University of Northern Iowa

UNI ScholarWorks

12-2017

Quantitative Evaluation of Heavy Metals in the Mastodon Tusk Ivory by Atomic Absorption Spectroscopy

Dmytro V. Kravchuck
University of Northern Iowa

Linda L. Wilson
University of Northern Iowa

Let us know how access to this document benefits you

Recommended Citation

Quantitative Evaluation of Heavy Metals in the Mastodon Tusk Ivory by Atomic Absorption Spectroscopy

Dmytro V. Kravchuk*, Linda L. Wilson

Department of Chemistry and Biochemistry, University of Northern Iowa, Cedar Falls, IA 50613

Introduction

One of the most important objects in the University of Northern Iowa Museum collection is the *Mammut Americanum* (American Mastodon) tusk, which was originally found in 1933 in a sand pit south of Hampton, Iowa. Since then, severe mechanical and chemical damage was done to the tusk in attempts of restoration and storage, as shown in Figure 1. In order to address these problems, the UNI Museum was awarded a Roy J. Carver Charitable Trust Grant to restore and preserve the American Mastodon tusk.[1]

Figure 2: Heavily damaged mastodon tusk[1]

The purpose of the project is quantitative determination of the heavy metal content in the core of the tusk ivory by atomic absorption spectroscopy. Information about trace heavy metals found in mastodon ivory, will help to draw conclusions about the dietary habits and the environment of the mastodon.[2] In addition, since heavy metals are toxic even low concentrations, the content of the heavy metals in ivory is needed to be known, in order to avoid the hazard of heavy metal poisoning for the scientists working on further restoration of the tusk.[3]

Technical Approach

The technique selected for the experimental setup was atomic absorption spectroscopy (AAS). The Perkin Elmer AAnalyst 200 Atomic Absorption spectrometer was used for the experiments described in this project. The instrument was equipped with Ca, Pb, Cd, Cr hollow cathode lamps, which serve as an element-specific line source. The AAS instrument was chosen due to its high sensitivity and low limits of detection for the metals of interest, as shown in Table 1 below.

Element	LOD of the AAS (ppm)	Wavelengths λ (nm)
Ca	**0.0015**	**422.67**
Cd	**0.0008**	**228.8**
Cr	**0.003**	**357.87**
Pb	**0.015**	**283.31**

Table 1: Limits of detection of Ca, Cd, Cr and Pb for the Perkin Elmer AAnalyst 200 spectrometer [4]

The flowchart of the instrument is shown in Figure 2 and follows the following steps[5]:

