




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



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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***



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Cast of Characters



State Lab of Hygiene

DeWayne Kennedy-Parker
Kevin Kaufman
Roger Schultz
Brian Clary
RJ Messling

Wisconsin DNR

Rick Mealy


Special thanks to

Paul Harris and **WELA** for both championing and sponsoring this event as well as providing the room and refreshments.




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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




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

Tell the audience what you're going to say, say it; then tell them what you've said.




QuoteHD.com

Dale Carnegie
American Writer
(1888-1955)



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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.**



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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

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Nebulizers need cleaning too

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

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Spray chambers (survey)



Nearly all lab use a cyclonic type spray chamber.

Also indicated:

Cyclonic, single pass

(2)Cyclonic Double Pass

Double Pass

Scott-type

Twister cyclonic



Generic cyclonic



Twister double pass



Single Pass



Double Pass



Cyclonic

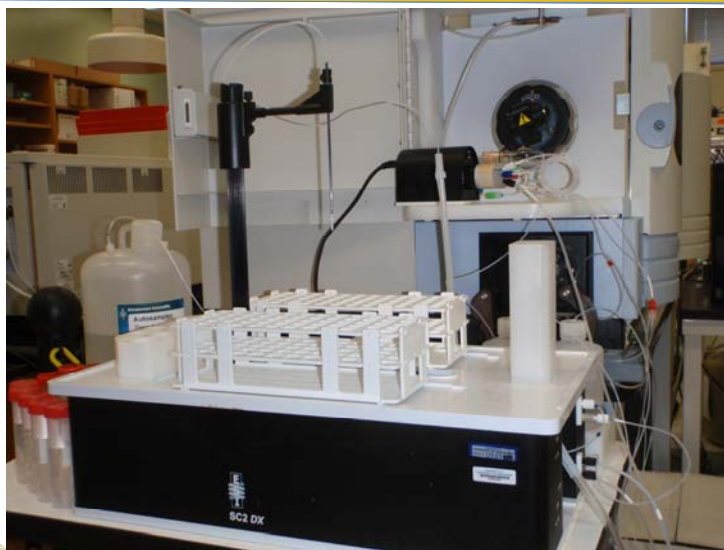
Scott type



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The FAST autosampler



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The FAST autosampler



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Instrument Set-up:

- Sample (and internal standard) flow check
- Spectral alignment using a single element (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
- conc. levels (MDLs and linear dynamic range),
- wavelengths

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Tell 'em


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A few words on... background correction



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Which comes first...



... IECs?
or background correction points?

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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



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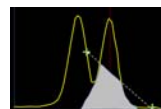
It's a trick question...

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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Conclusion:


You can achieve accuracy either way.

You just have to remember that IECs are inherently linked to the background correction points designated when the 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.




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INTERFERENCE CORRECTION




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Interference Correction Rules

1. **Not mandatory**
2. **No correction is a special case**
3. **Correction specific to configuration**
4. **Correction is subject to change**
5. **ICS= security. But it's not perfect**




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Interference Correction Rules

6. **Please...no more ICS-AB**
7. **Protection is only as good as ICS**
8. **INT > ICS requires dilution or re-do IECs**
9. **Size & resolution do not matter**
10. **Evaluate ICS samples properly**



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Which single elements? Level?


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

6010C, Table 2: 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?**




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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 interferences.
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).



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IEC Alternatives: FACT & MSF







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Fast Automated Curve-fitting Technique

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

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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

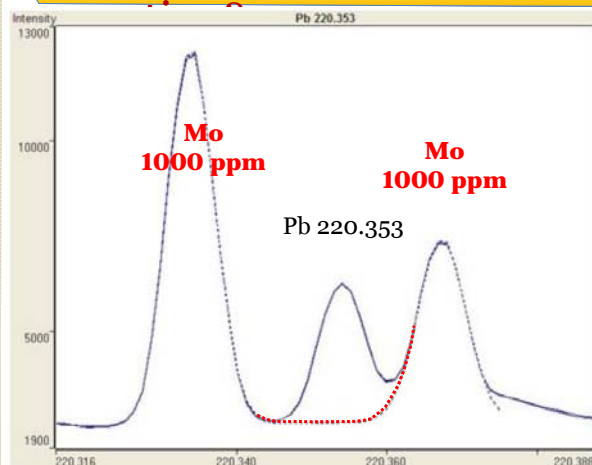
Publication number: 5991-0846EN

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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

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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 left of the analyte peak.**
 - c. **Any potential interference peak 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.
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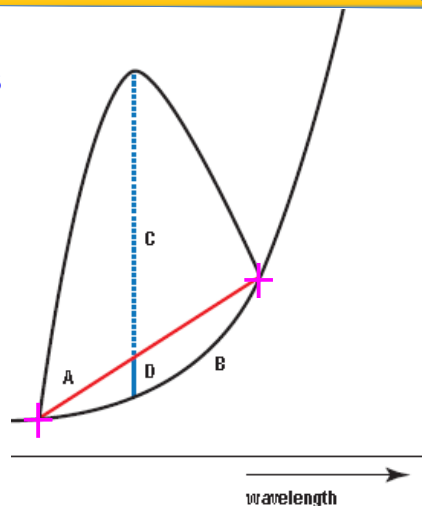


Fitted background correction



No off-peak background correction peak searches required.

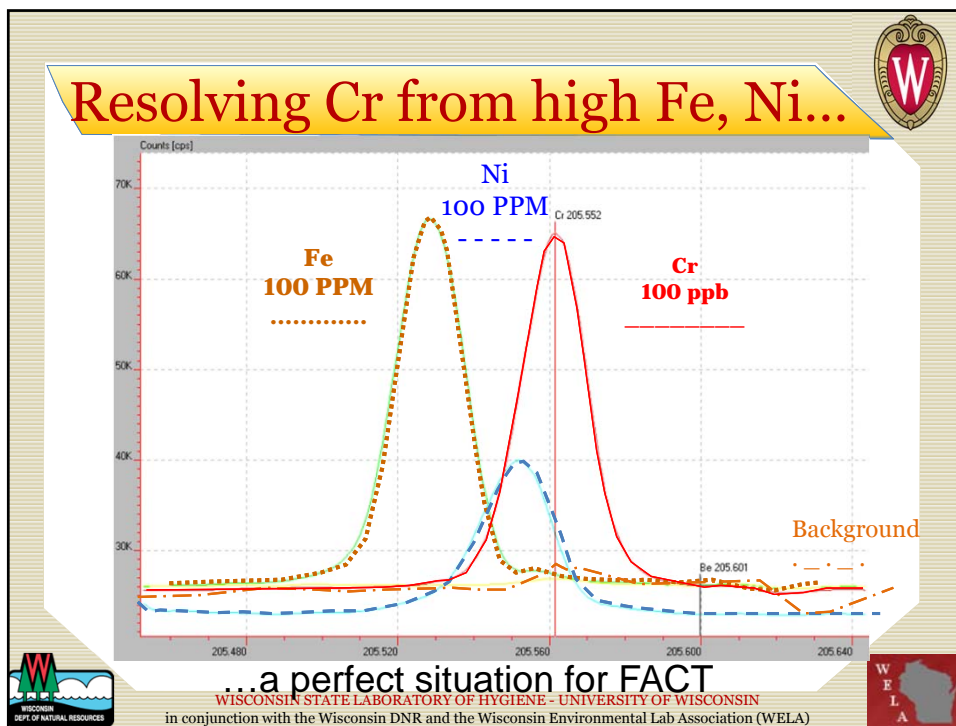
- A Off peak background correction
- B Fitted background correction (FBC)
- C Analytical wavelength
- D Error without using FBC



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

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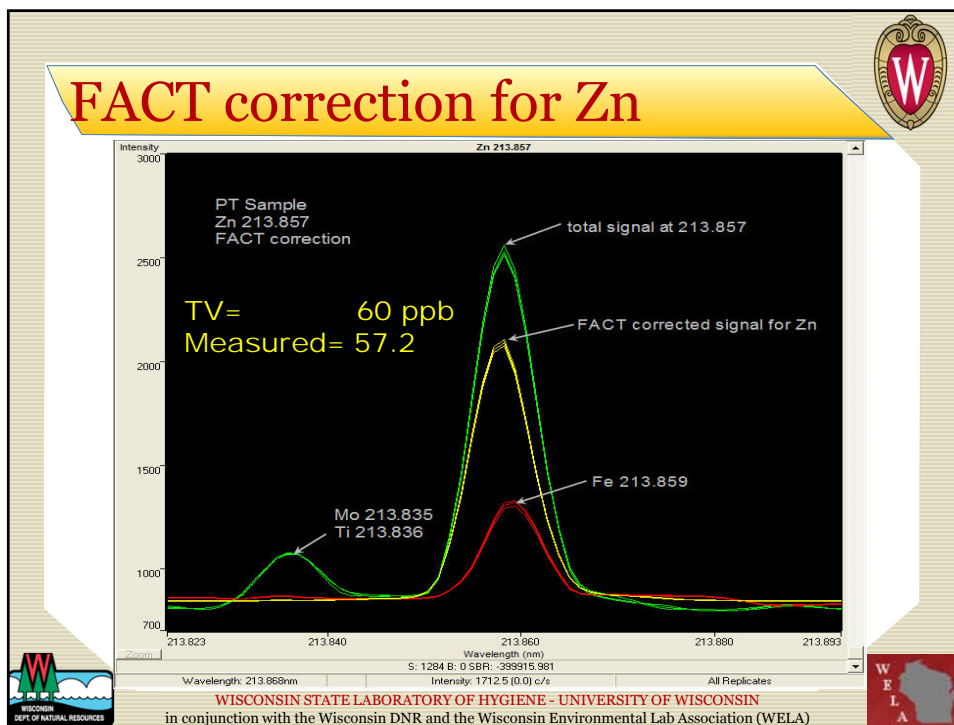
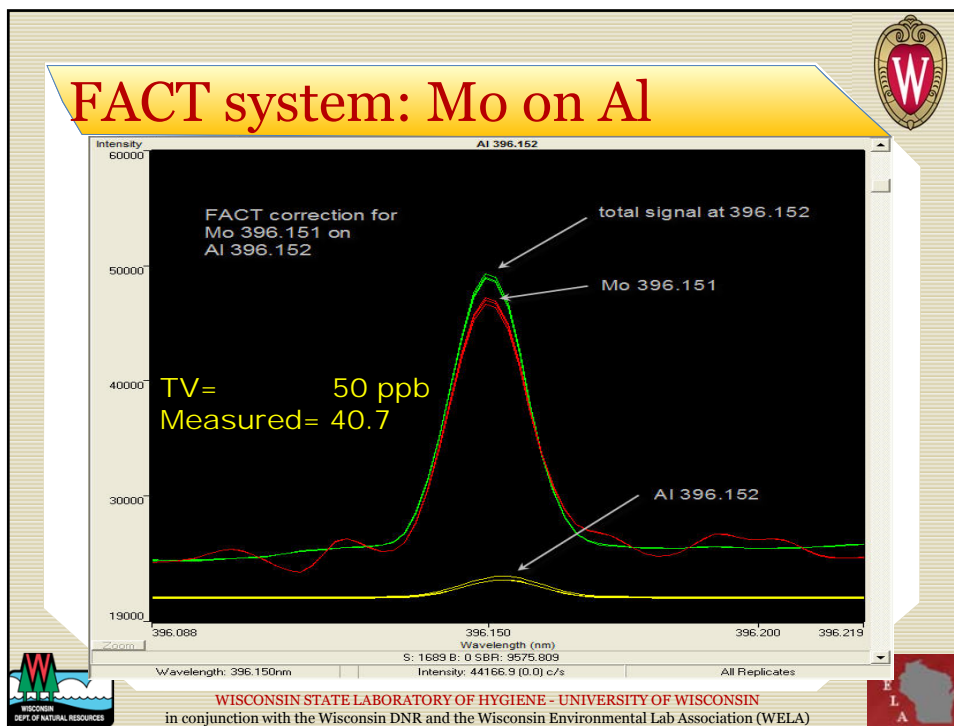
FACT in practice for the PT sample

