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CHROMATOGRAPHY-MASS SPECTROSCOPY ANALYSIS OF NATIVE AMERICAN POTTERY FOR MAPLE SYRUP RESIDUES

A Thesis Submitted

in Partial Fulfillment

of the Requirements for the Designation

University Honors

Alexis Wirtz

University of Northern Iowa

December 2022

This Study by: Alexis M. Wirtz

Entitled: Chromatography-Mass Spectroscopy Analysis of Native American Pottery for Maple Syrup Residues

Has been approved as meeting the thesis or project requirement for the

Designation University Honors

Date	Dr. Joshua Sebree, Honors Thesis Advisor
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TABLE OF CONTENTS

ABSTRACT

The research conducted regards whether or not Native Americans understood how to create maple syrup before the influence of Europeans. The analytical technique that was used is gas chromatography-mass spectrometry (GC-MS). This technique assisted in understanding what organic residues resided within the pottery and what those organic residues tell us about Native American history. An analysis of organic residues was performed on the following types of pottery: proof of concept pottery, weathered pottery (an analog of the proof of concept), and Native American pottery. The residues used in analysis were obtained through the usage of different solvent systems - Acetone: Dichloromethane and Methanol: Dichloromethane. The solvent systems liberated the compounds that remained inside the walls of the pottery. The thesis will also go in-depth regarding how accurate the usage of organic residues is when conducting research regarding archeology and chemistry. Understanding the reliability of these residues will either support or conflict with their usage in research.

INTRODUCTION

The background of this thesis first begins with an archeological debate that took place in the 1980s. Margaret Holman initiated the discourse with an article that came out in 1984. This article, “The Identification of Late Woodland Maple Sugaring Sites in the Upper Great Lakes”[1], goes in depth in describing the key indicators in determining if prehistoric sites can be identified as sugaring sites. According to Holman[1], “Collecting maple sap and processing it into syrup and sugar was a widespread practice in the eastern woodlands, including the Upper Great Lakes, throughout the Historic period.” Natives commonly collected maple sap as these products were used for consumption and medication. In addition to this, maple syrup could be stored as blocks of maple sugar making their longevity more applicable for prehistoric peoples.

In Holman’s[1] article, she lists a set of criteria that would identify a prehistoric site as a sugaring site. If a maple site were to be located in a hilly environment, maple trees would produce their sap at different times due to their elevations. This, in turn, would give a larger collection period during the year. If a site were to have limited food remains and a few stone tools, this is another indicator. A maple site’s culture/agriculture would revolve around cultivating maple trees so there would be less of a need for stone tools. Another criterion brought up by Holman is that maple sites, i.e., resource extraction sites, would need to be constructed in close proximity to a larger settlement.

In contrast, Carol Mason criticized Holman’s theories. She wrote the article, “Prehistoric Maple Sugaring Sites?”[2] For Mason, Holman’s criteria were inconclusive. She states, “Recent attempts to project maple sugaring patterns into the prehistoric past are questioned on the grounds that prehistoric maple sugaring has not yet been demonstrated…"[2] Mason’s argument goes in depth regarding the validity of Holman’s criteria as there are no existing descriptions of

Indigenous maple sugaring in the documentary record. The first descriptions appear after Europeans had been in contact with Native peoples. Her argument goes in depth as to why European colonizers had most likely brought maple sugaring technology and taught Indigenous groups the technique.

Now in 2022, the argument remains. Holman was able to provide many criteria and gave an outline to identify sugaring sites. Mason argued that a lack of written records inherently dismantles Holman's entire argument. No real conclusion has been identified. While this is the case, in 2008, a potential sugaring site was discovered in Cedar Falls, Iowa. This site is known as the Black Medicine site at Hartman Reserve Nature Center. The Black Medicine site not only contains few stone tools, but also fire cracked rock. Fire cracked rock (FCR) is rock that has been altered or split as a result of deliberate heating. Native Americans would often create FCR in hearths or fire pits as this is where they would heat, cook, or process foods to be eaten. This site exemplified Holman's criteria. This research is hopeful in the prehistoric Native American pottery will provide answers to this seemingly perpetual argument. In addition, this research will contribute data to acknowledge the significance of organic residues within archaeological and chemical research.

Dr. Donald Gaff, an archaeologist at the University of Northern Iowa, first gave rise to this project as he collected the Native American pottery from the Black Medicine site. His goal was to analyze different sherds of pottery for maple syrup residues in order to help solve the debate between Holman and Carol. This research has created an extraction technique in order to liberate maple syrup residues from the walls of the pottery sherds (Figure 1).

Figure 1: Native American pottery sherds collected from the Black Medicine site.

