Trace Metal Considerations when Phosphorus Removal Chemicals are Used

Rick Mealy, Program Chemist (DNR Certification Services)

What's the hub, bub?

RE300 RARE EARTH TECHNOLOGY

Product Data Sheet

Physical & Chemical Properties

Rare Earth Chloride Concentration:
39% - 42% w/w
615-671 g/L
5.13-5.59 lbs/gal

Physical State: Liquid
Color: Colorless to Amber
Odor: Mild
Freezing Point: -40°F (-40°C)

Aqueous Solubility: Miscible
Liquid pH (neat): 3.0 - 4.0
Specific Gravity: 1.55 - 1.63
Density: 1.55 - 1.63 g/ml (12.91 - 13.57 lb/gal)

Water weighs 8 lbs/gallon!

SECTION 3 COMPOSITION/ INFORMATION ON INGREDIENTS

CAS NUMBER	EC NUMBER (EINECS/ ELINCS)	CHEMICAL NAME	PERCENT (% Weight)
7732-18-5	215-185-5	Water	37-71
Proprietary	Proprietary	Rare Earth Chloride	29-63

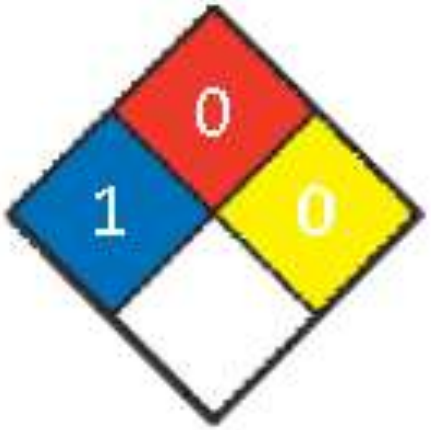
SECTION 16 OTHER INFORMATION

National Fire Protection Association (NFPA) Ratings:

Health: 1

Flammability: 0

Reactivity: 0



So... it's pretty harmless

Does it work? (Watertown data)

	Pre RE-300	RE-300 200 gpd	RE-300 135 gpd	RE-300 94 gpd
Influent TP	4.00	4.04	2.97	4.86
Effluent TP	0.510	0.133	0.172	0.291
Removal	*88%*	*97%*	*94%*	*94%*
Eff. PO4 (grab)	0.300	0.043	0.068	0.241
PO4 % of TP	60%	32%	40%	82%

Did not get down to 0.1 in limited trial, but…

… up to 75% reduction in effluent Total P

… up to 85% reduction in effluent PO4

Solution: A whole other talk

Theory: Communities of Watertown's size could get below 0.1 as long as they don't have a problem with Soluble non- reactive phosphorus (SNRP)

Parameter	Result	Units
Total Phosphorus	0.812	mg/L
Ortho Phosphorus	0.164	mg/L
Soluble Phosphorus	0.657	mg/L
Soluble Ortho Phosphorus	0.061	mg/L
SNRP	0.596	mg/L

So…if it works…what's the issue?

Kewaskum's experience...

- About 2 years ago we learned that products were available that contained over 30% Cerium (**Ce**).
- Note: EPA ICP method 200.7 warns of **Ce** interference. *(but SW-846 6010 does not!)*
- In late summer 2016, Kewaskum had trouble landspreading its biosolids; it was failing for Arsenic
- 3 different labs used; all said it exceeded arsenic (**As**) standards or that results were funky.
- Kewaskum never had **As** in biosolids before.
- But they *were* taking in a source using SorbX-100.
- Checked with labs. No correction for **Ce** on **As**.
- Once correction applied, **As** "disappeared".

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RE-100

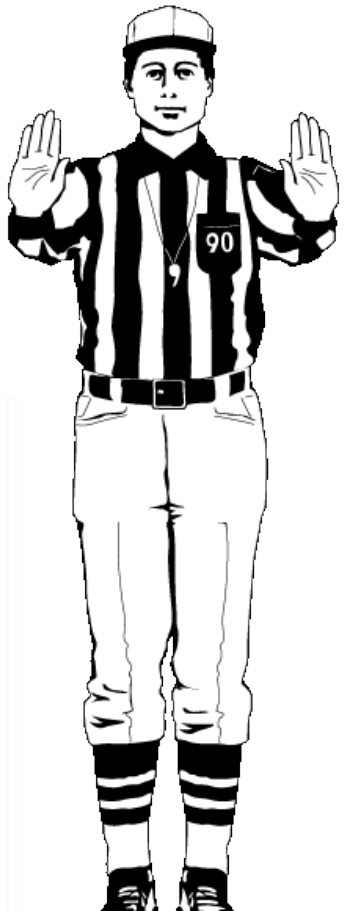
Kewaskum's Arsenic Results

(mg/kg dry weight)

Received	Lab	Result	Tech.	Line
		???		
		???		
		???		
		???		
		???		
		???		

Lab 3790 Summary

- Digested & analyzed using normal solids method.
- Upon learning about the **Ce** levels in the samples,
  - developed new solids method; added two **As** **λ**s (188.979 & 193.696) and a **Ce** **λ**.
  - **Ce** level in the samples was ~45,000 ppm.
  - Corrected for this interference on both **As** **λ** s.
  - 193.696 **λ** needed a huge correction
  - 188.979 did not need much of a correction.
- Since, results from the two **λ**s didn't agree… suspect an interference causing high **As** bias at 188.979 **λ**.
- Analyzed by ICP-MS to better assess the interference.



Whoa! Interference??

What's in RE-100/300 that's causing an interference?

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How to determine what's in it

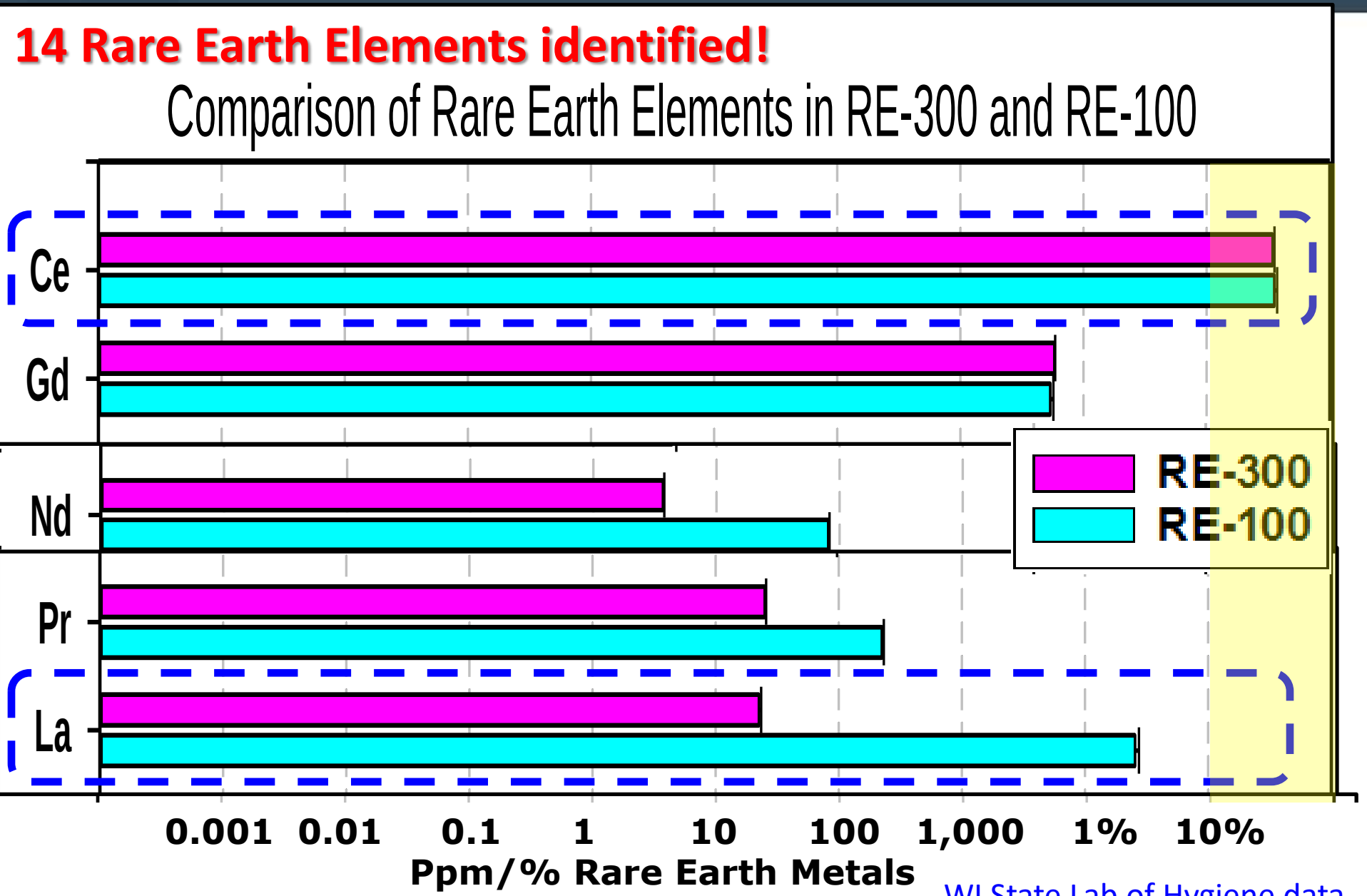
- High resolution ICP/MS is a powerful tool to identify and quantify with certainty any elements present.

