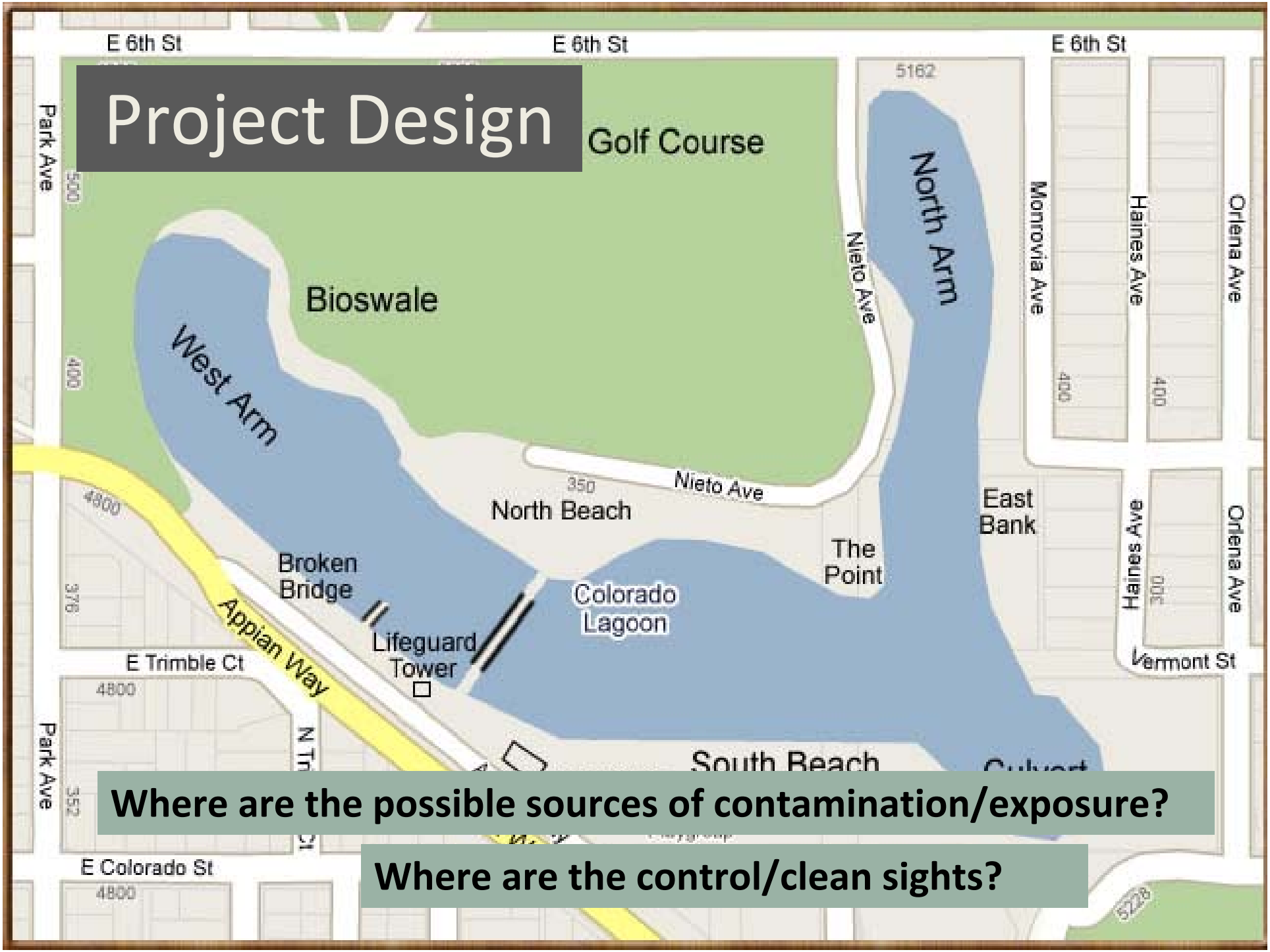
Introduction to Analytical Thinking and ICP-MS

