ICP:
You CAN'T Just Push Play

A discussion and compelling argument supporting the rationale behind and critical need for proper and effective use of inter-element correction factors (IEC) –or other interference correction tools--to obtain quality ICP-OES results on environmental samples.

Wisconsin DNR
Bureau of Science Services
Lab Certification Program

Wisconsin State Laboratory of Hygiene
UNIVERSITY OF WISCONSIN–MADISON

Wisconsin
Environmental
Laboratories
Association

Well, some can get away with it

Aerosmith can just push play;

most labs, however, cannot

Disclaimer

Any reference to product or company names does not constitute endorsement by any of the following:

- ***Wisconsin State Laboratory of Hygiene,***
- ***University of Wisconsin,***
- ***WI Dept. of Natural Resources***

Cast of Characters

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Special thanks to
Paul Harris and **WELA** for both championing and sponsoring this event as well as providing the room and beverages.

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Outline

- **Instruments, sample introduction, auto-samplers**
- **Brief instrument set-up and calibration**
- Background correction (pre-loaded vs. reality)
- Inter-Element Correction factors (IECs)
- Multi-Component Spectral Fitting (MSF) and Fast Automated Curve-Fitting Technique (FACT)
- Interference check samples (ICS)
- **PT sample results and examples of interference correction.**
- **Real World Sample Results**
- **Wrap-Up/ Q&A**

Tell 'em What You're Going to Tell 'em

Take home messages

- **Unless your samples are ultra-trace level and matrix free, some form of interference correction is required.**
- **Size does not matter.** Having a huge focal length is not a substitute for interference correction.
- **MSF and FACT are approved forms of interference correction.**
- **Test your interference correction technique by appropriate design of ICS samples.**
- **Use appropriate evaluation criteria for ICS.**
  Hint: referenced method criteria are not appropriate.
- **The "CLP" style ICS-AB offers NO value.**

Instrument array (survey)

5 **Agilent:** (3) 720-ES, (1) 720, (1) 710-E

3 **J-Y:** (2) Ultima 2, (1) Ultima 2C

1 **Leeman:** Profile Plus

6 **Perkin-Elmer:** 2100, 3500, 4300,
Optima: 5300, 7000, 7300

3 **Thermo:** (2) iCAP 6300, (1) iCAP 6500

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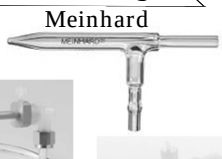
Nebulizers based on survey

6 Sea spray
3 Meinhard
3 Gem Cone
2 Concentric
1 Gem Tip Cross-Flow
1 MiraMist
1 Hildebrand Grid
1 Micro Flow PFA-ST
1 One Neb


Seaspray

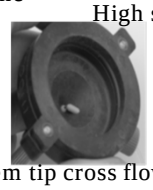

Meinhard


Concentric


Gemcone

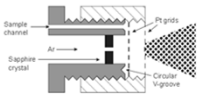

Gemcone High solids

MiraMist


gem tip cross flow

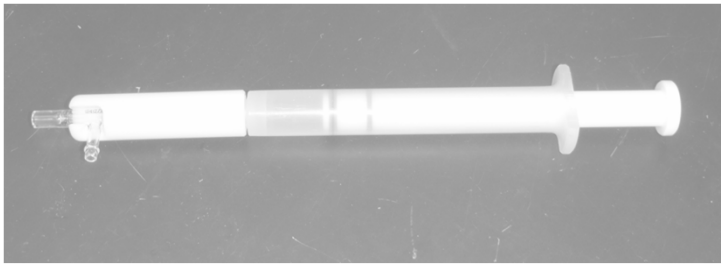

One Neb


Microflow PFA



Nebulizers need cleaning too

There may not be an APP for that, but there IS a tool for that…



Spray chambers (survey)

Nearly all lab use a cyclonic type spray chamber.

Generic cyclonic

Twister double pass

Also indicated:

Cyclonic, single pass

(2)Cyclonic Double Pass

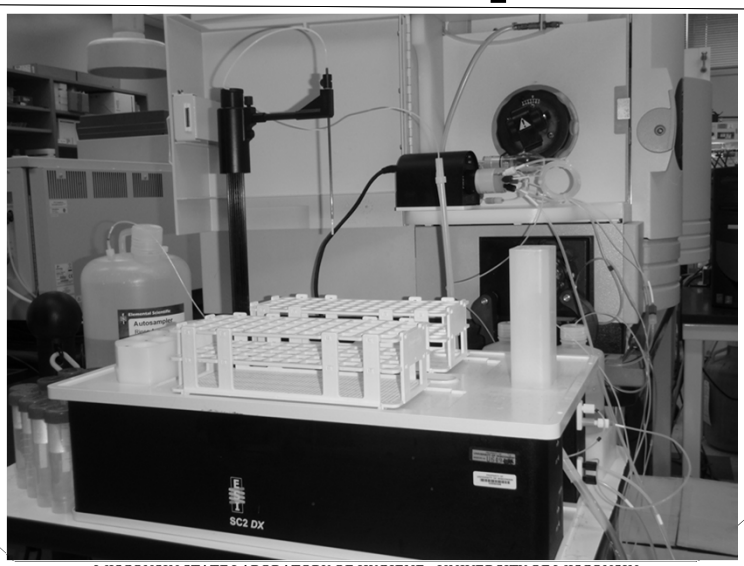
Double Pass

Scott-type

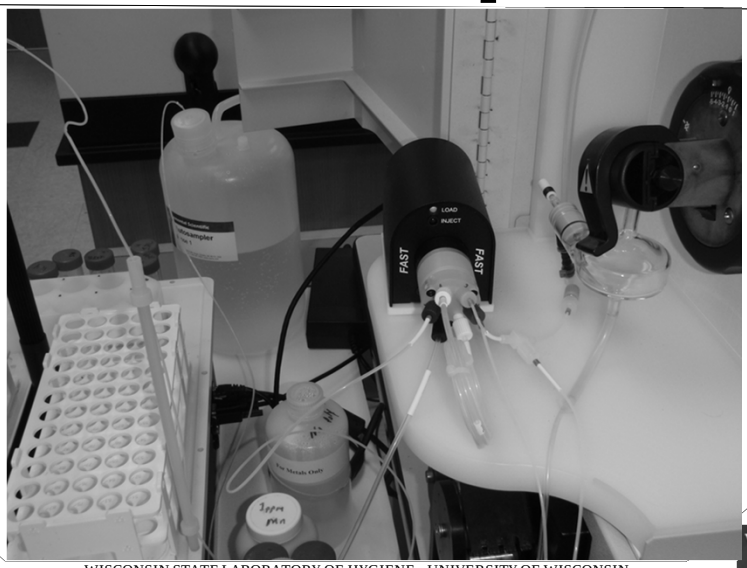
Twister cyclonic

Cyclonic Scott type

The FAST autosampler



The FAST autosampler



Instrument Set-up:

- Sample (and internal standard) flow check
- Spectral alignment using a single element (Cu/Mn, etc.),
- Internal instrument alignment (Hg),
- Equipment inspection
- Documentation as required by accrediting agency

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Calibration…a few words

- 1pt. vs. multi pt. (ELLAP),
- element separation (no IECs during calibration),
- conc. levels (MDLs and linear dynamic range),
- wavelengths

Tell ‘em

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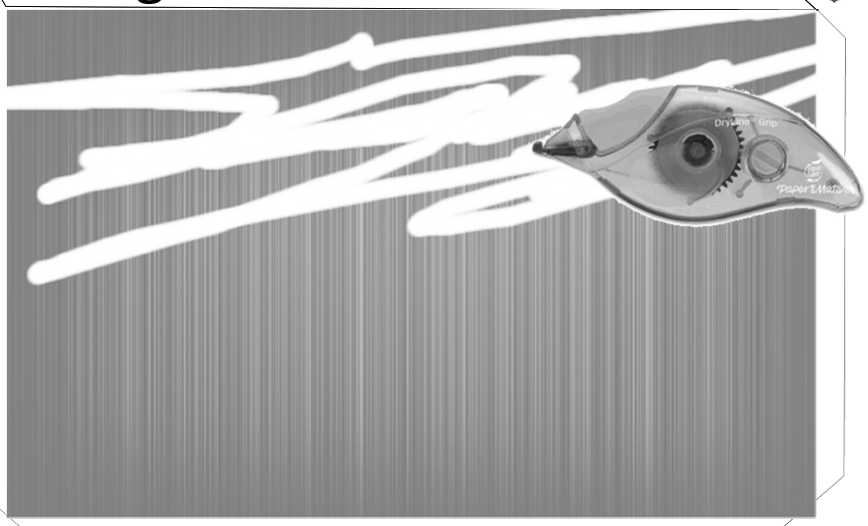
A few words on…
background correction



Which comes first…

… IECs?
or background correction points?

It's a trick question...

You can do these steps in either order, but because IECs have to be verified if background correction points change, it makes sense to set background points first.

You can update an IEC without changing background correction pts.

But if you change background correction (location of a point, going from 1 to 2 pts or 2 to 1 pt), you MUST re-assess any associated interference correction

It's a trick question...

Background correction points and IECs work in sync.

Proper background placement or switching from 2 to 1 pts is not necessarily a substitute for IECs.

2 background points is generally reserved for areas of sloping background.

When the sloping background is a shoulder of an interferent, you will need to have an IEC to recoup the area "shaved".

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INTERFERENCE CORRECTION

Interference Correction Rules

1. Interference correction is NOT mandatory, but proving that none is required IS mandatory.
2. You MAY be able to go without interference correction. But it's reserved for special cases.
3. Correction is specific to an instrument configuration. Change the torch or make adjustments to the plasma, nebulizer or spray chamber require repeating the determination.
4. Your correction may need adjustment.
   a) If all standards are mixed into one solution a co-interferant situation my exist. Although more time-consuming, multiple mixed standards works best.
   b) If IECs are established based on a single element standard at 2 ppm and you encounter the analyte at, say., 17 ppm, you'll have to re-check IECs at or above that level for all target analytes.
5. Interference check standards (ICS) are your security system. But no system is perfect.

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Interference Correction Rules

6. There is need for an ICS-A. There is also a need for an ICS-B (and possibly even an ICS-C,D,E). But <u>there is absolutely no need for an ICS-AB</u>
7. Your protection is only as good as your ICS and how your interference correction is established.
8. If you encounter an interferent level above the level at which you tested it, you must dilute the sample below the test level or re-do IECs for that element at a higher level.
9. Focal length and enhanced resolution may minimize interference, but they will not eliminate them.
10. Evaluate ICS properly. <u>+</u> 200ppb is unacceptable

Which single elements? Level?

<u>200.7, Table 2:</u> Requires evaluation of interference from 17 elements: Al,Be,Ba,Cd,Ce,Co,Cr,Cu,Fe,Mn, Mo,Ni,Si,Sn,Ti,Tl,V

<u>6010C, Table 2:</u> Requires evaluation of interference from 10 elements: Al,Ca,Cr,Cu,Fe,Mg,Mn,Ni,Ti,V

1000 ppm: Al,Ca,Fe,Mg *(that seems a bit high: 250? 500 ppm?*

200 ppm: all others *(that may also be a bit high; 10 ppm will work in most cases)*

Note that 6010 doesn't require evaluation from Mo. That wouldn't have ended well here, now would it?

Procedure to set IECs

1. Set background correction points.
2. Determine LODs.
3. Calibrate.
4. With IECs turned **OFF**, run single element standards for the 17 key interferents.
5. Populate an IEC table based on the results.
6. Analyze appropriate ICS standards designed to test for adequate correction of these interferences.
7. Verify that LODs are realistic (bouncing around the LOD).

Conclusion:

You can achieve accuracy either way.

You just have to remember that IECs are inherently linked to the background corrections points designated when then IECs were generated.

Changing background correction points requires

1. Re-standardization
2. re-evaluation of any associated IECs.
3. Run controls (ICS) to verify

But re-evaluating IECs does not require re-setting background correction points.

FACT v. MSF

MSF

Fast **A**utomated **C**urve-fitting **T**echnique

Minor wavelength offset or drift that may occur is accounted for by monitoring six plasma-based emissions lines across the wavelength range. This maintains the wavelength accuracy of the models for long-term use.

Unlike IEC, the known concentration of the analyte and interferent in the respective solutions is not required. The solution concentration only needs to be high enough for the signal peak to be easily distinguishable from the background (typically 50 x LOD).

Source: Agilent Technologies, Inc. 2009
Publication number: 5991-0846EN

How does FACT work?

Mathematically "deconvolutes" (or separate) the analyte signal from the raw spectrum**.**

Models built by measuring the expected components separately and the response for each. This typically includes measuring these solutions:

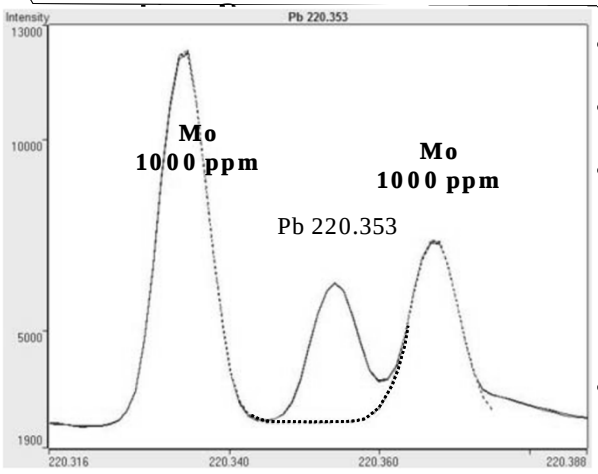
1. **A blank solution**
2. **A pure analyte solution**
3. **Pure interferent solutions**.

←Here, it's much like MSF

Up to 7 interference models per analyte

Source: Agilent Technologies, Inc. 2009
Publication number: 5991-0846EN

What is Fitted Background Correction?



- Not one point,
- Not 2 points,
- but a true polynomial function solution to drawing the baseline.
- Parallel = GC peak integration.

