Effect of Temperature Variation on LIBS Spectra of Molten Salts

Cynthia Hanson and Supathorn Phongikaroon
Nuclear Engineering Program, University of Idaho

Jeremy J. Hatch and Jill R. Scott
Interfacial Chemistry, Idaho National Laboratory

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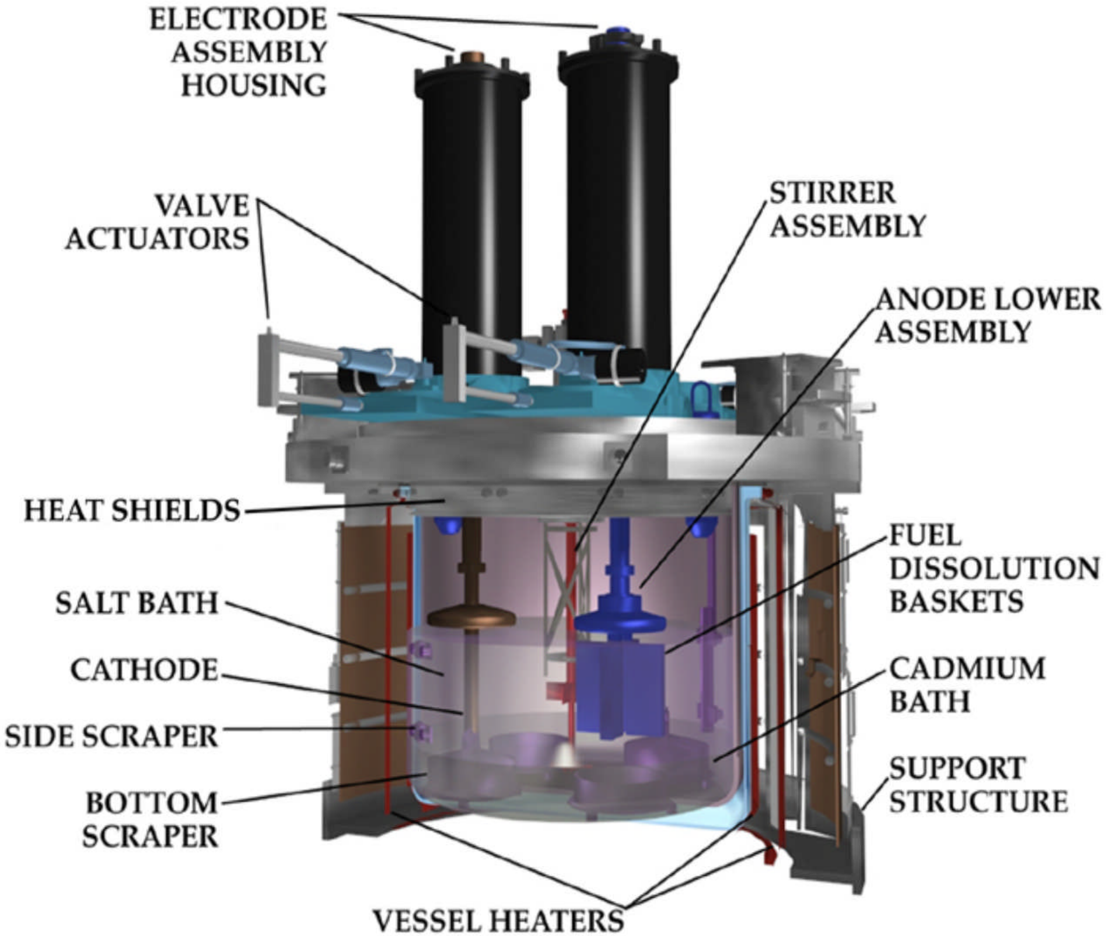
Agenda

- Mark-IV Electrorefiner
- Motivation
- Overview of LIBS (Laser-induced Breakdown Spectroscopy)
- Project Objective
- Experimental Set-up and Method Development
- Results
- Summary and Future Work

Mark-IV Electrorefiner



- Processes used nuclear fuel (UNF)
- Uranium from UNF is electrochemically transferred through the salt forming deposits on the cathode
- Build up of fission products, transuranics, etc. inhibits efficiency and creates liabilities

Motivation

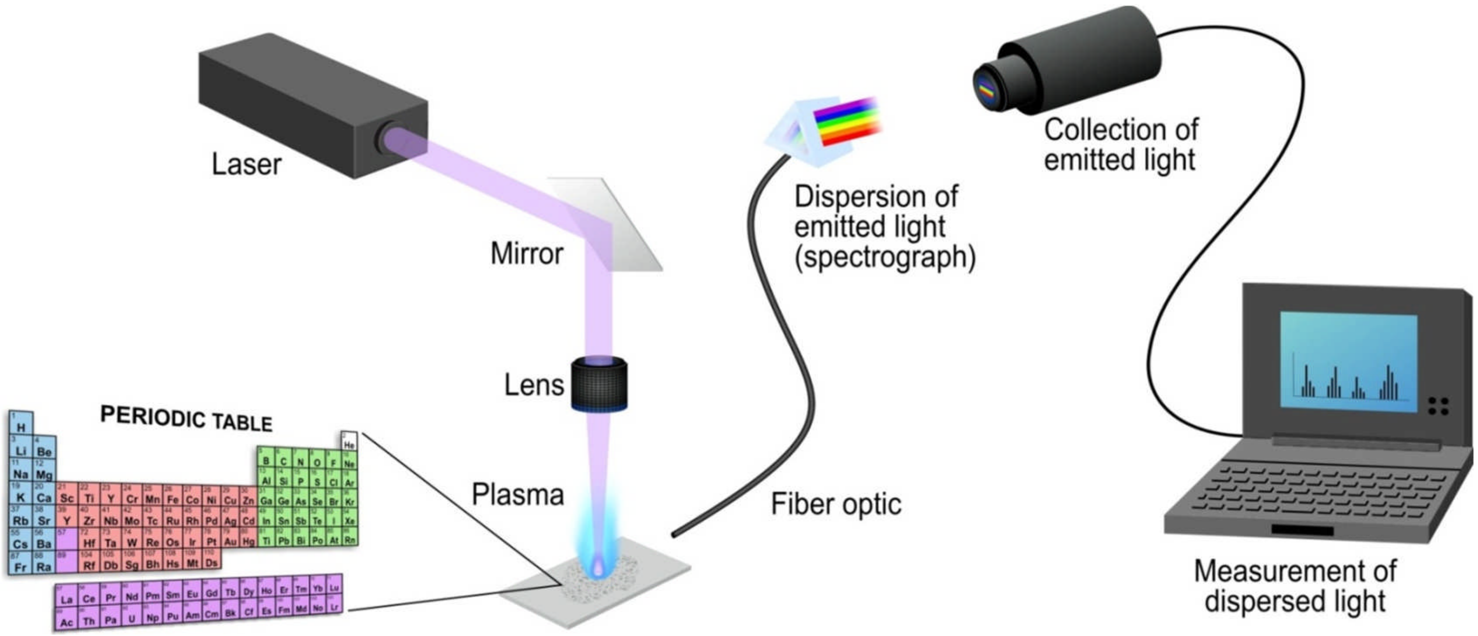
- Optimize operating conditions
- Material accountability and safeguards