Andrew Hamilton

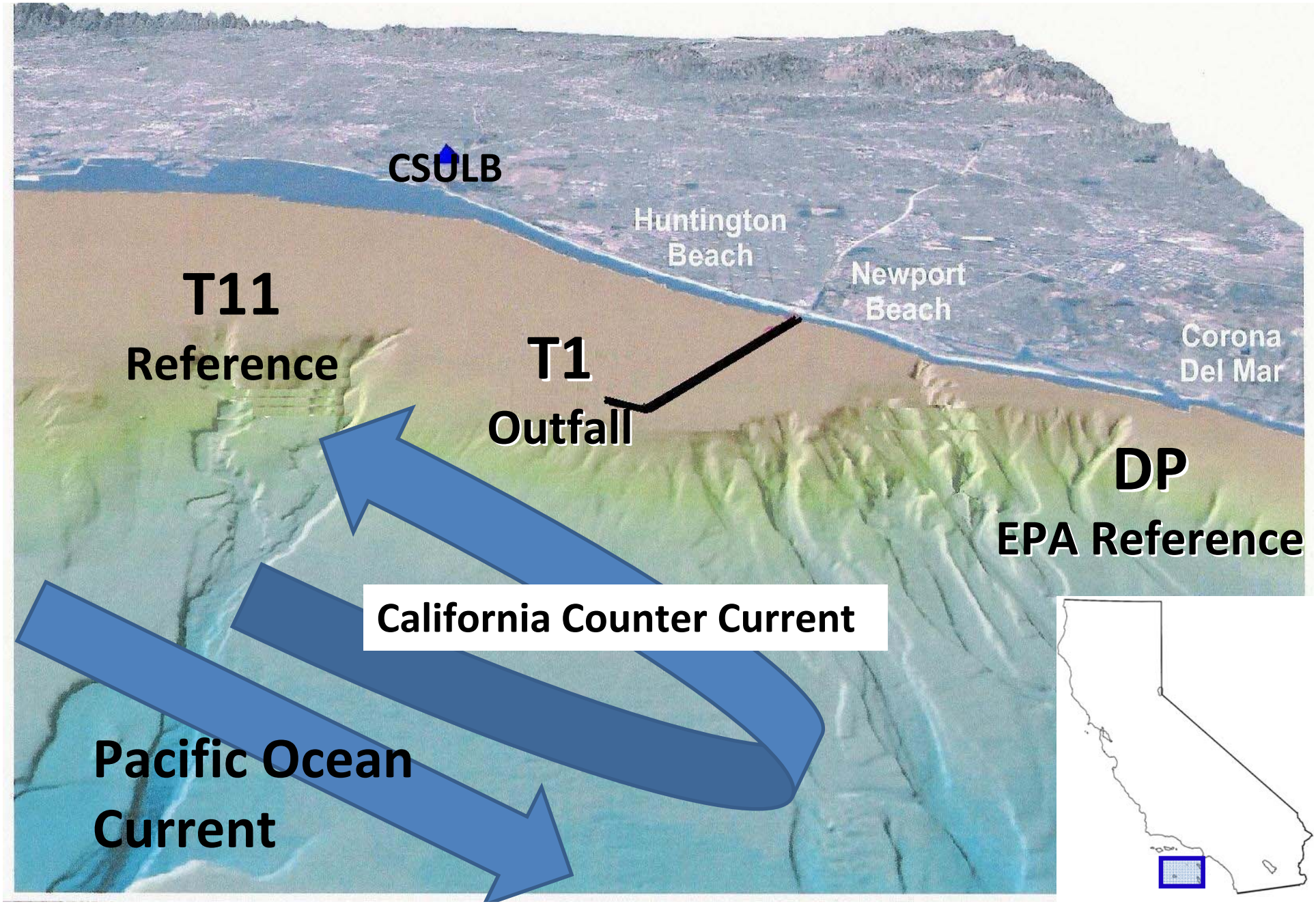
IIRMES

Understanding your project

- Project Design
  - What are the objectives of the study?
  - Where are the samples coming from? Study site?
  - What type of samples? Matrix? Preservation? Controls? Field Blanks?
  - Can we analyze the samples for the analytes of interest? Sample processing? Capabilities of the instruments?