Source: Agilent Technologies, Inc. 2012
Publication number: 5991-0841EN

Fitted background correction

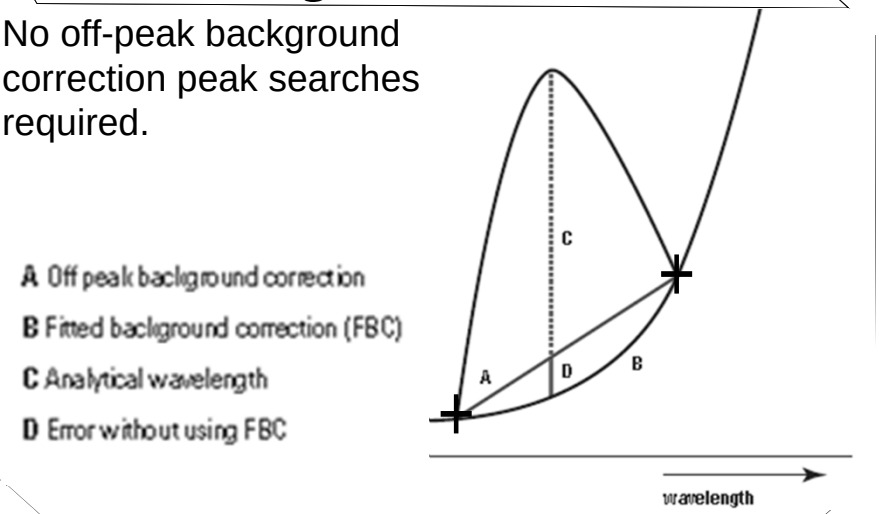
Mathematically models the measured spectrum :

1. Determining the **offset component** to model the unstructured continuum background.
2. Determining the **slope component to model the wings of large distant peaks.**
3. Applying three Gaussian peak components to model:
   a. The analyte peak.
   b. Any potential interference peak to the left of the analyte peak.
   c. Any potential interference peak to the right of the analyte peak.
4. Using an iterative procedure to estimate the width and position of the peaks.
5. Using a method of least squares to determine the magnitude of the offset, slope and peak heights.

Source: Agilent Technologies, Inc. 2012. Pub. number: 5991-0841EN.
'Fitted' — Fast, accurate and fully automated background correction.

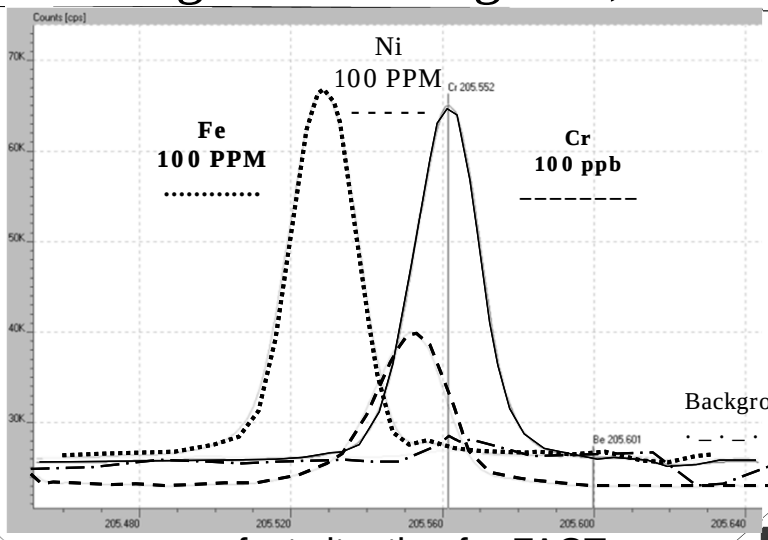
Fitted background correction

No off-peak background correction peak searches required.



Source: Agilent Technologies, Inc. 2012
Publication number: 5991-0841EN

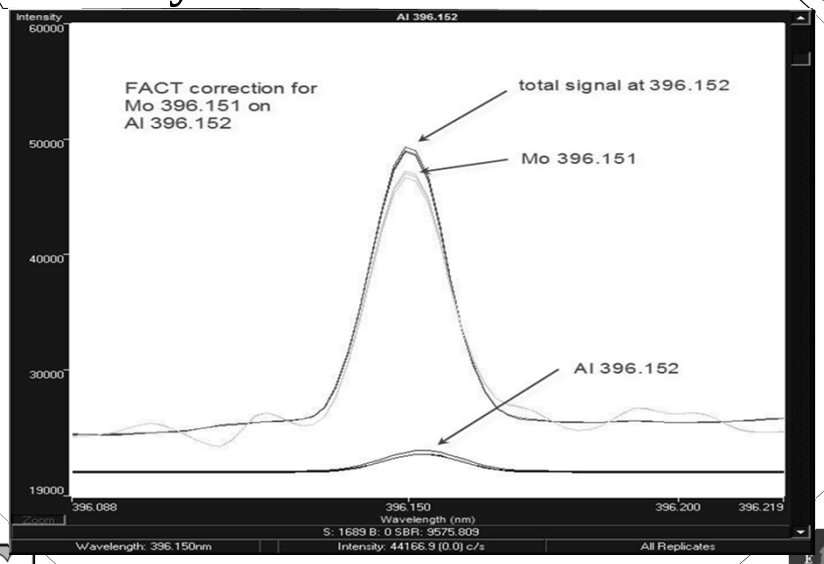
Resolving Cr from high Fe, Ni...



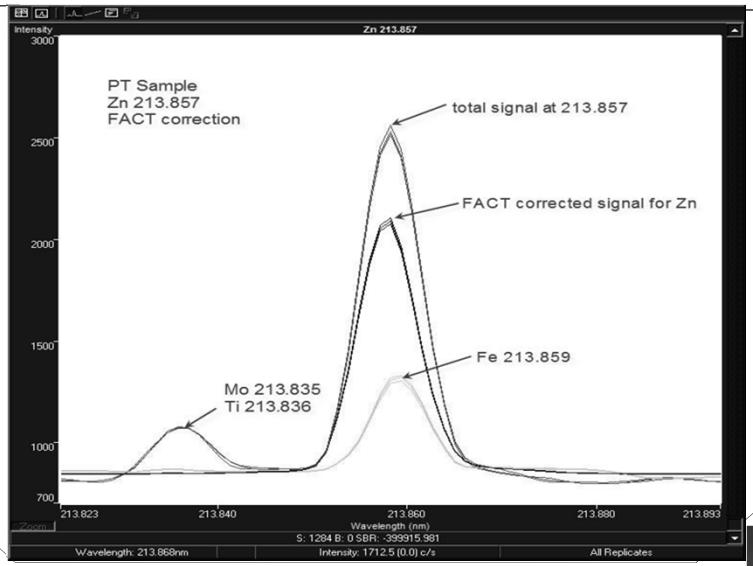
…a perfect situation for FACT

FACT in practice for the PT sample

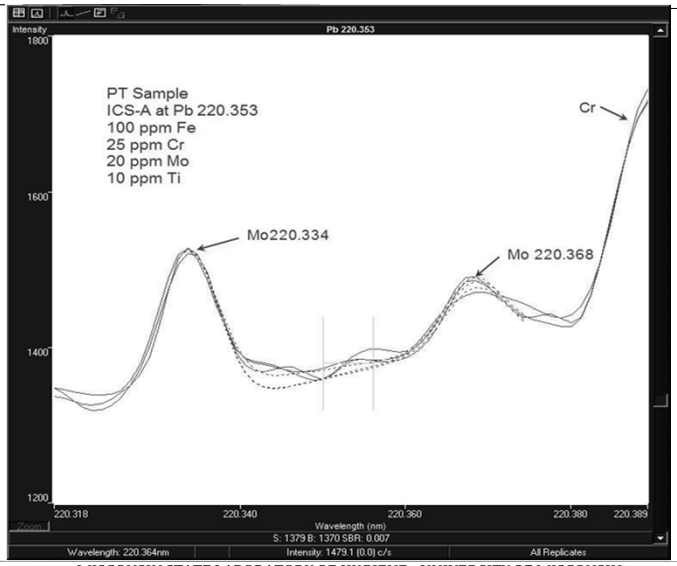
FACT system: Mo on Al



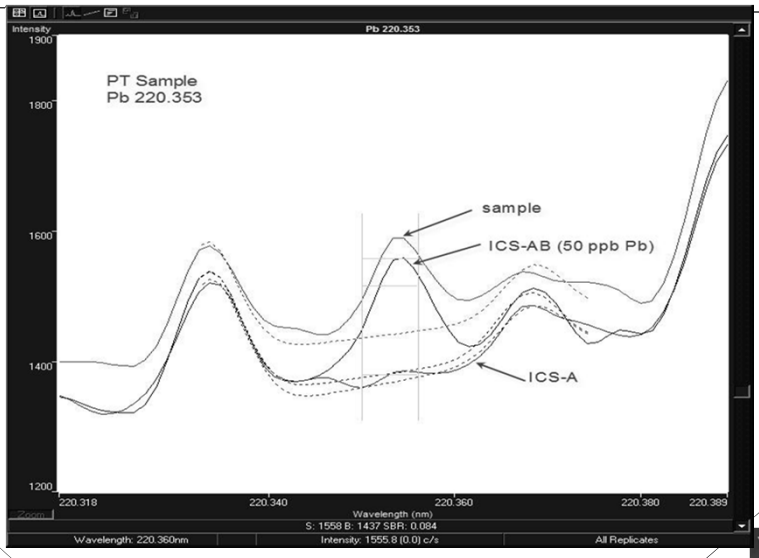
FACT correction for Zn



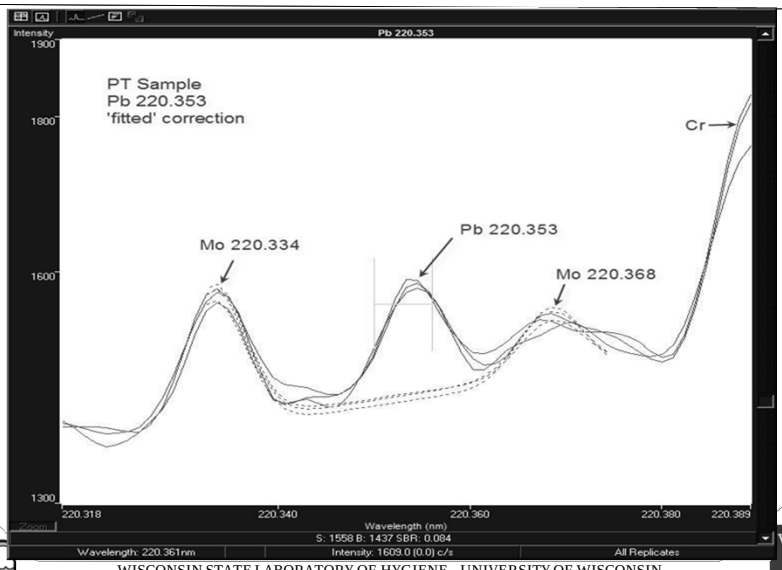
FACT/FBC for Pb in ICS A



FACT/FBC for Pb in ICS A/AB



FACT Fitted correction for Pb



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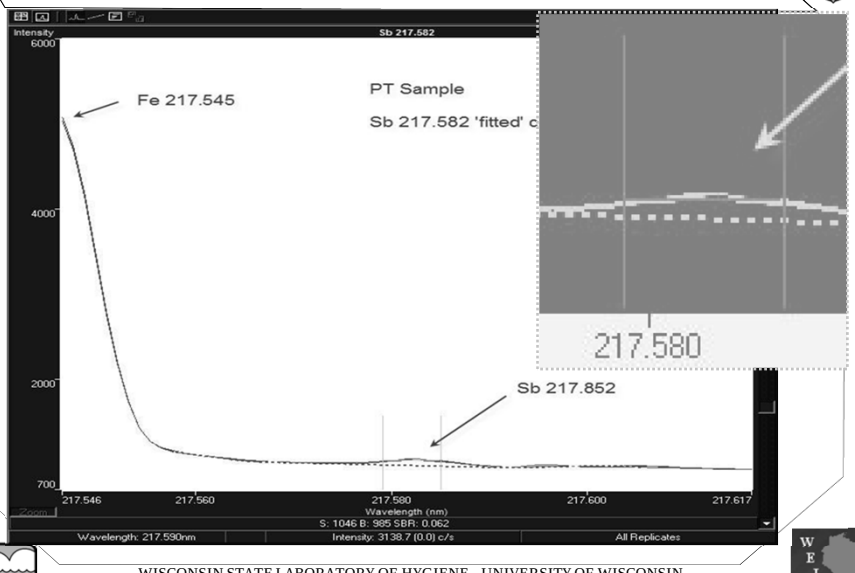
FACT Fitted correction for Fe on Sb



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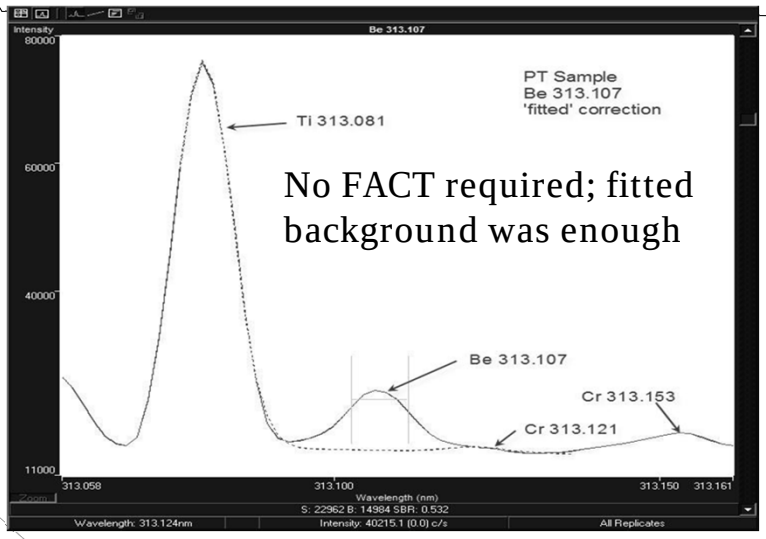
FACT scan on Be



LIMA on using FACT

(1) scan the sample

(2) make up individual single-element interferent samples & a mixed ICS-A containing all of the interferents at the concentrations in the sample.