- Unfortunately, few labs have this capability. The State Lab of Hygiene, however, has the instrument and a talented staff to run it.

- We used this as a first step to absolutely determine what elements are present in the Neo product as well as concentration levels

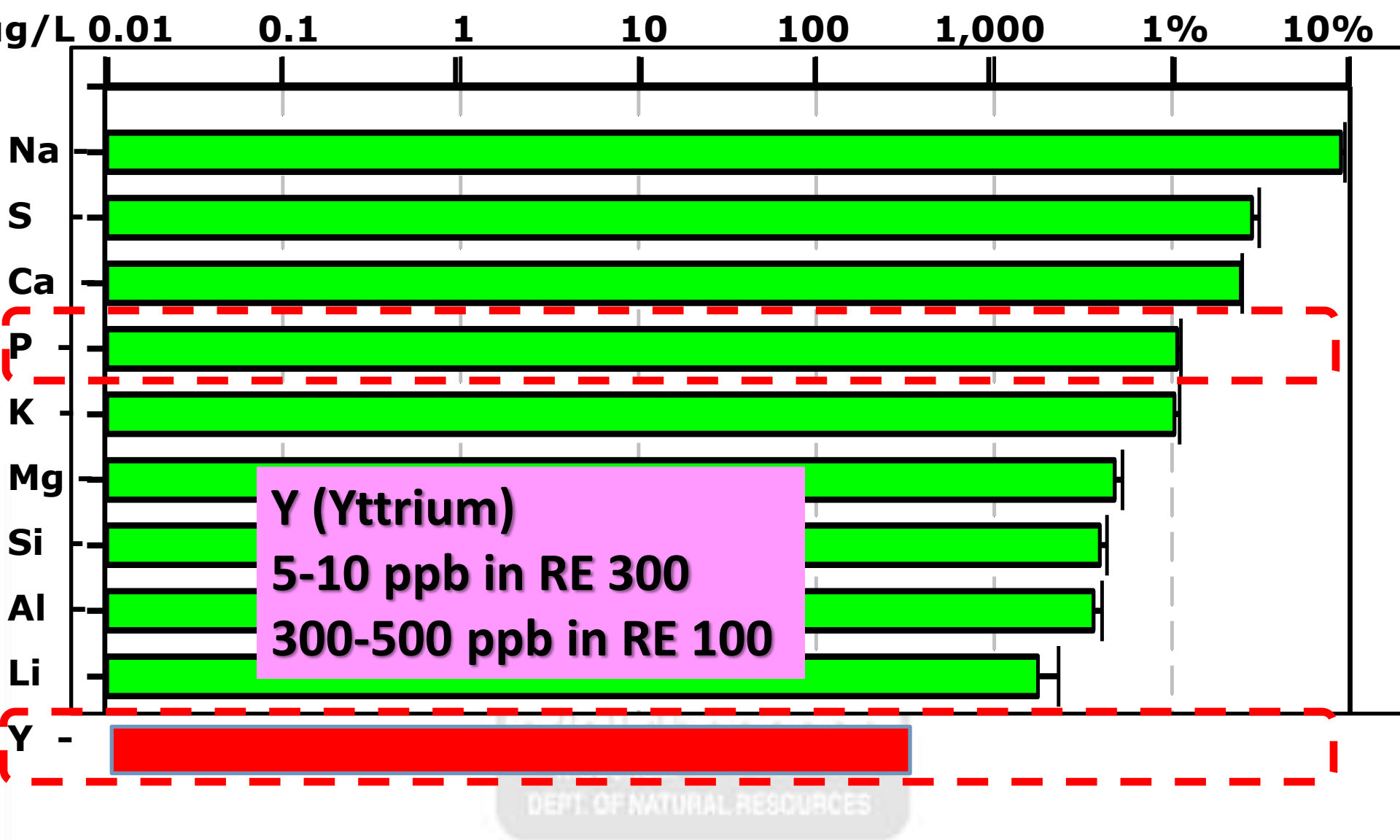
Rare Earths (RE) in RE300/100

14 Rare Earth Elements identified!



WI State Lab of Hygiene data

Other Elements in RE300/100



Metals testing 101

Now we need a low tech summary of metals testing and ICP Optical Emission Spectrometry

