Matrix Interferences in ICP-MS:

Causes, Effects, and Strategies to Reduce or Eliminate Them…

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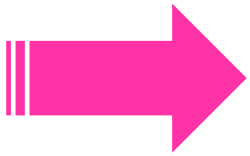
Ruth E. Wolf, Ph. D. and Daniel H. Jones

Matrix Effects in ICP-MS (and ICP-OES)

- Spectral Interferences
  - Isobaric or molecular overlaps
    - ^{64}Zn and ^{64}Ni
    - $^{40}Ar^{35}Cl$ on ^{75}As



- Collision/Reaction Cells
- High Resolution
- Matrix Separation….

- Non-spectral interferences[1]
  - Matrix induced changes in signal intensity
  - Concomitant elements may enhance or suppress analyte signals
    - Multiplicative effects that change slope of calibration curve

- Happen in sample introduction/plasma (known since the early 1970's)
  - Easily Ionizable Element (EIE) effects
  - Aerosol Ionic Redistribution Effects (AIR)
  - Organic Enhancement effects
  - Matrix/Acid washout

- Happen in the mass spectrometer
  - Space charge effects

[1] *Inductively Coupled Plasma Mass Spectrometry, Ed., Akbar Montaser, 1998, pp 543-548, ISBN: 0-471-18620-1*

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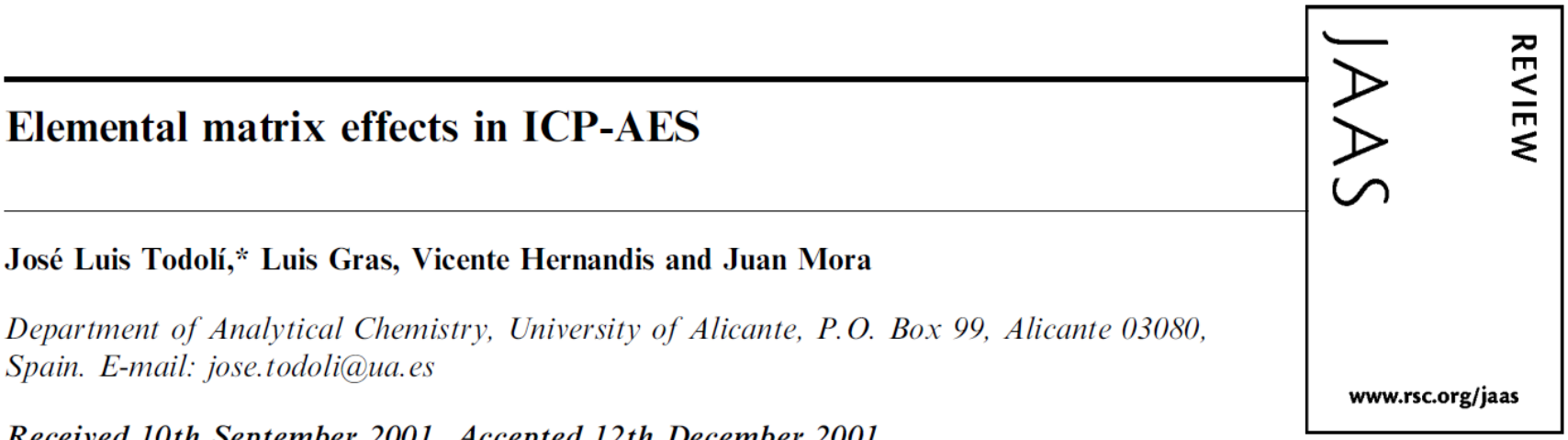
Sample Introduction/Plasma Effects

Good review article – although written for ICP-AES the effects in the spray chamber and processes in the plasma are the same in ICP-MS…



Elemental matrix effects in ICP-AES

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JAAS REVIEW

www.rsc.org/jaas

Organic Signal Enhancement Effects

- Organics can cause signal enhancements of high IP elements, e.g. arsenic (3-8 times) and selenium (2-6 times).
  - Attributed to the modification of the ionization equilibrium in the plasma
  - E.g. carbon acts as an electron sink….

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INVESTIGATIONS INTO NONSPECTROSCOPIC EFFECTS OF ORGANIC COMPOUNDS IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Easily Ionizable Element (EIE) Effects:

- Elements with low ionization potentials (IP)
- Traditionally been most studied cause of elemental matrix effects in ICP-AES (and ICP-MS).
- Responsible for changes in analytical signals because they modify:
  - (i) the state in which the analyte is being introduced into the plasma;
  - (ii) the plasma thermal characteristics; and
  - (iii) the analyte excitation efficiency as well as the spatial distribution of the emitting species.
- What are the EIEs?
  - Li (5.39 eV) **< Na (5.14 eV) < K (4.18 eV)** < Cs (3.89 eV)
    - The magnitude of the analyte emission signal variations induced by different EIEs is arranged according to the following increasing order
    - The higher the ionization potential (IP) the lower the interference effect

Internal Standards in ICP-MS

- Can be used to compensate for changes in sample introduction
  - Sample viscosity
  - Tubing wear
  - Changes in cone orifices (deposition over time)
- Can be used to compensate for matrix effects - MAYBE
  - However, depending on the cause of the matrix effect the internal standard may or may not correctly compensate for the signal changes
    - Depends in ionization potential of Internal Standard element and analyte
    - Depends on how internal standard elements and analytes are affected by concomitant elements in the plasma
- There is NO PERFECT internal standard for all samples!
  - May consider adding alternate internal standards
  - Reprocess data with different internal standard to see effects

EPA Method 200.8

- Approved elements:
  - Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn
- How many of you only monitor those elements?
- What about the major cations: Na, K, Mg, Ca?
  - Did you ever see a natural water without some level of these elements???
  - What are the typical concentrations of these elements in your samples?
    - Could be 10 - 50 ppm, depending on element and water source
  - Na and K are known EIE elements
    - High concentrations of EIE elements can affect elements with higher ionization potentials (e.g. Ge, As, Se)
  - Measured interference effects: K < Na < Mg < Ca
    - Based on IP, a non-thermal excitation mechanism was likely to take place
    - Calcium is regarded as one of the elements that produces the most serious interferences in ICP-AES (changes nebulization and vaporization characteristics)
- Do you have trouble keeping External QC's in limits when they contain ALL elements typically present in a water?

