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Indoor Chemistry: Development Of An Indoor Surface Extractor

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Indoor Chemistry: Development of an Indoor Surface Extractor

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Master of Science



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ABSTRACT

People spend around 90% of their time indoors. This means that indoor air can have an impact on human health. One of the main factors that makes indoor air differ from outdoor air is indoor areas have a higher surface area to volume ratio than outdoor areas. Surfaces give aerosol particles a place to deposit where they can partition or react. Some of this material can leave the surface and reenter the air. Being able to analyze the material on different indoor surfaces will help further the understanding of indoor surfaces' impact on indoor air. A surface extractor was developed to sample indoor surfaces for deposited material. The surface extractor allows samples to be taken from indoor surfaces in a reproducible way so the material can be analyzed. Extraction efficiency experiments were carried out to approximate how much material was being extracted each time. Samples were then taken with the surface extractor in a kitchen. This was done to learn more about what was on the surfaces as well as be able to optimize the surface extractor for taking real world samples. Finally, various cleaning products were tested on surfaces to see what they leave behind.

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Chapter 1. Introduction

Air quality has a large impact on human health. Around the world, an estimated 3.15 million deaths occur each year due to air pollution.¹ There are many components in the air we breathe and these components include gases and aerosol particles. Particles are usually categorized by size. The most common size categories are PM_{2.5} (diameter smaller than 2.5 μm) and PM₁₀ (diameter smaller than 10 μm). PM_{2.5} is also sometimes referred to as fine particles. Many of the deaths due to air pollution are believed to be caused by high concentrations of PM_{2.5} and PM_{2.5} has been linked to respiratory issues like asthma and cardiovascular disease.¹⁻⁸

Interestingly, most of what we know about air quality and its impacts are related to outdoor air; however, people spend around 90% of their time inside. Many people associate aerosol particles with outdoor sources like vehicle exhaust or burning coal.⁹ These activities can contribute to a lot of outdoor air pollution and they can be transported indoors through open windows and doors. However, they are not the only sources of aerosol particles indoors. Some other common sources for indoor aerosol particles include cooking and cleaning. Something that sets indoor air apart from outdoor air is that many times indoor air is somewhat isolated and contained within a building; however, most buildings still allow outdoor air to exchange with indoor air through windows, doors, and cracks or through heating, ventilation, and air conditioning systems (HVAC).

Buildings are leaky containers where the occupants have control over the environment through factors like lighting, ventilation, and filtration.¹⁰ Photolysis is a term for chemical reactions that are driven by the absorption of light and thus lighting can

control the amount of this type of chemistry that takes place in a building. Ventilation allows for air exchange with outdoor environments which can reduce the concentration of particulate matter indoors if the outdoor particulate matter is lower; however, it can also increase the concentration of ozone indoors since many areas have high outdoor ozone concentrations and surfaces act as ozone sinks.¹¹⁻¹⁴ When ozone enters a building, it immediately reacts with the material on surfaces lowering the indoor ozone concentration. Finally, air filtration can be used to actively remove particulate matter from indoor air.¹⁵

Another large difference between indoor air and outdoor air is that indoor areas have a much higher surface area to volume ratio. While it is known that surfaces can have an impact on indoor air, this is one area of indoor air research that has large knowledge gaps. Surfaces provide a place for material to come out of the air (or deposit) where they can stick, be re-suspended, or react.¹⁶ Compared to outdoors, surfaces play a much bigger role in indoor spaces due to the higher surface area indoors.¹⁷ In addition, over time buildings have been built to be more insulated to improve energy efficiency. The increased insulation reduces exchange with outdoor air.¹⁸ A reduction in air exchange can increase the time for reactions to occur with material deposited on surfaces by trapping the air in a confined space.

In addition to there being a high surface area to volume ratio inside, there is a large variety of surface types. Buildings are containers with floors, walls, and ceilings and the materials for these basic building foundational pieces vary from building to building.¹⁸ We also fill our spaces with various things like furniture and décor. Organic films that have formed over time have been found on most if not all surfaces.¹⁹ Surface

type and surface orientation¹⁹ can have an impact on the formation of organic films on indoor surfaces. Many of these surfaces differ in texture and surface area which causes them to have different partition coefficients between the surface and air.¹⁶ Within an indoor environment, organic films are believed to become more similar over time; however, they differ when they begin to form, for example right after a spot has been cleaned.²⁰ Not much sampling has been done on permeable surfaces due to them being more difficult to sample. Even though these surface films have an impact on indoor air quality, they have not been studied as extensively as indoor air due to the difficulty in collecting films off these surfaces.²¹

In the enclosed areas where we live and work, we use products that produce or release aerosol particles into our air and a portion of them deposit on surfaces. Some common sources include cooking, cleaning, and personal care products.^{18,22,23} Most people use cleaning and personal care products daily. Each company that produces these products has their own formulas (or mixture of chemicals). Even with companies creating their own formulas, there are some similarities between these products (Appendix 9). For example, common surfactants appear on the ingredient list for many cleaning products. One of these common surfactants is sodium lauryl sulfate. Surfactants are compounds that have a polar end and a nonpolar end. They are included in many cleaning products because they make it possible to dissolve nonpolar substances in water.

Another indoor pollution source are building occupants and the microbes they carry around.^{17,18} Microbes themselves as well as their emissions contribute to indoor air quality.^{24–26} Many of the microbes found inside came from outdoor environments, but

they have been observed in different levels outside than inside. Factors including temperature and moisture have an impact on the amount of bacteria and fungus in indoor environments.^{24,25} The emissions from microbes are aerosol particles that form during microbial metabolism. Some of these emissions are known allergens and toxins that can impact human health.²⁶

The diversity of surfaces and organic chemicals that can deposit on these surfaces contribute to a variety of complex systems. Additionally, the organic material on surfaces will age over time further increasing the chemical complexity. Since studying indoor air is a newer field, there are a lot of unknowns. For example, when studying surfaces, we may want to know what chemicals are partitioning off the surfaces out of the organic films and into our air. To measure this in one location is helpful, but it would be even more useful to understand the chemical nature of the mixtures across different indoor surfaces. This information can then be used in models to expand our knowledge across different indoor environments.

Given the complexity of the organic mixtures, a range of different analytical techniques are needed to provide a more complete picture. For example, mass spectrometry can provide different chemical information on the components in the mixture depending on the technique that is used. A soft ionization technique can provide molecular formula and sometimes the chemical identities. In contrast, a hard ionization technique generates characteristic mass spectra that provide insights into the chemical properties of the mixtures. One of the mass spectrometry techniques used here provides information on the bigger picture, or ensemble characteristics, rather than identifying each compound. This technique is called Aerosol Mass Spectrometry (AMS)

and researchers use this to provide quantitative oxygen to carbon ratios to determine how oxidized a sample is. They can also look at the amount of nitrogen in samples.¹¹ A particular strength of this technique is that AMS is typically used to do online sampling of aerosol particles which allows comparisons between material that was deposited on surfaces to material in the air.

When material deposits on surfaces, a lot of it sticks and can react and some is able to resuspend. The differences in the chemical mixtures makes it so that different materials can undergo different types of reactions and break or transform into different products. The common processes and aging reactions that occur on surfaces are sorption,^{19,22,23} ozonation,^{13,14,27-31} photolysis,^{11,32,33} biodegradation, hydrolysis,^{12,34} reactions driven by cleaning products, and pH dependent reactions.¹²

Ozonation occurs when ozone reacts with material. This is one of the main reaction types that material on indoor surfaces undergoes. Ozone mainly reacts with double bonds and, due to the high concentration of molecules with double bonds on surfaces, ozone can react very quickly with the material on indoor surfaces.¹⁴ Many different products can form through these reactions with ozone. One of the main products that is of concern is formaldehyde. This product is a concern because it is a known carcinogenic compound.^{14,29} Ozone will enter buildings from outside, printers, and ozone air purifiers/cleaners.^{13,29}

Emission source	Ozone reactive emissions
Some cleaning products	Limonene, α -pinene, terpinolene, α -terpinene and other terpenes, α -terpineol, linalool, linalyl acetate, and other terpenoids, longifolene and other sesquiterpenes
Occupants (breath, skin oils, and personal care products)	Isoprene, nitric oxide, squalene, unsaturated sterols, oleic acid and other unsaturated fatty acids, unsaturated oxidation products
Perfumes and other scented products	Limonene, α -pinene, linalool, linalyl acetate, terpinene-4-ol, γ -terpinene
Ventilation ducts and duct liners	Unsaturated fatty acids and esters, unsaturated oils, neoprene
Wood flooring	Isoprene, limonene, α -pinene, other terpenes and sesquiterpenes

Table 1.1 (highlights from Weschler 2006)¹⁴ Shows the variety of emissions in some common household products that can react with ozone. This demonstrates that there are many sources of material that can react with ozone.

Another type of reaction that occurs indoors is photolysis. Photolysis involves the absorption of photons by molecules followed by fragmentation reactions. The light that drives photolysis indoors comes from the sun through windows and lighting indoors. Light is not evenly distributed throughout buildings and it depends on the type of lights used and window placement. While photolysis does happen in indoor environments, it does not occur as much as it does in outdoor environments.¹¹

Cleaning products can also drive some indoor chemistry. Some cleaning products are formulated to remove material, some were formulated to react with material, and others do both. It has been observed that detergents can leave behind residue that can desorb from surfaces when heated.^{22,23} Bleach is reactive and performs redox reaction. Since bleach is a disinfectant, it can kill microbes and “cleans”

by breaking down material on surfaces through oxidation of material on surfaces. It is common for the volatile emissions in bleach cleaning to contain chlorine which can be linked to respiratory issues in people who use a lot of bleach. For example, in a recent study during some bleach cleaning events windows were left open. After cleaning was complete and windows were shut, the concentration of chlorinated compounds in the air increased. This is due to desorption of these compound off of indoor surfaces.³²

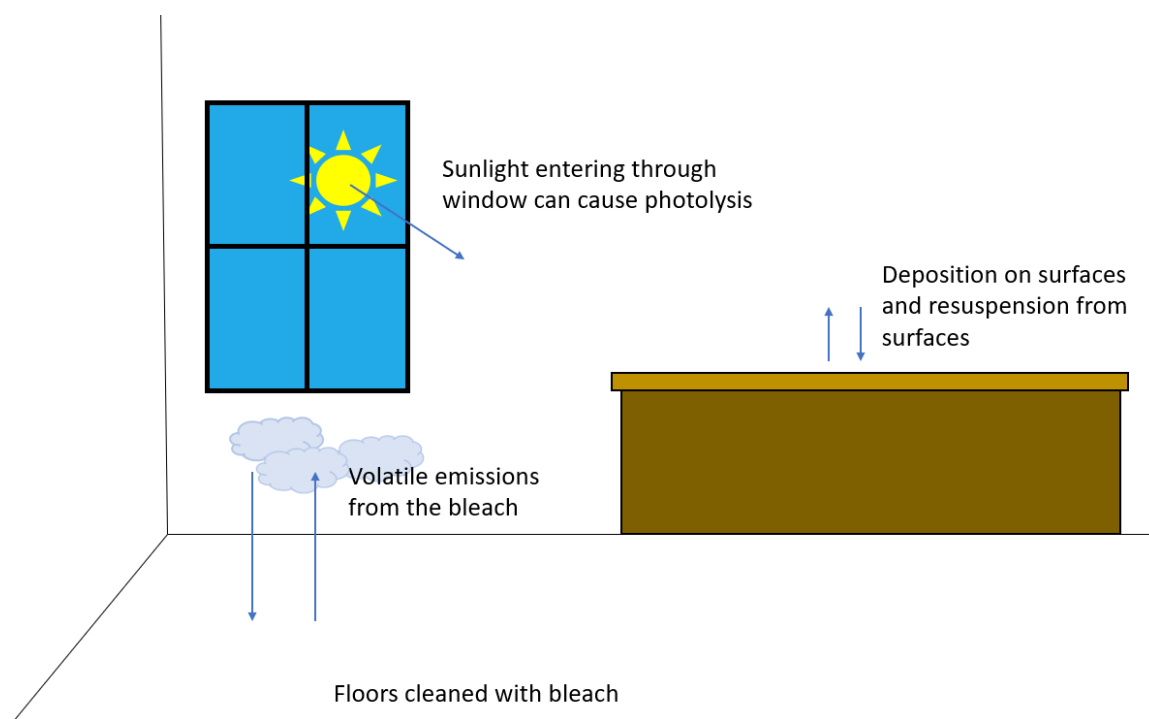


Figure 1.1 This figure shows a basic model of what can happen chemically when mopping with a bleach solution. Notice how the bleach solution is not the only factor causing reactions. There is also sunlight coming through a window that is making photochemistry take place.

Water is known to play an important role in indoor chemistry when it comes to surfaces, but there is not a lot of information about it. Based on sampling in 13 homes, indoor concentrations of water-soluble organic gases are around 15 times higher than outdoor environments. The amount of moisture inside buildings can vary and depends

on things like humidity and splashing water when cooking and bathing. It is likely that dampness on surfaces impact surface films and how they may react.³⁵

Given the range of different surface types, organic film mixtures, and aging processes, it is important to expand our understanding of surface films by collecting more samples from different areas. Surface wipes are a common method used to sample indoor surfaces. Surface wiping is when a Kimwipe or cotton cloth with solvent is used to wipe a surface; however, some problems can arise using this method.^{11,20} The two main problems are variability between different people sampling and how clean the wipes are. Different people may apply different amounts of pressure to the wipes and wipe for different amounts of time. Wipes can also be contaminated with organic material that could deposit on them prior to use.

To improve upon this extraction method, we have developed a new method: solvent extractions directly off of indoor surfaces. The surface extractor works by depositing a known amount of solvent on a surface and then extracting it into a sample vial. While the solvent is on the surface, it dissolves material from the surface so that when it is extracted, so is the material. The goal is to use this method to make sampling more reproducible and to enable surface film thickness to be calculated.

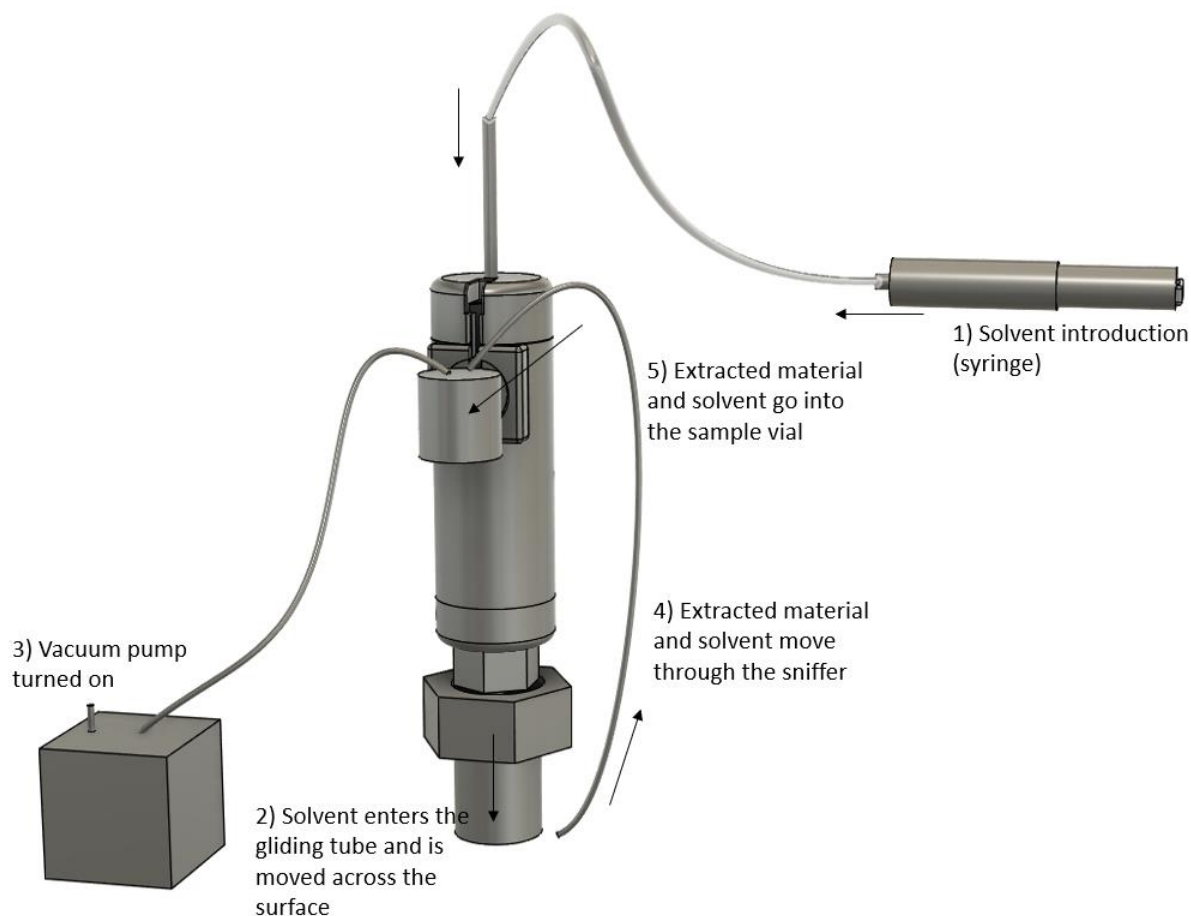


Figure 1.2 The above diagram shows how the extractor works. The syringe pump pushes solvent into the gliding tube part of the extractor. Solvent leaks out of the gliding tube as it is moved across a surface. The vacuum pump then pulls the solvent that leaked out of the gliding tube into the sniffer that leads to the sample collection vial. Once the sample is collected, the sample collection vial can be removed and replaced with the next one.