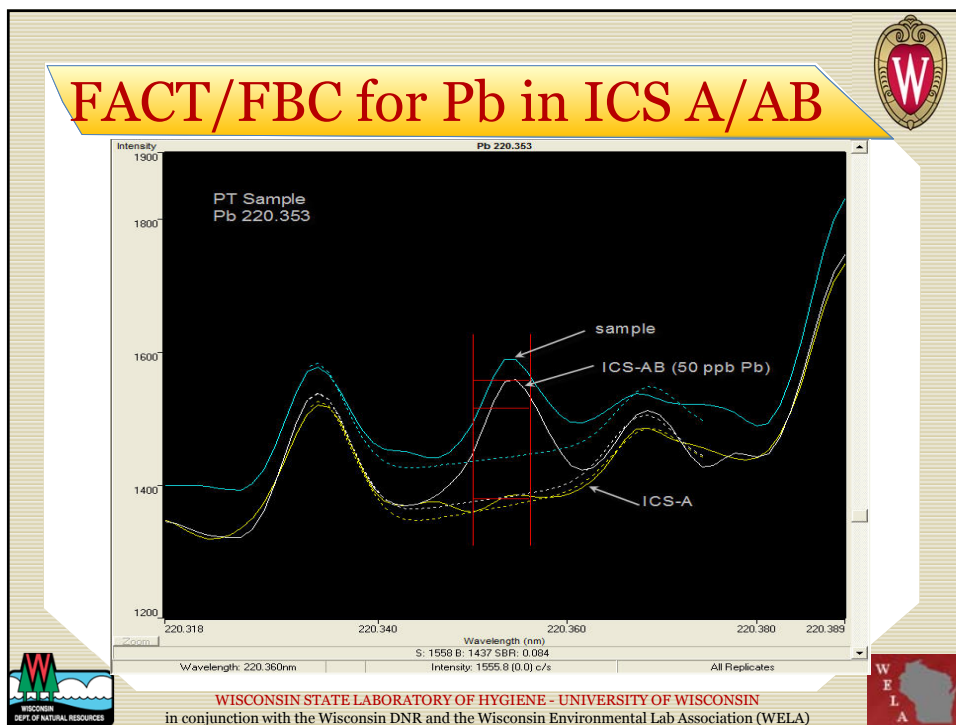
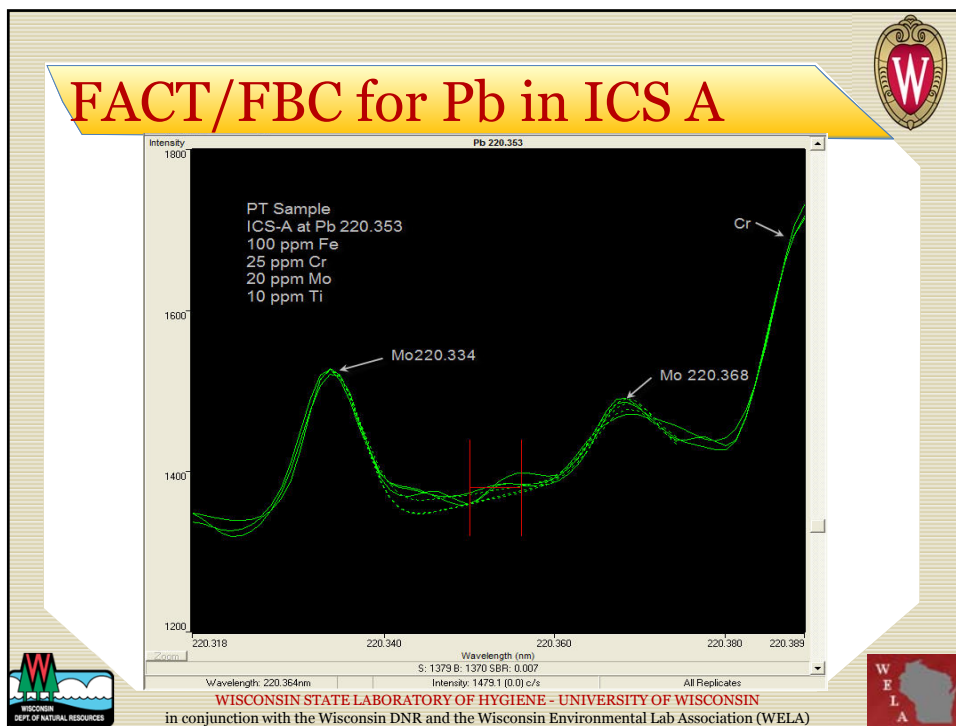
PRACTICE

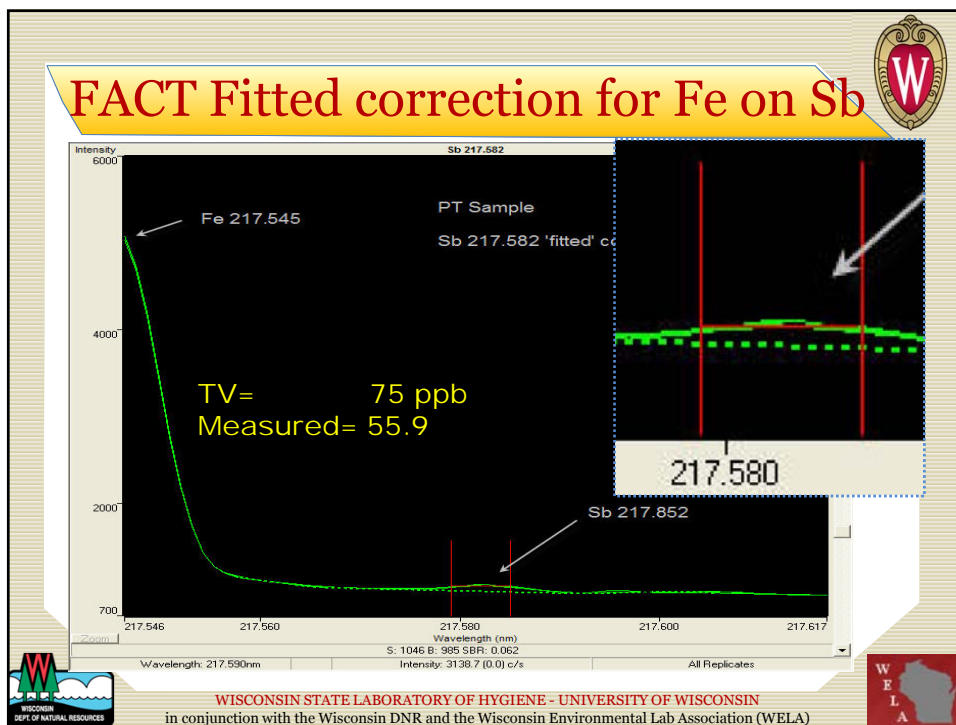
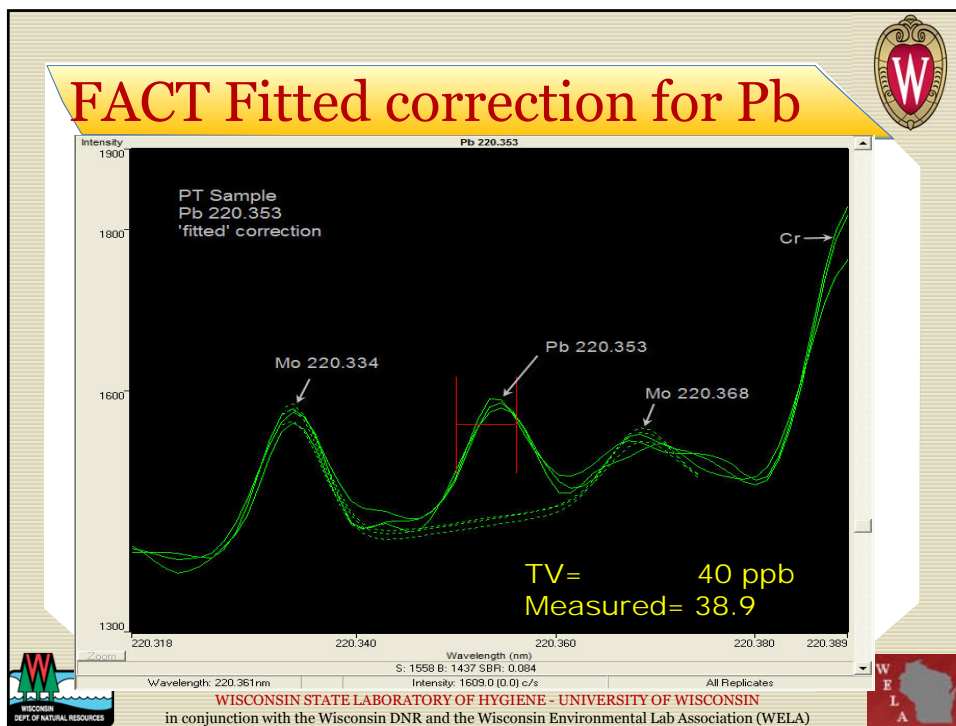
THEORY