Concentrations of Major Cations in Drinking Water

- **Mg, Ca, Na, and K present in all waters and highly variable**
- From: http://www.mgwater.com/mgrank.shtml
  - Accessed 06/26/2017
  - Not all states and only a few locations in each state, total N=99
- My own assignment to regions…

Region	States	Average Concentration mg/L (SD)			
		Mg	Ca	Na	K
North West	CA, HA, OR, WA	6.8 (4.6)	12.1 (11.1)	23.0 (24.5)	1.7 (1.3)
North Central	IA, IL, IN, KS, KY, MI, MN, MO, NE, OH, WI	14.7 (6.5)	46.1 (13.2)	21.0 (19.2)	1.7 (1.3)
North East	CT, DC, MA, MD, NJ, PA, RI, VA, NY	3.8 (2.9)	17.2 (11.4)	5.6 (2.9)	1.4 (0.6)
South West	AZ, CO, NM	10.6 (6.0)	43.7 (20.3)	36.1 (34.9)	2.1 (1.1)
South Central	AL, LA, MS, OK, TN, TX	6.6 (6.1)	23.8 (12.7)	29.5 (22.5)	2.5 (2.1)
South East	FL, GA, NC	4.1 (4.0)	26.1 (27.4)	5.6 (3.3)	1.4 (0.4)
Grand MEAN	**ALL STATES**	**9.4 (9.5)**	**31.8 (20.9)**	**22.5 (30.1)**	**2.5 (2.4)**

What Does an EIE effect look like???

- Calibrated at 1, 10, 50, 100 ppb in 1% nitric acid matrix
  - All elements present in same 10 ppm stock solution
  - Normal mode analysis (no cell or cell gas)
- ICV at 75 ppb analyzed in 1% nitric acid matrix
- ICV + Matrix: 25 ppm Ca, Na and 5 ppm Mg, K, Si

Internal Standard	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Ir	Ir	Ir	Ir
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**	**Ba 135 (ppb)**	**Tl-1 205 (ppb)**	**Pb-1 208 (ppb)**	**U-1 238 (ppb)**
ICV75	77.351	75.766	75.411	77.718	75.711	78.210	78.195	75.591	79.520	76.668	78.332	76.853	70.302	77.786	76.415	76.635
% RECOVERY	103.1%	101.0%	100.5%	103.6%	100.9%	104.3%	104.3%	100.8%	106.0%	102.2%	104.4%	102.5%	93.7%	103.7%	101.9%	102.2%
ICV75 MATRIX 10X	91.806	88.687	87.471	89.283	83.672	84.997	82.453	81.353	89.015	80.394	84.097	68.396	71.158	75.201	73.306	74.899
% RECOVERY	***122.4%***	***118.2%***	***116.6%***	***119.0%***	***111.6%***	***113.3%***	109.9%	108.5%	***118.7%***	107.2%	***112.1%***	91.2%	94.9%	100.3%	97.7%	99.9%

Element	V	Cr	Mn	Co	Ni	Cu	Cd	Zn	As	Se	Sr	Ag	Ba	Tl	Pb	U
1st IP	6.74	6.77	7.43	7.88	7.64	7.72	8.99	9.39	9.79	9.75	5.69	7.58	5.21	6.11	7.42	6.19

Element	Sc	Ge	Rh	Ir	In
1st IP	6.56	7.9	7.46	8.97	5.79

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Change the Internal Standards…

- Same raw data reprocessed with different internal standards
- Different Internal Standards behave differently…
- Indication you have EIE or other matrix effects occurring

Internal Standard	Ge	Ge	Ge	Ge	Ge	Ge	Ge	Ge	Ge	Ge	Ge	Ge
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV75	76.015	74.433	74.106	76.354	74.487	76.871	76.803	74.336	78.141	75.315	77.017	75.552
% RECOVERY	101.4%	99.2%	98.8%	101.8%	99.3%	102.5%	102.4%	99.1%	104.2%	100.4%	102.7%	100.7%
ICV75 MATRIX 10X	80.608	77.809	76.765	78.356	73.461	74.560	72.296	71.439	78.070	70.499	73.934	60.145
% RECOVERY	107.5%	103.7%	102.4%	104.5%	97.9%	99.4%	96.4%	95.3%	104.1%	94.0%	98.6%	***80.2%***
Internal Standard	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**	**Rh**
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV75	77.351	75.766	75.411	77.718	75.711	78.210	78.195	75.591	79.520	76.668	78.332	76.853
% RECOVERY	103.1%	101.0%	100.5%	103.6%	100.9%	104.3%	104.3%	100.8%	106.0%	102.2%	104.4%	102.5%
ICV75 MATRIX 10X	91.806	88.687	87.471	89.283	83.672	84.997	82.453	81.353	89.015	80.394	84.097	68.396
% RECOVERY	***122.4%***	***118.2%***	***116.6%***	***119.0%***	***111.6%***	***113.3%***	109.9%	108.5%	***118.7%***	107.2%	***112.1%***	91.2%
Internal Standard	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV75	74.765	73.153	72.893	75.070	73.307	75.615	75.536	73.159	76.855	74.114	75.814	74.354
% RECOVERY	99.7%	97.5%	97.2%	100.1%	97.7%	100.8%	100.7%	97.5%	102.5%	98.8%	101.1%	99.1%
ICV75 MATRIX 10X	75.422	72.696	71.806	73.266	68.748	69.749	67.635	66.863	73.057	65.945	69.215	56.240
% RECOVERY	100.6%	96.9%	95.7%	97.7%	91.7%	93.0%	90.2%	***89.2%***	97.4%	***87.9%***	92.3%	***75.0%***

