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Determination and Quantification of Lead Content in Mammut americanus Dentine Material by Anodic Stripping Voltammetry

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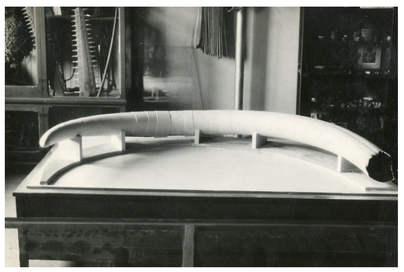
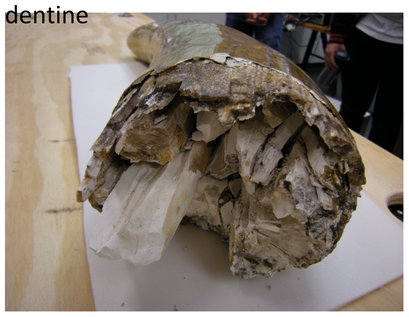
Background

A 120,000-200,000 year old mastodon tusk of species *Mammut americanus,* recovered from Hampton, Iowa in 1933 (right) was tested for lead using a lead test from Home Depot.[1] The lead test was returned positive, so Anodic Stripping Voltammetry (ASV) was undertaken to determine the concentration of lead in the dentine material of the tusk. The lead concentration is of interest because lead could affect both the health of the conservator and researchers and also inform about the diet of the mastodon. Tusk dentine material (left) functions similarly to human teeth, and studies have shown that 90% of lead in the human body concentrates in the hard tissues: skeleton and teeth.[2] Lead accumulation in teeth occurs because the calcium phosphate in teeth interacts with the stable Pb isotope, causing the calcium to be permanently replaced by the lead.[3] This enables teeth to be excellent records of the level of lead in the diet and environment of the organism.

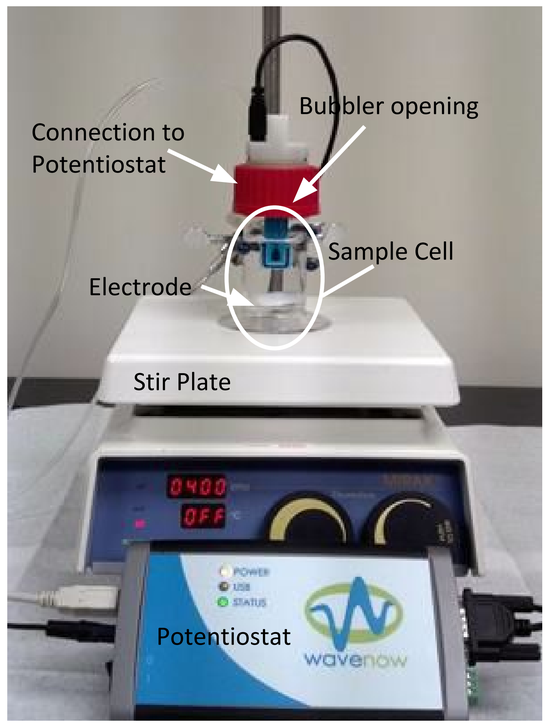




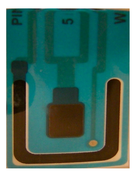
Importance of Lead

- Lead acts as a neurotoxin, and can bioaccumulate in the body[3]
- Potential lead exposure of the mastodon would most likely have come from its food sources
- Mastodons consumed vegetation
- Plants absorb lead from the soil they are grown in[4]
- The level of lead in the mastodon tusk will reveal information about both the diet of the mastodon and the environment in which it lived

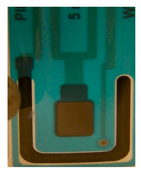
Instrumentation



Mercury Electrode



Pre-Deposition

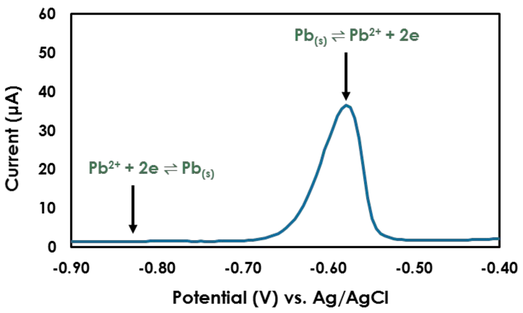


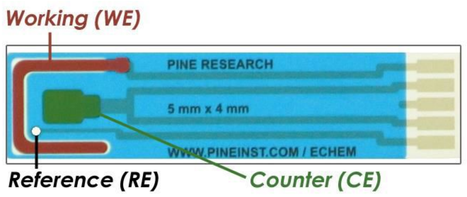
Post-Deposition

- Solid samples are dissolved in acid (nitric or glacial acetic)
- A buffer is typically added to the sample solution to control the pH[5]
- Mercury is coated on the electrode during a reductive deposition period (pre and post deposition shown above)
- The electrode is secured into the sample cell in a cap that also holds a pipette for N_2 bubbling and the connection to the potentiostat
- The sample cell is stirred during the deposition period
- Pb^{2+} is reduced and deposited at a Hg electrode, then oxidized and put back into solution while the current is recorded