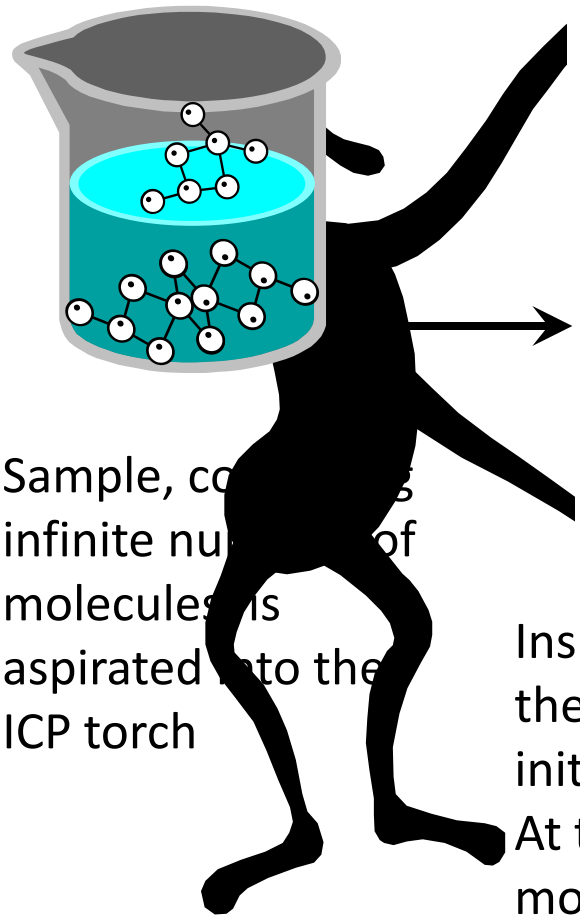
Metals instrumentation

FLAA 1,700-2,400 °C

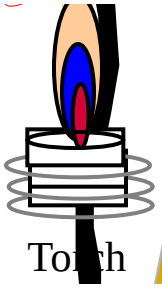
GFAA 2,000-2,500 °C

ICP ~**8,000 °C**

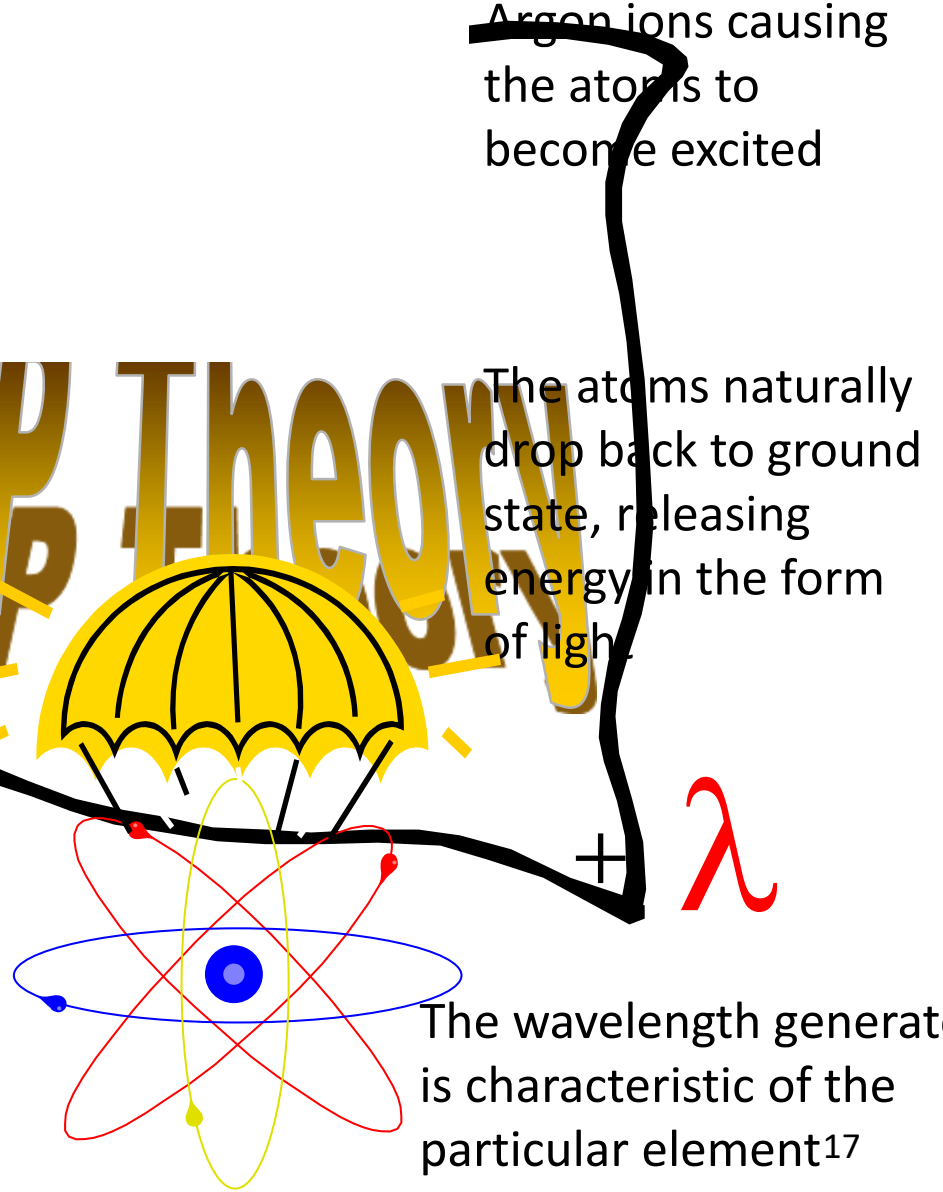
Basic theory



Sample, co g infinite nu of molecules is aspirated into the ICP torch



Inside the plasma, the sample is initially vaporized. At this point all molecules are atomized.



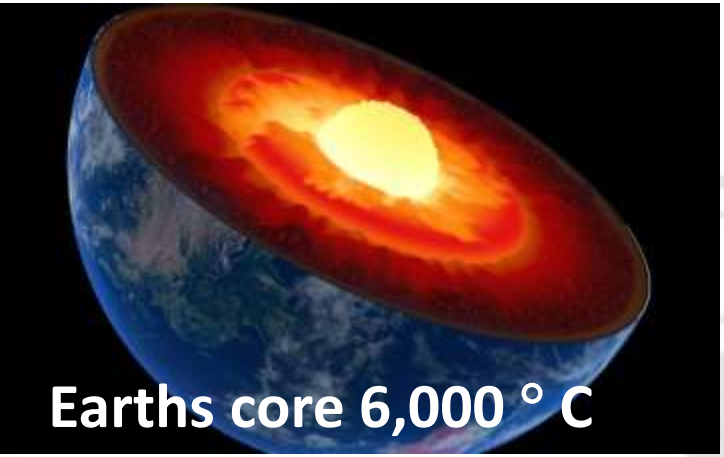
Then, atoms collide with electrons and Argon ions causing the atoms to become excited

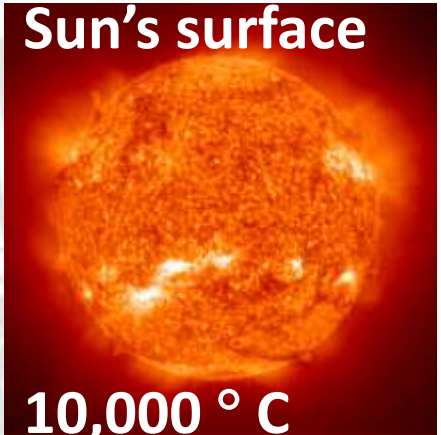
The atoms naturally drop back to ground state, releasing energy in the form of light

The wavelength generated is characteristic of the particular element

Relative hotness

8,000 °C



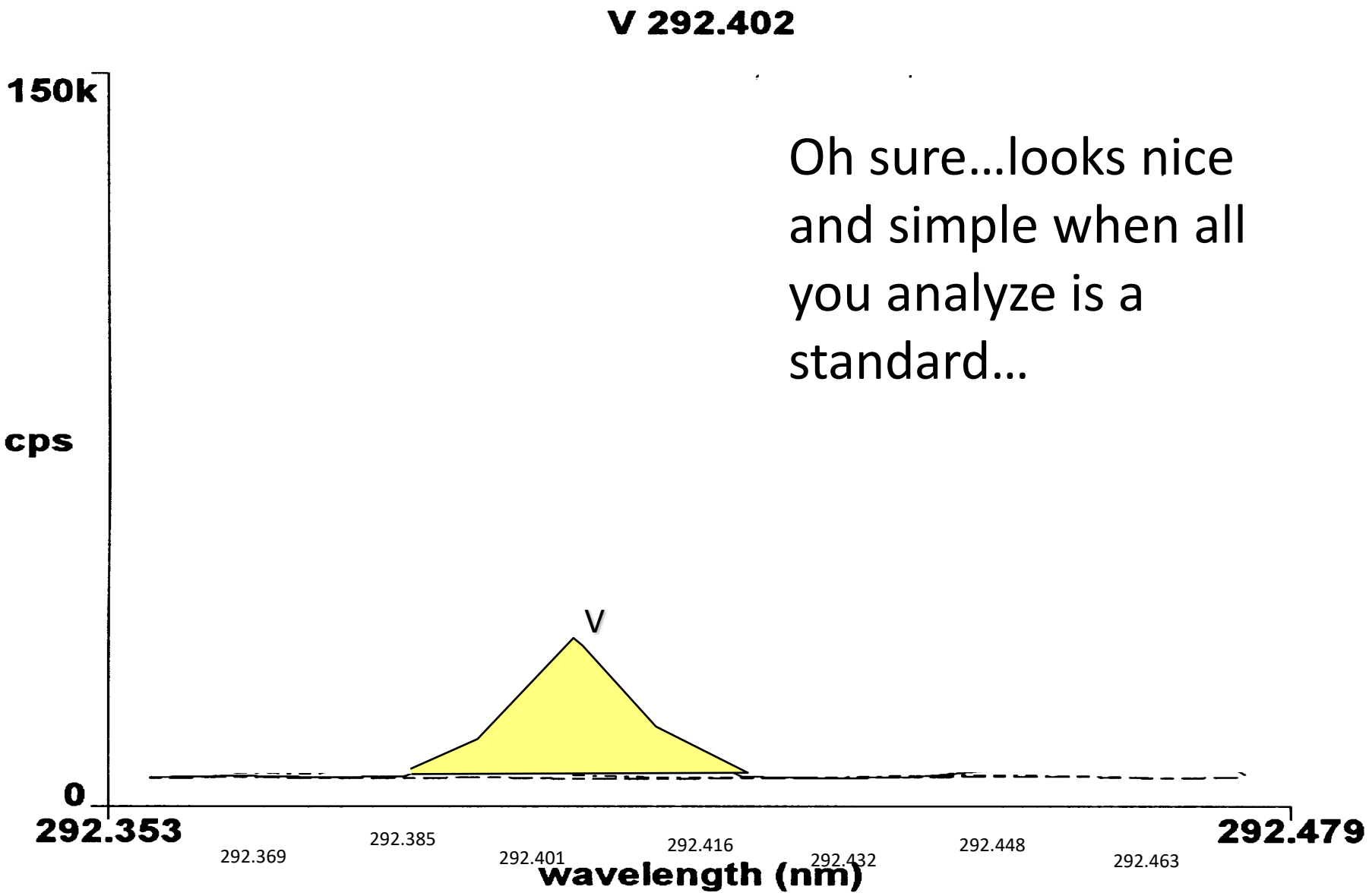


OK…so ICP is hot…

Why do we care about how hot something is?