(3) Spiked the ICS-A mix with low levels of analyte at 10 ppb and 50 ppb to run as our ICS-AB as a check against the sample spectra.

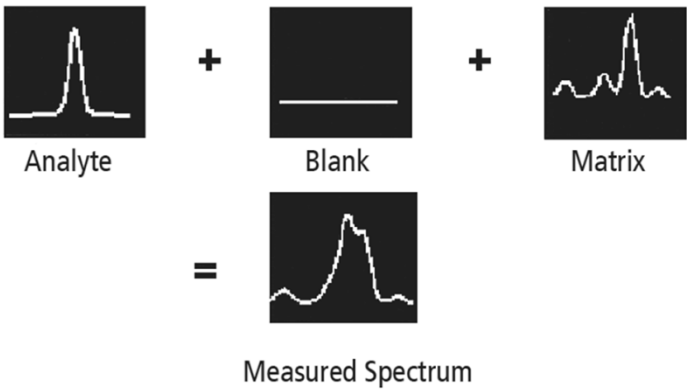
(4) Where fitted correction did not resolve the ICS-AB we employed the FACT correction and/or looked at alternate lines.

Red H-bar - a graphic used to indicate the pixel width at the desired λ used to adequately capture the peak for integration (default = 3 pixels wide)

MSF

MSF is…

Emission spectrum = sum of *n* contributions



Source: PerkinElmer Inc., 2009.
Multicomponent Spectral Fitting. Technical Note, 006081D_01.

Understanding MSF

Think of it as automatic simultaneous multi-point background correction.

Requires only that a minimum of three solutions are analyzed:

- the blank,
- a pure solution of the element being determined,
- and pure solutions for each of the potentially interfering elements in the matrix.

There are no limits on the number of interfering elements that can be included in a model.

Source: PerkinElmer, Inc. 2009
Multi-component spectral fitting. Pub. # 006081D_01

Understanding MSF

MSF looks at the spectral profile in the region around the wavelength of interest and not just at the target wavelength as is the case with IECs.

What MSF can't correct is direct spectral overlap. As long as there is some peak separation between the target element and the interference, then MSF will work.

In cases where the background interference involves multiple peaks from one element that creates "spectral grass", IECs simply do not work as background is larger than the target signal.

Bottom line is that neither IECs or MSF can handle all interferences. There are some specific interferences that can only be addressed by one vs the other.

Source: Personal communication, 2014
Perkin-Elmer Atomic Spectroscopy Product Specialist

MSF in practice

A user dialog box allows the analyst to select whether a particular line should be considered a blank, an analyte, or an interferent.

The scan appears no differently.

The SLH has MSF capability but generally does not use it because it's more sample specific. However, an MSF routine was quickly created for the PT sample.

State Lab PT sample by MSF

	TV	SLH by MSF			SLH by IEC		
Al	50	75.96	♥	152%	49.6	♥	99%
Sb	75	58.8	♥	78%	67.4	♥	90%
As	100	109.5	♥	110%	98	♥	98%
Ba	880	860.7	♥	98%	900	♥	102%
Be	5.5	5.556	♥	101%	5.2	♥	95%
B	750	679	♥	91%	842	♥	112%
Cd	35	33.59	♥	96%	35.2	♥	101%
Ca	13,500	13460	♥	100%	13292	♥	98%
Cr	25,000	24030	♥	96%	24610	♥	98%
Co	240	230.6	♥	96%	235.7	♥	98%
Cu	1,300	1275	♥	98%	1315	♥	101%
Fe	110,000	109400	♥	99%	112185	♥	102%
Pb	40	42.23	♥	106%	39	♥	98%
Mg	8,750	9027	♥	103%	8485	♥	97%

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State Lab PT sample by MSF

	TV	SLH by MSF			SLH by IEC		
Mn	430	415.4	♥	97%	420.4	♥	98%
Mo	17,000	16390	♥	96%	16239	♥	96%
Ni	30	30.5	♥	102%	31.2	♥	104%
P	100	85.38	♥	85%	105.2	♥	105%
K	7,500	7900	♥	105%	7462	♥	99%
Se	250	230.4	♥	92%	235.2	♥	94%
Ag	3000	-725.6	⤫ ↘	-24%	2957	♥	99%
Na	14,000	13960	♥	100%	14360	♥	103%
Sr	1,500	1437	♥	96%	1478	♥	99%
Tl	75	74.61	♥	99%	79	♥	105%
Ti	8,000	8361	♥	105%	8054	♥	101%
V	15	13.34	♥	89%	16.06	♥	107%
Zn	60	95.82	⤫ ↗	160%	53.5	♥	89%

ICS

COMPOSITION

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Can we please ditch the ICS-AB?

200.7 7.13.6 If **the instrument does not display negative concentration values**, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

6010 C 7.8 Spike the [ICS] with the elements of interest, particularly those with known interferences, at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If **the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.**

There, I Said It!

- The ICS-AB offers NO value in modern day ICP-OES instruments. It was intended for '80s instruments that read "0" for negative values.
- The value of an ICS is to observe the impact of interferents on target analytes that are not present!
- Therefore spiking everything defeats the purpose.
- And applying 20% as criteria at 1 ppm means that samples can be ± 200 ppb, which is 20-100 times the LOD for nearly all analytes.
- Would you allow your blank to be ± 200 ppb?

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I don't think so!

Blanks ±
200
ppb?

ICS Evaluation Criteria

- Can we all agree that using ± 20% as acceptance criteria for ICS samples is just plain silly?
- Yes, that's what the methods suggest, but…
- An ICS is no different than a standard
- ICV criteria are ± 5% (200,7) or ± 10% (6010)
- CCV criteria are ± 10% (200.7,6010)
- LCS criteria are ± 15% (200.7)
- At the ICS levels, shouldn't ± 5% be achievable?
- And for unspiked analytes, shouldn't they be the same as in a blank?
- **Using ± 20%? You may as well not do it at all.**

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Devising an Appropriate ICS

Check major interferents (cations)

ICS-A — Major interferent analytes only — **Al, Ca, Fe, Mg** — ± 5%

Add a simple, but overlooked evaluation step

ICS-B — Secondary interferents only — **Cr, Mo, V, Sn, Ti** — ± 10%

ICS-C? — **Be,Ba,Cd,Co,Cu,Mn,Ni**

Evaluate BOTH against

ICB — **± 2xLOD** — **Compare to blank for trends. Absolute ± 2xLOD**

For "unspiked" analytes...

Compare the ICB to the ICS-A

	LOD	Blank Avg	Al 50 + Fe 20 ppm	
Al	0.013	0.2974	49.14	LOD is questionable
Ba	0.001	-0.0001	0.2967	+300 ppb! IEC
Cu	0.001	0.0049	0.0042	Realistic LOD?
Mn	0.003	-0.0017	- 0.0040	Watch @ >Al/Fe
Mo	0.008	0.0012	- 0.0049	OK
Zn	0.007	0.0037	- 0.0175	Possible IEC

Compare the ICB to the ICS-B

	LOD	Blank	ICS-B*	
Ag	0.0005	0.0009	-0.0167	Some interference
Al	0.013	0.2974	0.7383	Significant ↑ IEC!
Cd	0.001	-0.0021	0.0003	Looks OK
Zn	0.007	0.0037	-0.0139	Small IEC needed?

*Cr,Cu,Mn,Ni,Ti,V @10ppm

PT Sample Results

In 2005, we presented The "Wibby"... In 2014, we upped the ante

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PT Sample Results

Remember…the point of these samples was analogous to an antiviral application for a computer; the sample was designed to highlight potential gaps in your interference security system. **If your lab did not fare well, please do not be discouraged**, we will be spending the majority of our time highlighting what the likely causes of these results are and how to correct them.

Please also understand that these results are in no way reflective of any lab's day-to-day performance using ICP. These samples, particularly the home brewed one, were specifically presented because of the challenge they pose in terms of interferents and actual levels of interferents. Most labs will not encounter samples with such severe interferences routinely, but in the event you do, this will help you come up with a plan to upgrade your defense systems.

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PT Sample Game Plan

Interferences:

Fe (110 ppm) Cr (25 ppm), Mo (17 ppm), Ti (8 ppm)

LOD challenges:

Al (50 ppb), Sb (75 ppb), Be (5,5 ppb), Pb (40 ppb), V (15 ppb)

Contaminant issues:

Zn (60 ppb)

Precipitation loss:

Ag (3 ppm)

Every lab did fine on the following elements: Ba, Ca, Cr, Cu, Fe, Mg, Mo, Na, Sr, Ti

10 out of 27 elements passed by all

...but there was trouble w/these

	#reptd	#ok	↑ bias	↓ Bias	False -
V	11	2	**3**	**2**	**4**
Sb	13	5	**7**	**0**	**1**
Be	14	6	**0**	**5**	**3**
Al	14	7	**6**	**0**	**1**
P	7	4	**3**	**0**	**0**
Zn	17	10	**7**	**0**	**0**
Tl	13	8	**1**	**2**	**2**
B	12	9	**2**	**1**	**0**
Pb	17	13	**0**	**3**	**1**

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PT Sample: IS and IEC effects

How important were IECs and IS for this sample?

Internal standards not as critical because there is no matrix!

	IS?	☒	☑	☒	☑	TRUE
	IEC?	☒	☒	☑	☑	Value
Al		453	428	56.2	48.3	50
Sb		381	367	62.1	58.9	75
As		296	285	101	91.3	100
Ba		890	867	899	873	880
Be		7.8	7.6	5.0	5.3	5.5
B		623	605	834	804	750
Cd		38.0	37.0	36.0	35.0	35
Ca		14.2	13.2	14.2	13.2	13.5
Cr		26230	25338	26243	25350	25000
Co		257	237	253	236	240
Cu		1256	1221	1328	1286	1300
Fe		117	111	118	111	110
Pb		-12.0	-13.4	40.4	40.0	40

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PT Sample: IS & IEC effects

How important were IECs and IS for this sample?

	IS?	☒	☑	☒	☑	TRUE
	IEC?	☒	☒	☑	☑	Value
Mg		8.9	8.4	8.9	8.4	8.75
Mn		426	418	430	422	430
Mo		16965	16390	16978	16403	17000
Ni		-3.7	-4.2	30.3	29.5	30
K		8.0	7.5	7.8	7.4	7.5
Se		131	130	245	238	250
Ag		3305	3322	3087	3110	3000
Na		15.1	14.1	15.1	14.1	14
Sr		1518	1448	1516	1448	1500
Tl		28	27	90	85	75
Ti		8790	8118	8788	8116	8000
V		-171	-160	6.7	16.1	15
Zn		1333	-151	55.2	55.9	60

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All axial

PT sample – Mo, -Mo,Ti IEC

	TV	–Mo IEC	–Mo,Ti IEC	all IEC	
Al 396.153	**50**	490	490	49.6	Mo
B 249.677	**750**	764	758	842	other
Be 313.107	**5.5**	5.1	**13.6**	5.2	Ti
P 178.221	**100**	**61.8**	**57.8**	105	Mo,?
Pb 220.353	**40**	**- 13.7**	**- 16.2**	39.0	Mo
Sb 206.836	**75**	**- 144**	**- 122**	67.4	Mo,Ti
Se 196.026	**250**	235	235	235	Neither
Tl 190.801	**75**	79.0	**2.0**	79.0	Ti
V 292.402	**15**	**- 7.2**	**- 0.9**	16.1	Mo,Ti
Zn 206.200	**60**	46.3	46.3	53.5	Mo

Just removing 2 IECs shows that Mo and Ti were major problems for difficult analytes

Examples from the (PT) sample

Interference of Mo on V

42 Mo Molybdenum 95.96

23 V Vanadium 50.9415

India	290.88
Kilo	290.88

Mike	292.4
Delta	292.401
November	292.401
* SLH *	292.402
Bravo	292.402
Juliet	292.402
Oscar	292.402
Papa P-E	292.402
Papa Thermo	292.402

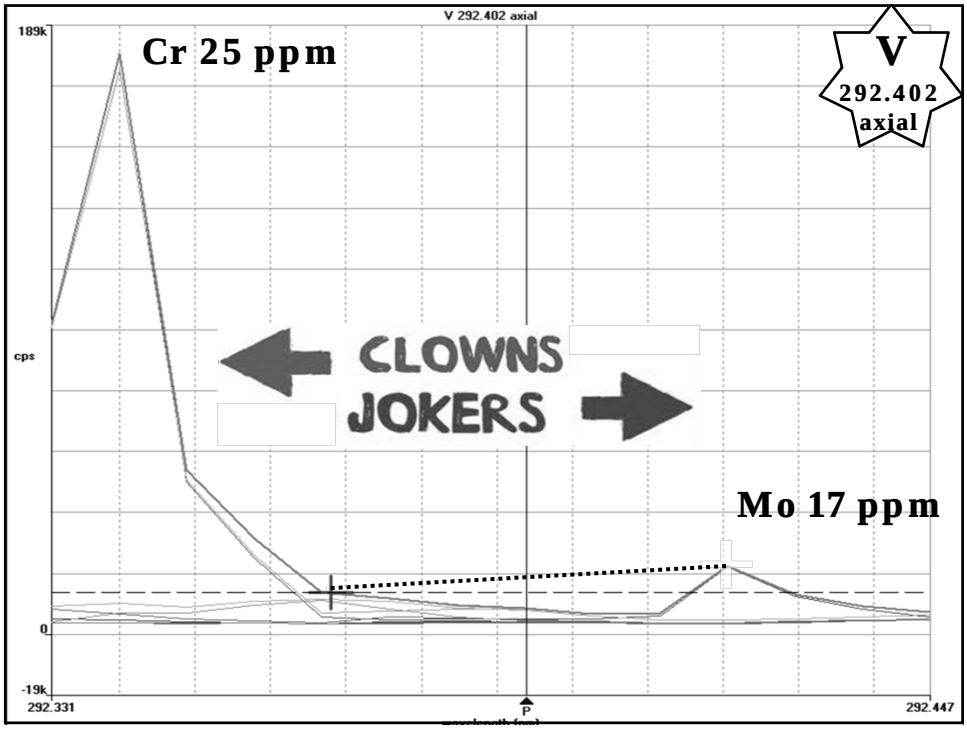
Alpha	292.464
Golf	292.464
Hotel	310.2
Lima	311.837

Interference of Mo on V

TV= 15 Acceptance = 12.8 – 17.3

November	- 2.24
Papa	< 0.34
Oscar	3
Bravo	< 5
Juliet	< 10.4
Delta	11.27
Lima	12.8
India	13.5
SLH	16.06

Alpha	18.6
Mike	22
Kilo	30.3
Hotel	< 20
Golf	< 28
Charlie	N/A
Echo	N/A
Foxtrot	N/A
Quebec	N/A



Interference of Mo on V

P-E default background correction points are at -27 and +27 pm off line from the peak maximum at 292.402 nm.