Similar previous research has been conducted by scientists through instrumentation including Gas Chromatography-Mass Spectroscopy and Direct Inlet Electron Ionization Mass Spectrometry.[3,4,5] Evershed[3] and Gregg et al.[4] in particular, conducted extensive GC-MS research on organic residues providing a basis for this work. These scientists all conducted research using binary solvent systems, a technique that will also be conducted during this research. An extraction procedure using binary solvent systems is a technique used to transfer unreacted reactants, salts, and other water-soluble impurities to the aqueous phase while leaving the organic compound of interest in the organic phase. This extraction will pull compounds out of the walls of the pottery sherds during the soaking process. The organic solvents are left to evaporate - leaving behind residue. This residue can then be analyzed using the GC-MS analytical technique. In this work, a GC-MS analysis was performed upon maple syrup, modern pottery, and Native American pottery. The results of these experiments will help to provide analytical evidence for the maple sugaring archeological debate.

LITERATURE REVIEW

It has been questioned in Native American history if Natives had the capability to cultivate maple syrup before the European colonization of the United States. In this research, the focus will be on the pottery itself, to see if Natives were using these pots as a means to make a maple syrup derivative. This thought process comes from the notion that Indigenous peoples, when transitioning from hunter-gatherers to agricultural-based, stored food items such as syrups.[1] While this is a known fact, it is not certain as to whether or not maple syrup is one of these syrups. An organic residue analysis to detect maple syrup residues may have the answer. In Grand Island, Wisconsin, a similar project identified nut oil processing in both stone boiling and ceramic vessels.[6] Skibo et al.[6] conducted research on pottery vessels that were originally in an environment similar to the landscape where Dr. Donald Gaff found his pieces of Native American pottery. This particular project shows that organic residue analysis has been achieved successfully upon food residues in a similar manner to my research.

Furthermore, EVERSHED[3] states the following, "Organic residue analysis utilizes analytical organic chemical techniques to identify the nature and origins of organic remains that cannot be characterized using traditional techniques of archaeological investigation." Organic residue analysis is building popularity within the archeological community due to its usefulness as a scientific tool. Gas Chromatography-Mass Spectroscopy (GC-MS) is an analytical technique used to identify substances within a sample. Once appropriate separation techniques (chromatography) and identification techniques (mass spectroscopy) have been applied to a set of samples, preserved biomolecular components within organic residues can be found and identified.[7] These biomolecular components hold information that provides an understanding of the structure and composition of the molecule being analyzed. In archeology, organic materials will often consist of different aging pathways and chemical environments.[7] Chromatographic and spectroscopic analyses of these materials supply details regarding what structures align in different pathways and chemical environments.

In this case, maple syrup is the organic residue under examination. Organic residues are carbon-based substances that come in many different forms - pottery vessels, food preparation, floor surfaces, and archaeological sediments. An analysis of residues conducted by Mayyas[8] showed the usage of GC-MS on five pottery sherds - which were collected from excavation sites in Jneneh, Sahab, and Tell Abu al-Kharaz - contained residues derived from plant and animal sources. Similarly, in our study, a GC-MS analysis will be performed upon pottery sherds in the hopes of detecting maple syrup components.

The analysis of the organic residue within different samples of pottery sherds will yield information about the identity of substances within the residue. According to Ball[9], maple syrup is composed of organic acids, amino acids, minerals, and sugars. Syrup is obtained by concentrating the sap from certain maple trees.[10] When maple syrup is made, concentrated compounds (sugars) are formed. This process is named the maillard reaction. Amino acids and sugars (carbohydrates), when exposed to high temperatures, react to produce organic, derived compounds. Due to the lack of longevity of sugars in the ground due to bacterial consumption and water solubility, it is anticipated that sugar data may not be collectable. Data including complex organic acids, amino acids, and minerals may prove more reliable as their decomposition is much more drawn out.

Maple syrup is defined as a natural sweetener obtained by thermal evaporation of sap collected from maple (Acer) species.[11] According to Li and Seeram,[11] "Maple syrup is the largest commercially available food product consumed by humans that is derived totally from the sap of deciduous trees." The sweet sap that comprises maple syrup is able to be derived from all native maple species; however, the sap from Acer saccharum yields a palatable sap used in commercial maple syrup.[12] This species can be found in the northern parts of the United States and in small portions of Canada. When large leaves of the Acer species are exposed to sunlight, large amounts of sugars are produced that are used for tree growth, respiration, and reproduction. A large amount of the sugar is primarily converted to starch and stored in the tree - this starch is used for tree growth in the next spring. As previously mentioned, these trees tend to grow in Northern parts of the United States and in portions of Canada. Since this is the case, most of the trees will face a cold wintertime with copious amounts of snow. As the weather cools down, starch gradually converts back to sugar due to its insolubility in water. Since the concentration of sugar reaches its peak during the latter part of winter, sap is tapped from the tree at this time. In order for the tree to remain healthy, only 10% of the sugar is removed from the Acer trees.[12]

