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Detection and determination of food residues in Native American pottery

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DETECTION AND DETERMINATION OF FOOD RESIDUES
IN NATIVE AMERICAN POTTERY

A Thesis Submitted
In Partial Fulfillment
Of the Requirements for the Designation
University Honors

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SIGNATURES

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ABSTRACT

The purpose of this research was to develop a new method of analyzing organic residues left on Native American pottery using linear Raman spectroscopy. Native American pottery was replicated using terra cotta and maple syrup was boiled in each of the pots using boiling stones. The pottery shards were then analyzed using Raman spectroscopy. Shards of pottery with maple syrup residue were compared to the standards and the syrup residue was not only detected, but also matched to compounds in the instrument library. Typically, the study of Native American pottery has been done in a variety of different ways, many of which require advanced instrumentation. However, as many universities do not have access to that level of instrumentation, this study demonstrates that the same type of analysis can also be done using linear Raman spectroscopy.

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I. INTRODUCTION

This project focused on developing a new technique to analyze the food residues left on Native American pottery, an example of which is pictured to the below in Figure 1^[1]. This research was also a collaboration between the Anthropology staff and the Department of



Figure 1. An example of Native American pottery^[1].

Chemistry and Biochemistry. Dr. Donald Gaff brought relevance to the project as he is searching for a way to analyze different shards of pottery that he has collected. He preferred that the method that was developed did not destroy the original structural integrity of the pottery^[2]. Additionally, this project added to existing knowledge of Raman spectroscopy of archaeological artifacts.

The study of Native American pottery has typically been done in a variety of different ways. However, this often requires advanced instrumentation techniques that universities like the University of Northern Iowa (UNI) do not have. It is because of this that the same types of analysis were done using linear Raman spectroscopy. Additionally, this research into the methodology behind linear Raman spectroscopy provided a new possible pathway for

universities like UNI to analyze samples of organic molecules on different types of archaeological artifacts, not just Native American pottery.

In addition to the methodology of analysis being used, the food residues on the pottery were also in question. Dr. Donald Gaff had postulated that the pots he had collected were used to boil a maple syrup derivative that the Native Americans had eaten. This ideology came from the idea that when the Native Americans transitioned from hunter-gatherers to sedentary horticulturists they began to store more complicated food items like syrup^[2].

Traditionally, pottery like the ones analyzed was used to store nuts and roots. A study done in 2009 demonstrated through the analysis of pottery from the land area around Lake Superior in Munising, Michigan that nut oil is the most common organic residue discovered in Native American pottery from that region^[2]. Dr. Donald Gaff's pottery which is from a similar region was determined to be newer than the pottery in the aforementioned study. This finding lead to the argument that his pottery could contain residues from more complex food groups like maple syrup and gave relevance to the development of a new methodology for the determination of food residues in Native American pottery.

II. LITERATURE REVIEW

The method that this project focused on is the analysis of different organic residues left in Native American pottery from foods using a DXR2 SmartRaman. The DXR2 SmartRaman focuses a monochromatic laser on a sample surface and records the scattering of the light off the sample. The scattering of light during Raman spectroscopy is due to the changes in vibrational, rotational, or electronic energy of the different molecules in the sample. The scattering of light is then passed through a filter and then a gradient which further refines it, and then finally is recorded by a computer^[3]. The recorded vibrations are then compared to the vibrations of known molecules and elements in the instrument library to determine the sample's composition.

In the past there have been many different methods of analyzing pottery. One of the most common methods is the use of Fourier Transform (FT) Raman. A 2006 overview of Raman Spectroscopy, noted that the most common wavelength of laser used to study biomolecules was 1065 nm. FT Raman only has that specific wavelength of laser making it the instrument of choice in studies of organic compounds^[4]. While it is similar to linear Raman spectroscopy, because it requires one specific wavelength of laser it is less common in universities like UNI.

The other most popular method of analyzing pottery is the usage of micro-Raman spectroscopy. According to the same study done in 2006, micro Raman was used to analyze the different pigmentation patterns used for coloration in Anasazi pottery^[5]. This is an effective method to determine which parts of pottery contain residue or pigmentation, but again is a form of instrumentation that UNI doesn't have.

