HIGH-PURITY STANDARDS

Application of Laser Induced Breakdown Spectroscopy to Quantify Beryllium Concentration in Soil

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Outline

- Introduction
- Objectives
- Experimental Design
- Results
- Method Evaluations and Conclusions
- Future Research

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Beryllium manufacturing

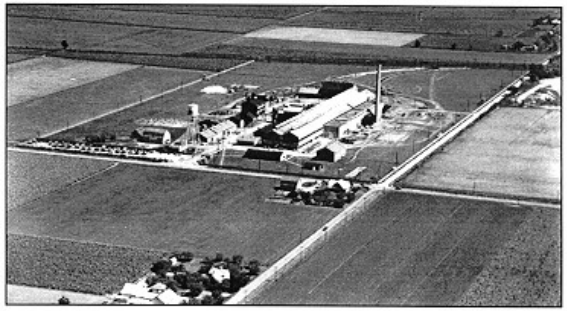
- a lightweight metal with
  - excellent heat conductivity
  - good electrical insulation
  - high tensile strength

- Used in nuclear operations, aluminum manufacturing, electronics, space exploration, mining, etc.

Beryllium Contamination

- In the 20th century Be was heavily utilized by the United States Atomic Energy Commission
- The U.S. Department of Energy has several legacy sites across the country that are eligible for FUSRAP due to beryllium contamination
- Monitoring underway by USDOE, USACE, EPA and state health departments
- Estimated cost to remediate 1 beryllium site: 600K-86M dollars

Handford Site, Washington



Beryllium Brush Co, Luckey, OH

Photos Courtesy of:
wmsym.org
Rt.com

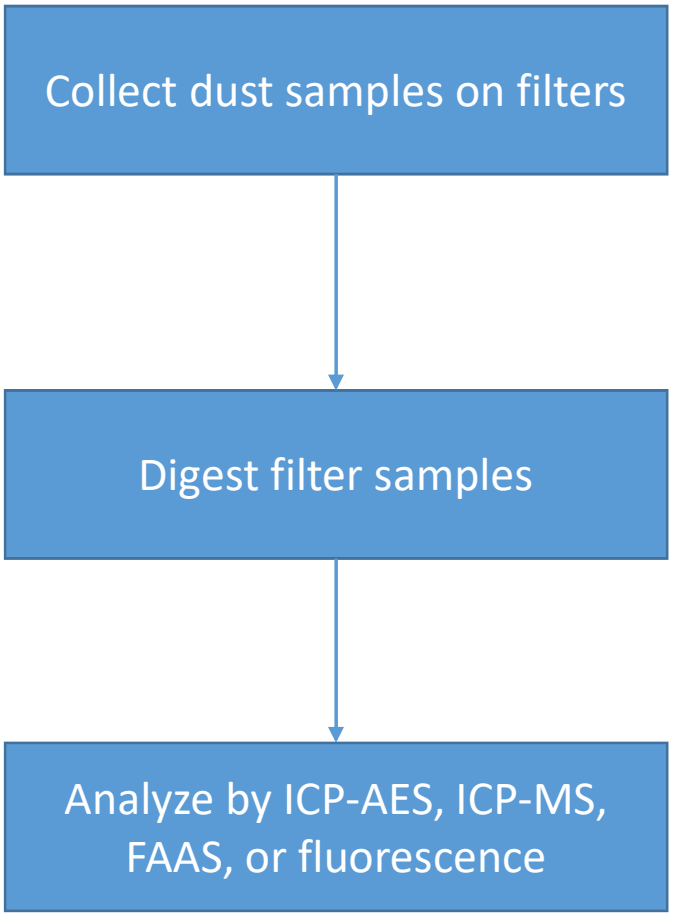
Beryllium Exposure Limits

Be is toxic due to it's high retention in mammalian tissues leading to cardiac strain, heart disease, beryllium sensitization (BeS) and chronic beryllium lung disease (CBD) in humans

-Mode of exposure: inhalation of Be aerosols

Agency	Permissible Exposure Limit (PEL)	Time Weighted Average (TWA)
DOE	0.2 µg/m^3 0.2 µg/100 cm^2	Air Surface
OSHA	2 µg/m^3	8 hours
ACGIH	1 µg/m^3	15 minutes