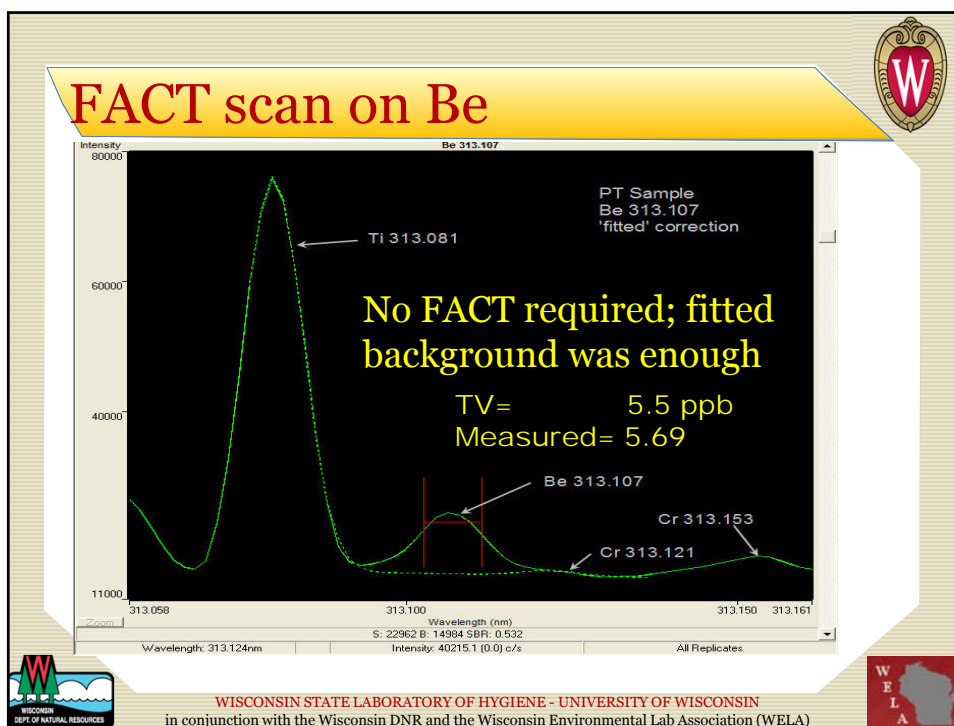
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LIMA on using FACT

- (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)

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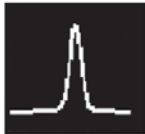

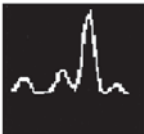
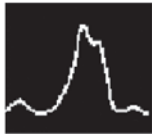


MSF

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MSF is...

Emission spectrum = sum of n contributions

	+		+	
Analyte		Blank		Matrix
=				
				
Measured Spectrum				

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

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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

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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

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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.



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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%



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ICS

COMPOSITION

ICS = Interference Check Standard


200.7 refers to these as “SIC”, or
spectral interference checks


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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.

STOP RIGHT THERE!



6010 C 7.8

If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

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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 interferences on target analytes not present!
- **Logic would dictate:** spiking everything defeats that purpose.
- And applying 20% as criteria at 1 ppm means that samples can be ± 200 ppb, which is 20-100X 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 \pm
200
ppb?



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ICS Evaluation Criteria

- Can we all agree that using \pm 20% as acceptance criteria for ICS samples is just plain silly?
- Yes, that's what the methods suggest, **but...**
- ICV criteria are \pm 5% (200,7) or \pm 10% (6010)
- CCV criteria are \pm 10% (200.7,6010)
- LCS criteria are \pm 15% (200.7)
- At the ICS levels, shouldn't \pm 5% be achievable?
- And for unspiked analytes, shouldn't they be the same as in a blank?
- **Using \pm 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** $\pm 5\%$

Add a simple, but overlooked evaluation step

ICS-B Secondary interferents only **Cr, Mo, V, Sn, Ti** $\pm 10\%$

ICS-C? **Be, Ba, Cd, Co, Cu, Mn, Ni**

Evaluate BOTH against **ICB** $\pm 2xLOD$ **Compare to blank for trends. Absolute $\pm 2xLOD$**

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For “unspiked” analytes... Compare the ICB to the ICS-A

	<u>LOD</u>	<u>Blank Avg</u>	<u>Al 50 + Fe 20 ppm</u>	
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

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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**

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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 interferences and actual levels of interferences.

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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If a window of
opportunity
appears, don't pull
down the shade.

~Tom Peters



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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 analyzing
 them did fine on the
 following elements:
 Ba, Ca, Cr, Cu, Fe, Mg,
 Mo, Na, Sr, Ti**

10 out of 27 elements passed by all

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...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?

	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	

Internal standards not as critical because there is no matrix!

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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	8279	8056	8276	8053	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
Ti 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

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Changes in IECs from 2 ppm to 17 ppm Mo, 8 ppm Ti

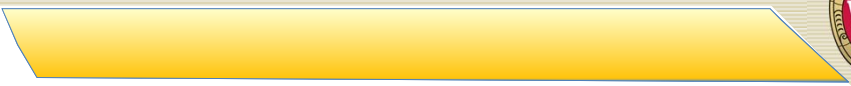
			Mo 202.031		% change	Ti 336.121		% change
			Before	After		Before	After	
			2 ppm	17 ppm		2 ppm	8 ppm	
Al	396.153	axial	24.7235	<u>26.9535</u>	109%			
Sb	206.836	axial	-14.0392	<u>-12.935</u>	92%		2.755	
As	188.979	axial	5.789	<u>7.2234</u>	125%	-1.97	<u>-3.7829</u>	192%
Ba	233.527	axial	-0.726	-0.726	no change			
Be	313.107	axial		<u>-0.00583</u>	new	0.85583	<u>1.06093</u>	124%
B	249.677	axial	-1.9665	<u>-4.79047</u>	244%			
Cd	214.440	axial						
Ca	317.933	radial						
Cr	205.560	axial	0.863444	<u>0.51334</u>	59%			
Co	228.616	axial	-1.62173	-1.62173	no change	2.34087	2.34087	no change
Cu	327.393	axial				-6	<u>-6.0604</u>	101%
Fe	238.204	radial						
Pb	220.353	axial	-2.22817	<u>-3.22628</u>	145%		<u>-0.3156</u>	new

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Changes in IECs from 2 ppm to 17 ppm Mo, 8 ppm Ti

			Mo 202.031		% change	Ti 336.121		% change
			Before	After		Before	After	
			2 ppm	17 ppm		2 ppm	8 ppm	
Mg	279.077	radial						
Mn	257.610	axial						
Mo	202.031	axial				<u>0.63785</u>	new	
Ni	231.604	axial	-2.43243	<u>-2.19289</u>	90%			
P	178.221	axial		<u>-2.66056</u>	new		<u>-0.4928</u> new	
K	766.490	radial						
Se	196.026	axial						
Ag	338.289	axial				-6.045	<u>-5.8001</u> 96%	
Na	589.592	radial						
Sr	407.771	radial						
Tl	190.801	axial				-11.6478	<u>-9.5717</u> 82%	
Ti	336.121	axial		<u>0.16409</u>	new			
V	292.402	axial		-1.4245		0.91222	<u>0.77957</u> 85%	
Zn	206.200	axial		<u>-0.43591</u>	new			
			9	14	# interferences	7	11	


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**Examples from
the (PT) sample**


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Interference of Mo on V

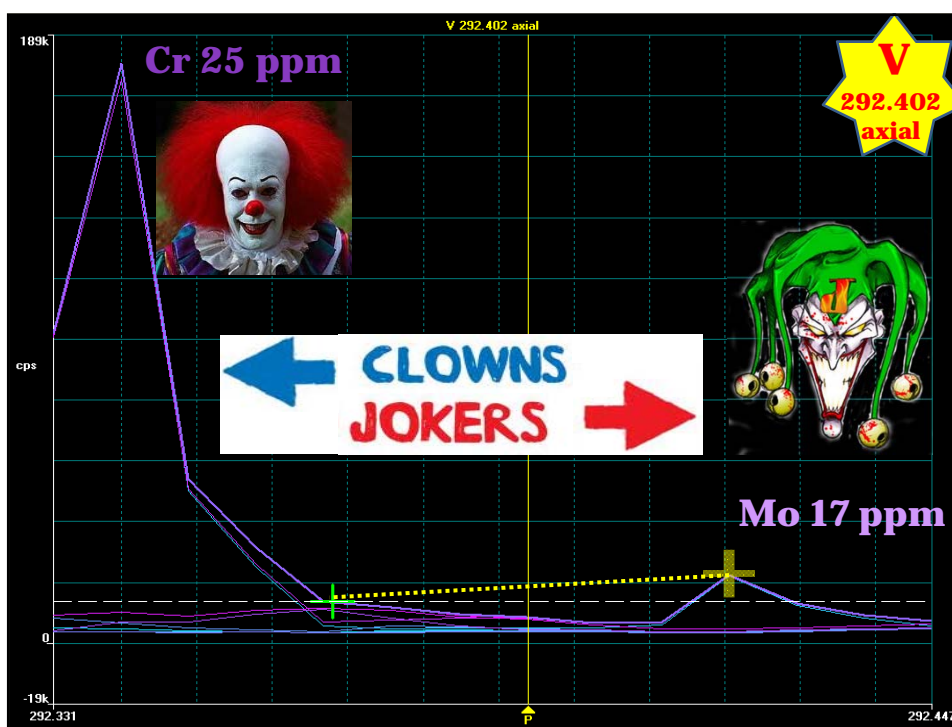
P-E default background correction points are at -27 and +27 μm off line from the peak maximum at 292.402 nm.

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.