Here I discuss the development of the surface extractor method and explore different factors that have been observed to impact surface extractions indoors. The first section covers surface and solvent characteristics. I find that water and acetonitrile make good solvents, but both of the solvents have pros and cons. In the second section I explore preliminary extraction efficiency experiments when using the indoor surface extractor. The extractor is able to pick material up, but the exact extraction efficiency is

still unknown. In our preliminary samples from a dorm room kitchen on campus, we saw some peak series that look like they may be from commercial products (Appendices A3-A5). This motivated me to investigate chemicals that may be left behind on surfaces after they are cleaned. The third section looks at various cleaning products that were aged on glass in an apartment kitchen. In this controlled study, in addition to seeing remains of cleaning products on surfaces, material that was deposited down from activities in the kitchen is also visible. I also observed many differences in the mass spectra between different cleaning products and what they leave behind on the surface.

Chapter 2. Experimental Methods

2.1 Surface Solvent Compatibility

Observational testing

Several surface samples were acquired from Home Depot to test how different solvents would interact with them. The surfaces that were tested were vinyl, rocky butte oak laminate, spice tan oak, HS strand woven hazelnut, crestwood gray oak laminate, hawthorne mill oak laminate, keller cherry laminate, hand scrapped strand woven sahara bamboo, high gloss jatoba laminate, Radcliff aged hickory laminate, and a ceramic tile- glossy. They were selected to represent different materials that are commonly used in buildings; vinyl, laminate, laminate, strand woven, and glossy ceramic. More details about each of the surfaces tested are in Appendix 2.

A few drops of solvent were applied to various types of surfaces that are found in buildings. The solvents that were tested were water, acetonitrile, toluene, and methanol. Visual observations were made about the physical properties and interactions of the surfaces and solvents. Observations were made at 1 minute 2 ½ minutes and 5 minutes.

Chemical testing

A few surfaces were selected for chemical testing. The surfaces were selected because they had different treatments (ie. Laminate and strand woven) which are expected to provide the largest differences, if any, in measurements. The hazelnut was selected because it was woven wood and seemed to be the most permeable. The crestwood gray oak was selected because it is laminate wood flooring which is

common. Finally, the vinyl was chosen because it was a manmade surface. The pieces of Hazelnut, vinyl, and crestwood gray oak were thoroughly cleaned with DI water then MilliQ water. An additional piece of glass was cleaned in the same manner. While they were being rinsed, they were also being scrubbed with the grain and against the grain. Once the surfaces were clean and dry, approximately 3 mL of methanol was used to extract from the surface. These samples were then run using an offline aerosol mass spectrometer (AMS) as described in section 2.5.1.

2.2 Surface Extractor Characterization

Two separate extraction efficiency experiments were carried out during the development of the indoor surface extractor (ISE). These experiments were performed by spotting down a known amount of a substance onto a clean glass plate and then extracting it.

Citric acid extraction

The first of these experiments was done using citric acid. 100 μg of citric acid dissolved in acetonitrile was deposited on a clean glass surface and allowed to dry. This citric acid was then extracted using the extractor with water as the solvent. These samples were dried under clean flow of nitrogen and were then analyzed using an AMS using the method as described in section 2.4.1.

Soy Oil extraction

The second experiment set was done using soy oil. Glass plates were prepped by drawing circles on the back side that were about 7 cm in diameter. The front side of

the glass plates were thoroughly rinsed with MilliQ water and then methanol. They were then set out to dry. Later, plates were prepped with soy oil by depositing 109 μL (about 0.1 mg) of soy oil on the front side of the glass in each circle.

Water was chosen as the solvent used to extract the soy oil. This was done because water is the solvent most likely to be used when taking real world samples off indoor surfaces as demonstrated in section 3.1. Here, 6 mL of water was used to extract 3 soy oil surface samples. A control was created by adding 109 μL of soy oil and 6 mL of water into a clean sample vial.

Samples were lyophilized to remove water. To do this, samples first had to be frozen in their vials. Once frozen, clean pieces of aluminum foil were secured on the tops of each vial and a small hole was poked in the foil. Once the lyophilizer was ready, the samples were placed inside. It took approximately one day for the samples to be lyophilized. More detail for this process is given in Appendix 7.

The soy oil samples were then analyzed gravimetrically. About 2 mL of methanol was added to each sample vial and then transferred into a second clean pre-weighed vial. This was then dried under clean nitrogen. Once the sample dried this was repeated two more times with the sample being transferred from its original vial into its second vial. Each time the same pipet was used for the same sample. Finally, approximately 1 mL of methanol was added to each original vial and then transferred and into the pre-weighed vial. These vials were then dried and reweighed so an extraction efficiency could be calculated.

2.3 Cleaning Product Characterization

Cleaning products are commonly used on indoor surfaces and there are nonvolatile components like surfactants present in them, so it would make sense for some cleaning product residue to be left on 'cleaned' surfaces. Some common cleaning products and their residues were analyzed to gain more insight into their composition. Glass plates were cleaned with MiliQ water and then rinsed with methanol. Once the plates were finished drying, cleaning products were added to their surface. One plate was treated with Windex, one with Simple Green, and one with Mrs. Meyer's Clean Day. The cleaning products were sprayed using the spray bottle they came in onto glass surface. The glass was then wiped with Kimwipes until it appeared dry. The process of adding cleaning product and wiping was completed three times with each product.

The glass plates were set out for about a day in lab. The Windex was extracted using approximately 4 mL of MiliQ water. Simple green and Miss Meyer's were extracted using approximately 6 mL of Milli-Q water. In between each sample a blank was taken from clean aluminum foil. Each extraction area was a circle that was about 7 cm in diameter. After the extractions, the samples were frozen overnight so that they could be prepped for lyophilization. The following day the samples in the vials were covered with clean aluminum foil with a small hole in the top. These samples were lyophilized for about a day. Samples were then frozen until they could be analyzed. Cleaning product samples were analyzed using an ion trap mass spectrometer and methods are described in Section 2.5.2.

Another experiment probed the changes that can occur when plates that had cleaning residue on the surface were located in an indoor area. For this, a second set of

glass plates was treated in a similar manner with cleaning products. Two plates were treated with Windex, two with Simply Green, two with Mrs. Meyer's, and four that were just cleaned with MiliQ water and methanol. The glass plates were sandwiched together with treated sides together. They were wrapped in aluminum foil.

This second set of glass plates were transported to an apartment kitchen. The foil packets were carefully opened and placed cleaning product face up on top of a refrigerator for around 3.5 months. One set of the clean plates were kept as a field blank. After the 3.5 months had passed, the glass plates were put back together and rewrapped in the aluminum foil. The glass was transported back to the lab and then extracted with 6 mL of acetonitrile. Samples were dried down under a gentle flow of ultra pure nitrogen and stored in a freezer.

To prepare all the samples from the kitchen for analysis, 8 mL of acetonitrile was added to the sample vials to re-dissolve the material. The sample was divided into two separate vials and filtered with a 0.2 μm Teflon filter to remove dust and larger particles that could clog the instrument. The samples were dried again under a gentle flow of ultra pure nitrogen.

Samples were prepped for analysis using an ion trap mass spectrometer. 500 μL of methanol was added to the vial. From that vial, 30 μL were transferred into a plastic centrifuge tube and an additional 500 μL were added to dilute the sample. The samples were run using an ion trap mass spectrometer instead of the Orbitrap because the signal in the Orbitrap was very low due to the long term instrument shut-down from the Covid 19 pandemic. The Orbitrap was used for the dorm kitchen samples that are described in section 2.4. Methods for the instrument are described in Section 2.5.2. If

the signal was below 10^3 counts, then additional sample was added to make the solution more concentrated.

2.4 Dorm Kitchen Surfaces

Real world samples were taken to test the indoor surface extractor to look at differences between different surfaces within the same area. The extractor was prepared following the SOP in Appendix 5 and was taken to a communal dorm kitchen.

Initial sampling

Extractions were collected in a dorm kitchen to test the extractor in a real world setting. Everything was precleaned in a lab with acetonitrile. In between samples, the sample lid was cleaned with methanol and the sniffing and gliding tubes were exchanged with freshly cleaned ones. The only sample where the sniffing tube was not exchanged was between the stove top sample and the stove hood sample where the sniffing tube was just thoroughly rinsed with methanol. After extractions, samples were brought back to the lab and placed in the freezer overnight. The counter sample was centrifuged for 5 minutes at the third speed level. The rest of the samples were filtered using a $0.2\ \mu\text{m}$ Teflon filter. The vials were then rinsed with an addition 2 mL of acetonitrile and filtered with the rest of the sample.

Later sampling

At the beginning of each sample, the gliding tube was exchanged for a new gliding tube. For some samples, the sniffer tube was exchanged and for some samples it was rinsed thoroughly with methanol before taking a new sample. A blank sample was

collected before each sample. The blank used here was aluminum foil that had been baked at 450 °C for at least 4 hours and thus was clean of any organic material. The aluminum foil was laid on a surface clean side up and the extraction from the foil was taken in the same manner as the surfaces. The sample was then extracted using the same tubes as the blank. The solvent used for the kitchen extractions was water. The counter and the stove top were horizontal surfaces, the stove hood was at an angle, and the windows were vertical. After extraction, samples were frozen and then lyophilized. 900 μL of acetonitrile was added to each vial and the sample was then divided into two smaller vials and dried down. Samples were analyzed using AMS and Orbitrap mass spectrometry as described in sections 2.5.1 and 2.5.2.

2.5 Analytical Methods

2.5.1 Aerosol Mass Spectrometer

Surface sample data was collected using an offline Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS).¹¹ Samples were run on the AMS at MIT or at NASA by Professor O'Brien. Before the samples were transported, they were dried down and frozen. They were transported in a cooler with ice packs.

Analyses with the AMS included an internal standard to enable quantification. The internal standard was ammonium iodide. In the syringe, 4-4.5 μL of the internal standard solution (0.25 g/L) and 0.5 μL of the sample solution were combined. The volumes were adjusted for optimization. The mixture was then placed on the small-volume nebulizer³⁶. The carrier gas was zero air (Aadco 737-13 Pure Air Generator). For the citric acid extraction efficiency experiment, citric acid was used to calibrate the

AMS. Each sample was replicated twice. These samples were then analyzed using Igor pro 7 packages. The packages were SQUIRREL (v1.571) and PIKA (v1.161).

2.2.2 Orbitrap Mass Spectrometer

Electrospray ionization Orbitrap mass spectrometer was used to characterize samples. The mass spectrometer was calibrated using Pierce LTQ ESI Positive Ion Calibration Solution (caffeine, MRFA, Ultramark 1621) and Pierce ESI Negative Ion Calibration Solution (SDS, sodium, taurocholate, Ultramark 1621). The Orbitrap has both a front ion trap and the Orbitrap mass spectrometer behind this. For some samples, the Orbitrap was used to collect high resolution data. The mass resolution used for high resolution runs was 60,000 $m/\Delta m$. Data was collected for about 10 minutes for each sample and the spectrum is an average over this sampling time. However, for many samples, only the ion trap was used as this has better signal.

MS/MS was used to fragment some ions in the 2D ion trap to learn more about them. Select ions were isolated in the ion trap and then fragmented. The fragmentation energy used was between 18 and 30 (arbitrary units within the program's software). The fragmentation was adjusted so the parent ion would have a relative intensity of about 50%.

Methanol was added to dried samples so they could be run. A portion of the sample was then diluted. If the sample was too dilute to see signal, more sample was added. For runs using the ion trap, the targeted signal was between 10^3 - 10^6 ion counts and for high resolution, the target signal was between 10^4 - 10^6 ion counts. Sheath gas

flow rate was between 12-20 arb, spray voltage was set between 4.00-4.50 kV, and the sample flow rate was set between 2.00-4.00 $\mu\text{L}/\text{min}$.

Raw files were converted using MSConvert (<http://proteowizard.sourceforge.net/tools.shtml>) and MMass version 5.5.0 (<http://www.mmass.org/download/>) was used to analyze the data. The peaks found in the mass spectra were picked using MMass and then put into Igor Pro version 7 to generate the reproduced mass spectra shown here.

Chapter 3. Results and Discussion

3.1 Surface Permeability

Observational testing

An indoor surface extractor was designed to extract material off of indoor surfaces so that it can be analyzed using different analytical techniques. The composition of this material can give some insight about what chemicals are found in indoor air. Being able to get good extractions is necessary to find out what is present on surfaces. In order to get a good extraction, a good solvent is needed. The ideal solvent for extractions would be a solvent that can be used on a large variety of indoor surfaces without damaging them, have enough surface tension to be easily extractable from the surface, and extract the material that is relevant to indoor air. The surfaces chosen for the following experiments were chosen because they are commonly used.

Being able to use the solvent on many indoor surfaces without causing damage is ideal because real world studies will involve extractions from a variety of surfaces and the materials will not always be identifiable. A solvent that might damage surfaces would limit the number of surfaces that can be tested. Data from previous studies show that different surfaces might grow surface films at different rates.³⁷ Limiting the number of surfaces that can be extracted limits the amount of surfaces that we can gather information on. This would then limit the understanding of how surfaces impact indoor air.

It is also important that the solvent has surface tension so that the extractor can remove the solvent from the surface after it has been deposited. If a solvent has low surface tension, it becomes more difficult to remove from the surface with the sniffing tube and vacuum I am using. The more solvent that the surface extractor can pick back

up, the more material it is able to pick up. If none or only a small portion of the solvent can be picked up, then that surface cannot be extracted efficiently with the indoor surface extractor. It can also make extracting from vertical or slanted surfaces more difficult if the solvent is able to move or drip more quickly. A solvent with poor surface tension can limit the variety of surfaces that can be tested.

The final thing to consider is that the solvent should dissolve the material that is relevant to indoor air. However, this could be tricky to gauge as it is not known what part of a surface has more of an impact on indoor air and this might vary from surface to surface. The chemicals that are on the surface of the material and the chemicals within the surface itself might both be relevant to indoor air.

The following data was collected from experiments that were conducted to compare the properties of different solvents. Water did not appear to interact or damage any of the surfaces. Water would be a good solvent for the sampling of a variety of indoor surfaces because it is unlikely to damage most indoor surfaces. There is also enough surface tension with water where the indoor surface extractor is able to pick up the water with the sample. The downside to water is its polarity. If a lot of the material on surfaces is nonpolar, it is less likely to get picked up by the water.

Table 3.1 Water was observed on different building materials that can be found indoors. The water did not appear to interact or absorb into these materials. No change in the table indicates no change in the appearance of the water since it was placed on the surface.

Surface	1 min	2.5 min	5 min
Vinyl	No change	No change	No change
Rocky Butte Oak laminate	No change	No change	maybe started to absorb
Spice Tan Oak	No change	No change	maybe started to absorb
HS Strand Woven Hazelnut	No change	No change	to absorb
Crestwood Gray Oak laminate	No change	No change	No change
Hawthorne Mill Oak laminate	No change	No change	No change
Keller Cherry laminate	No change	No change	No change
Hand Scraped Strand Woven Sahara bamboo	No change	No change	No change
High Gloss Jatoba laminate	No change	No change	No change
Radcliffe Aged Hickory laminate	No change	No change	No change
Ceramic Tile- glossy	No change	No change	No change

Table 3.2 Methanol was observed on different building materials that can be found indoors. Observations were made at 1, 2.5, and 5 minutes. No change in the table indicates no change in the appearance of the methanol since it was placed on the surface.

