The Characterization of Leather WWII Artifacts Using GC/MS and Raman Spectroscopy

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Background

Many museums face the challenge of protecting artifacts from deterioration. This process is often hampered by the history of the artifact, which can introduce factors that start or speed up the process of deterioration. An example of this is the method used during WW II to preserve leather. Mink oil or other fatty substances are used to help preserve and soften leather. A major component of mink oil is palmitic acid.[1] This fatty acid may have reacted with the brass in the same way that the oils from the hand react with coins to make that distinctive metallic smell, only in this case causing damage to the leather.[2] Since mink oil and other oils are commonly used to preserve leather, its components are expected to be found via GC/MS.

Introduction

Example of moderately well-preserved artifact

- The artifacts that were studied in this experiment are WW II leather and brass artifacts, including boots and a leather sheath.
- These items studied are on loan from the UNI museum, along with several other artifacts.
- These artifacts have some damage caused by a reaction of the brass fittings, called bronze disease, which has affected both the brass and the surrounding leather.[3]
- One of the goals was to find out how the bronze disease is affecting the degradation of the leather, if at all.

Example of bronze disease affected artifact containing Cu salts

- Another goal was to find out if the preservation methods used on the leather are still detectable chemically and if they helped preserve the leather or if they reacted with the brass.[4]
- The damage to leather could have been caused by either the removal of the protective fatty layer or by the products of the reaction between the fatty acid and the brass fittings.
- Material from around a severely damaged brass rivet provided a lot of data on the composition of the leather artifacts, as well as making a brilliant blue solution when dissolved in the solvents used.

$$HA_{(s)} + Cu_{(s)} \xrightarrow{\text{Atmospheric } H_2O} Cu^{2+}_{(aq)} + 2A^{-}_{(aq)}$$

Example of possible reaction damaging the artifact, with HA being a fatty acid.

Raman Analysis

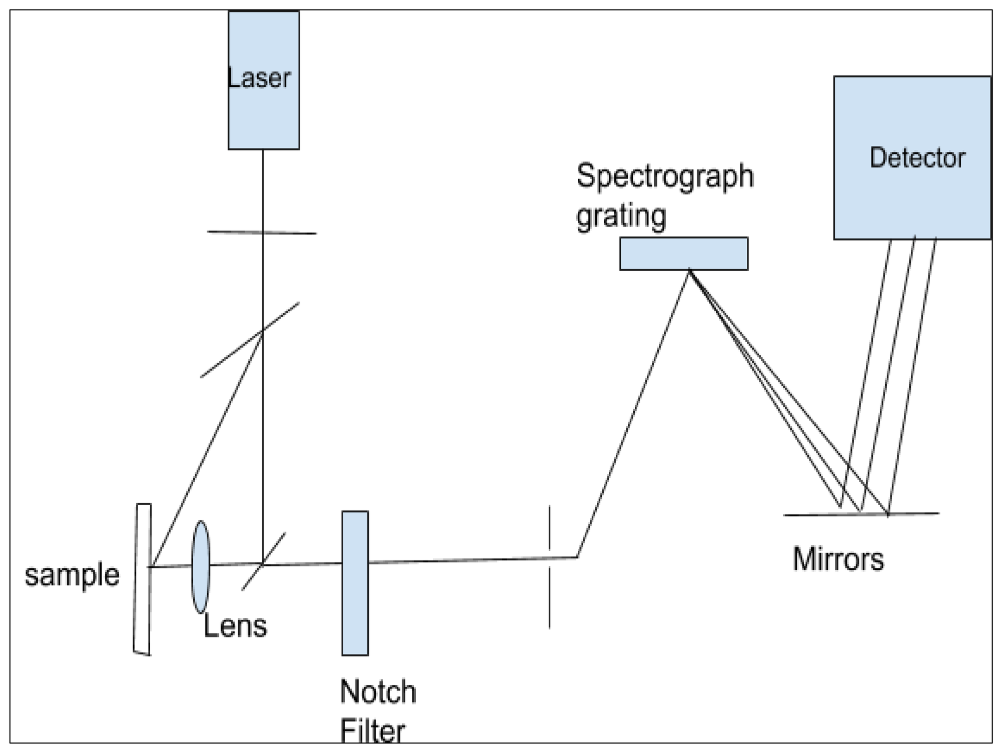
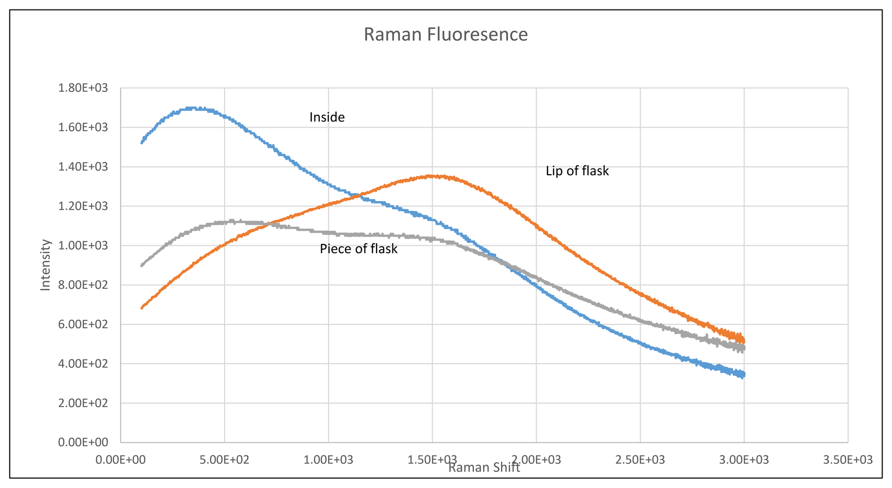