As this is the case, it is expected to identify sugars within the maple syrup analysis and the proof-of-concept analysis. In these two experiments, the identification of both tree byproducts and maillard reaction products is anticipated. The previous paragraph talks much about the production of maple sap within acer saccharum trees. Sucrose, a large component of sugar, is commonly found in most plants and would be an example of a compound identified in tree byproducts. Sucrose itself is created through the chemical process of photosynthesis. Plants growing on Earth remove carbon dioxide from the atmosphere and through a photochemical reaction, will convert CO_2 to carbohydrates.[13] This is able to be done through the presence of water. The resulting products of the reaction are glucose and oxygen. The process of photosynthesis then fuels the production of sap within a tree as the carbohydrates created are stored within the tree as starch.[13] Through a conversion process, (Figure 2), starch is converted to sucrose - a form of sugar. Lastly, the sucrose will dissolve into tree sap and is extracted through the maple syrup production process.

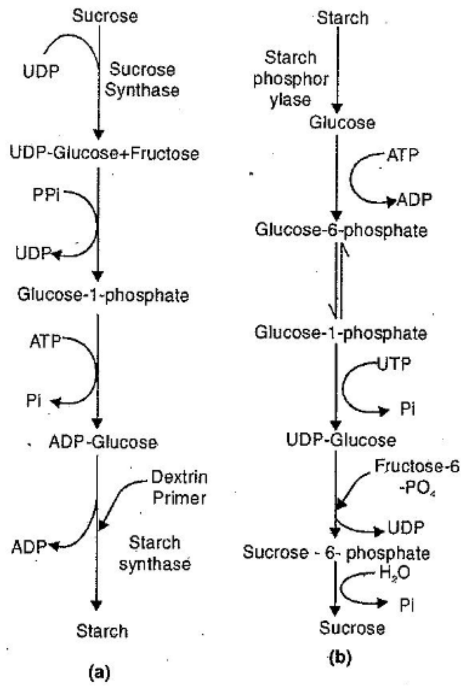

Figure 2: Photosynthesis chemical reaction process.

Canada, a nation in North America, is the leading producer of maple syrup across the world. Over 85% of maple syrup is produced in Canada specifically in the province Quebec.[11] A compound, 2,3,3-tri-(3-methoxy-4-hydroxyphenyl)-1-propanol, was named after the province due to its large amount of production. Quebecol - Figure 3 - is phenolic in nature, making it useful in an industrial setting. A study conducted by Li and Seeram[11] identified quebecol using nuclear magnetic resonance (NMR) and mass spectral (MS) analysis. It is in their opinion that quebecol is formed during the processing and/or extraction of maple syrup. This belief is supported through the MS analysis data that revealed quebecol is not originally present in maple sap.[11] Furthermore, much of the method development regarding the chromatography-mass spectroscopy will revolve around the identification of this quebecol. While the bulk components of maple syrup are of great interest, components that are only formed during the processing or the extraction stages will be the key identifiers that distinguish maple syrup from other food stuff.

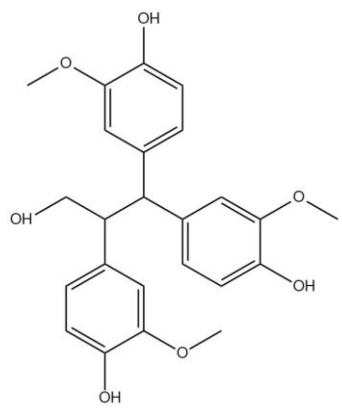

Figure 3: 2,3,3-tri-(3-methoxy-4-hydroxyphenyl)-1-propanol - Quebecol.

As stated previously, the question this thesis is trying to answer is whether or not Native Americans had the knowledge to create maple syrup before European colonization. Information regarding how maple syrup is created, and history of Native American technology provides useful details in understanding their capabilities as a civilization. While there is no conclusive analytical evidence to support that Natives did know, there is a copious amount of documentation to reinforce a narrative in showing that they did. Holman and Egan[14] went so far as to fully recreate the scenario (tools, environment) in which Natives would have curated maple syrup. A large portion of the argument against Native Americans having this knowledge regards the tools needed in order to create a syrup. Metal kettles were believed to be a necessary tool in the formation of maple syrup and maple sugar but Holman (the originator of the archaeological maple sugaring site debate) and Egan[14] proved this otherwise.

