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The Analysis of Heavy Metals in Samples of Honey using X-Ray Fluorescence and Anodic Stripping Voltammetry

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The Analysis of Heavy Metals in Samples of Honey using X-Ray Fluorescence and Anodic Stripping Voltammetry

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Introduction

- Honey bee colonies are shipped across the country to pollinate various crops throughout the year
- They are fed High Fructose Corn Syrup (HFCS) during transportation.[1]
- Fructose in HFCS is converted to a toxic chemical to bees, Hydroxymethylfurfural (HMF)
  - causes symptoms similar to dysentery
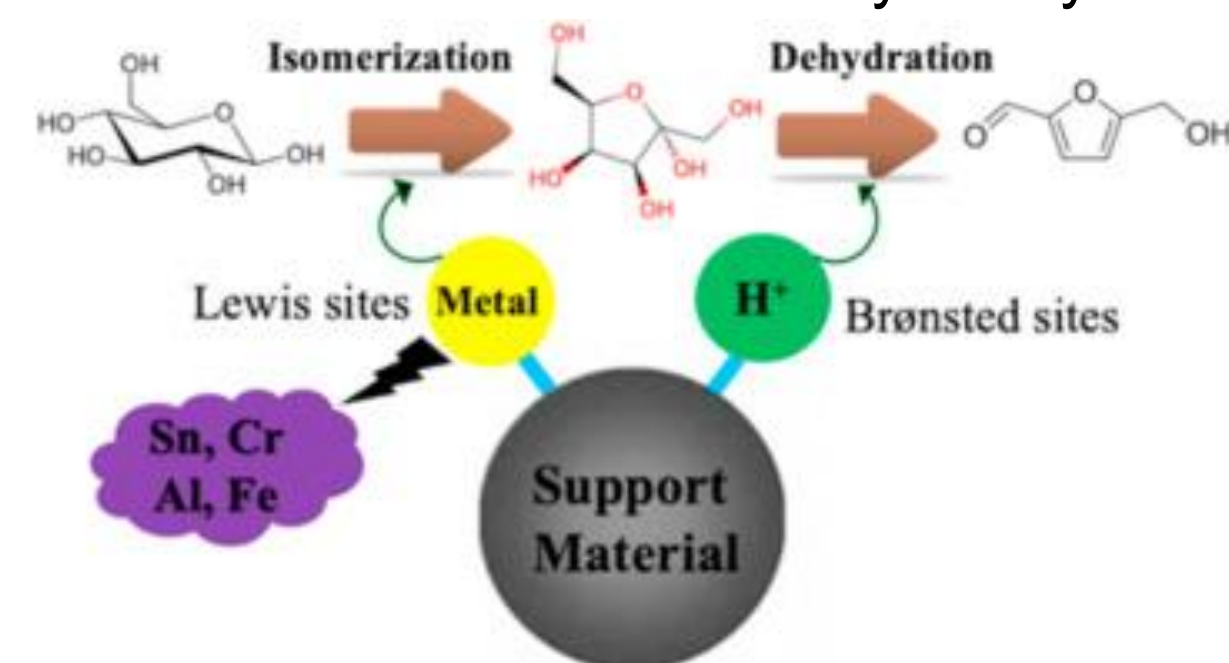- The production of HMF can be catalyzed by heavy metals

Figure 1. Catalyzation scheme of HMF by heavy metals.[3]

- High doses of HMF are suspected to be the cause of colony collapse disorder (CCD)
  - A drastic phenomenon in which populations of bee colonies are rapidly decreasing
- X-ray fluorescence (XRF) is a non destructive technique that works by emitting x-rays at a sample.
  - Each element present in the sample produces a set of distinct, characteristic fluorescent x-rays.[3]
- Anodic Stripping Voltammetry (ASV) is types of voltammetry in which the analyte is deposited on the electrode and is stripped away using a reduction-oxidation reaction.[4]

Figure 2. Honey sample 2 exploded in the muffle furnace during the dry ashing process due to residual moisture.