Challenge for in-situ Electrorefiner Analysis

- No current method for real time analysis of salt
- 500 °C operating temperature inside electrorefiner
- Radioactive environment

Possible Solution

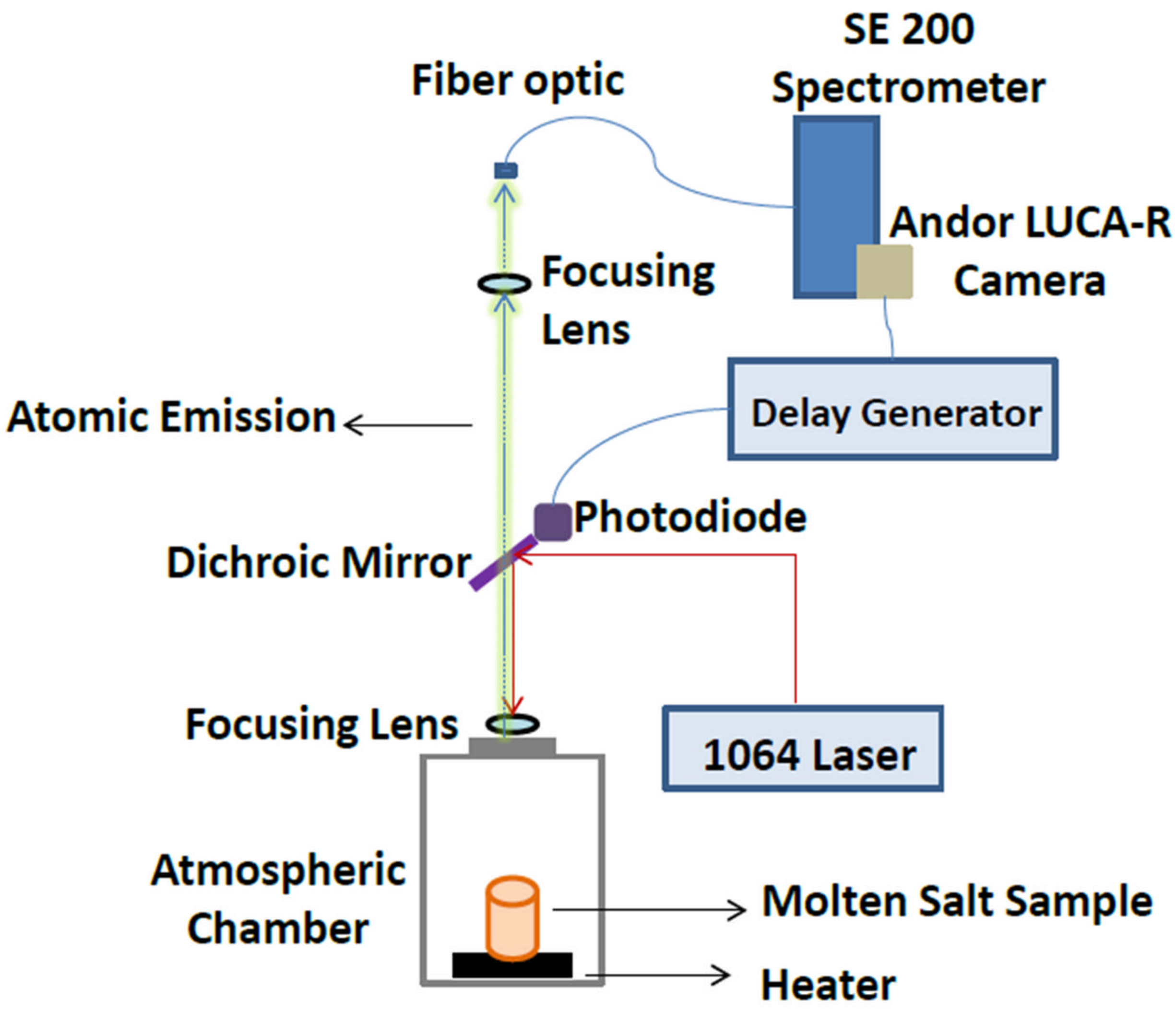
- Laser-Induced Breakdown Spectroscopy
  - No sample preparation
  - Real time
  - Performed with fiber optics