In their experiment, Holman and Egan[14] produced 61.5% concentrated maple syrup through the usage of shallow birch bark trays. Ceramic vessels, being also tested upon, yielded successful results. The ceramic vessel results were not as concentrated, but it was noted that maple syrup could be created through their usage. Research conducted in this way has proved successful results and, per the previous paragraph, there is also documentation to show Natives possessed these capabilities. Early European observers, in North America, have written evidence to support these claims. Munson,[15] an archaeologist, composed an article focusing on this written evidence. Muson[15] found that from 1675 to 1687, a man named Chrestien Le Clercq observed a group of Native Americans called the Mi'kmaq. The Mi'kmaq resided in the Northeastern Woodlands located in Canada and Maine. In reference to his time spent with the Mi'kmaq, he states, "... maple water… by virtue of boiling… hardens to something like sugar… It is formed into little loaves…" Another comment of similar significance was made by Dr. Robinson, "The Indians have practiced it time out of mind; the French begin now to refine it…"[15] Here, Dr. Robinson refers to Native Americans' capability to create a maple product and speaks about the French beginning to refine this method. As stated previously, it was probable that Natives would store their maple products as sugar rather than maple syrup. These written records provide evidence to support this claim.

When creating maple sugar, the process is slightly dissimilar to that of producing maple syrup. The proportion of water within the two products creates the dissimilarity. The syrup is created through a low temperate boil while the sugar must have a significant increase in temperature to materialize. Another trait of creating maple sugar regards its constant need for scraping - this is done in order to avoid scorching on the container. Sugar must also be vigorously stirred in order to break the granular pieces.[15] This breaking of the crystalized product introduces air between the granules and creates a well-formed product - maple sugar. The boiling utensils and techniques used by Natives (stone boiling, bark containers, ceramic vessels) are more successful at creating maple sugar. As it was more likely Natives would create maple sugar rather than maple syrup, their technology aligns with the sugaring technique.

Another concept to consider is that while researching organic residues is beneficial, there have been some disadvantages to this technique. Unfortunately, the question as to why organic residues survive in certain environments has not been thoroughly investigated. Most of the research that has been obtained regarding this subject has been collected through empirical observations - observations that are dependent on examination alone. Since there are multiple factors that increase the rate of decomposition, measures can be taken in order to protect/preserve the compounds. In nature, these measures happen spontaneously and naturally. Much of research in the archaeological field is dependent upon this spontaneity.[3]

As chromatographic and spectroscopic techniques improve, more reliable data can be obtained regarding archaeological research. Though, as these techniques improve, it has been seen that previous data and research may need to be retested. According to McGovern and Hall,[16] "As with any historical science which has time dimensions, biomolecular archaeology perforce bases its hypotheses and verification procedures on extremely limited databases." Extremely limited databases withhold the amount of information that could be deduced from research, leading to incorrect conclusions. This data then is unusable even though other journals have used said data to back up their hypotheses. Nonetheless, the data received from organic residue analysis, through the improvement of technology, is useful in archeological and chemical research.

RESEARCH QUESTIONS TO BE ANSWERED

The specific questions that this research will assist in answering are, “Did Native Americans have knowledge on how to produce maple syrup before the arrival/influence of European settlers?” and, “How accurate is the usage of organic residues in archaeological or chemical research?” In the future, should chemists/archaeologists depend upon organic residues as a means of research or is there potentially a different course that should be taken? Is there a technique that is viable at identifying organic residues within archaeological pottery?

METHODOLOGY

The project has been made possible due to the University of Northern Iowa Department of Chemistry and Biochemistry. The University of Northern Iowa Department of Sociology, Anthropology, and Criminology has also made this possible through the support of Dr. Donald Gaff who originally gave relevance to this research and is providing Native American pottery sherds to test. The project will also be using clay terra cotta pots made by the University of Northern Iowa Art Department.

Dr. Gaff first took these clay vessels and, through the usage of heated stones, boiled maple syrup within their walls. After the syrup had been allowed to cool, the substance was removed from the pots. A mallet was then taken to both plain/blank pots and the maple syrup sugar pots - many pieces were created so that many tests could be conducted (Figure 4). Much of this was done in 2018 by a previous University of Northern Iowa student.

Figure 4: Plain (no sugar) and Maple Sugar sherds.

In order to recreate the condition of the pots, as they would have been when used in Native American history, a weathering plan was created. The weathering plan for this project is to conduct research on two different time periods of burial. The periods being studied are as follows: the beginning of winter 2021 to the end of spring 2022 and the beginning of winter 2021 to the fall of 2022. These periods were chosen as a way to understand if different weather elements affected the composition of organic residues on pots. Both pots infused with syrup and plain pots were buried underneath the ground in December 2021 (Figure 5). Plain pots are used in order to have a blank sample - this is done to show the effects of soil on pottery for long periods of time. If there are natural materials that sink into the pot due to simply being underground, the plain pottery will help to gather this data.