Surface	1 min	2.5 min	5 min
Vinyl	No change	No change	No change
Rocky Butte Oak laminate	No change	No change	No change
Spice Tan Oak	No change	No change	No change
HS Strand Woven Hazelnut	about 50% absorbed	100% absorbed	Completely absorbed
Crestwood Gray Oak laminate	No change	No change	No change
Hawthorne Mill Oak laminate	No change	No change	No change
Keller Cherry laminate	No change	No change	No change
Hand Scraped Strand Woven Sahara bamboo	started to absorb	50% absorbed	100% absorbed
High Gloss Jatoba laminate	started to absorb	25-50% absorbed	50-75% absorbed
Radcliffe Aged Hickory laminate	maybe started to absorb	25-50% absorbed	50-75% absorbed
Ceramic Tile- glossy	spread out a lot	almost done evap	100% evap

Some variation in results were observed. The woven woods completely absorbed the methanol while only two of the laminate wood samples absorbed the methanol. The methanol had a lot less surface tension on the glossy ceramic tile than on the wood surfaces. Lower surface tension of the solvent would make it more difficult to sample with the extractor. Methanol would not be a good solvent to use for extractions with the indoor surface extractor because it cannot be used on a wide variety of surfaces. The surface tension was not good on smooth surfaces and it absorbed into more porous surfaces.

Table 3.3 Acetonitrile was observed on different building materials that can be found indoors. Acetonitrile did not appear to interact with the surfaces very much. No change in the table indicates no change in the appearance of the acetonitrile since it was placed on the surface.

Surface	1 min	2.5 min	5 min
Vinyl	No change	No change	No change
Rocky Butte Oak laminate	No change	No change	No change
Spice Tan Oak	No change	No change	No change
HS Strand Woven Hazelnut	No change	No change	maybe started to absorb
Crestwood Gray Oak laminate	No change	No change	No change
Hawthorne Mill Oak laminate	No change	No change	No change
Keller Cherry laminate	No change	No change	No change
Hand Scraped Strand Woven Sahara bamboo	No change	No change	No change
High Gloss Jatoba laminate	No change	No change	No change
Radcliffe Aged Hickory laminate	No change	No change	No change
Ceramic Tile- glossy	No change	No change	maybe started to evap

During this test, acetonitrile did not appear to get absorbed into any surfaces; however, in a later test, acetonitrile appeared to remove a waxy finish off a surface. Acetonitrile could be a good solvent to use with the indoor surface extractor if information is known about all surfaces being tested. It is useful for doing extractions off glass plates that are deployed in indoor spaces.

Table 3.4 Toluene was observed on different building materials that can be found indoors. Toluene did appear to absorb into the woven wood and it may have done something to one of the wood pieces. No change in the table indicates no change in the appearance of the toluene since it was placed on the surface.

Surface	1 min	2.5 min	5 min
Vinyl	No change	No change	No change
Rocky Butte Oak laminate	No change	No change	No change
Spice Tan Oak	No change	No change	surface felt less slick afterwards
HS Strand Woven Hazelnut	started absorbing	50% absorbed	almost 100% absorbed
Crestwood Gray Oak laminate	No change	No change	No change
Hawthorne Mill Oak laminate	No change	No change	No change
Keller Cherry laminate	No change	No change	No change
Hand Scraped Strand Woven Sahara bamboo	spread	started to soak in	50% absorbed maybe started to absorb
High Gloss Jatoba laminate	No change	No change	No change
Radcliffe Aged Hickory laminate	spread	No change	maybe started to absorb
Ceramic Tile- glossy	slight spread	No change	to evap

Toluene seemed to work well on most of the surfaces; however, it appeared to have been absorbed by the strand woven surfaces and it may have changed the slickness of one of the surfaces. Toluene probably would not work well on painted surfaces because it is a common component in paint thinners so it might remove paint from surfaces. It also has a strong odor that might not make sampling pleasant.

Based on the observations made, water and acetonitrile would make the best solvents to use with the indoor surface extractor. Water is a common component in household products and it is not very likely that it would damage any indoor surfaces

over the short sampling time period (~ 5 minutes). If there is a campaign where online gas-phase measurements are being taken, using water as a solvent to extract off surfaces would have a negligible impact on the online measurements. The downside to water is it is a very polar molecule so it is less likely to extract non polar molecules. On the other hand, acetonitrile is less polar. It performed well with the sample surfaces, but it did appear to remove a wax coating off part of a countertop. Another possible issue with acetonitrile is if gas-phase online measurements are being taken at the same time as an extraction, it might show up in the online data.

Chemical testing

A few of the surfaces from the observational testing were selected for chemical testing. These surfaces were thoroughly rinsed with MilliQ water and methanol before extractions were taken with methanol. The woven hazelnut was chosen because it appeared to be more permeable than the other surfaces. Laminate wood flooring is very common and the crestwood gray oak was selected as a representative for laminate wood. Finally, the vinyl was chosen because it was a different material all together.

Figure 3.1 below shows the AMS data that was collected from this chemical testing. AMS is a quantitative method that uses electron ionization to break apart molecules. The data from the AMS is then analyzed in a program where the mass of the organic material and the mass of the internal standard can be determined for each sample.

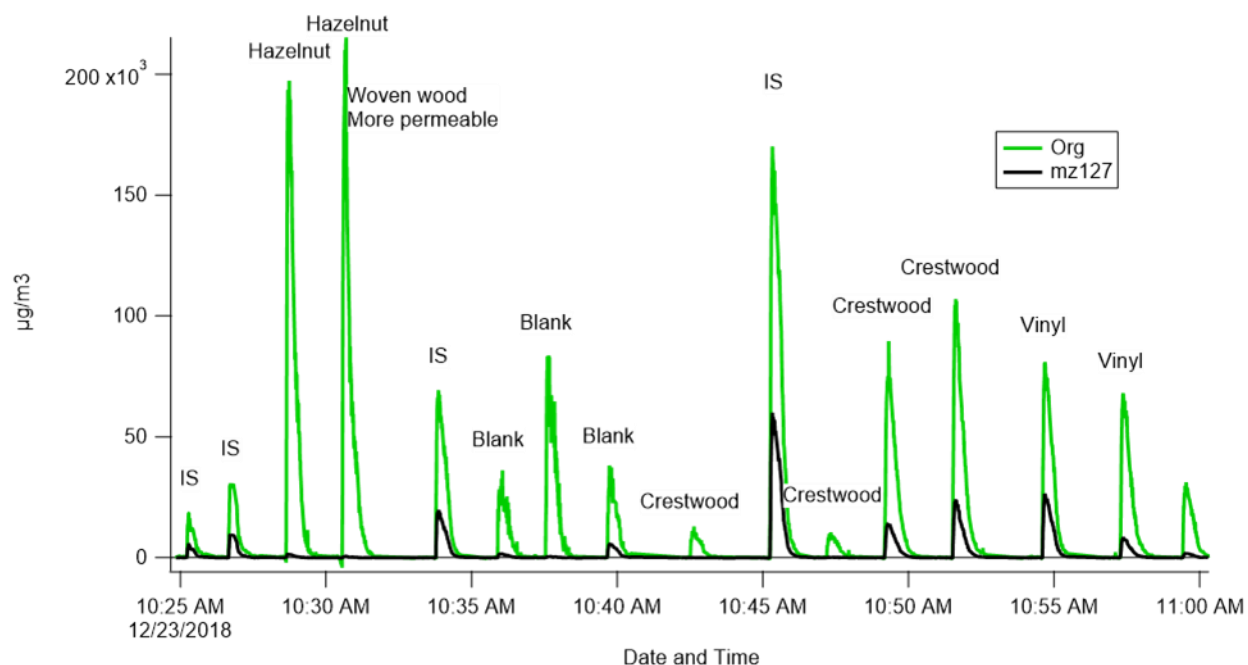


Figure 3.1 The figure shows a time series for offline AMS data from different methanol extracted surfaces. IS indicates internal standard. The peaks labeled 'Blank' were empty injections that were used to clean the instrument. The black line represents iodide which was used in the internal standard. The injections into this instrument were pulses, the rise and fall correspond to individual injections. The x-axis shows the times of the injections. Since the instrument creates aerosols to infect, the y-axis shows the μg .

The ratio of iodide and organic was compared between the internal standard and each sample in order to determine the amount of organic material from each surface. The strand woven hazelnut had the most amount of organic material in the extraction. Observations shown in **Table 3.2** said that methanol absorbs into the strand woven hazelnut wood. Some of the possible reasons for that wood having a higher organic signal than the others include: (1) that the methanol could be removing material from inside the wood, or (2) the wood might have a higher surface area allowing more material to have collected on its surface (material that was not cleaned off during the preparation).

Understanding how surfaces interact with a particular solvent is important in determining which solvent to use. The goal for extractions would be to remove the material on the surface that can interact with indoor air. A solvent should also be able to remove the material from the surface that is relevant to the study. Much of the material is organic and seems to be less polar or non-polar. This would mean an organic solvent can be useful in removing the material from the surface. It is possible that the surface itself or a chemical coating (i.e. a finish on a commercial surface) can impact the air; however, dissolving part of the surface itself with the solvent probably would not reveal useful information. Depending on what the surface is, an organic solvent might not be desirable.

As seen in the observational and chemical tests, permeability and materials can have an impact on the sample. The more permeable surface had more organic material extracted than the less permeable surfaces. Further testing is needed to see if another solvent, like water, would have similar results. The surface that absorbed the methanol had a higher concentration of organic material than those that did not. Water did not appear to absorb into any of the surfaces so it might yield different results. An important point to consider when collecting these samples is: does the solvent's ability to penetrate a surface impact the results? Overall, it is important to continue work to understand how solvents can interact with different surfaces so samples can be taken from buildings without damaging the surfaces.

3.2 Surface Extractor Characterization

The goal for the surface extractor is to be able to have quantitative and reproducible extractions. A few preliminary extraction efficiency experiments were carried out with known amounts of material on surfaces that are representative of organic compounds that can deposit on indoor surfaces. The first experiment used a known amount of citric acid and the second was carried out with a known amount of soy oil. The first experiment was depositing a known amount of citric acid onto a surface then extracting it. These extractions were analyzed using the quantitative AMS technique shown above and the data is shown in **Figure 3.2**. The technique gives the ability to calculate extraction efficiency of citric acid off a glass surface by measuring the concentration of citric acid in the extracted sample.

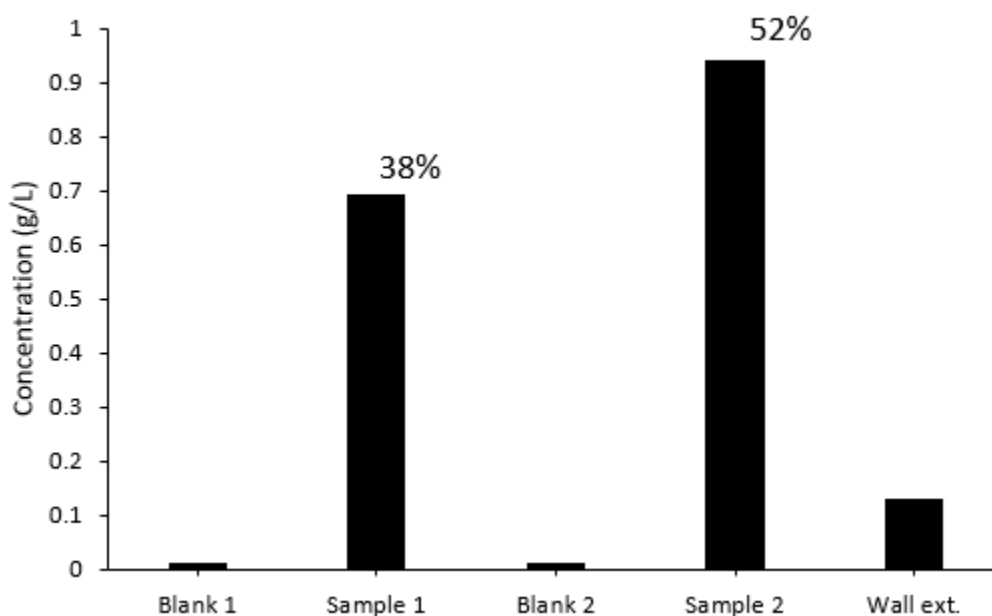


Figure 3.2 The approximate concentrations of citric acid measured in three different extracts using AMS. The two samples (Sample 1 and Sample 2) are from an extraction where a known amount of citric acid was placed onto a surface. The percentages labeled above these samples indicate the percent of citric acid that was recovered from the surface. The wall sample was extracted from a painted wall outside the O'Brien lab.

The expected concentrations for both samples was ~ 1.9 g/L and thus the extraction efficiency of citric acid off the glass was around 40-50%. This is a reasonable extraction efficiency, but it would be better to increase it. The wall extraction was performed to see if the extractor would work on a real world surface and to see how well the extractor worked on vertical surfaces. After these extractions, some changes were made to the extractor and the extractor method. Because the gliding tube was round, it made more sense to extract from circles and in circular patterns. The diameter of the gliding tube was also increased from $\frac{1}{4}$ of an inch to 1 inch. The smaller diameter made it harder for the extractor to remain upright and the solvent on the surface was more difficult to control. Improving the control over the solvent made it easier to collect the sample from a predetermined area.

The second extraction efficiency experiment used soy oil. Soy oil is common in cooking and therefore is likely to be present on kitchen surfaces. Water was used for these extractions because water will most likely be the solvent of choice when extracting off real world surfaces. A control was also created for this experiment in order to see how much soy oil would be lost through the lyophilization and transferring the soy oil into a separate container to be weighed. The control was the soy oil and water put directly into the sample vial instead of extracting it with the indoor surface extractor. Samples, including the control, were lyophilized in order to remove water. Gravimetric measurements were used to determine the extraction efficiency of this experiment.

Table 3.5 Soy oil in the amount of 0.100 g was deposited onto clean glass. A water extraction was performed with the indoor surface extractor. The extract was then lyophilized and the mass of the soy oil was recorded.

	Mass Recovered	Percent Recovery
Extraction 1	0.0753	75%
Extraction 2	0.0807	81%
Extraction 3	0.0848	85%
Control	0.0759	76%*

*Part of this sample was lost during lyophilization.

The percent recovery for soy oil during this experiment was between 75-85%. The control had a ~76% recovery, but the vial with the soy oil control broke during the lyophilization process and some of the sample was lost. Not only was the soy oil able to be extracted, but most of it was recovered. These results are promising because they show reproducible and quantitative results unlike what has been seen with surface wipes. The soy oil was still fluid when these extractions were performed so an organic film might behave differently.

These initial studies show that different material can be extracted using the indoor surface extractor. Extraction efficiency needs to be explored further once more data has been collected about the type of material deposited on surfaces. Based on data collected in the next section, I would suggest investigating the extraction efficiency of commonly used ingredients in cleaning products, off different types of surfaces with acetonitrile and water. Cleaning products are used on most if not all indoor surfaces and they have some commonly used similar ingredients.

In addition to extracting different material, experiments still need to be carried out to test extraction efficiency based on amount of solvent used or area extracted. Now that the solvent is easier to control, further experiments targeting extraction efficiency based on surface area and amount of solvent can be performed. So far I have found that extracting from a circle that is 6-7 cm in diameter and using 6 mL of water is effective for extracting material, but this might not be the optimal surface area or amount of solvent.

3.3 Cleaning Product Characterization

A preliminary real-world extraction experiment was done where various surfaces around a dorm kitchen were extracted (Mass spectra that were collected are reproduced in Appendices). When those samples were analyzed, material similar to that found in soap was detected. When fragmented, a fragment appeared around 97 m/z which is where sulfate would show up. Compounds with a sulfate group are commonly used in surfactants. A sulfate group is the polar end of the molecule and a long chain is the non-polar end. This characteristic makes surfactants good at cleaning because they can help dissolve both polar and non-polar substances. These initial studies raised the question: are we predominantly seeing cleaning products in the extracts?