Monitoring Beryllium

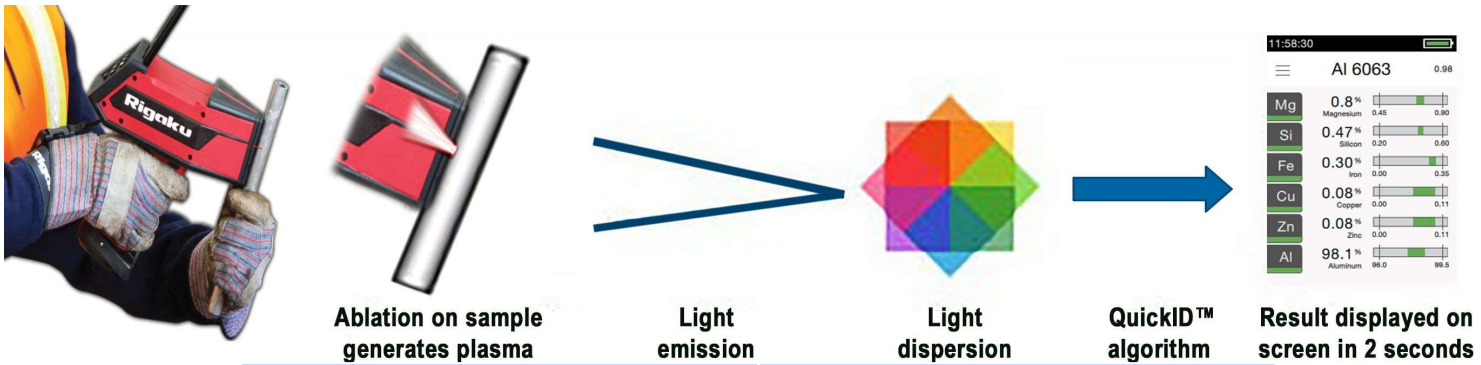


Challenges

- Variety of digestion protocols and methods
  - Results are dependent upon the digestion method
- Time consuming
- Not available for field analysis
- Suitable BeO reference material not readily available

Laser Induced Breakdown Spectrometer

Direct solid measurement technique



Pros	Cons
Limited sample preparation	Higher LOD
Field-portable units available	Lack of standards and inter-laboratory evaluations
Rapid results	Interferences & matrix effects undetermined

Photo courtesy of Rigaku Analytical Devices

Developing a Certified Reference Material (CRM)

- Currently no existing soil based beryllium reference material designed specifically for LIBS analysis
    - makes it difficult to evaluate digestion and analysis methods

*There is an urgent need for standardization of digestion methods

Developing a Certified Reference Material (CRM)

- Follow ISO Guide 34 and ISO 17025 guidelines

1. Detailed, traceable and consistent sample preparation

2. Homogeneity testing

3. Stability assessment

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Objectives

- Evaluate HPS's ability to produce soil samples spiked with BeO
- Evaluate the accuracy and precision of LIBS in determining Be concentration in soil