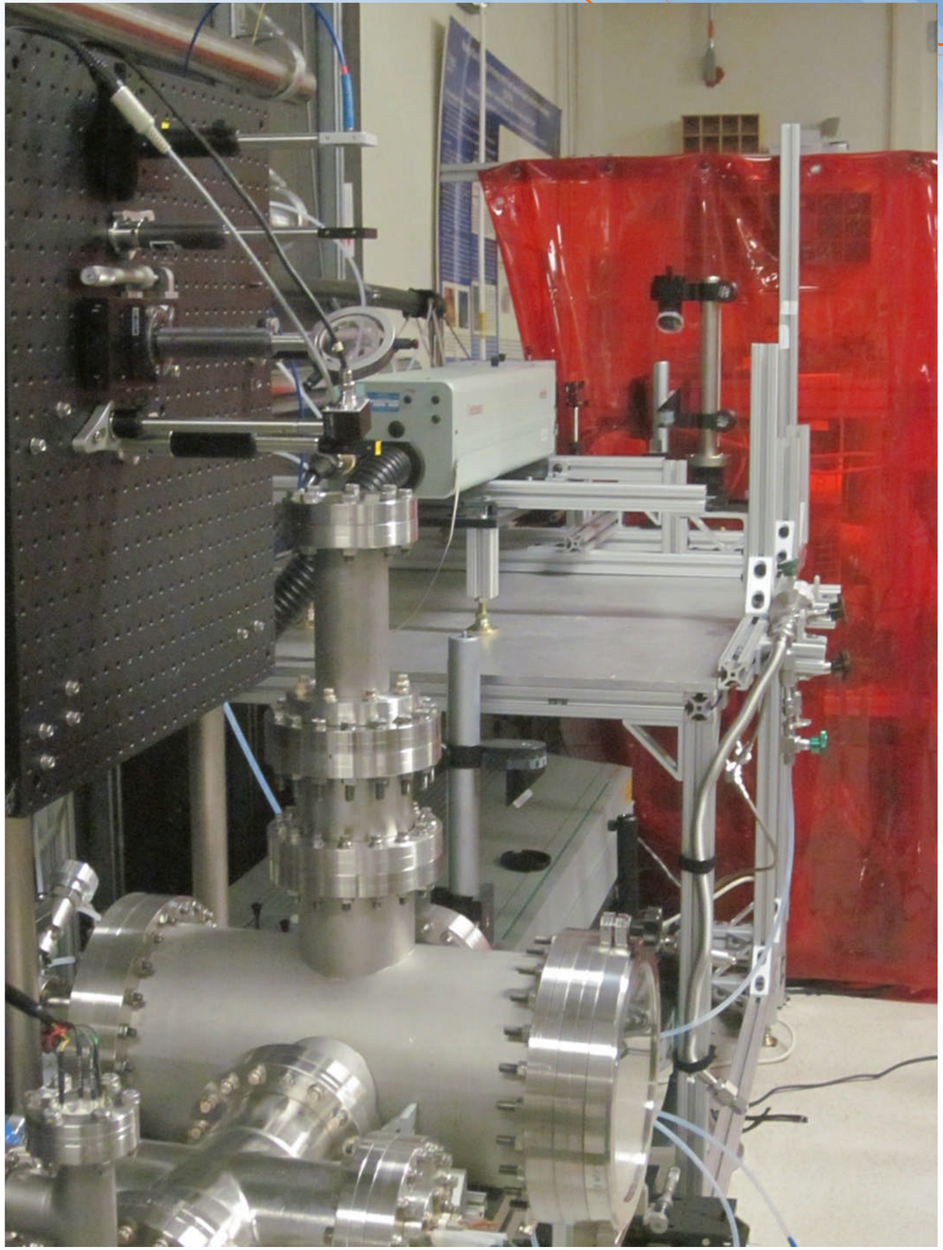


Objectives

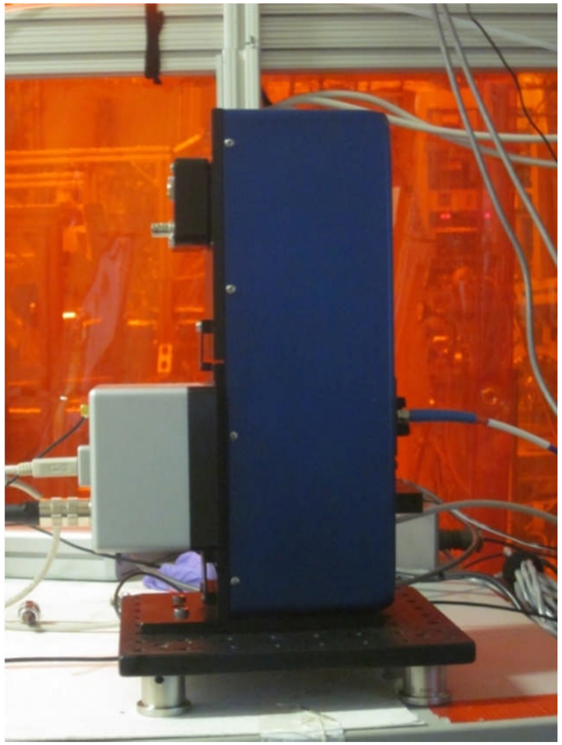
- Build a system to accommodate the experiment
  - Incorporating fiber optic collection system
- Determine a method to create a calibration curve
- Acquire calibration curves for $CeCl_3$ in molten LiCl-KCl
- Identify changes in spectra as temperature varies from 300–500°C with 50 degree increments

Experimental Set-up





- Continuum Surelite I Nd:YAG Laser
- SE 200 Echelle Spectrograph
- Andor LUCA-R EMCCD Camera

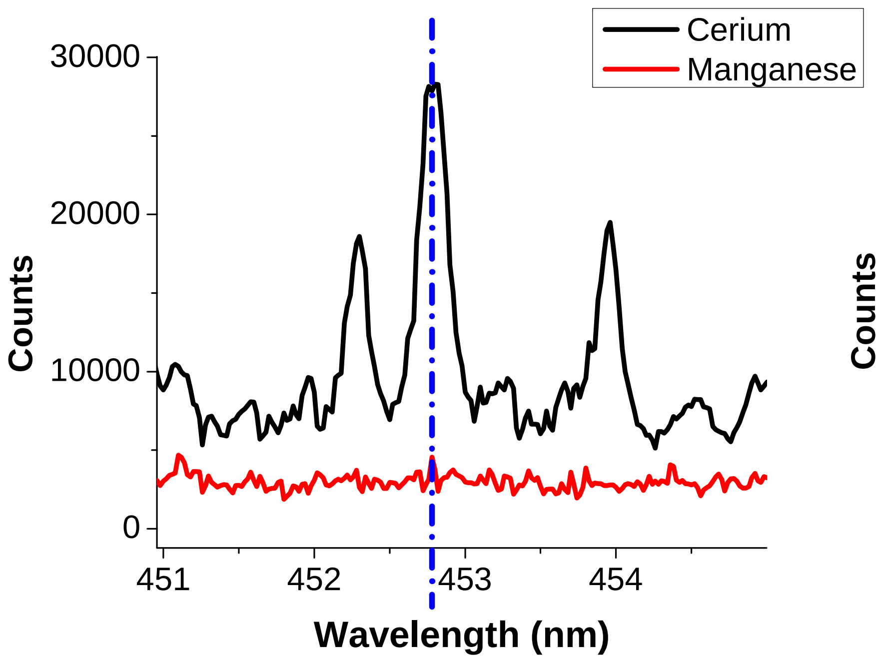


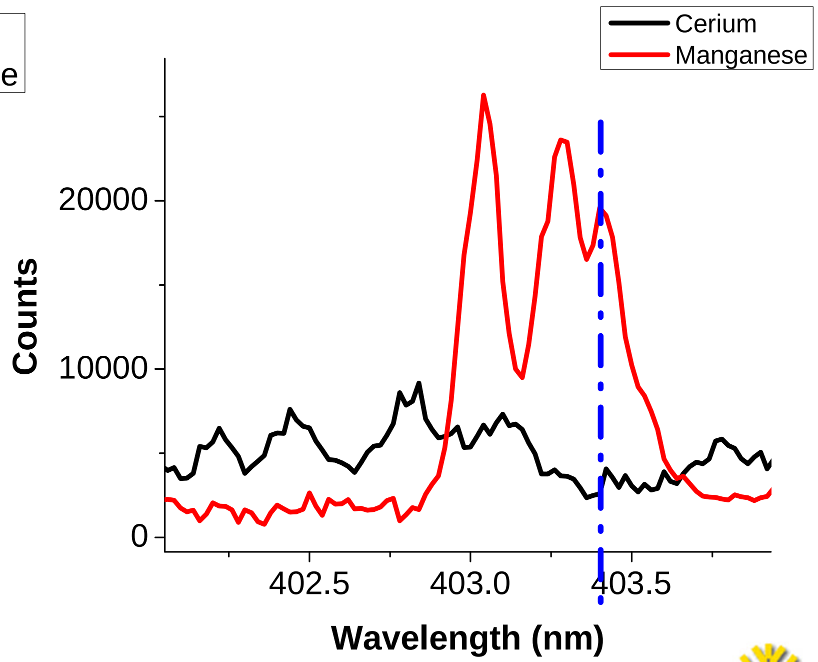
Calibration Scheme

- Internal Standard
  - Calibration based on peak ratios rather than absolute peak intensity or area
  - Avoid determining baseline
  - Avoid spectral changes due to laser energy fluctuations

