Introduction to Analytical Thinking and ICP-MS

Andrew Hamilton
IIRMES
Understanding your project

• Project Design
  – What are the objectives of the study?
  – Where are the samples coming from? Study site?
  – Can we analyze the samples for the analytes of interest? Sample processing? Capabilities of the instruments?
Where are the possible sources of contamination/exposure?

Where are the control/clean sights?
Study Sites from OCSD Ocean Monitoring Program

Pacific Ocean Current

California Counter Current

T11 Reference

T1 Outfall

CSULB

Huntington Beach

Newport Beach

Corona Del Mar

EPA Reference

DP
Sample Collection

• Correct collecting method
• Correct container: HDPE or glass; Clear or amber
• Preservatives or Filtering apparatus
• QA/QC requirements
  – Duplicates
  – Controls
  – Field Blanks
Laboratory Concerns

• QA/QC
  – Duplicates, matrix spike, blanks, blank spikes
• Accuracy
  – CRM of similar matrix
  – spikes
• Precision
  – Duplicates
  – CRM?
• Instrument Drift
  – Rare earth internal standards
Inductively Coupled Mass Spectrometry (ICP-MS)

• Can be used for:
  – Quantification of trace metals in liquid or solids
  – Examination of elemental speciation (isotopic abundances) or quantification of proteins and biomolecules (coupled with chromatograph)

• Different types (Quadrupole and TOF @ IIRMES)
  – Depends on application and sample state
ICP-MS cont’d

**INTRODUCTION**

**IONIZATION**

**ISOLATION AND DETECTION**

Detector: Detects on a Mass/Charge Ratio (m/z)
ICP-MS Concerns

• Sensitivity
  - Low, middle, and high masses

• Interferences
  - Doubly charged ions (Ba+/Ba++)
  - Oxides (Ce/CeO)
  - Chlorides (Fe/Pd & APDC Extractions)

• Resolution/Mass Axis
  - Is the instrument assigning the correct mass? Overlapping signal?

• Instrument Drift
  - Internal standard use (known concentration)
Daily Performance Report

Sample ID: dp 072408
Sample Date/Time: Thursday, July 24, 2008 11:39:38
Sample Description:
Method File: C:\elandata_zedmason\Method\Daily Performance.mth
Dataset File: C:\Elan\dataset\072208\dp 072408.113
Tuning File: C:\Elan\dataset\Tuning\default.tun
Optimization File: C:\Elan\dataset\Optimize\default.dac
Dual Detector Mode: Dual
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

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**Daily Performance Report**

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Dataset File: C:\elandata_zedmason\Dataset\061608\dp 061608.005  
Tuning File: C:\elandata_zedmason\Tuning\default.tun  
Optimization File: C:\elandata_zedmason\Optimize\default.doc  
Dual Detector Mode: Dual  
Acq. Dead Time (ns): 55  
Current Dead Time (ns): 55

**Summary**

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What’s Different?  Improvements?  Better Sensitivity, but at what cost??
What’s the problem with this tune?
Slight decreased Sensitivity for middle and high masses, but even more alarming is the increased interferences and RSD’s
Building a Standard Curve:
Remember those Laws and Formulas??

- Law of Conservation
- $M_1 V_1 = M_2 V_2$  ($C_1 V_1 = C_1 V_1$)
- Ex. 100 ppm Standard make a 10ml volume of 100ppb

  $100\text{ppm(ug/ml)} = 100000 \text{ ppb (ng/ml)}$
  
  $(100000 \text{ ppb})(x) = (100 \text{ ppb}) (10 \text{ ml})$
  
  $x = .01 \text{ ml or 100 ul}$
MULTIPLIERS:

• Samples are very rarely run at full strength.
  – Common Dilutions are 10x (1:10) and 500x (1:500)

• Dilutions are necessary to have sample responses fall in range of curves, and preserve the detector

• Need to account for Dilutions when Quantifying Data
Multipliers!!!

- Ex. Sample A – wt .543 g
- Digested with strong acids and brought to 50ml volume
- Ran at 10x dilution with a 10 ml running volume volume. Instrument quantifies in mass units (ng)

\[
\frac{X \text{ ng}}{\text{(total mass in 10 ml tube)}} \times 50 = \frac{50X \text{ ng (Total mass in 50 ml tube)}}{.543 \text{ g (wt of Sample)}}
\]

= 92.1 (Result in ng/g)
• Quantification of unknown samples based on standard curve
  • Must calculate slope, intercept, and r-sq (0.999...)

Quantification

![Graph showing various elements and their quantification based on standard curve.](image)
**Quick Case Study:**

<table>
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<tr>
<th>EL</th>
<th>MASS</th>
<th>RRF COUNTRAW COUNTS</th>
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**INTERNAL STANDARDS**

- Sc: 45, 9.39, 513.35
- Rh: 103, 264648.09
- Tm: 169, 393871.44
What’s a Secondary Source Standard???
QA Check: Blank Spike (Accuracy)
<table>
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Too Much Variation in the Internal Standards: Sample Run not reliable
DON’T WORRY!!!

His teaching philosophy is to have students "leave every lecture with a question that undermines the basic tenets and principles covered during that particular class. Provide enthusiasm and context but only partial answers. Challenge your students. They will rise to the occasion."

Taken from article regarding Dr. Zed Mason’s Distinguished Faculty Award