- Sample is introduced through the capillary tube from the solution
- Sample matrix is nebulized, converting it to the aerosol M
- Mist is mixed with acetylene and oxygen in the mixing chamber and swept into a Bunsen burner flame
- Flame evaporates the solvent and the sample is thermally decomposed into an atomic gas
- Hollow cathode lamp, which is doped with the specific metal of interest, emits the single wavelength of light specific to that element of interest
- Light emitted by the hollow cathode lamp goes through the flame that contains the atomized sample
- If present, the metal of interest absorbs the light transmitted through the flame
- Detector determines the percent transmittance or absorbance of the sample
- Absorbance is used to determine the concentration of the metal of interest in the sample
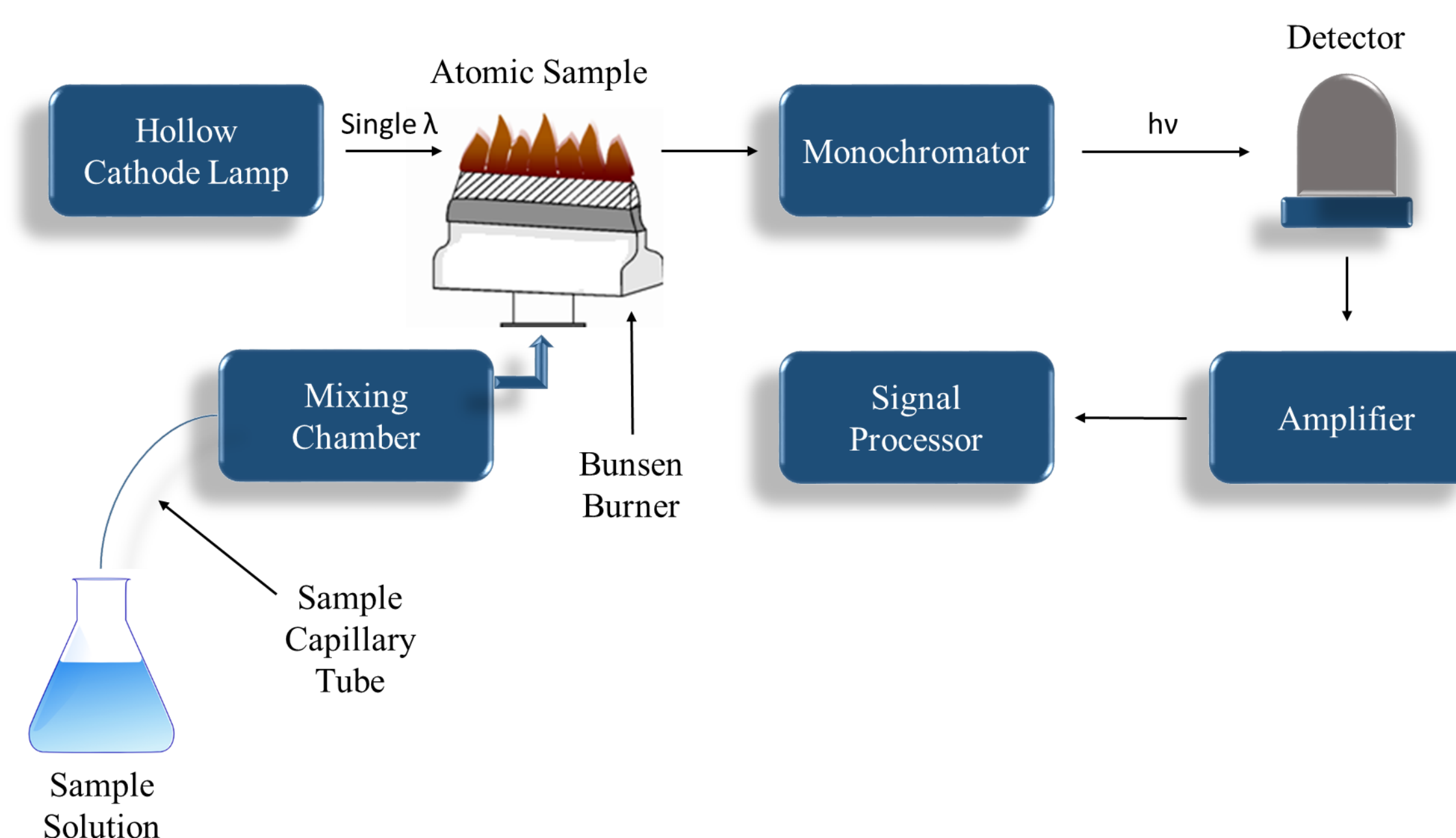
Technical Approach

Figure 2: The block scheme of the atomic absorption spectrometer setup

Experimental Procedure

- 1 gram of the tusk was dissolved in 100 ml volumetric flask in the mixture of glacial acetic and concentrated nitric acid overnight
- The acidic mixture was neutralized using 1M NaOH and NaOAc
- Three solutions of the tusk were made: original 10000 ppm tusk solution, 200 ppm tusk solution, 20 ppm tusk solution
- Cd standard (Aldrich Chemical Company 1010 ppm); Cr(III) standard (Aldrich Chemical Company 1005 ppm); lead acetate and calcium nitrate were used to make 5-7 standard solutions
- The standards were run on the Perkin Elmer AAnalyst 200 spectrometer, along with tusk solutions of various concentrations, as shown in Figure 3.