The +27 pt falls dead on top of a Mo peak (which would only be a problem at these Mo levels).

Kilo (202%) uses 290.88 line (P-E 1st recommended line). There is also a Mo peak at 290.912.

Lima passed but had low bias. They use λ 311.837 (5th recommended line). There is a Cr line at 311.865 nm.

Interference of Cr on Sb

24 Cr Chromium 51.9961

51 Sb Antimony 121.760

Alpha	206.833
Juliet	206.833
Papa P-E	206.833
Papa Thermo	206.833
Bravo	206.833
Delta	206.834
November	206.834
Charlie	206.835
* SLH *	206.836
Golf	206.836
India	206.836
Kilo	206.836

Hotel	206.8
Mike	206.8

Lima	217.582

Interference of Cr on Sb

TV= 75 Acceptance = 44 - 102

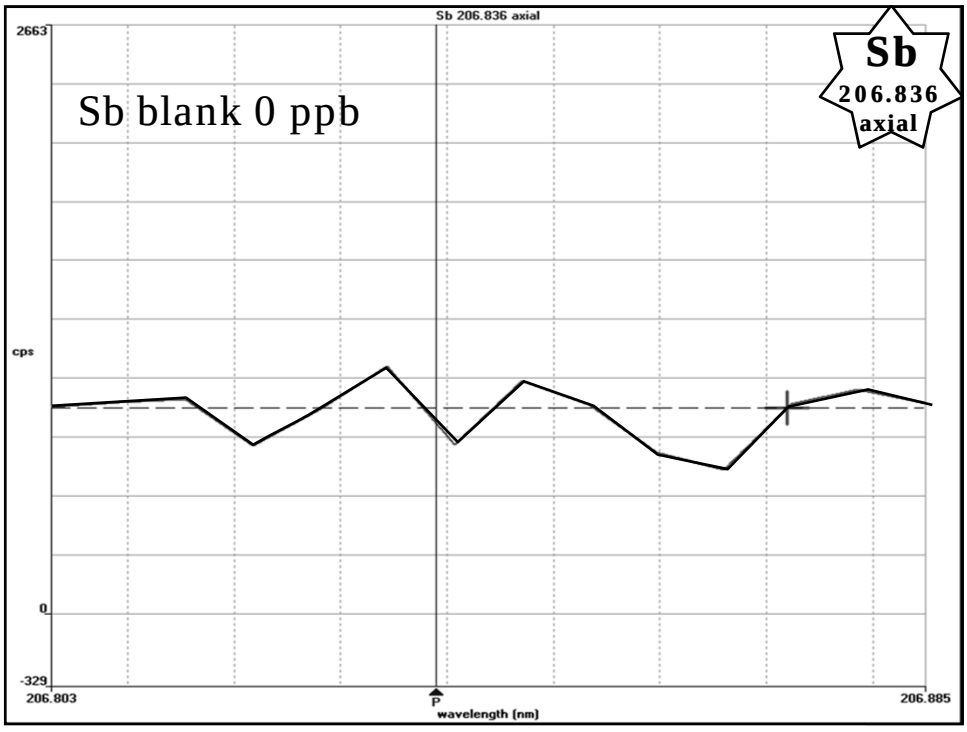
Lima	55.9
SLH	67.4
Alpha	74.5
Delta	75.7
November	78.9
Kilo	86.4
Juliet	117
Quebec	129

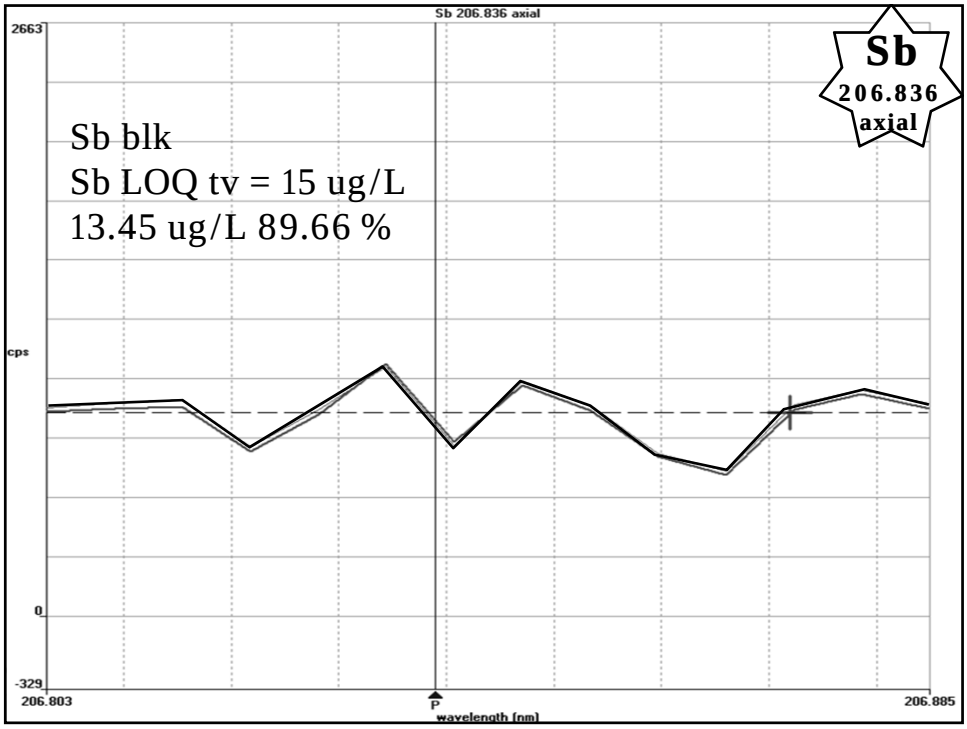
Mike	201
India	253
Charlie	288
Hotel	320
Golf	367
Bravo	**< 32**
Echo	N/R
Foxtrot	N/R

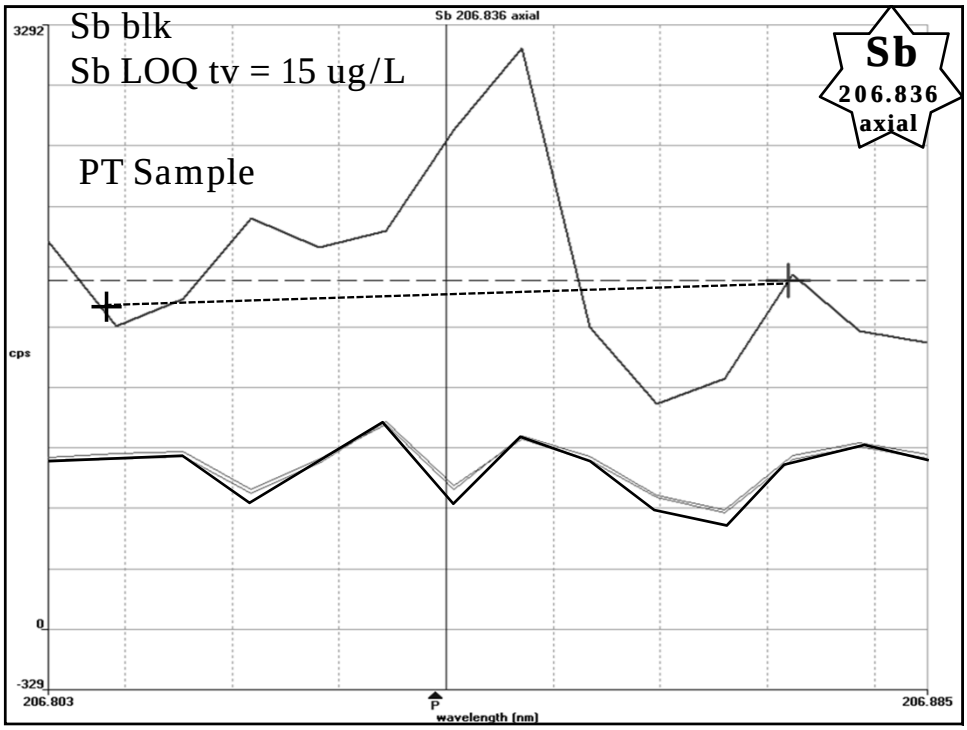
Interference of Cr on Sb

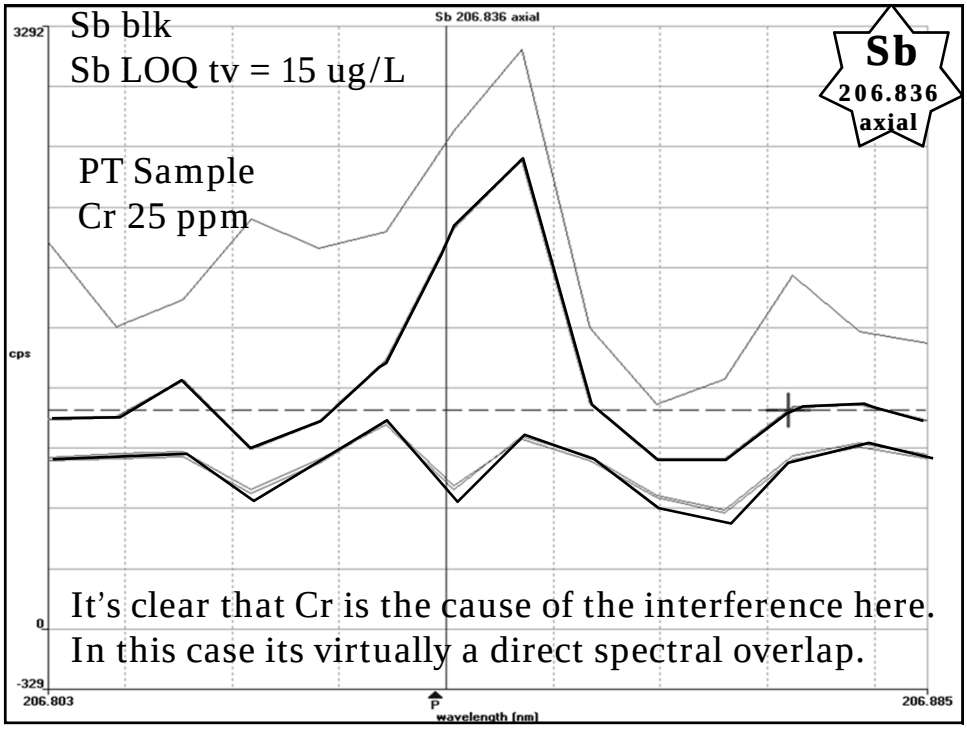
High bias will result (676% for SLH) if no correction was employed for interference due to Cr.

False "-" is most likely due to use of 2 background correction points. Cr is right on top of Sb.




Sb 206.836 axial
2663
cps
0
-329
206.803
206.885
wavelength (nm)
Sb
206.836
axial
Sb blk
Sb LOQ tv = 15 ug/L
13.45 ug/L 89.66 %


Sb 206.836 axial
3292
cps
0
-329
206.803
206.885
wavelength (nm)
Sb
206.836
axial
Sb blk
Sb LOQ tv = 15 ug/L
PT Sample



Interference of Ti on Be

Papa P-E	234.859
Alpha	234.861
November	234.861
Hotel	313
Mike	313
Bravo	313.042
Delta	313.042
India	313.042
Juliet	313.042
Kilo	313.042
Quebec	313.042

* SLH *	313.107
Charlie	313.107
Golf	313.107
Lima	313.107
Oscar	313.107
Papa Thermo	313.107

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Interference of Ti on Be

TV= 5.5 Acceptance = 4.68 – 6.33

Charlie	**< 0.79**	Quebec	5
Hotel	**< 1**	Delta	5.069
Kilo	**< 1.0**	India	5.14
Papa	**1.7**	Juliet	5.19
Oscar	**4**	SLH	5.2
November	**4.38**	Bravo	5.26
Mike	**4.4**	Lima	5.69
Alpha	**4.6**	Golf	< 7

Echo, Foxtrot N/R

Interference of Ti on Be

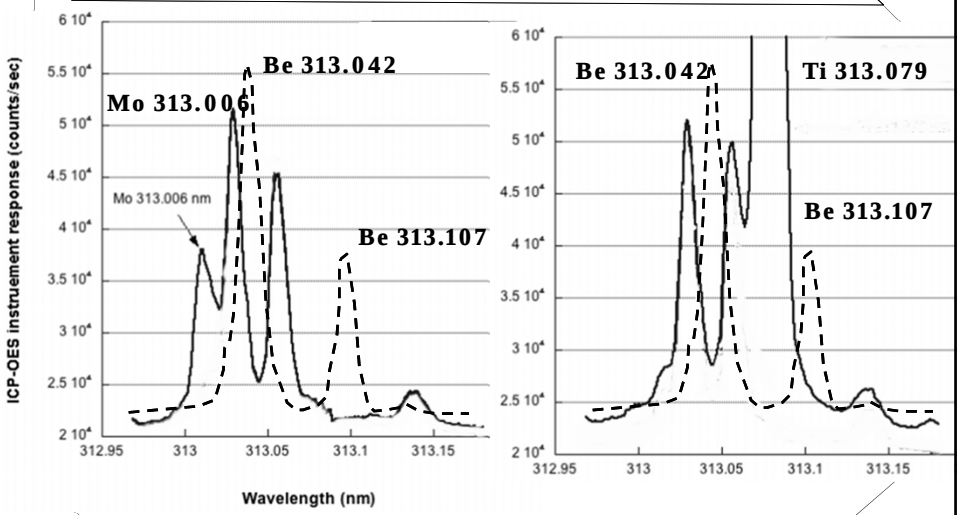
Beryllium is a doublet peak, with two very close lines.

