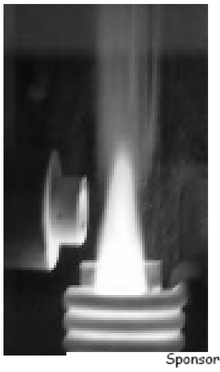
Advanced ICP Tips & Techniques



Sponsored by:

PROGRAM COORDINATORS

WI State Laboratory of Hygiene
DeWayne Kennedy Parker
Kevin Kaufman
Roger Schultz
George Bowman

WI DNR Lab Certification
Rick Mealy

W
E
L
A

Support provided by:

wibby
environmental

Disclaimer

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Discussion Topics

1. Calibration: Single point vs. multipoint
2. Selecting background correction points when dealing with challenging samples
3. Advanced techniques for the identification of interferences and setting proper IECs
4. Dealing with special case interferences: Multi-component spectral fit vs. IEC
5. Applying data evaluation tools to challenging round robin data submitted by participating laboratories

Objectives

- To provide an open forum where analytical problems and solutions can be openly shared among participants
- To better understand background and interference correction
- Provide troubleshooting tools that will be useful in data evaluation
- Learn from each other
- Improve the overall quality of ICP data in Wisconsin

Session Outline

- Suggested approach to setting up a new instrument
- Calibration
- Detection capabilities
- Background correction
- Interference correction
  - Interelement correction factors
  - Multicomponent spectral fit
- Daily interference checks
- Reprocessing data---application and ethics
- Postmortem of the Wibby Environmental PT sample…the PT sample from H_LL!

Initial Setup

Possible sequence for initial set-up

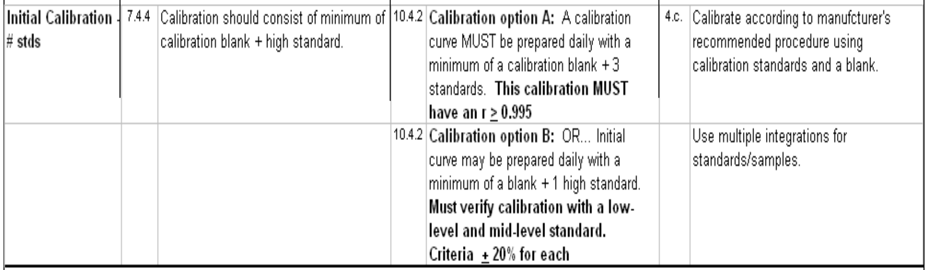
- Perform a viewing height alignment by analyzing a single element (i.e., Mn)
- Profile wavelengths by doing a Hg alignment (or similar, like Cu profile)
- Select elements and wavelengths from Periodic table and put into a method. May wish to have more than one wavelength for elements.
- Default background points are typically equidistant from the peak center.
- Decide which type of calibration to use: single pt. vs. multi-point
- Decide on concentration range based on samples or desired sensitivity.
  - Axial orientation is more sensitive, but has limited linear dynamic range.
  - Calibrating to a lower concentration may help improve detection limit.
- Calibrate with standards.

Initial Set-up Continued

- View spectra
  - Optimize peak position
  - Optimize background correction points.
- Calibrate with optimized conditions
- Determine linear dynamic range
- Analyze LOD standards (7 reps of std, 1 - 10 times the estimated LODs)
- Run single element standards; determine IECs based on LODs
- Prepare compatible calibration standard mixtures based on interferences.
- Calibrate using new standard mixtures and IECs
- Re-analyze LOD standards
- Evaluate IEC table based on new LODs
- Once method is set, validate method with a low level control (near LOQ concentration), a second source (QCS), interference check(s), a mid-range check, and a blank.

Calibration-
of stds

Method Comparison - # of Calibration Levels



	200.7		6010C		3120B	
Initial Calibration - # stds	7.4.4	Calibration should consist of minimum of calibration blank + high standard.	10.4.2	**Calibration option A:** A calibration curve MUST be prepared daily with a minimum of a calibration blank + 3 standards. **This calibration MUST have an r ≥ 0.995**	4.c.	Calibrate according to manufcturer's recommended procedure using calibration standards and a blank.
			10.4.2	**Calibration option B:** OR... Initial curve may be prepared daily with a minimum of a blank + 1 high standard. **Must verify calibration with a low-level and mid-level standard. Criteria ± 20% for each**		Use multiple integrations for standards/samples.

Calibration with blank and one standard acceptable for all 3

6010 incorporates stricter criteria when 1-pt calibration is used

Verify the calibration at low and mid-level, but…

…± 20% criteria is quite forgiving for a mid-level standard

…but may be difficult at LOQ level regardless of calibration

Note that only SM touches on the need for multiple integrations

Calibration…2 Schools of thought

Blank
+1 standard

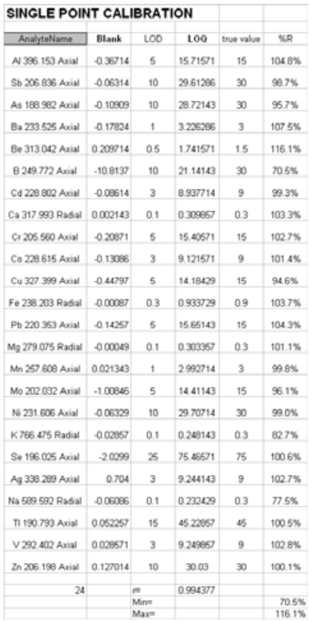
Blank +
Multiple standards

Manufacturers recommend: Blank + 1 standard.

SLH calibrates with 1 standard plus a blank and reads back an LOQ level standard. This procedure meets <u>NELAP requirements</u>.

Either is fine as long as you can demonstrate linearity and obtai acceptable results upon “reading back” an LOQ standard.

Calibration Debate: 1 pt or multi?



SINGLE POINT CALIBRATION

AnalyteName	Blank	LOD	LOQ	true value	%R
Al 396.153 Axial	-0.36714	5	15.71571	15	104.8%
Sb 206.836 Axial	-0.06314	10	29.61286	30	98.7%
As 188.982 Axial	-0.10909	10	28.72143	30	95.7%
Ba 233.525 Axial	-0.17824	1	3.226286	3	107.5%
Be 313.042 Axial	0.209714	0.5	1.741571	1.5	116.1%
B 249.772 Axial	-10.8137	10	21.14143	30	70.5%
Cd 228.802 Axial	-0.08614	3	8.937714	9	99.3%
Ca 317.993 Radial	0.002143	0.1	0.309857	0.3	103.3%
Cr 205.560 Axial	-0.20871	5	15.40571	15	102.7%
Co 228.615 Axial	-0.13086	3	9.121571	9	101.4%
Cu 327.399 Axial	-0.44797	5	14.18429	15	94.6%
Fe 238.203 Radial	-0.00087	0.3	0.933729	0.9	103.7%
Pb 220.353 Axial	-0.14257	5	15.65143	15	104.3%
Mg 279.075 Radial	-0.00049	0.1	0.303357	0.3	101.1%
Mn 257.608 Axial	0.021343	1	2.992714	3	99.8%
Mo 202.032 Axial	-1.00846	5	14.41143	15	96.1%
Ni 231.606 Axial	-0.06329	10	29.70714	30	99.0%
K 766.475 Radial	-0.02857	0.1	0.248143	0.3	82.7%
Se 196.025 Axial	-2.0299	25	75.46571	75	100.6%
Ag 338.289 Axial	0.704	3	9.244143	9	102.7%
Na 589.592 Radial	-0.06086	0.1	0.232429	0.3	77.5%
Tl 190.793 Axial	0.052257	15	45.22857	45	100.5%
V 292.402 Axial	0.028571	3	9.249857	9	102.8%
Zn 206.198 Axial	0.127014	10	30.03	30	100.1%
24		r=	0.994377		
		Min=			70.5%
		Max=			116.1%

Comparison of calibration approach

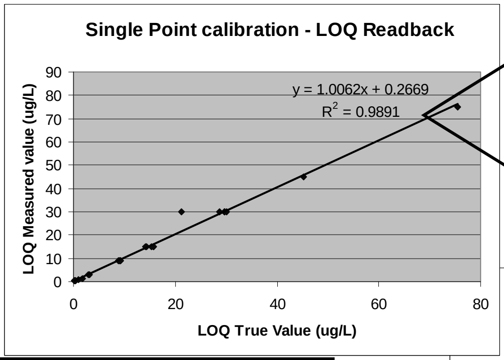
In each case, a standard was prepared at the SLH LOQ level for each target analyte.

These tables show the recovery for each analyte.

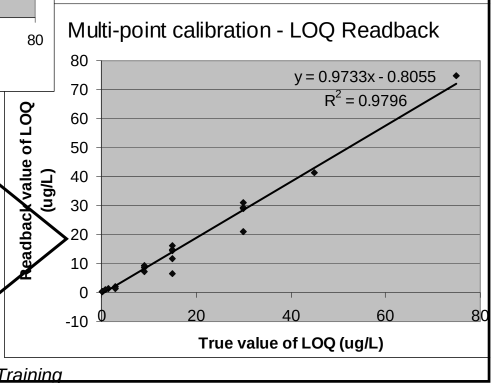
MULTI-POINT CALIBRATIO

AnalyteName	Blank	LOD	LOQ	true value	%R
Al 396.153 Axial	-10.0009	5	6.622	15	44.1%
Sb 206.836 Axial	0.659	10	30.90571	30	103.0%
As 188.982 Axial	-1.09194	10	29.15	30	97.2%
Ba 233.525 Axial	-1.28914	1	1.988143	3	66.3%
Be 313.042 Axial	-0.23186	0.5	1.423571	1.5	94.9%
B 249.772 Axial	-13.9143	10	21.17857	30	70.6%
Cd 228.802 Axial	-0.73686	3	8.493571	9	94.4%
Ca 317.993 Radial	-0.07029	0.1	0.245286	0.3	81.8%
Cr 205.560 Axial	-1.26229	5	14.59571	15	97.3%
Co 228.615 Axial	-0.15686	3	9.146714	9	101.6%
Cu 327.399 Axial	-3.27257	5	11.60429	15	77.4%
Fe 238.203 Radial	-0.04366	0.3	0.919143	0.9	102.1%
Pb 220.353 Axial	0.411286	5	16.35286	15	109.0%
Mg 279.075 Radial	0.057043	0.1	0.3658	0.3	121.9%
Mn 257.608 Axial	-1.48314	1	1.44	3	48.0%
Mo 202.032 Axial	-0.48424	5	14.89143	15	99.3%
Ni 231.606 Axial	-1.09614	10	29.08429	30	96.9%
K 766.475 Radial	0.036571	0.1	0.309286	0.3	103.1%
Se 196.025 Axial	-2.91071	25	74.88143	75	99.8%
Ag 338.289 Axial	-1.986	3	7.130571	9	79.2%
Na 589.592 Radial	0.006143	0.1	0.296	0.3	98.7%
Tl 190.793 Axial	-3.32286	15	41.31857	45	91.8%
V 292.402 Axial	-0.318	3	9.296571	9	103.3%
Zn 206.198 Axial	-2.12614	10	29.21429	30	97.4%
		r=	0.98974		
		Min=			44.1%
		Max=			121.9%

Calibration approach: accuracy at the LOQ

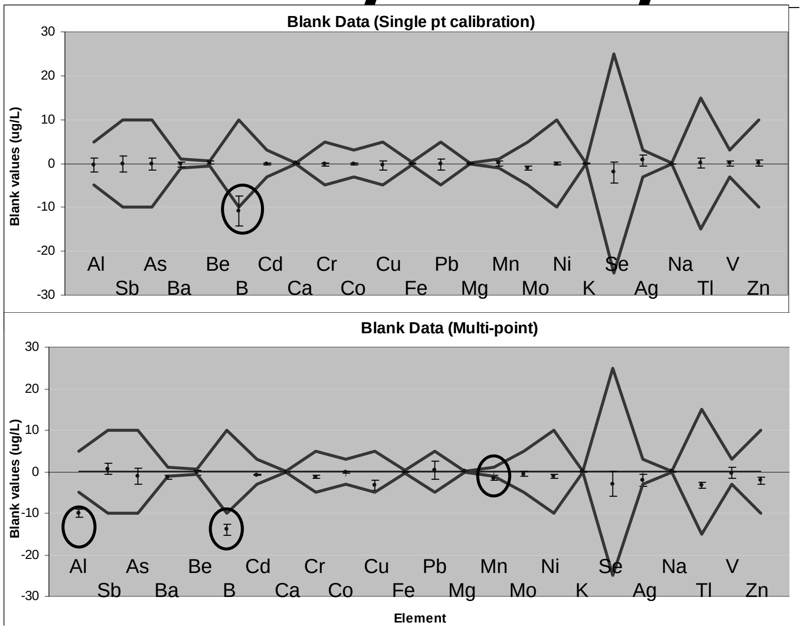

Single Point calibration - LOQ Readback

- 20 of 24 elements recovered w/ in ± 5% of True Value
- Only 4 elements outside of 90-110%: Be, B, K, Na
- Range = 70-116%
- Correlation= 0.994387


Multi-point calibration - LOQ Readback

- 16 of 24 elements recovered w/ in ± 5% of True Value
- 8 elements outside of 90-110%: Al, Ba, B, Ca, Cu, Mg, Mn, Ag
- Range = 44 -122%
- Correlation= 0.98974

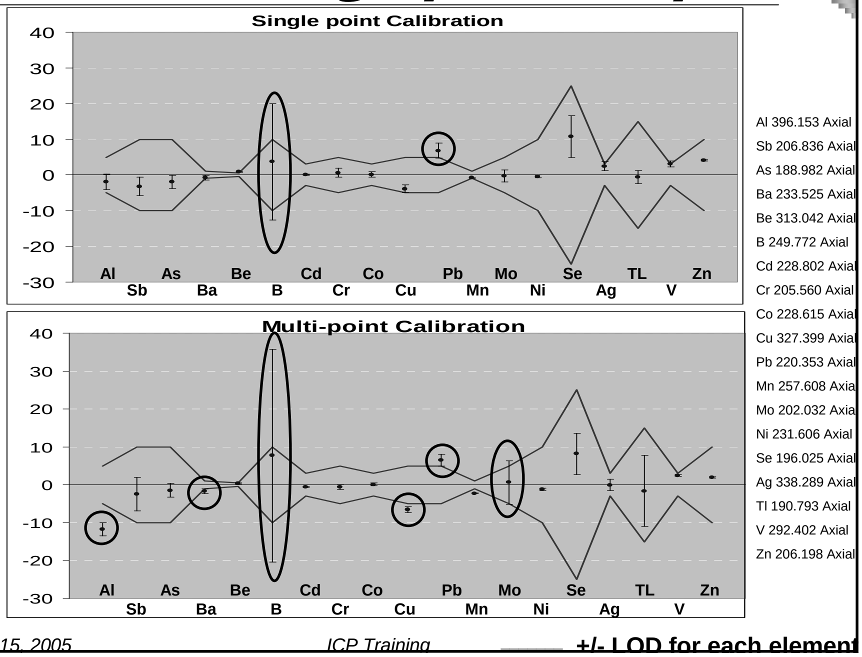
Blank Data: 1pt v. Multi pt


Blank Data (Single pt calibration)

Blank Data (Multi-point)

+/- LOD for each element

ICS-A Data: Single pt v. Multi pt



+/- LOD for each element

Comparison of calibration techniques: Low level accuracy statistics

Calibration followed by reading back 3 different standards with differing concentrations of 25 elements

	Single Point	Multi- Point
LOQ Standard	Mean recovery= 98.6% Range= 70.5 to 106.1%	Mean recovery= 90.8% Range= 44.1 to 121.9%
IPC Standard	Mean recovery= 100.6% Range= 95.5 to 103.8%	Mean recovery= 100.9% Range= 97.9 to 106.3%
QCS Standard	Mean recovery= 99.8% Range= 88.4 to 107.3%	Mean recovery= 101.2% Range= 95.3 to 108.7%

Calibration followed by reading back 3 different standards with differing concentrations of 20 elements (excludes radial elements (Ca, Fe, K, Mg, Na)

	Single Point	Multi- Point
LOQ Standard	Mean recovery= 99.9% Range= 70.5 to 116.1%	Mean recovery= 88.0% Range= 44.1 to 109.0%
IPC Standard	Mean recovery= 100.7% Range= 95.5 to 103.8%	Mean recovery= 100.9% Range= 97.9 to 106.3%
QCS Standard	Mean recovery= 100.9% Range= 97.4 to 107.3%	Mean recovery= 101.7% Range= 95.3 to 108.7%

1 pt vs. Multi-pt: Our Conclusions

- With older instrumentation (i.e., direct readers) the data was clear cut in favor of single point calibration
- With current technology (solid state, dual view), the line between the two becomes more gray
- BOTH approaches have been shown to work
- On close examination, however, the nod has to be given to single-point calibration:
  - Better control at low levels (blanks, LOQ standard)
  - Not only better accuracy, but better precision
  - More economical (time and $$$)

Limitations of Multi-point Calibration

- Calibration range must be short for successful measurement near the LOD (blanks, LOQ level standards and samples)
  - Multi-point calibration range for Ca: 0-10 ppm
  - Ca typically in the 10-100 ppm range
  - If try to bracket samples with calibration standards, frequent dilution maybe required
- Optional approach with multi-point
  - Calibrate with shorter range (e.g., Ca 0-10 ppm)
  - Run LDR standard daily (e.g., Ca 200 ppm)
  - Run samples without dilution to within 90% of LDR as per EPA method 200.7
- Extra effort to use multi-point calibration has little or no cost/benefit…..why bother!

