

University of Northern Iowa

UNI ScholarWorks

Fall 2021 - Chemical Analysis Class Projects

Chemical Analysis Class Projects

12-2021

Identification of Natural Dyes in Ancient Peruvian Mummy Cloths using LC/MS/MS

Shailah Mathews

University of Northern Iowa, mathesad@uni.edu

Joshua Sebree Ph.D.

University of Northern Iowa, joshua.sebree@uni.edu

Let us know how access to this document benefits you

Copyright ©2021 Shailah Mathews and Joshua Sebree

Follow this and additional works at: https://scholarworks.uni.edu/chemanaly_fa2021

 Part of the [Analytical Chemistry Commons](#)

Recommended Citation

Mathews, Shailah and Sebree, Joshua Ph.D., "Identification of Natural Dyes in Ancient Peruvian Mummy Cloths using LC/MS/MS" (2021). *Fall 2021 - Chemical Analysis Class Projects*. 1.

https://scholarworks.uni.edu/chemanaly_fa2021/1

This Open Access Poster is brought to you for free and open access by the Chemical Analysis Class Projects at UNI ScholarWorks. It has been accepted for inclusion in Fall 2021 - Chemical Analysis Class Projects by an authorized administrator of UNI ScholarWorks. For more information, please contact scholarworks@uni.edu.

Offensive Materials Statement: Materials located in UNI ScholarWorks come from a broad range of sources and time periods. Some of these materials may contain offensive stereotypes, ideas, visuals, or language.

Identification of Natural Dyes in Ancient Peruvian Mummy Cloths using LC/MS/MS

Shailah Mathews, Dr. Joshua Sebree
University of Northern Iowa

Artifact Introduction

- Collected in the 1960s by researchers from and donated to the museum in the 1970s
- Undetermined if the researchers violated UNESCO protocols
- Made of wool and dyed with a variety of natural dyes that are made of plants or insects
- Have different colors and patterns that represent status of the Peruvian mummy
- Possibly thousands of years old