Figure 5: Proof of concept analog (weathered pottery) in the ground.

During the spring of 2022, pre-analysis research began. Five blank pieces of pottery and five sugar pieces, that were not buried, were collected to conduct a proof-of-concept soak. A residue extraction was done upon these pieces and different solvent soaks followed. The latter part of the semester was spent analyzing this data and refining the methodology. During the summer of 2022, the first opportunity to remove buried pots from the ground arose. These pots underwent the same extraction/soaking process that was optimized above. An analysis of this pottery was conducted to note changes from the unweathered pots. Research during the summer of 2022 primarily focused on the analysis of the first set of weathered pot data. The results from the early data were then used in drafting the honors thesis while final weathering was taking place on the second set of buried sherd analogs. The final set of sherds were dug up and analyzed in late September/October of 2022. Lastly, during the fall of 2022, a cross-analysis was conducted between the blank/sugar pieces of terra cotta pot and the Native American pottery sherds.

From a technical approach, all of the analysis, as previously mentioned, occurred through gas chromatography-mass spectrometry (GC-MS). GC-MS, as can be seen in Figure 6, is an analytical technique that separates complex mixtures, through the usage of inert gases, in order to identify different compounds/substances within a sample. The compounds of a mixture are separated by injecting a gaseous sample into mobile phase - also called the carrier gas. This mobile phase is typically an inert gas - also known as a noble gas. In nature, noble gases do not react as they already contain the desired number of electrons in their valence shell. In this case, helium is used as the mobile phase as it is a noble gas. Once the carrier gas has been added to the mobile phase, the mobile phase will pass through to the stationary phase and separate the mixture. Once the mixture has been separated, the GC/MS identifies the substances as it has a large, complex library of mass spectra. Each sample placed in the machine yields a spectrum, the machine then compares the spectra to its library - leading to a potential identification. The instrument itself is a widely used analytical technique and can be found amongst many different work fields. For an initial proof of concept that is based in the intersection of chemistry and archaeology, the instrument is a perfect tool.

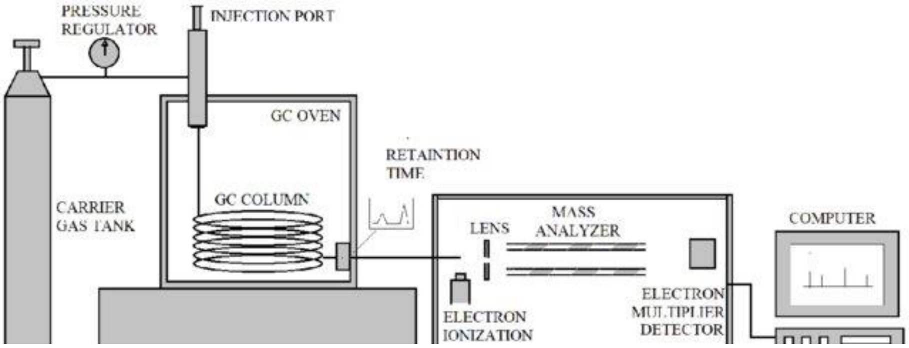

Figure 6: Schematic Representation of a GC-MS System[17]

EXPERIMENTAL

This research first began with a proof-of-concept soak. A proof-of-concept soak uses modern pottery, created by the University of Northern Iowa Art Department, that are similar in composition to the Native American pottery. A proof-of-concept is an analysis completed to determine if a technique is feasible in practice. In previous research, modern pottery was used to boil maple syrup and broken into different sherds. These same sherds were used for the proof-of-concept soak in my research. First, the pottery sherds underwent a 48-hour water soak, followed by an allotted drying time. After the sherds completely dried, they were placed into different solvent systems - found in Table 1. These solvent systems pulled compounds from the walls of the pottery during the soaking process (24 hours). The organic solvents were then left to evaporate - leaving behind residue. This residue, through the usage of methanol, was placed into GC/MS vials for an analysis. The purpose of the methanol was to be used as a solvent to dissolve the sludge-like residues, and to create a liquid sample to be placed in the GC/MS. Methanol itself appears very quickly due to its low molecular weight and can be identified very easily during analysis. Methanol will not show up as background noise due to this.

	1:1	1:1
Solvents	Methanol: Dichloromethane	Acetone: Dichloromethane

Table 1: Solvent Systems

A GC/MS analysis of pure maple syrup was conducted in order to compare and contrast what compounds were present in the proof of concept. The next step of this research was to conduct an analysis on weathered pottery. In December 2021, four different sets of pottery sherd samples were placed underneath the ground. In May 2022, two of the four samples were removed in order to begin analysis. Once removed, the sherds were cleaned of their dirt using a brush. The sherds then underwent the same residue extraction and analysis as the proof-of-concept pottery.