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Interference of Cr on Sb

24
Cr
Chromium
51.9961



51
Sb
Antimony
121.760

Hotel	206.8
Mike	206.8

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

Lima	217.582
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Interference of Cr on Sb

TV= 75 Acceptance = 44 - 102

Lima	55.9	Mike	201
SLH	67.4	India	253
<u>Alpha</u>	74.5	Charlie	288
Delta	75.7	Hotel	320
November	78.9	Golf	367
Kilo	86.4	Bravo	< 32
Juliet	117	Echo	N/R
Quebec	129	Foxtrot	N/R

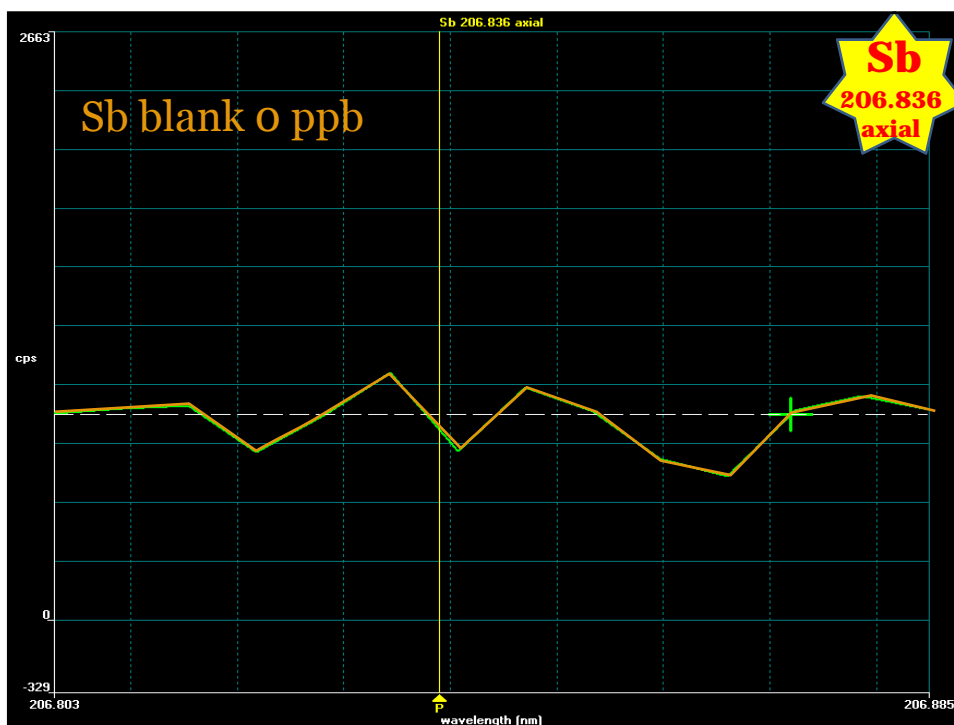
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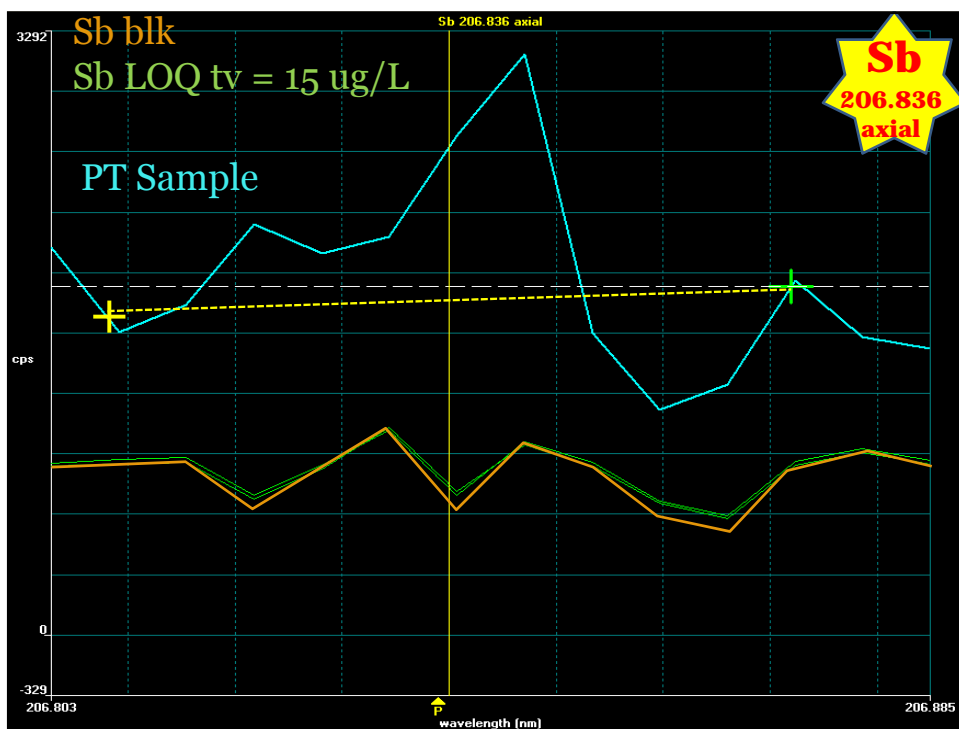
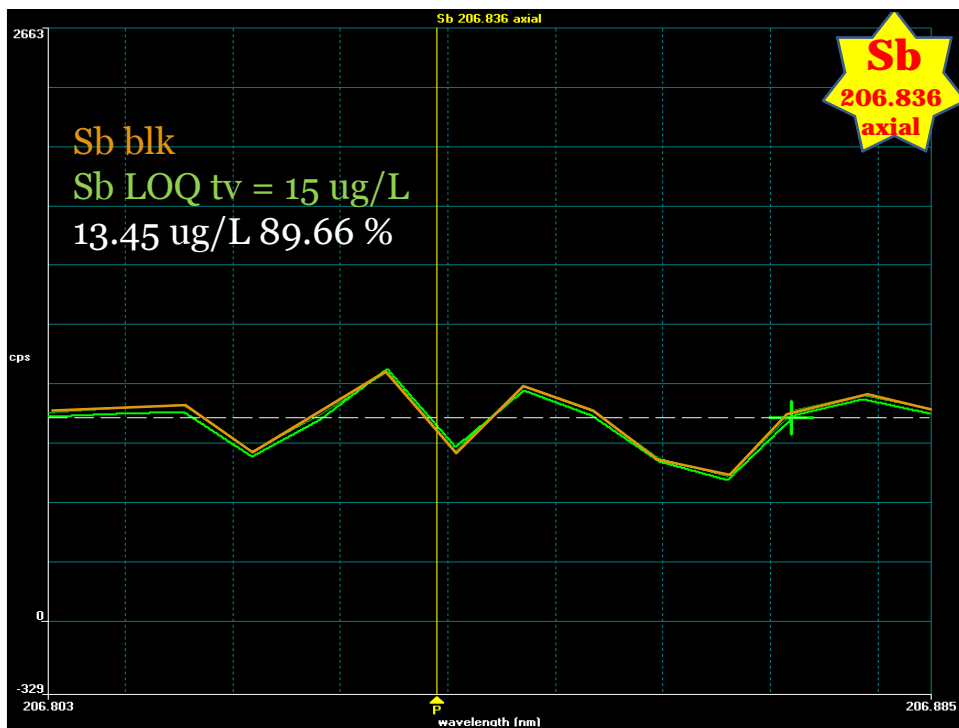
Interference of Cr on Sb

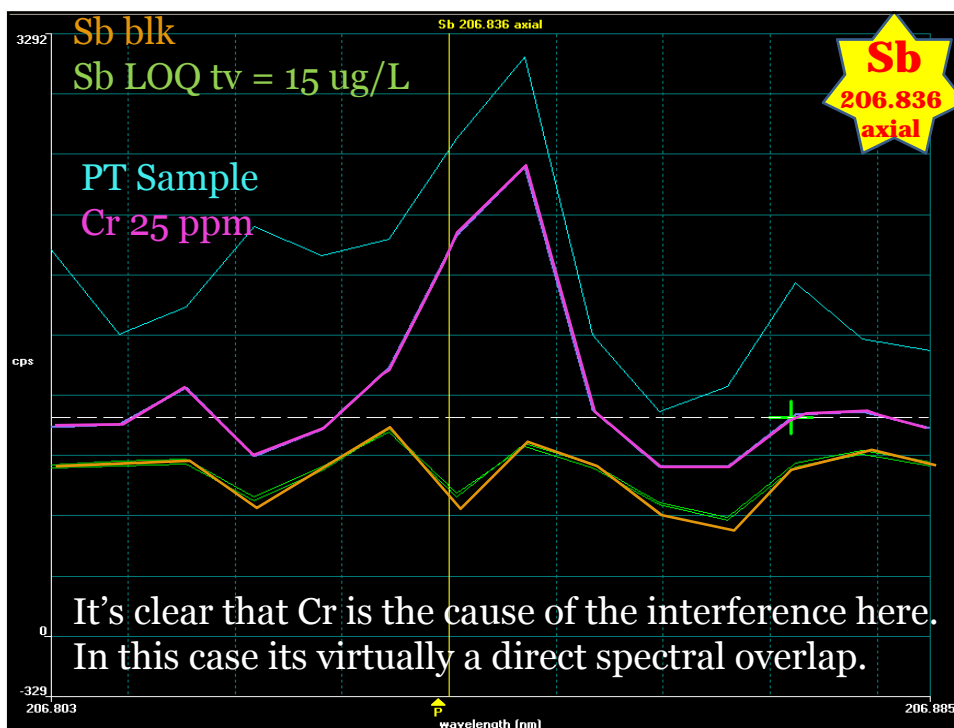
High bias will result (676% for SLH) if no correction was employed for interference due to Cr.

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

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Interference of Ti on Be

22
Ti
Titanium
47.867

4
Be
Beryllium
9.012182

Papa P-E	234.859	* SLH *	313.107
Alpha	234.861	Charlie	313.107
November	234.861	Golf	313.107
Hotel	313	Lima	313.107
Mike	313	Oscar	313.107
Bravo	313.042	Papa Thermo	313.107
Delta	313.042		
India	313.042		
Juliet	313.042		
Kilo	313.042		
Quebec	313.042		

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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