Calibration - Standard Preparation

- Compatibility Issues
  - Solubility concerns
  - Spectral interferences
  - Stability (Ag)
- How many groups?
  - Driven by compatibility
  - Plan on at least 5

Vendor	#Elements /#solutions
Spex	25 in 5
XAXO	25 in 5
Radian	25 in 6
Inorganic Ventures	31 in 6
High Purity Stds	26 in 4
RTC	31 in 2
SLH	28 in 5

Method Comparison - Standard Mixes

		200.7		6010		SM3120B
Instrument Optimization	7.9	Mixed calibration standards NOT prepared from primary standards must be initially verified using a certified reference solution	7.4	For all intermediate and working solutions (especially those < 1 ppm) stability MUST be demonstrated prior to use	3.e.	Before preparing mixed standards, analyze each stock standard separately to check for interferences/impurities. Verify calibration standards initially w2/ QCS; monitor weekly for stability.
	7.9	Acid content = 2% HNO3 / 2% HCl	10.4.11	Calibration standards should be prepared with the same acid combination/concentration as samples.	3.e.	Mixed calibration standard acid content = 1% HNO3 / 5% HCl
Suggested standard mixes	7.9	**Std I**: Ag, As, Ba, B, Ca, Cd, Cu, Mn, Sb, Se	7.4	**Std I**: Be, Cd, Mn, Pb, Se, Zn	3.e.	**Std I**: Be, Cd, Mn, Pb, Se, Zn
	7.9	**Std II**: K, Li, Mo, Na, Sr ,Ti	7.4	**Std II**: Ba, Co, Cu, Fe, V	3.e.	**Std II**: Ba, Co, Cu, Fe, V
	7.9	**Std III**: Co, P, V	7.4	**Std III**: As, Mo	3.e.	**Std III**: As, Mo, Li, Si, Sr
	7.9	**Std IV**: Al, Cr, SiO2, Sn, Zn	7.4	**Std IV**: Al, Ca, Cr, K, Na, Ni, Li, Sr	3.e.	**Std IV**: Al, Ca, Cr, K, Na, Ni
	7.9	**Std V**: Be, Fe, Mg, Ni, Pb, Tl	7.4	**Std V**: Ag, Mg, Sb, Tl	3.e.	**Std V**: Ag, B, Mg, Sb, Tl

Agree that mixed standards should be verified….disagree on "how"

Much variation on standard acid composition. 6010 makes best sense

Agree that 5 standard mixes are needed….disagree on composition

Method Comparison - Calibration Concentrations

Calibration Standard Concentrations

		200.7	3120B
Suggested standard concentrations	7.9	**Std I**:0.5 (Ag),1.0 (Ba), 2.0(B,Cd,Cu,Mn) 5.0 (Sb,Se), 10 (As,Ca)	**Std I**: 1.0 (Be), 2.0 (Cd, Mn), 5.0 (Se, Zn), 10 (Pb)
	7.9	**Std II**: 1.0 (Sr), 5.0 (Li), 10 (Mo,Na), 20 (K), ? (Ti)	**Std II**: 1.0 (Ba, Cu, V), 2.0 (Co), 10 (Fe)
	7.9	**Std III**: 2.0 (Co,V), 10 (P)	**Std III**: 1.0 (Sr), 5.0 (Li) 10 (As, Mo), 21.4 (Si)
	7.9	**Std IV**: 4.0 (Sn), 5.0 (Cr,Zn), 10 (Al,SiO2	**Std IV**: 2.0 (Ni), 5.0 (Cr), 10 (Al, Ca, K, Na)
	7.9	**Std V**: 1.0 (Be), 2.0 (Ni), 5.0 (Tl), 10 (Fe,Mg,Pb)	**Std V**: 1.0 (B), 2.0 (Ag), 10 (Mg, Sb, Tl)

	0.5ppm	1ppm	2ppm	5ppm	10ppm	20ppm
200.7	Ag	Ba,Sr,Be	Cd,Co,Mn,Ni B,Cu,V,	Cr,Li,Se,Zn Sb,Tl	Al,As,Ca,Fe, Mg,Mo,Na,Pb, Si	K
3120B	---	Ba,Sr, Be, Cu,V,B	Cd, Co, Mn,Ni, Ag	Cr,Li,Se,Zn,	Al,As,Ca,Fe, Mg,Mo,Na,Pb, Si, K, Sb, Tl	---

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Detection Capability

SLH LODs

(PE 5300 DV, 1 pt calibration, SeaSpray nebulizer, cyclonic spray chamber)

Element	Calib std.	LOQ stock	LOD
Ag	**2000**	**300**	3
Al	**2000**	**500**	5
As	**2000**	**500**	5
B	**2000**	**1000**	10
Ba	**2000**	**100**	1
Be	**200**	**50**	0.5
Cd	**2000**	**300**	3
Co	**2000**	**300**	3
Cr	**2000**	**500**	5
Cu	**2000**	**500**	5

Element	Calib std.	LOQ stock	LOD
Mn	**1000**	**100**	1
Mo	**2000**	**500**	5
Ni	**2000**	**500**	5
Pb	**2000**	**500**	5
Sb	**2000**	**500**	5
Se	**2000**	**1000**	10
Tl	**2000**	**1000**	10
V	**2000**	**300**	3
Zn	**2000**	**500**	5

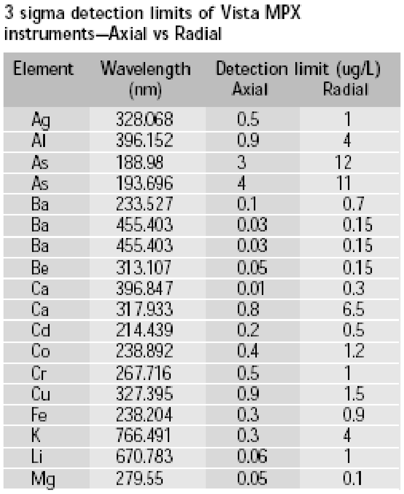
Element	Calib std.	LOQ stock	LOD
Ca	**200**	**10**	0.1
Fe	**30**	**10**	0.1
K	**30**	**10**	0.1
Mg	**100**	**10**	0.1
Na	**200**	**10**	0.1

P-E Optima 2100 DV 3-sigma IDLs

Perkin-Elmer
Field Application Note
Environmental Analysis Using the
Optima 2100 DV ICP System

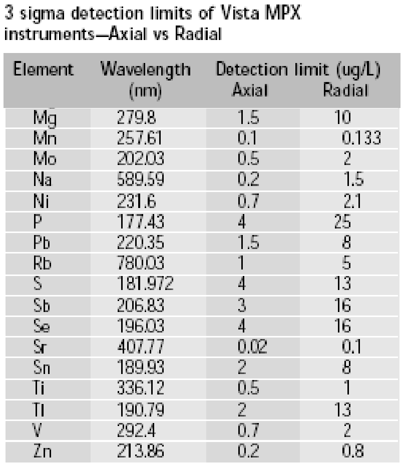
Analyte	IDL, ppb
Ag 328.068	0.549
As 188.979	4.29
Ba 233.527	0.555
Cd 226.502	0.607
Co 238.892	0.346
Cr 267.716	0.744
Cu 327.393	1.41
Mn 257.610	0.095
Na 589.592	15.5
Ni 231.604	0.839
Pb 220.353	2.21
Sb 206.836	4.68
Se 196.026	2.54
Tl 190.801	2.38
V 292.464	1.52
Zn 206.200	1.19

Varian Vista 3-sigma IDLs



3 sigma detection limits of Vista MPX instruments—Axial vs Radial

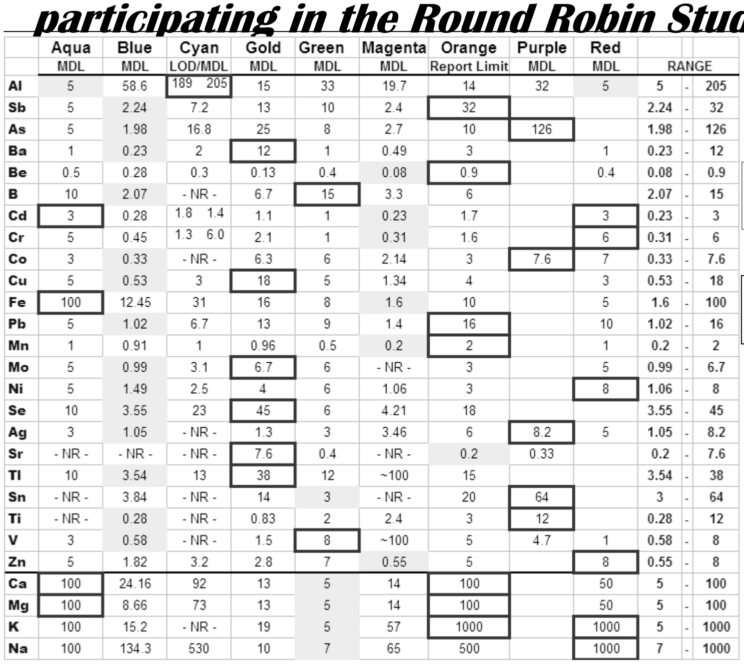
Element	Wavelength (nm)	Detection limit (ug/L) Axial	Radial
Ag	328.068	0.5	1
Al	396.152	0.9	4
As	188.98	3	12
As	193.696	4	11
Ba	233.527	0.1	0.7
Ba	455.403	0.03	0.15
Ba	455.403	0.03	0.15
Be	313.107	0.05	0.15
Ca	396.847	0.01	0.3
Ca	317.933	0.8	6.5
Cd	214.439	0.2	0.5
Co	238.892	0.4	1.2
Cr	267.716	0.5	1
Cu	327.395	0.9	1.5
Fe	238.204	0.3	0.9
K	766.491	0.3	4
Li	670.783	0.06	1
Mg	279.55	0.05	0.1



3 sigma detection limits of Vista MPX instruments—Axial vs Radial

Element	Wavelength (nm)	Detection limit (ug/L) Axial	Radial
Mg	279.8	1.5	10
Mn	257.61	0.1	0.133
Mo	202.03	0.5	2
Na	589.59	0.2	1.5
Ni	231.6	0.7	2.1
P	177.43	4	25
Pb	220.35	1.5	8
Rb	780.03	1	5
S	181.972	4	13
Sb	206.83	3	16
Se	196.03	4	16
Sr	407.77	0.02	0.1
Sn	189.93	2	8
Ti	336.12	0.5	1
Tl	190.79	2	13
V	292.4	0.7	2
Zn	213.86	0.2	0.8

Detection Limits of Labs participating in the Round Robin Study

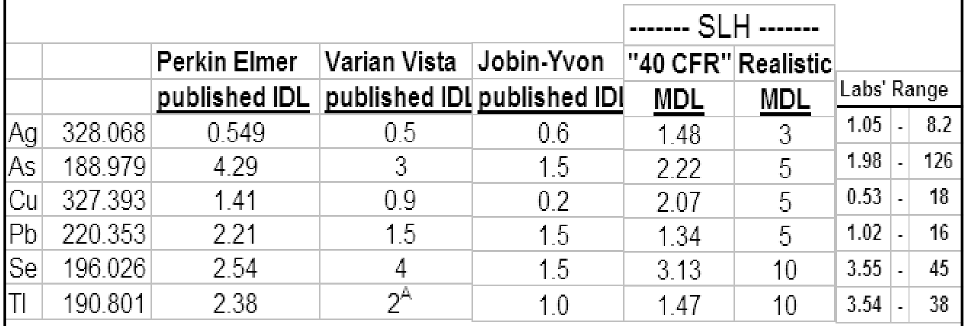


	Aqua	Blue	Cyan	Gold	Green	Magenta	Orange	Purple	Red			
	MDL	MDL	LOD/MDL	MDL	MDL	MDL	Report Limit	MDL	MDL	RANGE		
Al	5	58.6	189 205	15	33	19.7	14	32	5	5	-	205
Sb	5	2.24	7.2	13	10	2.4	32			2.24	-	32
As	5	1.98	16.8	25	8	2.7	10	126		1.98	-	126
Ba	1	0.23	2	12	1	0.49	3		1	0.23	-	12
Be	0.5	0.28	0.3	0.13	0.4	0.08	0.9		0.4	0.08	-	0.9
B	10	2.07	- NR -	6.7	15	3.3	6			2.07	-	15
Cd	3	0.28	1.8 1.4	1.1	1	0.23	1.7		3	0.23	-	3
Cr	5	0.45	1.3 6.0	2.1	1	0.31	1.6		6	0.31	-	6
Co	3	0.33	- NR -	6.3	6	2.14	3	7.6	7	0.33	-	7.6
Cu	5	0.53	3	18	5	1.34	4		3	0.53	-	18
Fe	100	12.45	31	16	8	1.6	10		5	1.6	-	100
Pb	5	1.02	6.7	13	9	1.4	16		10	1.02	-	16
Mn	1	0.91	1	0.96	0.5	0.2	2		1	0.2	-	2
Mo	5	0.99	3.1	6.7	6	- NR -	3		5	0.99	-	6.7
Ni	5	1.49	2.5	4	6	1.06	3		8	1.06	-	8
Se	10	3.55	23	45	6	4.21	18			3.55	-	45
Ag	3	1.05	- NR -	1.3	3	3.46	6	8.2	5	1.05	-	8.2
Sr	- NR -	- NR -	- NR -	7.6	0.4	- NR -	0.2	0.33		0.2	-	7.6
Tl	10	3.54	13	38	12	~100	15			3.54	-	38
Sn	- NR -	3.84	- NR -	14	3	- NR -	20	64		3	-	64
Ti	- NR -	0.28	- NR -	0.83	2	2.4	3	12		0.28	-	12
V	3	0.58	- NR -	1.5	8	~100	5	4.7	1	0.58	-	8
Zn	5	1.82	3.2	2.8	7	0.55	5		8	0.55	-	8
Ca	100	24.16	92	13	5	14	100		50	5	-	100
Mg	100	8.66	73	13	5	14	100		50	5	-	100
K	100	15.2	- NR -	19	5	57	1000		1000	5	-	1000
Na	100	134.3	530	10	7	65	500		1000	7	-	1000

Minimum LOD

Maximum LOD

Select Elements – DL Comparisons



		Perkin Elmer published IDL	Varian Vista published IDL	Jobin-Yvon published IDL	------- SLH ------- "40 CFR" MDL	------- SLH ------- Realistic MDL	Labs' Range		
Ag	328.068	0.549	0.5	0.6	1.48	3	1.05	-	8.2
As	188.979	4.29	3	1.5	2.22	5	1.98	-	126
Cu	327.393	1.41	0.9	0.2	2.07	5	0.53	-	18
Pb	220.353	2.21	1.5	1.5	1.34	5	1.02	-	16
Se	196.026	2.54	4	1.5	3.13	10	3.55	-	45
Tl	190.801	2.38	2^A	1.0	1.47	10	3.54	-	38

^{A} used wavelength 190.790

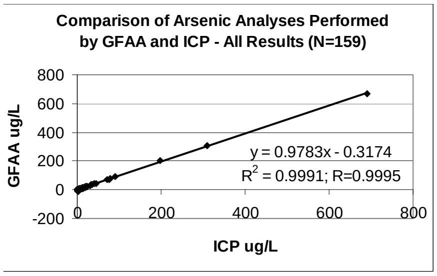
Determining Realistic LODs: One Approach

- Determine LODs using the EPA approach (which is based on precision and may not reflect actual detection capability)
- If your blank results are frequently outside of ± the LOD, the LOD is unrealistic
- Read back standards at the LOQ.
- If you cannot achieve recoveries of 70-130% the LOD is too low and should be raised.
- Increase the LOQ concentration to a reasonable level and repeat replicate measurements. If you can measure this level within 70-130% your LOQ estimate is likely good.
- Divide the LOQ by 3.333 (per NR 149) to obtain the LOD.
- Talk with your auditor and show him/her the data to see if they concur with you.

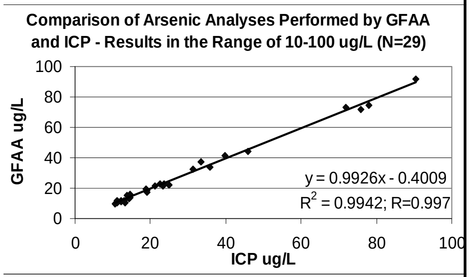
Detection Capability and Arsenic

- The new generation instrumentation strongly suggests that achievable detection limits will allow ICP to virtually replace GFAA
- With the push to lower SDWA MCLs (and NR 140 PALs) for elements such as Pb and As, is ICP still a viable option for low level analysis of arsenic?
- The SLH looked at a 2004 groundwater study for arsenic when both ICP and GFAA techniques were performed on the same sample.

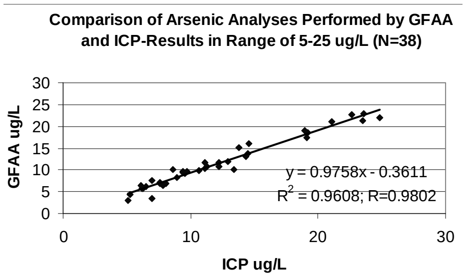
Arsenic; ICP vs. GFAA


Comparison of Arsenic Analyses Performed by GFAA and ICP - All Results (N=159)

Correlation for ALL data looks good, but don't be fooled by limitations of the correlation coefficient

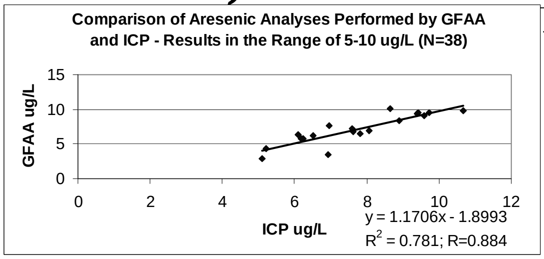

Comparison of Arsenic Analyses Performed by GFAA and ICP - Results in the Range of 10-100 ug/L (N=29)

Looking a bit closer, we see that the correlation DOES drop, but agreement still looks good


Comparison of Arsenic Analyses Performed by GFAA and ICP-Results in Range of 5-25 ug/L (N=38)

Narrowing the range further, we start to see data scattering

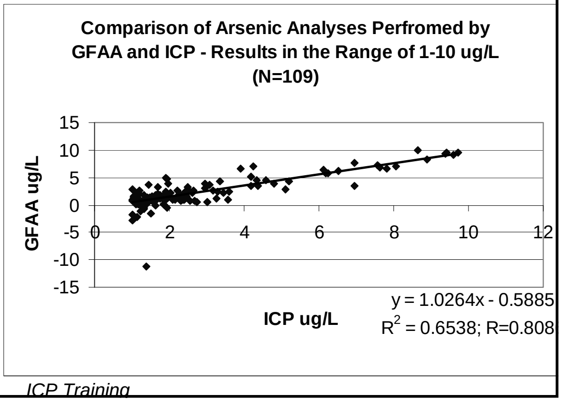
Arsenic; ICP vs. GFAA


Comparison of Aresenic Analyses Performed by GFAA and ICP - Results in the Range of 5-10 ug/L (N=38)

y = 1.1706x - 1.8993
R^2 = 0.781; R=0.884

Narrowing the range further, we start to see data scatter.

ICP shows a little high bias over GFAA


Comparison of Arsenic Analyses Perfromed by GFAA and ICP - Results in the Range of 1-10 ug/L (N=109)

y = 1.0264x - 0.5885
R^2 = 0.6538; R=0.808

Looking only at data in the 1-10 ug/L range, it is clear that GFAA is better below 5 ug/L.

Note that as of Jan. 2006, the EPA will no longer approve use of ICP for compliance testing of As in drinking water

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BGC
Background Correction

Background Correction

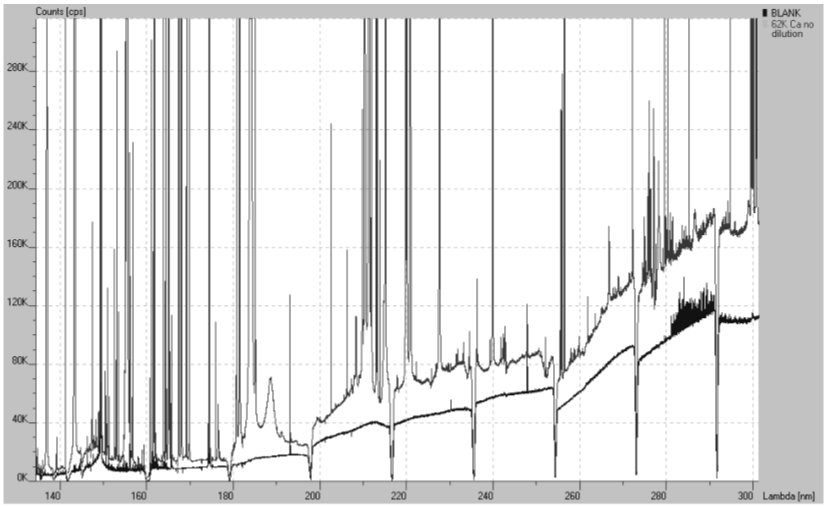
6010C
10.1.1 Before using this procedure to analyze samples, data must be available documenting the initial demonstration of performance. The required data **document the selection criteria for background correction points**; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. These data must be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data must be kept on file and be available for review by the data user or auditor.

6010C4.1.2 AND 200.7 4.1.4
4.1.2 To determine the appropriate location for off-line background correction, **the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes**. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations.