That being said, FT Raman and micro-Raman instruments tend to not be cost effective purchases for universities who will have little usage for them other than the study of an occasional compound. This means that most universities, such as the University of Northern

Iowa (UNI), opt for a linear Raman with a spectral range from 50-3500 cm^{-1} and a maximum wavelength of 785 nm. This type of Raman spectroscopy has many applications, not only in the analysis of food residues, but can also be used to study a variety of samples. This versatility in its ability to study a vast array of samples is something that the other two types of Raman lack, which ultimately makes them less attractive to budget conscious universities. Researching the methodology behind using linear Raman spectroscopy provides a new path for universities, like UNI, to analyze samples of organic molecules on not only pottery, but also on other archaeological samples as well.

III. RESEARCH QUESTION TO BE ANSWERED

Due to the additional cost and specificity of micro-Raman and FT Raman, this research aims to develop a technique that is able to utilize linear Raman spectroscopy in organic residue determination. Additionally, in order to preserve the pottery, the technique needed to have little to no sample preparation and allow for samples to be analyzed as is. The main question to be answered by this research is: Can linear Raman spectroscopy detect and accurately determine the presence of different food residues in Native American pottery?

IV. METHODOLOGY

Several sample terra cotta pots were made by the UNI Art Department and delivered to Dr. Donald Gaff. Dr. Gaff used stones to heat maple syrup in the pots to boiling, allowed the syrup to cool, and then remove the syrup. After the pots were dry, mallets were used a mallet to break the pots into more manageable sizes, similar to the shards often found by archeologist. The pieces were labeled and marked as the pots were broken down. An example of this process can be seen below in Figure 2. The outside of the pot was used as a background to which the residues from the inside of the pot can be compared.



Figure 2. Example of how the terra cotta pot was broken down and labeled.

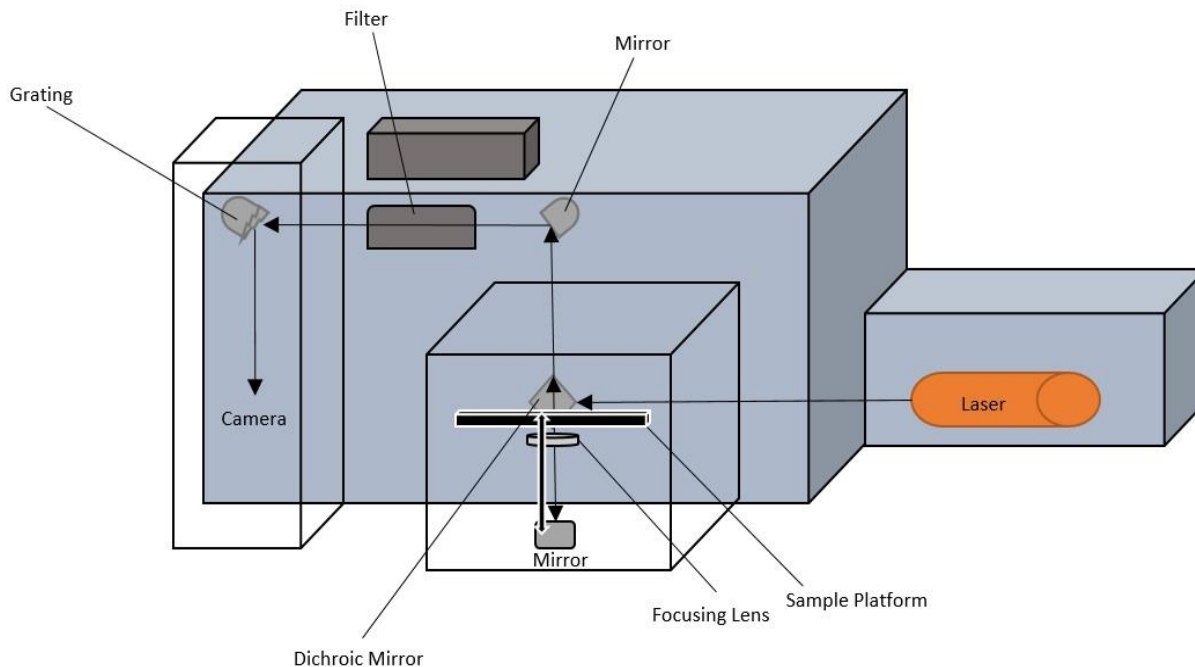


Figure 3. Diagram of the DXR2 SmartRaman.

Each piece of the pot was analyzed using the 785 nm laser on the DXR2 SmartRaman, which can be seen above in Figure 3, with other laser wavelengths being used as necessary. The vice grip sample holder was used to ensure that the sample did not move during analysis. By comparing these two spectra, we expected to discern an extra peak that will indicate the different food residue, in this case a compound found in maple syrup called Quebecol^[6]. The structure for Quebecol is pictured below in Figure 4.