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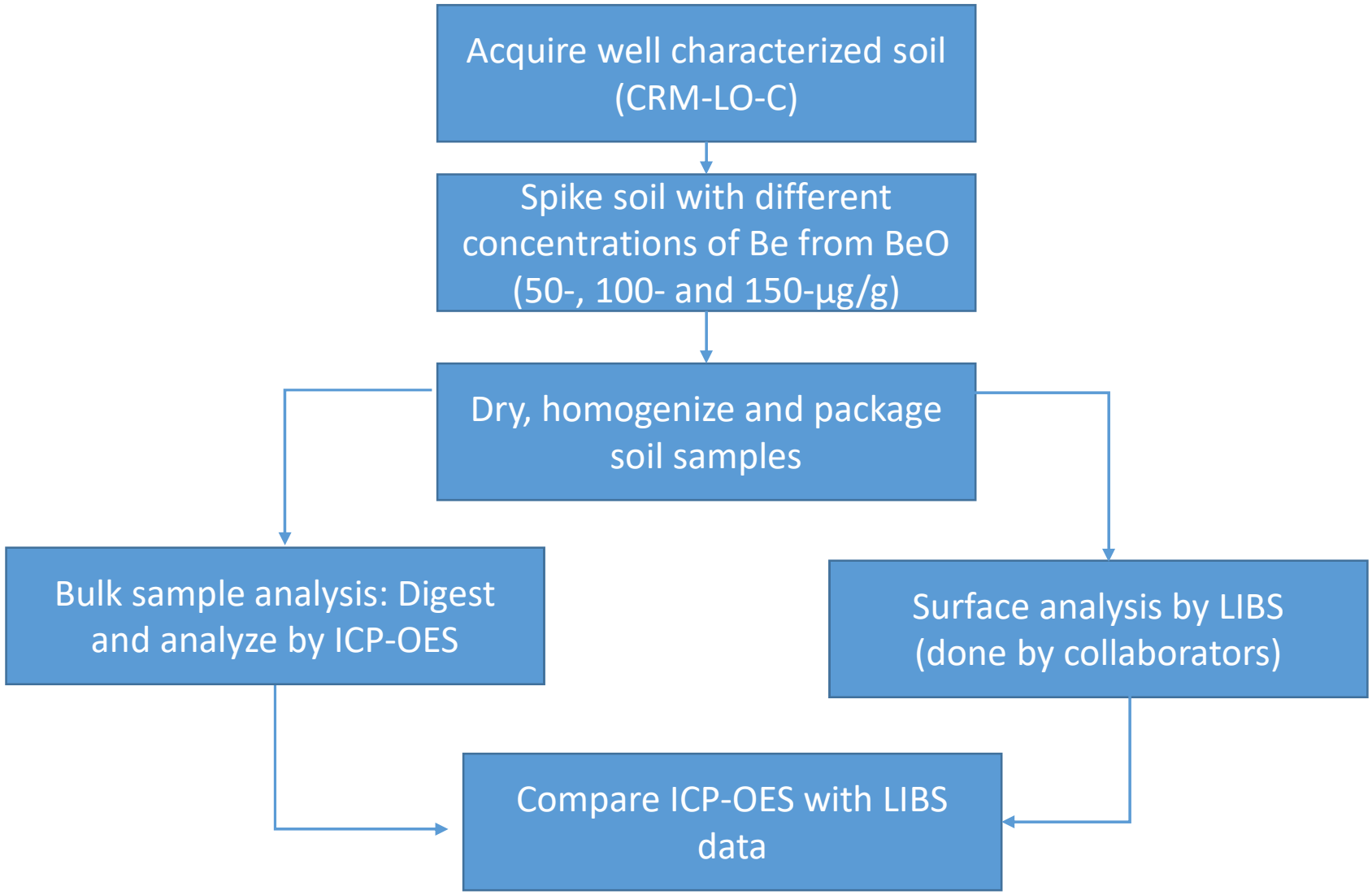
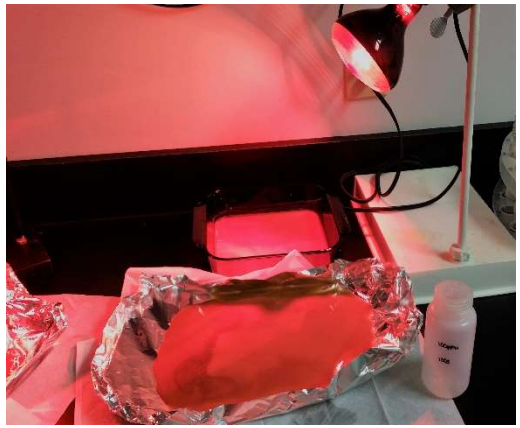
Experimental Design



Sample Manufacturing Process

Spiking method developed in house



Packaging and Shipping

Digestion and Analysis

- Digestion performed using Milestone ETHOS UP Microwave digestion system
  - EPA3052 “Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices”
  - Digestion reagent: 10 mL of HNO_3 and 5 mL HF
- Analysis performed with Perkin Elmer ICP-OES Optima 5300