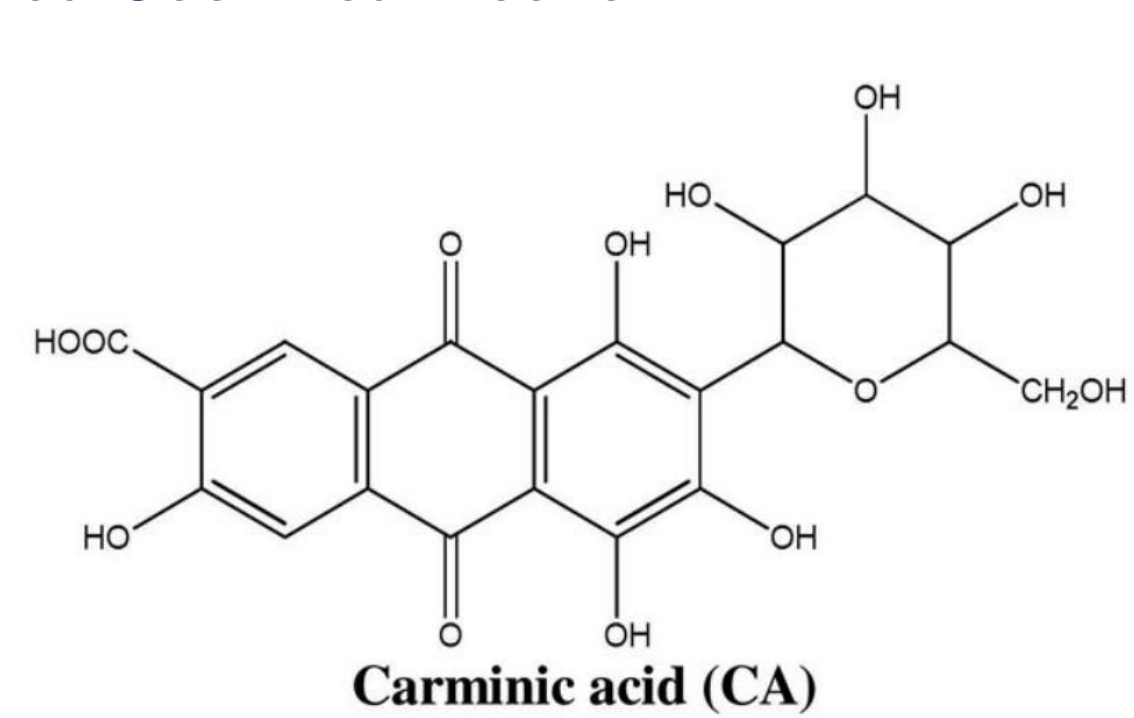
Chemical Introduction

- The spun yarn is boiled with the dyestuff and mineral salts are added to help the color stick to the wool
- Dyestuff in ancient Peru were often made of plant or animal materials
- Many natural wool colors such as black, brown, and tan are often just washed with a natural detergent made from the Jabonera plant