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Interference of Ti on Be

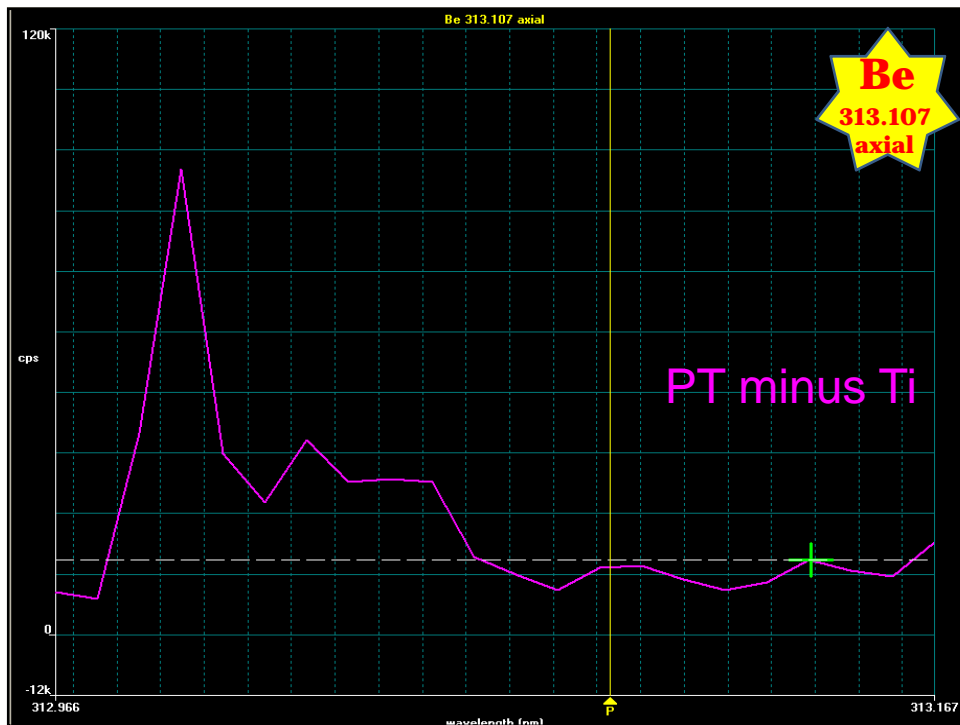
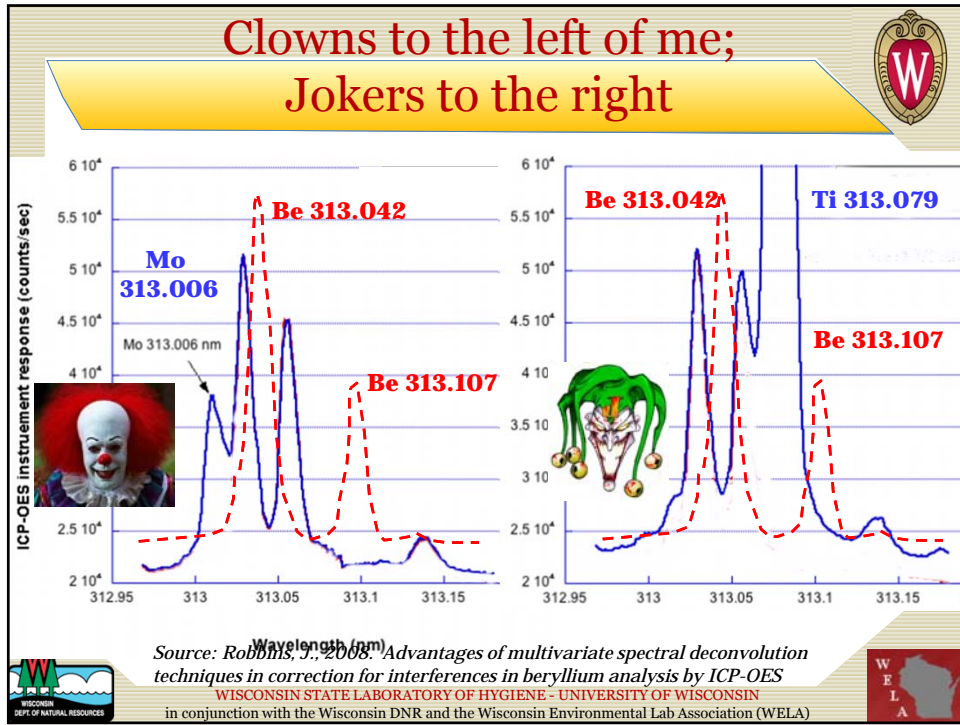
Beryllium is a doublet peak, with two very close lines.

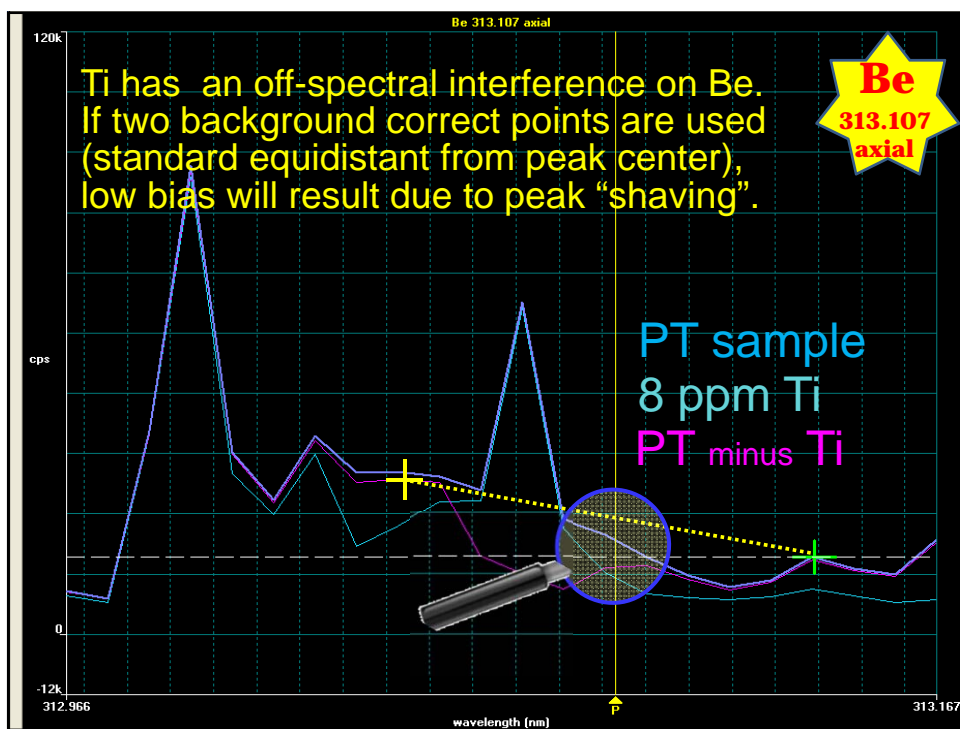
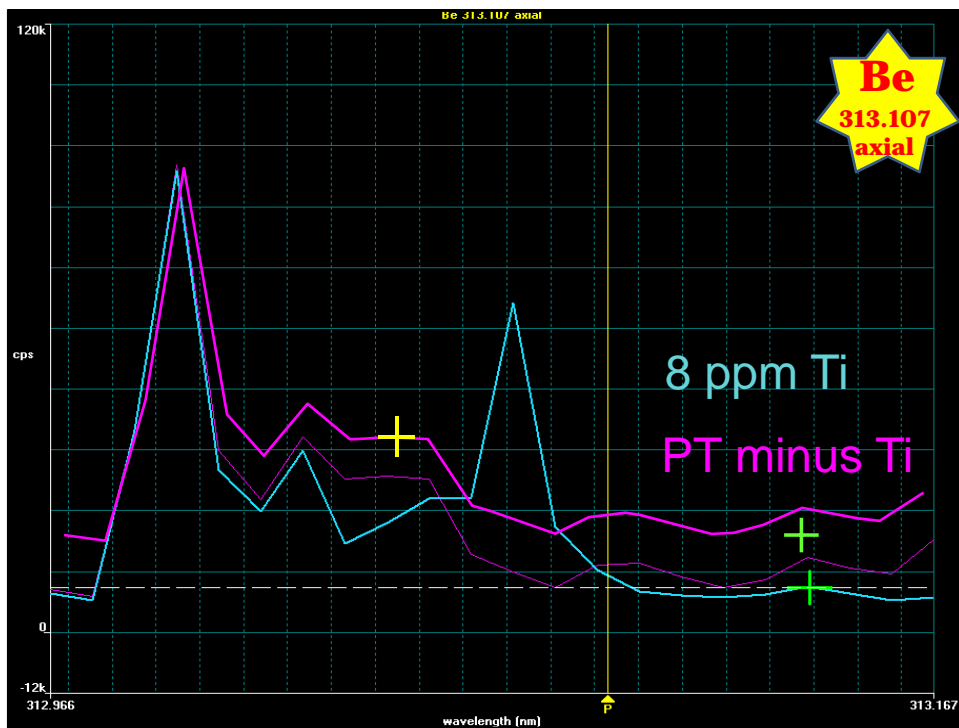
Due to Ti, even if using only 1 background correct point, low bias can result. Mo can also be an issue.

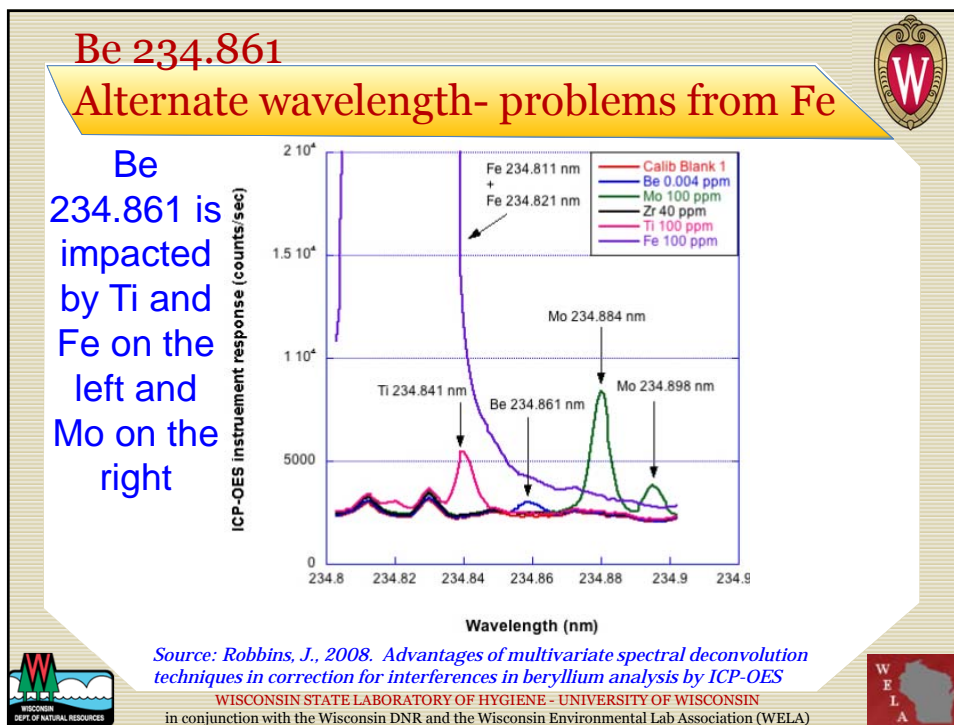
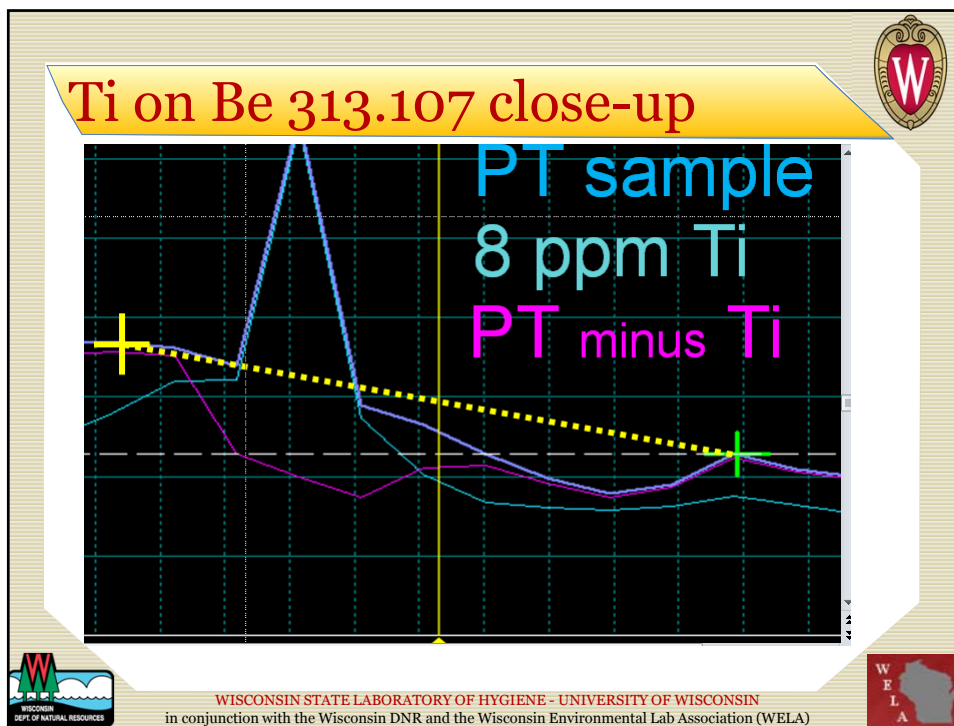
Will yield slight negative result if not using an IEC (or some other form of correction).