Experimental

Standard Addition- Honey samples were adulterated with varying amounts of heavy metals

Dry Ashing- Honey samples were dried in a crucible for 72 hours at 105°C. The dried honey was then placed in a muffled furnace and heated for 20 minutes at 200°C, 20 minutes at 300 °C, and 16 hours at 550 °C. The crucible was removed, cooled, and the mass of the honey residue was obtained.

Wet Digestion- Honey was dissolved with HNO_3. The mixture was boiled, and H_2O_2 was added. The solution was heated until almost dry and 5 mL of HNO_3 were added. The solution was then diluted to 50 mL with DI water.

Standards- Standard solutions of copper, lead, and iron were created at various concentrations using stock solutions.

XRF- A Bruker Tracer V X-ray fluorometer was used. The ashes were placed in a sample container before being x-rayed.

ASV- A Gamry potentiostat with a carbon printed electrode with an Ag/AgCl reference electrode was used to analyze the external standards and honey samples prepared through wet digestion.

Results

Contrary to what was expected, there was more Fe than Mn. Using the equation of the line for each calibration curve, the concentration of manganese was calculated to be 2.5 µg/g honey, iron had a concentration of 2.7 µg/g honey, and zinc had a concentration of 1.0 µg/g honey. Using ASV, lead had a concentration of 5.25 ppm.
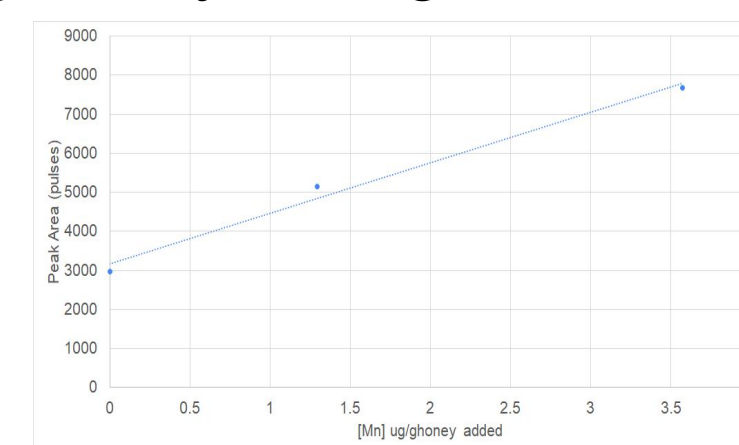

Figure 3. Calibration curve for Manganese comparing the concentration of honey added ([Mn], ug/g) to the peak area (pulses).
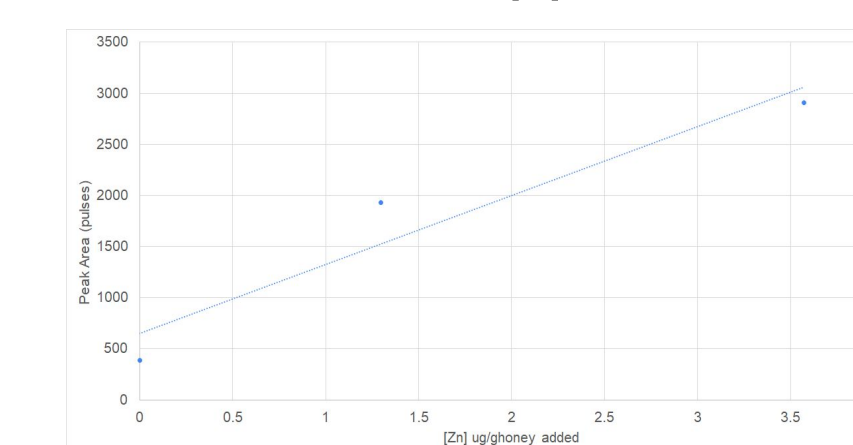