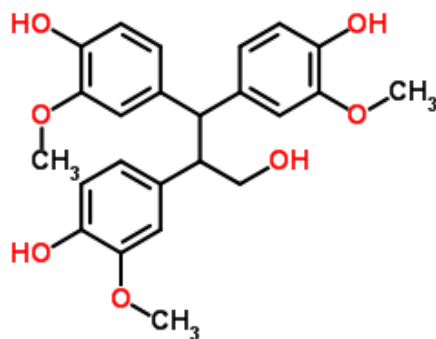


Figure 4. Molecular structure of Quebecol^[7].

V. PROCEDURE

The pottery was broken down with a hammer covered by a towel to create pieces that would fit inside the spectrometer. Each piece was marked on each side by a small line which matched up to the other pieces surrounding it. The piece was then numbered and placed into a secure tub for later analysis.

A piece (piece 21) was chosen and analyzed with the DXR2 SmartRaman using the 785 nm laser. The outside was first analyzed to create a background of terra cotta to compare to the residues. The residue was then analyzed in the vice grip 180 degree holder and then compared to the outside background spectra.

Three pieces were then chosen (pieces 11, 16, 21) and rinsed with acetone, methanol, and methylene chloride respectively. The rinses were collected and placed into capillary tubes. The rinses were analyzed with the 785 nm laser using the capillary tube holder. The rinses were then evaporated in petri dishes for 3 days. The residue left in the bottom of the dishes was then analyzed using the universal sample holder.

The residues itself was then analyzed by placing maple syrup and the sap that the pots were doped with into two different NMR tubes. The NMR tubes with the residues were also analyzed using the 785 nm laser and compared to each other.

VI. ANTICIPATED RESULTS

In conclusion, linear Raman spectroscopy was used to develop a new method of detecting and determining organic food residues in Native American potter. Residue peaks were expected to be seen at approximately 900 cm^{-1} . Additionally, the peak indicating the presence of terra cotta is expected to be seen at $460\text{ cm}^{-1[6]}$. Each of the peaks was analyzed and identified using the DXR2 SmartRaman library.

VII. RESULTS

Piece 21 was selected and analyzed using the 785 nm laser and generating two different spectra. One which was used as the background to compare the residue to and the other of the residue. These can be seen below in Figures 5 and 6 respectively. It was determined that the terra cotta alone produces peaks at 142, 462, and 625 cm^{-1} . Conversely, the residue produced peaks at 142, 1,350, 1,500, and 3,300 cm^{-1} . The peak at 142 cm^{-1} can be attributed to titanium dioxide, a common ingredient used to make terra cotta. The rest of the peaks in Figure 3 can be attributed to the residue on the terra cotta².

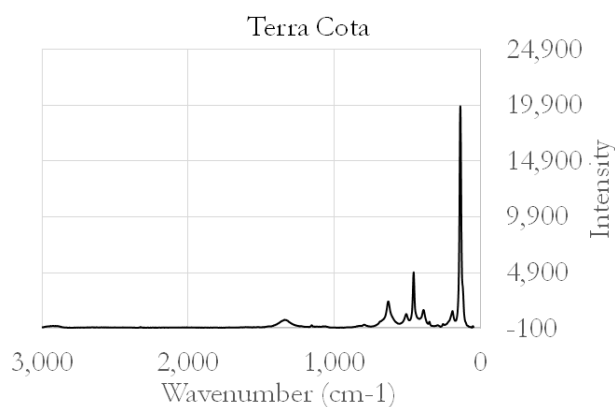


Figure 5. Spectra of terra cotta using the 785 nm laser.

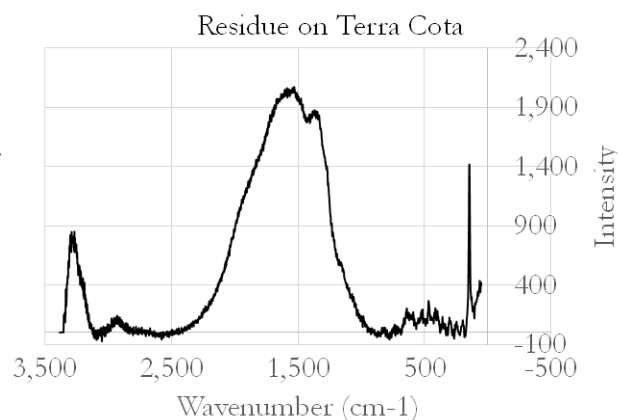


Figure 6. Spectra of residue on terra cotta using the 785 nm laser.