200.7
4.1.4 If a wavelength other than the recommended wavelength is used, the **user must determine and document both the on-line and off-line spectral interference** effect from all method analytes and provide for their automatic correction on all analyses.

Bottom Line: What BGC points were selected and why?

Background Correction Basics



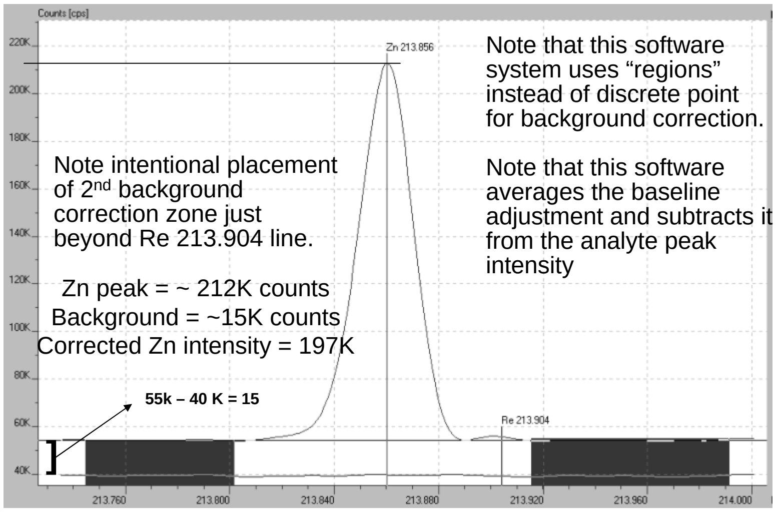
An example showing how a sample with very high levels of Calcium will increase background radiation/intensity over the whole spectrum.

www.ivstandards.com/tech/icp-ops/part08.asp

Background correction:

Flat but elevated baseline

Zn peak with straight-line baseline noise increase due to 62000 ppm Ca.



Note that this software system uses "regions" instead of discrete point for background correction.

Note that this software averages the baseline adjustment and subtracts it from the analyte peak intensity

Note intentional placement of 2nd background correction zone just beyond Re 213.904 line.

Zn peak = ~ 212K counts
Background = ~15K counts
Corrected Zn intensity = 197K

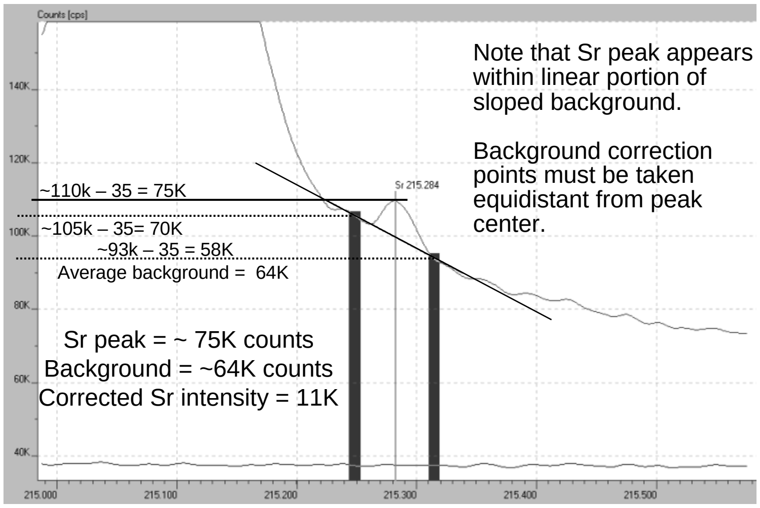
55k – 40 K = 15

Illustration from:
http://www.ivstandards.com/tech/icp-ops/part08.asp#icp-types

Background correction:

sloping linear

Sr peak with sloping/linear baseline due to 62000 ppm Ca.



Note that Sr peak appears within linear portion of sloped background.

Background correction points must be taken equidistant from peak center.

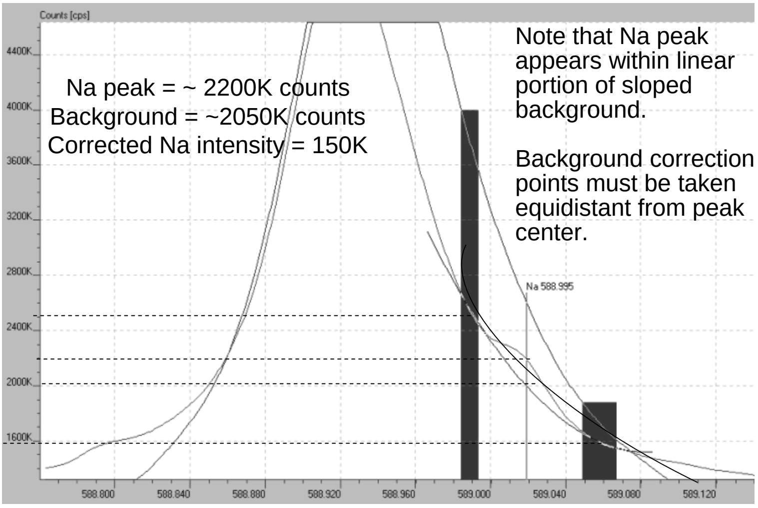
~110k – 35 = 75K
~105k – 35= 70K
~93k – 35 = 58K
Average background = 64K

Sr peak = ~ 75K counts
Background = ~64K counts
Corrected Sr intensity = 11K

Illustration from:
http://www.ivstandards.com/tech/icp-ops/part08.asp#icp-types

Background correction: sloping non-linear

Sr peak with sloping/linear baseline due to 62000 ppm Ca.



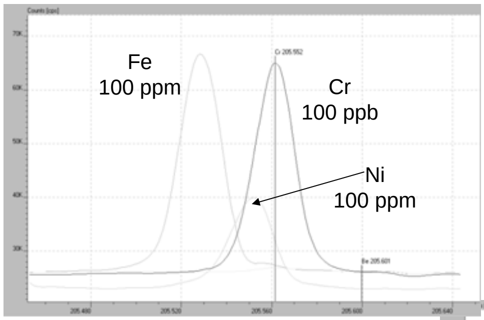
Na peak = ~ 2200K counts
Background = ~2050K counts
Corrected Na intensity = 150K

Note that Na peak appears within linear portion of sloped background.

Background correction points must be taken equidistant from peak center.

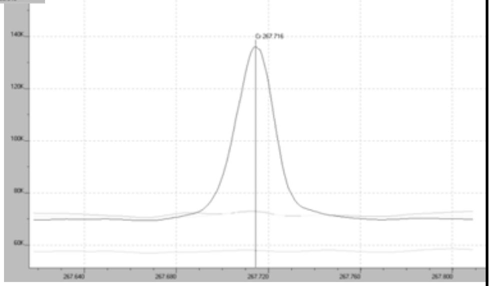
Illustration from:
http://www.ivstandards.com/tech/icp-ops/part08.asp#icp-types

Deciding to use an alternate line



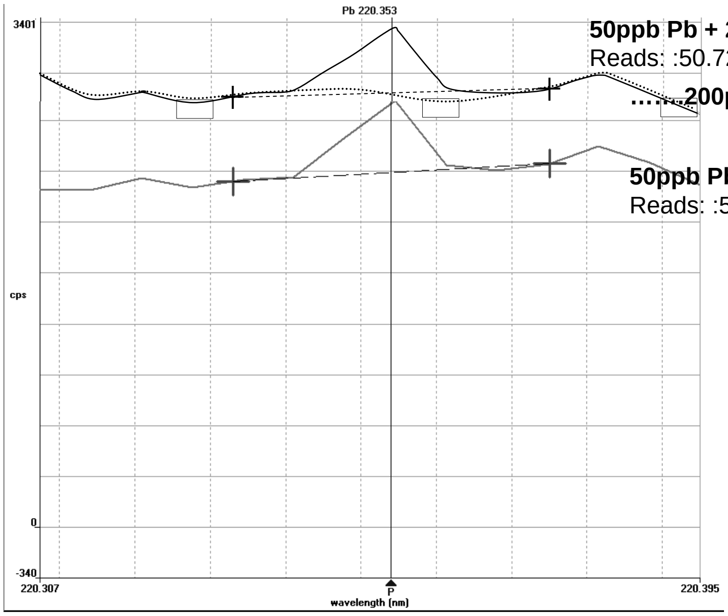
Initially looking at the 205.552 line for Cr,. The decision is that other analytes in this sample make the use of this line too challenging

Switching to the 267.716 line, it looks very clean



http://www.ivstandards.com/tech/icp-ops/enlarge/07/fig1.asp

Background shifts

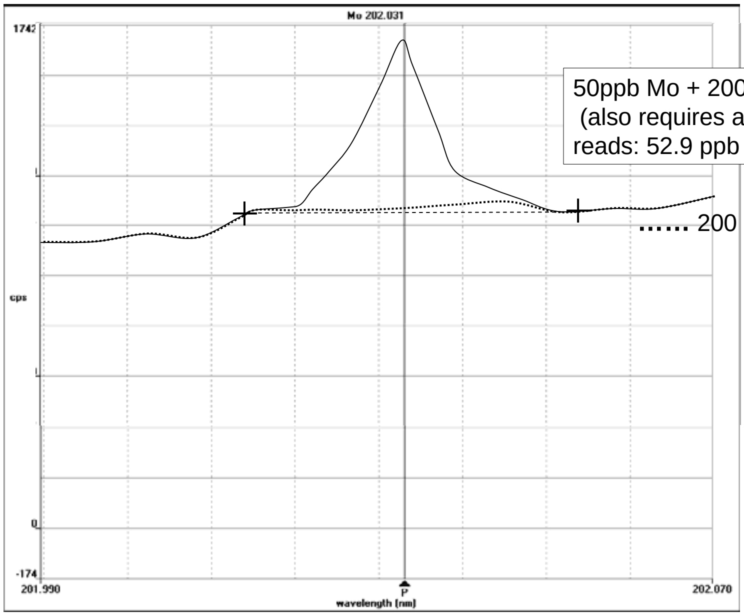


50ppb Pb + 200 ppm Ca
Reads: :50.72

……200ppm Ca

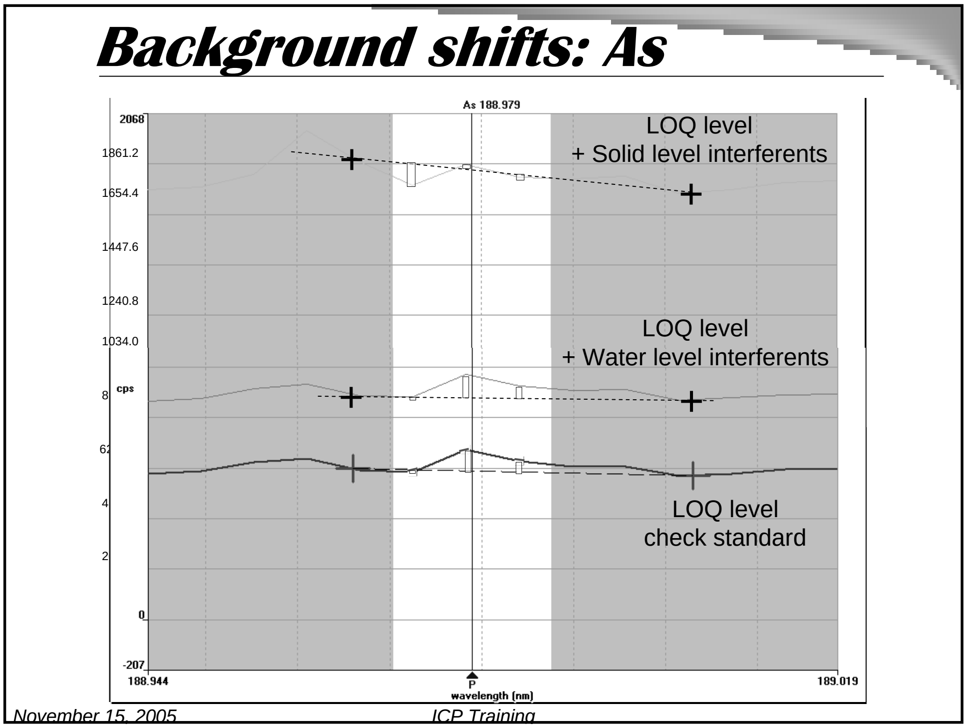
50ppb Pb only
Reads: :50.86

Background shifts: Ca on Mo



50ppb Mo + 200ppm Ca
(also requires an IEC)
reads: 52.9 ppb

…… 200 ppm Ca

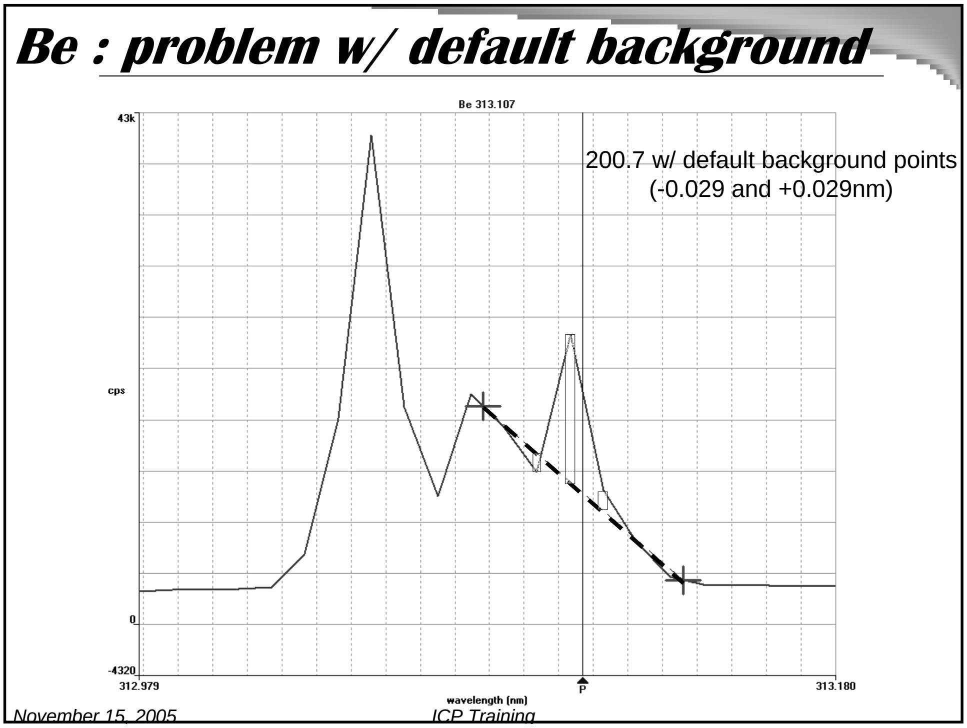


Background shifts: As

LOQ level
+ Solid level interferents

LOQ level
+ Water level interferents

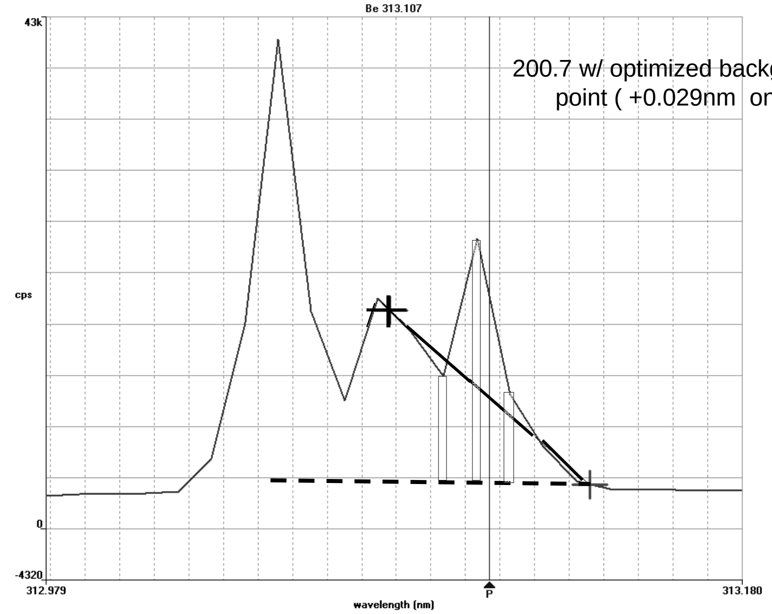
LOQ level
check standard



Be : problem w/ default background

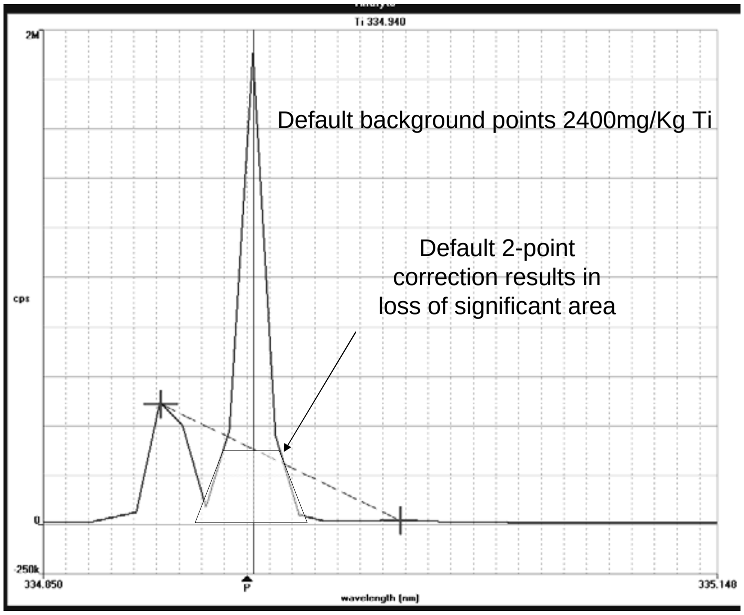
200.7 w/ default background points
(-0.029 and +0.029nm)

Be : optimized background



200.7 w/ optimized background point (+0.029nm only)

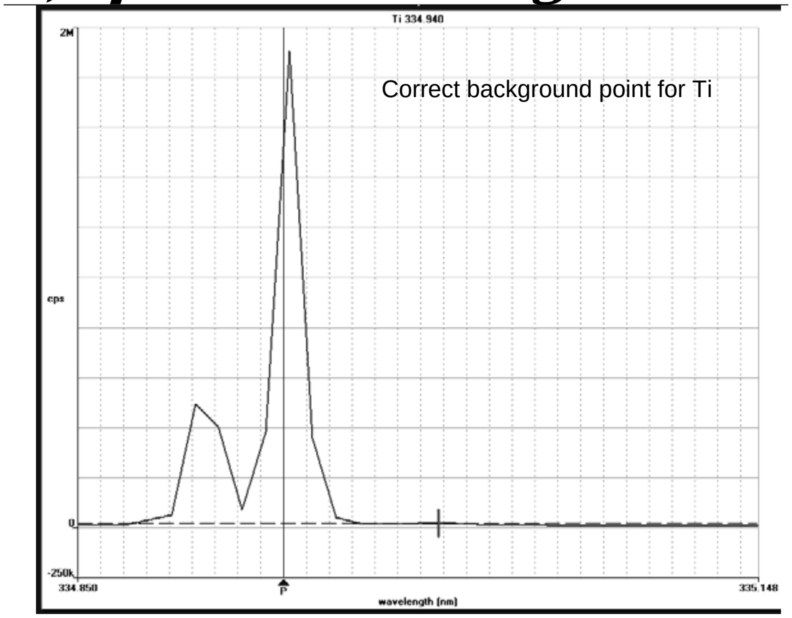
Ti : Default background



Default background points 2400mg/Kg Ti

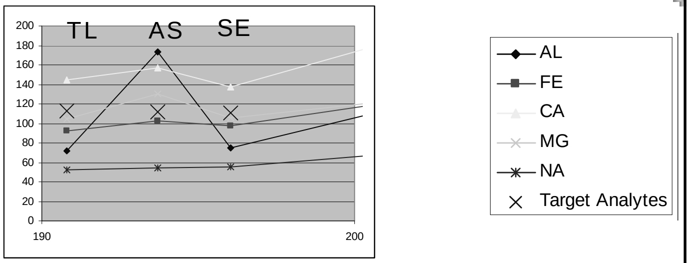
Default 2-point correction results in loss of significant area

Ti; optimimized background

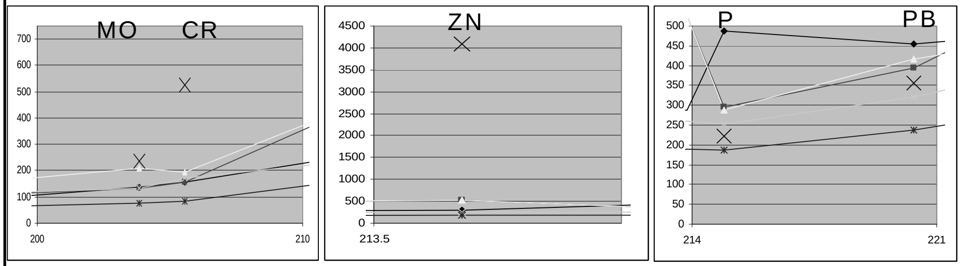


Correct background point for Ti

Major interferents (ICS-A) effect at wavelength of main target analytes at a concentration equal to their LOQ

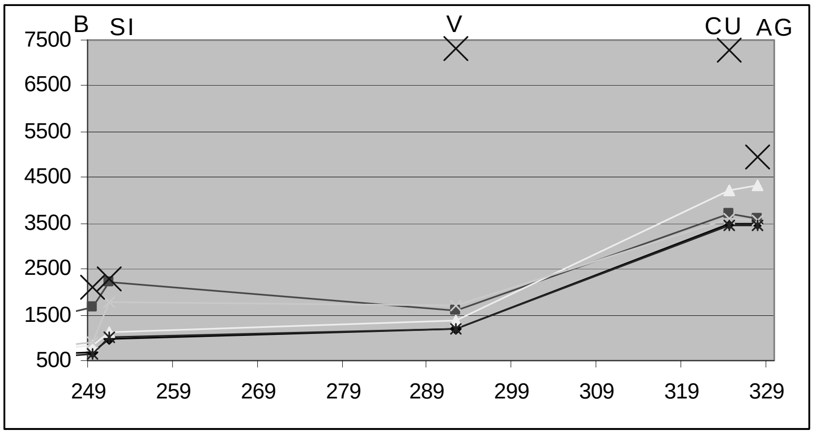


This shows effect of Ca and Fe on Tl, As, and Se.



