS Spectrum and TIC*

*A m/z threshold of 29 was used for this sample

1.809 minute propylene oxide match



4.710 minute toluene match



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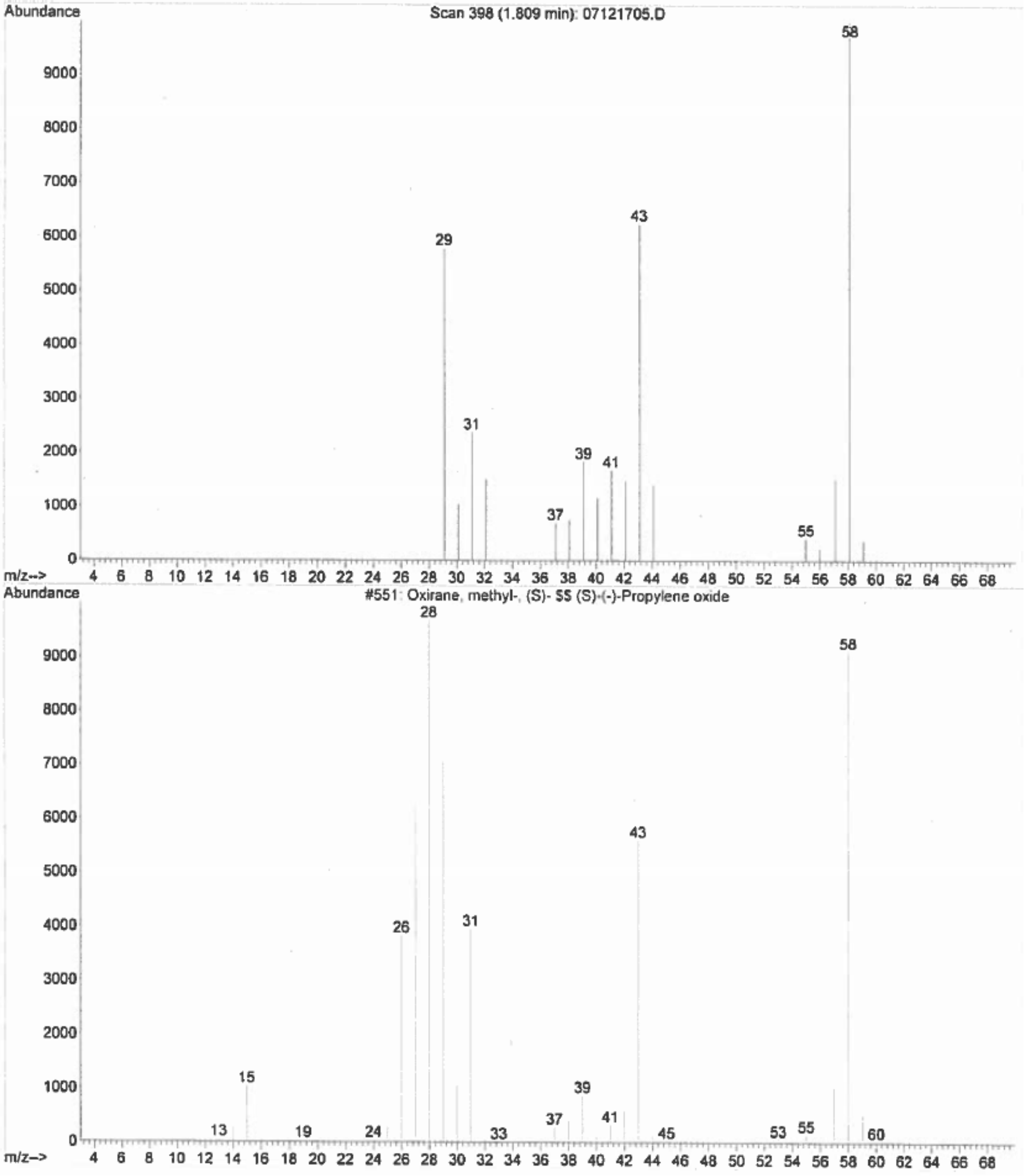