Diagram of Raman Instrument

- Raman spectra of the artifacts were taken to try and help characterize the compounds in and on the artifact, but any distinctive peaks were covered by fluorescence.
- The artifacts that were sampled included a belt and a hip flask that may have contained gunpowder.
- Useful data may be possible with a 1064 nm laser, but UNI does not have one for use with the Raman instrument.

- The Raman instrument was warmed up with the 785 nm laser installed.
- The sample holder was changed as needed to hold the various artifact and artifact pieces.
- A polystyrene disc was used as a background prior to sample collecting.
- Artifacts were placed inside the instrument to be measured by Raman.
- The focus was then adjusted for each artifact so that the detector could acquire data.
- All artifacts sampled fluoresced with the 785 nm laser, so no useful data was obtained.
- Each artifact did fluoresce with their own distinct peak shape and intensity.
- The noise in the data was partially removed by increasing the number of scans taken, resulting in the smoothing of the graphs shown below.



Graph of Leather Fluorescing (Inside and Lip of Leather Flask)

GC/MS Analysis

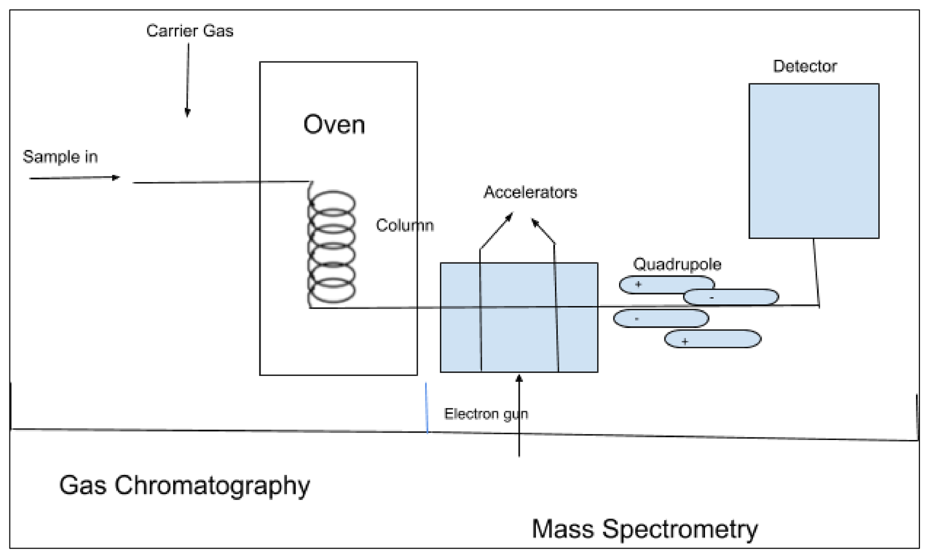
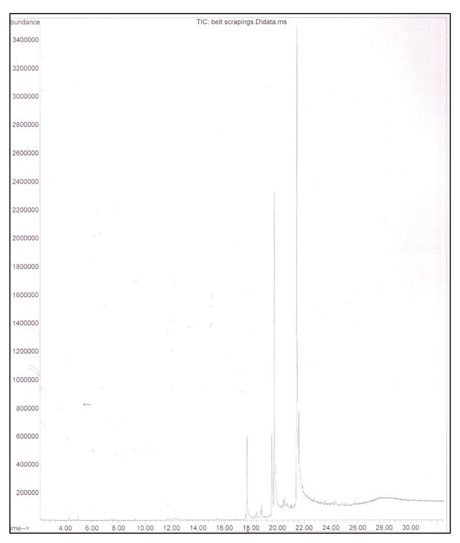


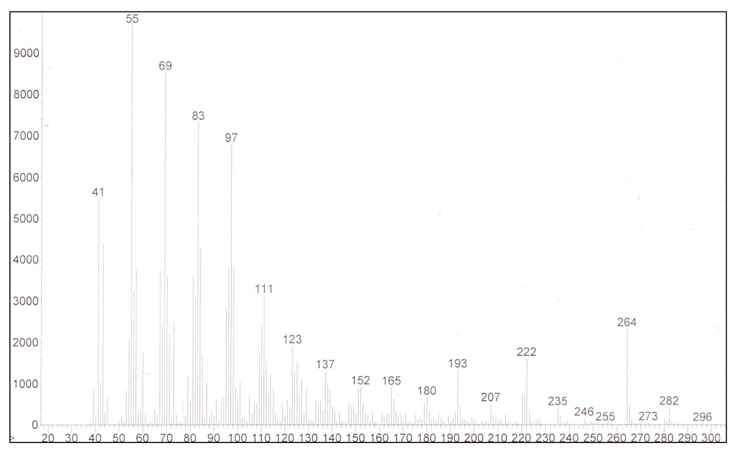
Diagram of GC/MS Instrument

- The sample vials were then loading into the GC, where a needle punctured the lid of the vial and draws some of the sample into the GC.
- The sample was moved through the GC, where the different chemicals in the sample are separated by mass and polarity.
- The chemicals are then sent through the mass spectrometer, where they are blown apart via electron gun and the fragments measured and identified.