Figure 4. Calibration curve for Iron comparing the concentration to the peak area.
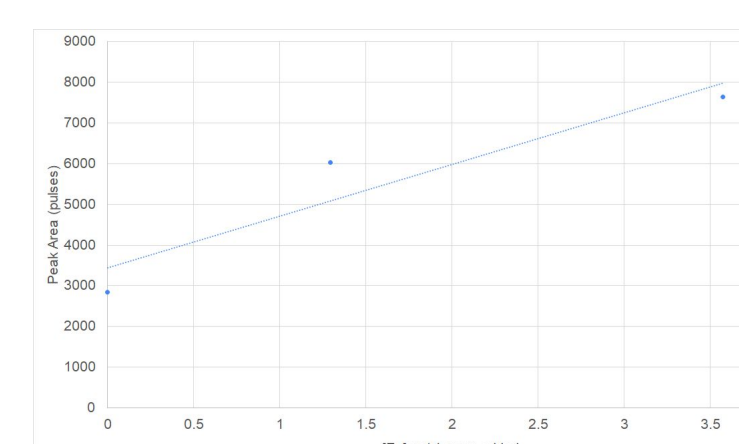

Figure 5. Calibration curve for zinc comparing the concentration to the peak area.
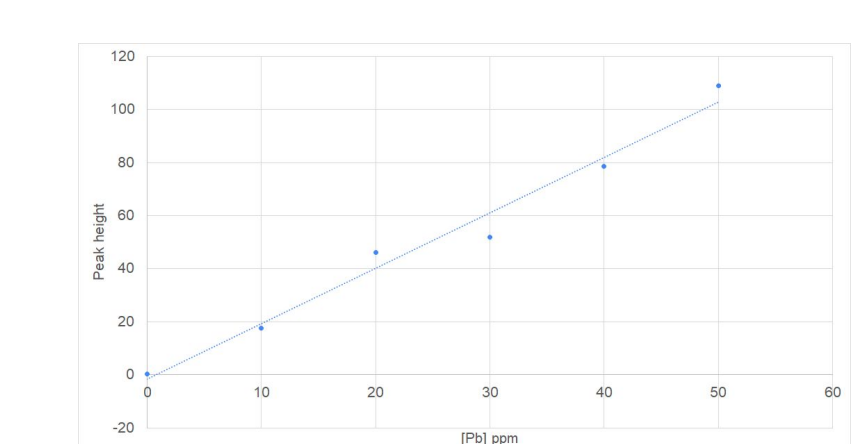

Figure 6. Calibration curve for lead comparing the concentration to the peak area.

Conclusions

- Issues with measuring certain elements using XRF methods
- Found in The Case study of the missing bees, this study supported the large amount of Mn found in honey samples.
- The study contained elevated levels of lead, low levels of zinc, and an average amount of iron.
- Because of the data found from this study, it would be likely that HMF would be catalyzed by the chosen samples of honey.