In September of 2022, the same process used in the first set of weathered pottery was recreated with the second set of weathered pottery. The sherds were cleaned of their dirt then underwent the water and solvent extractions. In November of 2022, the Native American pottery was experimented upon using the same binary solvent techniques as the proof of concept and analog.

RESULTS

In this preliminary analysis, both tree byproducts and maillard reaction products were identified. The maple syrup analysis yielded three compounds: maltol, 5-(hydroxymethyl)-2-Furancarboxaldehyde, and sucrose (Figures 6,7,8). This is done by comparing the peaks and retention times of the maple syrup spectra to the spectra within the GC/MS library. All three were identified using this method.

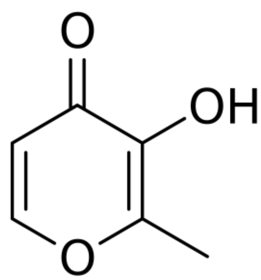

Figure 6: Molecular Structure of Maltol.

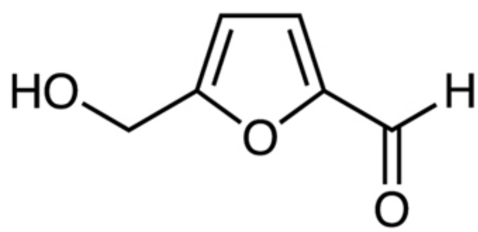

Figure 7: Molecular Structure of 5-(hydroxymethyl)-2-Furancarboxaldehyde.

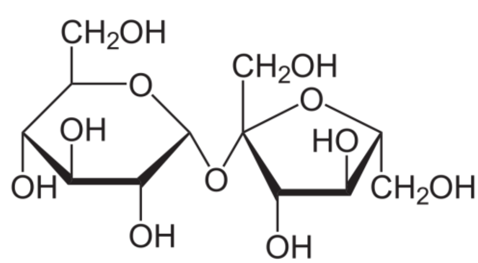

Figure 8: Molecular Structure of Sucrose.

The proof-of-concept analysis that was conducted yielded two identified compounds. Spectra from the six different samples was compared to spectra within the GC/MS. The methanol: dichloromethane “sugar” sample yielded the two identified compounds. One was a byproduct of the maple tree - sucrose. The second compound identified was 5-(hydroxymethyl)-2-Furancarboxaldehyde also known as a product of the maillard reaction. Not only were these two compounds identified in the proof of concept but also in the analysis of the Hartman reserve maple syrup. As can be seen by the figures, both spectra have a retention time labeled. This particular peak is the 5-(hydroxymethyl)-2-Furancarboxaldehyde compound. Since both spectra have this similar peak with a similar retention time and absorbance level, it can be concluded that the compound is found to be in both the proof of concept and the modern sample (Figures 6 and 7).

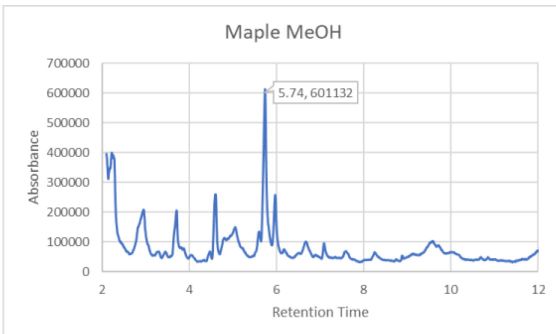

Figure 6: GC-MS Chromatogram of Maple Analysis

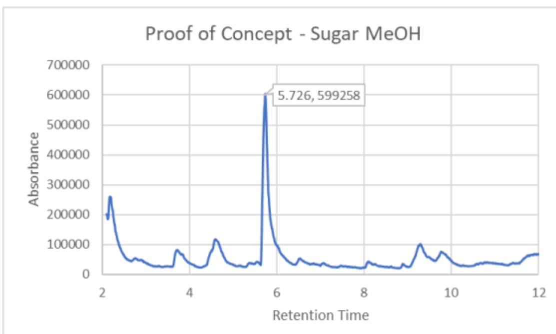

Figure 7: GC-MS Chromatogram of Proof-of-Concept Analysis - Sugar MeOH

Regarding the first and second set of weathered pottery samples, no maple syrup residue compound was clearly able to be identified within the samples (Figures 8 and 9).