Wavelength Selection

- Ce 452.74 nm
  - Pu 453.63 nm
- Mn 403.44 nm
  - U 409.01 nm





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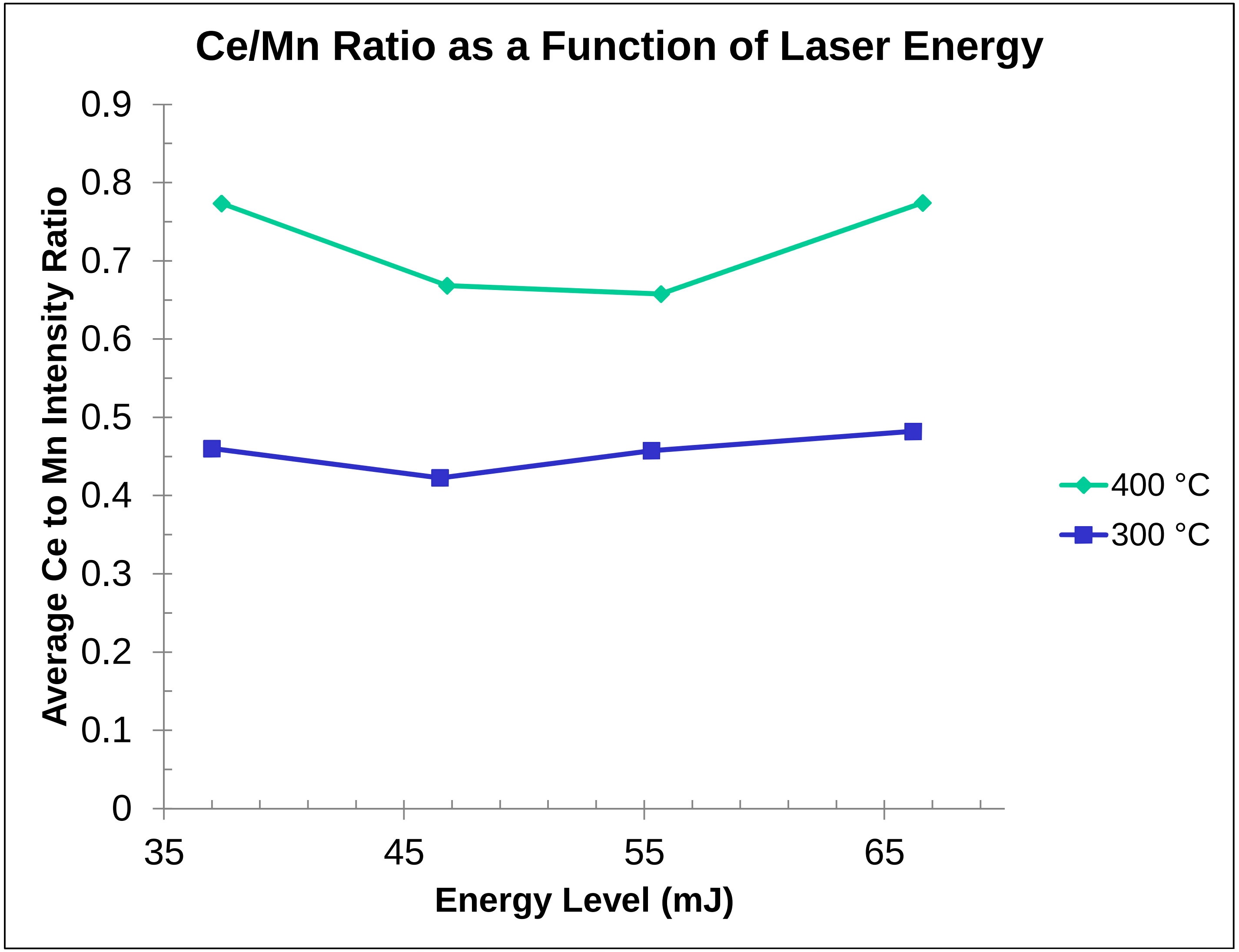
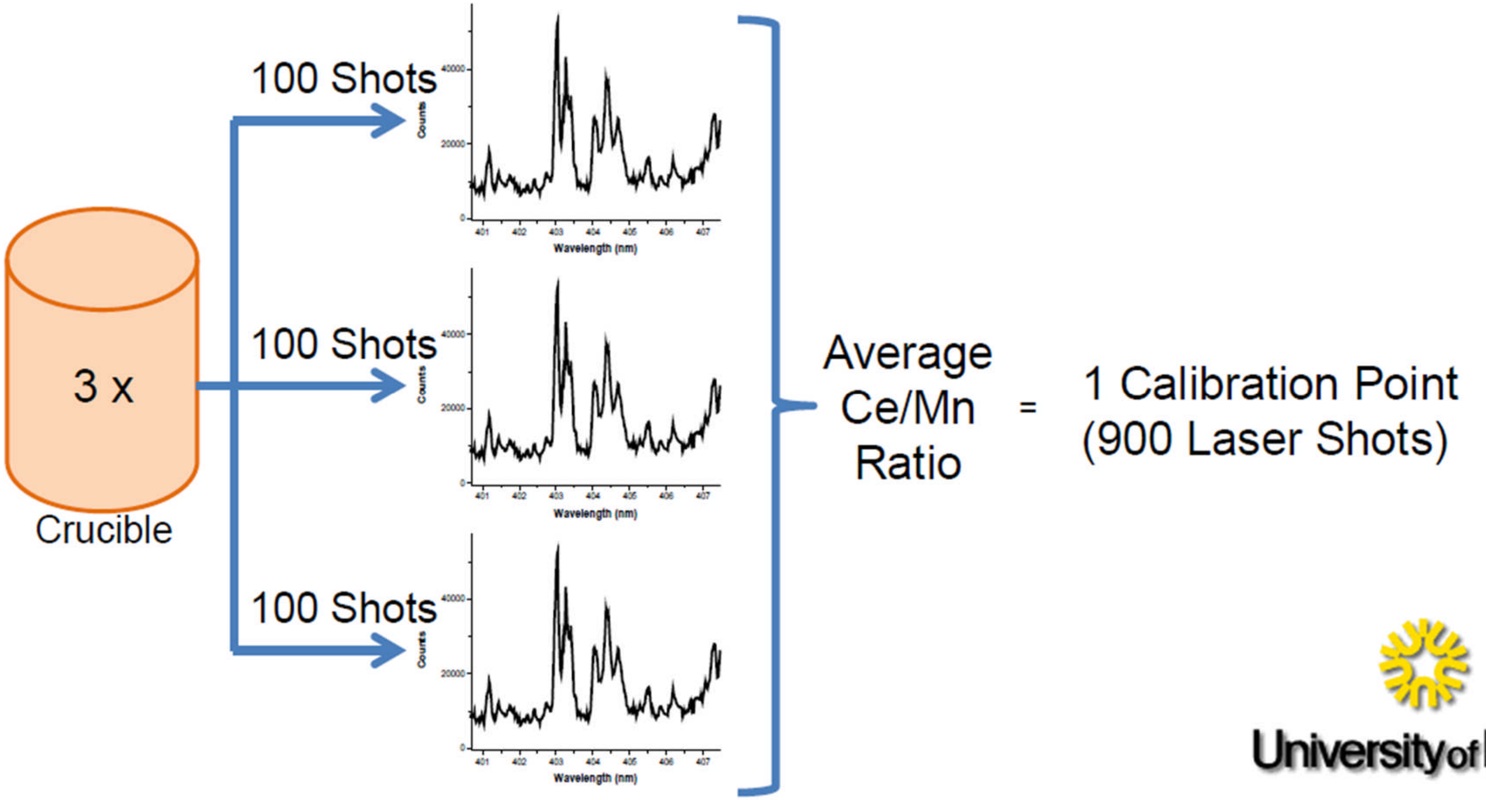
Effect of Laser Energy