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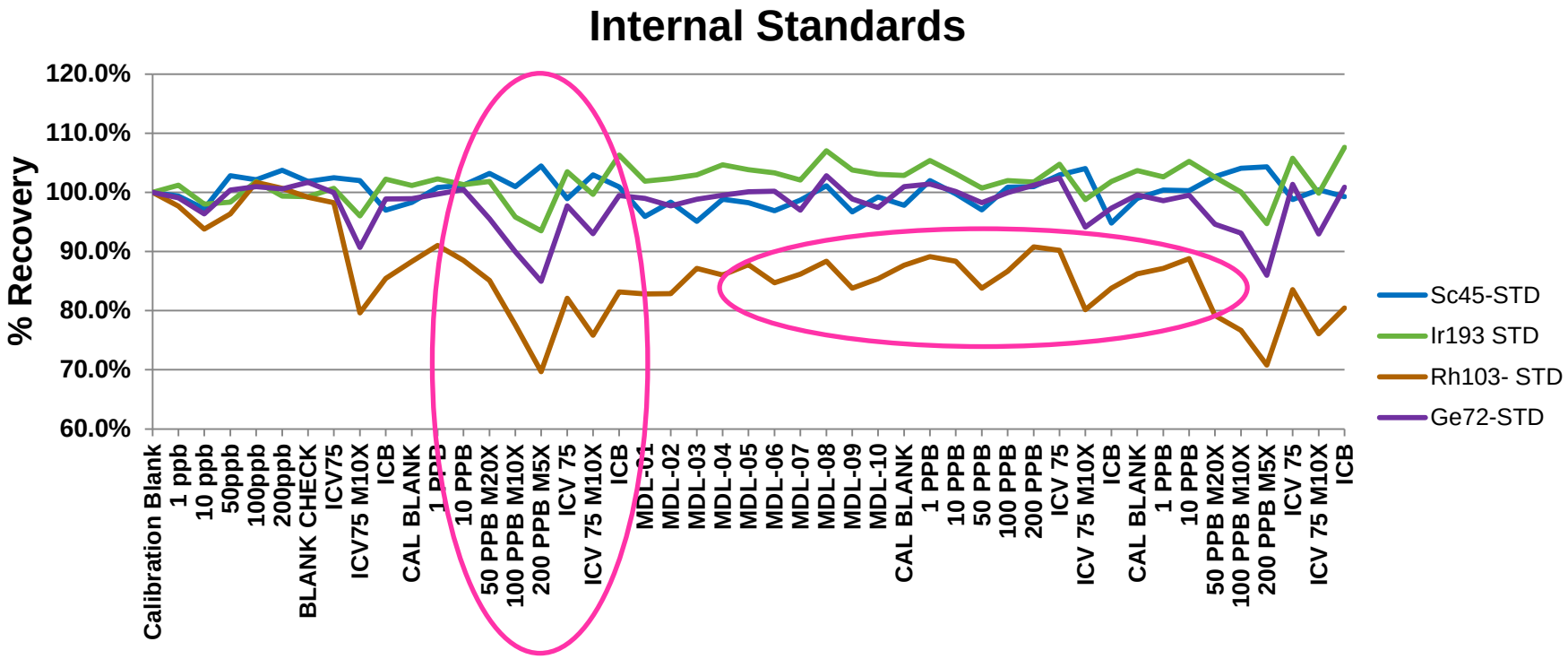
Look at what Internal Standards are doing…

- Presence of Na, K, Mg, Ca, Si matrix suppresses Ir and Rh
- As Matrix concentrations increase so does suppression
  - Matrix 20X = 12.5 ppm Ca, Na + 2.5ppm Mg, K, Si
  - Matrix 10x = 25 ppm Ca, Na + 5 ppm Mg, K, Si
  - Matrix 5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si



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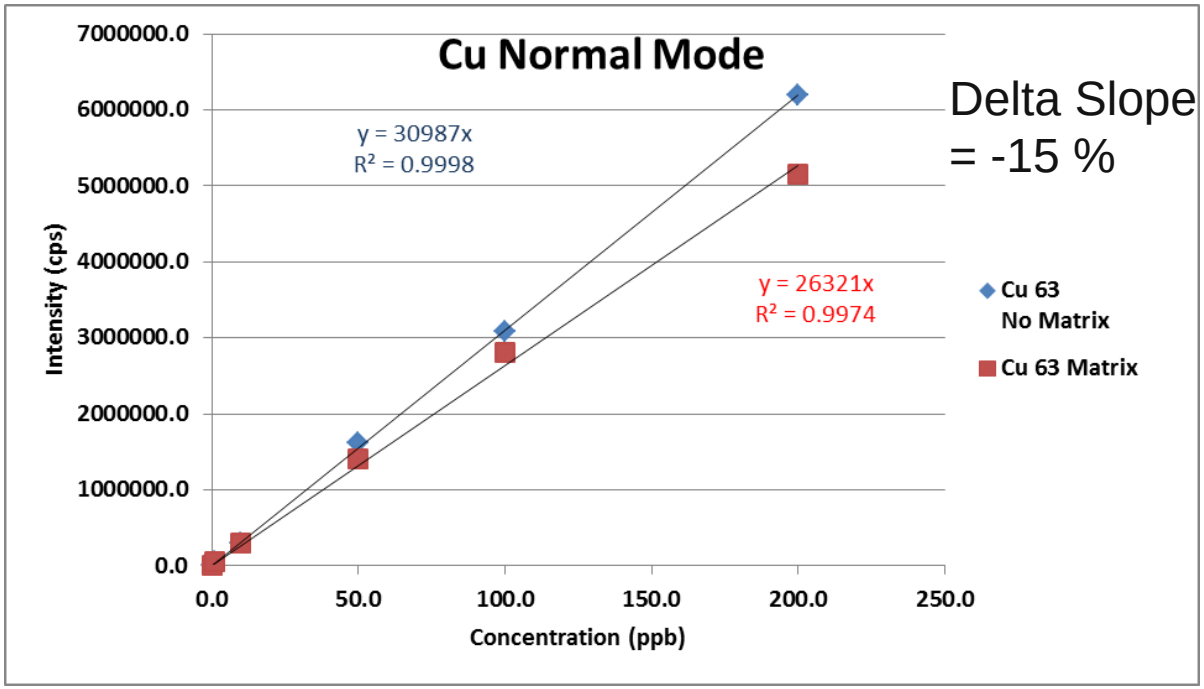
Suppression of Calibration Standards with Matrix