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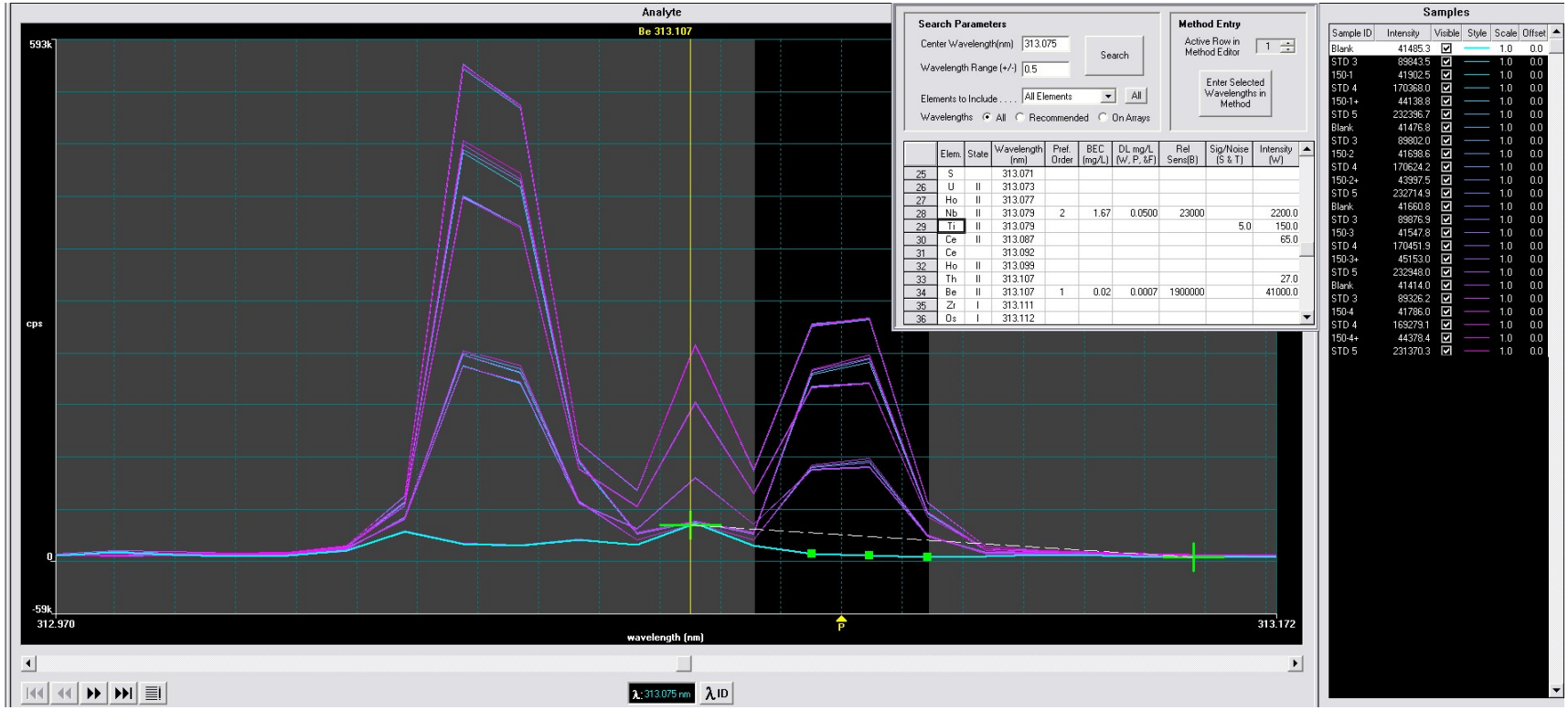