Future Directions

- High concentrations of other elements were detected in the honey samples
  - additional research should be conducted on these metals
- Alternative methods should be used for further investigation of honey contents for metals with varying weights
  - lead was not detected in these methods
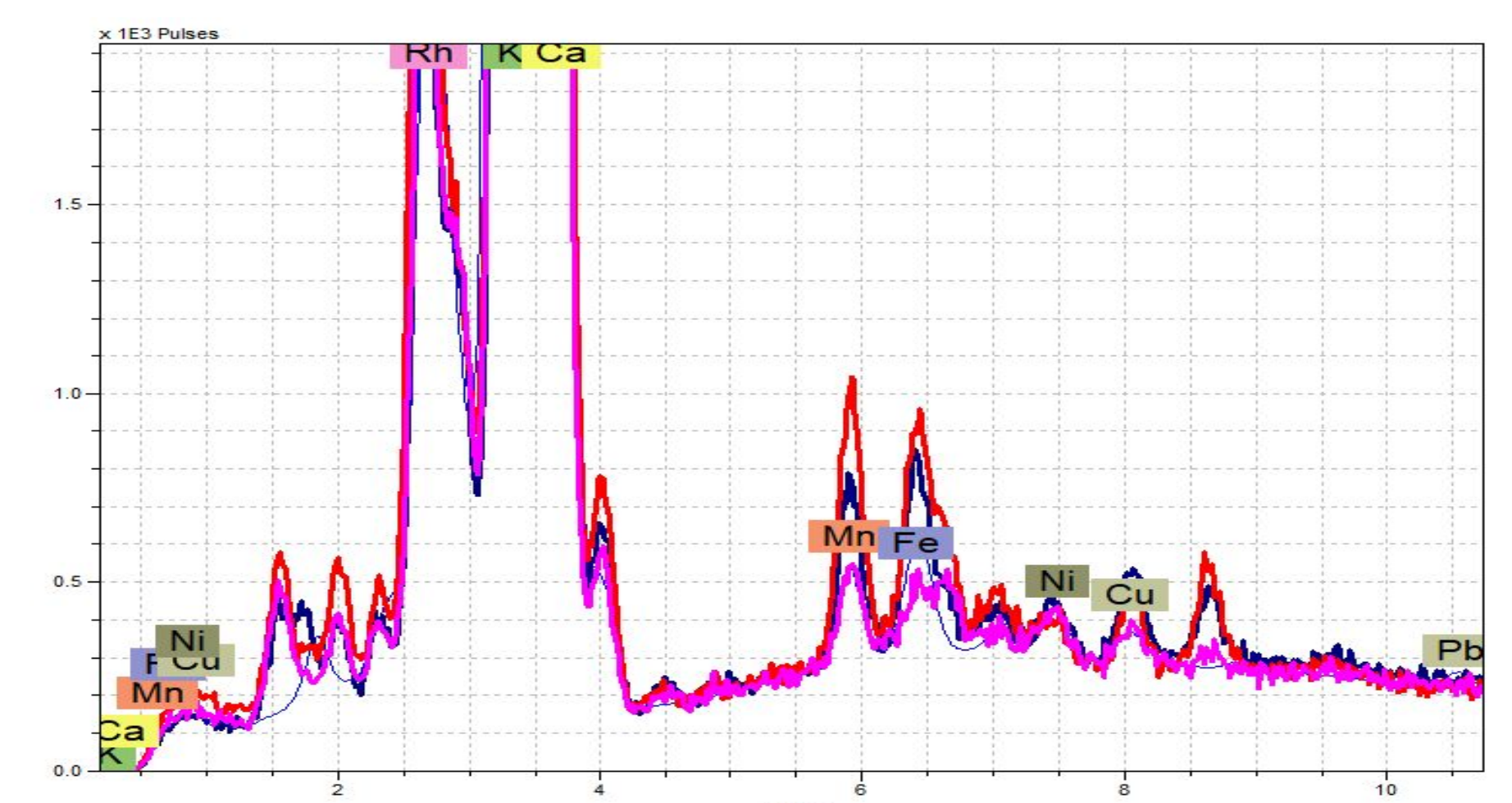- Be sure honey sample is fully dry to prevent overflow.
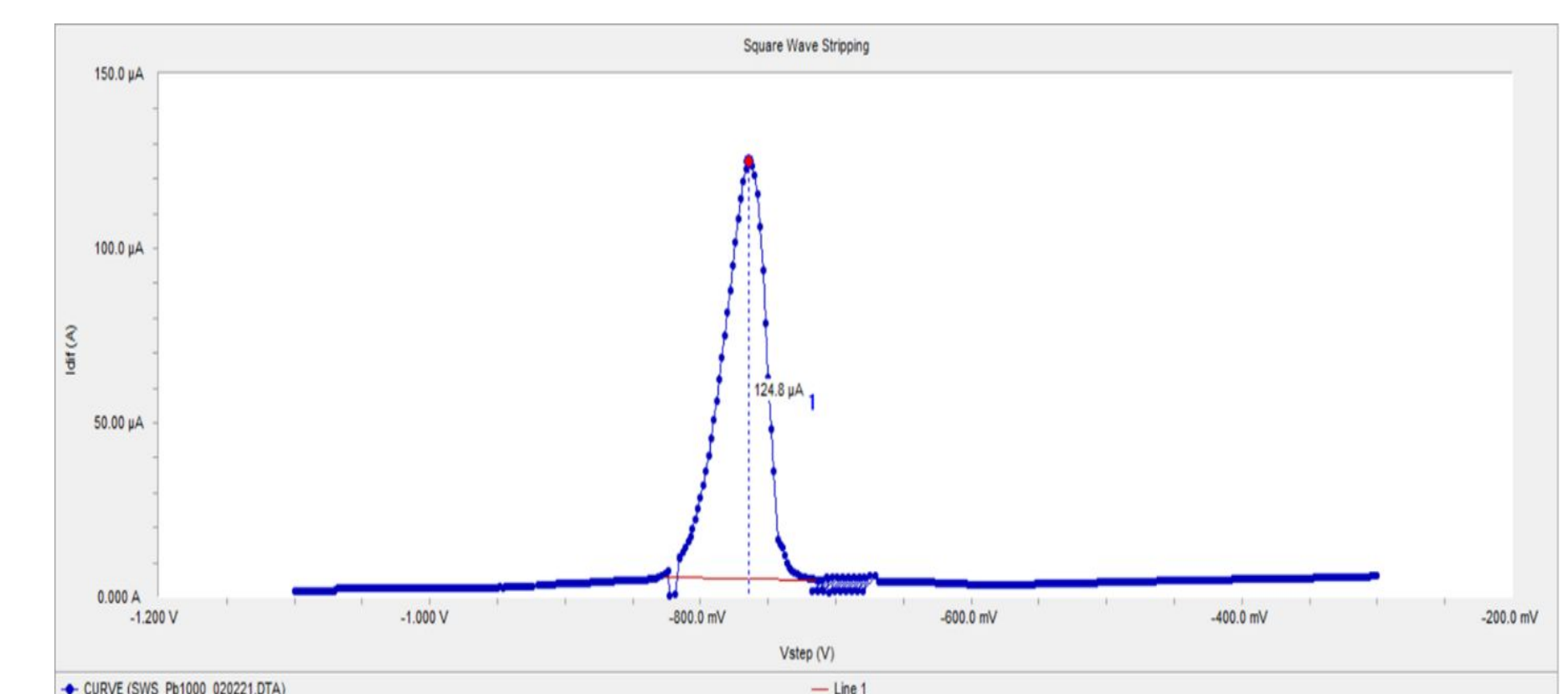