Matrix / no Matrix
Ratio of Rh Int Std:
200 ppb = 69.0 %
75 ppb 92.5 %

Ratio of Ir Int Std:
200 ppb = 94.0 %
75 ppb = 96.3 %

Ratio of Ge Int Std:
200 ppb = 84.0 %
75 ppb = 90.7 %

Matrix Stock: 250 ppm Ca, Na + 50 ppm Mg, K, Si
Blank, 1 ppb, 10 ppb stds: no matrix
Matrix added to 50 (20x), 100 (10x), 200 (5x) ppb
5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si
75 ppb ICV: without matrix = 76.648, with matrix = 84.700 (10% enhancement), Rh Int Std
10x = 25 ppm Ca, Na + 5 ppm Mg, K, Si

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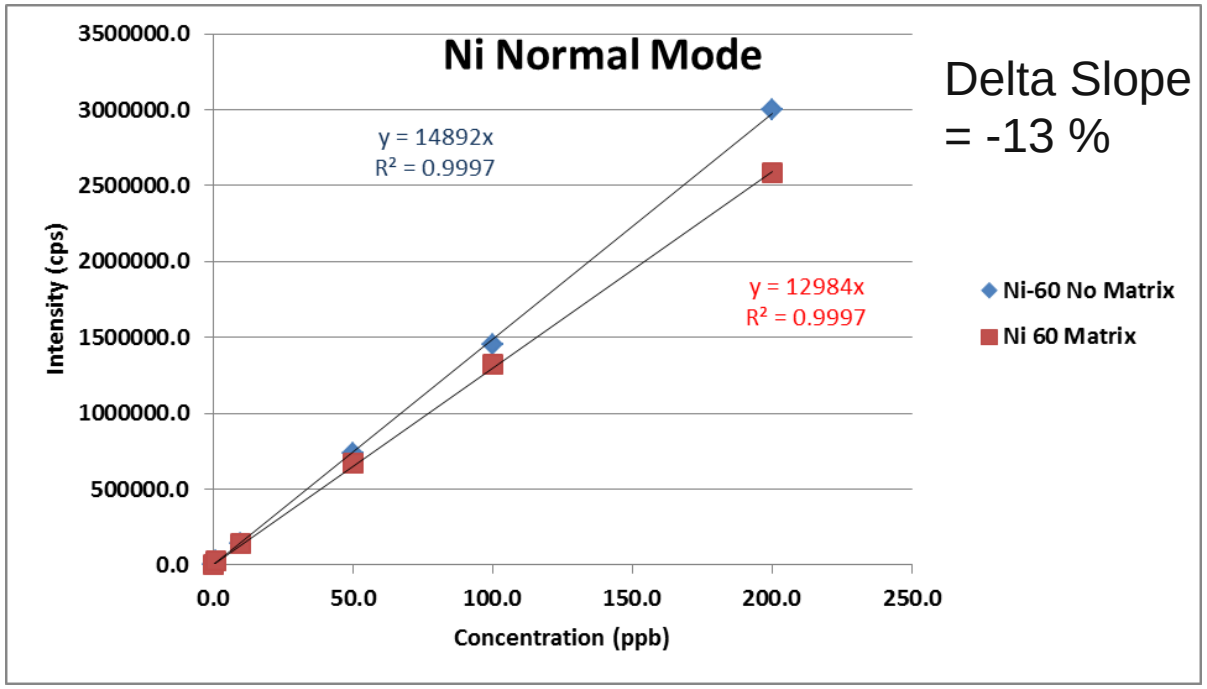
Suppression of Calibration Standards with Matrix



Delta Slope
= -13 %

Matrix / no Matrix
Ratio of Rh Int Std:
200 ppb = 69.0 %
75 ppb 92.5 %

Ratio of Ir Int Std:
200 ppb = 94.0 %
75 ppb = 96.3 %

Ratio of Ge Int Std:
200 ppb = 84.0 %
75 ppb = 90.7 %

Matrix Stock: 250 ppm Ca, Na + 50 ppm Mg, K, Si
Blank, 1 ppb, 10 ppb stds: no matrix
Matrix added to 50 (20x), 100 (10x), 200 (5x) ppb
5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si
75 ppb ICV: without matrix = 78.130, with matrix = 85.052 (9% enhancement), Rh Int. Std.
10x = 25 ppm Ca, Na + 5 ppm Mg, K, Si

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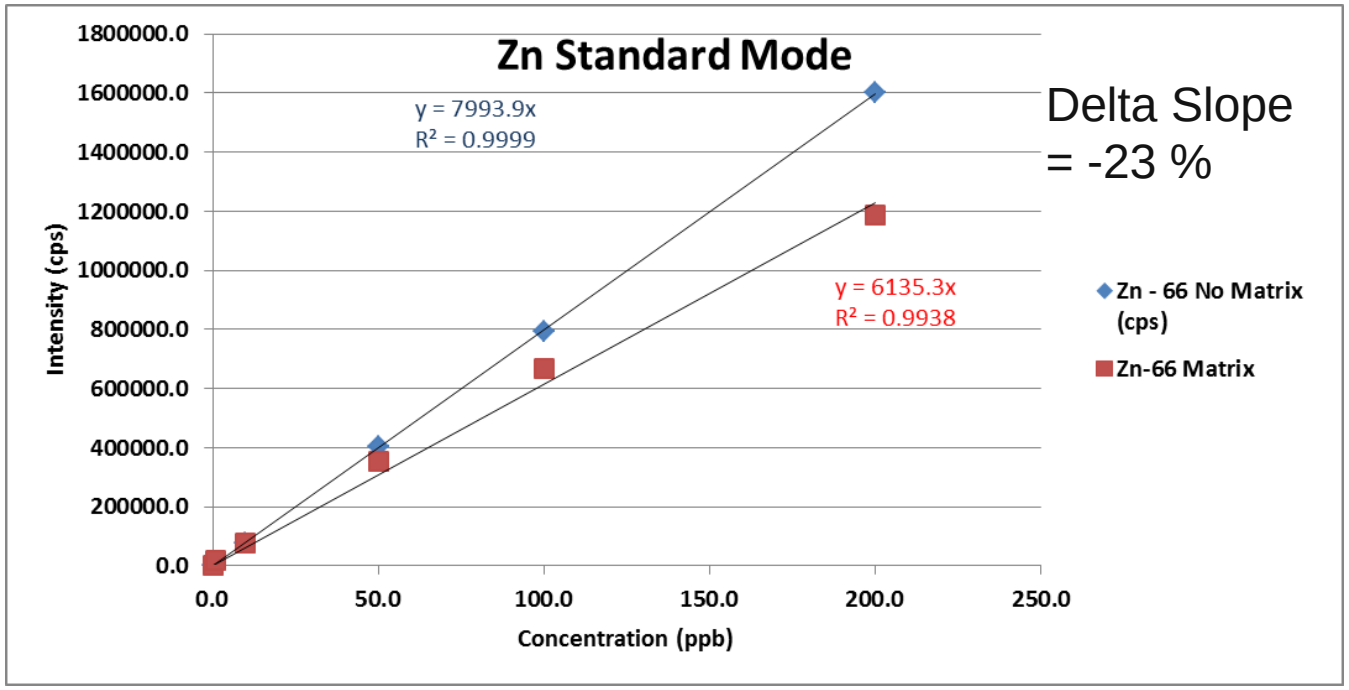
Suppression of Calibration Standards with Matrix