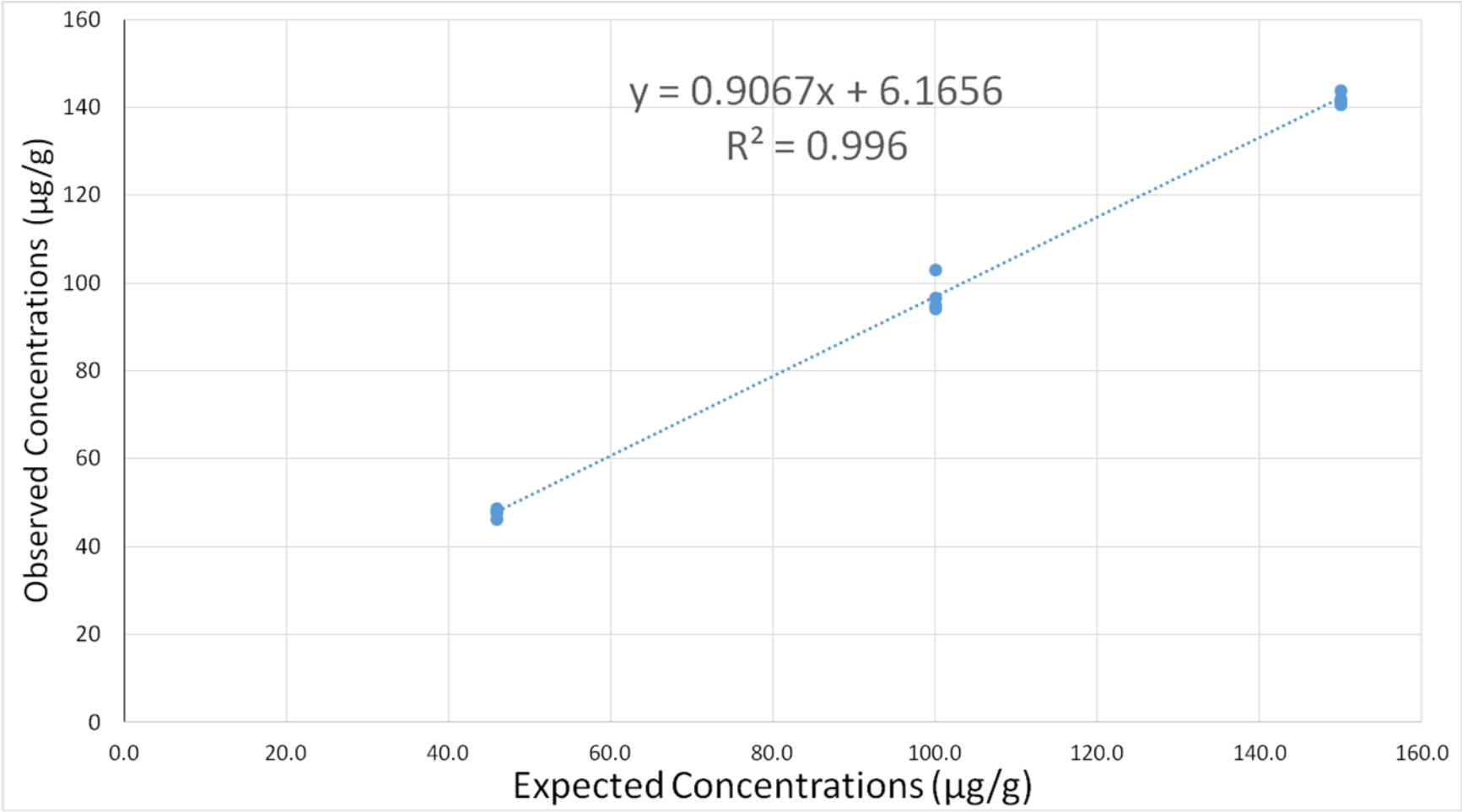
ICP-OES Analysis