Due to Ti, even if using only 1 background correct point, low bias can result. Mo can also be an issue.

Will yield slight negative result if not using an IEC (or some other form of correction).

The false negative (Kilo) is suspected to result from using the lower wavelength. The background correction point (or one if using two points) is affected by neighboring Mo peak

Clowns to the left of me; Jokers to the right



Source: Robbins, J., 2008. Advantages of multivariate spectral deconvolution techniques in correction for interferences in beryllium analysis by ICP-OES

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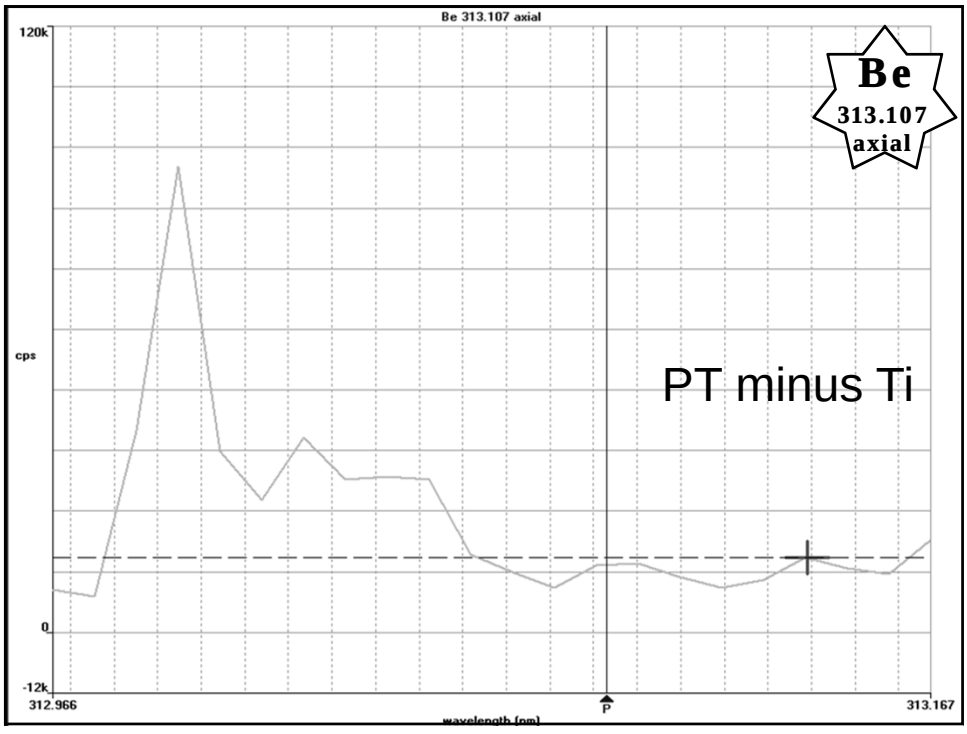
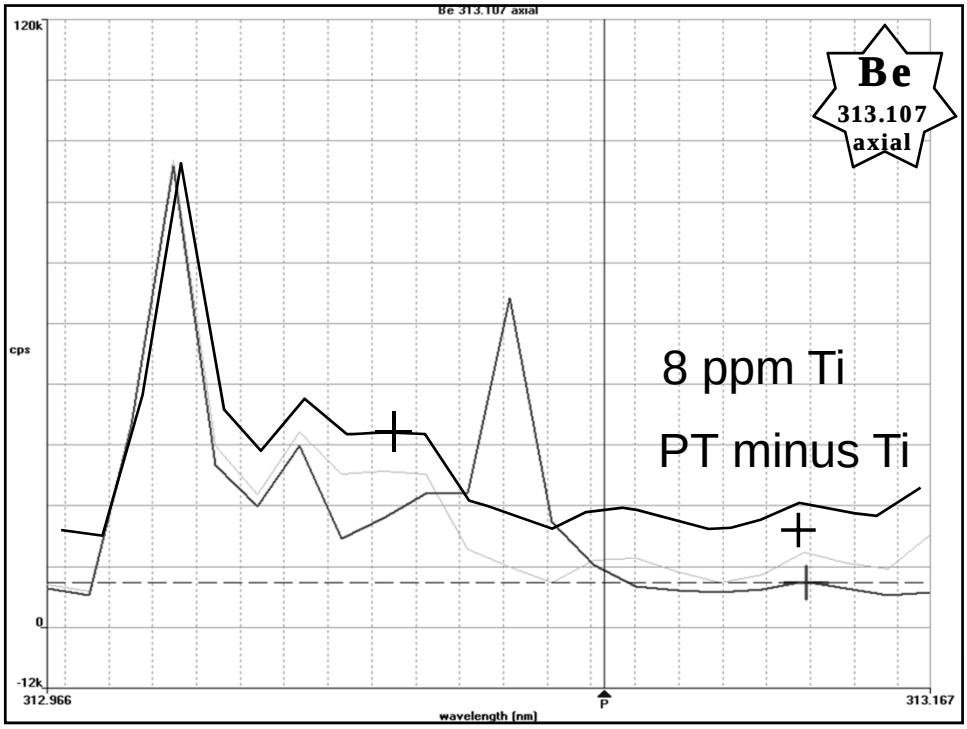
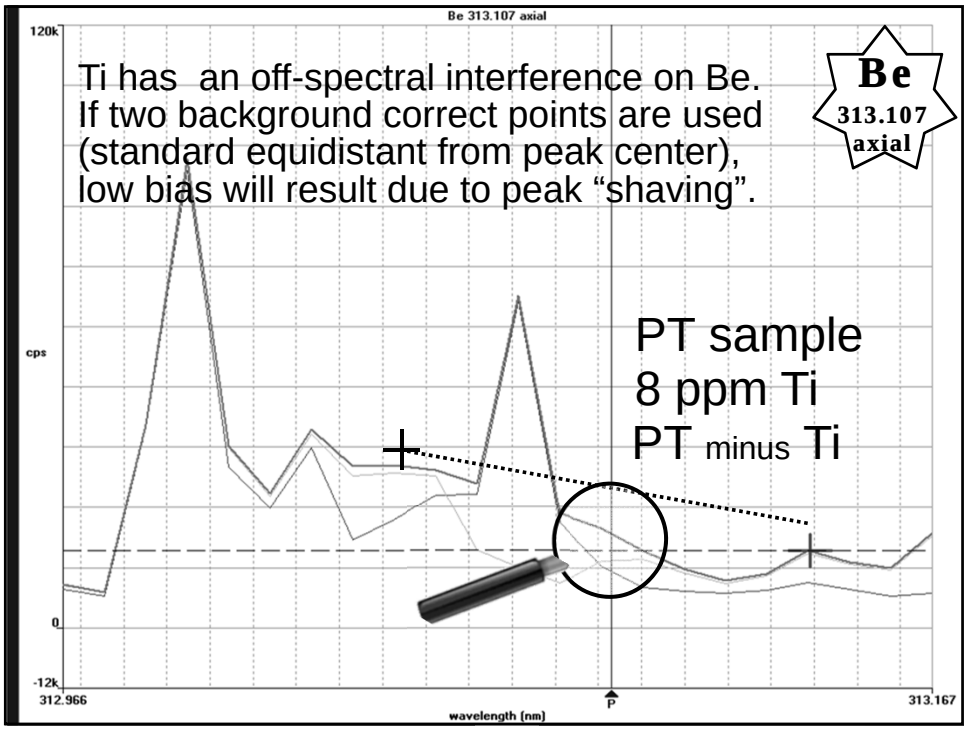
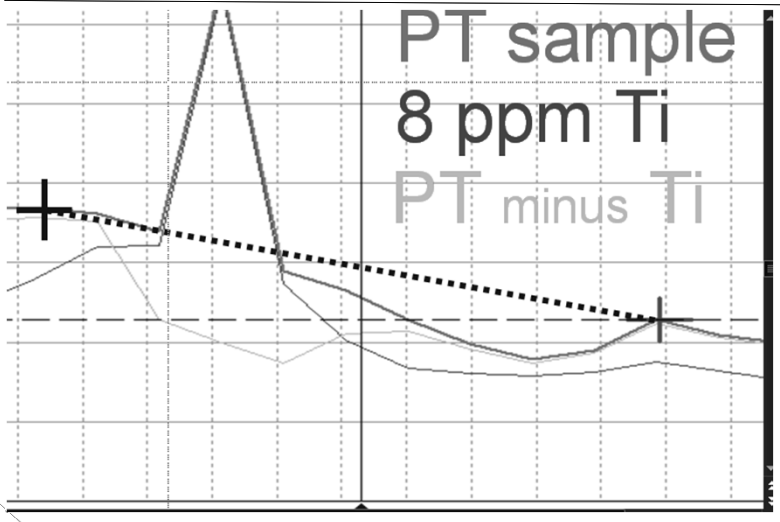



Be 313.107 axial
120k
cps
0
-12k
312.966
P
313.167
wavelength (nm)
Be
313.107
axial
8 ppm Ti
PT minus Ti

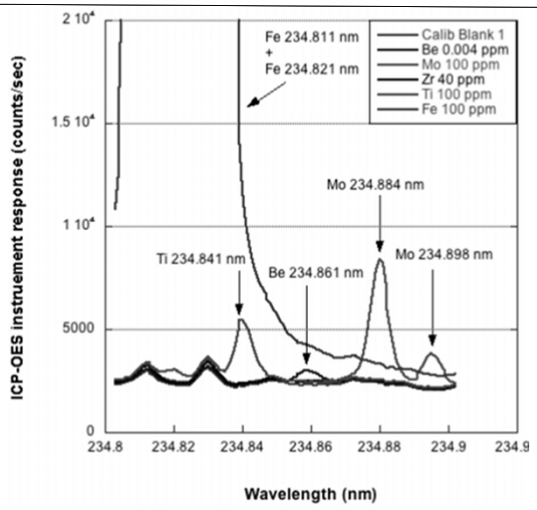

Be 313.107 axial
120k
cps
0
-12k
312.966
P
313.167
wavelength (nm)
Ti has an off-spectral interference on Be.
If two background correct points are used
(standard equidistant from peak center),
low bias will result due to peak “shaving”.
Be
313.107
axial
PT sample
8 ppm Ti
PT minus Ti

Ti on Be 313.107 close-up



Alternate wavelength- problems from Fe

Be 234.861 is impacted by Ti and Fe on the left and Mo on the right



Source: Robbins, J., 2008. Advantages of multivariate spectral deconvolution techniques in correction for interferences in beryllium analysis by ICP-OES

Interference of Mo on Al

November	237.312
Papa	237.312
Charlie	237.313
Delta	308.215
Echo	308.215
Juliet	308.215
Quebec	308.217
Hotel	396.1
Mike	**396.1**

Bravo	396.152
Alpha	396.152
Lima	396.152
Quebec	396.152
* SLH *	396.153
Golf	396.153
India	396.153
Kilo	396.153
Oscar	396.153

Interference of Mo on Al

TV= 50 ug/L Acceptance = 18 - 99

Lima	40.7
Oscar	46.2
November	48.4
SLH	49.6
Delta	58
Kilo	66.6
Mike	82
Juliet	120
Alpha	231

Charlie	350
India	575
Golf	696
Hotel	710
Echo	< 120
Quebec	< 65
Bravo	**< 20**
Foxtrot	N/R