Figure 3: 10000ppm tusk solution being run on the AAS instrument

Data Analysis

- Calibration curves obtained from Ca, Cd, Cr, Pb STD solutions, as shown in Figure 4, were linearly fit to get the Beer's law plot
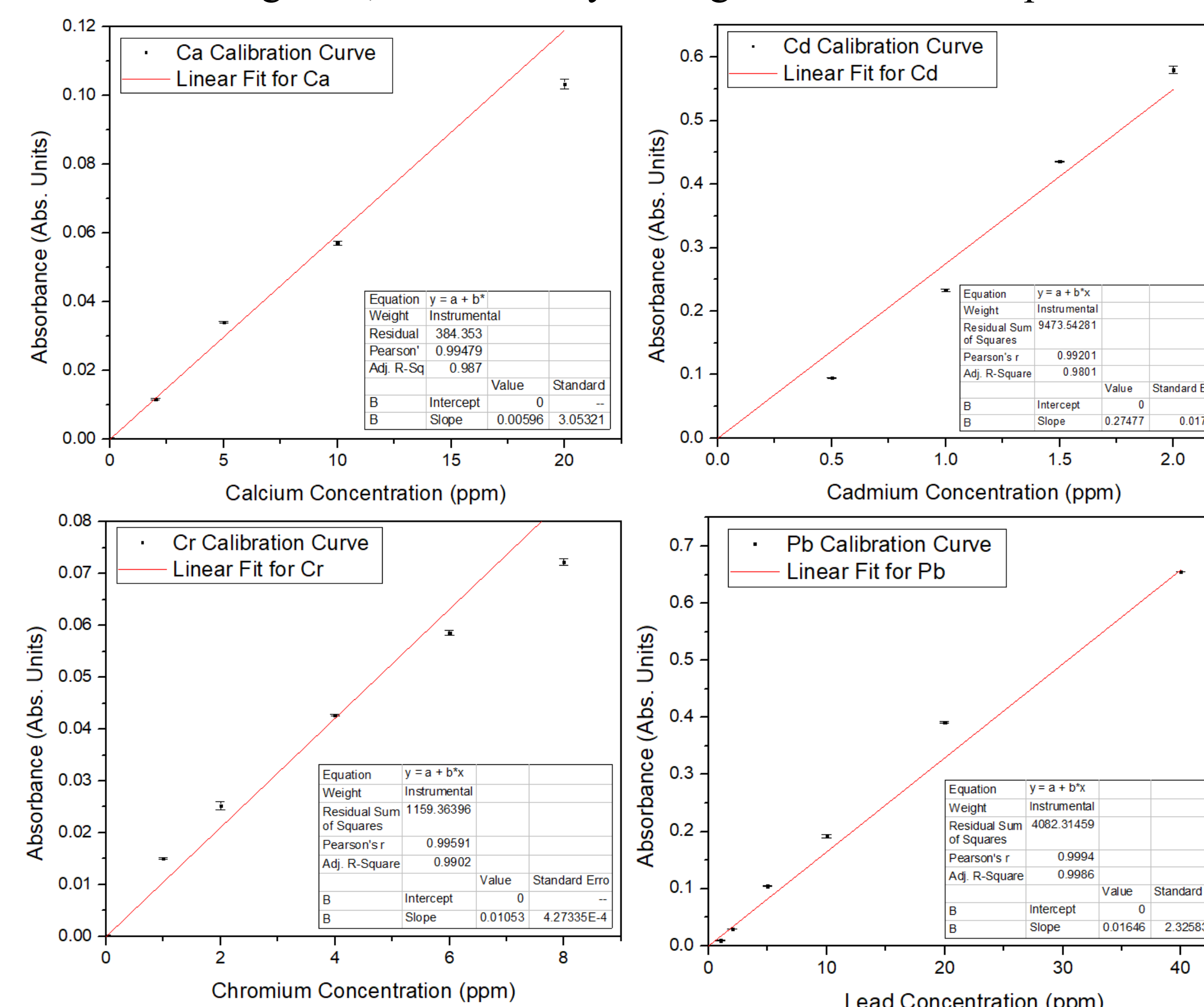

Figure 4: Calibration curves for calcium (Ca), cadmium (Cd), Chromium (Cr), and lead (Pb).