To investigate this, we started by characterizing pure cleaning solutions. First, some preliminary data was gathered using Windex. Three glass plates were thoroughly cleaned with MiliQ water and methanol. The first plate had Windex sprayed on it and left to dry. The other two plates had Windex sprayed on them, but then the Windex was wiped off with Kimwipes. While wiping the Windex off, one hand was gloved and the other hand was not. Two days later all surfaces were extracted using 4 mL of MiliQ

water. Before extractions were taken, it was observed that the plate that had not been wiped had visible residue from the Windex, but the wiped surfaces appeared very clear and clean. While the surfaces were being extracted, it was noted that the surfaces were far more slick than extractions taken from glass surfaces where cleaning products had not been applied. There was also less control over the solvent than previous extractions. For example, during previous extractions, there was more control over where the solvent was going. For these extractions, due to the slickness, the water would just move.

The experiment was set up in this way to see if Windex straight from the bottle looked the same as the residue Windex would leave behind on a surface being cleaned. Samples were then analyzed using 60k high resolution electrospray ionization mass spectrometry. Overall, we observed that there were differences between all three methods, but the samples from the plates that were wiped appeared very similar. It is important to know if there are differences between what comes in the bottle and what remains on a surface after the cleaning product is wiped off because most people wipe surfaces after spraying them down.

In addition to the Windex study, a second study using multiple fresh and aged cleaning products was run. Here, the glass surfaces were cleaned and then deployed in an actively used kitchen. This allowed for direct comparisons to be made between freshly dried cleaning products and surfaces that were deployed for a long period of time with dried cleaning products on them. The data from direct comparison would show if anything besides cleaning products would be visible on thoroughly cleaned surfaces using the analytical methods here. It would also give an idea of how different cleaning

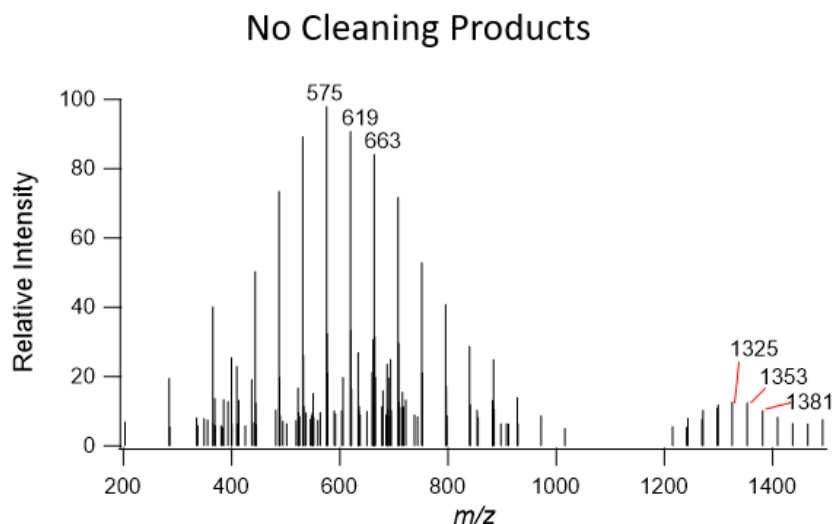
products might appear in mass spectrometry data. The cleaning products that were selected were Windex, Simple Green, and Mrs. Meyer's Clean Day. Windex is a commonly used glass cleaner. Simple Green is supposed to be an environmentally friendly and non-toxic household cleaner. Finally, Mrs. Meyer's was chosen because it is a brand that uses a lot of natural ingredients and incorporates essential oils.

The fresh cleaning products were applied to a clean glass surface and wiped. This was repeated to make sure the glass was coated with the cleaning product. The glass was left out in lab for two days so it could dry and then the glass was extracted with water using the indoor surface extractor. The aged cleaning products were tested in a similar manner, except they were left in a kitchen for 3.5 months and then extracted with acetonitrile. Acetonitrile was chosen for the aged extractions in order to save time because drying samples down with a gentle flow of nitrogen does not take as long as lyophilizing water samples. While extracting the aged and unaged cleaning product samples, the extractor felt different for each product as it glided across the glass. Some of the fresh samples felt smooth and glided easier while some of the aged seemed to feel a bit more gritty or rough.

Data was collected using an LTQ ion trap mass spectrometer with the exception of the fresh Windex sample which was run using high resolution. This is because the other samples were run after the COVID-19 shut down and the ion trap offers better sensitivity. The better sensitivity from using the ion trap is useful for a first look at the data because more of the material is visible when using the ion trap than getting the high-resolution data. High resolution is used more for identifying the material because the higher resolution shows the exact masses for the compounds. Neither method is

quantitative, they show a portion of the material that is present in the sample. It is important to consider that other material is likely to be present just not observed.

a)



b)

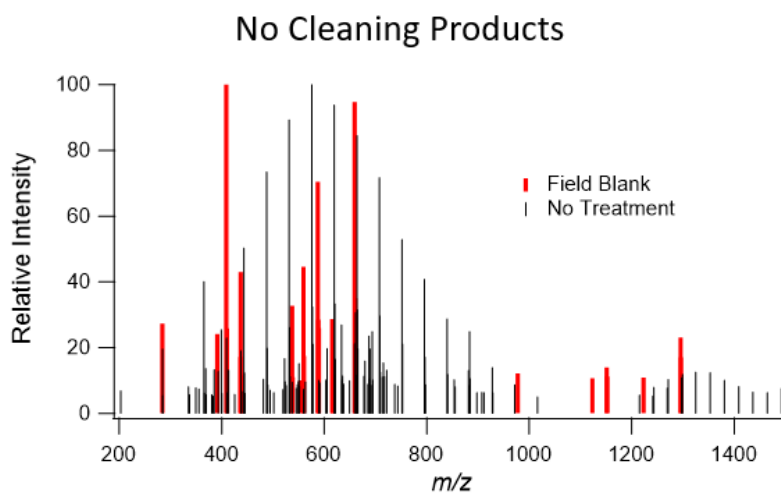
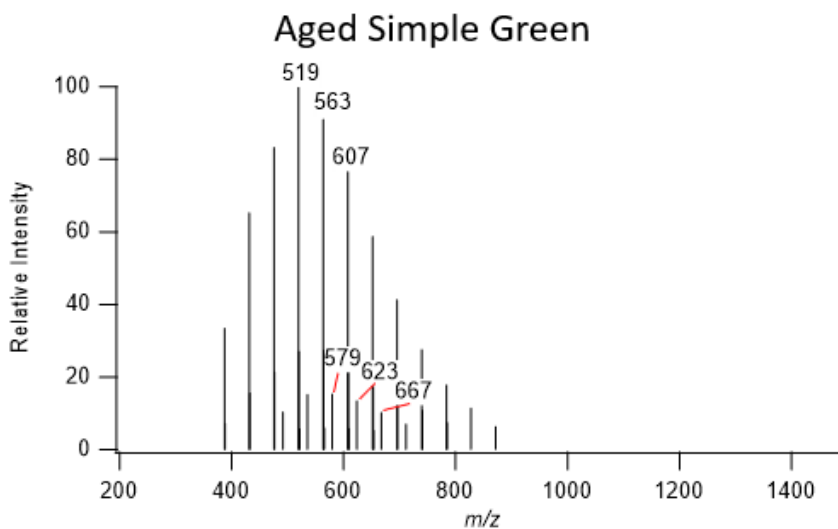


Figure 3.3 Mass spectra showing data from both the field blank (red) and the glass without cleaning products (black, replicated in a and b). The glass without cleaning products was left out for 3.5 months in a kitchen that was actively used. Extractions were taken from both a clean glass field blank and the glass that was sitting in a kitchen. Samples were run using electrospray ionization Orbitrap mass spectrometry with the ion trap. In **a**) masses in two oligomeric series are highlighted centered at 575 m/z and 1325 m/z . In **b**) the field blank mass spectrum (red) and the mass spectrum from the glass that was sitting out in a kitchen (black, same spectrum as in a) are overlaid on top of each other.

Discussion

For the glass plate that was deployed in the kitchen for 3.5 months with no cleaning supplied applied, an oligomeric pattern was observed (Figure 3.3a). The lower mass series from the No Cleaning Products sample increases by 44 m/z . This is a pattern that is observed in polyethylene glycol (PEG). The masses that would be observed for an unmodified PEG in this mass range include (503, 547, 591, 635 m/z). The observed masses do not correspond to this or to sodium adducts, suggesting that this may be an unknown modified PEG. The second series has a difference of 28 m/z this is possibly either a difference of C_2H_4 or CO. The series were seen in the samples from the glass that was sitting out and not in the field blank (Figure 3.1b). Based on this comparison between the field blank and the glass without cleaning products, the series likely came from activity in the kitchen. Further testing is needed to identify what these chemicals are. In the future, high mass resolution in the Orbitrap MS can be used to find the exact mass of the material which can be used to calculate the molecular formulas.

a)



b)

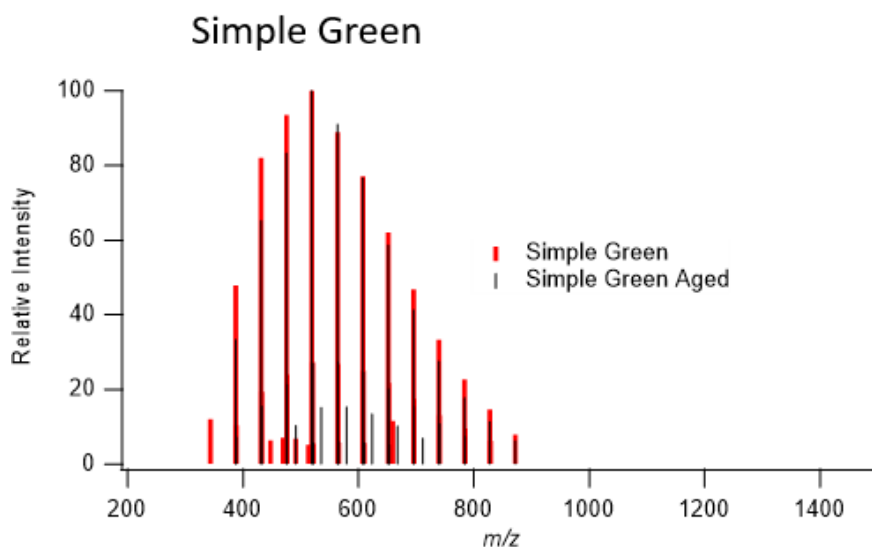


Figure 3.4 Mass spectra of extracts from glass with both freshly applied and aged Simple Green. The glass with Simple Green was aged by leaving it out in a kitchen that was being used for 3.5 months. The extracted samples were run using electrospray ionization Orbitrap mass spectrometry. The ion trap was used to analyze these samples. In **a)** two series are highlighted. In **b)** the freshly applied Simple Green mass spectrum (red) and the mass spectrum from the glass with Simple Green that was sitting out in a kitchen (black) are on top of each other.

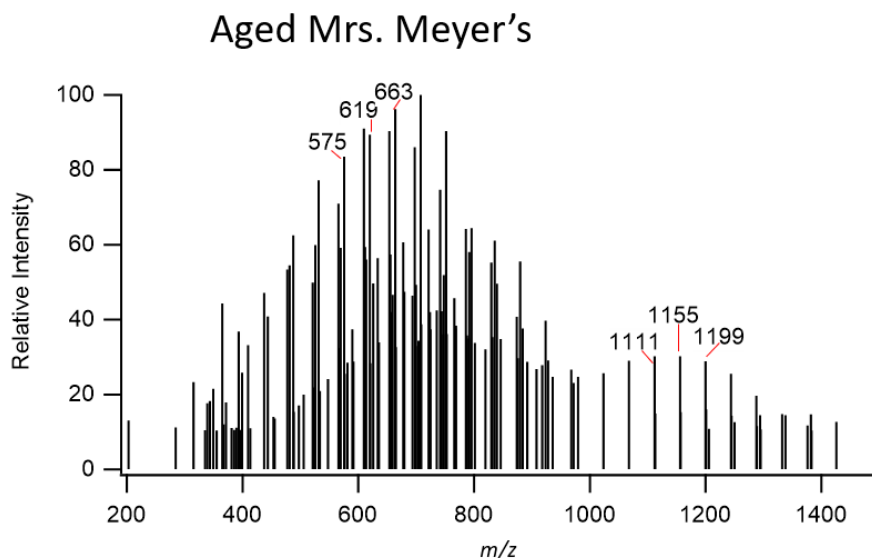
Discussion

The glass plate with aged Simple Green and the glass plate with fresh Simple Green both look like they have similar material in the mass spectrum. The series around 519 m/z was observed in the fresh sample and appears in the aged sample. The relative intensity of the series around 519 m/z does appear to shift more towards the higher mass in the aged sample. It is possible that this could be due to the lower mass material re-suspending, but this needs to be investigated further since the method used is not quantitative. This series has a spacing of 44 m/z . There is another series around 579 m/z that has a mass spacing of 44 m/z . A mass spacing of 44 m/z has been observed in PEG and modified PEG. The series around 519 m/z was present in both the fresh and aged samples, but the series around 579 m/z was only present in the aged Simple Green sample. The 579 m/z series was likely from the kitchen since it was not present in the fresh Simple Green sample; however, this series was not observed in the extractions from the other glass that was set out. Further analysis to characterize the samples can include different spray optimizations to try to de-emphasize these oligomers, which appear to spray very well, or separating the material in the samples using chromatography.

Electrospray ionization is a good technique for detecting a wide range of molecules. It allows for characterization of the material in the ion trap through fragmentation. Seeing mass distributions allows for series, such as the ones observed here, to be easily picked out and is ideal for seeing oligomers. However, everything might not be seen and thus not everything can be characterized that is present in the samples. Electrospray ionization works by ionizing compounds, but different

compounds ionize in different ways. In positive mode, the compounds compete for adding protons. The compounds that are outcompeted might not appear in the mass spectrum. Electrospray ionization is a good technique for initially looking at complex organic mixtures, but further analysis is still needed to fully characterize the samples. For example, quantitative techniques like AMS can be used to analyze all the material in the sample. Separation techniques, like liquid chromatography, can also be used. Gas chromatography might not be the best separation technique because the mixture on surfaces that have been targeted by this extraction method generally has low volatility.

a)



b)

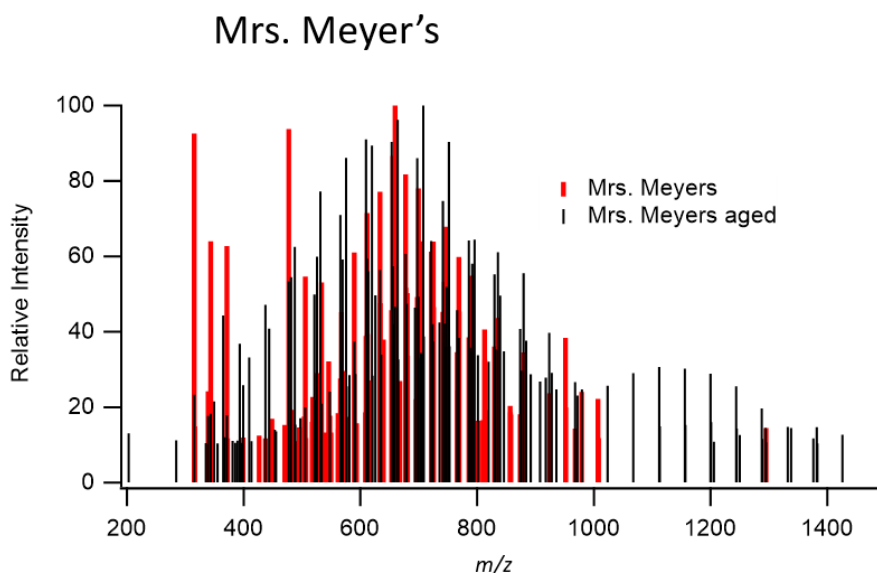


Figure 3.5 Mass spectra showing extracts from glass where Mrs. Meyer's was freshly used and where Mrs. Meyer's was aged. The glass with Mrs. Meyer's was aged by leaving it out in a kitchen that was being used for 3.5 months. Extractions were taken from both the glass with fresh Mrs. Meyer's and the glass that was sitting in a kitchen. The extraction samples were run using electrospray ionization Orbitrap mass spectrometry to produce the mass spectrums in the figure. The ion trap was used to look at these samples. In **a)** two series are highlighted. In **b)** the freshly applied Mrs. Meyer's mass spectrum (red) and the mass spectrum from the glass with Mrs. Meyer's that was sitting out in a kitchen (black) are on top of each other.