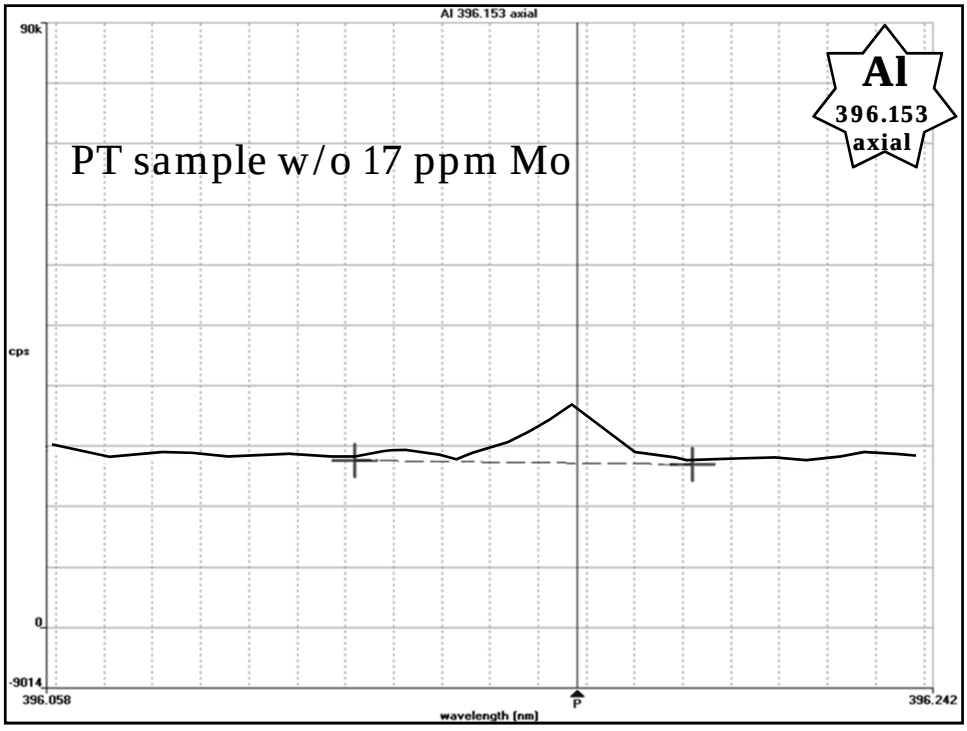
Interference of Mo on Al

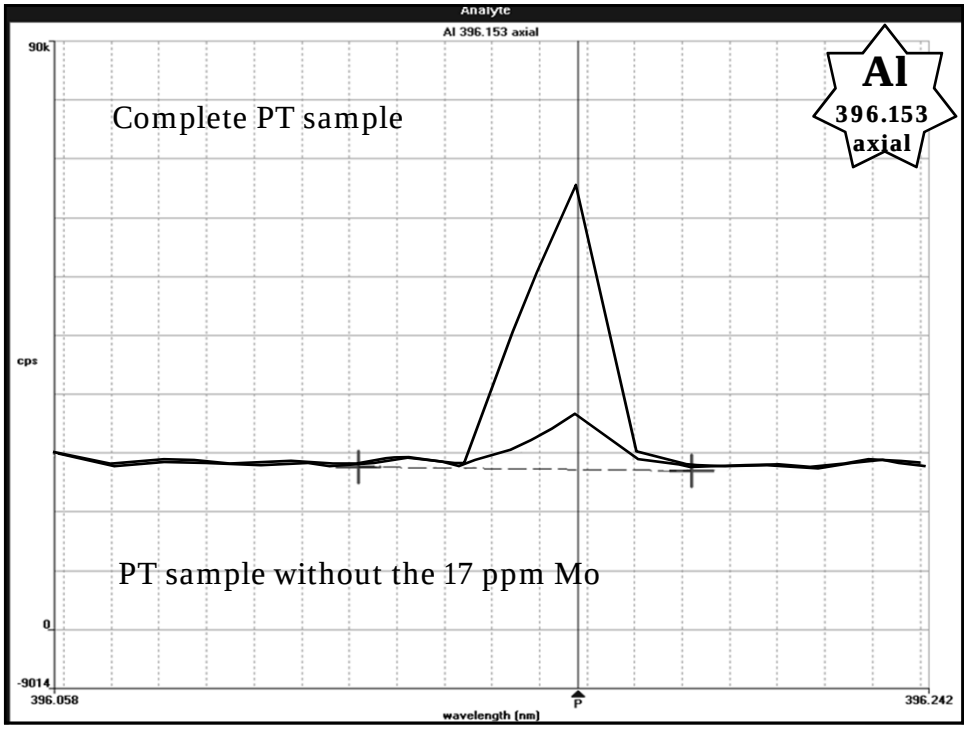
Problems with Al on the PT sample were purely related to interference from Mo.

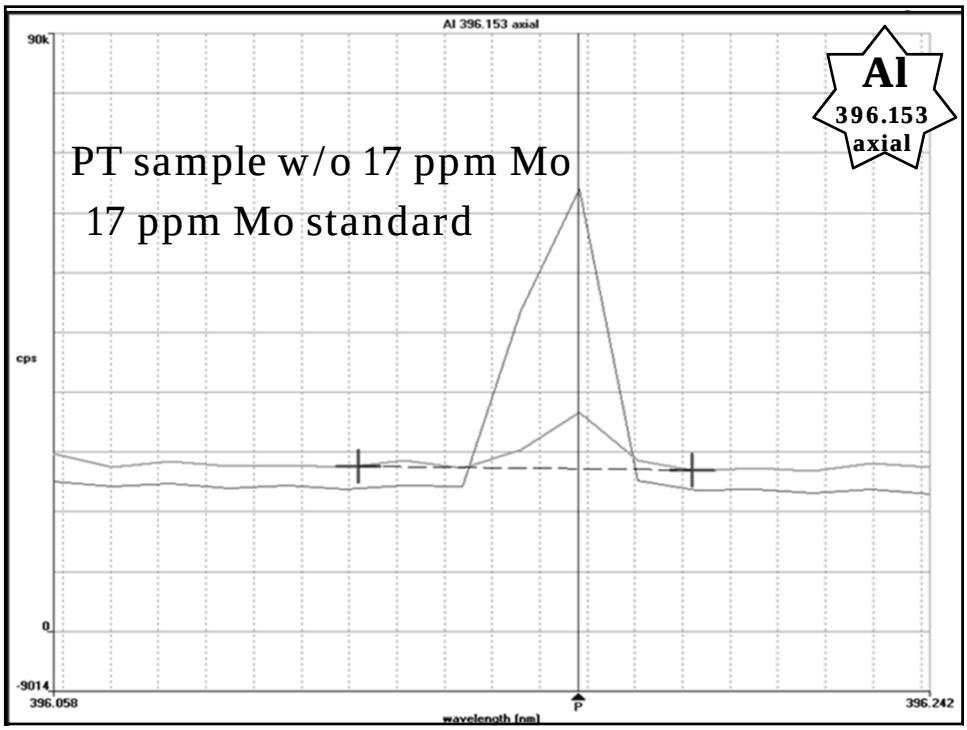
At 50 ppb, the level Al was somewhat of a challenge, but well above the mean/median LODs reported.

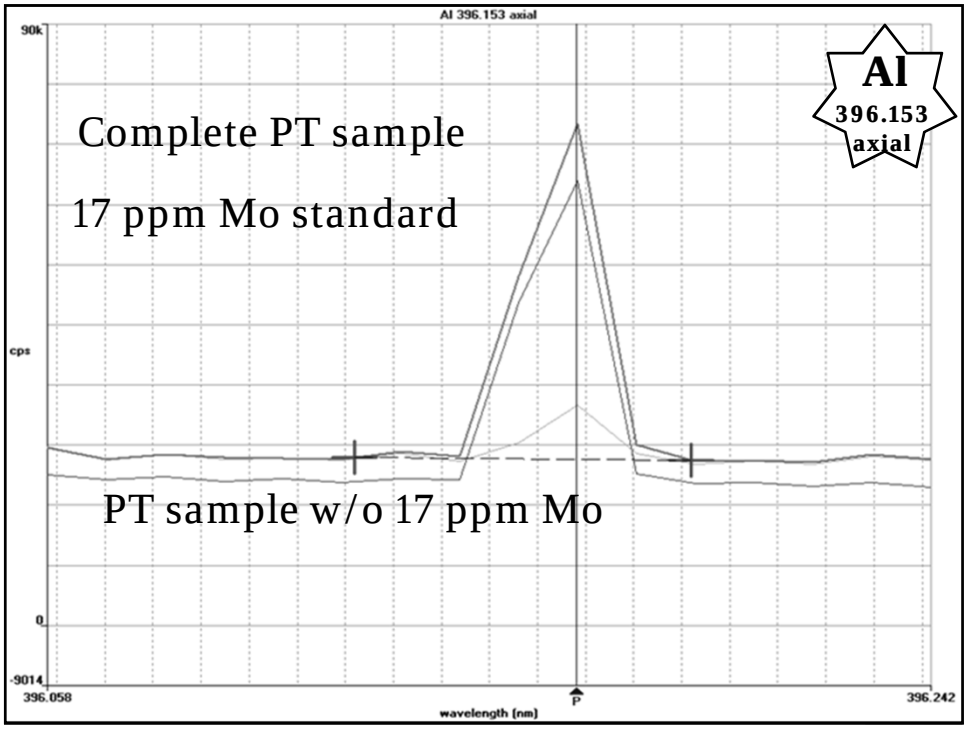
High bias observed is related to either not having interference correction for Mo, or having set the correction at a much lower level than that of Mo (17 ppm) in the PT sample.

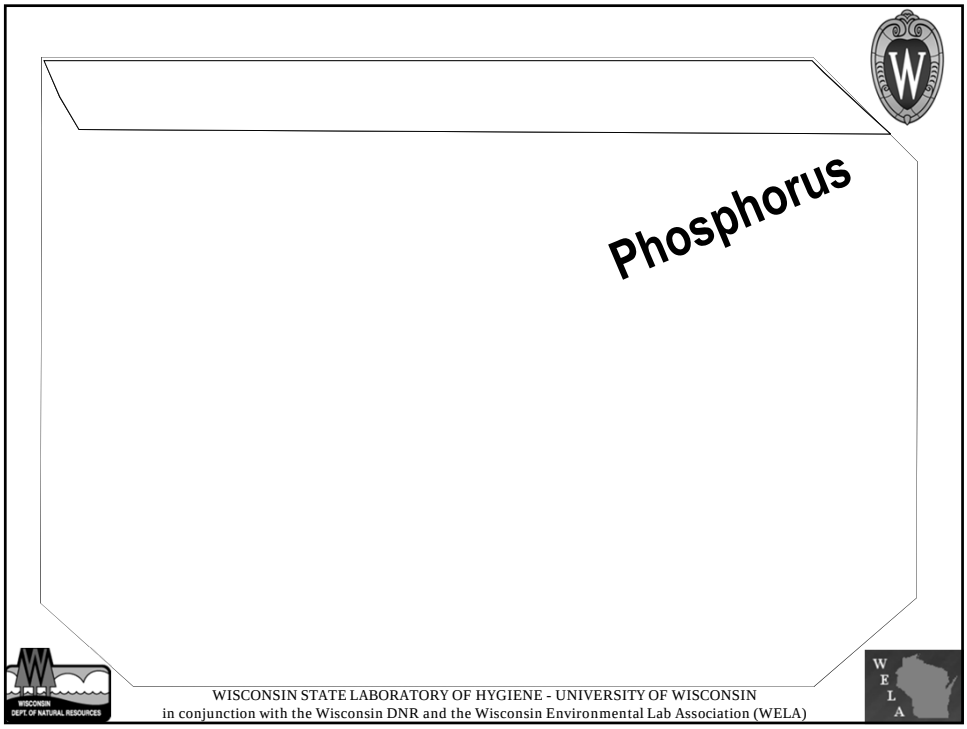
We suspect the false negative to be a result of either an unrealistic LOD or over-correction.




Analyte
Al 396.153 axial
90k
cps
0
-9014
396.058
P
396.242
wavelength (nm)
Al
396.153
axial
Complete PT sample
PT sample without the 17 ppm Mo


Al 396.153 axial
90k
cps
0
-9014
396.058
P
396.242
wavelength (nm)
Al
396.153
axial
PT sample w/o 17 ppm Mo
17 ppm Mo standard


Al 396.153 axial
90k
cps
0
-9014
396.058
P
396.242
wavelength (nm)
Al
396.153
axial
Complete PT sample
17 ppm Mo standard
PT sample w/o 17 ppm Mo


Phosphorus
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Interference of Cu on P

Papa Thermo	177.495
* SLH *	178.221
Papa P-E	213.616
Oscar	213.617
Delta	213.618
Lima	213.618
November	213.618
Quebec	213.618
Hotel	214.9
Kilo	214.914

Oscar	< 200
November	**92.7**
Quebec	**101**
Papa	**101.7**
Lima	**105**
SLH	**105.2**
Kilo	**205**
Delta	**216.3**
Hotel	**500**

TV= 100
84-115

The trouble with Phosphorus

The SLH uses the 178.221 line because 213.618 and 214.914 both suffer from significant interference from Cu.

This also partially explains why the Dept. has not been keen on the use of ICP for phosphorus.

While only 8 labs supplied results, 3 of the eight (37%) succumbed to high bias (and the sample contained 1.3 ppm Cu).

The good news is that the interference CAN be controlled.

Copper lines interfering with P

178.221 none

213.618

Ion	Observed Wavelength Air (nm)	Rel. Int. (?)
Cu II	213.4341	420
Cu II	213.5981	900

214.914

Cu II	214.8984	400

The trouble with Phosphorus

Notably, of the three labs that had trouble with P, all of them used one of the problem lines. Delta uses the 213 line and Hotel and Kilo use the 214 line.

While the 178 line is less sensitive, the SLH is able to obtain an LOD of 20 ppb which, while perhaps a little high for Adaptive Management needs, is well within LOD needs for routine P in wastewater.

Interference on B

Mike	208.9
Papa P-E	208.957
Papa Thermo	208.959
* SLH *	249.677
Golf	249.677
India	249.677
Bravo	249.678
Delta	249.678
Juliet	249.678
Lima	249.678
Hotel	249.7
Kilo	249.772
November	249.772
Quebec	249.772
Alpha	249.773

TV = 750 ppb

638 to 863

632	**Golf**
718	Lima
729.4	Delta
737	Bravo
738	November
743	Juliet
749	India

764 Quebec
790 Mike
842 SLH
850 Hotel
1770 Kilo
2574 Papa

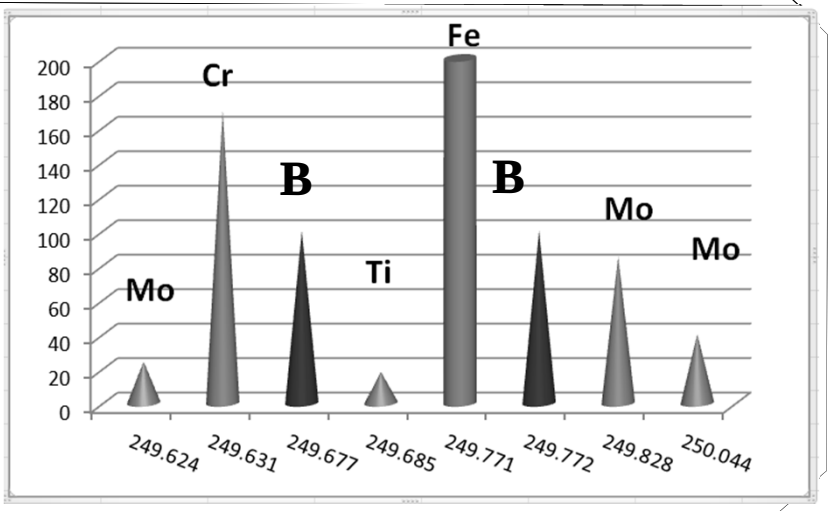
N/A: Alpha, Charlie , Echo, Foxtrot, Oscar

Why Papa had high bias for B

Element, Wavelength and Order	Use?	# IECs	IEC	k1	k2	Calc-in-fit?
As 189.042 (478)	☒	1	Mo	0.001424	0.000000	No
B 208.959 (461)	☐	11	Al	0.000779	0.000000	No
			Ca	0.000886	0.000000	No
			Cr	0.022993	0.000000	No
			Cu	0.022399	0.000000	No
			Fe	0.002208	0.000000	No
			Mg	0.000953	0.000000	No
			Mo	0.046550	0.000000	No
			Ni	0.023264	0.000000	No
			Ti	0.028057	0.000000	No
			V	0.025402	0.000000	No

IECs established but “Use” being unchecked means that , while they have IECs for Boron, they did not use them!