Sample Preparation

- 65/35 mol% LiCl/KCl (~400 °C melting point)
- Five Concentration Points for Ce (0.1, 0.3, 0.5, 0.8,1.0 wt%)
- Internal standard of Mn (~0.44 wt%)

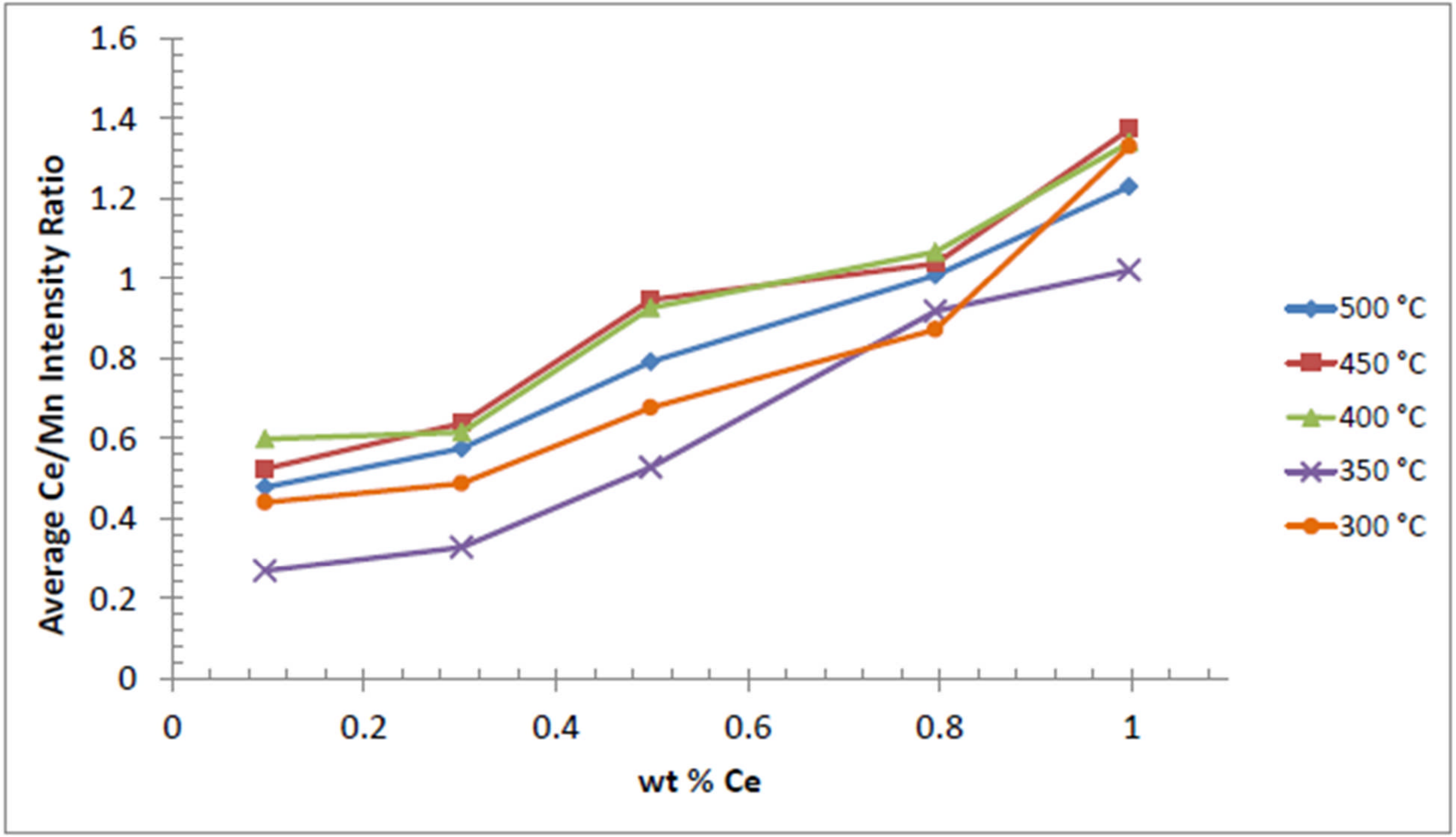
5 g Sample



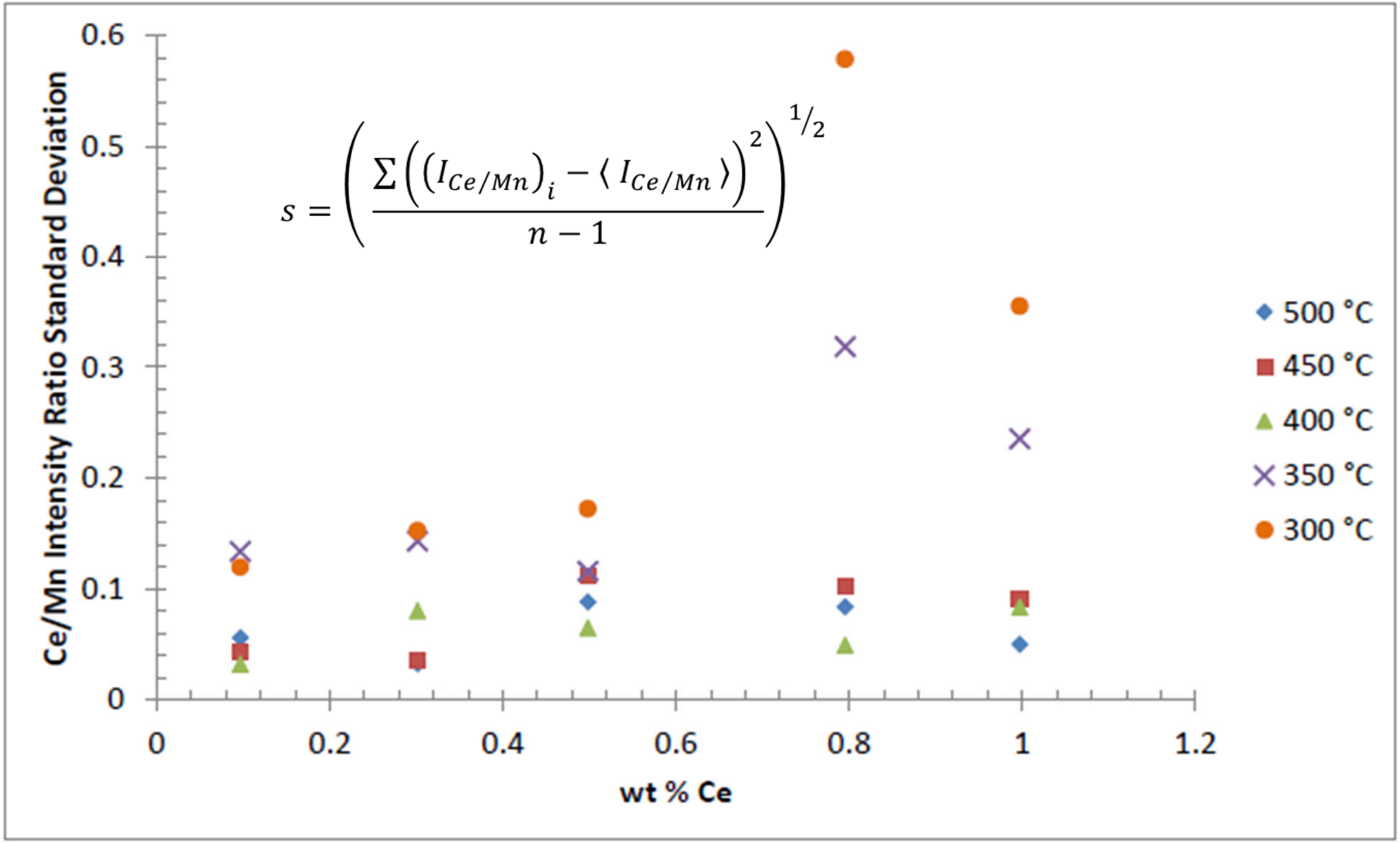
Sample Preparation

- Samples prepared in a glovebox