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

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Interference of Mo on Al


42
Mo
Molybdenum
95.96




13
Al
Aluminum
26.981538

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




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Interference of Mo on Al

TV= 50 ug/L Acceptance = 18 - 99

Lima	40.7	Charlie	350
Oscar	46.2	India	575
November	48.4	Golf	696
<u>SLH</u>	<u>49.6</u>	Hotel	710
Delta	58	Echo	< 120
Kilo	66.6	Quebec	< 65
Mike	82	Bravo	< 20
Juliet	120	Foxtrot	N/R
Alpha	231		



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Interference of Mo on Al

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

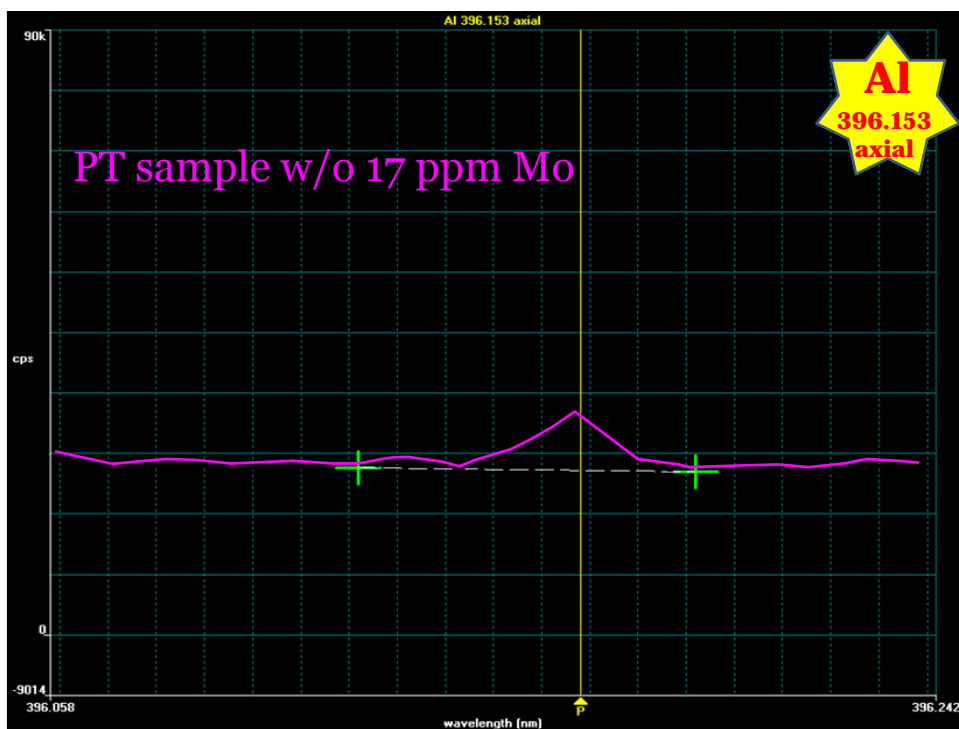
At 50 ppb, the level Al was somewhat of a challenge, but well above the mean/median LODs reported.

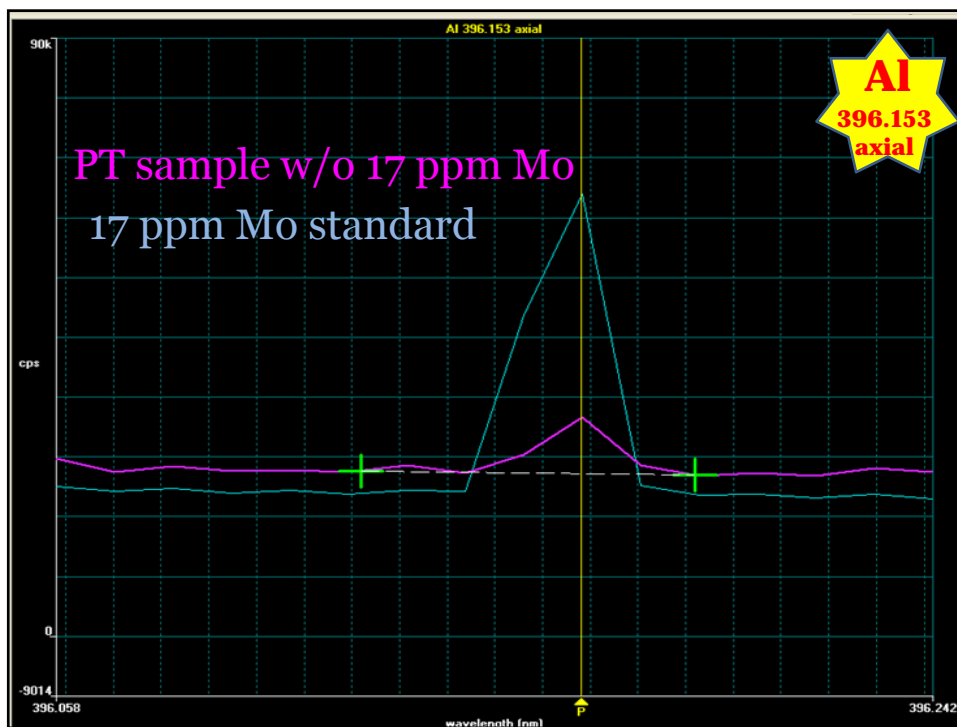
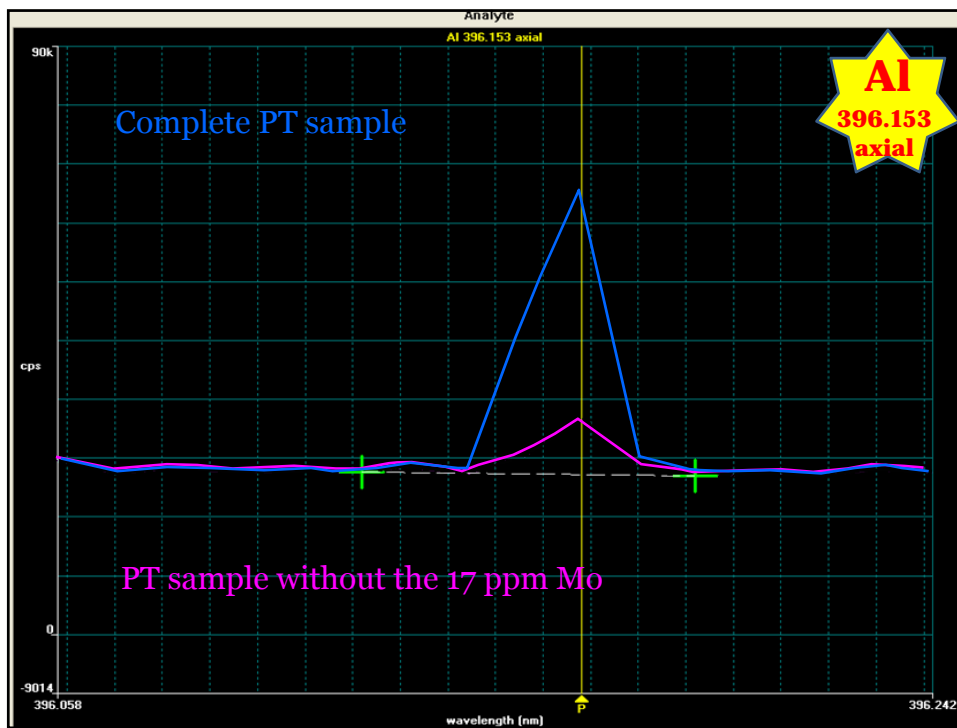
High bias observed is related to either not having interference correction for Mo, or having set the correction at a much lower level than that of Mo (17 ppm) in the PT sample.