Interference on B



Boron: Plenty of trouble areas

Pb and background correction

Pb issues: intentional (back)gounding

Pb and background correction

P-E Out of the box defaults for Pb = λ 220.353 and 2 background correction points: -22 and + 20 pm.
All labs used the default wavelength.

Papa Thermo	182.205
Hotel	220.3
Mike	220.3
Charlie	220.351
Bravo	220.353
* SLH *	220.353
Alpha	220.353
Delta	220.353
Echo	220.353
Foxtrot	220.353
Golf	220.353
India	220.353
Juliet	220.353
Kilo	220.353
Lima	220.353
November	220.353
Oscar	220.353
Quebec	220.353
Papa P-E	220.354

< 1.2	Charlie	37	Quebec
22	Oscar	37.7	India
26	Golf	38.9	Lima
27.4	Papa	39	SLH
30	Bravo	40.1	November
30	Hotel	40.4	Alpha
30.9	Kilo	40.4	Echo
31	Foxtrot	46	Mike
33.53	Delta	49	Juliet

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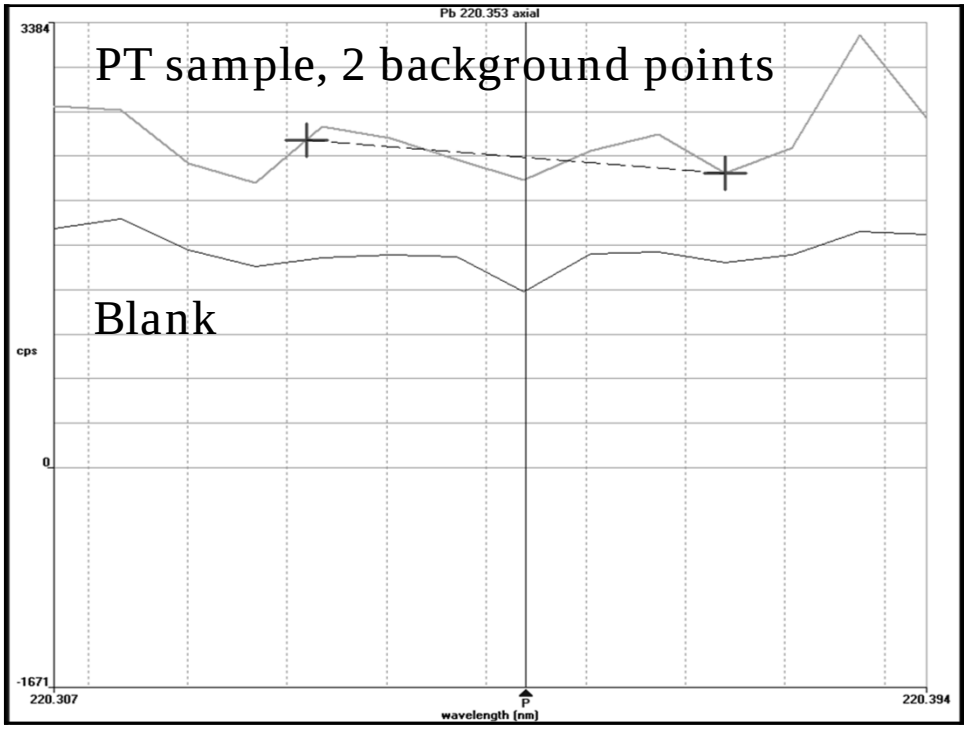
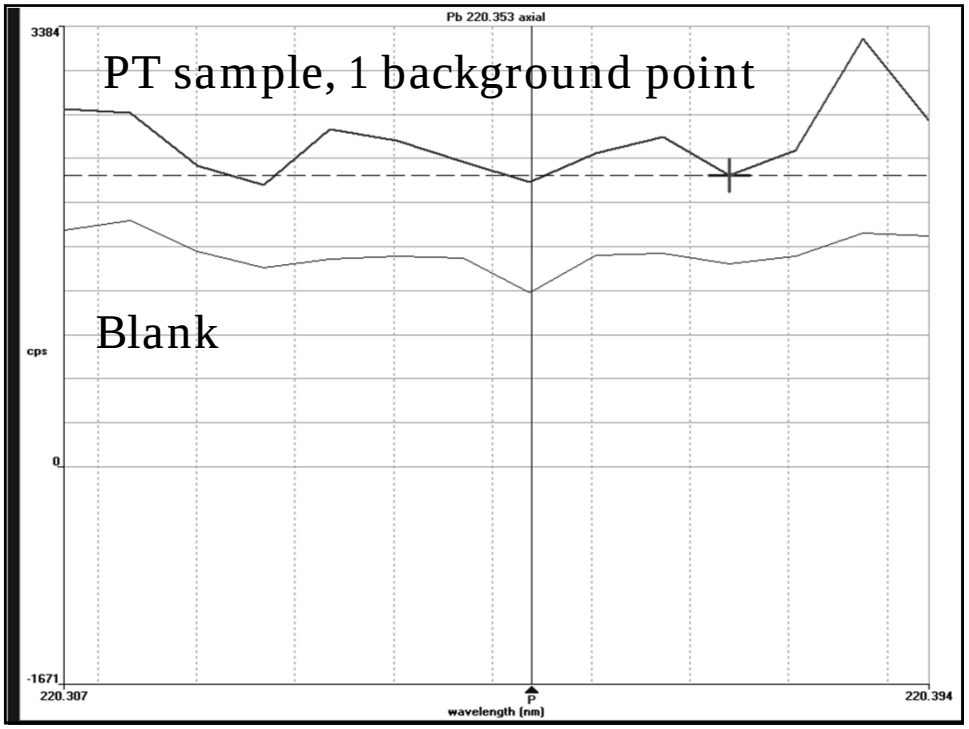
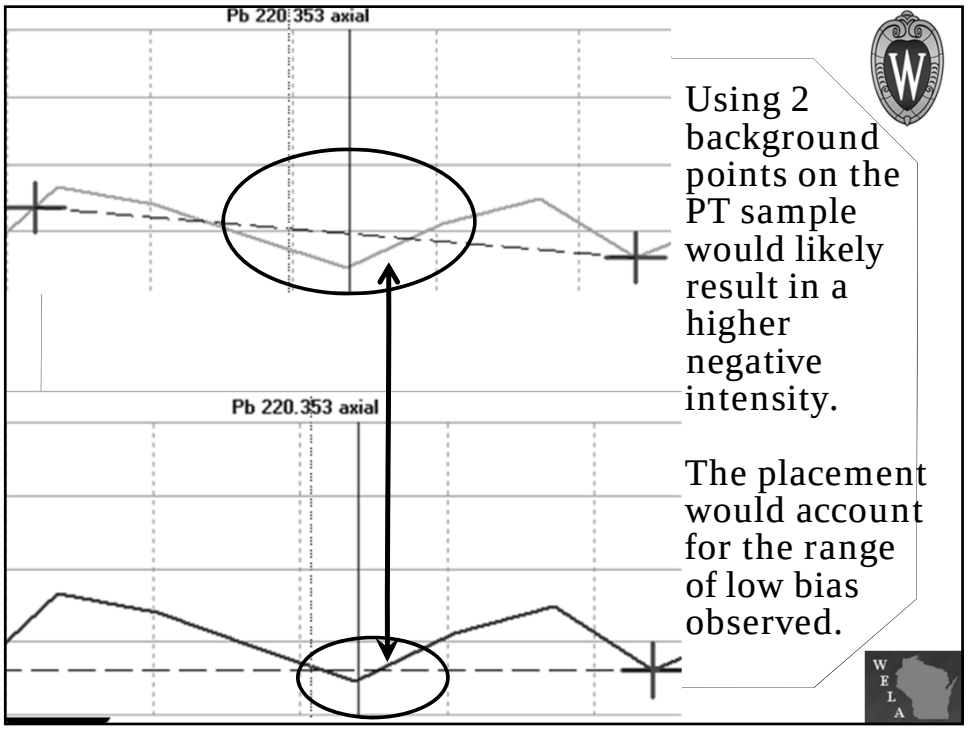
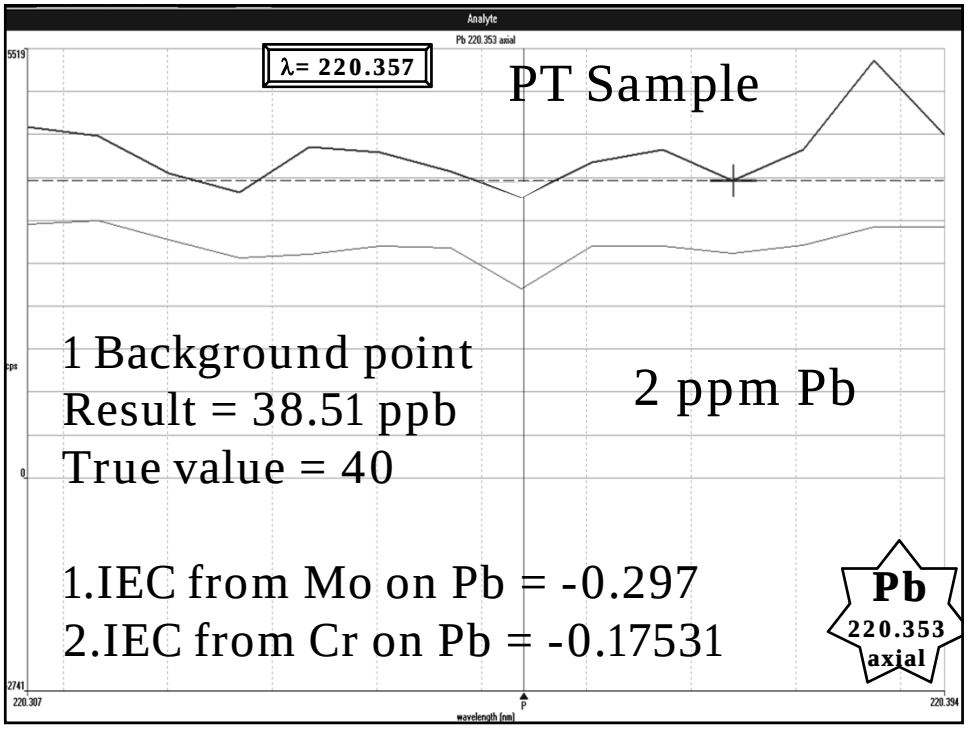
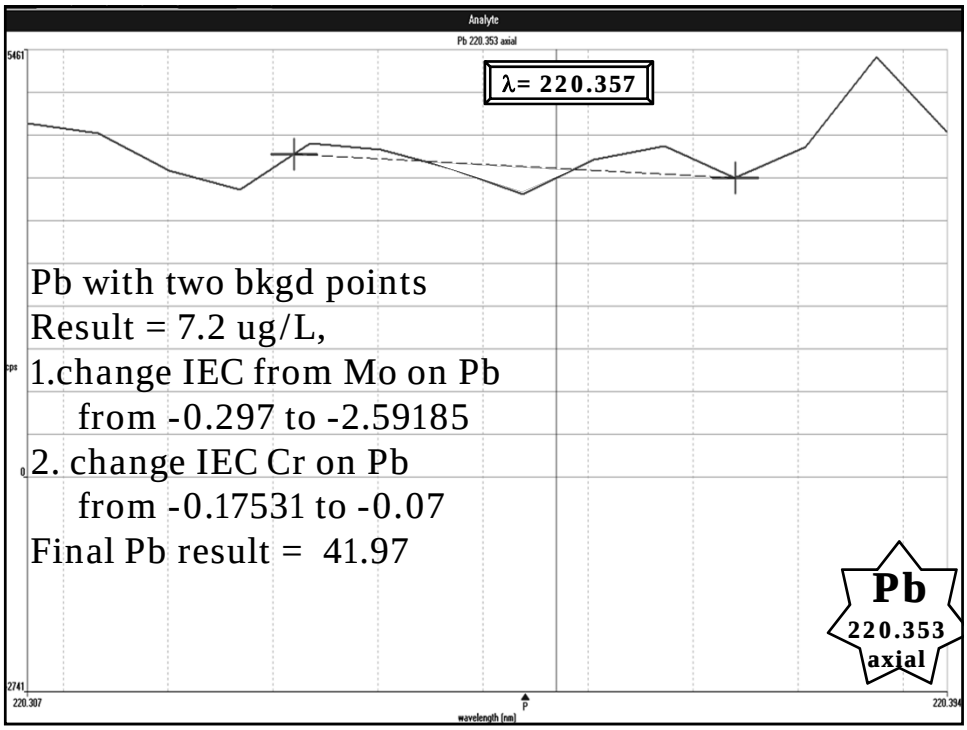



Pb 220.353 axial
3384
PT sample, 1 background point
Blank
cps
0
-1671
220.307
P
220.394
wavelength (nm)


Pb 220.353 axial
Pb 220.353 axial
Using 2 background points on the PT sample would likely result in a higher negative intensity.
The placement would account for the range of low bias observed.
W E L A


Analyte
Pb 220.353 axial
λ= 220.357
PT Sample
1 Background point
Result = 38.51 ppb
True value = 40
2 ppm Pb
1.IEC from Mo on Pb = -0.297
2.IEC from Cr on Pb = -0.17531
Pb
220.353
axial
220.307
220.394
wavelength (nm)

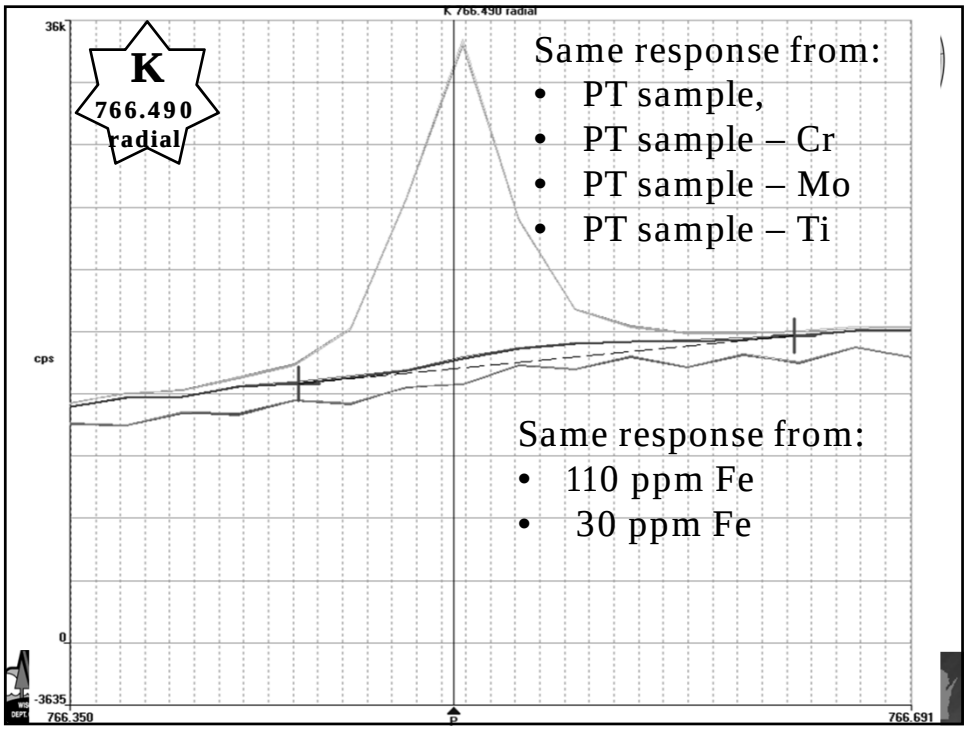

Analyte
Pb 220.353 axial
λ= 220.357
Pb with two bkgd points
Result = 7.2 ug/L,
1.change IEC from Mo on Pb
from -0.297 to -2.59185
2. change IEC Cr on Pb
from -0.17531 to -0.07
Final Pb result = 41.97
Pb
220.353
axial
220.307
220.394
wavelength (nm)

How many background correction points?