-Initial analysis revealed significant spectra interference, likely due to Ti

-Prior to data processing Be recovery ~65% for all samples, after baseline adjustment Be recovery ~95%



ICP-OES Analysis

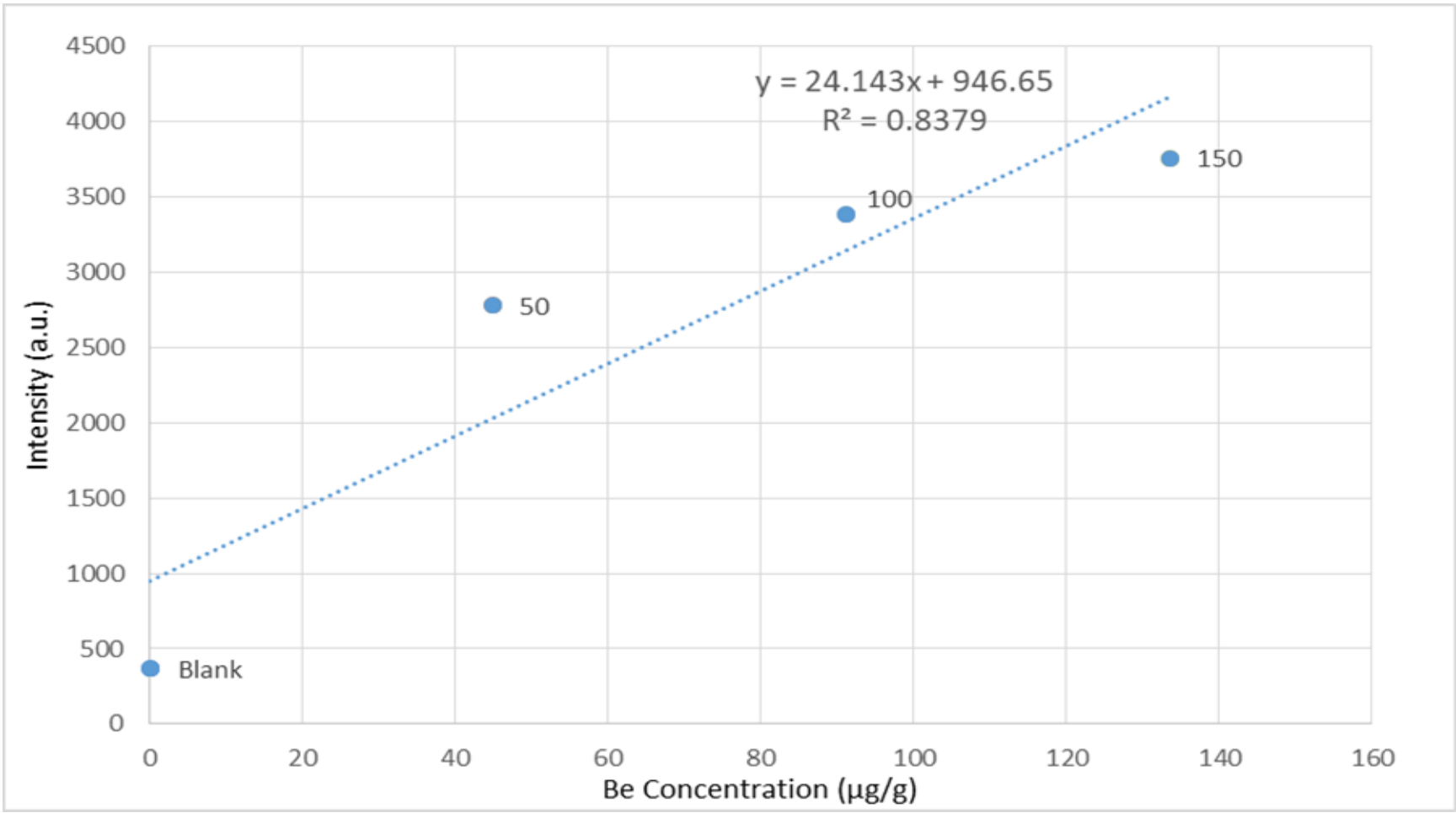


Calibration curve from ICP-OES data for all samples calculated via method of standard addition