…while elements such as Cr and Zn do not seem to be affected

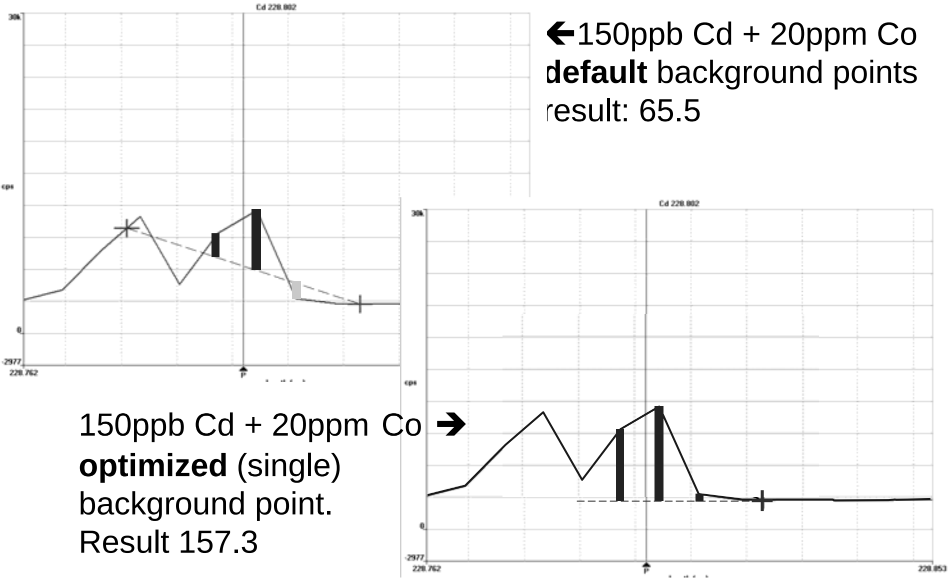
Major interferents (ICS-A) effect at wavelength of main target analytes at a concentration equal to their LOQ



Vanadium shows itself to be another analyte not effected by a high cation background.

Co interference on Cd series

no IECs involved…just background correction



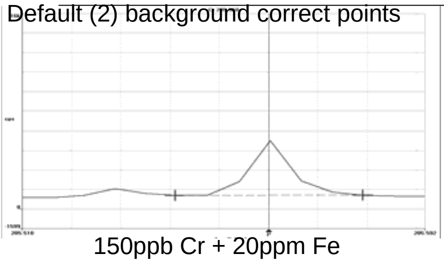
🡐150ppb Cd + 20ppm Co
default background points
result: 65.5

150ppb Cd + 20ppm Co ➔
optimized (single) background point.
Result 157.3

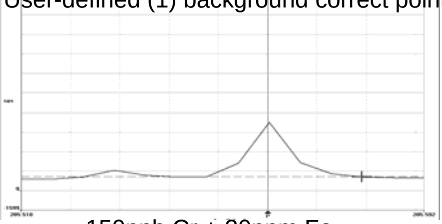
Fe interference on Cr series

Default (2) background correct points

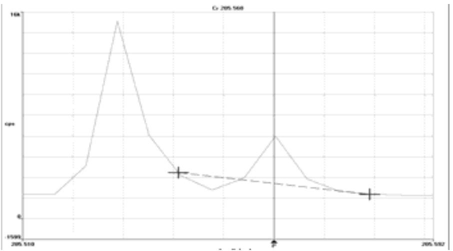
User-defined (1) background correct point



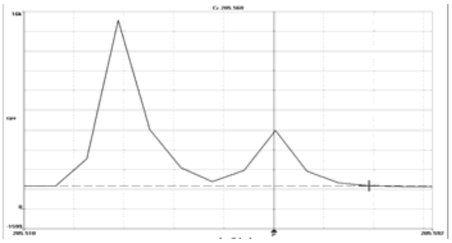
150ppb Cr + 20ppm Fe
Result 158.9
IECs on but no IEC for Fe on Cr



150ppb Cr + 20ppm Fe
Result 161
IECs on but no IEC for Fe on Cr



150ppm Cr + 400ppm Fe
Result= 114.2
IECs on but no IEC for Fe on Cr



150ppb Cr + 400ppm Fe
Result= 165
IECs on but no IEC for Fe on Cr

IECS

Interference Correction

Determining what Interferences exist

Spectral overlap? Or background correction?

Generating correction factors

Verifying adequate correction

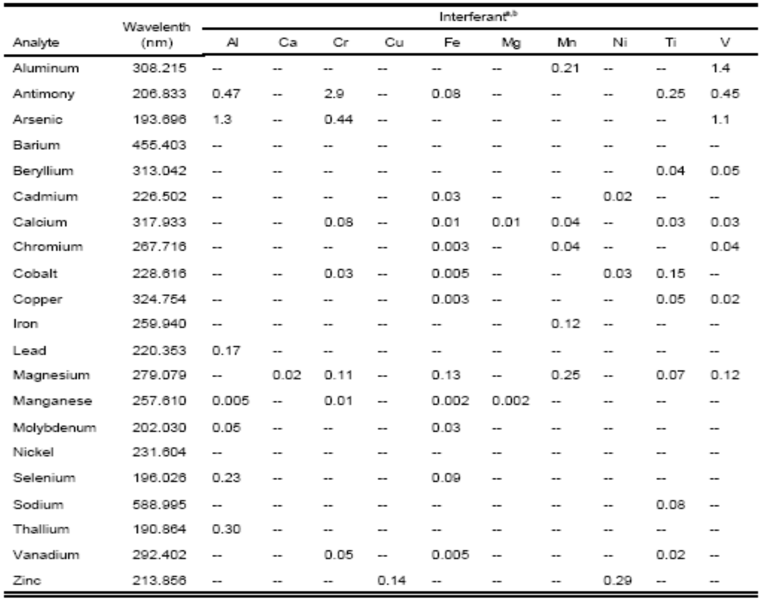
- what the methods require
- common sense approach
  - calibration blank
  - ICS-A….1º interferents (major cations)
  - ICS-B?? 2º interferents (other elements that might interfere)
  - ICS-AB

Method Comparison
-What Elements Must be Tested?

		200.7		6010C		3120B
Option A: Interference Correction using method wavelngths	4.1.4	Interferences must be evaluated for each instrument. When using method suggested λ, analyst must determine and document for each λ the effect of interferences in Table 2 (and use a computer routine for auto-correction	4.1.4	Interferences must be evaluated for each instrument. When using method suggested λ, analyst must determine and document for each λ the effect of interferences in Table 2		Determine interelement CFs by analyzing single element stock solutions of appropriate concentration under conditions matching as closely as possible those of samples.
	Table 2	Requires evaluation of interference from 17 elements: Al,Fe,Cu,Ni,Cr,Mn,V,Be,Ba,Co,Mo,Sn,Ti, Cd,Tl,Si,Ce	Table 2	Requires evaluation of interference from 10 elements: Al, **Ca**, **Mg**, Fe, Cu, Ni, Cr, Mn, V, Ti 1000 ppm: (Al, Ca,Fe,Mg) used by EPA 200 ppm: all others used by EPA		
		NOTE what's missing: Ca, Mg, Na		*NOTE what's missing: Na only*		

200.7 (4.1.4)
6010C (4.1.2)
If a wavelength **other than the recommended wavelength is used**, the user must **determine and document both the <u>on-line</u> and <u>off-line</u> spectral interference** effect **<u>from all method analytes</u>** and provide for their automatic correction on all analyses.

6010 suggested IECs – but not plug n’ play

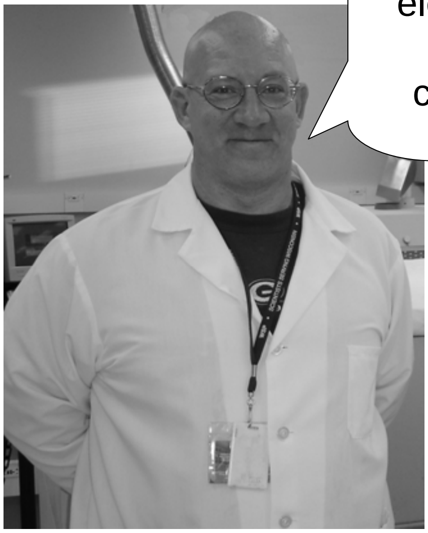


		Interferant[a,b]									
Analyte	Wavelenth (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

Procedure for Generating IECs (PE 5300 DV)

- Calibrate instrument as usual.
- Run single element standards at levels equal to calibration standards.
- If no previous IEC table is in the method, create a new one by entering standards as samples and choosing which element is the possible interferent.
- Check all standards against a table of LODs or reporting limits.
- If any analyte exhibits a response greater than the LOD:
  - calculate an IEC as “apparent” analyte concentration (ppb) per ppm of interferent
- If the method already had an IEC table in it, then the analytes that were greater than the LODs will be manually calculated, as above, and the current IEC will be edited.
- Once the table is complete the single element standards should be analyzed again to ensure they worked and were accurate.
- Some minor editing of the IEC table may be required.
- Reprocessing the analytical run used to collect the data, with the IEC table, will not give an accurate indication of the IECs at work.
- It is best to re-evaluate LODs after IECs have been calculated.

No. 1 Rule for determining IECs



Be sure that your single element standards do not contain significant concentrations of target elements

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Validating IECs

Breaking New Ground

Task *(since it's not clear in the methods)*
Identify an Interference Check Solution(s)...
and a set of evaluation criteria
that ensures adequacy of IECs and BGC points

Objective: Apply the...

... KISS Principle

eep t imple

Devising an Appropriate ICS

Take what we have (CLP) and update it

ICS-A — Major interferent analytes only

This is critical

Add a simple, but overlooked evaluation step

ICB — No analytes of interest — For non-interferent target analytes in ICS-A results should be equivalent to this sample

Consider substituting an evaluation step

ICS-A+ (*aka ICS-AB*) — Major interferents spiked with all analytes

VS.

ICS-B — Secondary interferents only

Re-evaluate acceptance criteria (QA)
Re-think analytical frequency

What about the ICS-AB sample?

- Typically, the "B" means that all target analytes are spiked in with the interferents at a concentration from 0.5 to 1.0 ppm
- Using +/- 20% acceptance criteria, this amounts to allowing +/- 100-200 ppb as "acceptable"
- When trying to analyze trace levels (below 50 ppb), +/- 100-200 ppb represents a huge difference that can mask potential inter-element interferences
- The original reason for the ICS-AB sample was for early instruments that could not display negative numbers (*further suggesting validity of +/- LOD*)
- If you remain caught up in the ICS-AB concept, at least consider spiking target analytes at a much lower level (3-5 times LOQ)

ICS Recommendations: How do we know our IECs are working.

Analyze & Evaluate Initial Calibration Blank (ICB)

All target analytes should be within ± LOD

Analyze & Evaluate an ICS-A standard

ICS-A = Some combo of : Al, Ca, Mg, Fe, K, Na

Use levels = 99% level of expected concentration

May use different ICS-A levels for different matrices

ex. Soils: Al, Ca, Mg, Fe all at 500 ppm

ex: drinking water: Al, Ca, Mg, Fe all at 50 ppm

ex:The "Wibby Sample":????

Interferents should be within ± 5% of true value

All unspiked target analytes should be within ± LOD

Optimally, checks should be made with each run

(Methods allow weekly if control is demonstrated)

ICS Recommendations:
How do we know our IECs are working.

Analyze & Evaluate an ICS-B standard

ICS-B = 2° Interferents only (e.g., Be,Ba,Cd,Co,Cr,Cu,Mn,Ni,V)

Use levels = 99% level of expected concentration

Suggest 10-50 ppm for each

Interferents should be within + 10% of true value

All unspiked target analytes should be within + LOD.

Analyze & Evaluate an ICS-A+ *[ICS-B+]* standard

ICS-A+/ B+ = Interferents at regular level + all target analytes

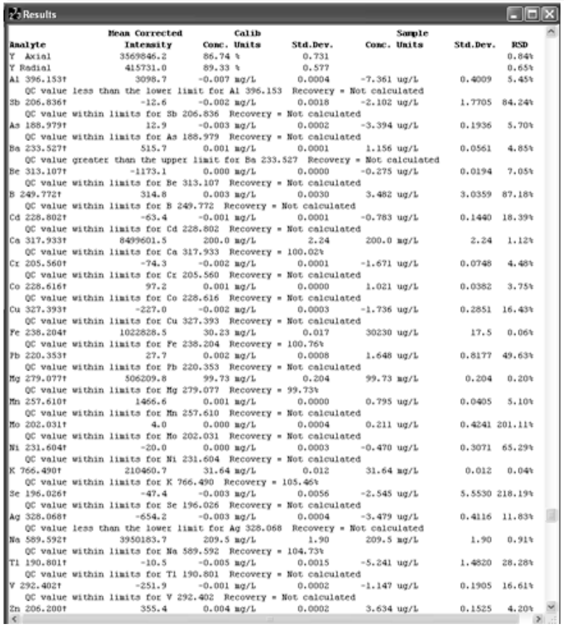
Design target analyte spike levels to detect bias near LOD

Suggest 3 x LOQ for each analyte

All analytes should be within + 10% of true value

At 3 x LOQ, target analyte recovery should be + LOD

Example: ICS-A



```
                     Mean Corrected       Calib                                Sample
Analyte                  Intensity    Conc. Units       Std.Dev.     Conc. Units          Std.Dev.   RSD
Y  Axial                 3569846.2    86.74 %             0.731                                    0.84%
Y Radial                  415731.0    89.33 %             0.577                                    0.65%
Al 396.153†                 3098.7   -0.007 mg/L         0.0004     -7.361 ug/L           0.4009   5.45%
   QC value less than the lower limit for Al 396.153  Recovery = Not calculated
Sb 206.836†                  -12.6   -0.002 mg/L         0.0018     -2.102 ug/L           1.7705  84.24%
   QC value within limits for Sb 206.836  Recovery = Not calculated
As 188.979†                   12.9   -0.003 mg/L         0.0002     -3.394 ug/L           0.1936   5.70%
   QC value within limits for As 188.979  Recovery = Not calculated
Ba 233.527†                  515.7    0.001 mg/L         0.0001      1.156 ug/L           0.0561   4.85%
   QC value greater than the upper limit for Ba 233.527  Recovery = Not calculated
Be 313.107†                -1173.1    0.000 mg/L         0.0000     -0.275 ug/L           0.0194   7.05%
   QC value within limits for Be 313.107  Recovery = Not calculated
B 249.772†                   314.8    0.003 mg/L         0.0030      3.482 ug/L           3.0359  87.18%
   QC value within limits for B 249.772  Recovery = Not calculated
Cd 228.802†                  -63.4   -0.001 mg/L         0.0001     -0.783 ug/L           0.1440  18.39%
   QC value within limits for Cd 228.802  Recovery = Not calculated
Ca 317.933†              8499601.5    200.0 mg/L           2.24      200.0 mg/L             2.24   1.12%
   QC value within limits for Ca 317.933  Recovery = 100.02%
Cr 205.560†                  -74.3   -0.002 mg/L         0.0001     -1.671 ug/L           0.0748   4.48%
   QC value within limits for Cr 205.560  Recovery = Not calculated
Co 228.616†                   97.2    0.001 mg/L         0.0000      1.021 ug/L           0.0382   3.75%
   QC value within limits for Co 228.616  Recovery = Not calculated
Cu 327.393†                 -227.0   -0.002 mg/L         0.0003     -1.736 ug/L           0.2851  16.43%
   QC value within limits for Cu 327.393  Recovery = Not calculated
Fe 238.204†              1022828.5    30.23 mg/L          0.017      30230 ug/L             17.5   0.06%
   QC value within limits for Fe 238.204  Recovery = 100.76%
Pb 220.353†                   27.7    0.002 mg/L         0.0008      1.648 ug/L           0.8177  49.63%
   QC value within limits for Pb 220.353  Recovery = Not calculated
Mg 279.077†               506209.8    99.73 mg/L          0.204      99.73 mg/L            0.204   0.20%
   QC value within limits for Mg 279.077  Recovery = 99.73%
Mn 257.610†                 1466.6    0.001 mg/L         0.0000      0.795 ug/L           0.0405   5.10%
   QC value within limits for Mn 257.610  Recovery = Not calculated
Mo 202.031†                    4.0    0.000 mg/L         0.0004      0.211 ug/L           0.4241 201.11%
   QC value within limits for Mo 202.031  Recovery = Not calculated
Ni 231.604†                  -20.0    0.000 mg/L         0.0003     -0.470 ug/L           0.3071  65.29%
   QC value within limits for Ni 231.604  Recovery = Not calculated
K 766.490†                210460.7    31.64 mg/L          0.012      31.64 mg/L            0.012   0.04%
   QC value within limits for K 766.490  Recovery = 105.46%
Se 196.026†                  -47.4   -0.003 mg/L         0.0056     -2.545 ug/L           5.5530 218.19%
   QC value within limits for Se 196.026  Recovery = Not calculated
Ag 328.068†                 -654.2   -0.003 mg/L         0.0004     -3.479 ug/L           0.4116  11.83%
   QC value less than the lower limit for Ag 328.068  Recovery = Not calculated
Na 589.592†              3950183.7    209.5 mg/L           1.90      209.5 mg/L             1.90   0.91%
   QC value within limits for Na 589.592  Recovery = 104.73%
Tl 190.801†                  -10.5   -0.005 mg/L         0.0015     -5.241 ug/L           1.4820  28.28%
   QC value within limits for Tl 190.801  Recovery = Not calculated
V 292.402†                  -251.9   -0.001 mg/L         0.0002     -1.147 ug/L           0.1905  16.61%
   QC value within limits for V 292.402  Recovery = Not calculated
Zn 206.200†                  355.4    0.004 mg/L         0.0002      3.634 ug/L           0.1525   4.20%
```