Pieces 11, 16, and 21 were rinsed with different solvents and the spectra of these rinses can be seen in Figure 7. It was very difficult to determine the difference between the residue and the solvents it was dissolved in and further analysis was required as the solvent background was much stronger than the syrup residue. The solvents were then evaporated and the leftover residue was analyzed. It was determined that Methanol (MeOH) was the best solvent to remove the residue, as seen in Figure 8, it removed the most residue and exhibited the highest intensity.

Finally, the residue alone was analyzed and it was determined that they both have identical peak structures at 500 and 2,900 cm^{-1} , as shown in Figure 9. While they have identical peak structures, they do not have the same intensities. This can be attributed to the maple syrup alone having a more crystalline structure due to the intense boiling process. The sap, which has not been boiled at such a high temperature, is seen at a lower intensity due to the smaller amount of crystalline structures^[6].

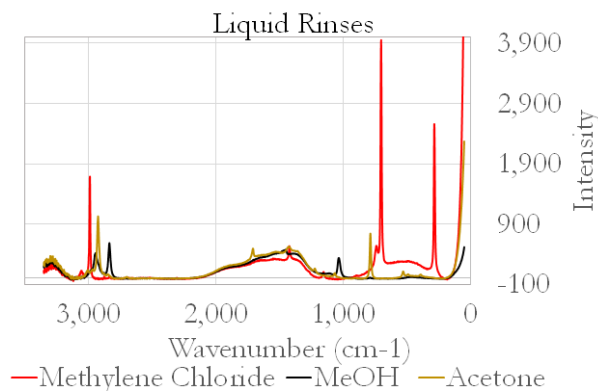


Figure 7. Liquid rinses of the residue off the terra cotta.

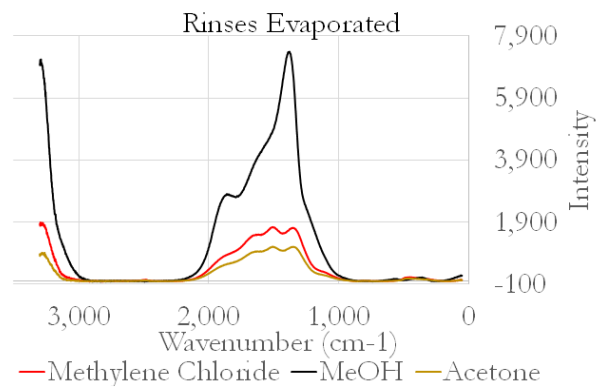


Figure 8. Evaporated liquid rinses of the residue.

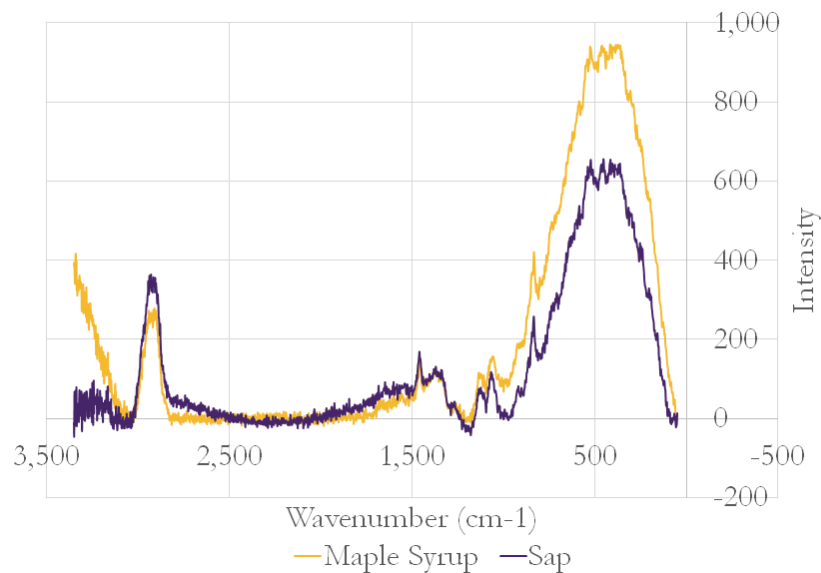


Figure 9. Spectra of the two different types of residues.

VIII. DISCUSSIONS

In terms of the residue on the pottery, the terra cotta proved to be more difficult to separate from the residue peaks as was seen in Figures 5 and 6. The terra cotta produced peaks that were different from the spectrum of the residue and some were easily discernable in the residue spectrum as in the case of the peak at 142 cm^{-1} . The presence of this peak indicates that the residue peaks needed to be separated completely from the pottery sample.