ICP-OES Analysis

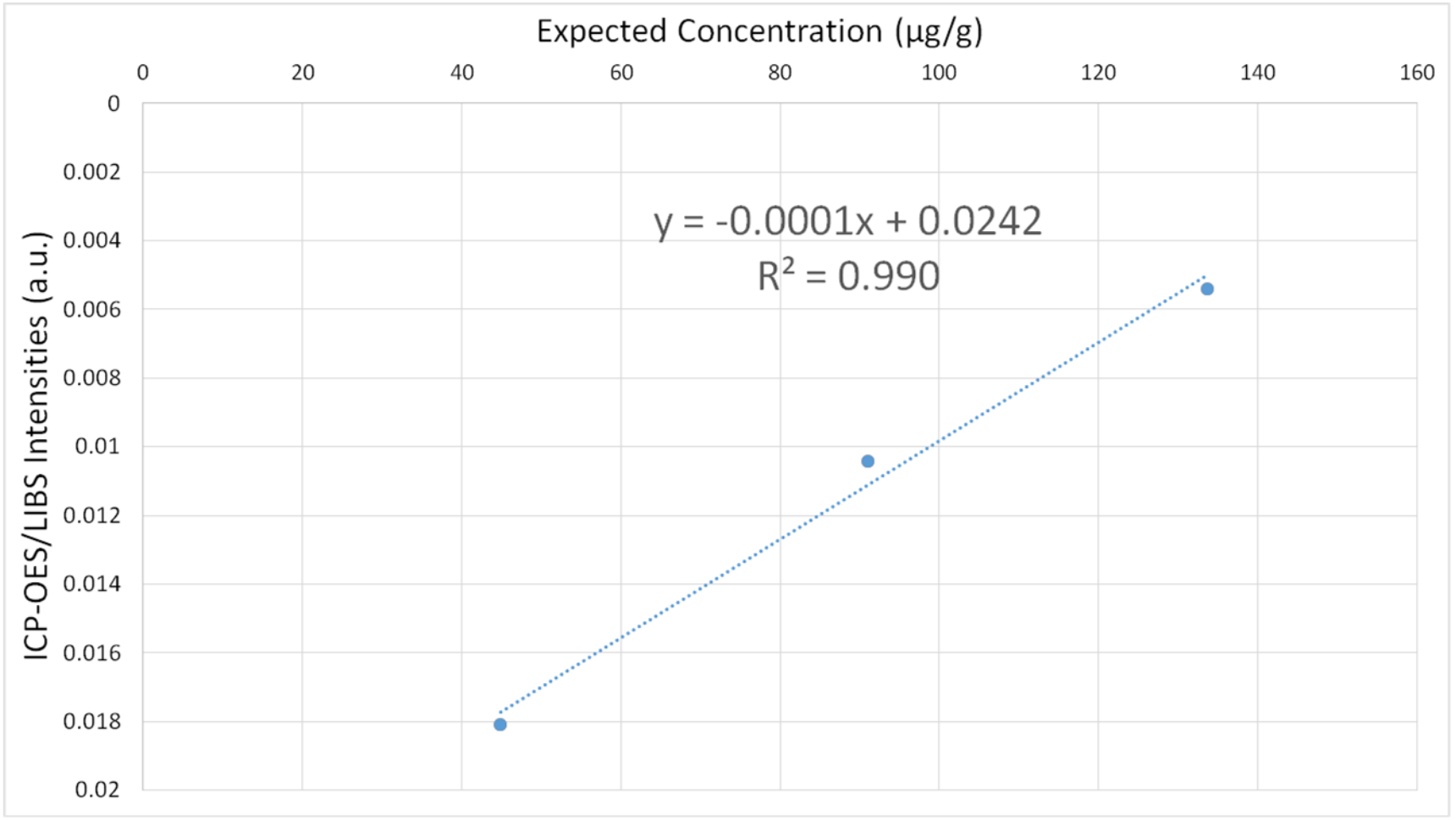
Calculated Concentrations		
ID	**µg/g**	**Recovery**
50-1	46.151	100%
50-2	47.738	104%
50-3	48.815	106%
50-4	47.917	104%
50 Average	**47.655**	**104%**
STDEV	**1.108**	
100-1	94.851	95%
100-2	96.468	96%
100-3	103.165	103%
100-4	94.331	94%
100 Average	**97.204**	**97%**
STDEV	**4.077**	
150-1	142.0568	95%
150-2	144.0240	96%
150-3	140.6477	94%
150-4	141.3405	94%
150 Average	**142.0172**	**95%**
STDEV	**1.4563**	

LIBS Analysis



Calibration curve from averaged LIBS data for each sample concentration.

LIBS and ICP-OES Correlation



LIBS intensities correlated to ICP-OES intensities plotted against precise expected concentrations

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Evaluating methods

Possible sources of error

- Sample becomes in-homogeneous during spiking/drying process

- Loss of sample during extraction

- Some samples damaged during shipping

Conclusions

- Established proof of concept
- ICP-OES analysis determined the recovery for Be greater than 95%
- Spectra analysis showed significant interferences from Ti, adjustments are required to get accurate results
- Accuracy and precision decrease in samples with higher concentration Be

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Future Research

1. Include more labs with various LIBS instrument models

2. Evaluate the effect of moisture on accuracy of determining Be in soil by LIBS

3. Evaluate the effect of soil particle size on accuracy of determining Be in soil by LIBS

4. Develop a Be soil CRM amenable to LIBS analysis

Acknowledgements

High Purity Standards

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