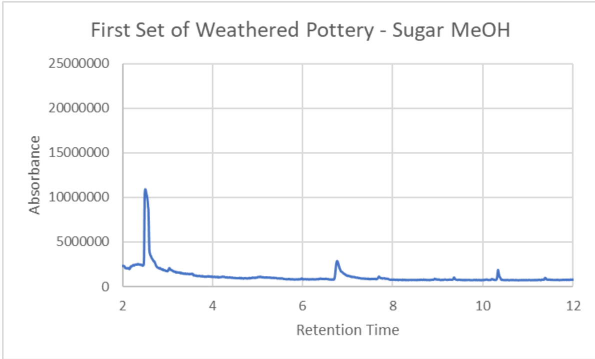

Figure 8: GC-MS Chromatogram of First Set of Weathered Pottery Analysis *Scales are Relative

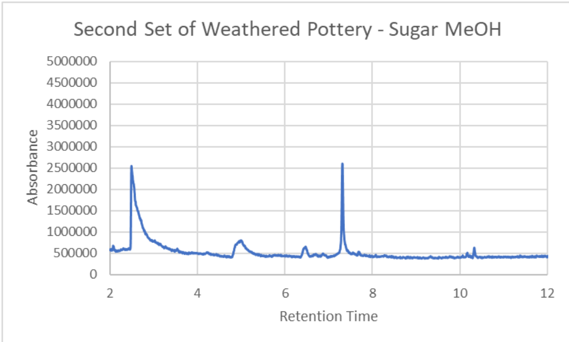

Figure 9: GC-MS Chromatogram of Second Set of Weathered Pottery Analysis *Scales are Relative

The data gathered from the Native American pottery is shown in the following chromatograms (Figures 10, 11, 12, 13).

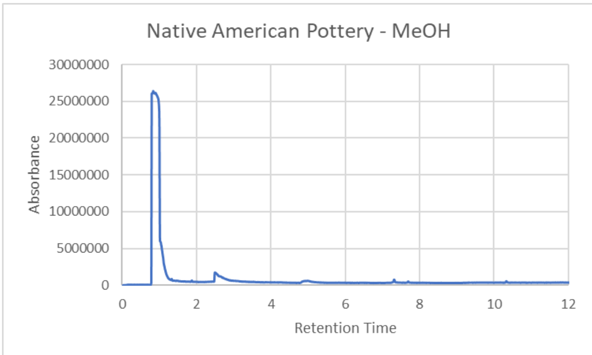

Figure 10: GC-MS Chromatogram of Native American Pottery - MeOH

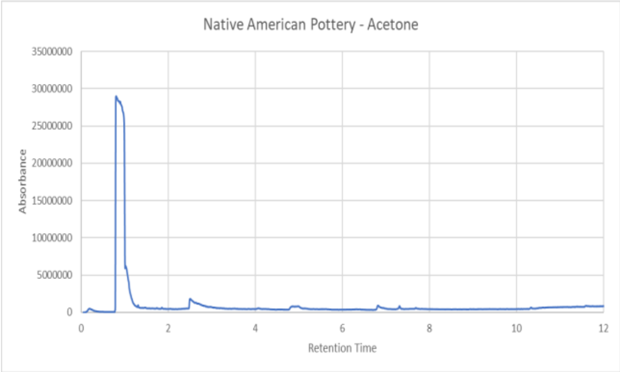

Figure 11: GC-MS Chromatogram of Native American Pottery - Acetone

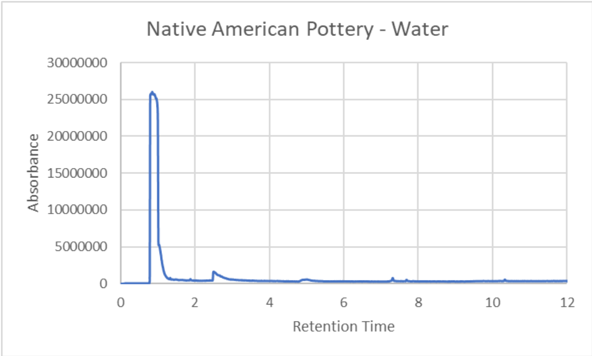

Figure 12: GC-MS Chromatogram of Native American Pottery - Water

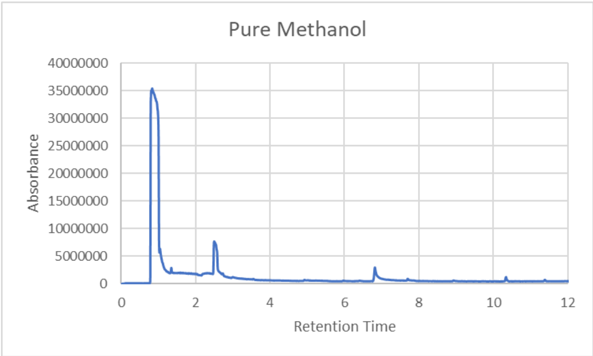

Figure 13: GC-MS Chromatogram of Pure Methanol

DISCUSSION

Maltol, 5-(hydroxymethyl)-2-Furancarboxaldehyde, and sucrose were all compounds identified in the maple syrup analysis. Maltol, in particular, is an organic compound that naturally occurs in the bark of trees, pine needles, and roasted malt. This compound was most likely found as a byproduct of the maple tree, found in its bark. The second compound, 5-(hydroxymethyl)-2-Furancarboxaldehyde, is an organic compound found through the dehydration of reducing sugars. The maillard reaction products are formed through a similar process most likely making this compound a product of said reaction. Sucrose is a naturally occurring compound found in plants.