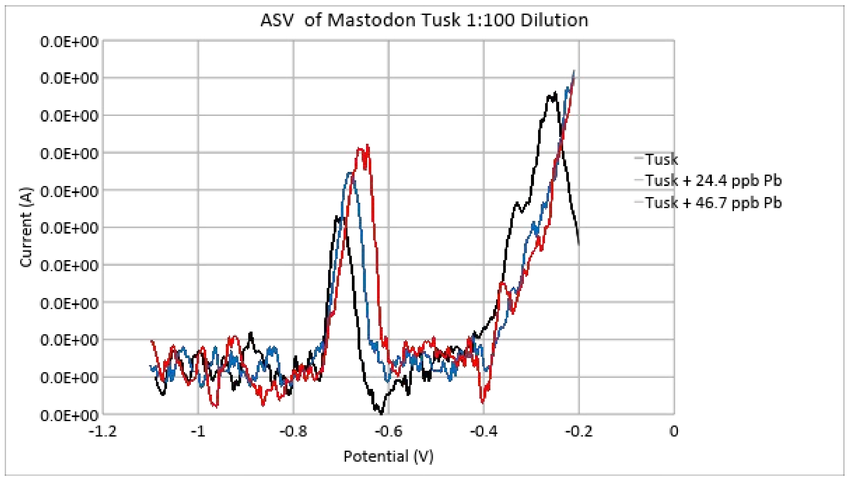
Methodology

- ASV is a highly selective technique that is widely used to determine lead content in liquids
- The technique uses three electrodes to make electrochemical measurements by ramping the electrode potential over time (right)
- Reaction takes place at working electrode
- The standard electrode contains an internal standard reference for cell potential
- The counter electrode balances changes in the cell's potential caused by changes at the working electrode
- High surface area to volume ratio increases mass transfer rate
- Ideal voltammograms of lead in water have little noise and show a clear lead peak (below)

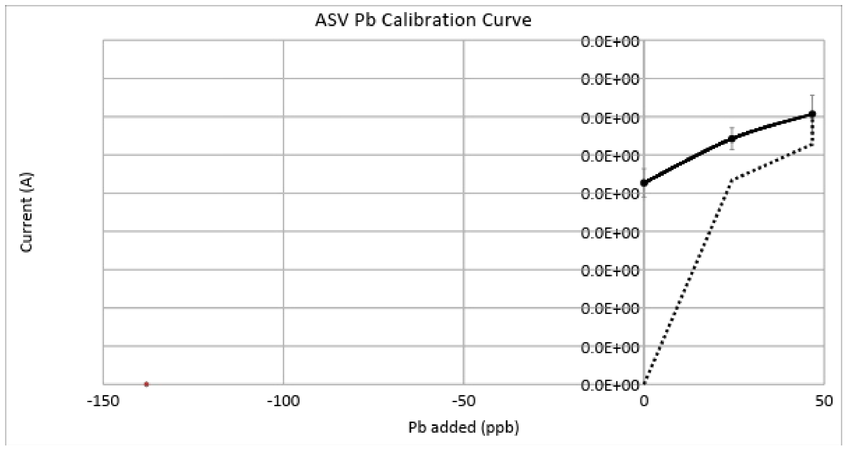




Results



- The lead peak can be seen around -0.7 V
- The large peak at -0.2 V is caused by matrix effects from the tusk material
- Noise can be seen along the baseline, and is averaged and represented as error below. The signal to noise ratio of the sample was ~14



- Based on the calibration curve, the concentration of lead in the dentine material was determined to be 1.4±0.1 parts per thousand (w/w)

Conclusions

- The concentration of lead in the dentine material was found to be 1.4±0.1 parts per thousand (w/w)
- Lead could not be detected using EDX, which indicates that the lead in the tusk is unevenly distributed
- The detectable presence of lead indicates that the mastodon lived in a relatively lead-enriched environment, though without values of lead in other tusks to compare to it cannot be determined if this is standard for the time and location
- The EPA limit in bare soil is 1.2 ppt, so the soil near where the tusk was removed should be checked for lead content[6]
- The lead content should not pose any imminent risks to those working on the tusk

Acknowledgements

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- Dr. Martin Chin for Potentiostat
- Dr. Joshua Sebree

References

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[2]Steenhout, A. (1982). Kinetics of Lead Storage in Teeth and Bones: An Epidemiologic Approach. Archives of Environmental Health: An International Journal, 37(4), pp.224-231.
[3]Sharon, I. (1988). The Significance of Teeth in Pollution Detection. Perspectives in Biology and Medicine, 32(1), pp.124-131.
[4]Hevesy, G. (1923). The Absorption and Translocation of Lead by Plants. Biochemical Journal, 17(4-5), pp.439-445.
[5]Pine Research. (2016). Highly Sensitive Electrochemical Determination of Lead in T Tap Water: Anodic Stripping Voltammetry with Disposable Screen Printed Carbon Electrodes. pp.1-5.
[6]Hazard Standards for Lead in Paint, Dust and Soil (TSCA Section 403) | US EPA https://www.epa.gov/lead/hazard-standards-lead-paint-dust-and-soil-tsca-section-403 (accessed Nov 15, 2017).