- Transferred to atmospheric chamber exposing to air
- Sample heated to ~500 °C
- Vacuum pulled to ~10^{-3} Torr backfilled with argon repeated once
- Spectra collected at 50 degree increments between 300-500 °C

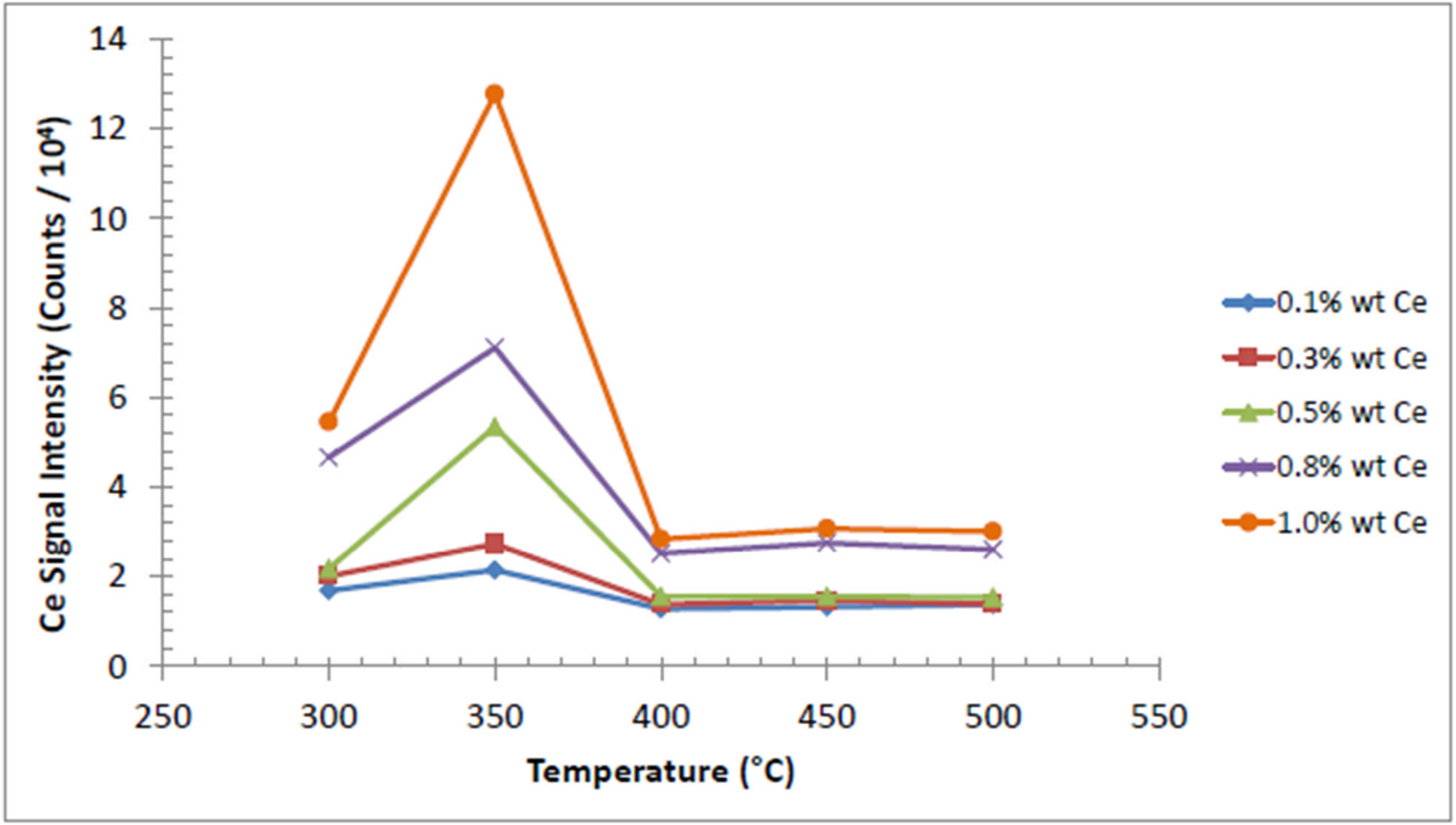
Ce Calibration Curves at Various Temperatures