When is using 2 background correction points a requirement?

Whenever the background is sloping, you MUST use two background correction points (at least on a P-E system).

Potassium, at the upper end of the spectrum is a perfect example



PT Sample: Ag

Several labs expressed concern about the "trick" regarding analysis of silver.

Only two labs had trouble with the silver (3 ppm). Both reported results around 400-450 ppb.

One of the two reported consecutive results of : 2171, 432, and 241 ppb. All were low, but clearly silver was dropping…why?

Silver and Chloride

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ (precipitate)

Many analysts experience low Ag recoveries when working in HNO_3 media. The problem is due to trace chloride contamination.

But….I don't see a precipitate!

Ag has already **photo-reduced** onto the container walls. Silver is very light sensitive. You won't see a precipitate, even though it has "fallen" out.

Handling Ag

If Ag is prepared in just a 0.5% HNO3 solution, it will not be stable for very long.

The SLH prepares Ag standard fresh daily.

Under about 2 ppm, the presence of a small amount of HCl will actually keep the silver in solution.

We chose the 3 ppm level for Ag because at that concentration, any HCL becomes a problem and the Ag falls out of solution.

Rinse solution should have ~5% HCL (even though standards and samples are HNO3 only) to keep Ag from plating onto walls of the spray chamber

High Bias/ False Positives

If you had high bias or false positives…

Did you neglect to correct for a bias?

Ex. Mo on Al

Did you neglect to correct for a synergistic bias?

- Y interferes with Z
- But X is also an interferent on Y

Interferent concentration greater than that tested to generate IECs

2 BGC pts vs. 1 (INT bleeds into BGC pt)

Generally Speaking, Low Bias

If you had low bias or "false negatives"…

False negative: Is your LOD too low?

- Ex.: Reporting < 0.34 ppb for V [15 ppb]

Did you overcorrect interference due to a 2nd interference? A background correction point?

Is a background correction point too close to an interferent? (integrated intensity gets reduced)

Using 2 BGC points when 1 would be better? (INT bleeds into BGC pt).

REAL WORLD SAMPLE

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Our "Real World" sample.

Real World Sample Scoring

	SLH	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
As	ND	FP	ND	ND	ND	ND	ND	ND	FP	FP	FP	ND	ND	FP	ND		FP
Ba	✓	✓	✓	✓	✓	NA	NA	✓	✓	OUT	✓	✓	✓	ok	OUT	✓	✓
Cd	ND	ND	ND	ND	FP	FP	ND	ND	FP	FP	FP	ND	ND	FP	ND	ND	FP
Cr	✓	✓	ND	✓	✓	✓	30%	✓	OUT	✓	✓	OUT	✓	✓	✓	30%	OUT
Cu	✓	✓	ND	OUT	✓	✓	ND	✓	✓	✓	✓	30%	✓	✓	✓	✓	✓
Fe	✓	✓	✓	✓	✓	✓	OUT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Mg	✓	✓	✓	OUT	✓	✓	NA	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Mn	✓	✓	✓	✓	✓	NA	OUT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ni	30%	✓	ND	30%	✓	✓	30%	✓	30%	✓	✓	✓	✓	✓	✓	✓	✓
Se	ND	ND	FP	ND	ND	ND	FP	ND	FP	FP	FP	ND	ND	ND	FP		ND
Ag	ND	ND	ND	FP	NA	NA	ND	ND	FP	ND	ND	ND	ND	FP	ND	ND	FP
Zn	✓	✓	OUT	✓	✓	✓	OUT	30%	✓	30%	✓	✓	✓	✓	✓	✓	✓

OUT Outlier result | FP False positive | 30% Result outside 30% of mean

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Real World: IEC and IS impact

	Acceptance Limits			IEC: ☒ IS: ☒	IEC: ☑ IS: ☒	IEC: ☒ IS: ☑	IEC: ☑ IS: ☑
	-30%	Mean	+30%				
As	Not Present			69.6	TOO NEGATIVE	111	< 5.0
Ba	222	318	413	240	237	323	319.2
Cd	Not Present			3.9	< 1.0	6.5	< 1.0
Cr	76	109	141	65	58.7	87	79.6
Cu	62.5	89.3	116	44.4	60.9	60.6	82.2
Fe	9450	12600	15750	10150	10150	11770	11770
Mg	7725	10300	12875	7642	7642	8863	8863
Mn	1550	2220	2880	1667	1365	2240	1890
Ni	187	267	347	159	112	218	164
Se	Not Present			TOO NEGATIVE	74.3	TOO NEGATIVE	< 10
Ag	Not Present			< 2	< 10	4.8	< 2
Zn	257	367	477	197	212	260	277.2

Real World Sample Concerns

1. **False positives.** We determined that As, Cd, Ag, and Se were not present in the sample.
2. **Outliers.** We tested the data set for each element for outliers and, after identifying them, we removed them from the data set.
3. Next we calculated the mean of the remaining data.
4. We set acceptance criteria at +/- 30% of the mean.
5. Any values the fell outside of 30% were marked.

Assessing Real World sample performance

	outliers	False +		> 30%
Alpha		As		
Bravo	Zn	Se		
Charlie	Cu,Mg	Ag		Ni
Delta		Cd		
Echo		Cd		
Foxtrot	Fe.Mn	Se		Cr, Ni
Golf			→ Pass...on to finals	Zn
Hotel	Cr	Ag,As,Cd,Se		Ni
India	Ba	As,Cd,Se		Zn
Juliet		As,Cd,Se		
Kilo	Cr			Cu
Lima			→ Pass...on to finals	winner →
Mike		Ag,As,Cd		
November	Ba	Se		
Oscar			→ Pass...on to finals	Cr
Papa	Cr	Ag,As,Cd		
SLH			→ Pass... on to finals	Ni

Lima

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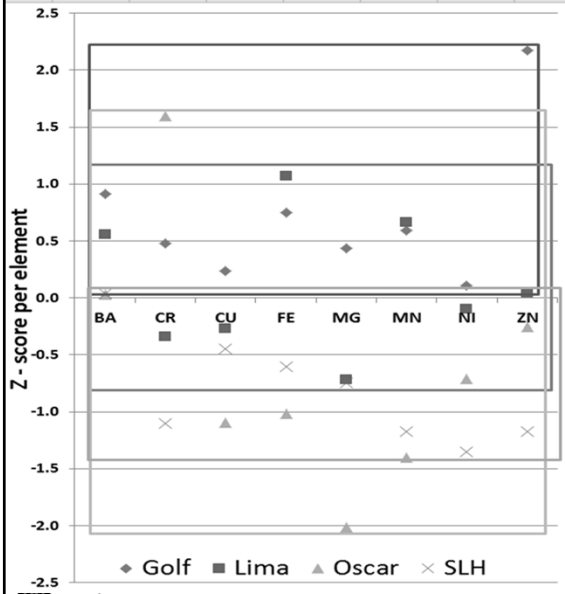
Real World Sample Finals



Lima wins:

Best data with no skewing. No values outside 30% of mean.

Oscar: broadest
Golf: fairly tight but skewed high
SLH: tight data but skewed slightly low

Golf, **Oscar** and **SLH** each had one result outside 30%; **Lima** had none.

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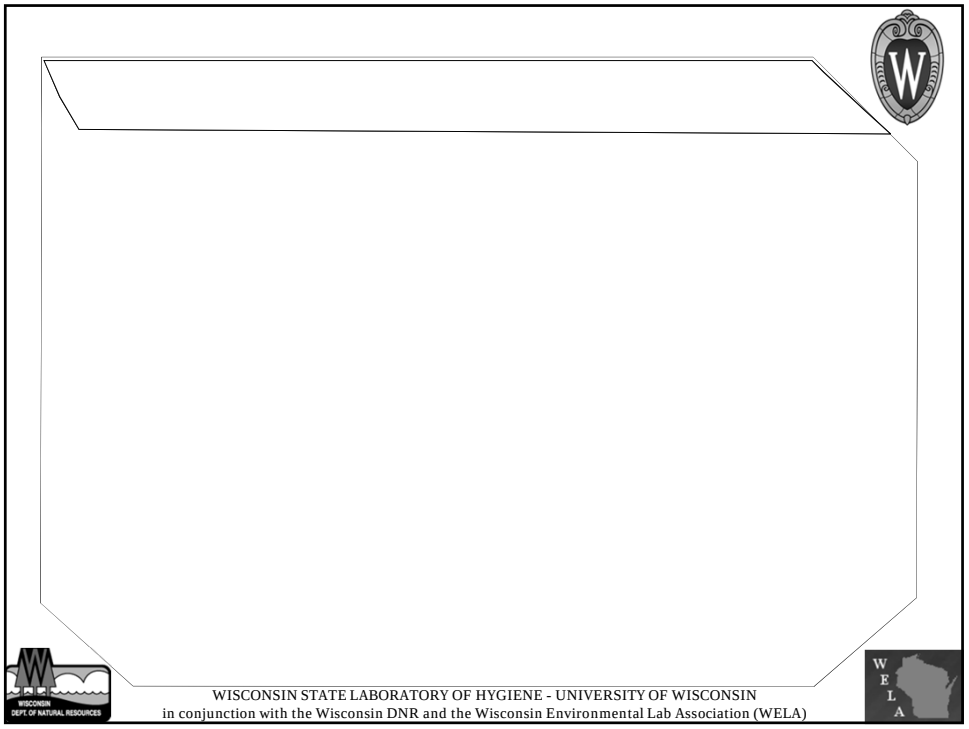
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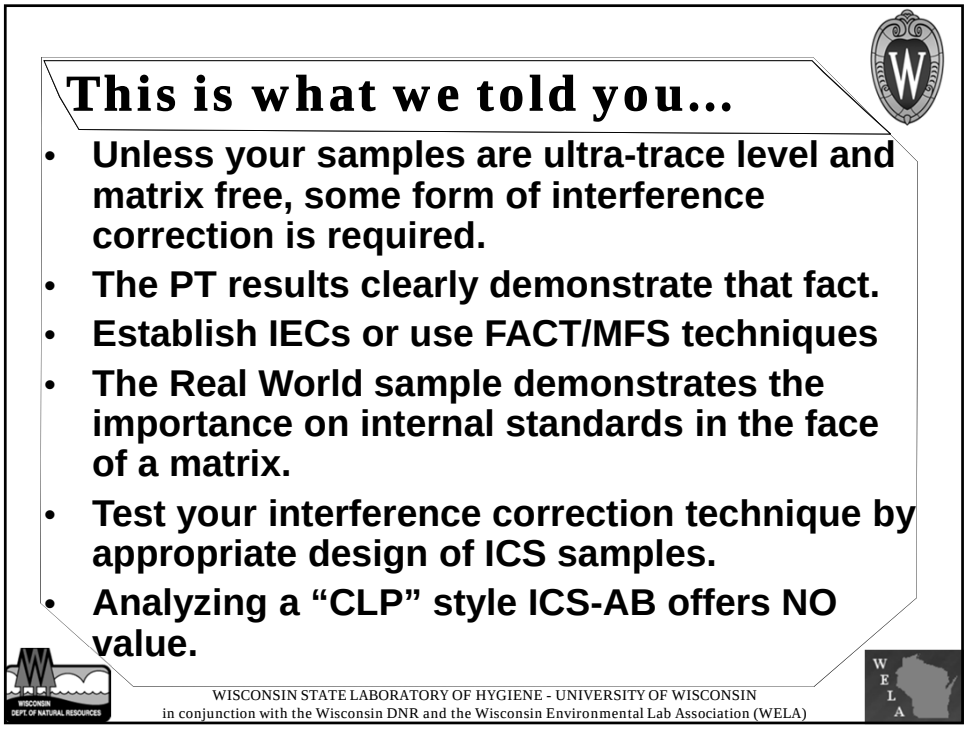
This is what we told you…
• Unless your samples are ultra-trace level and matrix free, some form of interference correction is required.
• The PT results clearly demonstrate that fact.
• Establish IECs or use FACT/MFS techniques
• The Real World sample demonstrates the importance on internal standards in the face of a matrix.
• Test your interference correction technique by appropriate design of ICS samples.
• Analyzing a "CLP" style ICS-AB offers NO value.
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Questions?

Thanks for coming!

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