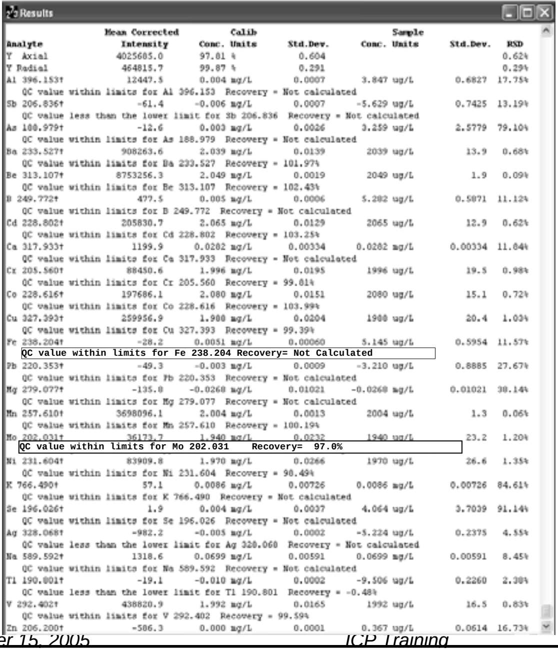
ICS-"A"
200ppm Ca, Na
100ppm Mg
30ppm Fe,K

Control Limits: + LOD

LODs of failed elements

Al	5ppb	(-7.4 ppb)
Ba	1ppb	(1.2 ppb)
Ag	3ppb	(-3.5 ppb)

Example: ICS-B

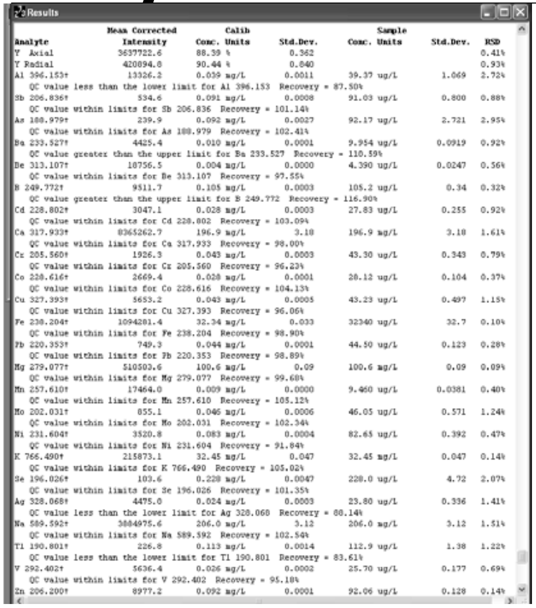


```
                   Mean Corrected       Calib                               Sample
Analyte               Intensity     Conc. Units        Std.Dev.       Conc. Units        Std.Dev.    RSD
Y  Axial              4025685.0      97.81 %             0.604                                      0.62%
Y Radial               464815.7      99.87 %             0.291                                      0.29%
Al 396.153†             12447.5      0.004 mg/L         0.0007        3.847 ug/L          0.6827   17.75%
   QC value within limits for Al 396.153  Recovery = Not calculated
Sb 206.836†               -61.4     -0.006 mg/L         0.0007       -5.629 ug/L          0.7425   13.19%
   QC value less than the lower limit for Sb 206.836  Recovery = Not calculated
As 188.979†               -12.6      0.003 mg/L         0.0026        3.259 ug/L          2.5779   79.10%
   QC value within limits for As 188.979  Recovery = Not calculated
Ba 233.527†            908263.6      2.039 mg/L         0.0139         2039 ug/L            13.9    0.68%
   QC value within limits for Ba 233.527  Recovery = 101.97%
Be 313.107†           8753256.3      2.049 mg/L         0.0019         2049 ug/L             1.9    0.09%
   QC value within limits for Be 313.107  Recovery = 102.43%
B 249.772†                477.5      0.005 mg/L         0.0006        5.282 ug/L          0.5871   11.12%
   QC value within limits for B 249.772  Recovery = Not calculated
Cd 228.802†            205830.7      2.065 mg/L         0.0129         2065 ug/L            12.9    0.62%
   QC value within limits for Cd 228.802  Recovery = 103.25%
Ca 317.933†              1199.9     0.0282 mg/L        0.00334       0.0282 mg/L         0.00334   11.84%
   QC value within limits for Ca 317.933  Recovery = Not calculated
Cr 205.560†             88450.6      1.996 mg/L         0.0195         1996 ug/L            19.5    0.98%
   QC value within limits for Cr 205.560  Recovery = 99.81%
Co 228.616†            197686.1      2.080 mg/L         0.0151         2080 ug/L            15.1    0.72%
   QC value within limits for Co 228.616  Recovery = 103.99%
Cu 327.393†            259956.9      1.988 mg/L         0.0204         1988 ug/L            20.4    1.03%
   QC value within limits for Cu 327.393  Recovery = 99.39%
Fe 238.204†               -28.2     0.0051 mg/L        0.00060        5.145 ug/L          0.5954   11.57%
   QC value within limits for Fe 238.204 Recovery= Not Calculated
Pb 220.353†               -49.3     -0.003 mg/L         0.0009       -3.210 ug/L          0.8885   27.67%
   QC value within limits for Pb 220.353  Recovery = Not calculated
Mg 279.077†              -135.8    -0.0268 mg/L        0.01021      -0.0268 mg/L         0.01021   38.14%
   QC value within limits for Mg 279.077  Recovery = Not calculated
Mn 257.610†           3698096.1      2.004 mg/L         0.0013         2004 ug/L             1.3    0.06%
   QC value within limits for Mn 257.610  Recovery = 100.19%
Mo 202.031†             36173.7      1.940 mg/L         0.0232         1940 ug/L            23.2    1.20%
  QC value within limits for Mo 202.031    Recovery=  97.0%
Ni 231.604†             83909.8      1.970 mg/L         0.0266         1970 ug/L            26.6    1.35%
   QC value within limits for Ni 231.604  Recovery = 98.49%
K 766.490†                 57.1     0.0086 mg/L        0.00726       0.0086 mg/L         0.00726   84.61%
   QC value within limits for K 766.490  Recovery = Not calculated
Se 196.026†                 1.9      0.004 mg/L         0.0037        4.064 ug/L          3.7039   91.14%
   QC value within limits for Se 196.026  Recovery = Not calculated
Ag 328.068†              -982.2     -0.005 mg/L         0.0002       -5.224 ug/L          0.2375    4.55%
   QC value less than the lower limit for Ag 328.068  Recovery = Not calculated
Na 589.592†              1318.6     0.0699 mg/L        0.00591       0.0699 mg/L         0.00591    8.45%
   QC value within limits for Na 589.592  Recovery = Not calculated
Tl 190.801†               -19.1     -0.010 mg/L         0.0002       -9.506 ug/L          0.2260    2.38%
   QC value less than the lower limit for Tl 190.801  Recovery = -0.48%
V 292.402†             438820.9      1.992 mg/L         0.0165         1992 ug/L            16.5    0.83%
   QC value within limits for V 292.402  Recovery = 99.59%
Zn 206.200†              -586.3      0.000 mg/L         0.0001        0.367 ug/L          0.0614   16.73%
```

ICS - "B"
2ppm each of
Ba,Be,Cd,Cr,Cu,Co,Mn,Mo,V

<u>LODs of failed elements:</u>
Sb 5ppb (-5.6)
Ag 3ppb (-5.2)

Example: ICS-A+



```
                   Mean Corrected       Calib                               Sample
Analyte               Intensity     Conc. Units        Std.Dev.       Conc. Units        Std.Dev.    RSD
Y  Axial              3637722.6      88.39 %             0.362                                      0.41%
Y Radial               420894.8      90.44 %             0.840                                      0.93%
Al 396.153†             13326.2      0.039 mg/L         0.0011        39.37 ug/L           1.069    2.72%
   QC value less than the lower limit for Al 396.153  Recovery = 87.50%
Sb 206.836†               534.6      0.091 mg/L         0.0008        91.03 ug/L           0.800    0.88%
   QC value within limits for Sb 206.836  Recovery = 101.14%
As 188.979†               239.9      0.092 mg/L         0.0027        92.17 ug/L           2.721    2.95%
   QC value within limits for As 188.979  Recovery = 102.41%
Ba 233.527†              4425.4      0.010 mg/L         0.0001        9.954 ug/L          0.0919    0.92%
   QC value greater than the upper limit for Ba 233.527  Recovery = 110.59%
Be 313.107†             18756.5      0.004 mg/L         0.0000        4.390 ug/L          0.0247    0.56%
   QC value within limits for Be 313.107  Recovery = 97.55%
B 249.772†               9511.7      0.105 mg/L         0.0003        105.2 ug/L            0.34    0.32%
   QC value greater than the upper limit for B 249.772  Recovery = 116.90%
Cd 228.802†              3047.1      0.028 mg/L         0.0003        27.83 ug/L           0.255    0.92%
   QC value within limits for Cd 228.802  Recovery = 103.09%
Ca 317.933†           8365262.7      196.9 mg/L           3.18        196.9 mg/L            3.18    1.61%
   QC value within limits for Ca 317.933  Recovery = 98.00%
Cr 205.560†              1926.3      0.043 mg/L         0.0003        43.30 ug/L           0.343    0.79%
   QC value within limits for Cr 205.560  Recovery = 96.23%
Co 228.616†              2669.4      0.028 mg/L         0.0001        28.12 ug/L           0.104    0.37%
   QC value within limits for Co 228.616  Recovery = 104.13%
Cu 327.393†              5653.2      0.043 mg/L         0.0005        43.23 ug/L           0.497    1.15%
   QC value within limits for Cu 327.393  Recovery = 96.06%
Fe 238.204†           1094281.4      32.34 mg/L          0.033        32340 ug/L            32.7    0.10%
   QC value within limits for Fe 238.204  Recovery = 98.90%
Pb 220.353†               749.3      0.044 mg/L         0.0001        44.50 ug/L           0.123    0.28%
   QC value within limits for Pb 220.353  Recovery = 98.89%
Mg 279.077†            510503.6      100.6 mg/L           0.09        100.6 mg/L            0.09    0.09%
   QC value within limits for Mg 279.077  Recovery = 99.60%
Mn 257.610†             17464.0      0.009 mg/L         0.0000        9.460 ug/L          0.0381    0.40%
   QC value within limits for Mn 257.610  Recovery = 105.12%
Mo 202.031†               855.1      0.046 mg/L         0.0006        46.05 ug/L           0.571    1.24%
   QC value within limits for Mo 202.031  Recovery = 102.34%
Ni 231.604†              3520.8      0.083 mg/L         0.0004        82.65 ug/L           0.392    0.47%
   QC value within limits for Ni 231.604  Recovery = 91.84%
K 766.490†             215873.1      32.45 mg/L          0.047        32.45 mg/L           0.047    0.14%
   QC value within limits for K 766.490  Recovery = 105.02%
Se 196.026†               103.6      0.228 mg/L         0.0047        228.0 ug/L            4.72    2.07%
   QC value within limits for Se 196.026  Recovery = 101.35%
Ag 328.068†              4475.0      0.024 mg/L         0.0003        23.80 ug/L           0.336    1.41%
   QC value less than the lower limit for Ag 328.068  Recovery = 88.14%
Na 589.592†           3884975.6      206.0 mg/L           3.12        206.0 mg/L            3.12    1.51%
   QC value within limits for Na 589.592  Recovery = 102.54%
Tl 190.801†               226.8      0.113 mg/L         0.0014        112.9 ug/L            1.38    1.22%
   QC value less than the lower limit for Tl 190.801  Recovery = 83.61%
V 292.402†               5636.4      0.026 mg/L         0.0002        25.70 ug/L           0.177    0.69%
   QC value within limits for V 292.402  Recovery = 95.18%
Zn 206.200†              8977.2      0.092 mg/L         0.0001        92.06 ug/L           0.128    0.14%
```

Interferent A+
200ppm Ca, Na
100ppm Mg
30ppm Fe,K
Added to Challenge Level std.
Warning Limits ±10% true valu

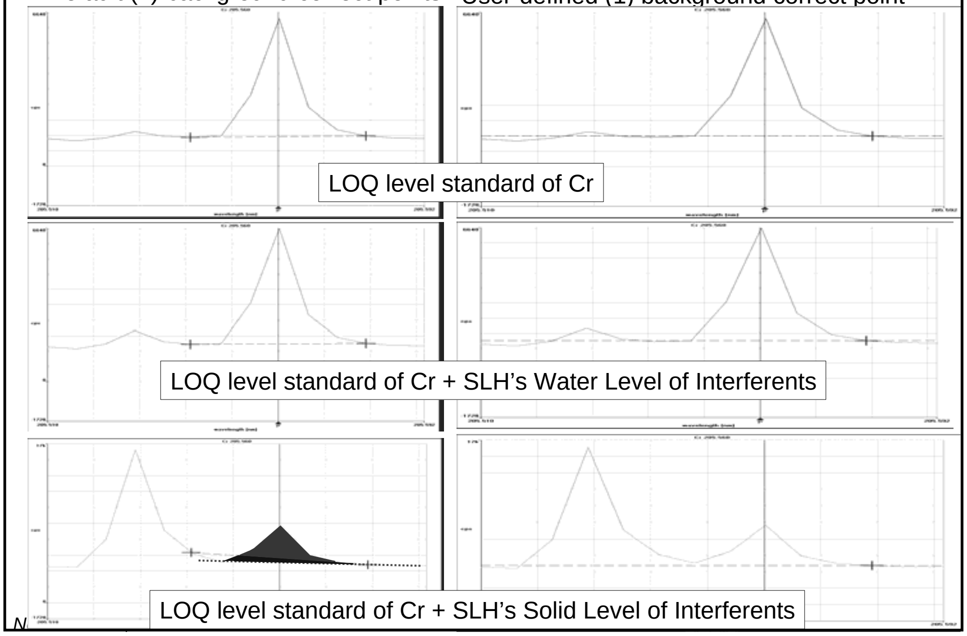
		Challenge Level st	
Se	101.4%	225ppb	Se
Tl	83.6%	135ppb	Tl
As	102.4%	90ppb	As,
B	116.9%	↓	B,
Ni	91.8%		Ni,
Sb	101.1%		Sb,
Zn	102.3%		Zn
Al	87.5%	45ppb	Al,
Cr	96.2%	↓	Cr,
Cu	96.1%		Cu,
Mo	102.3%		Mo,
Pb	98.9%		Pb
Ag	88.1%	27ppb	Ag,
Cd	103.1%	↓	Cd,
Co	104.1%		Co,
V	95.2%		V
Ba	110.6%	9ppb	Ba,
Mn	105.1%		Mn
Be	97.5%	4.5ppb	Be

Background Correction & IECs

Fe on Cr Summary

Default (2) background correct points

User-defined (1) background correct point



LOQ level standard of Cr

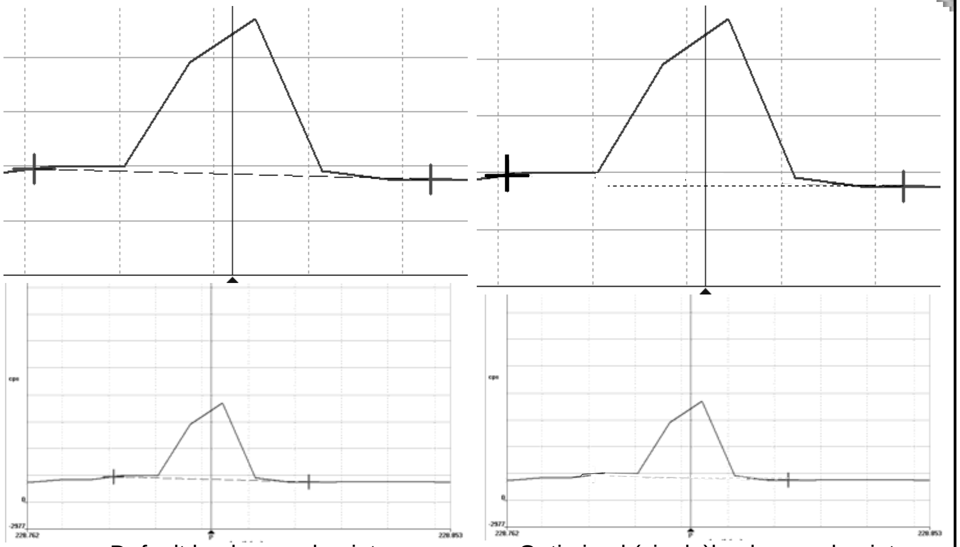
LOQ level standard of Cr + SLH’s Water Level of Interferents

LOQ level standard of Cr + SLH’s Solid Level of Interferents

Summary: Cr @ 150 ppb

	NO INT	Water level INT	Solid level INT
Default 2 BC	156.9	155.1	119.6
Default 2 BC **+ IEC**	157.5	156.5	146.9
User-select 1 BC	158.0	156.5	159.3
User-select 1 BC**+IEC**	158.8	158.3	158.8

Co interference on Cd series

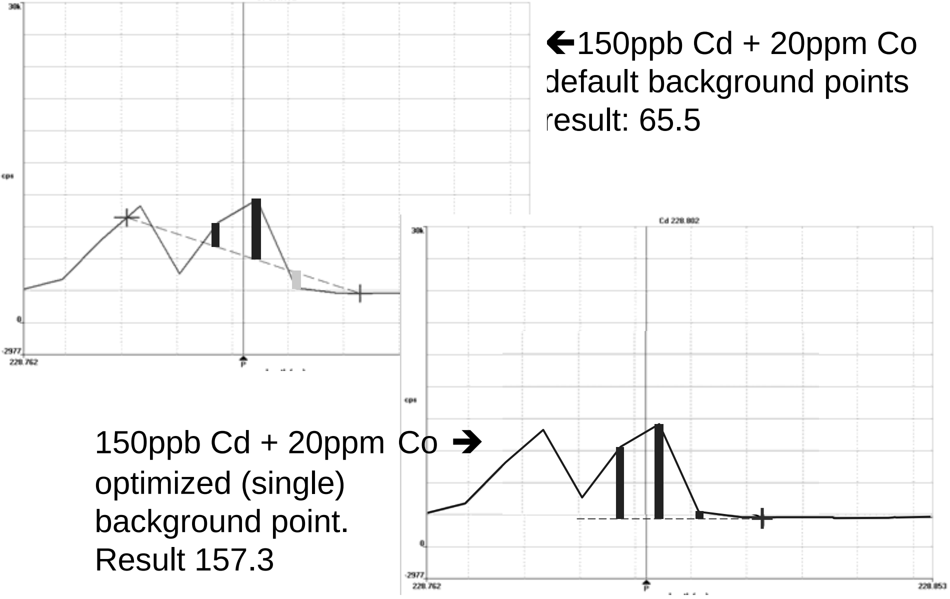


Default background points
150ppb Cd + 2ppm Co
Result 145.2

Optimized (single)background points
150ppb Cd + 2ppm Co
Result 154.2

Co interference on Cd series

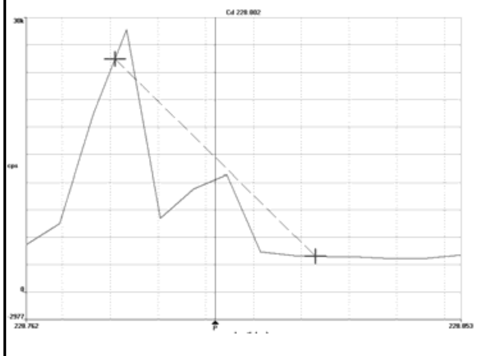
no IECs involved…just background correction