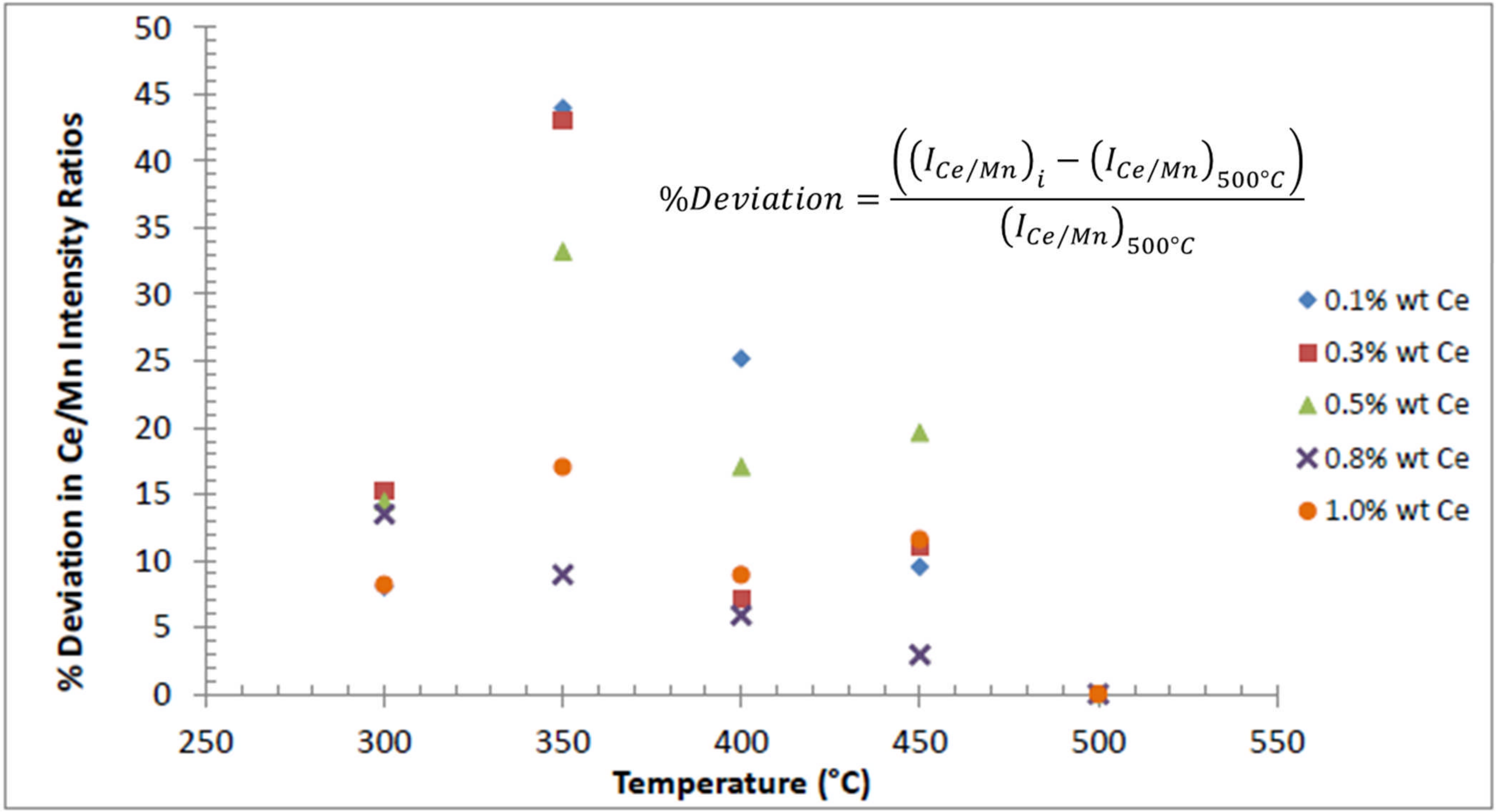
Standard Deviation at Various Temperatures



Ce Signal Intensity as a Function of Temperature at Varying % wt Ce



%Deviation from 500 C line at Various Concentrations



Summary

- Calibration curves indicate Ce/Mn ratios are affected by temperature
- Signal intensity is it's at 350 °C but has the lowest Ce/Mn intensity ratio
- Ce/Mn ratios are not significantly affected by laser energy
- Higher temperature regimes (i.e., molten phase) have the least Ce/Mn ratio variance between samples
- As Ce wt% increases, the variations decrease between liquid and solid samples

Future Work

- Incorporate dual pulse LIBS system
- Improve light collection system
- Perform work on other species