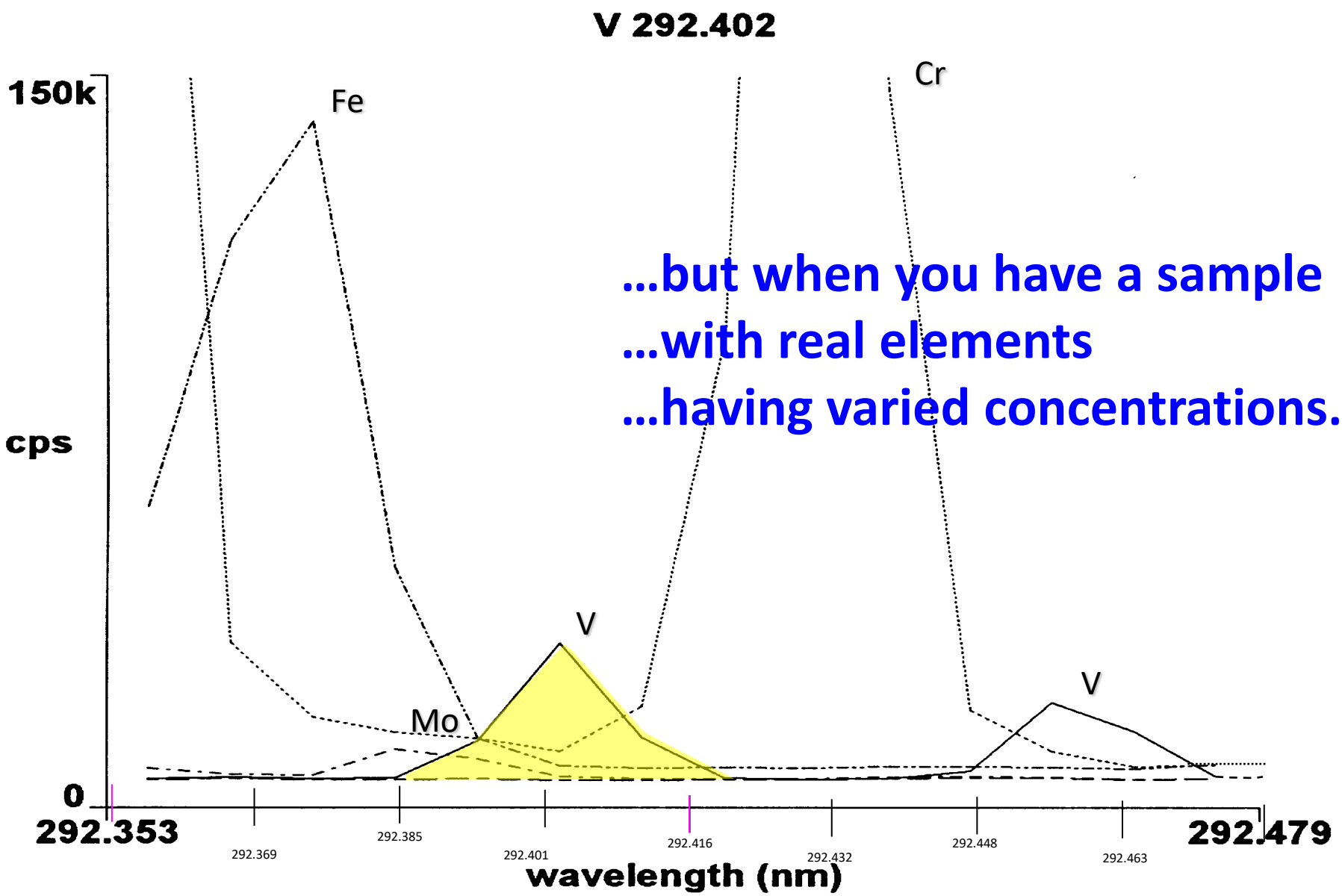
- The ICP torch is really plasma energy.
- EVERYTHING is atomized.
- Background matrix interferences are essentially non-existent (*what could survive 8,000 °C?*).
- **The only interferences we need to worry about are spectral interferences.**
- **Spectral interference** occurs when an emission line from one element "bleeds" into another element's emission.

Spectral interference 101



Oh sure…looks nice and simple when all you analyze is a standard…

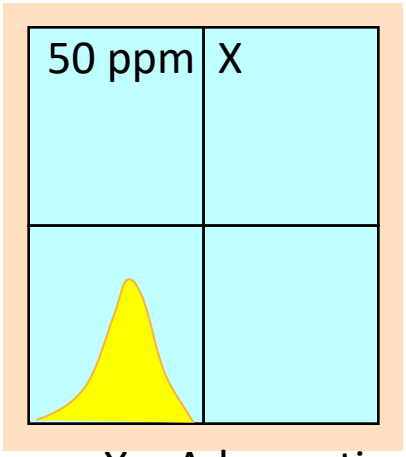
Spectral interference 101

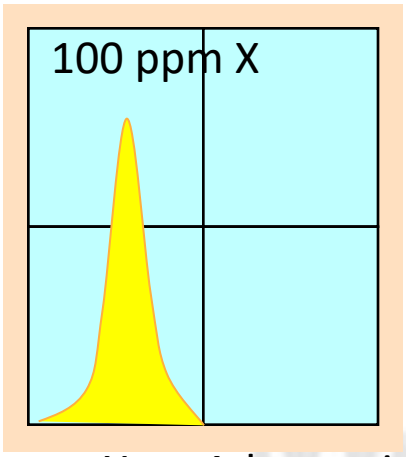


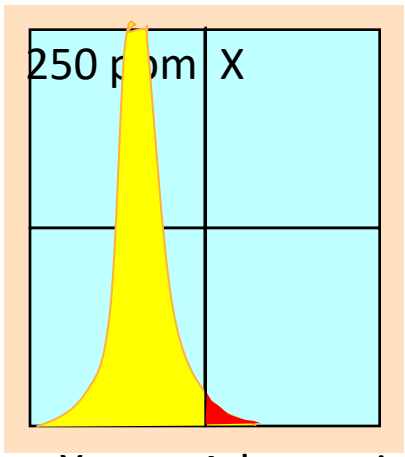
…but when you have a sample
…with real elements
…having varied concentrations…

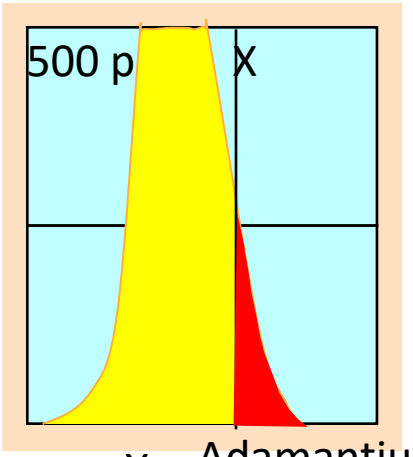
Spectral overlap

Spectral overlap is simply when another element has an emission line very close to another target element, and as concentration increases, it “bleeds” into the other element’s window.