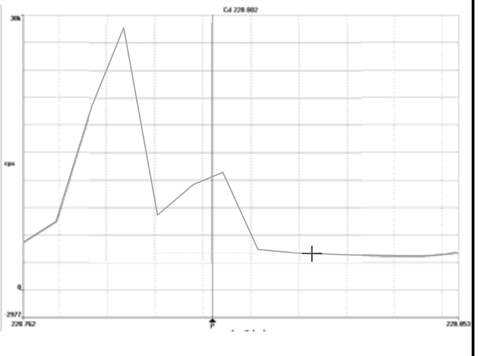
🡐150ppb Cd + 20ppm Co
default background points
result: 65.5

150ppb Cd + 20ppm Co 🡒
optimized (single)
background point.
Result 157.3

Co interference on Cd series



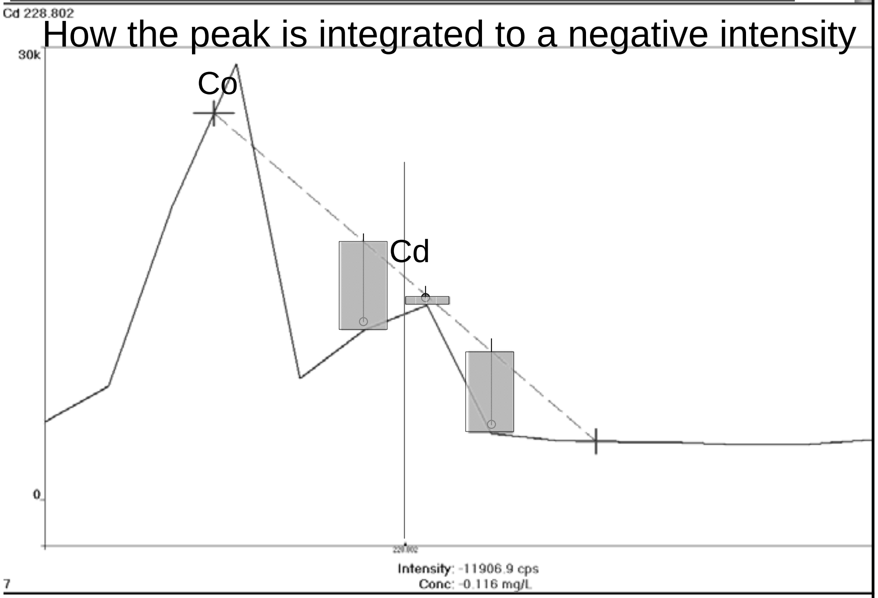
Default background points
150ppb Cd + 60ppm Co
Result: -113.9



Optimized (single) background point
150ppb Cd + 60ppm Co
Result: 168.3

Co interference on Cd series

How the peak is integrated to a negative intensity



Intensity: -11906.9 cps
Conc: -0.116 mg/L

Area calculated for 150ppb Cd + 60ppm Co default bkgrd no IECs

Co interference on Cd series

Without any IECs ----------------- *150 ppb Cadmium* ----------------

Background correction	+ 2 ppm Co	+ 20 ppm Co	+ 60 ppm Co
Default (2 pt)	145.2	65.5	(-113.9)
Optimal (1 pt)	154.2	157.3	168.3

With IECs based on analysis of 2 ppm CO standard applied

Background correction	+ 2 ppm Co	+ 20 ppm Co	+ 60 ppm Co
Default (2 pt)	147.8	91.7	(-35.0)
Optimal (1 pt)	156.7	153.5	150.9

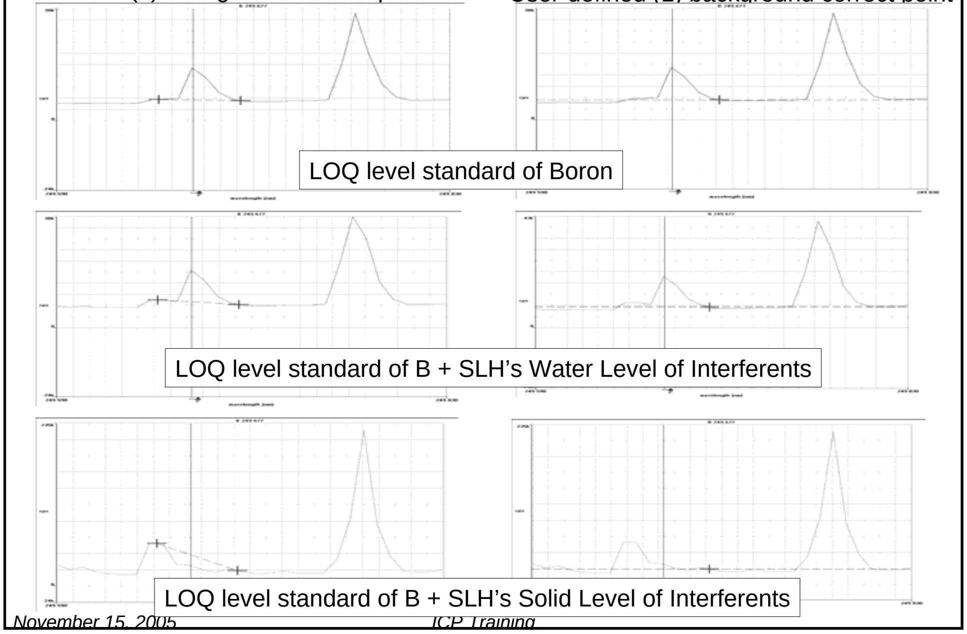
With IECs based on analysis of 60 ppm CO standard applied

Background correction	+ 2 ppm Co	+ 20 ppm Co	+ 60 ppm Co
Default (2 pt)	154.1	157.0	161.6
Optimal (1 pt)	153.6	150.9	149.2

Fe on B Summary

Default (2) background correct points

User-defined (1) background correct point



LOQ level standard of Boron

LOQ level standard of B + SLH’s Water Level of Interferents

LOQ level standard of B + SLH’s Solid Level of Interferents

Summary: Fe on B @ 300 ppb

	NO INT	Water level INT	Solid level INT
Default 2 BC	293.3	292.4	- 761.2
Default 2 BC + IEC	288.3	281.9	- 968.2
User-select 1 BC	311.8	332.9	115.8
User-select 1 BC+IEC	288.3	281.9	- 54.5

MSF:
Multi-Component Spectral Fitting

What is MSF?

MSF- What is it?

- Proprietary software algorithm provided with Perkin-Elmer ICP instruments. It uses multiple regression technique.

What does it do?

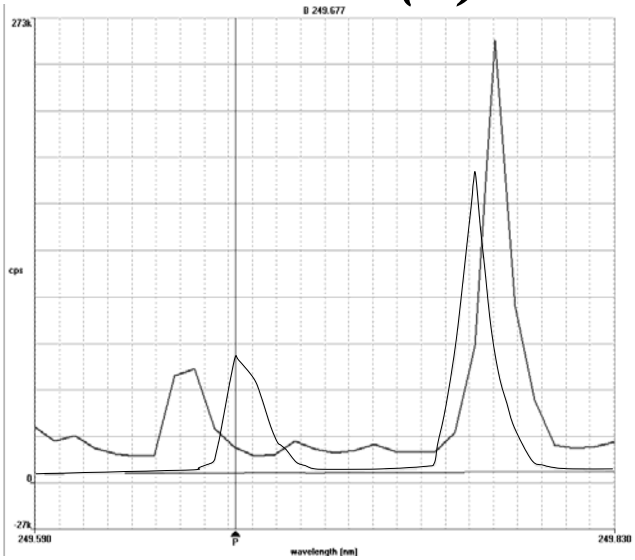
- An advanced form of IEC correction. By feeding it ICP spectra of blank, standard and interferents, the software “de-constructs” a sample spectrum in order to resolve and integrate only the peak related to the analyte

Are there limitations?

- MSF will not work for direct spectral overlap
- Certainly, it’s best to “feed” the algorithm data that closely matches the real sample.
- This is really a sample specific or interference-specific correction rather than a universal correction

Perfect example of need for MSF

Interference of Iron (Fe) on Boron (B)

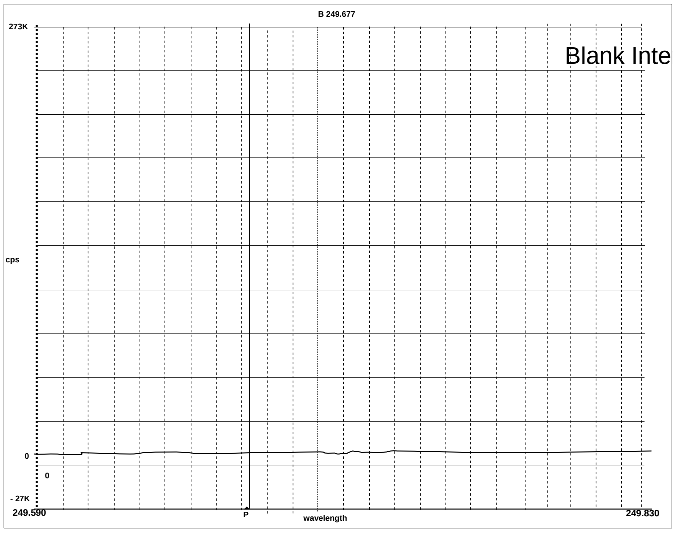


Iron has strong spectral overlap on both of the main wavelengths used for Boron.

Even MSF is difficult because of strong overlap of peaks at 249.772.

Poor peak shape at 249.677 makes it difficult as well.

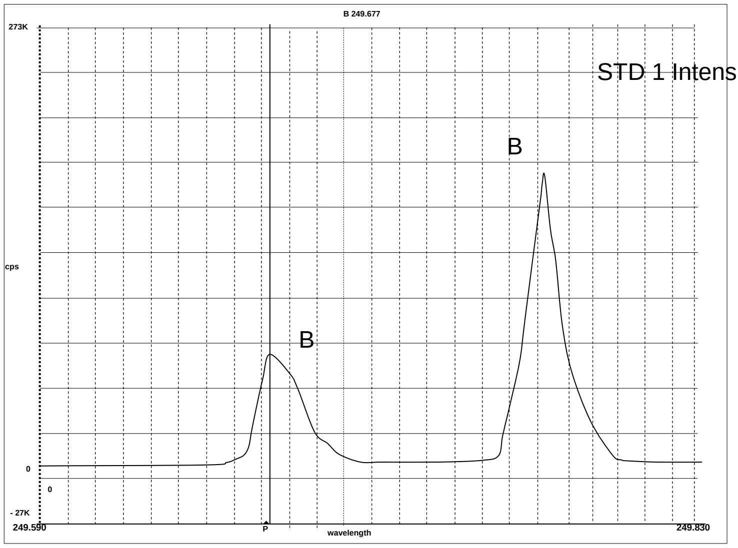
MSF development: 1. Blank



Blank Intensity 5732.2

Data used to create a MSF file for Fe interference on B at 249.677
This is the spectrum for the blank in the region of the Boron peak

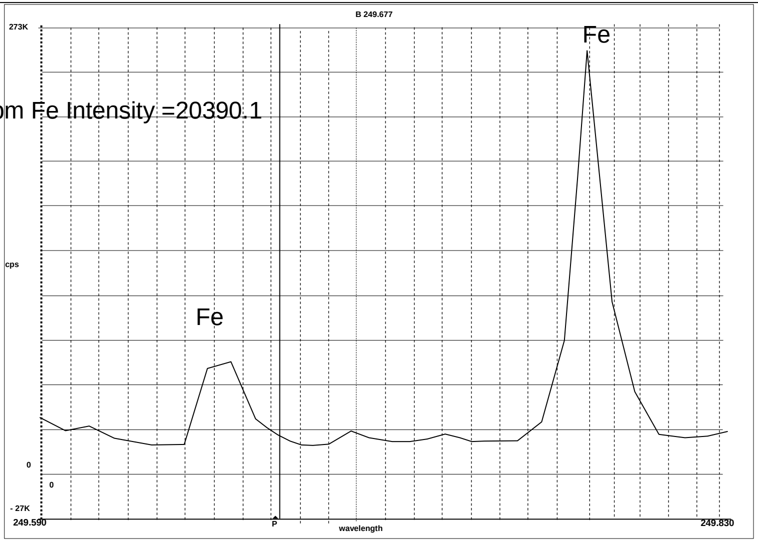
MSF Development : 2. Boron only



STD 1 Intensity = 73462.0

Data used to create a MSF file for Fe interference on B at 249.677
This is the spectrum of the Boron std (2ppm) used to develop the MSF

MSF Development: 3. Fe 400 ppm only

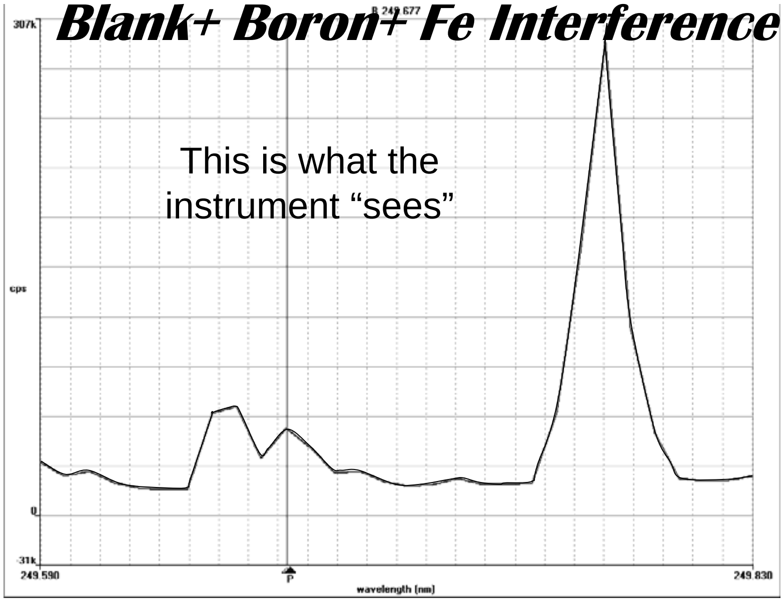


400 ppm Fe Intensity =20390.1

Data used to create a MSF file for Fe interference on B at 249.677
This is the spectrum of the Iron std (400 ppm) used to develop the MSF

MSF Development:

Blank+ Boron+ Fe Interference

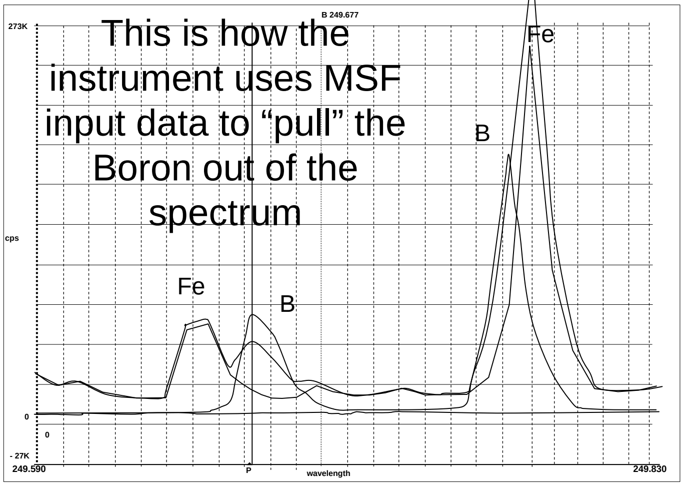


This is what the instrument "sees"

This shows the sample with 1ppm B and 400ppm Fe 53537.4

MSF Development:

Blank+ Boron+ Fe Interference



This is how the instrument uses MSF input data to "pull" the Boron out of the spectrum

Electronically, the instrument determines and then subtracts the background (blank) and iron components of the sample to leave only the boron component which can then be easily integrated.

MSF vs. IEC comparison

The results for analyzing a 1000 ug/L (ppb) single element Boron standard to which 400 ppm of Iron was added are as follows:

With no IECs : 1249 ppb ~ 25% high bias

Background correction is insufficient

With water IECs: 1067 ppb ~ 7% high bias

This correction is based on Fe at 20 ppm

With solid IECs : 1026 ppb ~ 3% high bias

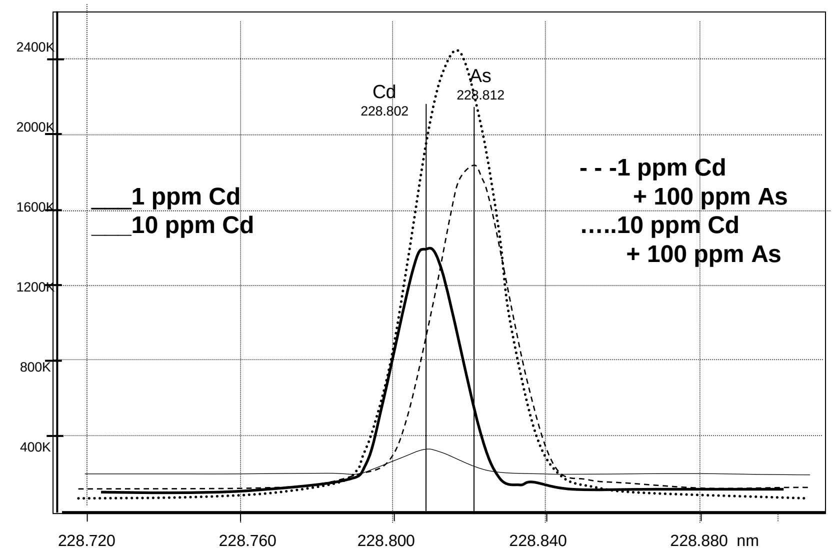
This correction is based on Fe at 400 ppm

Using MSF: 1016 ppb ~ 2% high bias

While the solid IEC gives good results, the MSF-derived value is slightly better.