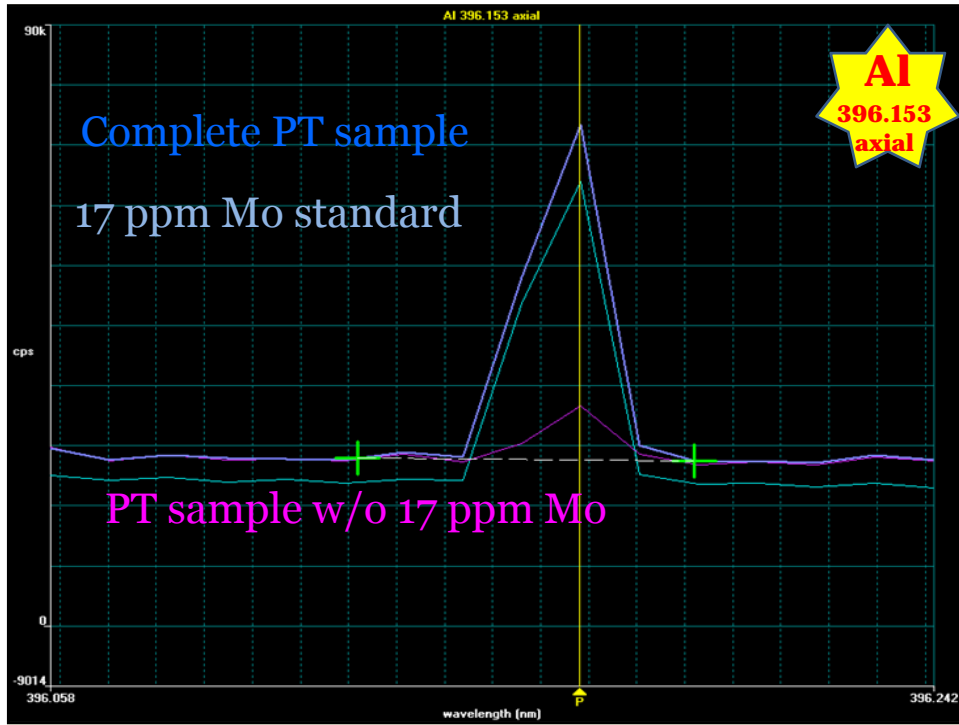
We suspect the false negative to be a result of either an unrealistic LOD or over-correction.



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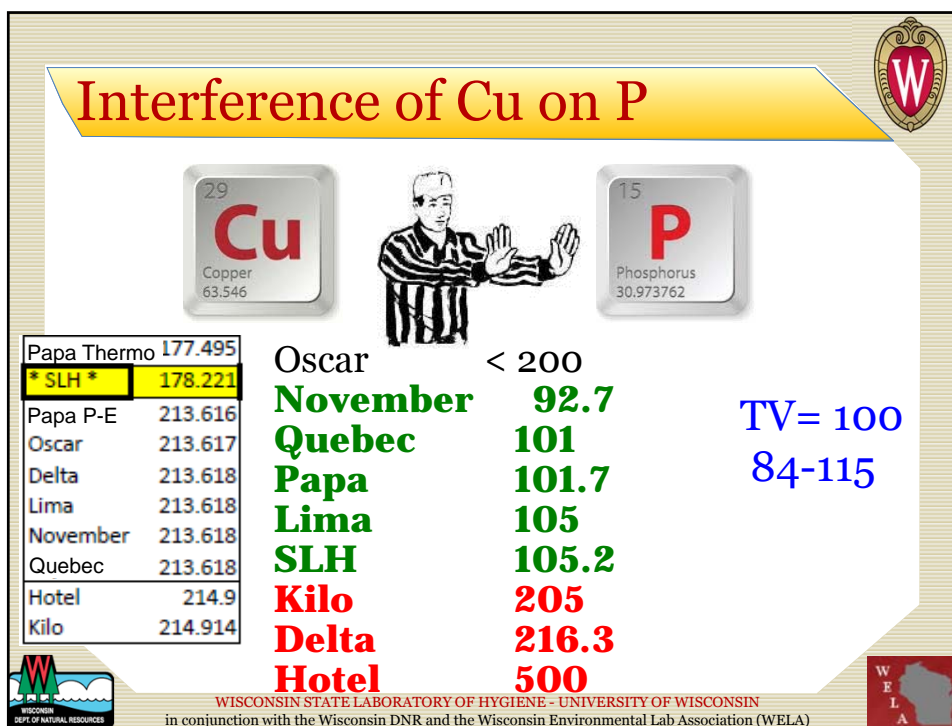


“THE TROUBLE WITH ~~TRIBBLES~~ Phosphorus”

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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.


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Copper lines interfering with P

178.221 **none**

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

214.914

Cu II	214.8984	400
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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.

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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	764 Quebec
718	Lima	790 Mike
729.4	Delta	842 SLH
737	Bravo	850 Hotel
738	November	1770 Kilo
743	Juliet	2574 Papa
749	India	




N/A: Alpha, Charlie, Echo, Foxtrot, Oscar
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Why Papa had high bias for B

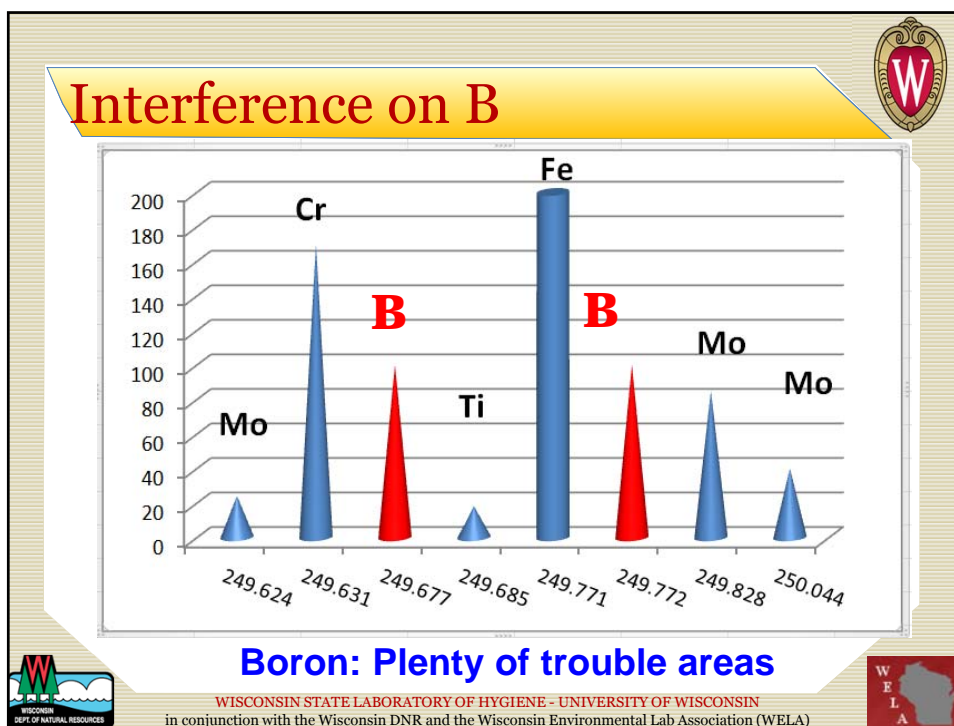
Element, Wavelength and Order	Use?	# IECs	IEC	k1	k2	Calc-in-fit?
As 189.042 (478)	<input checked="" type="checkbox"/>	1	Mo	0.001424	0.000000	No
B 208.959 (461)	<input type="checkbox"/>	11	Al	0.000779	0.000000	No
			Ca	0.000886	0.000000	No
			Cr	0.022993	0.000000	No
			Cu	0.022399	0.000000	No
			Fe	0.002208	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!



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Pb and background correction

82

Pb

Lead

207.2


Pb issues: intentional (back)gounding

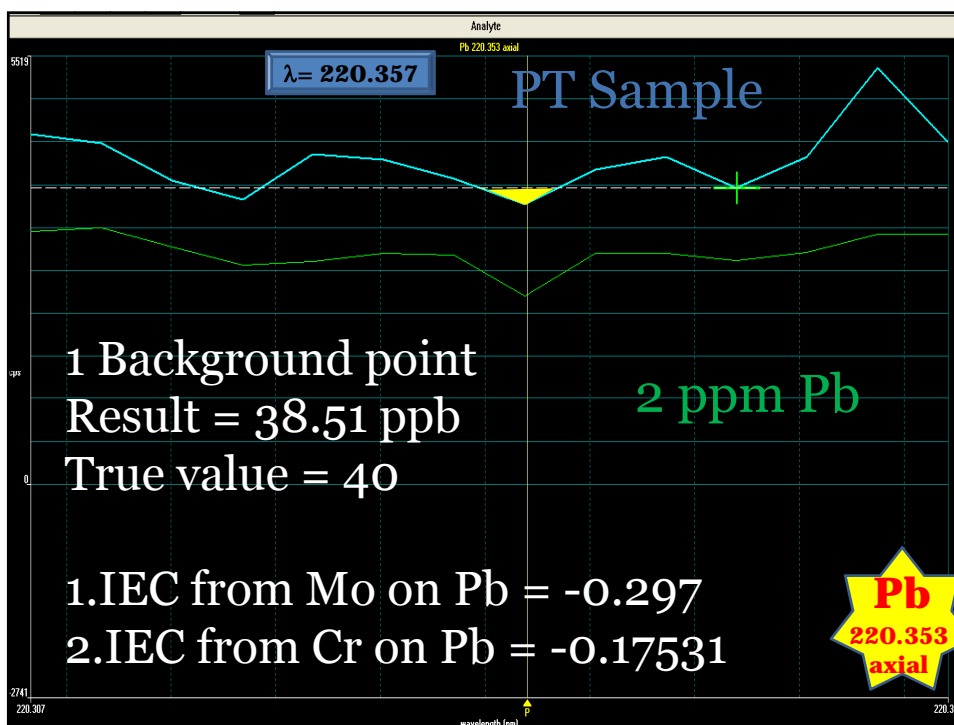
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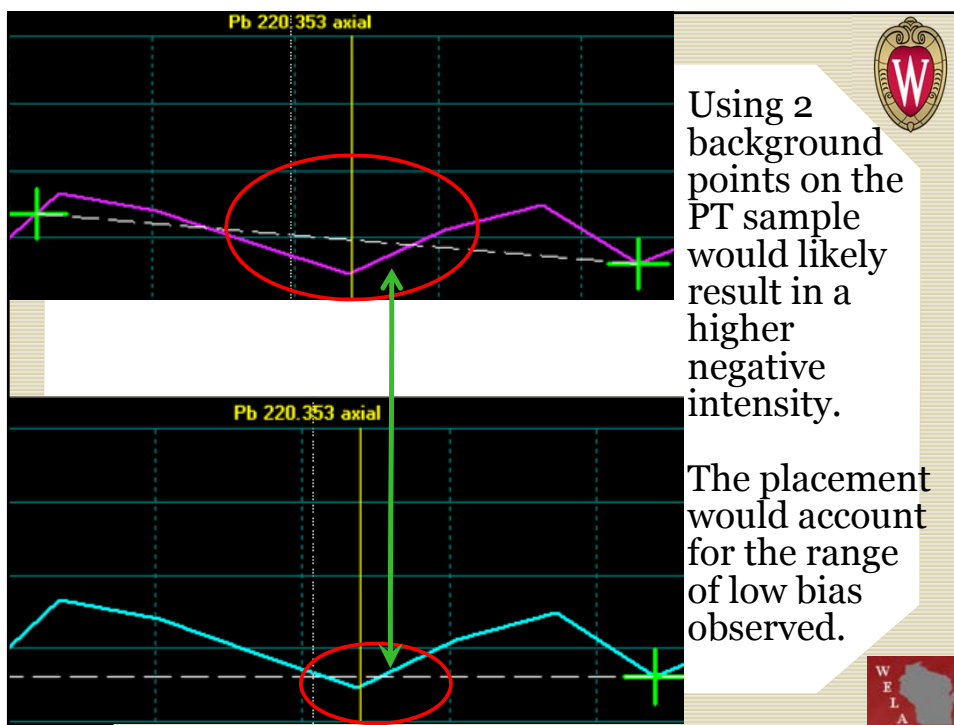
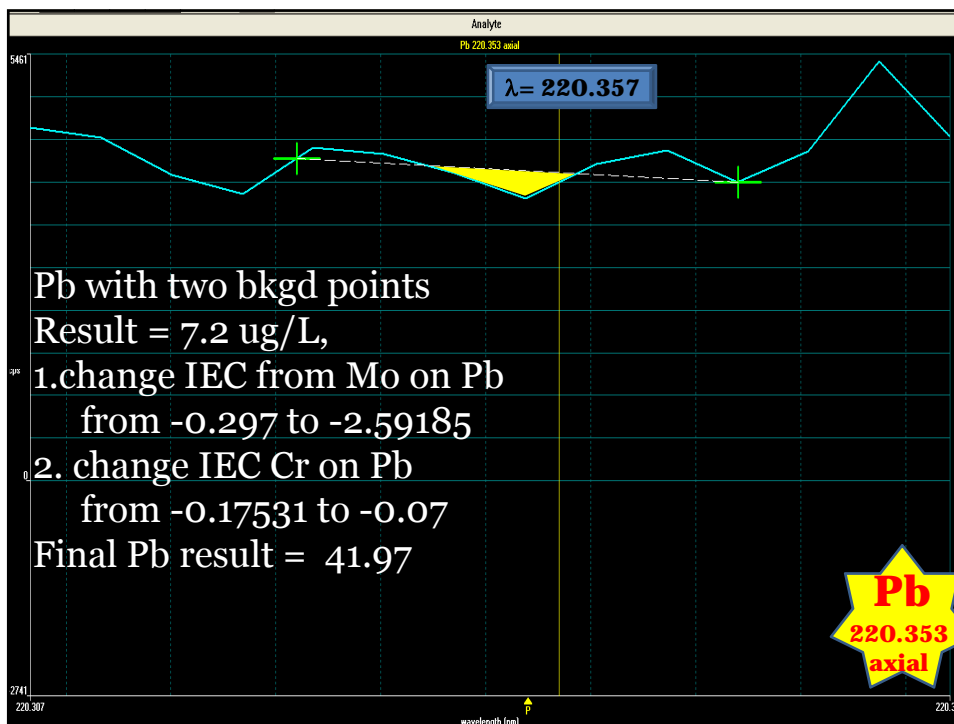
Pb and background correction