The residue was removed from the pottery samples using different solvents by rinsing three different pieces with different solvents. The solvents, acetone, methanol (MeOH), and methylene chloride, all which are Raman active hindered the analysis of the residue in the rinses. This was due to the solvent peaks overlapping with the residue peaks and generating a mixed spectrum.

In order to solve this problem, the rinses were evaporated in petri dishes and the residue left behind was analyzed in a similar fashion. The residue from the evaporated rinses demonstrated that MeOH was able to remove the greatest amount of material from the pottery due to its high intensity peak. Acetone and Methylene chloride were determined to have removed the same parts of the residue due to the similar peak shapes seen in Figure 8. While all three residues were able to remove the residue from the pottery, it remained uncertain if all of the residue was removed.

In further analysis of that pathway, the residue and pure maple syrup were analyzed alone in small glass tubes. The tubes were mounted in the tube holder of the Raman instead of the vice grip which had been in use in order to generate two different spectra. These spectra demonstrated that the residue has a different spectrum when it is in liquid form versus when it is dry.

When the residue is in liquid form, it displays a peak at 500 cm^{-1} this is the same for both maple sap and for syrup. The maple syrup has a more complex crystalline structure than the sap due to boiling which leads to the higher intensity peak. When the residue is dried onto the pottery

or is in solid form on after all liquid has been evaporated, the peaks is shifted to $1,500\text{ cm}^{-1}$. This is most likely due to the dried form of the residue having a more complex crystalline structure than the liquid form as all the water would have been removed from the residue. All of the spectra were run through the SmartRaman library and it was determined that the residue exhibits two areas of interest in Raman spectroscopy.

The first area of interest is the largest peak area, shown at $1,500\text{ cm}^{-1}$ in solid form and at 500 cm^{-1} in liquid form. It was determined that this area would most likely correspond to the aromatic rings on Quebecol, seen Figure 4^[8]. These rings and their Raman bands would change in the presence of water and would explain the shift between $500\text{-}1,500\text{ cm}^{-1}$ seen between the solid and liquid forms. While it is likely that this band contains the aromatic rings, due to how broad the peak is, it is likely that other functional groups are present as well in this band.

The second area of interest was determined to be the area at $3,300\text{ cm}^{-1}$ in both solid and liquid forms of the residue. This area most likely corresponds to the alcohol groups on the side chains of the benzene rings of Quebecol. This side chains would exhibit one to two different peaks in that band area. One for the trans isomer of the side chain and one for the cis isomer of the side chain. The cis isomer would show up closest to $3,000\text{ cm}^{-1}$ and the trans isomer of the alcohol would show up farther up field in the spectrum^[9].

These two areas of interest demonstrate that the residue is able to be detected on the pottery and once it has been removed from the pottery. However, it is impossible to break down all that the peak at $1,500$ or 500 cm^{-1} actually contains, as many different compounds display peaks in that band area. Other possible peaks the band could contain are ketone, nitrogen, and carboxylic acid groups all which display Raman activity in this area^[8]. Further analysis needs to be done to break apart this broad peak to determine the actual molecular structure of the residue.

IX. CONCLUSIONS

It was determined that the residue can be detected both when it is on the pottery and after it has been removed from the pottery. However, the molecular structure of the residue cannot be effectively determined using Raman spectroscopy alone. Further studies need to be done into how different spectral groups can combine to form the residue peaks in order to elucidate the actual structure of the residue. Specifically, within the band at $1,500\text{ cm}^{-1}$, which is a combination of several similar functional groups.

The bands at $3,300$ and $1,500\text{ cm}^{-1}$ correspond to functional groups which can be found in the chemical compound Quebecol. The band at 500 cm^{-1} in Figure 9 demonstrated what the band at $1,500\text{ cm}^{-1}$ would look like if all its bonds were saturated with water. These spectral bands are in agreement with our maple syrup residue with which the pottery was doped, further supporting that the residue was correctly detected.

In addition to these findings, further work should be done on how the solvents affected the overall structural integrity of the terra cotta to determine if any significant damage was done in the removal of the residue. It is important to know how much the terra cotta was affected by the different solvents in terms of not only preservation techniques, but also in terms of how contaminated the residue would be. This is a vital next step in the future work on this project.

Finally after this, preliminary work should be done using authentic Native American pottery to determine if the method works as predicted. Different challenges may arise in authentic pottery that could not have been foreseen when using modern samples, so it is important to consider every angle of analysis before this is attempted.

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