Discussion

Mrs. Meyer's Clean Day is the most natural cleaning product of the products tested and it seems to have the most complex mixture based on the mass spectra. Despite common comments from the public and advertising tactics, having a large variety of compounds present in a product does not make the product more or less harmful than other products. In addition to that, natural ingredients do not necessarily make a product safer or better. How harmful a product is depends on the specific compounds present and their amounts. It can also depend on how the material breaks down over time. These initial experiments were conducted to learn about what cleaning products leave on surfaces and are not an evaluation of how good or safe they are.

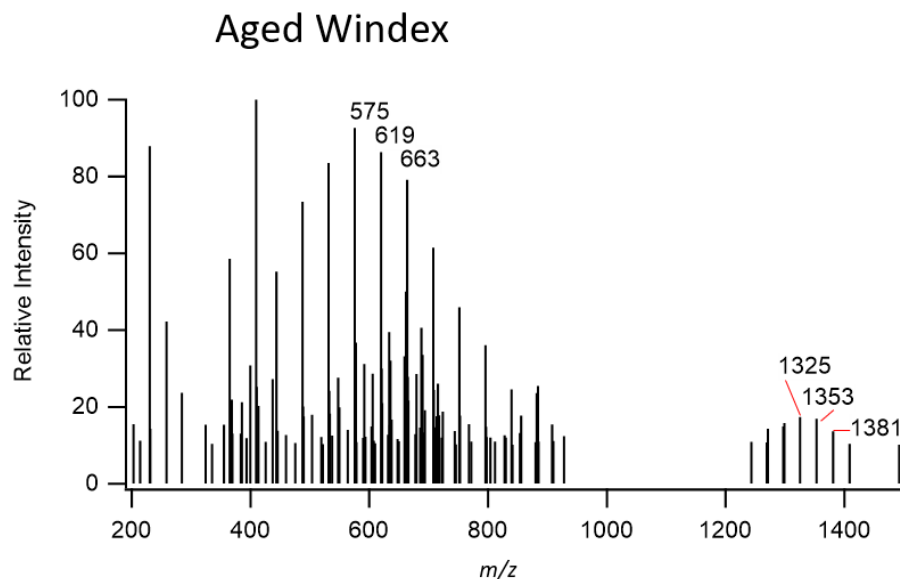
Mrs. Meyer's extractions have multiple series. These extractions show the most variety in material out of all the cleaning products that were tested. As seen in figures for the no treatment and for the aged Mrs. Meyer's, both share some of the same series (the same masses and spacings). As seen in the Simple Green samples, the series that are in both the aged and fresh samples seem to have similar relative intensity shifts towards a higher mass. For example the 575, 619, and 663 m/z series is found in both. The main peak in the no cleaning product series is observed at 575 m/z (Figure 3.3a), but in the aged Mrs. Meyer's sample it is shifted to 707 m/z (Figure 3.5a). While both Mrs. Meyer's and the no cleaning product samples have the same masses and mass spacing, the centroid of Mrs. Meyer's is shifted up. However, the series that was centered around 1325 m/z that was observed in the no cleaning product sample did not show up in the Mrs. Meyer's aged sample. This could simply be because there was not enough signal for this material to show up, or something could have caused it to break

down after depositing. Not being able to see everything in a sample and the variation in what gets ionized with ESI due to the difference in composition between samples is a limitation of this technique.

An interesting detail that differed between the samples was there were a few series present in the aged Mrs. Meyer's sample that we not present in the fresh Mrs. Meyer's sample or the aged clean glass. An example of this series is centered around 1155 *m/z*. Many natural products have the ability to biodegrade because microbes exist that can break their components down. The reason why it is easier for these products to biodegrade is because these compounds are found in nature so there is bacteria that can break them down. Many of the natural ingredients in Mrs. Meyer's are plant based. Produce, if left out for too long in a kitchen begins to break down, so it would make sense that there are microbes present in a kitchen that can break down plant based material. That being said, it takes time for these microbes to grow in numbers and these glass plates were left out for 3.5 months. If some of these compounds are a result of biodegradation, their concentrations might be lower in a kitchen cleaned with Mrs. Meyer's once a week.

More of a variety in material showed up in the fresh Mrs. Meyer's extractions than in the fresh extractions from the other cleaning products. Mrs. Meyer's also had more ingredients than the other cleaning products and many of the ingredients were natural. This could mean that each ingredient includes multiple compounds. The reason why a larger variety of material appeared in the fresh Mrs. Meyer's samples could be because there was more variety or that more of the material can be ionized.

a)



b)

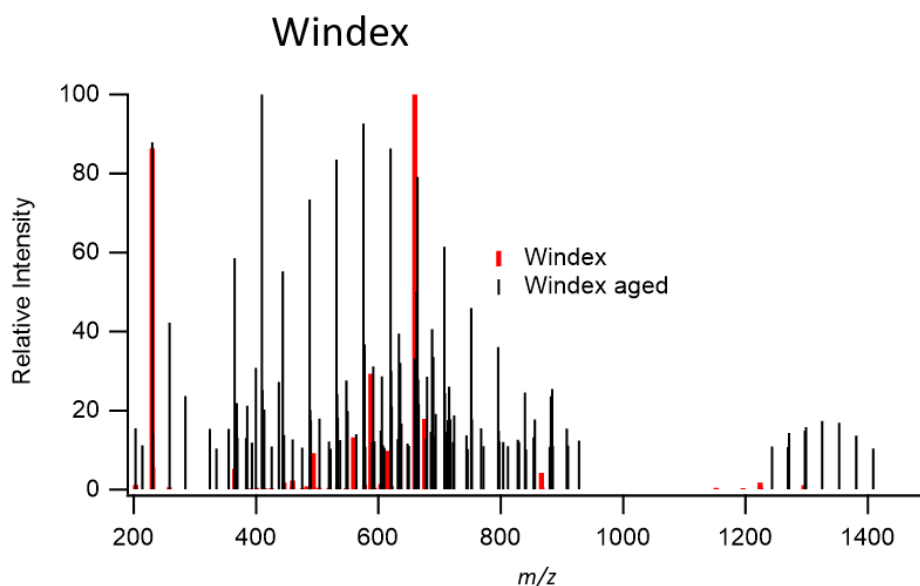


Figure 3.6 Mass spectra showing extracts from glass where Windex was freshly used and where Windex was aged. The glass with Windex was aged by leaving it out in a kitchen that was being used for 3.5 months. Extractions were taken from both the glass with fresh Windex and the glass that was sitting in a kitchen. The extraction samples were run using electrospray ionization Orbitrap mass spectrometry to produce the mass spectrums in the figure. The ion trap was used to look at the aged Windex and 60k high resolution was used to look at the fresh Windex. In **a)** two series are highlighted. In **b)** the freshly applied Windex mass spectrum (red) and the mass spectrum from the glass with Windex that was sitting out in a kitchen (black) are on top of each other.

Discussion

The mass spectrum from the aged Windex looks very similar to the mass spectrum from the glass that was not treated with cleaning products (Figure 3.1a). This would mean that the material deposited on the glass surface is visible in addition to the material that came from Windex. While it is possible that components in Windex could have degraded over time, much of the new material shown in the mass spectra deposited on the surface.

The data in this section show that at least some material from cleaning products used on indoor surfaces stays on the surfaces. Additional material was also deposited onto the surfaces. Each of the mass spectra from the three cleaning products appeared different from each other. Differences between the residues that different cleaning products leave on surfaces adds to the idea that indoor surfaces and what is on them is very complex and affected by many variables. Not only would this mean that there is variation between buildings because different people use different cleaning products, but the variation due to cleaning products can cause differences within buildings and even rooms. Most people do not use just one cleaning product in their homes or offices. People tend to use a variety of cleaning products for a variety of surfaces and what the surfaces are used for. It should also be noted that the glass was left out for 3.5 months in a kitchen and it is recommended that kitchen surfaces get cleaned more often than that.

Quantitative analysis can be used to determine how much of the material is from cleaning products and how much was deposited on the surface. Extractions from surfaces that are cleaned with cleaning products can be analyzed using the AMS as

demonstrated above. Once the material is identified in the Orbitrap, cleaning product calibration standards can be created. Since the AMS can be a quantitative technique, standards can be run alongside samples to see how much clean product residue is left on surfaces right after cleaning and after the surface has had other material deposited on it.

Chamber experiments with cleaning materials could be set up to age the cleaning material to see how it decomposes and if the decomposed material remains on the surface. A chamber could be used for this because it can exclude other material from depositing on a surface while exposing the surface to other environmental conditions that can age the material like light and ozone.

Another thing to consider is the downside to using water as a solvent. Water is polar and so it will extract the polar material while leaving down the non-polar material. Surfactants aid in dissolving both polar and non-polar molecules because they have polar and non-polar ends. Extractions from kitchen surfaces and the deployed surfaces that were cleaned with cleaning products had surfactants like sodium lauryl sulfate. The exact concentrations for these surfactants are unknown, but while extracting from kitchen surfaces, the water appeared soapy. Depending on how much surfactant is present on a surface, they might be able help remove other compounds that water would be a poor solvent for. This is not to suggest that soaps should be added to the extraction solvent, but rather that they are already present on many real world surfaces and there is the possibility that they could impact the material that ends up being extracted.

Chapter 4. Conclusions

An indoor surface extractor has been designed and created to sample surfaces for deposited material. The method allows material to be extracted off surfaces in a reproduceable manner. Different researchers that use wiping methods tend to use different wiping methods and different wipes.³⁸ In addition to the different methods, some researchers have discussed seeing different extraction efficiencies within their own sampling methods. There are many factors that should be taken into consideration when choosing a solvent for the surface that is being extracted. Some of these factors include surface tension, the permeability of the surface itself, how deep the grain is, if it can damage the surface, and what the user is trying to extract. Based on these observations, surfaces with similar treatments tend to interact the same or similar ways with the same solvents. For example, the woven wood appeared to absorb some of the different solvents while only some of the laminate wood absorbed solvents.

Out of the tested solvents, water appears to be the better solvent to extract from building surfaces, especially if not a lot is known about the type of surface. The reason why water is probably better to use with real world surfaces relates to the high surface tension observed on all surfaces as well as the facts that it is common and it probably will not damage the surface. Water is a common ingredient in many cleaning products so most indoor surfaces should be able to handle water. Further testing is needed to see if water extracts different amounts of organic material on different surfaces.

When testing extraction efficiency, replicates extracted similar amounts of the deposited material. This suggests that not only was the extractor method able to extract the material from the surface, but that it can be done in a reproduceable manner. More

testing is needed to optimize extraction efficiency. Additional testing of real-world surfaces can be used to determine if the method is as reproducible in real world scenarios as it is with controlled lab tests. However, the real-world testing will need to take into account variations in deposition that can occur across an area. For example, looking at a kitchen counter, the distance from the stove could have an impact on what can be observed. Aerosols that cannot travel as far would deposit in higher concentrations closer to the stove than a space farther away. To account for these differences, multiple samples can be extracted in close proximity. With the surface extractor, extractions are made in circles with a diameter of 6-7 cm so taking samples close to each other is possible.

In some preliminary tests, it was found that some cleaning product material can be extracted off surfaces. Many people use a variety of products on their surfaces. Each product is made up of many ingredients, some are the same, but many differ. Many differences were also visible in the mass spectrum. For example, the aged Windex sample looks very similar to the glass that was deployed with no cleaning products. Some of the variations observed in the aged material did not appear on the clean glass. For example, the aged Mrs. Meyer's sample had material that was not seen in the fresh Mrs. Meyer's sample or the glass that did not have cleaning products on it. Not only did the initial material appear to differ, but the aged material did as well. This could be because the material in the cleaning product could have aged or it could be a difference in optimization. Out of all the cleaning products tested, Mrs. Meyer's had the most naturally derived ingredients. Natural ingredients tend to be able to biodegrade over

time and the glass was left out over a 3.5 month period in a kitchen. Clean product ingredients are listed in Appendix 8.

The differences between the fresh and aged cleaning products show that material is deposited on surfaces over time and the material can be observed using electrospray ionization mass spectrometry. Using electrospray ionization is a good technique for analyzing what is present in these samples and more material is visible using this technique than using gas chromatography, but it is not quantitative. Another issue that can occur when using electrospray ionization is that if a compound is very good at ionizing and it found in high concentrations, then signal for other compounds that are not as good at ionizing will not be visible. This probably occurred with the Simple Green samples (Figure 3.4). It appears that something in Simple Green is much better at ionizing than other material that is likely present in the samples. Part of the optimization for electrospray ionization is having the sample concentrated to a point where there is signal for the sample but not having the signal dominated by a small fraction of what is present. Further testing is needed to see how the cleaning products themselves age over time.

Once these samples have been analyzed with high resolution mass spectrometry, a cleaning product standard and a surrogate standard can be designed. The cleaning product standard would consist of common surfactants found in many household cleaners while the surrogate standard would be added to the surface before an extraction. These standards could be used to explore the extraction efficiency of the residual material left behind by cleaning products and it could be used to calibrate the AMS so that the concentrations of cleaning products on surfaces can be calculated.

Additional testing on the aging of different cleaning products is needed. Using high resolution mass spectrometry would make identifying the chemicals easier. Here, the lower resolution ion trap was predominantly used because the ion trap has higher signal. The higher signal is good for getting an overview of what is present, but the high resolution is good for getting exact masses and identifying what compounds are present. Aging cleaning materials in a more controlled environment could help differentiate what is aged cleaning material and what has been deposited on the surface. The extractor has been shown to have reproducible results between samples when tested for extraction efficiency. On real world surfaces, the extractor has been shown to be able to extract a variety of material. The body of the extractor was designed on Fusion 360 so it can be 3D printed. The extractor was designed so that it only needs one person in order to operate it and it can be easily transported in a backpack.

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Appendix 1 Surface Extractor Design

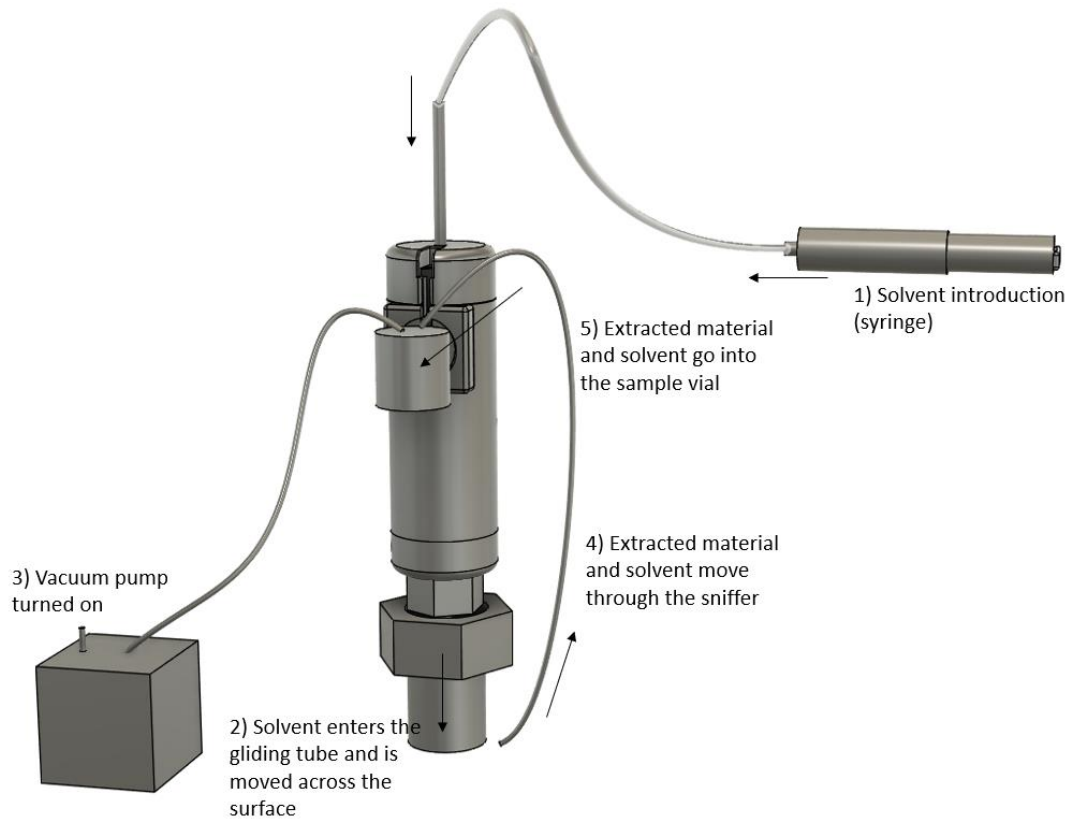


Figure A1 The solvent is loaded into the syringe which is how it gets into the extractor. It will travel through 1/16" Teflon tubing to the extractor and then it will go through 1/16" stainless steel tubing. Once the solvent leaves the stainless-steel tubing, it goes directly onto the surface inside the gliding tube. The extractor is moved around the surface and the solvent leaks out. The vacuum pump allows the sniffer to suck the solvent and material off the surface and into a collection vial.