- According to Beer's law, shown in Equation 1 below, where A is absorbance, ε is molar absorptivity, l is the pathlength of the sample holder and [C] is concentration, absorbance is directly proportional to the concentration of the element of the interest[5].

Equation 1
$$A = \varepsilon l [C]$$

Data Analysis

- Tusk solutions were analyzed according to the calibration curves and the Beer's law equation, results are shown in Table 3 below.

Metal	Conc. of the Tusk (ppm)	Absorbance (Abs. Units)	Concentration of the M (ppm)	M in the Tusk
Ca	20	0.129 ± 0.001	24.1 ± 0.3	$120 \pm 1\%$
Cd	10000	0.009 ± 0.002	0.035 ± 0.002	3.5 ± 0.2 ppm
Cr	10000	-0.004 ± 0.002	-0.4 ± 0.2	-40 ± 20 ppm
Pb	20	0.012 ± 0.009	0.7 ± 0.5	$3.5 \pm 2.5\%$

Table 3 : Metal concentrations and percentage per gram of tusk

Discussion and Conclusions

- Complex matrix complicated the analysis of the data. A high concentration of Ca in the matrix caused inconclusive results for the amounts of Ca and Cr in the tusk. The negative amount of Cr can be explained by the emission spectra of Ca and Cr, shown in Figure 5.
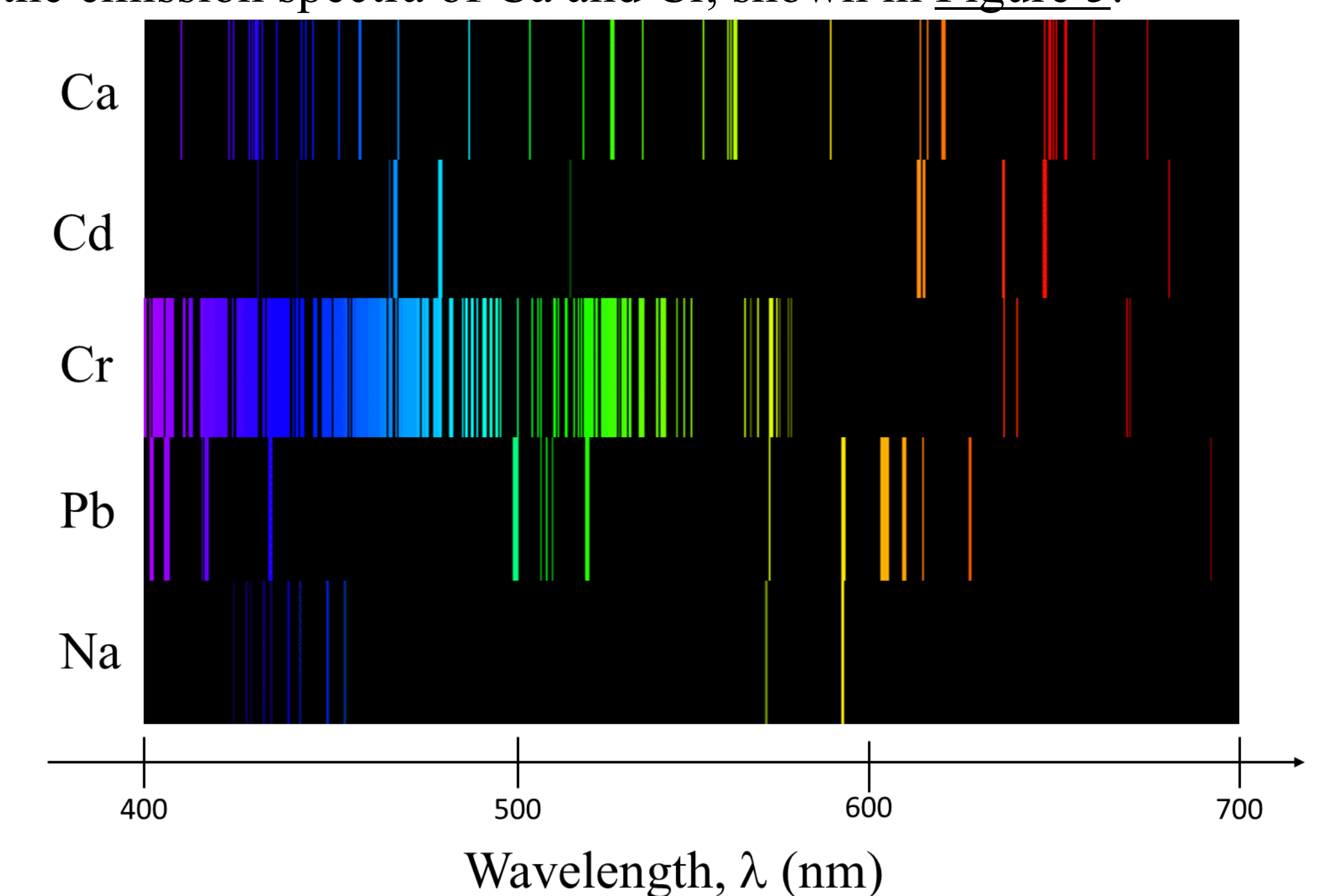