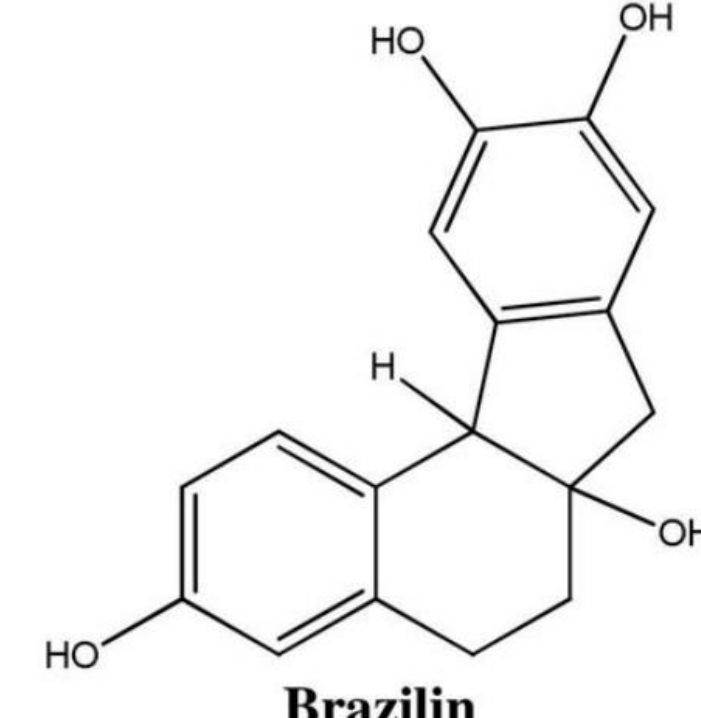
Dyes

- The common dyes used in Peru are listed below

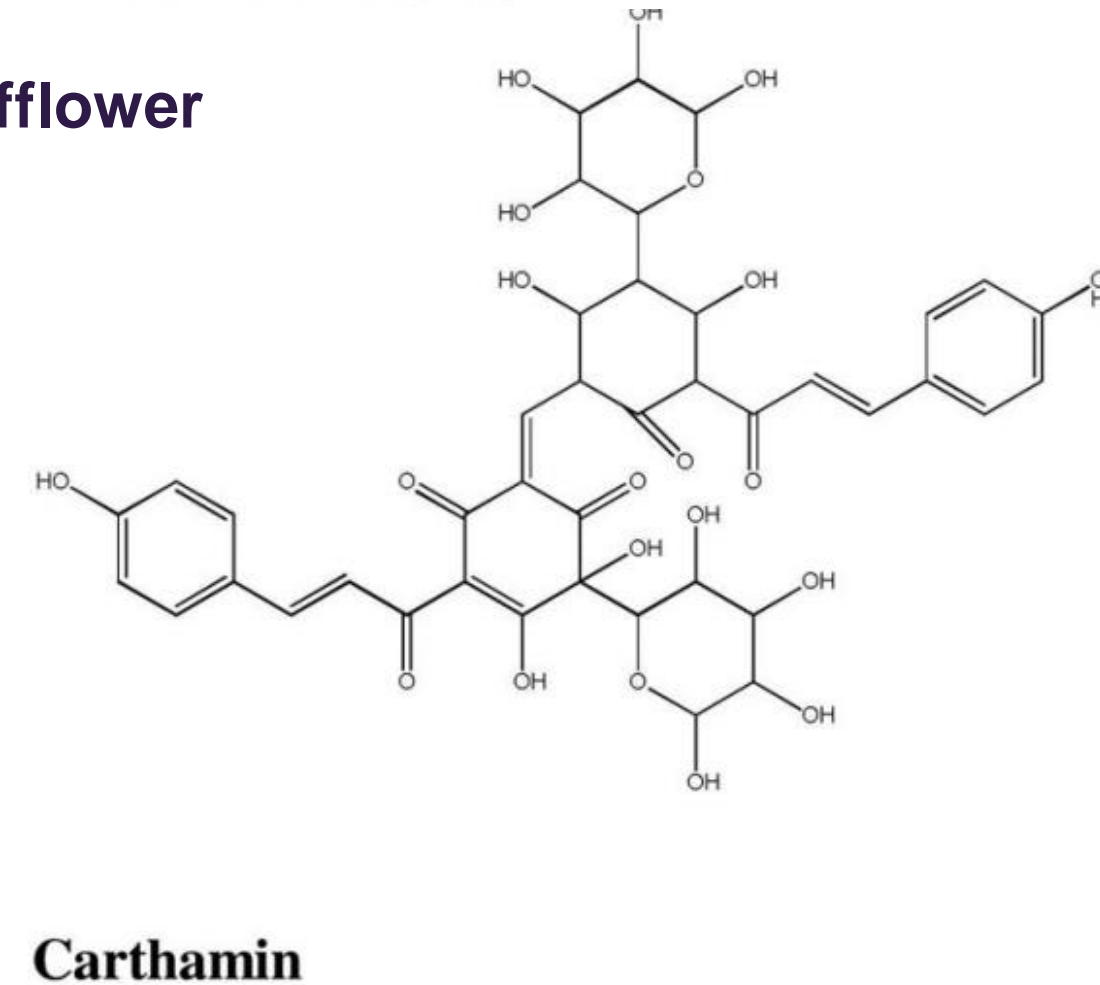
- Red-Cochineal Beetle



- Red- Brazilwood



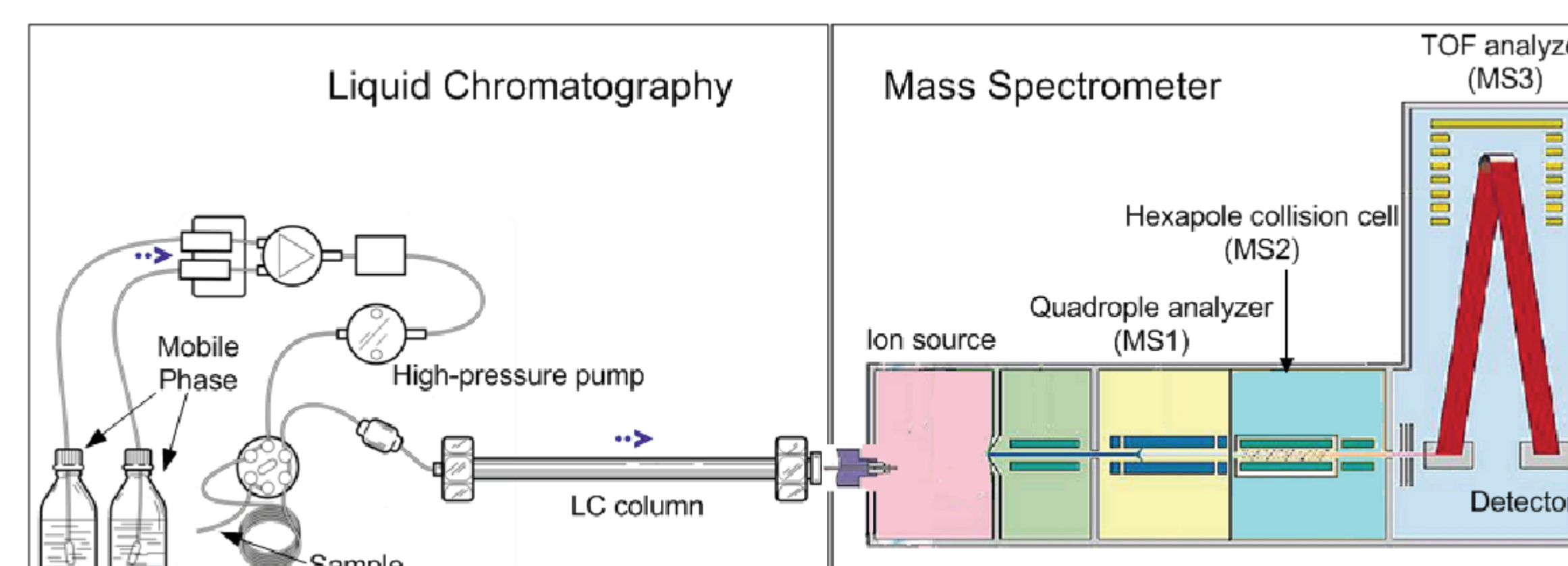
- Yellow- Safflower



Dye Extraction Method

- An acid extraction was performed on the fabrics because the acid can hydrolyze dye molecules from their inorganic mordants