Appendix 2

This table includes manufacturing and other information about the surfaces that were tested with different solvents in section 3.1. The table includes basic information about the type of wood and the model information.

Mono/Dicot	Family	Genus	Coating/finish	Model	SKU	Surface
			Authentic Textured Finish	I114813L	1002-145-275	Vinyl
Dicot	Fagaceae	Quercus	high gloss, traditional finish	HC19	1002-913-756	Rocky Butte Oak-THS laminate
Dicot	Fagaceae	Quercus	7 layered aluminium oxide finish	SHD5214	1000-025-055	Spice Tan Oak-THS
Dicot	Betulaceae	Corylus	Embossed Register (EIR) Finish	HL661H	1003-176-280	HS Strand Woven Hazelnut-THS
Dicot	Fagaceae	Quercus	Embossed Register (EIR) Finish	HL1318	1003-063-418	Crestwood Gray Oak-THS laminate
Dicot	Fagaceae	Quercus	Embossed Register (EIR) Finish	HL1317	1003-043-769	Hawthorne Mill Oak laminate
Dicot	Rosaceae	Prunus	high gloss finish	HL82	822-240	Keller Cherry-THS laminate
Monocot	Poaceae		7 layered aluminium oxide finish	HL655H, HL655S	1001-869-345, 1001-869-339	Hand Scraped Strand Woven Sahara-THS bamboo
Dicot	Fabaceae	Hymenaea	High Gloss, Piano Finish	HL1044	897-469	High Gloss Jatoba-THS laminate
Dicot	Juglandaceae	Carva	EIR (Embossed in register) finish	HL1251	1001-775-585	Radcliffe Aged Hickory-THS laminate

Appendix 3

Real world samples from a dorm kitchen analyzed using ESI/MS. These extractions were made with acetonitrile.

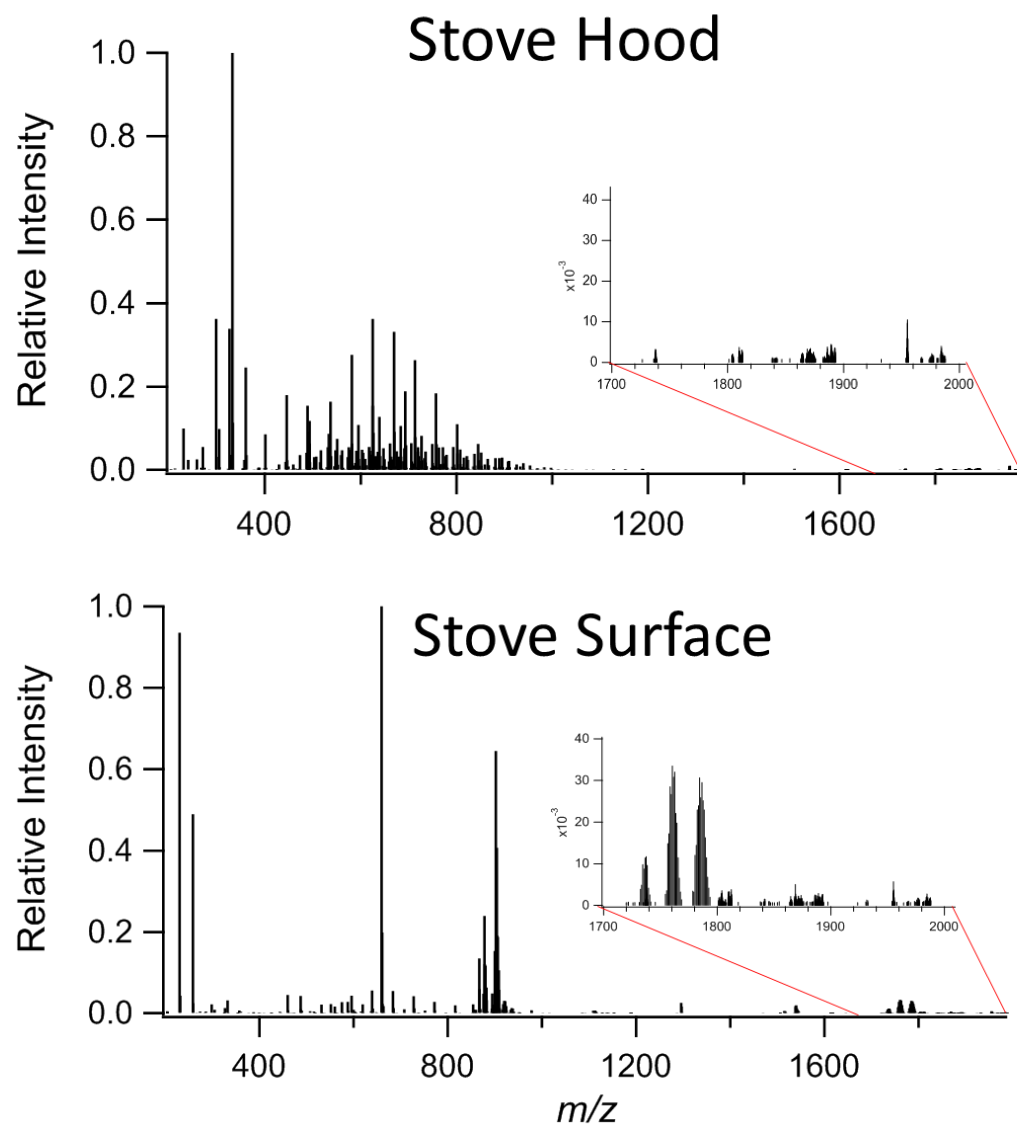
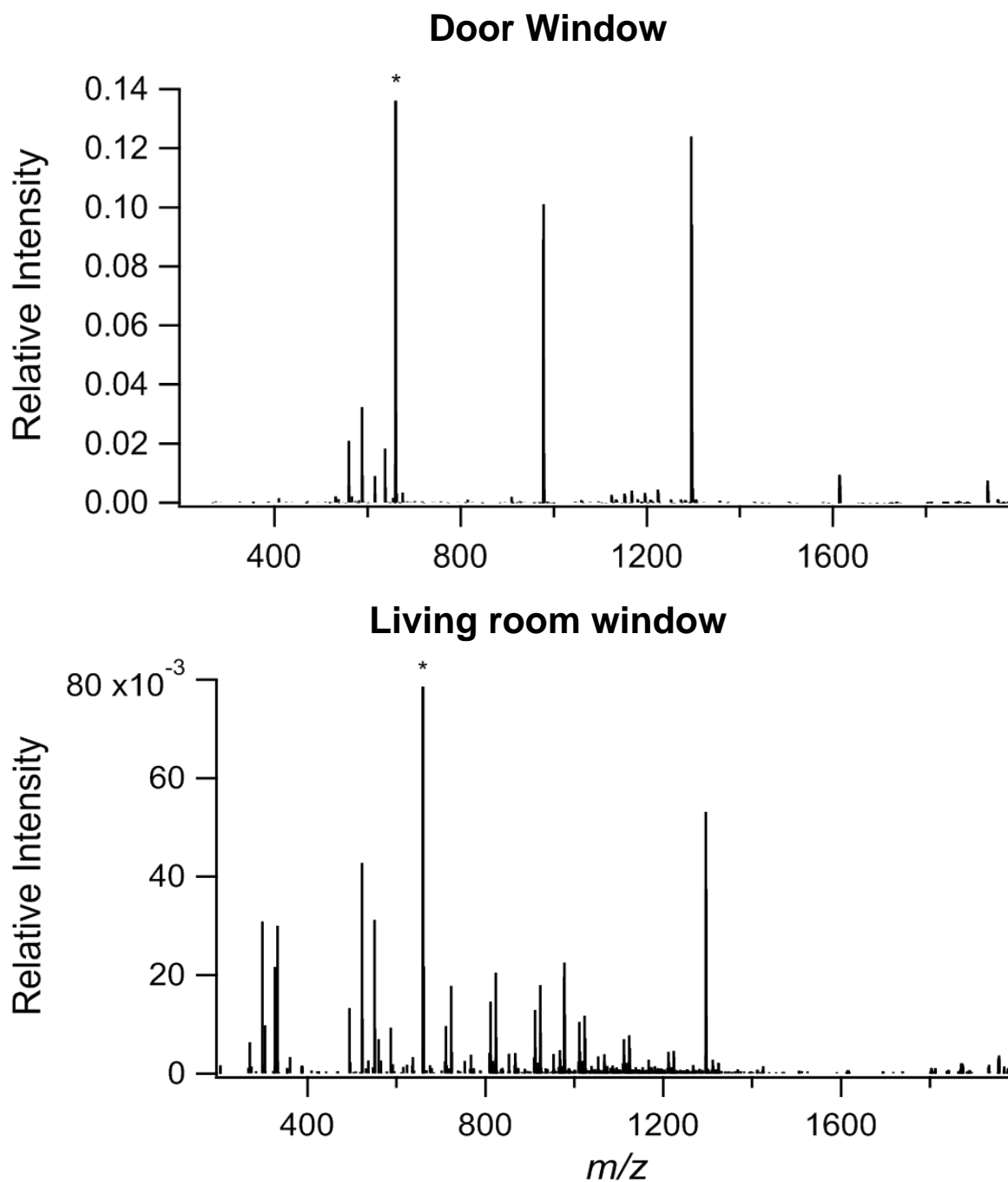


Figure A3.1 A stove hood and glass stove top were sampled using acetonitrile. While both of these samples were taken close together, their mass spectra appear very different. Both samples were found to have high mass components. The high mass components could be triglycerides and oligomers formed from di- and triglycerides. The pattern looks very similar to them and it matches the environment because of the cooking that took place there.

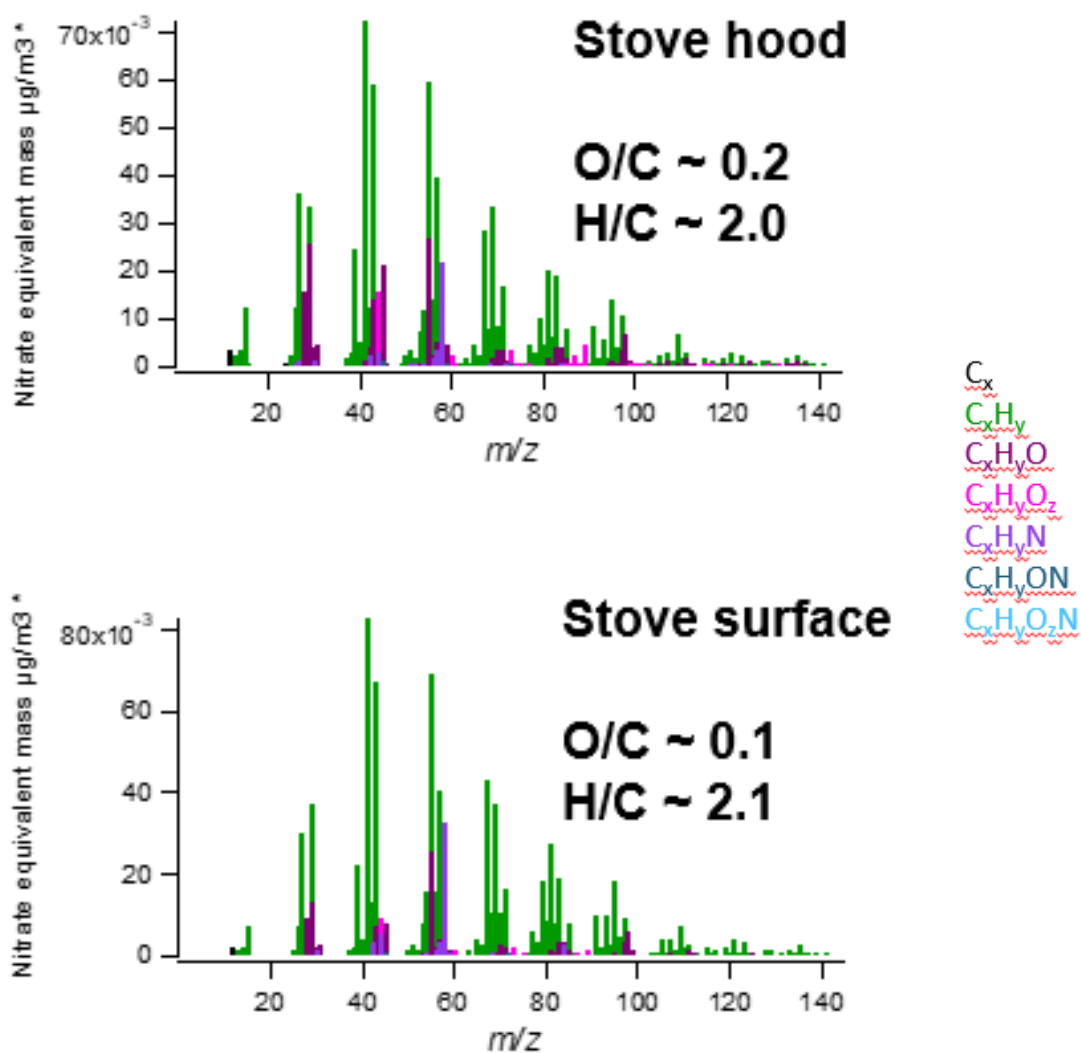


*indicates a relative intensity of 1

Figure A3.2 These samples were from two different windows. The door window was a small circular window on an interior door. The side of the window that was sampled was in a kitchen. The living room window was an exterior window. The side of the window that was sampled was in a common space within a dorm.

Appendix 4

These are samples from the same dorm kitchen samples as Appendix 3, but this is data was collected using the AMS. Note, this Figure has 4 mass spectra, the second two and the caption are on the following page.



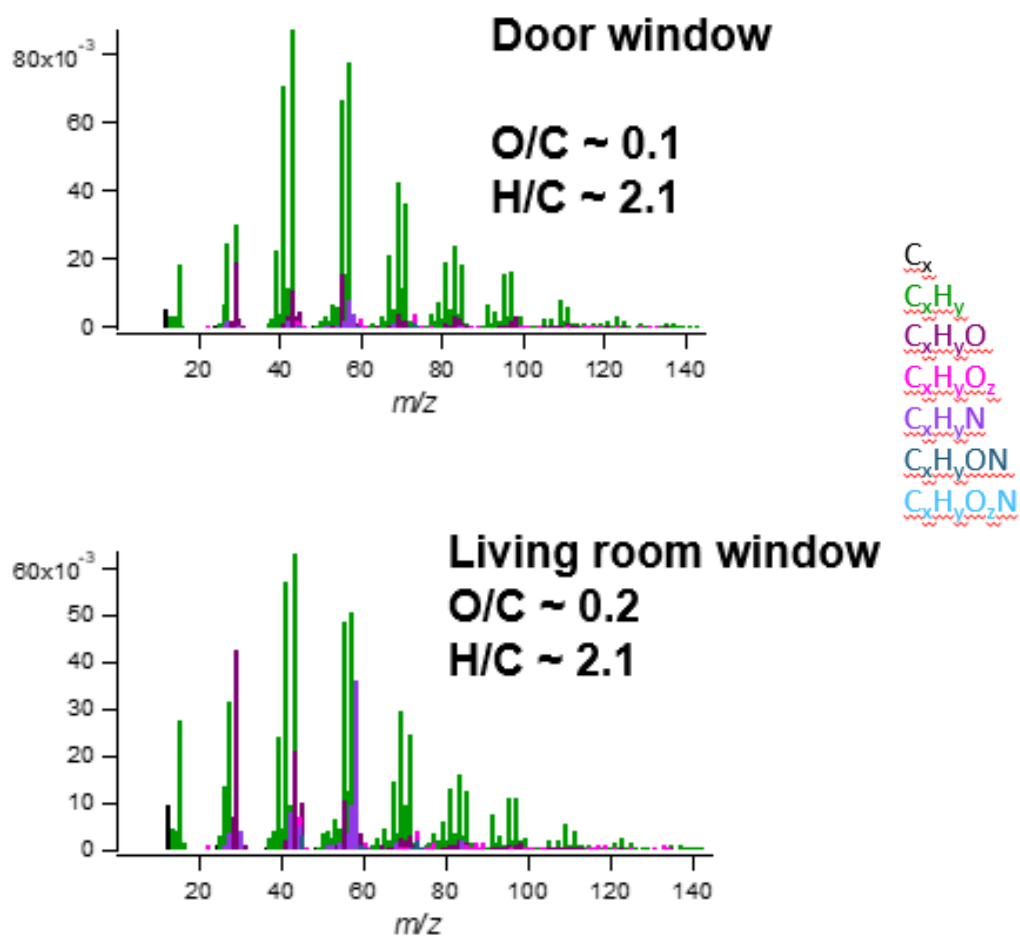


Figure A4. The above mass spectra are the AMS data from the acetonitrile kitchen extractions. The stove that was sampled was a glass top stove. The door window that was sampled was a window on an interior door between the kitchen and living room area. The kitchen side was the side that was sampled. The living room window was a large window in a room that was next to the door kitchen. Some acetonitrile dripped out of the gliding tube and the extractor was modified to reduce this problem. The spectra are colored by the type of ion that was measured (see keys on each page). This color scheme is standard for online AMS data sets.