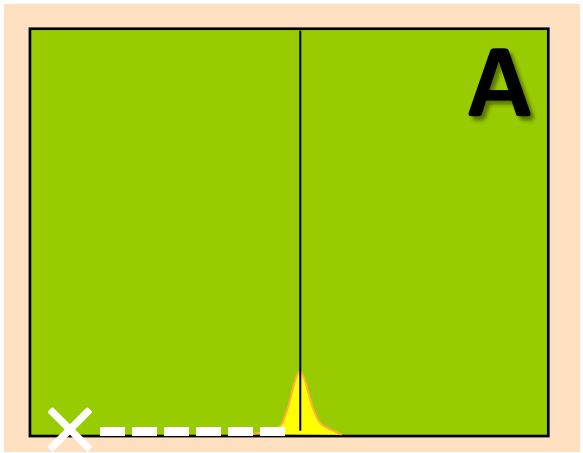


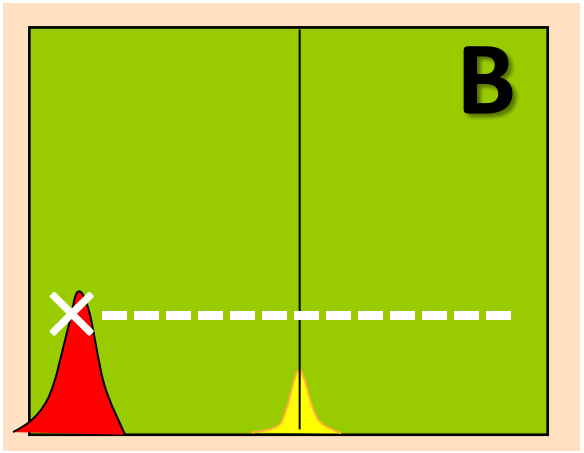
At 50 ppm, element X has no impact on Adamantium

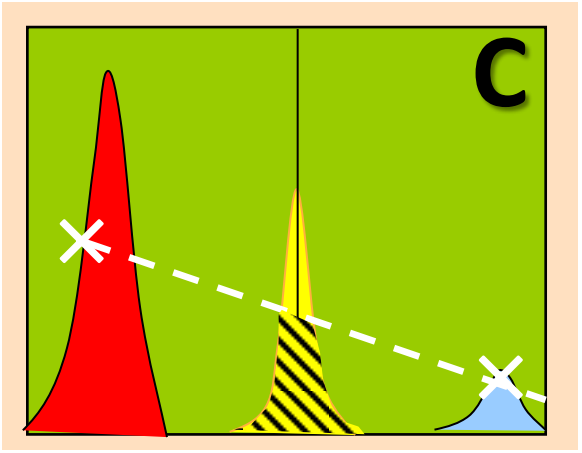
But at 500 ppm, X’s emission bleeds into and is counted as Adamantium

Background correction issues

Improper background correction can also occur. If a background correction point is placed where an interferent emits, it can cause peak reduction.







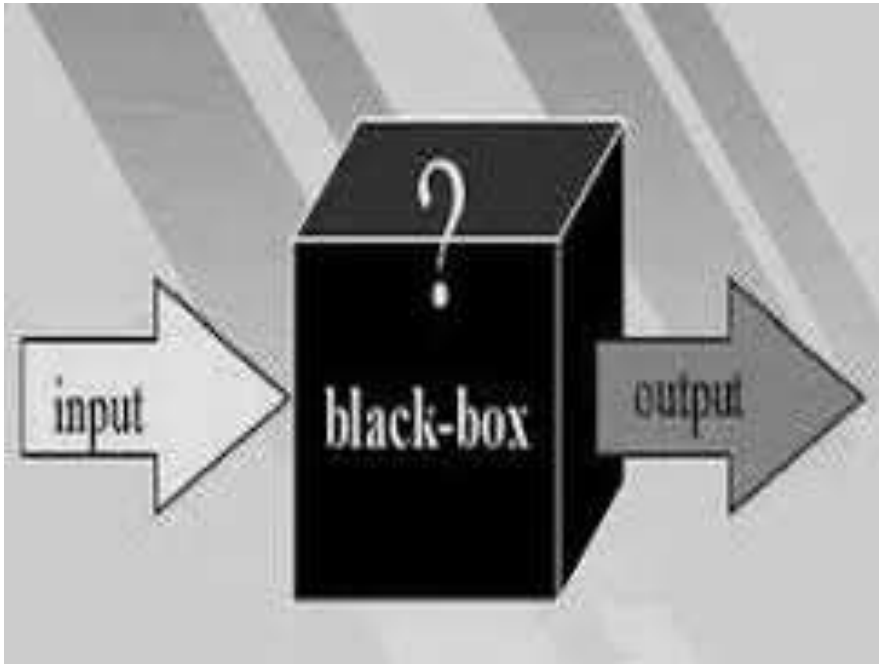
Scenario A Nothing present, background correction point becomes peak integration baseline.

Scenario B 1 background point. If an interferent exists, the baseline is re-set, creating negative peaks.

Scenario C 2 background points. If interferents affect both sides of the target peak, the peak can be shaved off and a new baseline created.

Correcting for interferences

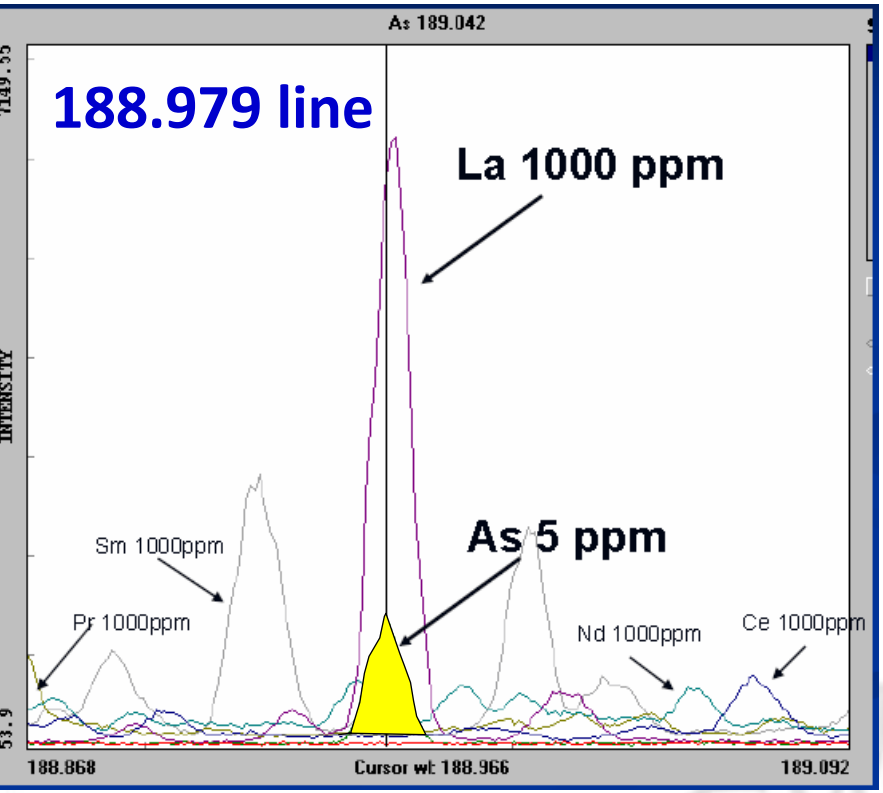
- Analyze a bunch of individual pure element standards.
- Determine what elements should be **absent—but aren't**