Project Design
E 6th St
E 6th St
E 6th St
Golf Course
Park Ave
Bioswale
West Arm
North Arm
Nieto Ave
Monrovia Ave
Haines Ave
Orlena Ave
5162
500
400
420
400
350
Nieto Ave
North Beach
East Bank
The Point
4800
Broken Bridge
Colorado Lagoon
Haines Ave
Orlena Ave
376
300
Appian Way
Lifeguard Tower
E Trimble Ct
Vermont St
4800
Park Ave
352
South Beach
Culvert
Where are the possible sources of contamination/exposure?
E Colorado St
4800
Where are the control/clean sights?
5228

Study Sites from OCSD Ocean Monitoring Program



Sample Collection

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

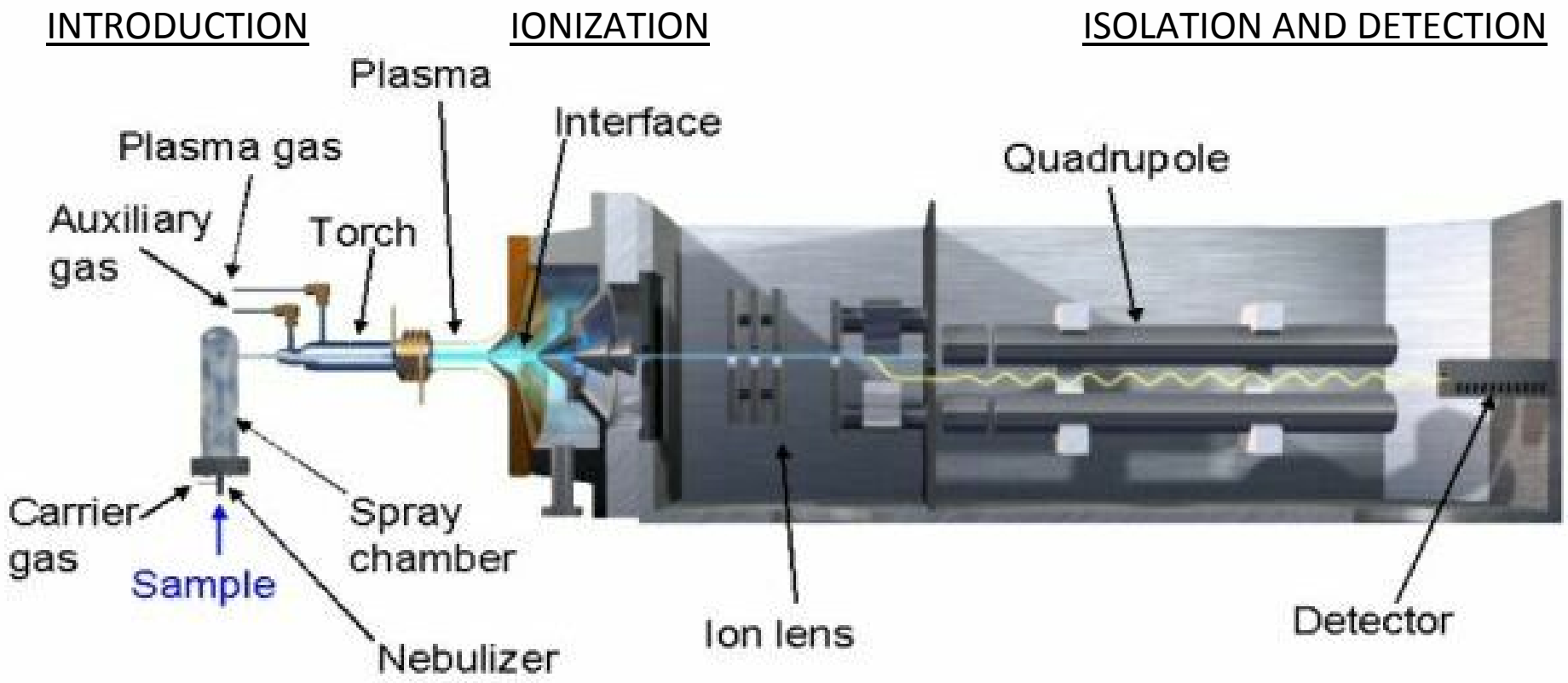
Laboratory Concerns

- 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 (Quadrapole and TOF @ IIRMES)
  - Depends on application and sample state