RE-PROCESS FUNCTION

Interference: As on Cd



Using RE-PROCESS to update an IEC

- The lab noted that although a little high biased, the Cd in their LOQ check standard was acceptable.
- On this day, however, they were analyzing a new TCLP internal blind PT
- Things that should have no Cd (blanks, INTRF) looked good.
- Things that had relatively high As (QCS, LFB) showed high Cd bias. It was noted that these As levels exceeded the level at which IECs had been determined.
- The background correction points looked fine
- Closer examination, however, shows an As line at 228.812 nm (Cd peak is at 228.802)
- This looks to be a clear spectral overlap problem

Uncovering an IEC problem

Sample	Cd 228.802 LOD= 0.005 ppm Mean Corr. Intensity	mg/L	Recovery	As 188.979 NEW INTERFERENT Mean Corr. Intensity	mg/L	Recover
Cal. Blank	- 296.5	[0.00]		-105.8	[0.00]	
STD 1	48397.7	[0.50]		------------------		
STD 2	------------------			3962.6	[1.00]	
●LOQ ppm	931.2	0.010	(106.9%)	121.4	0.031	(102.1%)
●QCS	49184.7	0.508	(127.0%)	15927.2	4.019	100.5%)
INTRF	- 480.6	-0.005		- 92.5	- 0.023	
●I-IPC	26452.6	0.273	(109.3%)	2022.4	0.510	102.0%)
CB	6.2	0.000		- 3.7	- 0.001	
DLRB	4.2	0.000		- 5.2	- 0.007	
●DLFB	44170.2	2.282	(114.1%)	8535.1	10.77	107.7%)
●DQCS	12256.9	0.633	(126.6%)	4048.5	5.108	102.1%)

24 elements 0.5, 2 or 4 ppm)

Ca, Fe, Na: 200 ppm; Mg: 100ppm; Al, K:20 ppm

Uncovering an IEC problem

Sample	Cd 228.802 Mean Corr. Intensity	mg/L	Recovery	As 188.979 Mean Corr. Intensity	mg/L	Recover
2nd Source	47523.7	**0.491**	(98.2%)	-2.7	-0.001	------
2 ppm As	6105.1	**0.063**	--------	8088.3	2.041	(102.1%)

Single element standard, different from normal 2nd source

This clearly indicated that additional IEC correction for As on Cd is required
Updated IEC table to reflect an IEC correction of **-0.03087** ppm per 1 ppm As

Update IEC Table and use “Reprocess” feature to regenerate the entire run from beginning to end.

Why wasn’t this need for an IEC identified earlier?
IECs were run at 500 ppb for As because samples at or above this level are not typically encountered.
At 500 ppb As, the apparent Cd is 0nly 0.0039 ppm, which is below the LOD of 0.005 ppm

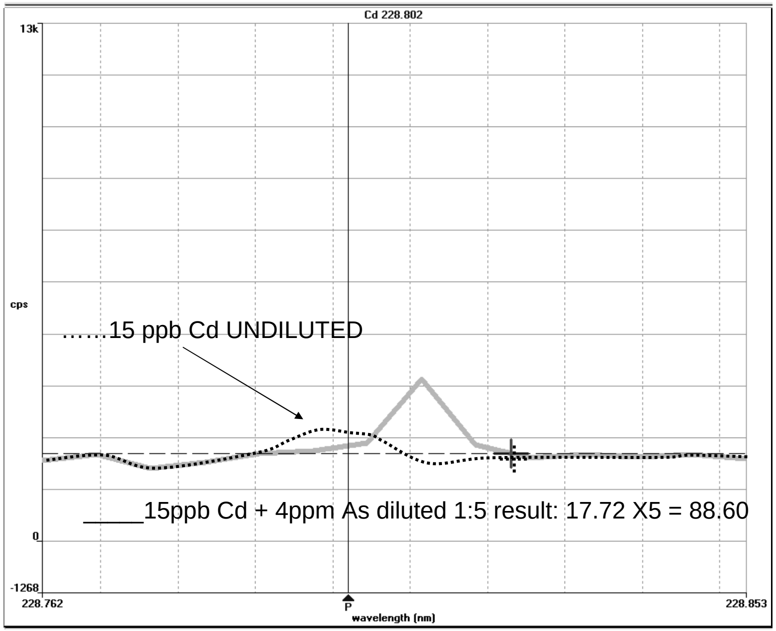
…after "REPROCESS" feature

Sample	Cd 228.802			As 188.979		
	Mean Corr. Intensity	mg/L	Recovery	Mean Corr. Intensity	mg/L	Recovery
Cal. Blank	-296.5	[0.00]		-105.8	[0.00]	
STD 1	48397.7	[0.50]		-------------------		
STD 2	-------------------			3962.6	[1.00]	
LOQ ppm	931.2	0.009	(96.3 %)	121.4	0.031	(102.1%)
QCS	49184.7	0.384	(96.0%)	15927.2	4.019	(100.5%)
24 elements 0.5, 2 or 4 ppm)						
INTRF	-480.6	-0.004		- 92.5	-0.023	
Ca, Fe, Na: 200 ppm; Mg: 100ppm; Al, K:20 ppm0						
I-IPC	26452.6	0.258	(103.0%)	2022.4	0.510	(102.0%)
CB	6.2	0.000		-3.7	-0.001	
DLRB	4.2	0.000		-5.2	-0.007	
DLFB	44170.2	1.949	(97.5%)	8535.1	10.77	107.7%)
DQCS	12256.9	0.475	(95.0%)	4048.5	5.108	102.1%)

After "REPROCESS" function

Sample	Cd 228.802			As 188.979		
	Mean Corr. Intensity	mg/L	Recovery	Mean Corr. Intensity	mg/L	Recover
2nd Source	47523.7	**0.491**	(98.2%)	-2.7	-0.001	------
Single element standard, different from normal 2nd source						
2 ppm As	6105.1	**0.000**	--------	8088.3	2.041	(102.1%)

As on Cd: Serial Dilution Fails



……15 ppb Cd UNDILUTED

_____15ppb Cd + 4ppm As diluted 1:5 result: 17.72 X5 = 88.60

As on Cd: Serial Dilution

Analyzed a 15 ppb single element Cd standard: 16.29 ppb
Mixed 15 ppb Cd with 4 ppm As standard: 85.57 ppb
Note: an IEC for As on Cd WAS in place
Correction was -0.0096391 ppm Cd per 1 ppm As

Prepared & analyzed a 1:5 serial dilution of the
15 ppb Cd with 4 ppm As standard: 17.72 ppb
times 5 x dilution = 88.60 ppb
Agreement is within10%

From 6010C 9.6.2 Dilution test
If the analyte concentration is sufficiently high (minimally, a factor of 10 above the method detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

CAUTION: If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

This is why serial dilution may be misleading. It may work for flame and furnace AA, but it does not work when very near spectral overlap is involved

As on Cd: Serial Dilution

Instead of dilution, adjusting the IEC is best option

Analysis of 4 ppm single element As standard: 70.02 ppb

70.02 ppb Cd / 4 ppm As= 0.01754 ppm Cd/ppm As

Already had an IEC of 0.0096391 Cd per 1 ppm As

Must ADD the additional IEC

0.0096391 + 0.01754 = 0.027185

Change IEC for As on Cd to 0.027185

Prepared & analyzed a 1:5 serial dilution of the

15 ppb Cd with 4 ppm As standard: 3.61 ppb

times 5 x dilution = 18.06 ppb

Agreement is within15%

Note proximity of diluted sample to LOD (3 ppb)

Re-processing: Pros & Cons

Pros	**Cons**
Easy, a time-saver	Makes auditors uneasy
Allows flexibility	Practice can be abused
Excellent for dealing with unique sample issues	Requires a good deal of thought to decide WHAT to reprocess
Excellent method development tool	How to document precisely what was done (and that nothing else changed in the process)
Raw data are unchanged	

Where reprocessing maybe appropriate

- Method development
- IEC needs to be adjusted
- Background correction point is incorrect
- If mis-entered calibration standard concentration
- Atypical samples (the “Wibby”)

Reprocessing ICP Data & Ethics

- New generation ICP-OES digitally captures all data
- Modern software has the ability to alter test results by changing method parameters and by reprocessing the data.
- This can present an ethical conundrum if used carelessly or inappropriately
- Strict rules MUST be followed or … the auditors will be on you like a monkey on a cupcake!

Suggested Reprocessing Guidelines

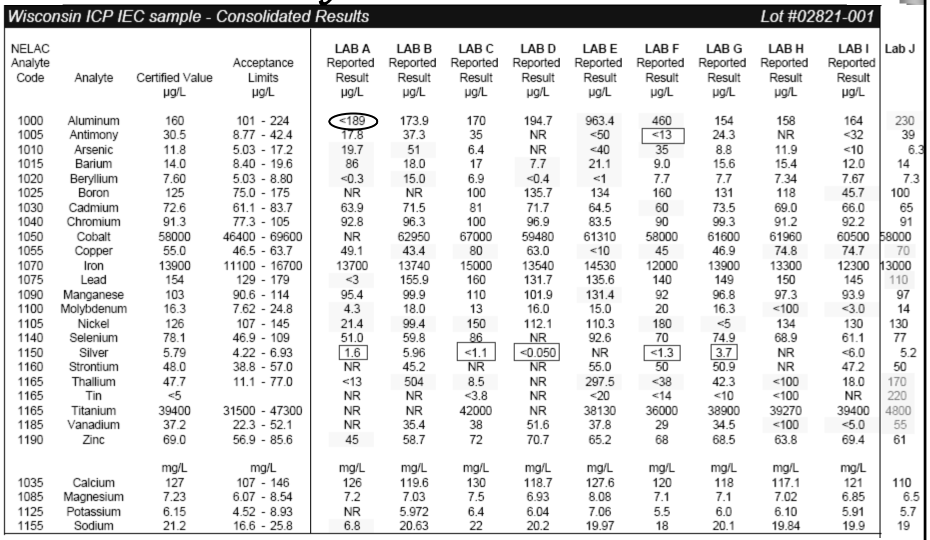
- Only experienced personnel with a good understanding of instrumental analysis should be allowed to reprocess data.
- ALL DATA including the calibration and QC checks must be reprocessed.
- ALL adjustments must be clearly documented on the initial and the reprocessed printouts.
- The adjustments must be approved, initialed and dated by the analyst and supervisor or QA Officer.
- As a general rule, changes must make good data better not bad data acceptable.

The Wibby

"The Wibby" PT Sample Design

- Wibby Environmental used a stock lot of WP Trace Metals diluted an additional 10X as the main ingredient in the sample. The idea was to challenge the lower end of the working range of the ICPs.
- Wibby Environmental used a matrix that included the common cations Ca, K, Mg and Na at levels found in a typical ground water sample. The purpose of the cations was to provide some level of background for the labs to deal with.
- The three main interferents added, Co, Fe and Ti, were chosen for different reasons. Co was chosen because it has a specific impact on Pb and also because it can cause interference with a number of other analytes depending on the type of ICP being used and the line selected by the lab. Fe was chosen because it can be a common contaminant that has the potential to interfere with a number of analytes. Ti was chosen because it does interfere with a number of elements and is not commonly found in water samples.

The "Wibby"- all lab results



Wisconsin ICP IEC sample - Consolidated Results Lot #02821-001

NELAC Analyte Code	Analyte	Certified Value µg/L	Acceptance Limits µg/L	LAB A Reported Result µg/L	LAB B Reported Result µg/L	LAB C Reported Result µg/L	LAB D Reported Result µg/L	LAB E Reported Result µg/L	LAB F Reported Result µg/L	LAB G Reported Result µg/L	LAB H Reported Result µg/L	LAB I Reported Result µg/L	Lab J
1000	Aluminum	160	101 - 224	<189	173.9	170	194.7	963.4	460	154	158	164	230
1005	Antimony	30.5	8.77 - 42.4	17.8	37.3	35	NR	<50	<13	24.3	NR	<32	39
1010	Arsenic	11.8	5.03 - 17.2	19.7	51	6.4	NR	<40	35	8.8	11.9	<10	6.3
1015	Barium	14.0	8.40 - 19.6	86	18.0	17	7.7	21.1	9.0	15.6	15.4	12.0	14
1020	Beryllium	7.60	5.03 - 8.80	<0.3	15.0	6.9	<0.4	<1	7.7	7.7	7.34	7.67	7.3
1025	Boron	125	75.0 - 175	NR	NR	100	135.7	134	160	131	118	45.7	100
1030	Cadmium	72.6	61.1 - 83.7	63.9	71.5	81	71.7	64.5	60	73.5	69.0	66.0	65
1040	Chromium	91.3	77.3 - 105	92.8	96.3	100	96.9	83.5	90	99.3	91.2	92.2	91
1050	Cobalt	58000	46400 - 69600	NR	62950	67000	59480	61310	58000	61600	61960	60500	58000
1055	Copper	55.0	46.5 - 63.7	49.1	43.4	80	63.0	<10	45	46.9	74.8	74.7	70
1070	Iron	13900	11100 - 16700	13700	13740	15000	13540	14530	12000	13900	13300	12300	13000
1075	Lead	154	129 - 179	<3	155.9	160	131.7	135.6	140	149	150	145	110
1090	Manganese	103	90.6 - 114	95.4	99.9	110	101.9	131.4	92	96.8	97.3	93.9	97
1100	Molybdenum	16.3	7.62 - 24.8	4.3	18.0	13	16.0	15.0	20	16.3	<100	<3.0	14
1105	Nickel	126	107 - 145	21.4	99.4	150	112.1	110.3	180	<5	134	130	130
1140	Selenium	78.1	46.9 - 109	51.0	59.8	86	NR	92.6	70	74.9	68.9	61.1	77
1150	Silver	5.79	4.22 - 6.93	1.6	5.96	<1.1	<0.050	NR	<1.3	3.7	NR	<6.0	5.2
1160	Strontium	48.0	38.8 - 57.0	NR	45.2	NR	NR	55.0	50	50.9	NR	47.2	50
1165	Thallium	47.7	11.1 - 77.0	<13	504	8.5	NR	297.5	<38	42.3	<100	18.0	170
1165	Tin	<5		NR	NR	<3.8	NR	<20	<14	<10	<100	NR	220
1165	Titanium	39400	31500 - 47300	NR	NR	42000	NR	38130	36000	38900	39270	39400	4800
1185	Vanadium	37.2	22.3 - 52.1	NR	35.4	38	51.6	37.8	29	34.5	<100	<5.0	55
1190	Zinc	69.0	56.9 - 85.6	45	58.7	72	70.7	65.2	68	68.5	63.8	69.4	61
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
1035	Calcium	127	107 - 146	126	119.6	130	118.7	127.6	120	118	117.1	121	110
1085	Magnesium	7.23	6.07 - 8.54	7.2	7.03	7.5	6.93	8.08	7.1	7.1	7.02	6.85	6.5
1125	Potassium	6.15	4.52 - 8.93	NR	5.972	6.4	6.04	7.06	5.5	6.0	6.10	5.91	5.7
1155	Sodium	21.2	16.6 - 25.8	6.8	20.63	22	20.2	19.97	18	20.1	19.84	19.9	19

Certified Values = "100% true concentration" of each analyte as determined from gravimetric and volumetric measurements made during standard manufacture
Acceptance limits = 99% confidence limits calculated using nvironmental Laboratory Accreditation Conference (NELAC) criteria (ref: 2005-06 NELAC PT FOT tables) for all elements except for Ba, B, Co, Fe, Se, Ti and V. Limits set at +/-20% for Co, Fe and Ti. Limits set at +/-40% for Ba, B, Se and V.
NR = Not reported.

▭ = Failure by WI DNR PT scoring ⬭ = unusually high LOD

How SLH Handled "the Wibby"

- Analyzed sample for regular 24* elements using IECs based on water levels (20ppm Fe,K, 100ppm Mg, 200ppm Ca,Na).
    - Gallium internal standard failed high. ~160% axial, ~240% radial.
- Noticed cobalt at ~60ppm.
- Calibrated for Gallium, but found no gallium in sample
- Cerium and titanium peak near gallium line.
- Created new method to include cerium, tin, strontium, and titanium (not in regular method) and used Yttrium only as internal standard. Added Indium as possible internal standard.
- Calibrated new method

* Don't normally analyze Sr, Sn, Ti

How SLH Handled "the Wibby"

- Using EXAMINE tool in software; optimized peaks and background points
- Analyzed single element standards at the calibration level to calculate IECs.
- Reprocessed above run with new IECs.
- Analyzed Wibby sample, plus duplicate and spiked sample
- 16 of the 27 elements worked at this point (controls, blanks, and QC all acceptable)
- The remaining 11 elements required further investigation. Many had interferences from Cobalt (~60ppm) and Titanium (~40ppm)

* Don't normally analyze Sr, Sn, Ti

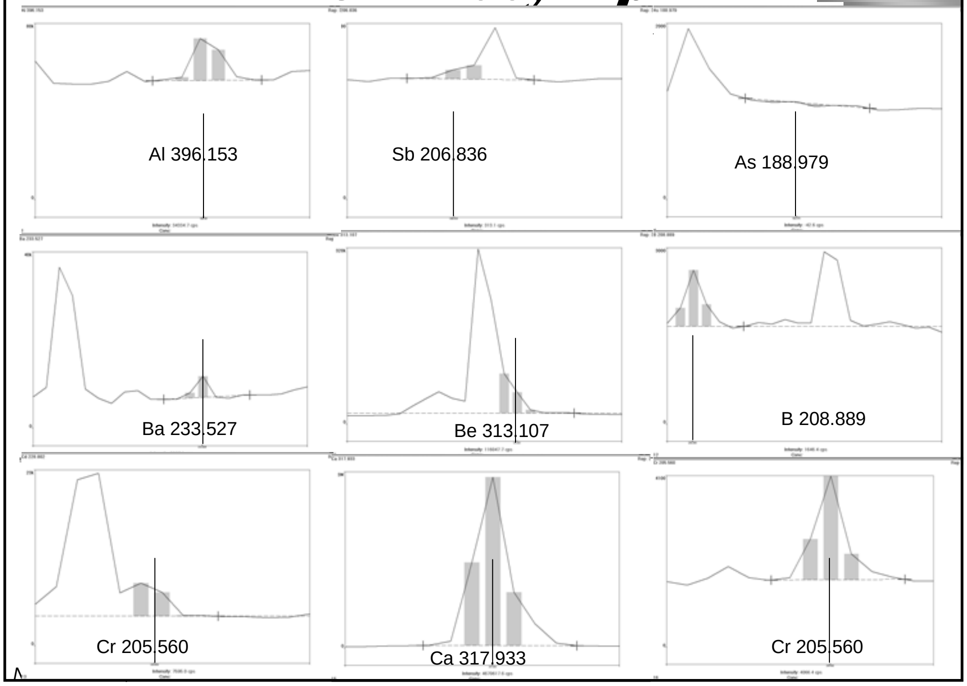
How SLH Handled "the Wibby"

- EXAMINED sample spectra and single element standards (used for IECs),
  - readjusted some background points and
  - added multiple lines for Sb,As,Be,B,Cd,Cu,Pb,Ni,Se,Ag,Tl,Sn, and Sr.
  - Re-determined IECs using new background points and new wavelengths.
- Ran interferences at the levels seen in the sample (Co=60ppm, Ti=40ppm, Fe=15ppm, Ca=120ppm). *..since these appeared to be the main interferents*.
- Calculated new IECs and ran calibration, controls, sample, duplicate, and spike. Diluted 100x for Co and Ti.
- All elements passed except: B, Cu, Ni, Se, Ag, Tl, Sn