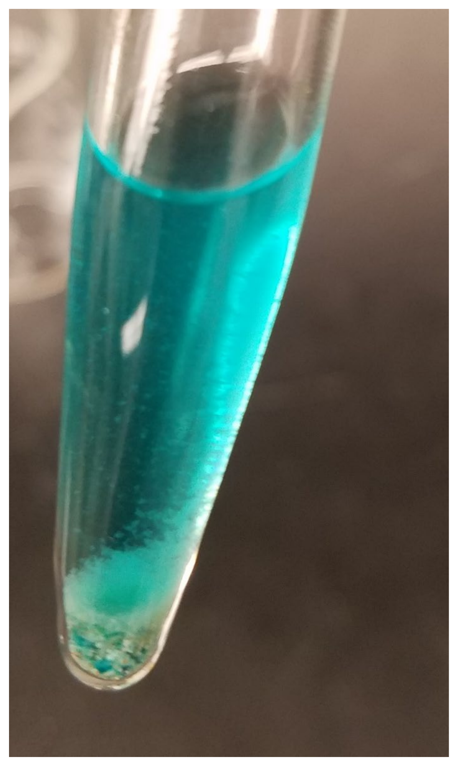
- Two methods of obtaining GC samples were used: swabbing and soaking.
- Various areas on the flask and belt artifacts were swabbed with cotton tipped swabs dipped in solvent to collect surface material.
- The swabs were then soaked in solvent to get a useable sample.
- Enough material was removed to color the solvent in the GC vial.
- A background of just cotton swabs soaked in solvent was collected to make sure no contaminants were introduced by them.
- Two items were soaked to see if any different substances were liberated from the artifacts, a piece of the leather flask and debris from around the decayed rivet.
- Solvent used for GC/MS was a 50/50 mixture of acetone and methylene chloride to ensure all molecules could dissolve were dissolved.



Example of GC Spectra



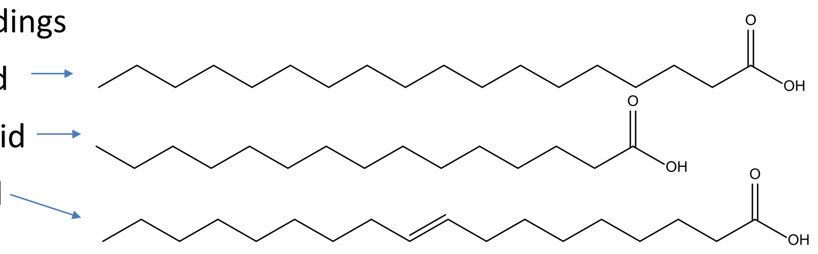
Example of MS spectra



Example of GC sample

Discussion

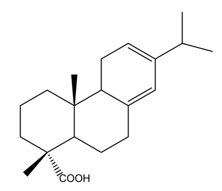
- Many fatty acids and other chemicals were identified by the mass spectrometry of material from each of the artifacts swabbed, but material from around the destroyed brass fitting provided the clearest data.
- GC/MS analysis of swabs from the damaged areas of the artifacts were taken
- GC/MS findings
- Stearic acid
- Myristic acid
- Elaidic acid



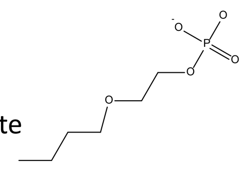
- All of these fatty acids are found in animal products that are used to preserve leather, with elaidic acid being particularly good at preventing mold growth.[2]

Possible contaminants

- 2-butoxy-phosphate ethanol, an industrial cleaner was found in most of the samples. This indicates that they may have been cleaned or otherwise come in contact with this chemical.
- Levopimaric acid, commonly found in pine resin, was also found via GC/MS. Pine resin is sometimes used to seal leather against the elements, so the presence of levopimaric acid is possible.



Levopimaric acid structure



2-butoxy-phosphate ethanol structure

Conclusion

The leather of these artifacts contained various acids. The acids present were all weak acids and in low concentrations. However, the acids are constantly in contact with the brass and water from the atmosphere. This means that the small amount of damage that they do to the metal would add up over time. The formation of the blue liquid indicates that copper is being liberated from the brass fittings and reacting with something. These copper ions may be complexing with the fatty acids to produce the blue-green solid on and around the brass fittings. The components of the leather may also function as a catalyst to speed up the reaction of the brass. The levopimaric acid from the pine resin may also have affect on the brass, as well as the 2-butoxy-phosphate ethanol. The 2-butoxy-phosphate ethanol may also make acidic conditions if present in a large enough amount.

Acknowledgements

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