ICP-MS cont'd



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:\Elandata_zedmason\Dataset\072208\dp 072408.113
Tuning File: C:\Elandata_zedmason\Tuning\default.tun
Optimization File: C:\Elandata_zedmason\Optimize\default.dac
Dual Detector Mode: Dual
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

	Analyte	Mass	Meas. Intens. Mean	Net Intens. Mean	Net Intens. SD	Net Intens. RSD
	Mg	24.0	76612.7	76612.686	642.459	0.8
	In	114.9	510965.9	510965.923	2748.010	0.5
	U	238.1	685105.4	685105.364	5208.000	0.8
⌈>	Ce	139.9	514643.5	514643.474	2581.015	0.5
⌊	CeO	155.9	14349.5	0.028	0.000	1.4
⌈>	Ba	137.9	420269.6	420269.570	2818.664	0.7
⌊	Ba++	69.0	7989.6	0.019	0.000	1.4
	220	220.0	0.9	0.900	0.548	60.9
	8.5	8.5	3.4	3.400	0.962	28.3

Daily Performance Report

Sample ID: dp 061608
Sample Date/Time: Monday, June 16, 2008 18:00:13
Sample Description:
Method File: C:\elandata_zedmason\Method\Daily Performance.mth
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.dac
Dual Detector Mode: Dual
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

	Analyte	Mass	Meas. Intens. Mean	Net Intens. Mean	Net Intens. SD	Net Intens. RSD
	Mg	24.0	145363.0	145363.009	7805.184	5.4
	In	114.9	663329.2	663329.186	4779.285	0.7
	U	238.1	691879.7	691879.717	8887.848	1.3
>	Ce	139.9	715060.9	715060.929	9987.740	1.4
	CeO	155.9	25762.5	0.036	0.001	1.6
>	Ba	137.9	597043.4	597043.435	4946.917	0.8
	Ba++	69.0	15511.6	0.026	0.000	1.8
	220	220.0	0.4	0.400	0.418	104.6
	8.5	8.5	5.5	5.500	1.369	24.9

What's Different? Improvements?
Better Sensitivity, but at what cost??

Daily Performance Report

Sample ID: 10ppb daily performace
Sample Date/Time: Wednesday, June 18, 2008 14:36:14
Sample Description:
Method File: C:\elandata_zedmason\Method\Daily Performance.mth
Dataset File: C:\elandata_zedmason\DataSet\061808\10ppb daily performace.031
Tuning File: C:\Elandata_zedmason\Tuning\default.tun
Optimization File: C:\elandata_zedmason\Optimize\default.dac
Dual Detector Mode: Dual

Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

	Analyte	Mass	Meas. Intens. Mean	Net Intens. Mean	Net Intens. SD	Net Intens. RSD
	Mg	24.0	220872.4	220872.417	3316.544	1.5
	In	114.9	308828.9	308828.898	17127.233	5.5
	U	238.1	380224.2	380224.198	42521.536	11.2
>	Ce	139.9	681782.2	681782.195	78061.967	11.4
	CeO	155.9	17981.2	0.026	0.000	1.4
>	Ba	137.9	721226.6	721226.573	6959.853	1.0
	Ba++	69.0	23159.6	0.032	0.004	13.5
	220	220.0	1.4	1.400	0.652	46.6
	8.5	8.5	14.0	14.000	4.650	33.2

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
- $M_1V_1 = M_2V_2$ $(C_1V_1 = C_1V_1)$
- Ex. 100 ppm Standard make a 10ml volume of 100ppb

100ppm(ug/ml) = 100000 ppb (ng/ml)