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	< 1.2	Charlie	37 Quebec
Mike	220.3			
Charlie	220.351	22	Oscar	37.7 India
Bravo	220.353			
* SLH *	220.353	26	Golf	38.9 Lima
Alpha	220.353	27.4	Papa	39 SLH
Delta	220.353			
Echo	220.353	30	Bravo	40.1 November
Foxtrot	220.353			
Golf	220.353	30	Hotel	40.4 Alpha
India	220.353			
Juliet	220.353	30.9	Kilo	40.4 Echo
Kilo	220.353			
Lima	220.353	31	Foxtrot	46 Mike
November	220.353			
Oscar	220.353	33.53	Delta	49 Juliet
Quebec	220.353			
Papa P-E	220.354			



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Special K



Perfect example of a background correction rule



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How many background correction points?


When is using 2 background correction points a requirement?

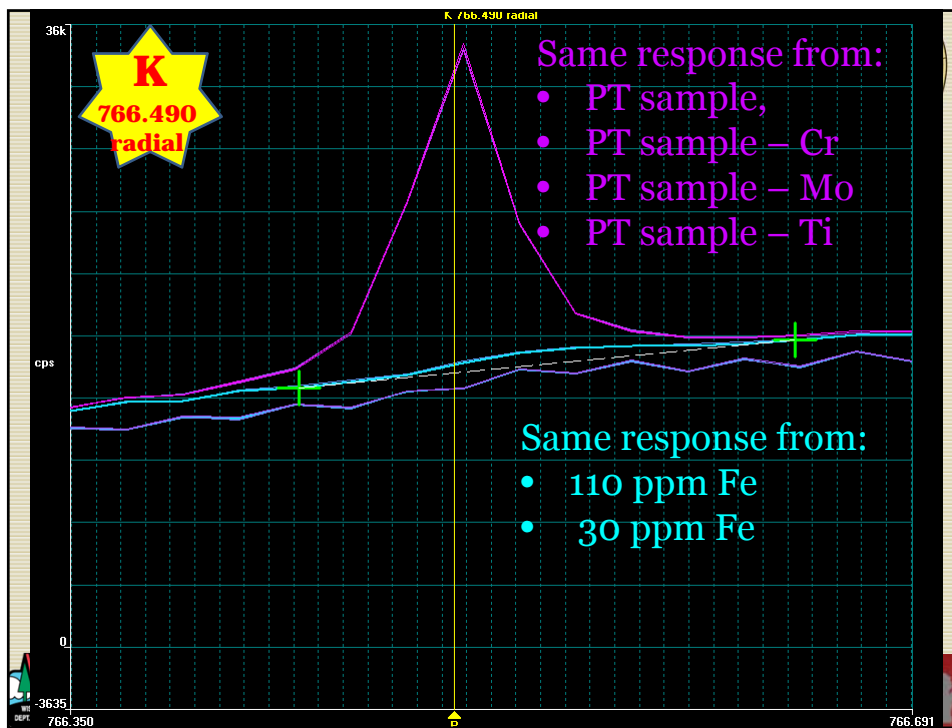
Whenever the background is sloping, you **MUST** use two background correction points (at least on a P-E system).

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



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PT Sample: Ag

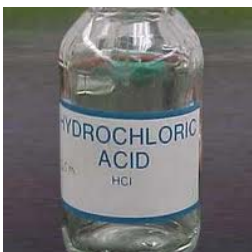
Several labs expressed concern about the “trick” regarding analysis of silver.

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?

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Silver and Chloride



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.



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Handling Ag

If Ag is prepared in just a 0.5% HNO_3 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 HNO_3 only) to keep Ag from plating onto walls of the spray chamber



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REAL WORLD SAMPLE




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Our “Real World” sample.



As one analyst put it,
“...a mix of milk of magnesia, Elmer’s glue, and ...something else”



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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	NA	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	NA	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: <input checked="" type="checkbox"/>	IEC: <input checked="" type="checkbox"/>	IEC: <input checked="" type="checkbox"/>	IEC: <input checked="" type="checkbox"/>
	-30%	Mean	+30%	IS: <input checked="" type="checkbox"/>	IS: <input checked="" type="checkbox"/>	IS: <input checked="" type="checkbox"/>	IS: <input checked="" type="checkbox"/>
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


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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.




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Assessing Real World sample performance

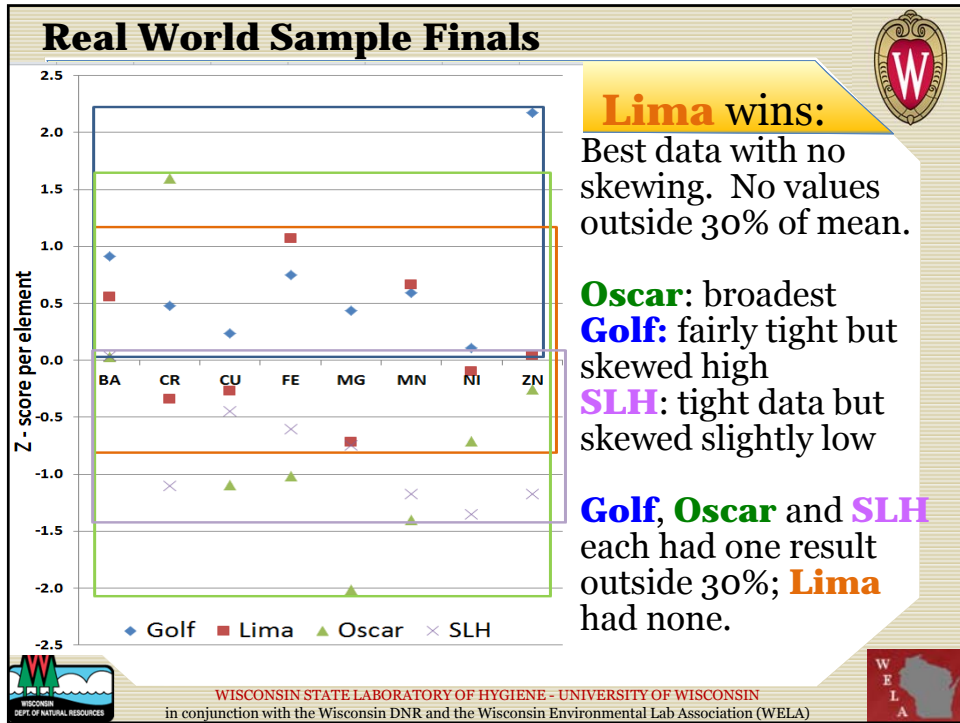
	outliers	False +		> 30%
Alpha		As		
Bravo	Zn	Se		
Charlie	Cu,Mg	Ag		Ni
Delta		Cd		
Echo		Cd		
Foxtrot	Fe.Mn	Se		Cr, Ni
Golf	→	→ Pass...on to finals	Zn	
Hotel	Cr	Ag,As,Cd,Se	Ni	
India	Ba	As,Cd,Se	Zn	
Juliet		As,Cd,Se		
Kilo	Cr		Cu	
Lima	→	→ Pass...on to finals		winner →
Mike		Ag,As,Cd		
November	Ba	Se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

Lima



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Tell the audience what you're going to say, say it; **then tell them what you've said.**


Dale Carnegie
American Writer
(1888-1955)


QuoteHD.com


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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/MSF 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?




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Thanks for coming!



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