Appendix 5

The following mass spectra are from a second set of dorm kitchen extractions using ESI/MS. These extractions were done using water as the solvent. Methods were described in Section 2.4 under the later sampling subheading.

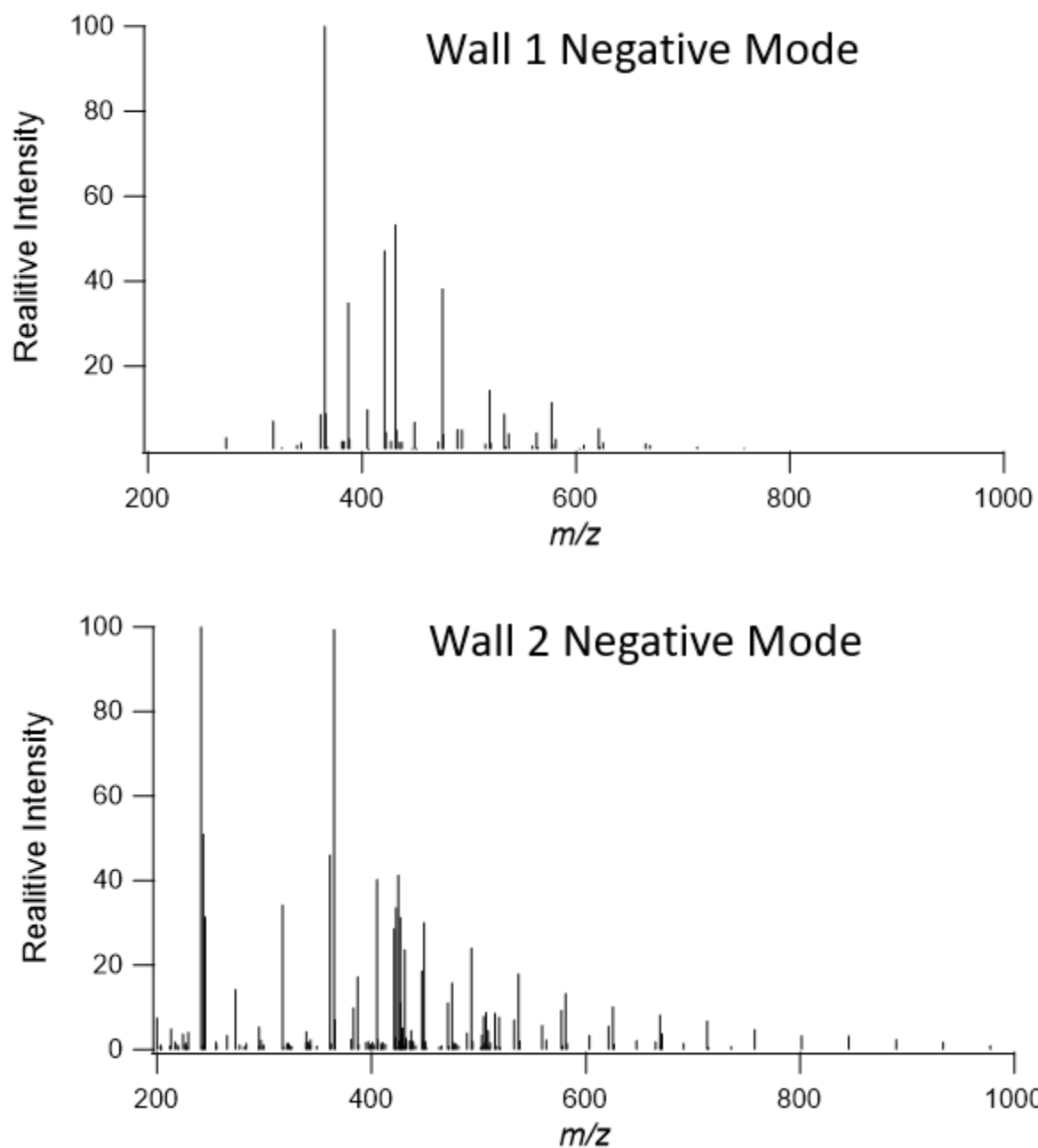


Figure A5.1 These are two negative mode mass spectra from wall samples that were taken close to each other.

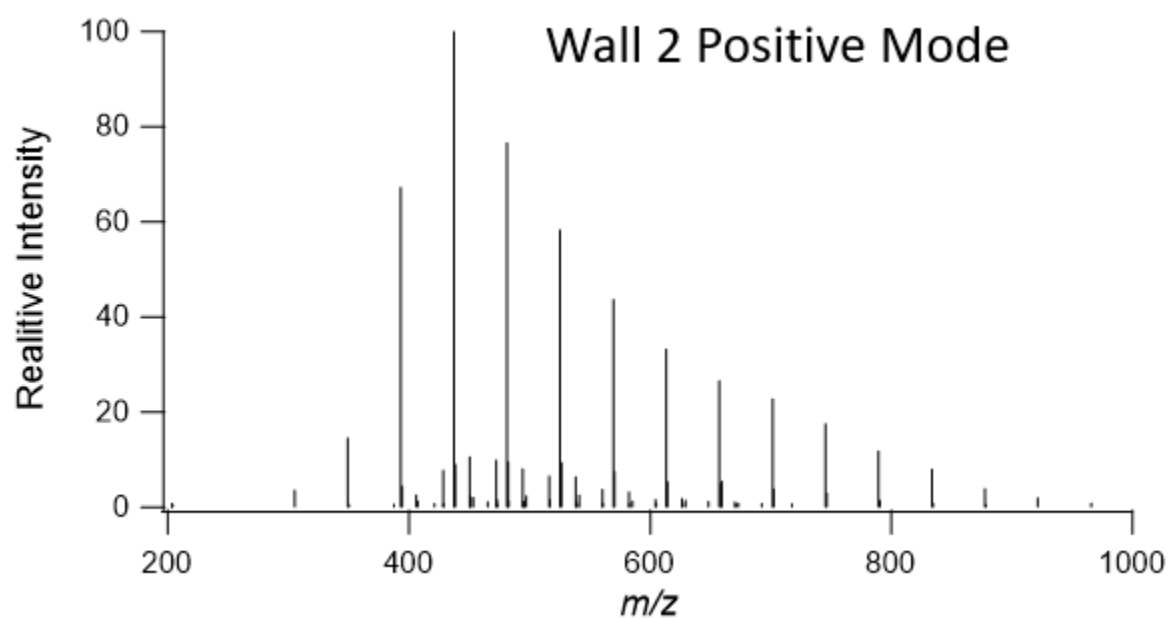
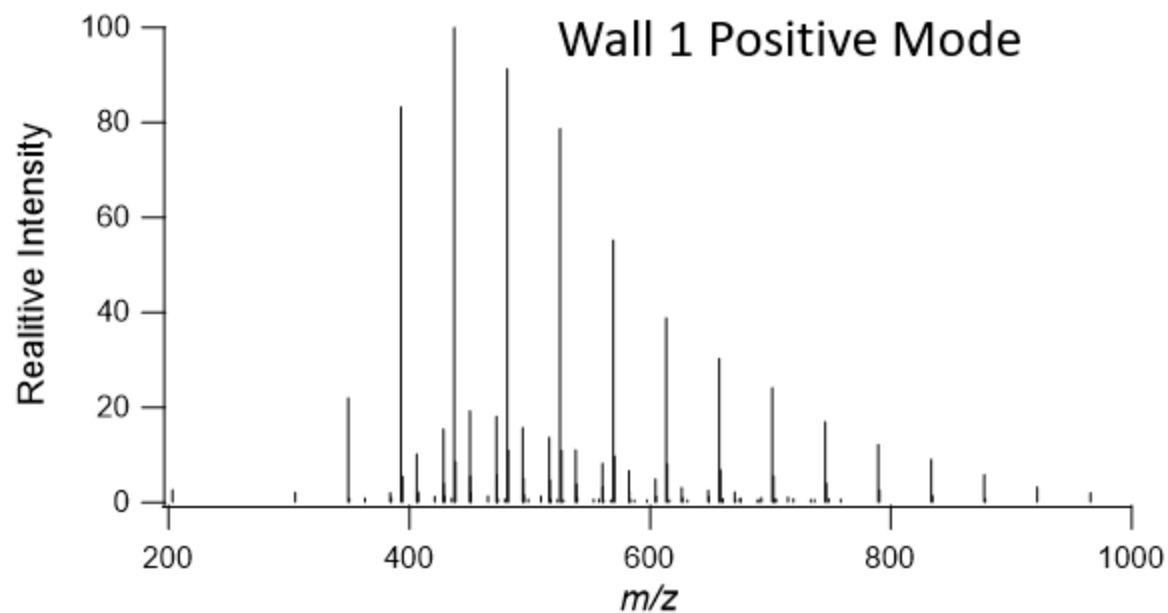


Figure A5.2 The above figures are the same samples from **Figure A5.1** but these are the positive mode run. The samples look more similar in positive mode than they did in negative mode.

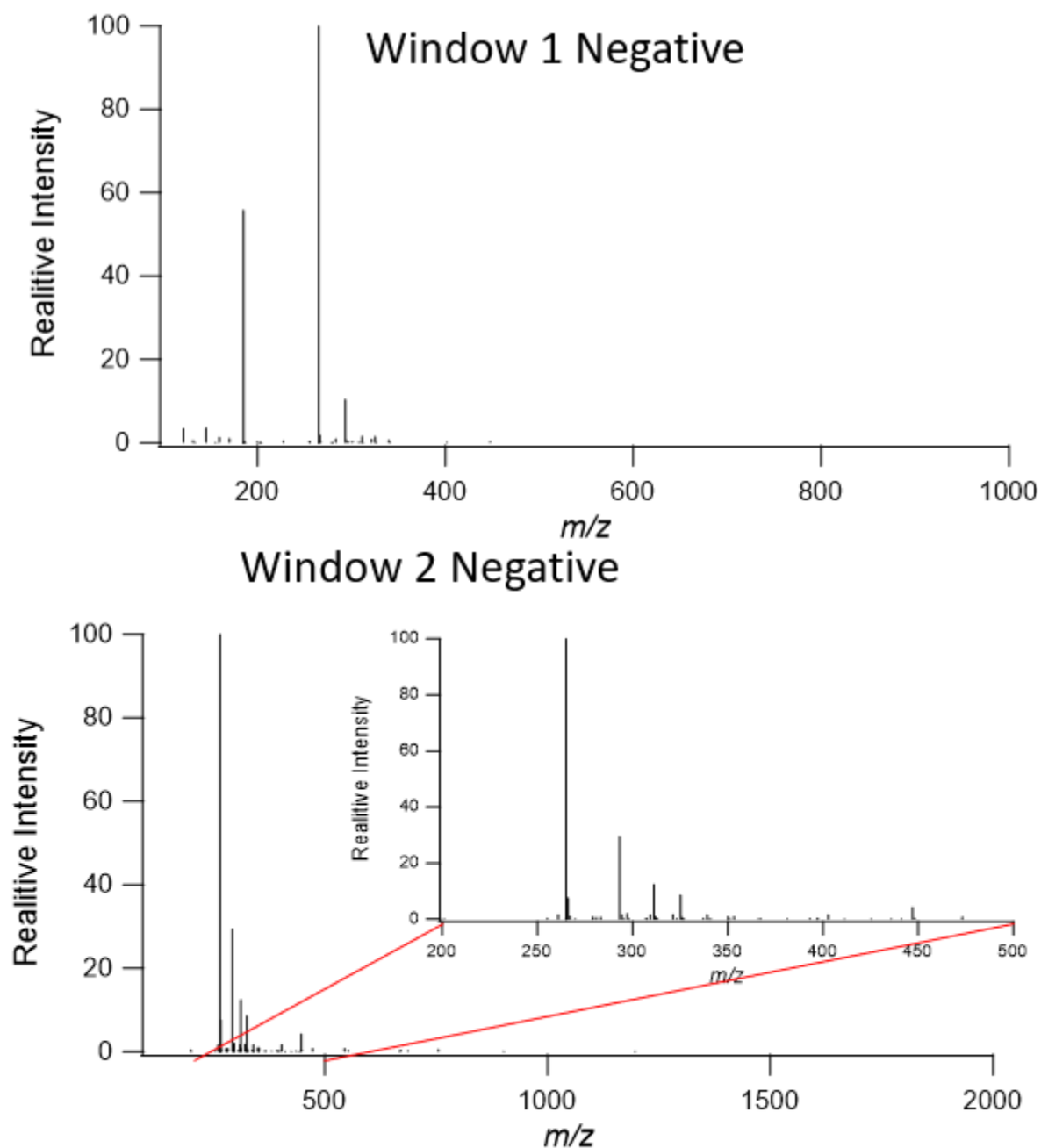


Figure A5.3 Both of the window samples were taken from neighboring exterior windows from the internal side. Sampled windows were located in a living room area next to a dorm kitchen. The negative mode mass specs look different even though samples were taken at neighboring windows.

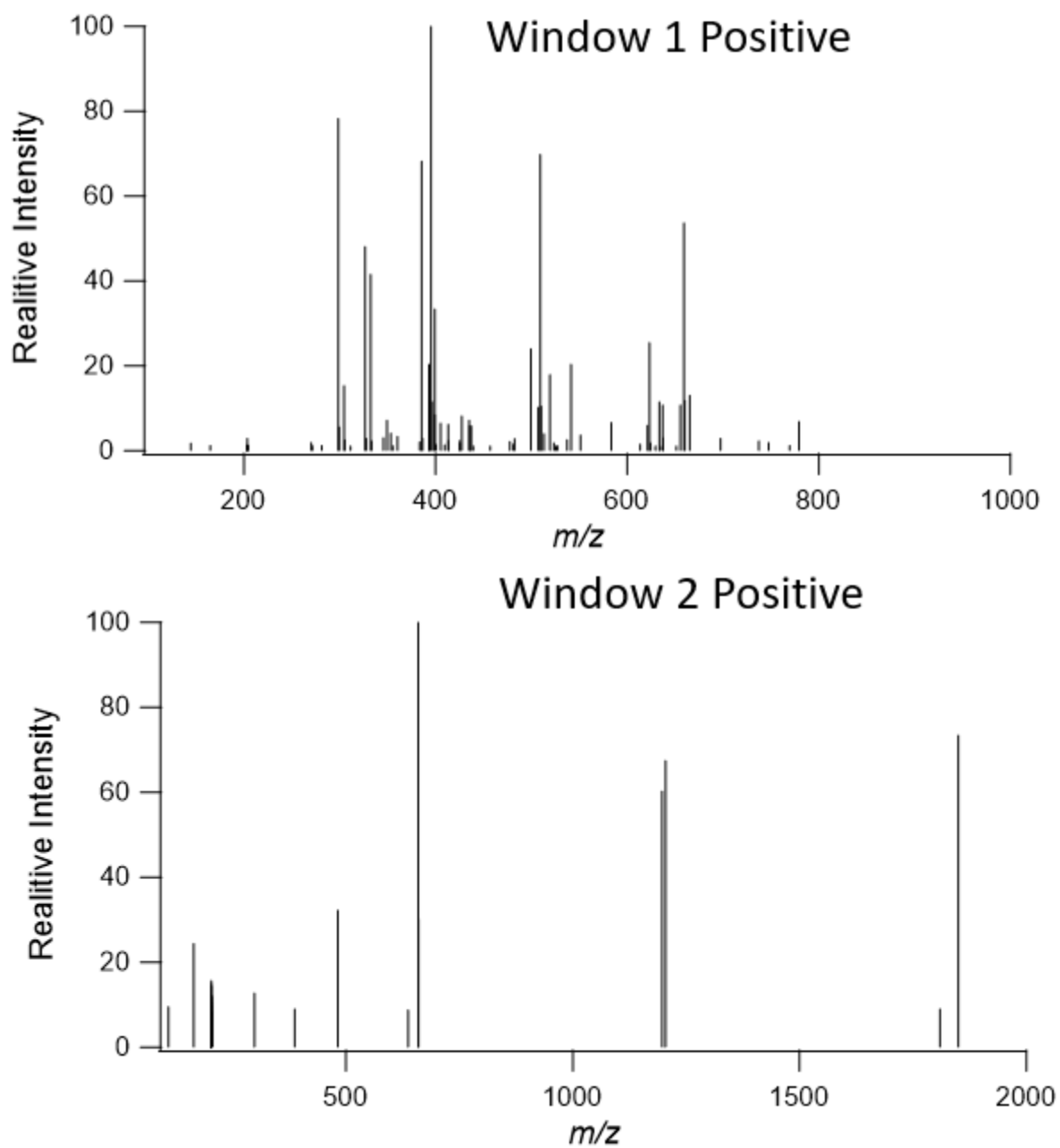


Figure A5.4 Similar to the negative mode runs, the signal from each sample is very different.