(100000 ppb)(x) = (100 ppb) (10 ml)

x = .01 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

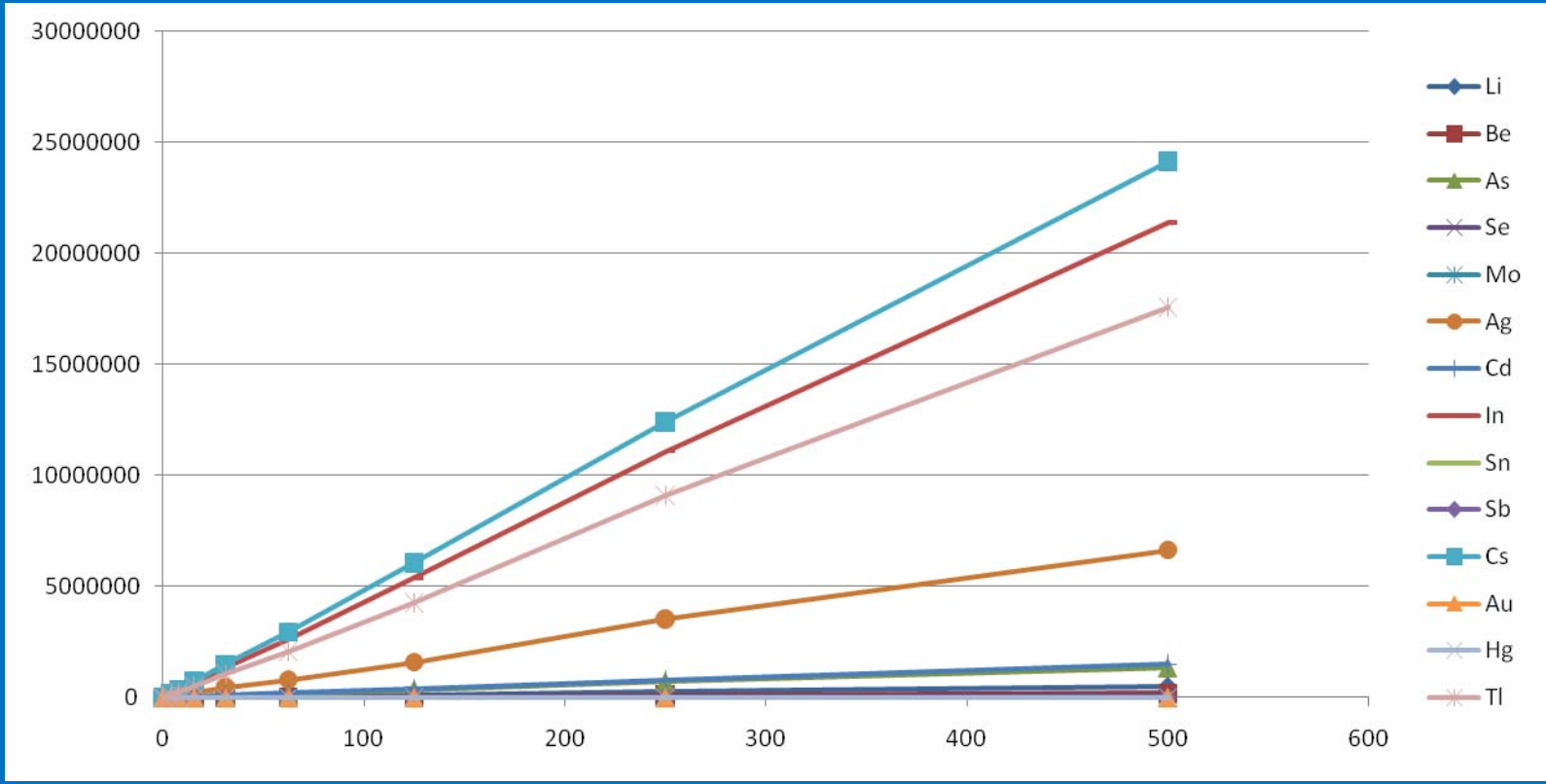
Multipliers!!!