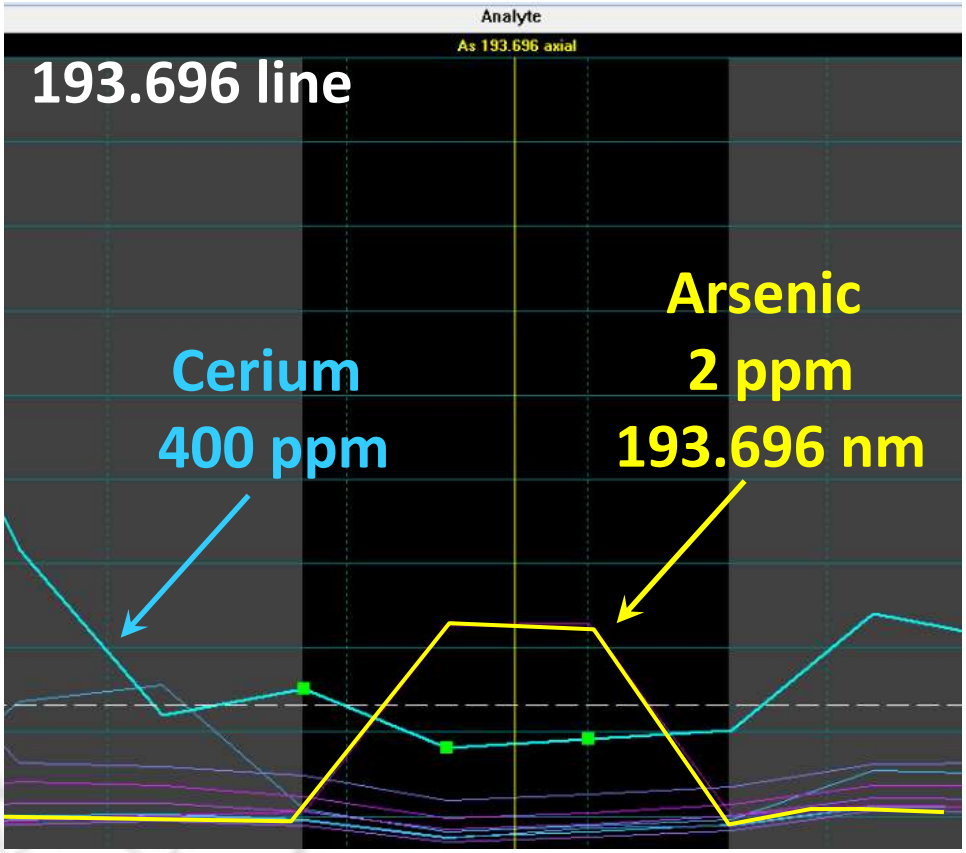
Inter-element Correction (IEC) Factors!

Flashback to Kewaskum data

Lanthanum (La)
Direct overlap



Cerium (Ce)
Background correction issue

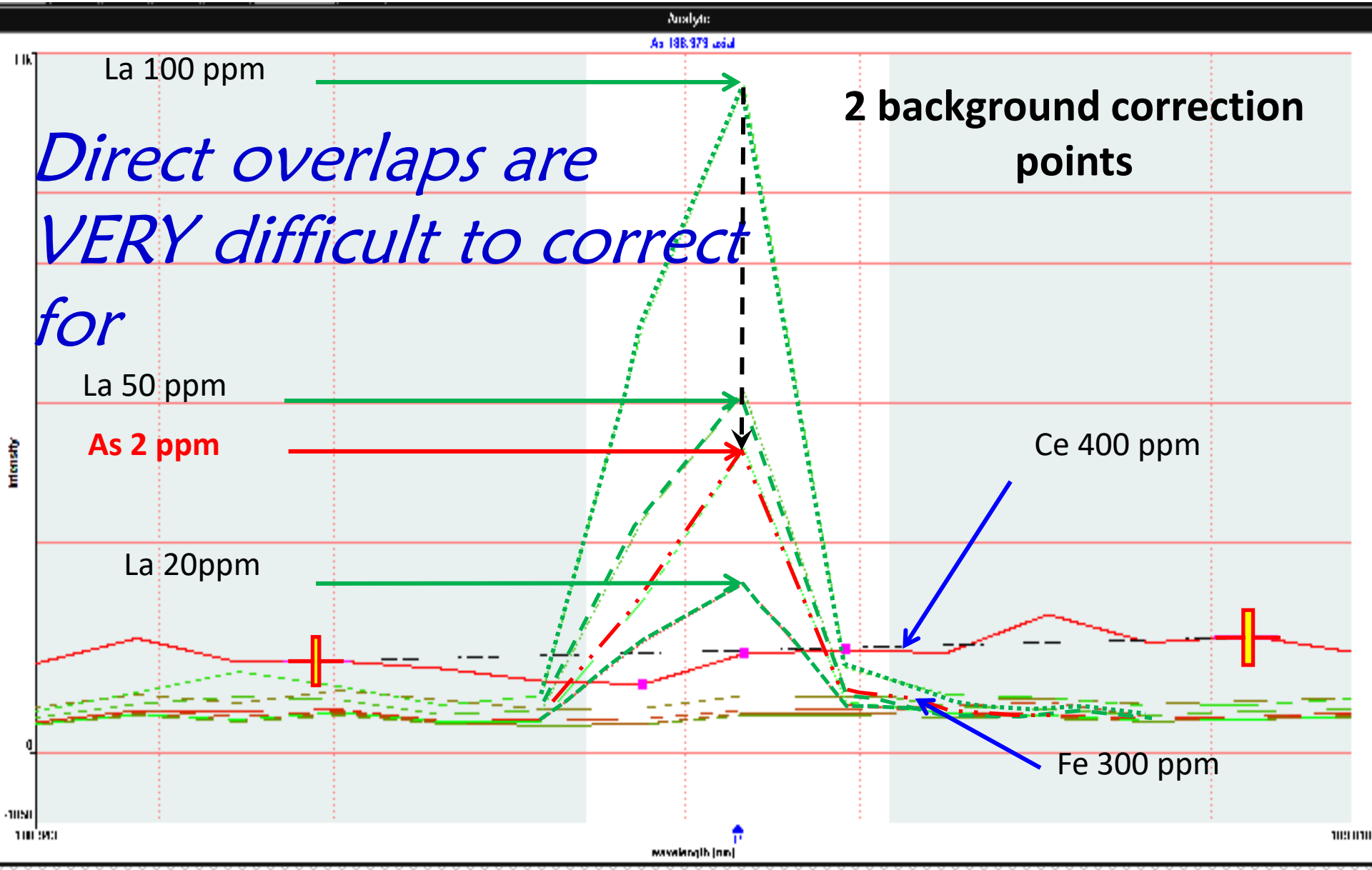


Direct overlaps are VERY difficult…
what if BOTH are present?

Problems with Arsenic Detection:
https://www.aiha.org/aihce06/handouts/po122gunderson.pdf