Appendix 6

Extractor SOP

Purpose:

Collect surface samples in a reproducible manner.

Safety:

If using organic solvents, follow organic solvent safety.

Know the surface that will be sampled.

- Can organic solvents dissolve it?
- Is it porous?
- Coatings that can be removed on surface

Supplies needed:

- MeOH bottle
- Lab notebook
- Tape measure
- Pen
- Extractor body
- Clean sniffers
- Syringe
- Pump
- Power somehow
- Extractor vial lid
- Clean sample vials
- Clean surface tubes
- Waste container
- Clean solvent container
- Tape
- Waste vial

Procedure:

1. Initial cleaning
 - a. Syringe
 - i. Glass
 1. Push MiliQ water through
 2. Push organic solvent to be used through or MeOH if water will be solvent
 - ii. Plastic
 1. Ultra-sonicate both pieces in a beaker of MiliQ water for 20 min
 - b. 1/16" tubing (Teflon and stainless steel) from syringe to surface
 - i. Push solvent through many times using the syringe
 - ii. Have this solvent go into waste
 - c. 1" Teflon tubing in contact with surface (gliding tube)
 - i. Ultra-sonicate in ACN for 20 min
 - ii. Rinse with MeOH
 - d. 1/16" tubing sniffer
 - i. Use MeOH bottle to push MeOH through to clean
 1. This is easier if the tube is connected to the sample vial lid and the methanol is pushed through the 1/16" Swagelok piece
 2. It might be a bit difficult to line it up
 - e. Vial collection lid
 - i. Use MeOH to thoroughly rinse the lid
 1. ***Don't get MeOH on O-ring if you can help it
 2. Get the top inside of the lid
 3. Rinse both Swagelok pieces thoroughly
2. Sampling
 - a. Cleaning parts in the field
 - i. Enough gliding tubes for the surface should be cleaned before going out into the field, packing a few extra would be a good idea
 - b. Actively Sampling

- i. Place the clean gliding tube on a surface and hold it there
- ii. Using the syringe, deposit $\frac{1}{2}$ mL to 1 mL of solvent at a time onto the surface you want to extract
 1. If using syringe pump, set for 60 mL/hour and set it for a limit of 6 mL
- iii. Move the extractor around on the surface allowing the solvent to leak out of the tube on the surface
- iv. Turn on the vacuum pump and use the sniffer to pick up the solvent that has leaked out of the tube
- v. (if not using syringe pump) When most of the first $\frac{1}{2}$ mL-1 mL has been collected, add more
- vi. Repeat until ~6-8 mL have been deposited and recollected

***I was originally using 8 mL, but I think 6 mL would be enough

c. Post sampling

- i. Water samples
 1. Freeze
 2. Lyophilize samples in order to remove water
 3. Store in a freezer
- ii. Other organic solvents
 1. Dry down under a gentle flow of ultra-pure nitrogen
 2. Store in a freezer

Appendix 7

Lyophilizer SOP

Purpose:

Dry down water samples using a freeze drying process.

Safety:

Lyophilizer gets very cold

Some organic solvents can harm the lyophilizer

Pre-prep:

1. Freeze samples
2. Remove caps and replace with Al foil that has a hole in the top
 - a. These can be put back in freezer for a few min before the lyophilizer is ready to go

***Optional: add dry ice to the lyophilizer

Procedure:

1. Check connections- power cord is typically removed
 - a. Turn it on, power button in on a side facing wall
2. Start cool down- it needs to get to -55°C
 - a. Turn on the manual switch, not auto because auto will also turn on the vacuum
3. Check that the vacuum can seal
 - a. Turn on the vacuum and see that the pressure decreases and there are no hissing sounds
 - b. Release the vacuum (the turn valve on the lid)
 - i. Should hear a hissing noise coming from the valve
4. Once the temperature has cooled to -55°C , remove lid and put samples in- see sample prep to see how samples should be prepared
 - a. This might be when dry ice can be added as well
5. Replace lid, close valve and turn on the vacuum.

6. The freeze drying process will take several hours and might need to run overnight.
7. When it is done, turn off vacuum and release the pressure slowly with the valve
8. Turn off freezer
9. When there is no longer a vacuum, samples can be removed and stored in freezer until they are ready to be run
10. After the lyophilizer has returned to room temperature, make sure there is no water left in it
 - a. There is a drain hole at the bottom- doesn't actually drain
 - b. Wipe it down with paper towels

Things that can go wrong

- Vial cracks
 - Typically happens if sample is not completely frozen and freezes while in the lyophilizer
- Sample comes out of vial
 - The vacuum can pull the ice out of the vial, therefore it is important to place clean aluminum foil on the vial. A hole is placed in the foil so that water can escape.
- If water doesn't get wiped up, it can cause errors when setting up for the next use

Appendix 8

Form 3 SOP

Probably a good idea to sign up for the printer online. Preform has a link. It lets you know when things have to be changed, resin is getting low, and how far a print is.

Safety

Uncured resin can irritate skin

Troubleshooting

Complete non-adherence

- Check to make sure resin in resin tank is “clean”
- Clean build platform extra well

Mixer comes off

- It clicks when it is back in place
 - This is held in place with magnets and is designed to pop off if there is cured resin stuck to the bottom of the resin tank
 - Can easily be removed if it needs to be cleaned or something

Resin tank not attached

- Needs to be pushed all the way back
- There is a thing that can get dirty where the printer meets the resin tank
 - If this is dirty, the printer might not recognize the resin tank
 - Wipe clean

Dos and don'ts

Scraping

- Build platform- yes
- Resin tank- no

Washing with Isopropyl alcohol

- Finished print- yes
- Build platform- yes

- Resin tank- no

Parts

Build platform

Resin tank

- Replace every 35 weeks or 5 liters of resin

Resin cartridge

Cleaning stuff

- Scraper
- Resin tank tool

Loading files

Save STL

- If using Fusion 360
 - Right click the body in the body list
 - “save as STL”
 - A box pops up on the right → click OK
 - Name and save the file somewhere

Setup Preform

- Printer is ClearMeerkat
- Choose resin type

Open Preform (specific formlabs print set up)

- File → open
- Open saved STL file to print
- Click magic wand
 - On the right side, a printability thing will pop up
 - If it isn't ok to print, play around with things or attempt suggestions
- Choose layer thickness- I just choose 100 nm
 - If pieces need to fit together, make sure measurements are to the nearest 100 nm

- Print on ClearMeerkat

Printing

- Follow instructions on printer screen
- Check on the print when the build platform is high enough to check
- The printer displays the amount of time left for a print
- If a print needs to be aborted, click pause then abort print

Finishing print

Removing print

- Open printer
- Removed build platform by pulling up tab and sliding the build platform towards yourself
- Slide build platform onto the stand
- Remove print with scraper
 - The more the build platform is scraped, the better prints will stick
 - It is ok if it gets scratched
 - It can be tricky to get off and it can fly off, don't aim towards people
- Rinse build platform with isopropyl alcohol and wipe down
 - If there are solids left of the build platform, re-scrape, the next print will fail if cured resin remains on the platform

Cleaning print

- Current resin
 - Rinse 5 min in isopropyl alcohol
 - Switch to second isopropyl bin and rinse for additional 5 min
 - Isopropyl alcohol must remain over 90% isopropyl alcohol
 - Overtime uncured resin will accumulate in bins

Curing print

- Put print outside (cures with UV)
 - If it has shiny or wet looking parts, it is not fully cured
 - Might need to be spun around or angled

Appendix 9

Cleaning product ingredients

Mrs. Meyer's	Simple Green	Windex
Decyl Glucoside	C9-11 Alcohols	2-Hexoxyethanol
Polysorbate 20	Ethoxylated	Isopropanolamine
<i>Betula alba</i> Bark Extract	*Sodium Citrate	Ammonia
<i>Citrus limon</i> Peel Oil	Sodium Carbonate	Lauryl Dimethyl Amine Oxide
<i>Abies alba</i> Leaf Oil	*Tetrasodium Glutamate Diacetate	Sodium Dodecylbenzene Sulfonate
<i>Cymbopogon schoenanthus</i> Oil	*Citric Acid	Fragrance
Fragrance	Blend of Polyoxyalkylene Substituted Chromophores (Cyan and Yellow)	<ul style="list-style-type: none"> • benzyl acetate • butylphenyl methylpropional • c9-11 pareth-3 • Citronellol • <i>Citrus X aurantium</i> var. <i>dulcis</i> (orange) peel oil • dipropylene glycol • Ethoxydiglycol • hexyl cinnamal • Linalool • Terpeneol
*Sodium Citrate	Fragrances	
Glycerin	Anethole	
Sodium Methyl 2-Sulflaurate	Eucalyptol	
*Citric Acid	*Methylchloroisoithiazoli none,	
*Tetrasodium Glutamate Diacetate	Methylisothiazolinone	
Sodium Sulfate		
PEG-5 Cocoate		
*Methylisothiazolinone		
Benzisothiazolinone		Liquitint Sky Blue Dye

*Indicates that ingredient is in more than one of the cleaning products tested

Figure Lists the ingredients in each cleaning product used in section 3.2. Ingredients vary greatly between products.

Appendix 10

The following figures are the design for the indoor surface extractor that were designed with Fusion 360. They are followed by images of the actual printed design that has been assembled.

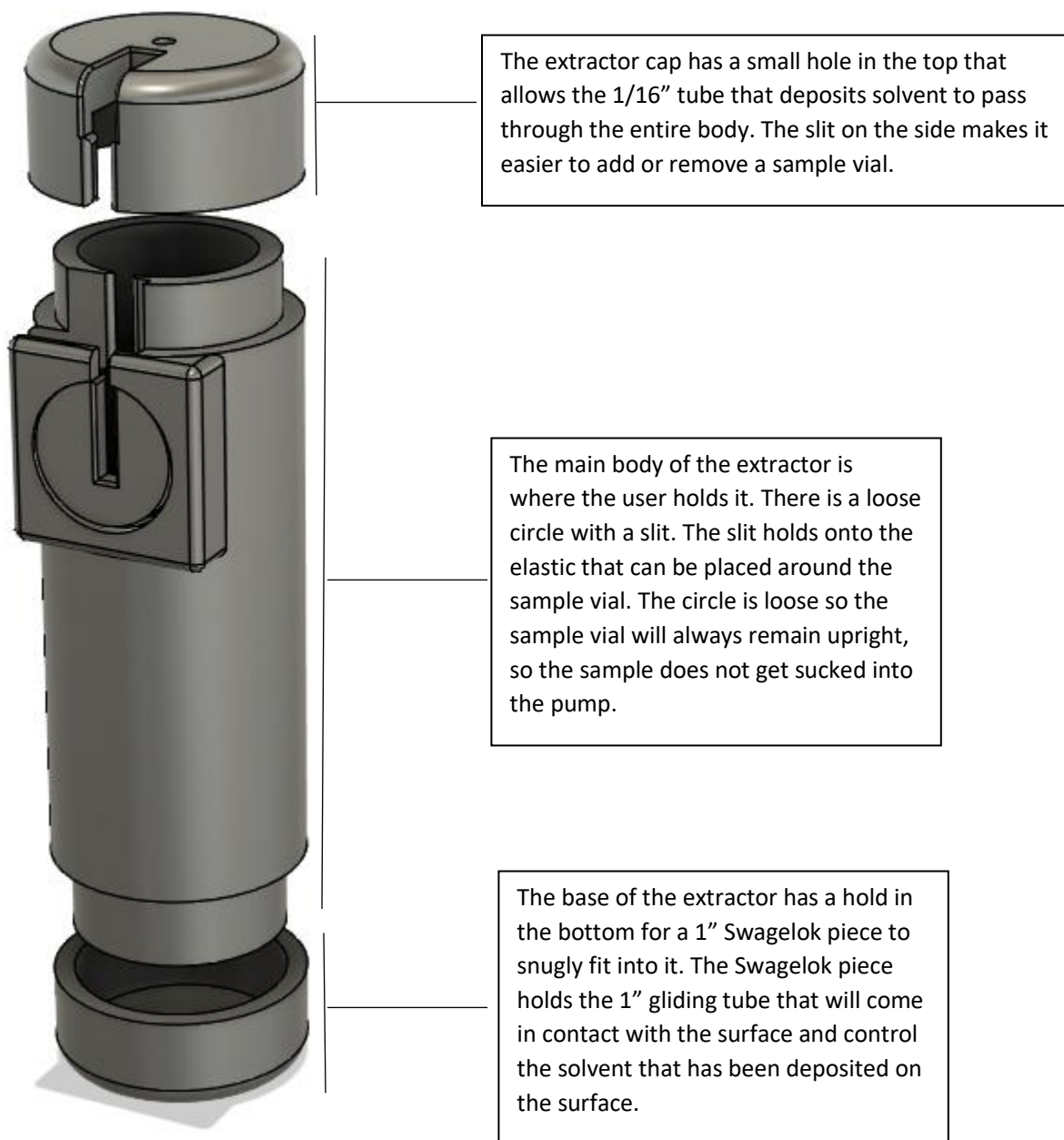




Figure A10.1 The image on the previous page shows the exterior of the extractor while the image on the current page also shows interior lines.



Ribbon crimps were added to the ends of the elastic

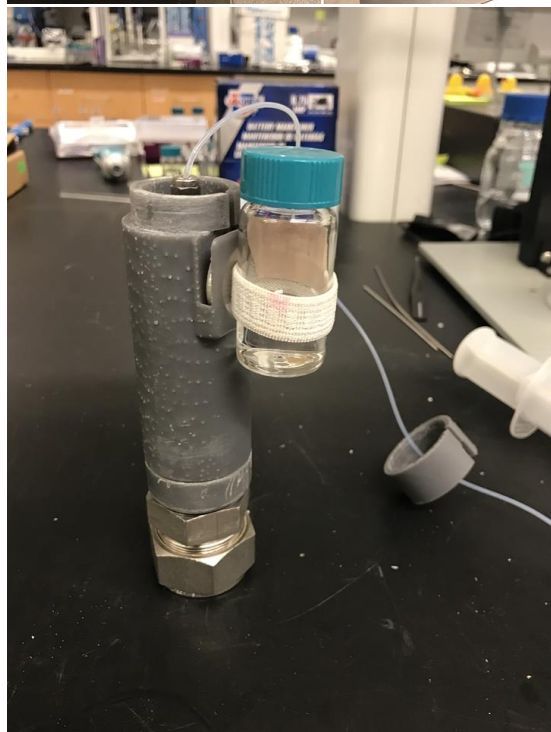


Figure A10.2 The above images show the extractor body printed and assembled.