- Small (1cm) pieces of fabric were placed into micro test tubes with a 250µl solution of HCl/MeOH/H₂O (2:1:1 v/v/v)
- The samples were placed in 105°C water and heated for 10 minutes
- Then evaporated inside a centrifuge under vacuum at 40°C
- The residue of the samples were rehydrated with 200µl solution of MeOH/H₂O (1:1 v/v)
- They were then extracted and placed into MS vials for analysis

Instrument



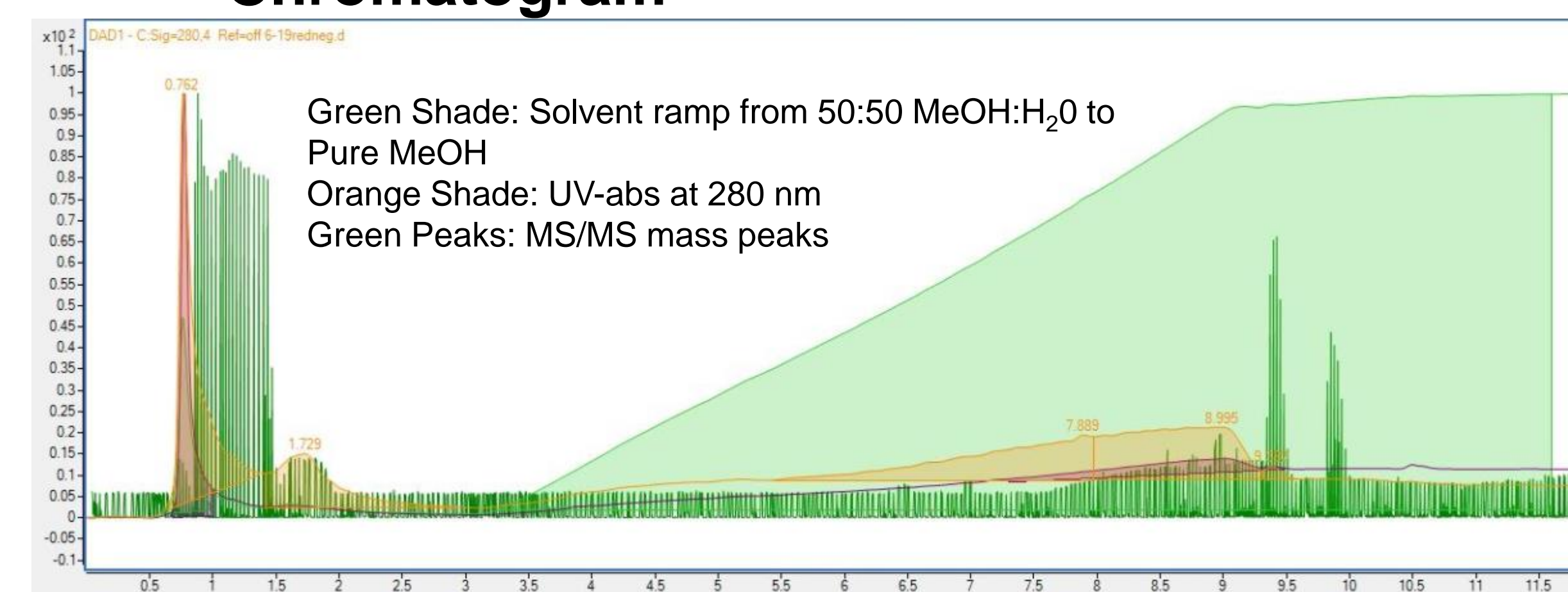
- Liquid chromatography (LC) separates the sample components
- The Mass Spectrometer (MS) creates and detects charged ions
- LC/MS data may be used to provide information about the molecular weight, structure, identity and quantity of specific sample components
- Used negative ion mode
- 50:50 MeOH/ H₂O