Matrix / no Matrix
Ratio of Rh Int Std:
200 ppb = 69.0 %
75 ppb 92.5 %

Ratio of Ir Int Std:
200 ppb = 94.0 %
75 ppb = 96.3 %

Ratio of Ge Int Std:
200 ppb = 84.0 %
75 ppb = 90.7 %

Matrix Stock: 250 ppm Ca, Na + 50 ppm Mg, K, Si
Blank, 1 ppb, 10 ppb stds: no matrix
Matrix added to 50 (20x), 100 (10x), 200 (5x) ppb
5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si
75 ppb ICV: without matrix = 78.130, with matrix = 80.453 (3% enhancement), Rh Int. Std.
10x = 25 ppm Ca, Na + 5 ppm Mg, K, Si

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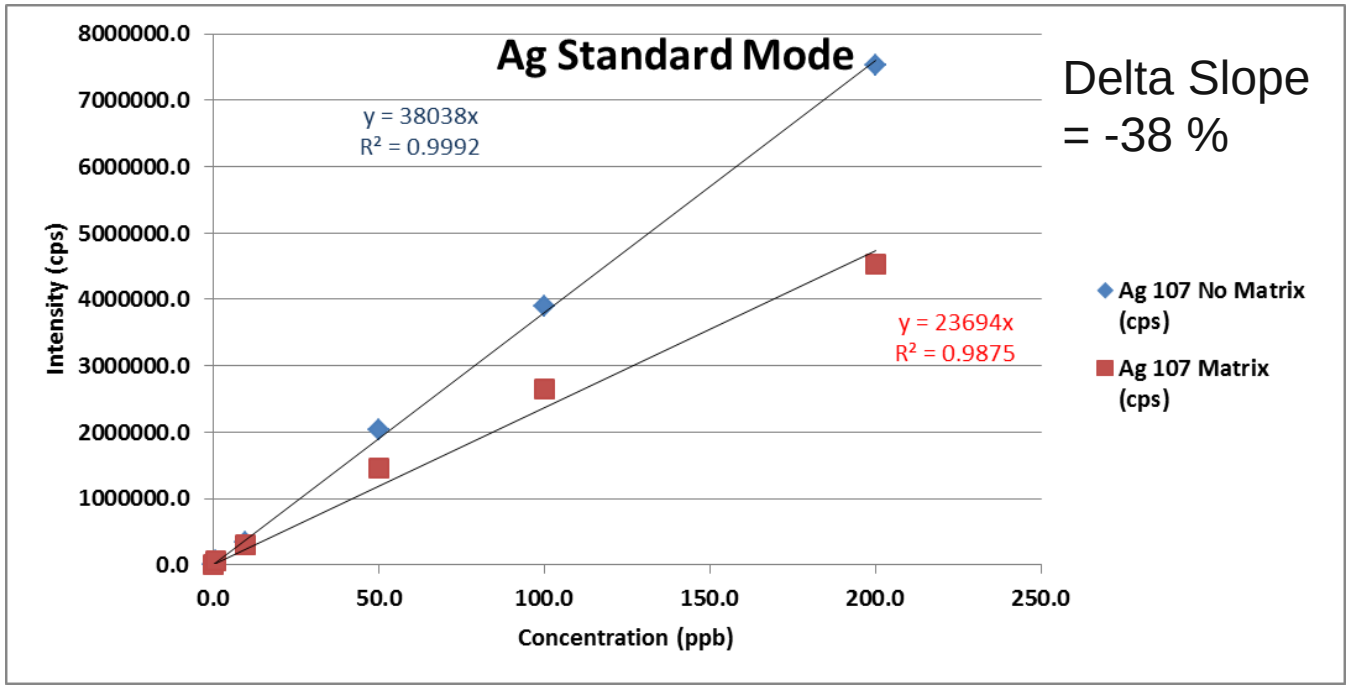
Suppression of Calibration Standards with Matrix



Delta Slope = -38 %

Matrix / no Matrix
Ratio of Rh Int Std:
200 ppb = 69.0 %
75 ppb 92.5 %

Ratio of Ir Int Std:
200 ppb = 94.0 %
75 ppb = 96.3 %

Ratio of Ge Int Std:
200 ppb = 84.0 %
75 ppb = 90.7 %

Matrix Stock: 250 ppm Ca, Na + 50 ppm Mg, K, Si
Blank, 1 ppb, 10 ppb stds: no matrix
Matrix added to 50 (20x), 100 (10x), 200 (5x) ppb
5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si
75 ppb ICV: without matrix = 76.796, with matrix = 69.096 (11% suppression), Rh Int. Std.
10x = 25 ppm Ca, Na + 5 ppm Mg, K, Si

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Matrix Match the Calibration…

- Calibration with increasing concentrations of major cations
  - Na, Ca, K, Mg, Si
- Minimizes EIE effects
- Internal standard less critical…

Matrix Stock: 250 ppm Ca, Na + 50 ppm Mg, K, Si
Blank, 1 ppb, 10 ppb stds: no matrix
Matrix added to 50 (20x), 100 (10x), 200 (5x) ppb
5x = 50 ppm Ca, Na + 10 ppm Mg, K, Si