- **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)**

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

= 92.1 (Result in ng/g)

Quantification



- **Quantification of unknown samples based on standard curve**
  - **Must calculate slope, intercept, and r-sq (0.999…)**

Quick Case Study:

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HP4500 ICPMS Data Report

Data File Name:	010SMPL.D	Method:	Rich.M
Sample Name:	500ng	Calibration File:	110111.C
Comments:		Units:	ng/ml
Date Acquired:	Jan 11 2011 01:18 pm	Number of Masses:	39
Total Dilution Factor:	1.0000	Vial Number:	1206

EL	MASS	RRF COUNT	RAW COUNTS	IS	MODE	RESULT	UNITS
Tl	205	229.08	450733.41	169	P	494.60	ng/ml
Sn	118	112.44	148560.50	103	P	498.90	ng/ml
Ti	47	34.44	45468	103	P	543.60	ng/ml
V	51.00	440.62	582112	103	P	513.40	ng/ml
Zn	66	44.55	58802	103	P	491.8000	ng/ml

INTERNAL STANDARDS

Sc	45	0.39	513.99	P	
Rh	103	264648.09	264648.09	P	
Tm	169	393871.44	393871.41	P	
In	115	1.66	2202.38	P	

What's a Secondary Source Standard???

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HP4500 ICPMS Data Report

Data File Name:	014SMPL.D	Method:	Rich.M
Sample Name:	500ng S.S. cali check	Calibration File:	110111.C
Comments:		Units:	ng/ml
Date Acquired:	Jan 11 2011 01:34 pm	Number of Masses:	39
Total Dilution Factor:	1.0000	Vial Number:	1212

EL	MASS	RRF COUNT	RAW COUNTS	IS	MODE	RESULT	UNITS
Tl	205	238.34	471481.50	169	P	514.60	ng/ml
Sn	118	120.61	155440.70	103	P	536.30	ng/ml
Ti	47	34.95	44692	103	P	552.10	ng/ml
V	51.00	438.12	560997	103	P	510.50	ng/ml
Zn	66	45.46	58557	103	P	502.2000	ng/ml
INTERNAL STANDARDS							
Sc	45	0.39	501.13		P		
Rh	103	257910.13	257910.09		P		
Tm	169	395592.34	395592.41		P		
In	115	1.78	2284.61		P		

QA Check: Blank Spike (Accuracy)

HP4500 ICPMS Data Report

Data File Name:	018SMPL.D	Method:	Rich.M
Sample Name:	Blank spike 10x	Calibration File:	110111.C
Comments:		Units:	ng/ml
Date Acquired:	Jan 11 2011 01:50 pm	Number of Masses:	39
Total Dilution Factor:	1.0000	Vial Number:	1305

EL	MASS	RRF COUNT	RAW COUNTS	IS	MODE	RESULT	UNITS
Tl	205	466.81	949558.81	169	P	1008.00	ng/ml
Sn	118	231.33	339063.19	103	P	1029.00	ng/ml
Ti	47	55.78	81916	103	P	899.30	ng/ml
V	51.00	743.23	1090849	103	P	871.20	ng/ml
Zn	66	69.67	102073	103	P	779.5000	ng/ml
INTERNAL STANDARDS							
Sc	45	2.67	3924.94		P		
Rh	103	292902.69	292902.69		P		
Tm	169	406850.81	406850.81		P		
In	115	3.15	4617.25		P		

Sample 1:

INTERNAL STANDARDS			
Sc	45	6.32	15538.16
Rh	103	492879.63	492879.59
Tm	169	708366.06	708366.13
In	115	0.13	320.01

Sample 2:

INTERNAL STANDARDS			
Sc	45	2.78	5516.53
Rh	103	401929.28	401929.31
Tm	169	552284.38	552284.38
In	115	0.07	136.67

Sample 3:

INTERNAL STANDARDS			
Sc	45	2.48	4171.68
Rh	103	336451.50	336451.50
Tm	169	494767.31	494767.31
In	115	3.18	5358.55

Sample 4:

INTERNAL STANDARDS			
Sc	45	4.73	9453.67
Rh	103	399476.38	399476.41
Tm	169	567149.06	567149.00
In	115	0.08	166.67

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 Facuty Award