Auto MS/MS

- Parent ions are fragmented during the LC/MS these fragmentations sorted by time of flight
- Each ion will have a different fragmentation pattern
- The pattern is recorded and stored in a library
- When the fragmentation matches something in the library it will show the compound

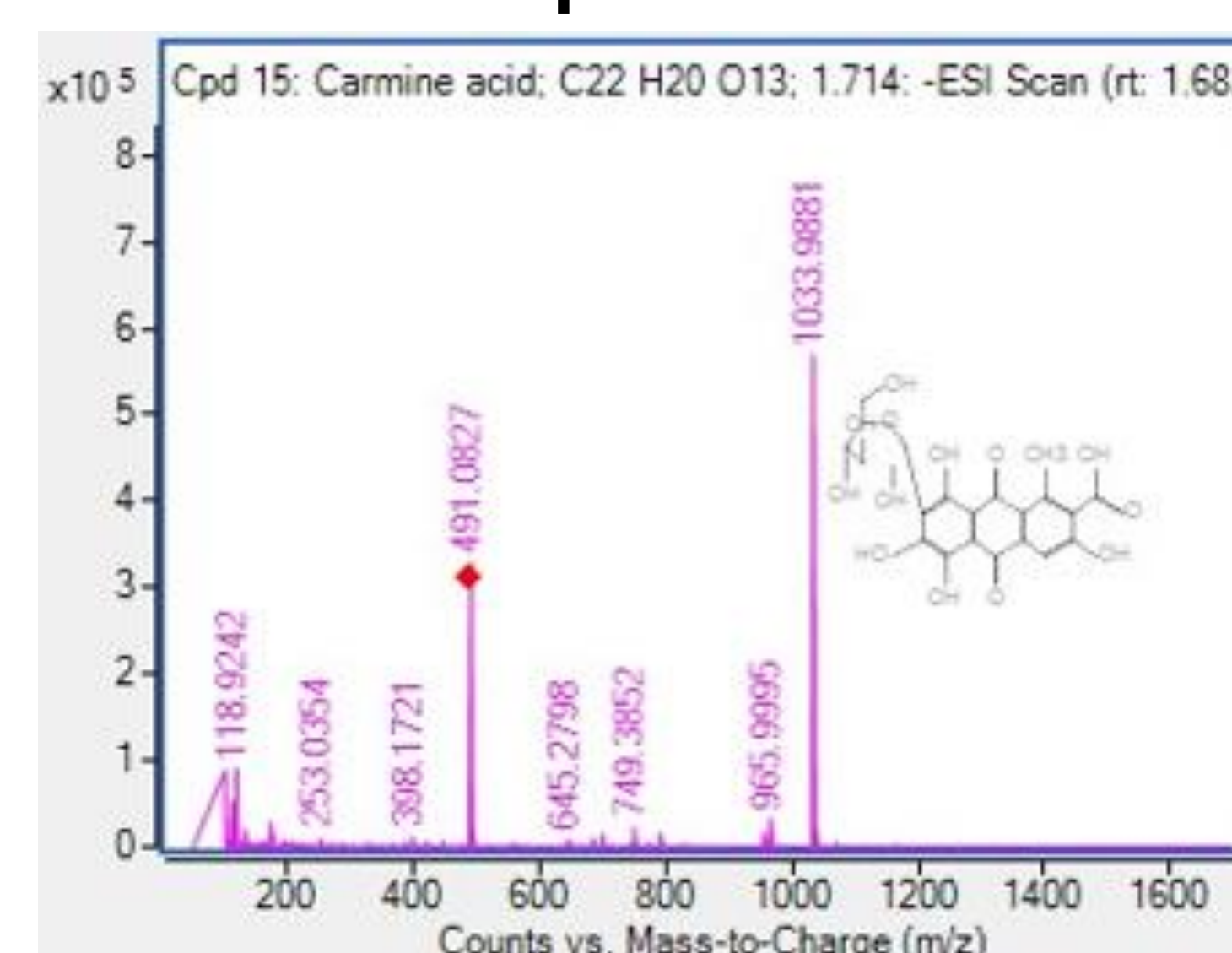
Results

- Chromatogram