Figure 7. X-ray fluorescence spectrum.

Figure 8. Concentration of Pb in honey samples shown in voltammogram. Significant due to fluorescence spectroscopy could not detect any Pb.

References

1) Bohlsceid, j; Dinan. F. "The Case of the Missing Bees" *National Center for Case Studies.* 2) LeBlanc, B.W., et al. 2009. Formation of hydroxymethylfurfural in domestic high-fructose corn syrup and its toxicity to the honeybee (*Apis mellifera*). *J. of Ag. and Food Chem.* 57(16): 9369–9376. 3) Shao, Y.; Ding, Y.; Dai, J.; Long, Y.; Hu, Z. 2020. "Synthesis of 5-hydroxymethylfurfural from dehydration of biomass-derived glucose and fructose using supported metal catalysts." *Green Syn and Catalysts.* 4) "How does XRF work?" XRF Technology. *ThermoFisher Scientific* 5) Opoka, W.; Szlosarczyk, M.; Maslanka, A.; Piech, R.; Bas, B.; Wlodarczyk, E.; Krzek, J. 2013. "Optiization of method for zinc analysis in several bee products on renewable mercury film silver based electrode." *Acta Polonia Pharm.-Drug Res.* 70(6): 961-965.6)Shapla U. M.; Gan S. H., et al., 5-Hydroxymethylfurfural (HMF) levels in honey and other food products: effects on bees and human health, *NCBI*, 2018.