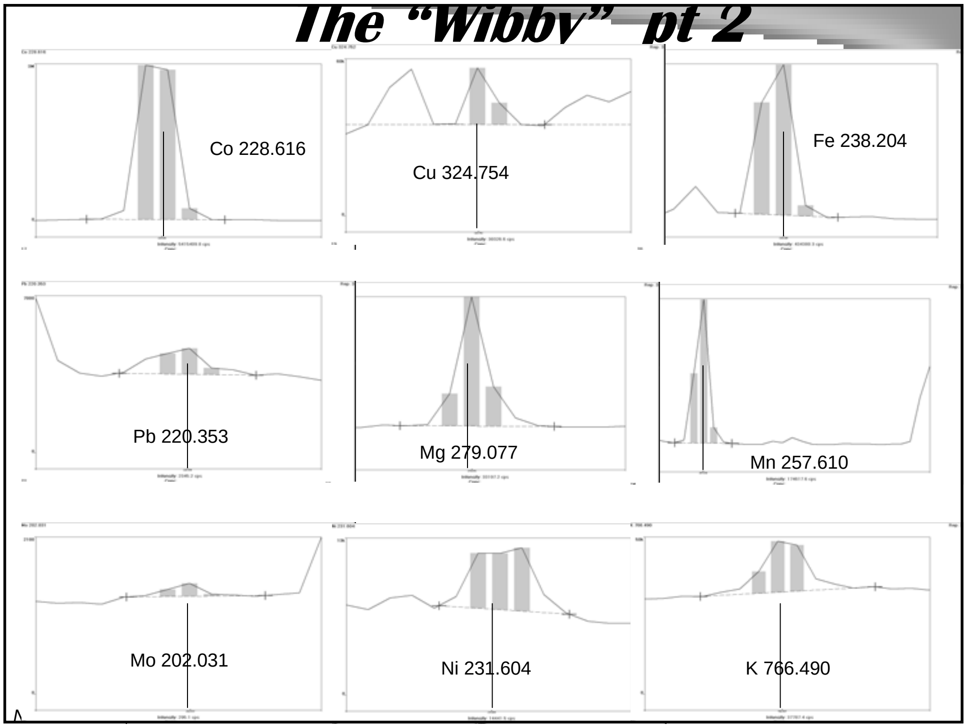
How SLH Handled "the Wibby"

- Decided to use MSF on remaining elements. Created MSF file and reprocessed data.
- All acceptable except for: Ni, and Sn.
  - Ni was ~ - 15ppb on all wavelengths,
  - Sn was ~100ppb on 1st wavelength, ; ~1ppb on alternate
- Prepared & analyzed a sample with 100ppb Sn plus interferences (Co=60ppm, Ti=40ppm, Fe=15ppm, Ca=120ppm).
  - Chose result from routine wavelength (189.927) ➔ 96%
  - Alt.wavelength= -31% recovery.
  - Concluded: No Sn in sample <LOD=10ppb
- Prepared & analyzed samples with 10ppb and 20ppb Ni plus interferences as above.
  - Concluded Ni not present in sample = < 5ppb
  - Recoveries ~92% to 96 on two lines

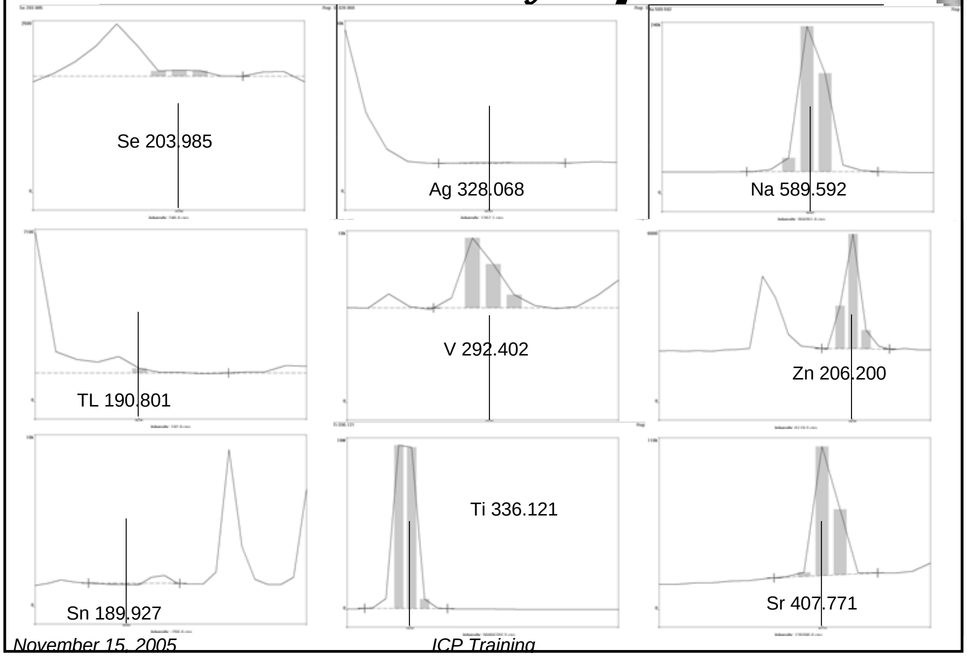
The “Wibby” pt 1



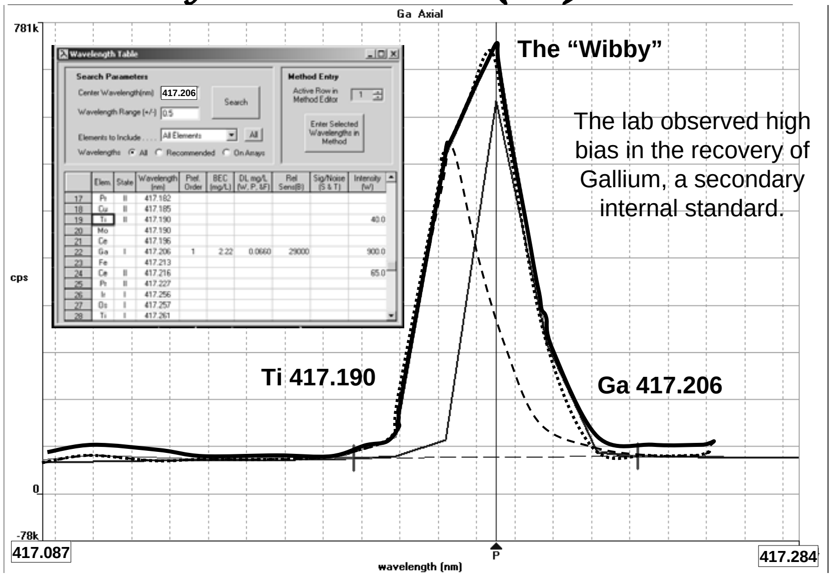
The “Wibby” pt 2



The "Wibby" pt 3



The "Wibby": Gallium (IS) Glitch



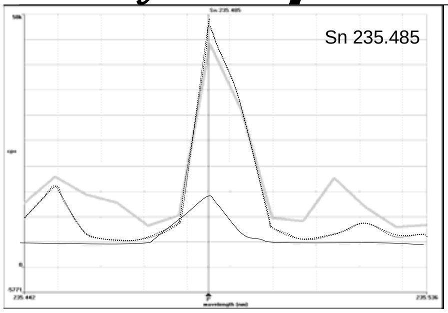
Center Wavelength(nm) 417.206
Wavelength Range (+/-) 0.5
Elements to Include . . . . All Elements
Wavelengths ● All ○ Recommended ○ On Arrays
Active Row in Method Editor 1

	Elem.	State	Wavelength (nm)	Pref. Order	BEC (mg/L)	DL mg/L (W, P, &F)	Rel Sens(B)	Sig/Noise (S & T)	Intensity (w)
17	Pr	II	417.182						
18	Cu	II	417.185						
19	Ti	II	417.190						40.0
20	Mo		417.190						
21	Ce		417.196						
22	Ga	I	417.206	1	2.22	0.0660	29000		900.0
23	Fe		417.213						
24	Ce	II	417.216						65.0
25	Pr	II	417.227						
26	Ir	I	417.256						
27	Os	I	417.257						
28	Ti	I	417.261						

The lab observed high bias in the recovery of Gallium, a secondary internal standard.

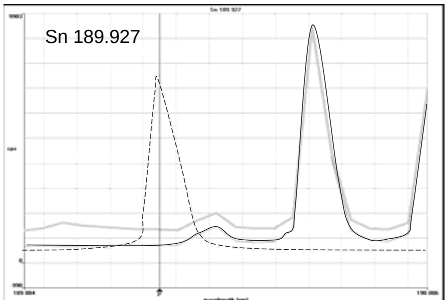
Calibration blank (yellow) vs. Wibby sample (blue/dotted) shows increased Gallium (internal standard) intensity.

Wibby sample – Tin Trouble



The thick (red)line = the sample
The dotted (white) line = 15ppm Fe
The small (yellow) peak = 2ppm Sn

Strong Fe interference; direct overla



Different wavelength doesn't help

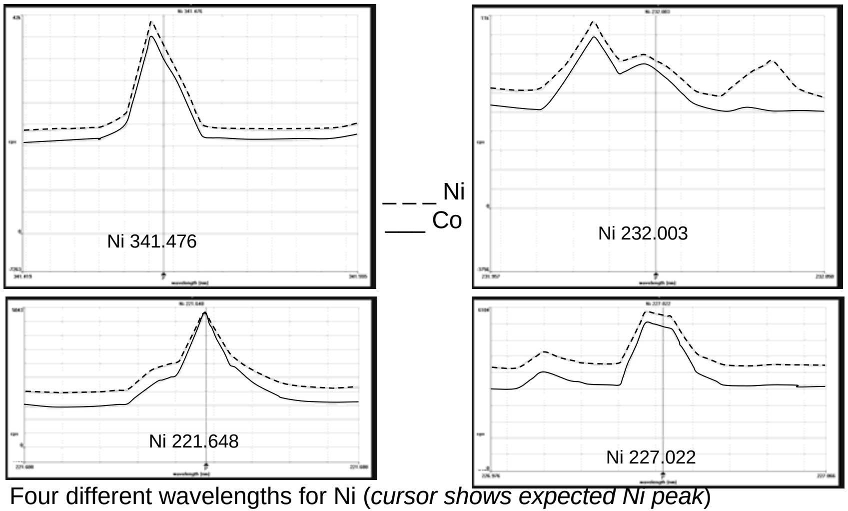
Thick (red) line = sample
Blue line = 40ppm Ti
Red (dash) line is 2ppm Sn

MSF yields 1.6ppb
100 ppb spike = 96% recovery

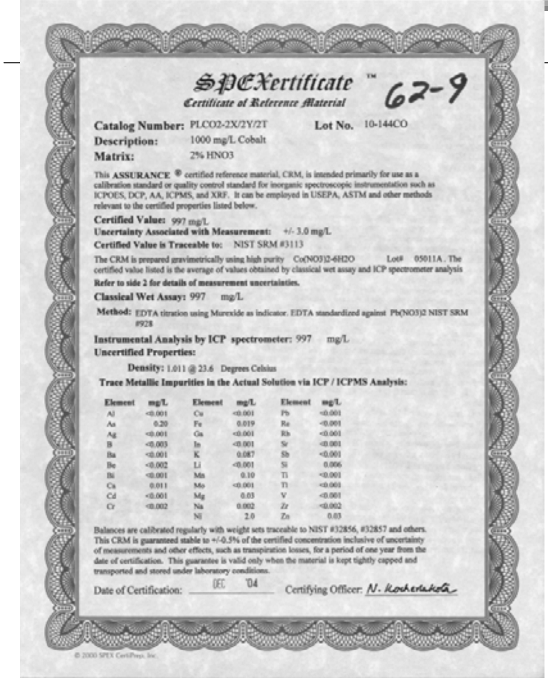
Convinces that Sn is not present

The "Wibby" - Nickel Nightmare

Cobalt at the level it was in the sample interfered with Nickel at multiple wavelengths



Four different wavelengths for Ni (*cursor shows expected Ni peak*)
Each shows the sample + 60ppm Cobalt superimposed.
SLH base IEC for Cobalt on Nickel yielded negative results (~ - 20 to – 30ppb).
MSF also yielded negative results (~ - 25 to - 30ppb). Yet a 10ppb Ni spike= 92%



SPEXertificate ™ 62-9

Certificate of Reference Material

Catalog Number: PLCO2-2X/2Y/2T **Lot No.** 10-144CO
Description: 1000 mg/L Cobalt
Matrix: 2% HNO3

This **ASSURANCE** ® certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 997 mg/L
Uncertainty Associated with Measurement: +/- 3.0 mg/L
Certified Value is Traceable to: NIST SRM #3113

The CRM is prepared gravimetrically using high purity Co(NO3)2-6H2O Lot# 05011A . The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis

Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 997 mg/L

Method: EDTA titration using Murexide as indicator. EDTA standardized against Pb(NO3)2 NIST SRM #928

Instrumental Analysis by ICP spectrometer: 997 mg/L
Uncertified Properties:

Density: 1.011 @ 23.6 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

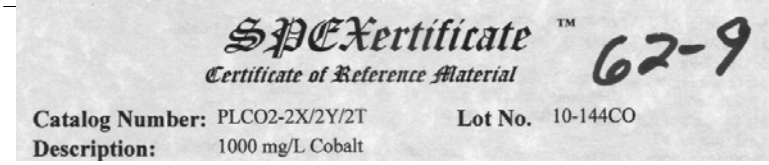
Element	mg/L	Element	mg/L	Element	mg/L
Al	<0.001	Cu	<0.001	Pb	<0.001
As	0.20	Fe	0.019	Re	<0.001
Ag	<0.001	Ga	<0.001	Rb	<0.001
B	<0.003	In	<0.001	Sr	<0.001
Ba	<0.001	K	0.087	Sb	<0.001
Be	<0.002	Li	<0.001	Si	0.006
Bi	<0.001	Mn	0.10	Ti	<0.001
Ca	0.011	Mo	<0.001	Tl	<0.001
Cd	<0.001	Mg	0.03	V	<0.001
Cr	<0.002	Na	0.002	Zr	<0.002
		Ni	2.0	Zn	0.03

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: DEC '04 Certifying Officer: N. Kocherlakota

Certificate of Analysis for the 1000 ppm Co standard used to prepare IECs for Ni.

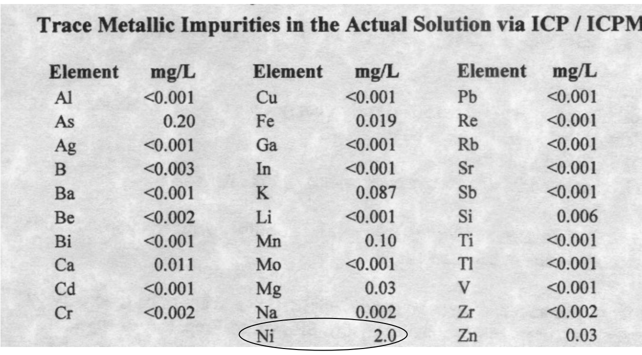
"The Problem Revealed"



SPEXertificate ™ 62-9

Certificate of Reference Material

Catalog Number: PLCO2-2X/2Y/2T **Lot No.** 10-144CO
Description: 1000 mg/L Cobalt



Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	<0.001	Cu	<0.001	Pb	<0.001
As	0.20	Fe	0.019	Re	<0.001
Ag	<0.001	Ga	<0.001	Rb	<0.001
B	<0.003	In	<0.001	Sr	<0.001
Ba	<0.001	K	0.087	Sb	<0.001
Be	<0.002	Li	<0.001	Si	0.006
Bi	<0.001	Mn	0.10	Ti	<0.001
Ca	0.011	Mo	<0.001	Tl	<0.001
Cd	<0.001	Mg	0.03	V	<0.001
Cr	<0.002	Na	0.002	Zr	<0.002
		Ni	2.0	Zn	0.03

When this standard was diluted to 60 ppm of Co, the Ni concentration was 120 ppb

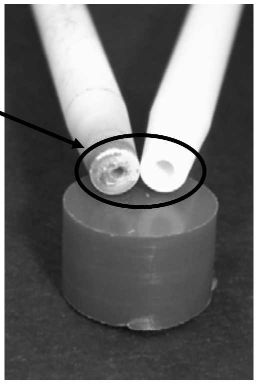
Lesson learned…Can't develop IECs if the standard contains the analyte of interest!

The Nickel solution

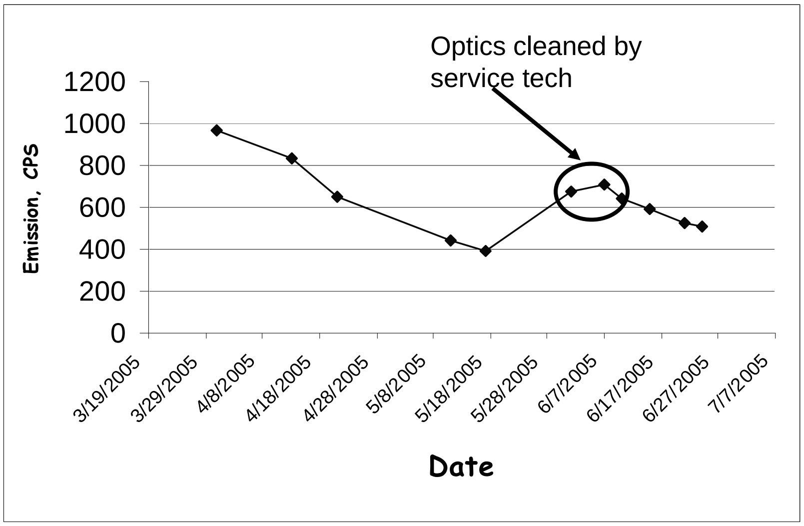
- Using a pure Co standard, new IECs were developed and “the Wibby” (true value= 126 (107-145)), was re-analyzed
- Ni 231.604 – 122.0 ppb
- Ni 221.648 – 121.7 ppb
- Ni 232.003 – 119.6 ppb
- Ni 227.022 – 124.0 ppb

WSLH Emission Tracking Experience

- Noticed sensitivity deteriorating
- “Backtracked” and plotted emissions over several months
- Found UV lines dropped the most
- Sample introduction as injector problems ruled out.
- Service revealed optics coated – technician cleaned them.

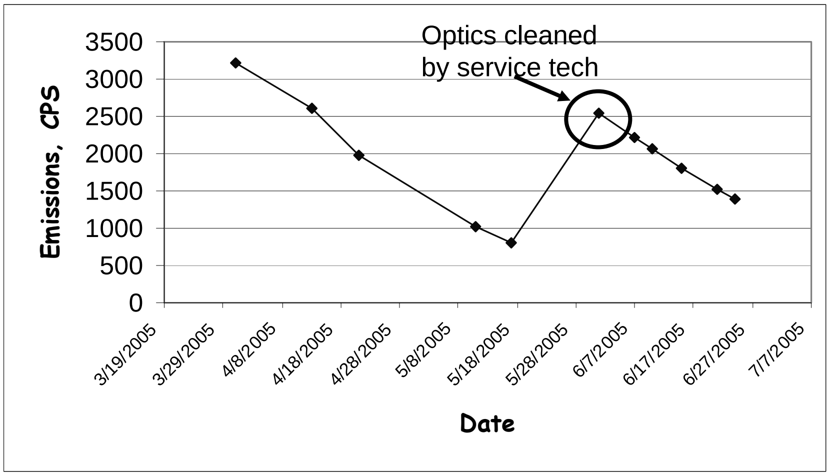


Emissions Tracking for Arsenic: 250 ppb at 188.979 ηm



Optics cleaned by service tech

Emissions Tracking for Selenium: 1000 ppb at 196.025 ηm



Optics cleaned by service tech

WSLH Emission Tracking Experience

- Problem returned
- Instrument replaced,
- Problem returned-again
- Problem: Leak in gas line
  - Leaks allow impurities to enter gas stream and coat optics
- Final Corrective Action:
  - Fix leak
  - Add in-line gas filter & dessicant
  - Clean optics

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- S-F Analytical Laboratories, Inc.
- TestAmerica, Inc., Watertown
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