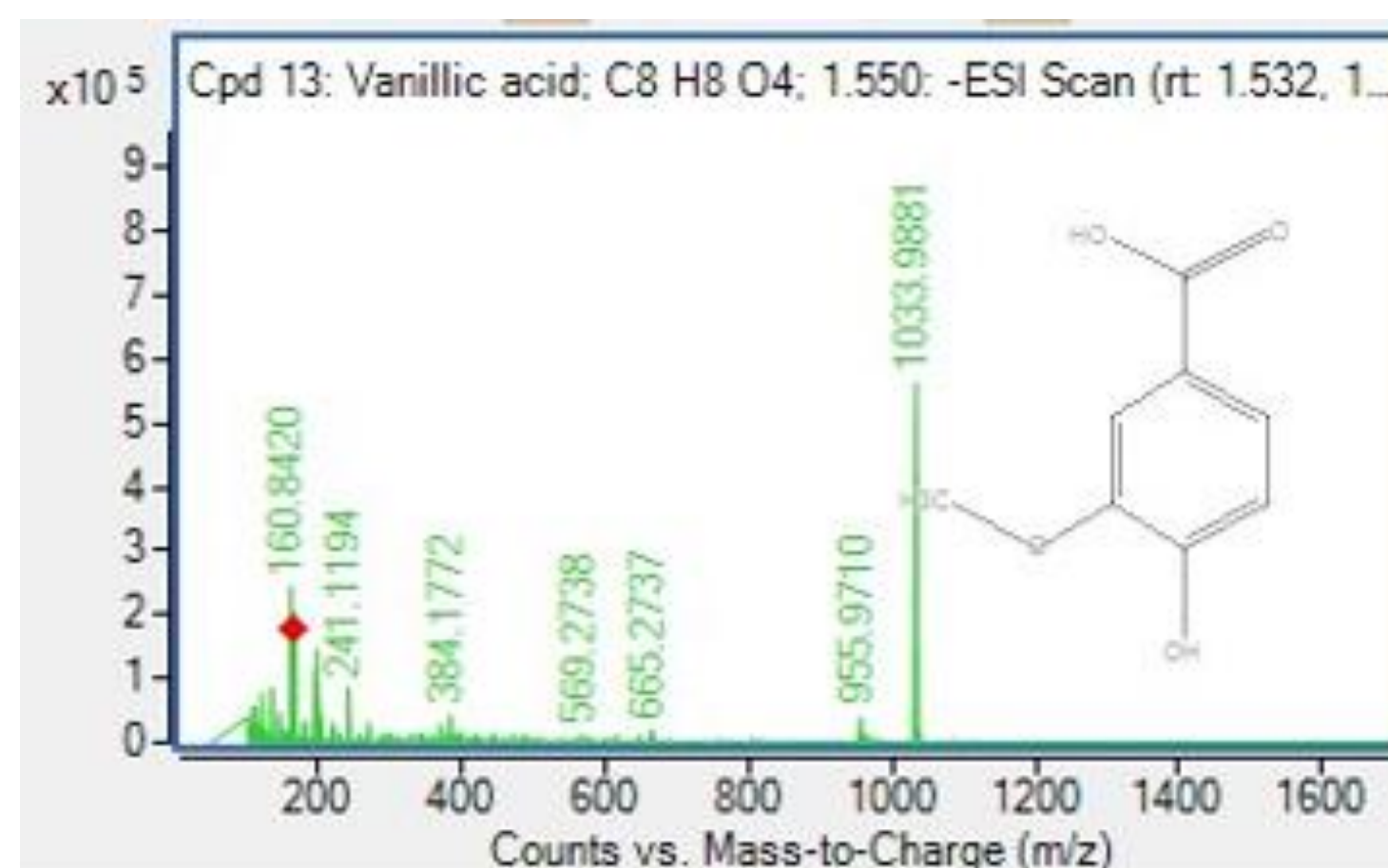


- Dye molecules should show unique absorbances (difference from blank) in a UV-chromatogram.
- Mass without UV-absorbances were not analyzed for dye properties.

- Mass Spectrometer



- From sample 1970.9.0019 from the red fiber.
- Shows carmine acid
- Carmine acid is an indicator it was dyed using the Cochineal Beetle