Internal Standard	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Ga-1 69 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV 75	72.214	72.141	73.911	71.124	73.341	72.975	75.074	72.680	75.910	72.135	77.455	70.208	74.940
% RECOVERY	96.3%	96.2%	98.5%	94.8%	97.8%	97.3%	100.1%	96.9%	101.2%	96.2%	103.3%	93.6%	99.9%
ICV 75 M10X	73.085	73.128	72.930	72.032	73.990	75.698	74.353	73.886	75.865	74.217	76.498	71.736	73.497
% RECOVERY	97.4%	97.5%	97.2%	96.0%	98.7%	100.9%	99.1%	98.5%	101.2%	99.0%	102.0%	95.6%	98.0%
Internal Standard	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**	**Ge**
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Ga-1 69 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV 75	75.304	75.230	77.074	74.163	76.436	76.081	78.236	75.664	79.101	75.161	80.733	73.177	78.107
% RECOVERY	100.4%	100.3%	102.8%	98.9%	101.9%	101.4%	104.3%	100.9%	105.5%	100.2%	107.6%	97.6%	104.1%
ICV 75 M10X	72.732	72.773	72.607	71.693	73.588	75.361	73.998	73.379	75.478	73.767	76.135	71.390	73.121
% RECOVERY	97.0%	97.0%	96.8%	95.6%	98.1%	100.5%	98.7%	97.8%	100.6%	98.4%	101.5%	95.2%	97.5%
Internal Standard	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**	**Ir**
Sample Id	**V-1 51 (ppb)**	**Cr-1 52 (ppb)**	**Mn-1 55 (ppb)**	**Co-1 59 (ppb)**	**Ni-1 60 (ppb)**	**Cu-1 63 (ppb)**	**Ga-1 69 (ppb)**	**Cd-1 111 (ppb)**	**Zn-1 66 (ppb)**	**As-1 75 (ppb)**	**Se-1 82 (ppb)**	**Sr-1 88 (ppb)**	**Ag-1 107 (ppb)**
ICV 75	73.611	73.552	75.386	72.523	74.712	74.406	76.508	73.899	77.351	73.521	78.953	71.510	76.324
% RECOVERY	98.1%	98.1%	100.5%	96.7%	99.6%	99.2%	102.0%	98.5%	103.1%	98.0%	105.3%	95.3%	101.8%
ICV 75 M10X	71.298	71.334	71.197	70.320	72.174	73.884	72.535	71.877	73.960	72.378	74.631	69.942	71.659
% RECOVERY	95.1%	95.1%	94.9%	93.8%	96.2%	98.5%	96.7%	95.8%	98.6%	96.5%	99.5%	93.3%	95.5%

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Tips for Calibrating for Method 200.8

- Figure out range of major elements typically seen in lab – including external QC samples
  - Example: Ca = 30 mg/L, Na = 38 mg/L, K = 5 mg/L, Mg = 9 mg/L
    - An Internet USDA report listed the above Mean Concentrations (https://www.ars.usda.gov/ARSUserFiles/80400525/Articles/NDBC32_WaterMin.pdf)
- Make up a Matrix Standard 5 – 10 X higher in concentration
  - Use this to spike increasing levels of your matrix elements into your calibration standards
  - Be careful you are using ultrapure standards if you make your own
    - Recommend purchasing a multi-element standard from reputable supplier to contaminants are reported
- Example Calibration Scheme:
  - Add increasing spike amounts of the matrix standard to each calibration standard (see below)
    - Can use no matrix in lowest 1 or 2 standards – to prevent contamination
  - Monitor what your internal standards (and alternates) are doing

Analytes	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)	Standard 4 (µg/L)
Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, U, Fe*	1	10	50	100
Hg	0.05	0.5	2.5	5
Na*, Mg*, K*, Ca*	100	1000	5000	10000
Internal Standards	^{45}Sc, ^{71}Ga, ^{72}Ge, ^{115}In, ^{193}Ir			

https://www.perkinelmer.com/lab-solutions/resources/docs/APP-NexION-2000-ICP-MS-EPA-200-Point-8-Standard-Mode-013121B_01.pdf

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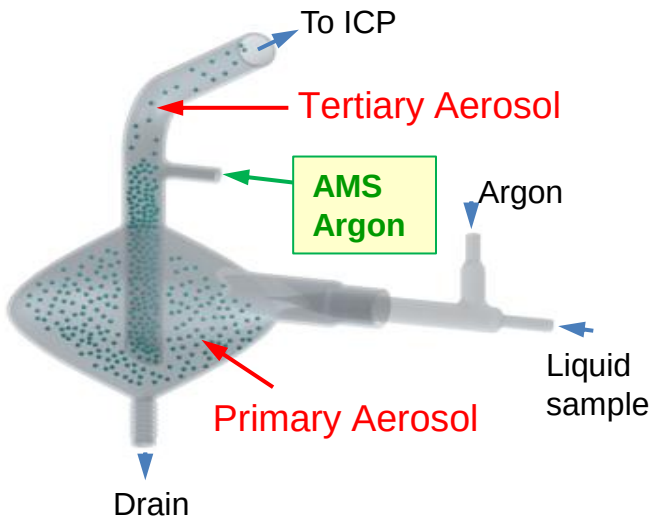
Gas Dilution – Another Alternative to Reduce Matrix Effects

- All Matrix Solution (AMS)
  - Simplifies the analysis of high-matrix samples

- Introduces a flow of argon into the spray chamber neck, the aerosol stream is diluted, allowing for:
  - More efficient ionization
  - Fewer matrix effects
  - Less deposition on the interface cones

- Simplifies sample preparation
- Improves internal standard stability



PerkinElmer All Matrix Solution (AMS)

- Signal attenuation through gas dilution
- Over 100x dilution
- Predictable response across mass range