Figure 5: Emission spectra of metals in the studied matrix[6]

- High concentration of Ca resulted in a broader band at 422 nm, which caused the amount of Cr to show up as a negative number. Thus both the value of Ca and the value of Cr are inconclusive.
- Results showed a high percentage of Pb in the sample. However, the results can not be considered statistically significant due to a low signal to noise ratio. This could have been caused by the overlap of the Cr and Pb emission bands.
- The amount of Cd in the tusk 3.5 ppm is below the EPA Standard in soil, which sets the upper limit of Cd in the soil to 85 ppm[7]
- Overall, the results of Ca, Cr, and Pb are inconclusive and further research is needed to determined the amount of each metal in the tusk material. Adequate personal protective equipment is needed to work on the restoration of the tusk.

Acknowledgements and References

References

1. Nathan Arndt, J. C., Preserving the Past: Scientific Study, Conservation, and Interpretation of the Mammut Americanum (American Mastodon). 2016.
2. Safaa Sabri Najim*, M. A. A., Dental Erosion by Beverages and Determination of Trace Elements in Teeth by Atomic Absorption Spectrometry *American Journal of Analytical Chemistry* **2016**, 548-555
3. Duruibe, J. O., Ogwuegbu, M. O. C.and Egwurugwu, J. N., Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences* **2007**, *Vol. 2*, 112-118.
4. PerkinElmer, A Guide to Selecting the Appropriate Technique and System. Inc., P., Ed. Waltham, MA, 2011.
5. Robert Granger, H. Y., Jill Granger, Karl Sienerth, Atomic Absorption Spectroscopy. In *Instrumental Analysis*, 1 ed.; Oxford University Press: New York, 2016; pp 208-242.
6. Jircitano, Alan J. Periodic Table, chemistry.bd.psu.edu/jircitano/periodic4.html.
7. "Environmental Health and Medicine Education." Centers for Disease Control and Prevention, Centers for Disease Control and Prevention, www.atsdr.cdc.gov/csem/csem.asp?csem=6&po=7.