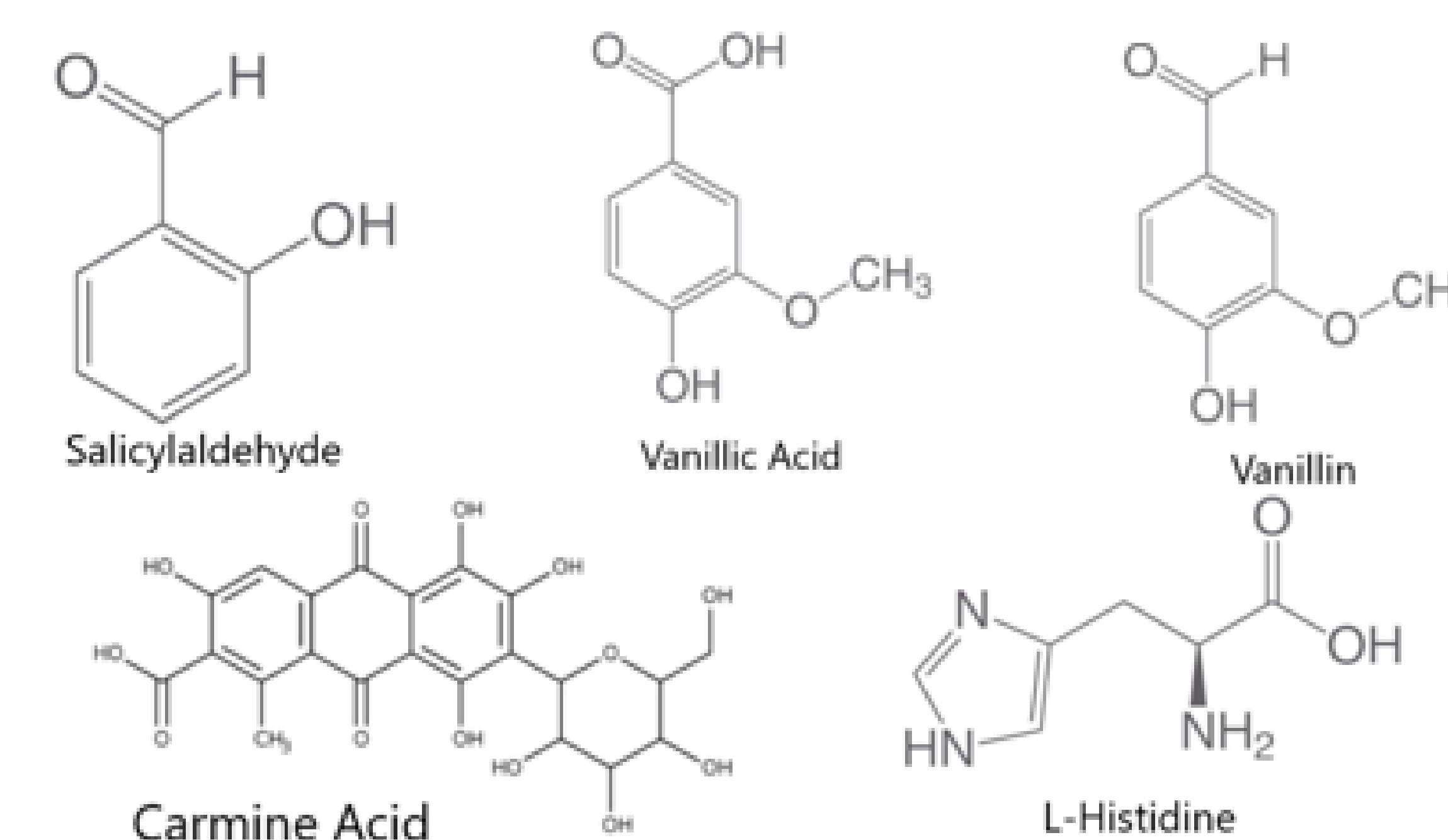


- From sample 1970.9.0034 from the brown fiber
- Shown the MS of the Vanillic Acid
- Vanillic Acid is an indicator that the fabric was dyed with a type of plant.

Table Summary

Fiber	Compounds Found/ Identified	Key Compounds Identified
1970.9.0019 (Tan)12	34 Found 13 Identified	N/A
1970.9.0019 (Red)6	51 Found 23 Identified	Carmine Acid
1970.9.0024 (Tan)13	51 Found 17 Identified	Salicylaldehyde
1970.9.0024 (Black)7	52 Found 15 Identified	L-Histidine
1970.9.0025 (Brown)8	55 Found 18 Identified	Vanillin Salicylaldehyde
1970.9.0025 (Red)11	76 Found 25 Identified	Vanillin Salicylaldehyde
1970.9.0031 (Brown)9	36 Found 17 Identified	Carmine Acid
1970.9.0032 (Brown)10	48 Found 15 Identified	Vanillin
1970.9.0034 (Brown)5	65 Found 24 Identified	Vanillic Acid Salicylaldehyde
1970.9.0034 (Tan)14	51 Found 17 Identified	Chymostatin

Example Structures of Identified Natural Products



Conclusions

- In the brown samples, they have been dyes with a type of plant
- The red samples have been dyed with Cochineal Beetle
- The black sample was most likely made of natural black wool

Future

- Make a larger library of dyes so they can be identified by the auto MS/MS

Acknowledgements

UNI Department of Chemistry and Biochemistry
UNI Museum
Nathan Arndt
Anne Marie Gruber
Kirk Manfredi

Citations

- Kay K. Antúnez de Mayolo. "Peruvian Natural Dye Plants." Economic Botany, vol. 43, no. 2, New York Botanical Garden Press, 1989, pp. 181–91
- Romanian Reports in Physics, Vol. 64, No. 2, P. 507–515, 2012
- Smith, G. D.; Esson, J. M.; Chen, V. J.; Hanson, R. M. In Forensic dye analysis in cultural heritage: Unraveling the authenticity of the earliest Persian knotted-pile silk carpet 2020, DOI:10.1016/j.fsisc.2020.11.004
- A Primer.; Howard-Packard Company, 1998.
- Serrano, A., Sousa, M.M., Hallett, J. et al. Analysis of natural red dyes (cochineal) in textiles of historical importance using HPLC and multivariate data analysis. Anal Bioanal Chem 401, 735–743 2011, DOI: 10.1007/s00216-011-5094-0
- : Daria Zasada-Kłodzińska, Elżbieta Basiul, Bogusław Buszewski & Michał Szumski (2021) Analysis of Natural Dyes from Historical Objects by High Performance Liquid Chromatography and Electromigration Techniques, Critical Reviews in Analytical Chemistry, 51:5,411-444, DOI: 10.1080/10408347.2020.1743640