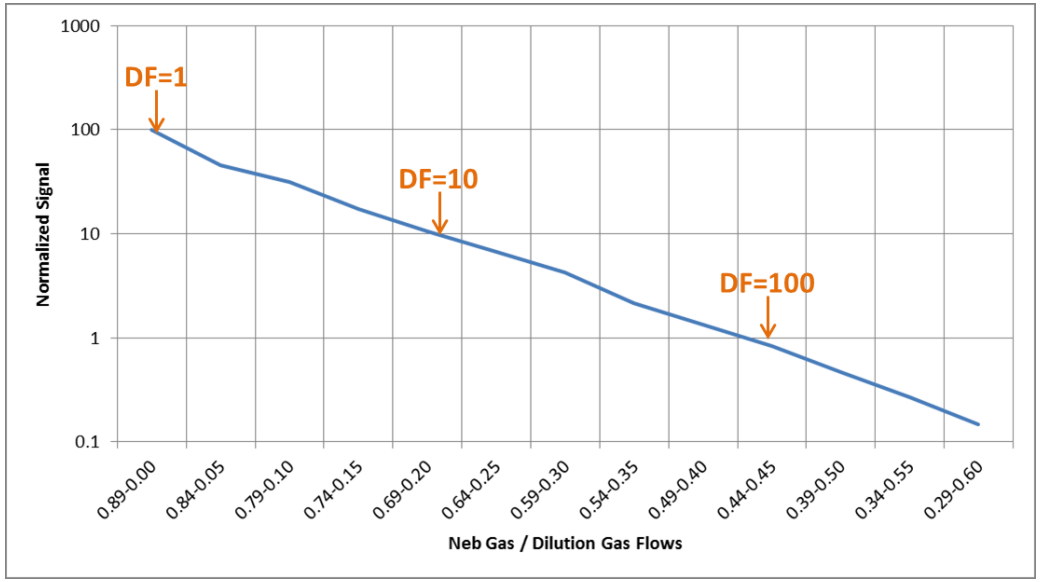


Figure 2. Spike recovery in undiluted seawater NASS-5 with humidifier.

http://www.perkinelmer.com/CMSResources/Images/44-175832PRD_NexION-AMS-Systems-Product-Note-012394_01.pdf

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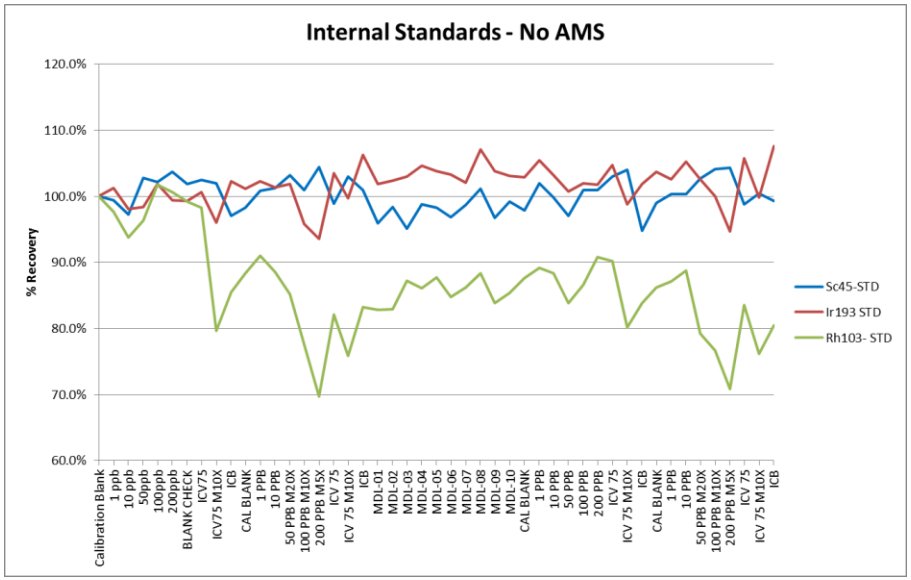
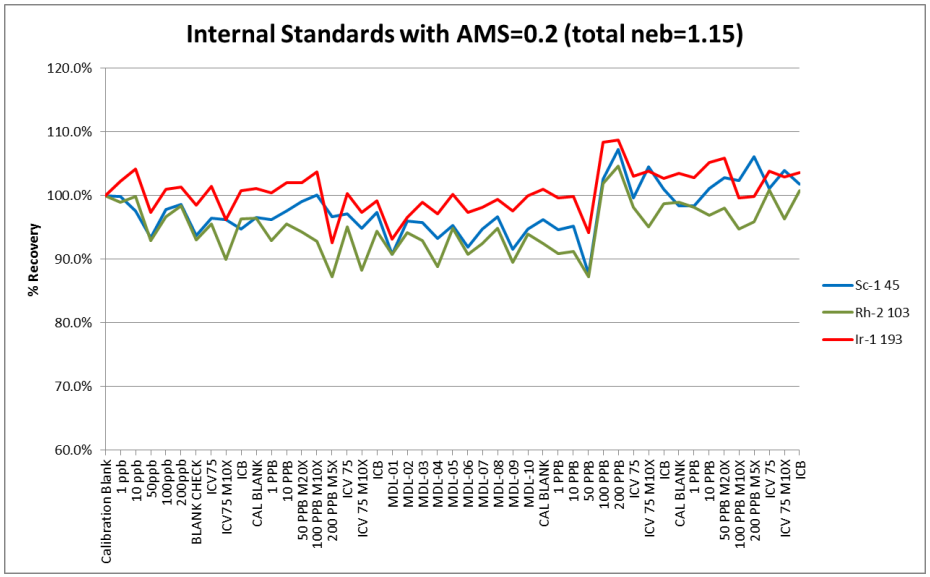
AMS Stabilizes Internal Standards

- Calibrated at 1, 10, 50, 100 ppb in 1% nitric acid matrix
  - All elements present in same 10 ppm stock solution
  - Normal mode analysis (no cell or cell gas)
- ICV at 75 ppb analyzed in 1% nitric acid matrix
- ICV 75 + Matrix: 25 ppm Ca, Na and 5 ppm Mg, K, Si
- Large Rh suppression with 5x and 10x matrix added to standards
  - Drastically reduced using AMS





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Other Considerations in Matrix Matching

- Always match the acid type and content of standards and samples
  - Some elements are very sensitive to acid content (Mg, Co, Zn, Se)
  - Some elements have interferences in certain acids:
    - Hydrochloric, phosphoric, sulfuric, etc.