Acknowledgements

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  - Timothy R. McJunkin

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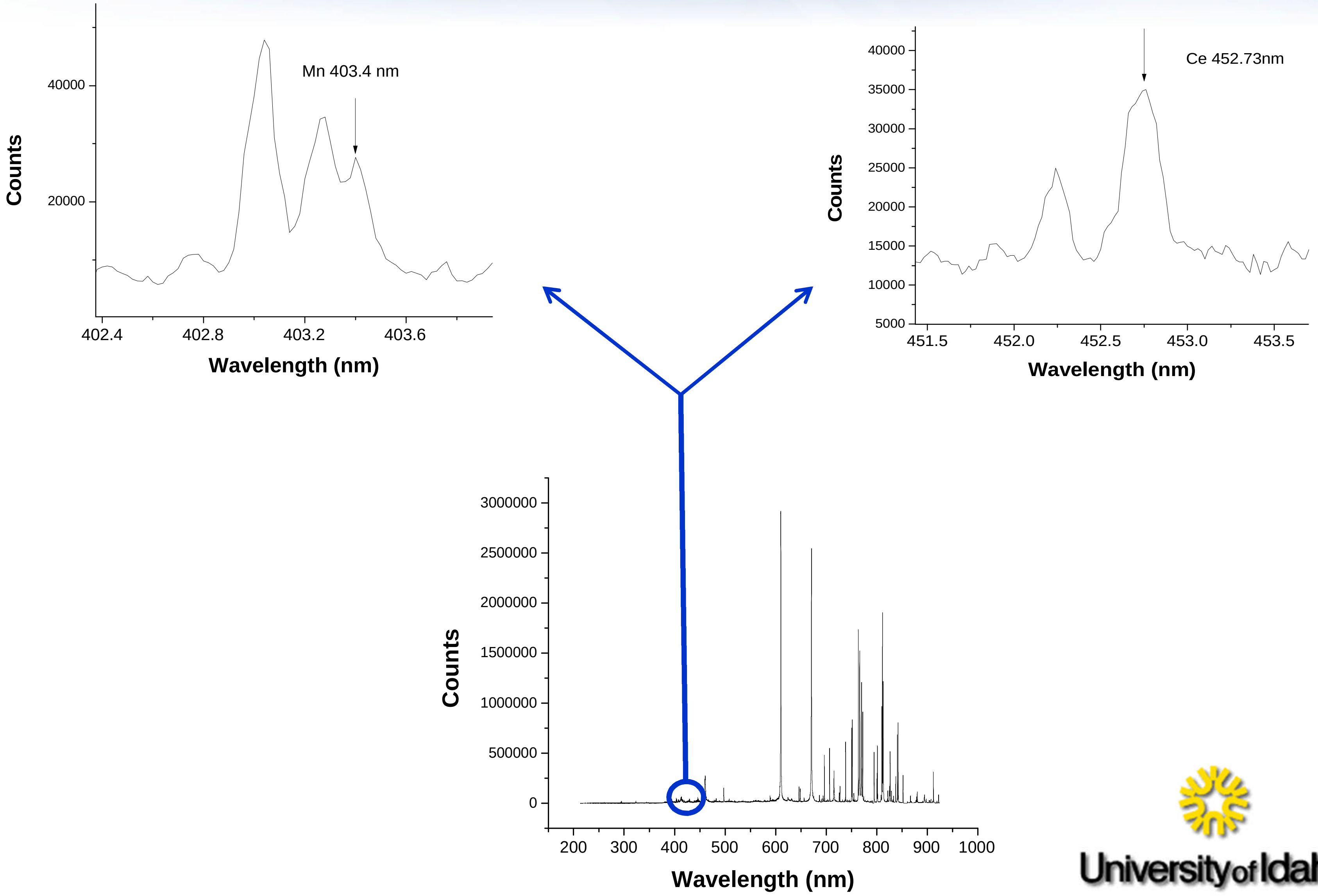
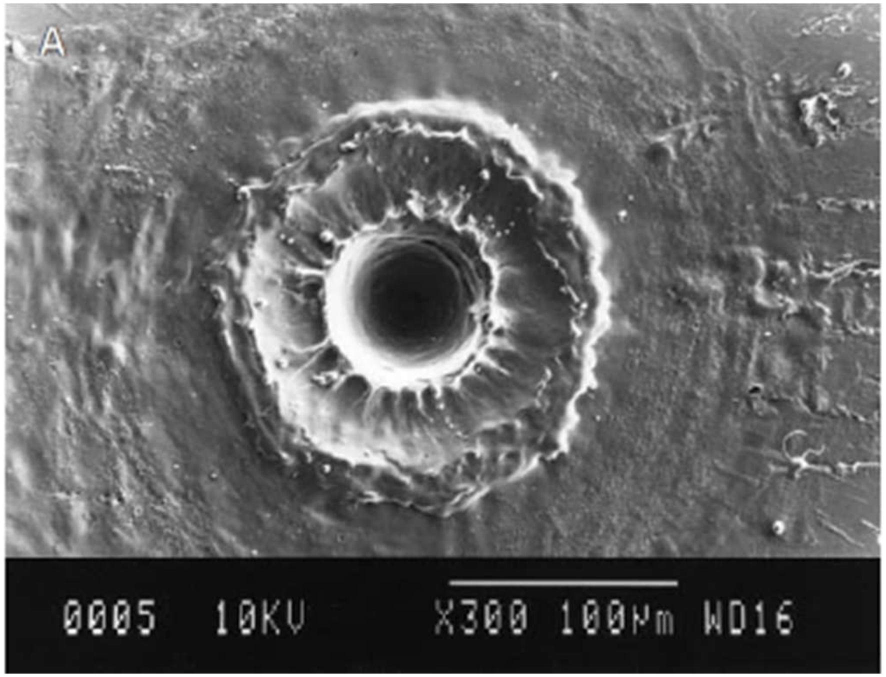
Questions?



Counts
40000
20000
402.4
402.8
403.2
403.6
Wavelength (nm)
Mn 403.4 nm
Counts
40000
35000
30000
25000
20000
15000
10000
5000
451.5
452.0
452.5
453.0
453.5
Wavelength (nm)
Ce 452.73nm
Counts
3000000
2500000
2000000
1500000
1000000
500000
0
200
300
400
500
600
700
800
900
1000
Wavelength (nm)

Ce wt %	LiCl wt %	KCl wt %	$CeCl_3$ wt %	$MnCl_2$ wt %
0.1	50.81	48.03	0.16	1.00
0.3	50.47	47.99	0.53	1.00
0.5	50.14	47.99	0.87	1.00
0.8	49.59	48.02	1.39	1.00
1.0	49.24	48.00	1.76	1.01



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Double Pulse

- Babushok, V. I., F. C. DeLucia, et al. (2006). "Double pulse laser ablation and plasma: Laser induced breakdown spectroscopy signal enhancement." Spectrochimica Acta Part B-Atomic Spectroscopy **61**(9): 999-1014.

CF-LIBS Method

$$\overline{I_{\lambda}^{ki}} = F C_s A_{ki} \frac{g_k e^{-(E_k/k_B T)}}{U_s(T)}$$

- I = Intensity of light at wavelength λ
- F = efficiency of light collection system
- Cs = Concentration of species s
- A = Transition probability
- g_k = degeneracy
- E_k = Energy at level k
- k_B = Boltzmann's constant
- U_s = Partition function

CF-LIBS Assumptions

- Stoichiometric Ablation
  - The constituents of the plasma are equivalent to that which was ablated
- Local Thermal Equilibrium (LTE)
  - Isothermal for the temporal and spatial window
- Optically thin plasma
  - No self absorption

Local Thermal Equilibrium

- McWhirter Criterion
  - Minimum electron density needed to allow for LTE
  - Assumes the plasma plume is stationary and homogenous

$$n_e(cm^{-3}) > 1.6E^{12}T^{0.5}(\Delta E_{ik})^3$$

- Electron density is calculated by observing line broadening due to the Stark effect

Statistical Outliers

- Outlier definition: Any observation farther than 1.5fs from the closest fourth is an outlier.

- Order observations from smallest to largest
  - Upper forth = median of the largest half
  - Lower forth = median of the smallest half
  - f_s = "A measure of spread that is resilient to outliers"

- f_s = upper forth – lower forth