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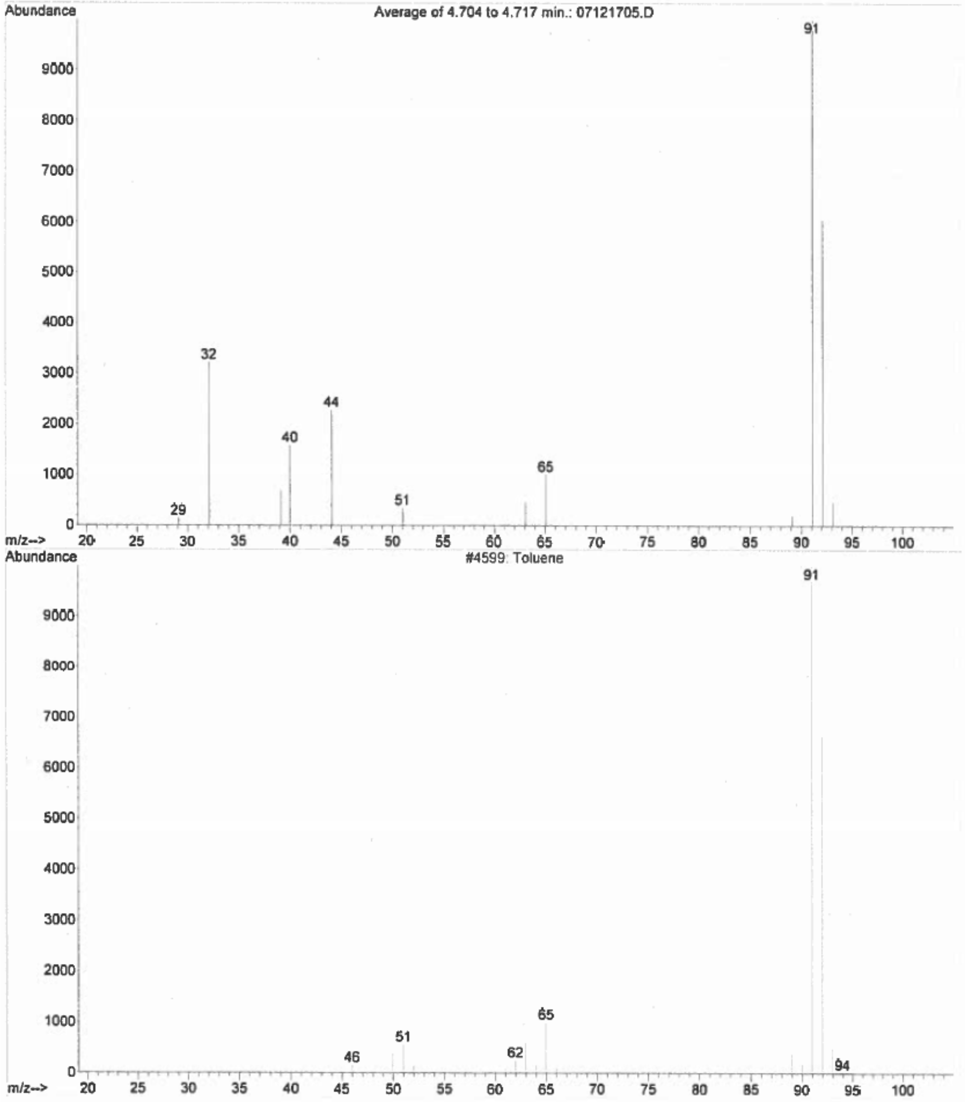

EP-102 Curing GC-MS Spectrum and TIC

CC Epoxy GC-MS Spectrum and TIC

Foam-iT! 8 GC-MS Spectrum and TIC