Sample Id	Be 9 (ug/L)	Mg 24 (ug/L)	V 51 (ug/L)	Cr 52 (ug/L	Mn 55 (ug/L)	Co 59 (ug/L)	Ni 60 (ug/L)	Cu 63 (ug/L)	Zn 66 (ug/L)	As 75 (ug/L)	Se 78 (ug/L	Mo 95 (ug/L)	Ag 107 (ug/L)	Tl 205 (ug/L)	Pb 208 (ug/L)
10PPB 1-HNO3	10.07	10.69	10.00	9.60	9.58	9.66	9.64	9.08	10.02	10.01	10.56	10.21	9.29	9.89	10.24
10PPB 5-HN03	9.35	13.14	9.83	9.80	9.19	11.66	9.85	9.45	9.27	9.61	9.72	10.45	9.17	10.45	10.35

Effects of Acid Mismatch – Samples/Stds and QCs

- Calibrated in 20% nitric acid – samples in 20% nitric acid
- QC sample in 1% nitric acid
  - Values for some elements off until acid matrix matched

Lab No	Field No		Ag ppb	As ppb	Ba ppb	Be ppb	Ca ppm
T-183		MATRIX IS 1-2% HNO3	2.2	5.7	31.2	1.33	9.66
T-183 MPV			2.7	4.5	29.9	0.82	11.6
	% Recovery		81.48%	126.67%	104.35%	162.20%	83.28%
T-183 ACID		Concentrated nitric acid (4mL) added to 20mL of T-sample.	2.27	3.6	26.3	0.8	9.94
T-183 acid MPV		MPVs adjusted for dilution by addition of acid	2.25	3.8	24.9	0.68	9.67
	% Recovery	Recoveries of acid matched concentration	100.89%	94.74%	105.62%	117.65%	102.79%

Lab No	Field No	Cd ppb	Co ppb	Cr ppb	K ppm	Mg ppm	Pb ppb	Se ppb	Tl ppb	U ppb	Zn ppb
T-183		6.72	3.83	1.9	2.01	5.97	6	3.1	0.681	1.67	119
T-183 MPV		5.35	3.94	2.1	2.57	7.39	5.89	2.1	0.68	1.69	86.4
	% Recovery	125.61%	97.21%	90.48%	78.21%	80.78%	101.87%	147.62%	100.15%	98.82%	137.73%
T-183 ACID		4.64	3.4	1.8	2.23	7	5.34	1.8	0.61	1.5	72
T-183 acid MPV		4.46	3.28	2	2.14	6.16	4.91	1.8	0.57	1.41	72
	% Recovery	104.04%	103.66%	90.00%	104.21%	113.64%	108.76%	100.00%	107.02%	106.38%	100.00%

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Other Effects to Be Aware Of…

- Switching acid concentrations between samples and washes may have lingering effects on sensitivities
- May need to test stabilization times in plasma
  - Can be minutes!!

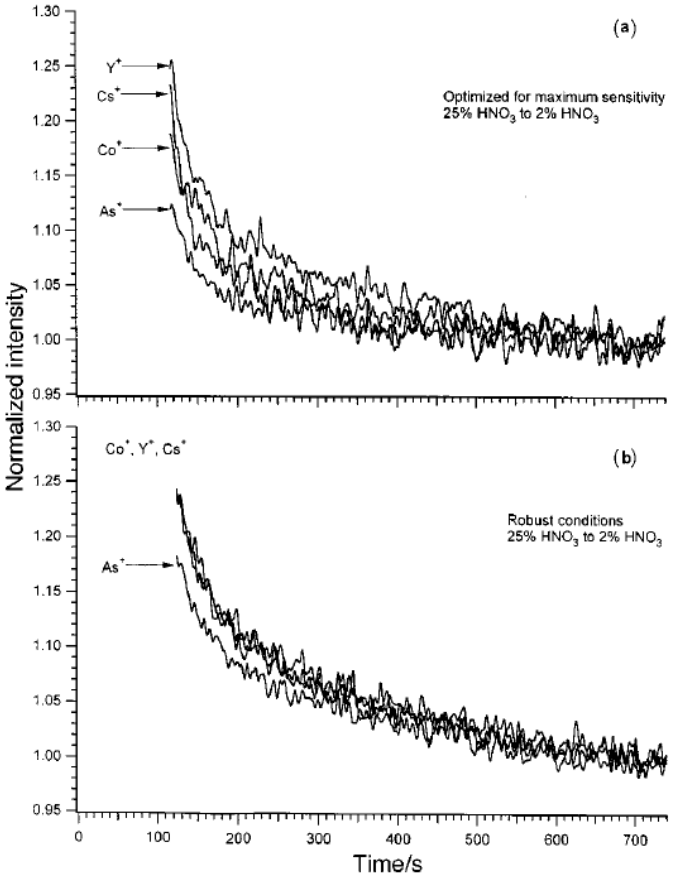

Fig. 8 Transient ICP-MS response for the analytes listed in Table 2 on going from the spray chamber conditioned with 25% to 2% HNO_3 as a function of operating conditions. The two responses correspond to (a) optimized conditions (nebulizer gas flow rate 0.70 l min^{-1} and power 750 W) and (b) robust conditions (nebulizer gas flow rate 0.70 l min^{-1} and power 1300 W).

Transient acid effects in inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry†

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Steps to Successful Sample Analysis

- Sample Preparation
  - Pick sample preparation/digestion method to fit your sample
    - Some cases dictated by regulatory method
  - Solid samples – complete digestion or “leach”

- Calibration
  - Pick appropriate calibration range
  - Matrix match standards to samples!
    - Acid content and concentration
    - Major element concentrations
    - Organic content (in the case of high carbon samples or presence of organics)
      - E.g. Methanol, ethanol, etc…

- Pick appropriate internal standards
  - Can’t be in the sample! Includes elements you don’t look for
    - Can use TotalQuant to screen samples for possible IS elements
  - Can’t be interfered with by matrix elements in sample

Final Thoughts….

- Seeing weird effects/results on certain samples for certain elements isn't generally the result of an instrument (mass spectrometer) problem!
  - Remember the detector on the mass spectrometer is NOT element specific
- If some result is different than expected it is generally because something changed BEFORE the mass spectrometer and/or detector
- Examine ALL the RAW data… what trends do you see in intensity counts for your samples, internal standards
  - Look at RSD's - High RSD's indicate stability issue somewhere…
- 95% of all issues in ICP/ICP-MS occur in the sample introduction system!
  - All these interference effects apply to ICP-OES as well – Axial View in particular!

Questions??

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