Similarly, the proof of concept yielded identification of 5-(hydroxymethyl)-2-Furancarboxaldehyde and sucrose. The identification of these compounds both within the maple syrup analysis and within the proof of concept shows that maple organic residues found within a basic sample of maple syrup can be found in pottery that has undergone an extraction process. For the first set of weathered pottery, no compound was able to be clearly identified within the range of samples. The pots themselves were buried underneath the ground from the beginning of winter and were removed at the end of spring. Since this is the case, the pots dealt with snow melt from the wintertime and also spring showers. Due to this, it is believed that weather elements washed any compounds that were able to be identified within the maple syrup analysis and the proof-of-concept analysis.

Similar to the first set of weathered pottery, there was no identification of a maple residue compound when analyzed in the GC-MS. The second set of weathered pottery was buried in the ground at the beginning of winter and was removed in the fall of the following year. Due to this, the pots had to withstand the elements of winter, spring, summer, and the beginning of fall. The second set of weathered pottery is akin to the first set in that it is entirely clear that the weather elements removed compounds that were able to be previously identified. This can be seen in both Figure 8 and Figure 9 as the 5-(hydroxymethyl)-2-Furancarboxaldehyde peak (found both in the maple syrup analysis and the proof of concept) can no longer be identified. This is evidential as a peak no longer resides at the retention time of 5.47 minutes, shown in Figures 6 and 7.

Even though no compound was found to be within the first and second set of weathered pottery, the position of this thesis is to prove the techniques being conducted are viable in the archaeological field. The weathered pottery itself is not unsuccessful in its results. This analog provides information to archaeologists about the longevity of residues when pottery has been discovered underneath the ground. According to Evershed,[3] the rate of decomposition of residues within pottery is, unfortunately, very spontaneous. Organic residues have been proved to survive in certain environments while unable to remain in others. The Native American pottery sherds were found much deeper within the Earth compared to the modern sherds placed in the ground. The Native American pottery sherds were also found to be in a hilly environment with plenty of tree coverage. The modern pieces were placed in a stable environment with different conditions than that of the Indigenous pottery. The conditions of prehistoric pottery were recreated to the best of our ability but conditions in archaeological fashions can never be recreated exactly. Research in the archaeology field is very dependent upon spontaneity.

For the Native American pottery analysis, no maple residues were able to be identified. No organic residues, in general, were identified. Figures 10, 11, 12, and 13 all have peaks similar in heights at similar retention times. So, what that tells us, is that unfortunately, the GC/MS was unable to detect any compounds dissimilar to those that are in methanol. When creating GC/MS samples, methanol is used as a solvent to dissolve residues left within the beaker. When performing an analysis, it is practice to include samples of the pure chemicals used throughout the process. Figure 13 is the chromatogram of a pure methanol sample. It is noted that all peaks within the methanol chromatogram can be identified in Figures 10, 11, and 12.

CONCLUSION

Did Native Americans contain the knowledge of creating maple sugar before European influence? The answer to this question is still not clear. In the maple syrup analysis and in the proof-of-concept analysis, it was discovered that the binary solvent extraction technique was successful at extracting maple syrup residues from the walls of pottery. The technique itself has yielded results that show the approach is viable. In contrast, the proof-of-concept analog (weathered pottery) did not produce data. This was able to be foreseen as it is impossible to replicate archaeological conditions to their exact criteria. Oftentimes, whether or not the identification of organic residues within archaeological contexts is spontaneous and dependent upon the conditions of the pottery. Even though the proof-of-concept analog did not produce much data, this does not disprove the technique at hand as it could be viable with pottery that has conditions that are well suited for archaeological research.

In a similar manner to the weathered pottery, the Native American pottery did not produce data. Any peak that was able to be identified was a peak caused by a chemical that was used during experimentation. Even though no maple organic residues were identified within the Native pottery, there is still much work to be done within this project. The extraction technique is viable and shows that maple residues can be extracted from the walls of terra cotta pottery. What must then be determined is what analytical technique is best for a project such as this. A proficient technique, combined with the extraction procedure, could produce more results.

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