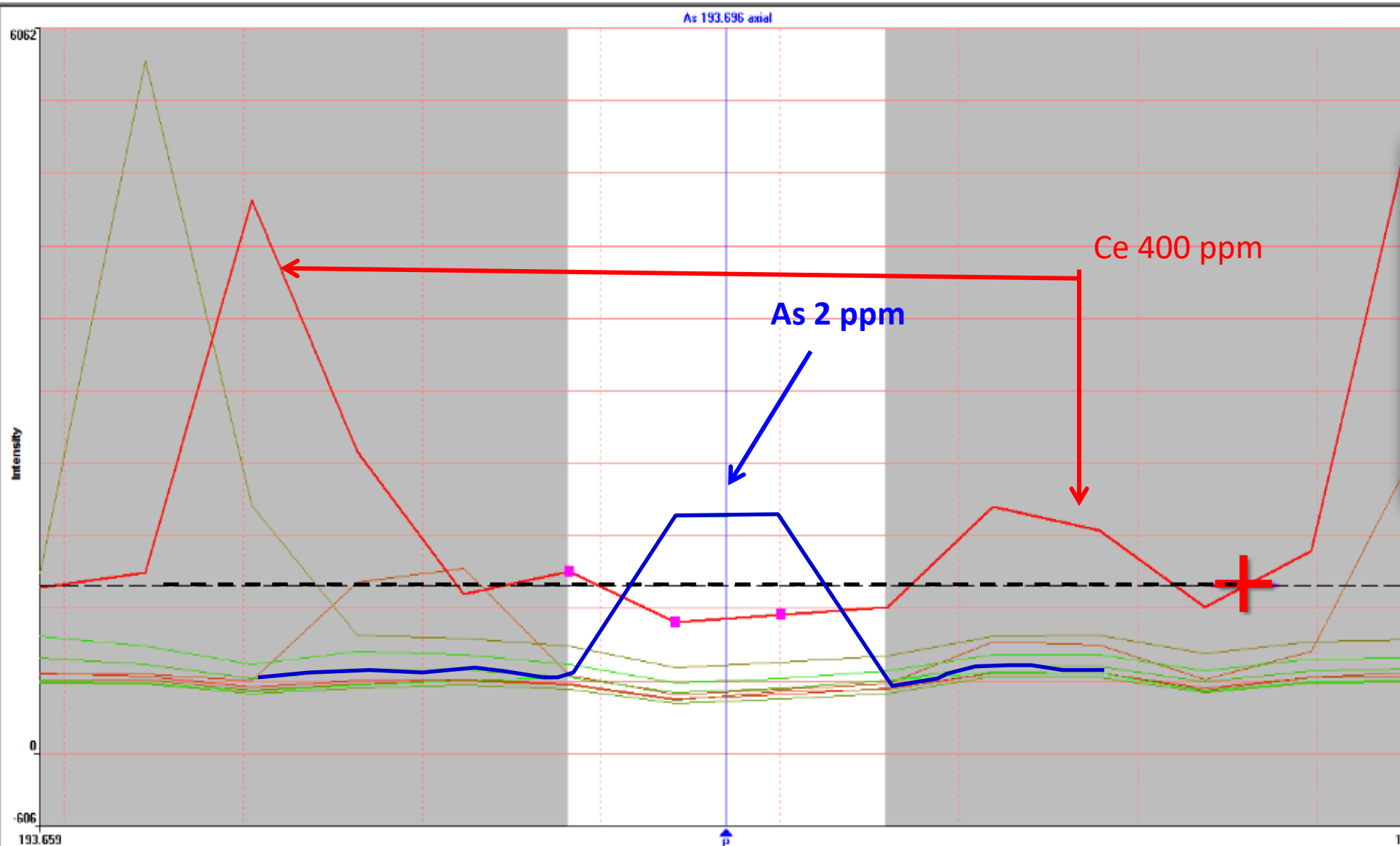
WI State Lab of Hygiene data

Arsenic 188.979 line



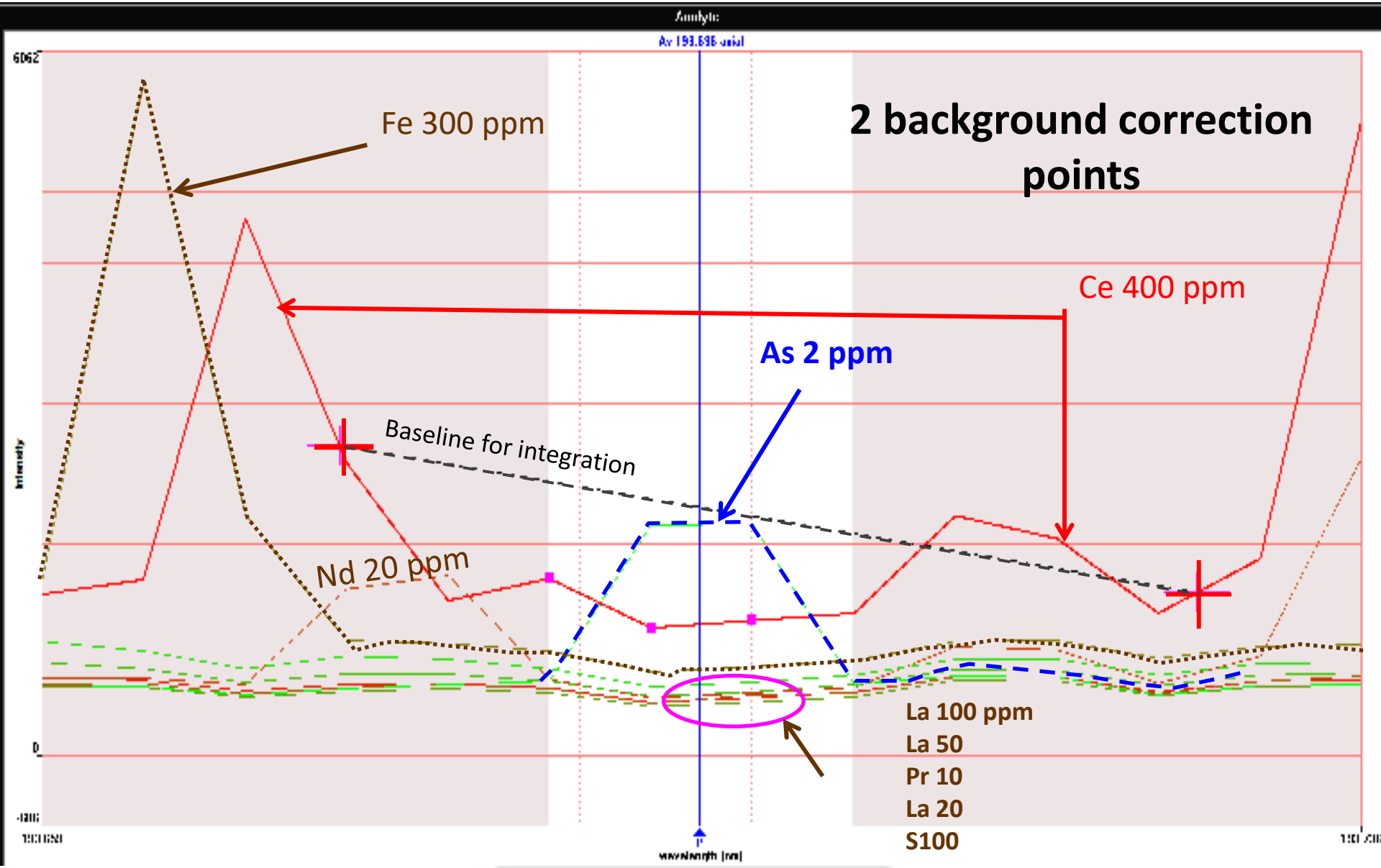
Arsenic 193.696 line (1 pt)

Arsenic 193.696 line



Arsenic 193.696 line (2 pts)

Arsenic 193.696 line



Putting what we learned to work

- We wanted to analyze biosolids data of facilities using RE100/300 and look at data with and without proper correction.
- We also wanted to look at effluent trace metals data to see if any of the REEs appear in the effluent (and thus may need correction) or potentially lead to permit issues.

Effluents: Good News!

EHD-Metals ICP-OES Data of WWTP Effluents (ug/L

these are interference corrected

Minerals

RE Elements

Element	Town of Norway	Village of Sussex	Watertown	Juneau
Al 396.153 R	26.81	10.41	29.18	71.95
Sb 217.582	ND	ND	ND	ND
As 188.979	ND	ND	ND	ND
As 193.696	ND	ND	ND	ND
Ba 233.527	44.92	54.54	64.71	13.57
Be 313.107	ND	ND	ND	ND
B 249.677	171.18	126.33	465.23	100.90
Cd 226.502	ND	ND	ND	ND
Ca 317.933 R	92,861.39	88,295.96	86,059.95	50,078.76
Cr 205.560	ND	ND	1.63	ND
Co 228.616	ND	ND	ND	ND
Cu 324.752	7.86	13.13	15.79	10.55
Fe 238.204 R	ND	ND	150.00	ND
Pb 220.353	ND	ND	ND	ND
Mg 279.077 R	52,316.17	39,551.09	47,796.95	34,634.26
Mn 257.610	21.21	5.12	32.99	ND
Mo 202.031	3.78	ND	ND	ND
Ni 231.604	2.62	2.09	7.91	2.72
P 213.617	346.09	463.40	321.00	875.94

Element	Town of Norway	Village of Sussex	Watertown	Juneau
K 766.490 R	7.84	7.94	33.94	49.72
Se 196.026	ND	ND	ND	ND
Ag 328.068	ND	ND	ND	ND
Na 589.592 R	302,984.69	219,168.01	272,587.82	269,568.59
Sr 407.771 R	539.65	7,632.94	339.82	1,524.00
S 181.975	7,513.99	5,275.65	8,637.19	10,244.24
Tl 190.801	ND	ND	ND	ND
Sn 189.927	ND	ND	ND	ND
Ti 336.121	ND	ND	ND	ND
V 292.402	ND	ND	1.47	1.11
Zn 206.200	20.83	17.60	30.18	14.91
Ce 413.764 R	ND	11.53	1640.25	ND
Gd 342.247 R	ND	ND	ND	ND
La 408.672 R	ND	ND	ND	ND
Nd 406.109 R	ND	ND	ND	ND
Pr 390.844 R	ND	ND	ND	ND
Sm 359.260 R	ND	ND	ND	ND
Ho 345.600 R	ND	ND	ND	ND

Effluent levels (ppb)

Element	Town of Norway	Village of Sussex	Watertown	Juneau
Ca 317.933 R	92,861.39	88,295.96	86,059.95	50,078.76
Mg 279.077 R	52,316.17	39,551.09	47,796.95	34,634.26
K 766.490 R	7,840	7,940	33,940	49,720
Na 589.592 R	302,984.69	219,168.01	272,587.82	269,568.59
Sr 407.771 R	539.65	7,632.94	339.82	1,524.00
S 181.975	7,513.99	5,275.65	8,637.19	10,244.24
P 213.617	346.09	463.40	321.00	875.94
Ce 413.764 R	ND	11.53	1640.25	ND
La 408.672 R	ND	ND	ND	ND

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Semi-final data Biosolids (mg/kg)

Element	Norway	*Norway (w/o IEC)*	Sussex	*(w/o IEC)*	Watertown	*Watertown (w/o IEC)*	Juneau	*(w/o IEC)*
Al 396.153 R	**3,066.8**	*3,135.5*	**1,962.6**	*1,984.0*	**3,111.2**	*3,101.9*	**1,218.3**	*1,187.6*
As 188.979	**4.3**	*127.2*	**(8.6)**	*196.2*	**(32.2)**	*466.4*	**(50.9)**	*848.7*
As 193.696	**61.0**	*(675.4)*	**12.6**	*(265.4)*	**28.0**	*(324.4)*	**18.6**	*(276.1)*
Cd 228.802	**(4.8)**	*10.8*	**(6.2)**	*4.8*	**(15.4)**	*4.8*	**(29.8)**	*4.1*
Cd 214.440	**1.9**	*3.0*	**1.4**	*1.9*	**1.4**	*4.7*	**0.3**	*0.5*
Cd 226.502	**2.7**	*(5.3)*	**1.6**	*(1.2)*	**1.2**	*5.1*	**(0.1)**	*(4.6)*
Cr 205.560	**16.0**	*27.9*	**25.8**	*29.3*	**101.7**	*102.1*	**2.4**	*3.4*
Cr 283.563	**14.3**	*124.4*	**25.1**	*67.9*	**102.1**	*212.7*	**1.2**	*41.7*
Pb 220.353	**10.3**	*128.1*	**15.2**	*54.9*	**31.4**	*49.5*	**25.7**	*64.2*
Pb 217.000	**7.0**	*319.1*	**17.8**	*132.3*	**36.2**	*136.0*	**13.7**	*148.7*
P 213.617	**40,328.6**	*40,518.2*	**35,126.7**	*35,492.5*	**37,613.4**	*37,708.0*	**17,017.1**	*17,059.8*
P 178.221	**36,926.9**	*36,845.5*	**32,801.6**	*32,774.3*	**34,885.5**	*34,857.5*	**17,137.4**	*17,100.7*
Sr 407.771 R	**314.0**	*258.7*	**3,100.0**	*???*	**225.2**	*101.5*	**787.9**	*553.7*
S 181.975	**5,807.6**	*6,612.7*	**5,690.2**	*6,704.6*	**5,338.2**	*10,154.5*	**3,584.3**	*924.1*
Tl 190.801	**15.5**	*(568.0)*	**4.5**	*(210.1)*	**6.7**	*(130.4)*	**5.7**	*(259.2)*
Y (IS)	**272.6**	*(509.1)*	**255.1**	*(185.5)*	**274.4**	*(119.5)*	**94.1**	*(234.2)*
Y (IS) **R**	**237.3**	*(445.3)*	**217.4**	*(167.5)*	**237.4**	*(106.6)*	**82.0**	*(204.7)*
Ce 413.764 R	**76,871.3**	*76,809.4*	**28,252.0**	*28,249.7*	**18,005.4**	*18,039.8*	**34,721.2**	*34,788.1*
La 408.672 R	**3,437.7**	*2,610.6*	**4,166.6**	*3,860.8*	**8,979.8**	*8,781.4*	**16,860.6**	*16,478.8*
Nd 406.109 R	**4,218.4**	*2,959.3*	**1,216.1**	*749.9*	**118.2**	*(172.7)*	**208.4**	*(350.4)*
Pr 390.844 **R**	**705.3**	*15,014.7*	**359.3**	*5,638.5*	**(53.0)**	*3,350.9*	**(192.3)**	*6,365.5*
Gd 342.247 **R**	**(16.0)**	*484.6*	**(9.1)**	*174.9*	**12.3**	*129.3*	**(10.4)**	*216.4*
Sm 359.260 **R**	**(8.6)**	*103.9*	**(2.9)**	*26.6*	**(2.2)**	*0.5*	**6.9**	*7.9*

Semi-final data Biosolids (mg/kg)

- **Arsenic:** Significant changes when IECs (inter-element correction factors) are applied.
- Still disagreement between the 2 lines.
- Suspect background correction issues.

Element	Norway	*Norway (w/o IEC)*	Sussex	*(w/o IEC)*	Watertown	*Watertown (w/o IEC)*	Juneau	*(w/o IEC)*
As 188.979	**4.3**	*127.2*	**(8.6)**	*196.2*	**(32.2)**	*466.4*	**(50.9)**	*848.7*
As 193.696	**61.0**	*(675.4)*	**12.6**	*(265.4)*	**28.0**	*(324.4)*	**18.6**	*(276.1)*
Pb 220.353	**10.3**	*128.1*	**15.2**	*54.9*	**31.4**	*49.5*	**25.7**	*64.2*
Pb 217.000	**7.0**	*319.1*	**17.8**	*132.3*	**36.2**	*136.0*	**13.7**	*148.7*
P 213.617	**40,328.6**	*40,518.2*	**35,126.7**	*35,492.5*	**37,613.4**	*37,708.0*	**17,017.1**	*17,059.8*
P 178.221	**36,926.9**	*36,845.5*	**32,801.6**	*32,774.3*	**34,885.5**	*34,857.5*	**17,137.4**	*17,100.7*
Sr 407.771 **R**	**314.0**	*258.7*	**3,100.0**	*???*	**225.2**	*101.5*	**787.9**	*553.7*
S 181.975	**5,807.6**	*6,612.7*	**5,690.2**	*6,704.6*	**5,338.2**	*10,154.5*	**3,584.3**	*924.1*
Y (IS)	**272.6**	*(509.1)*	**255.1**	*(185.5)*	**274.4**	*(119.5)*	**94.1**	*(234.2)*
Y (IS) **R**	**237.3**	*(445.3)*	**217.4**	*(167.5)*	**237.4**	*(106.6)*	**82.0**	*(204.7)*
Ce 413.764 **R**	**76,871.3**	*76,809.4*	**28,252.0**	*28,249.7*	**18,005.4**	*18,039.8*	**34,721.2**	*34,788.1*
La 408.672 **R**	**3,437.7**	*2,610.6*	**4,166.6**	*3,860.8*	**8,979.8**	*8,781.4*	**16,860.6**	*16,478.8*
Nd 406.109 **R**	**4,218.4**	*2,959.3*	**1,216.1**	*749.9*	**118.2**	*(172.7)*	**208.4**	*(350.4)*

FINAL data Biosolids (mg/kg)

Semi-final data Biosolids

Element	Norway	*Norway (w/o IEC)*	Sussex	*(w/o IEC)*	Watertown	*Watertown (w/o IEC)*	Juneau	*(w/o IEC)*
Al 396.153 R	3,066.8	*3,135.5*	1,962.6	*1,984.0*	3,111.2	*3,101.9*	1,218.3	*1,187.6*
As 188.979	4.3	*127.2*	(8.6)	*196.2*	(32.2)	*466.4*	(50.9)	*848.7*
As 193.696	61.0	*(675.4)*	12.6	*(265.4)*	28.0	*(324.4)*	18.6	*(276.1)*

EHD-Metals ICP-OES Data of WWTP Biosolids for As using individual IEC tables

Element	Norway	Sussex	Watertown	Juneau	units
As 188.979 axial	14.0	1.4	4.6	-23.0	mg/kg
As 193.696 axial	-1.6	-10.0	3.2	0.0	mg/kg

Single background correction point for both wavelengths. 193 is preferred wavelength due to interference from La
Unique IEC table developed for each sample based on the concentrations of elements found in that sample

WISCONSIN DNR
Department of Natural Resources

Bob?

What about BOB?

How SLH addressed the problems

Calibration: added 15 REEs/25 wavelengths (based on HR ICP/MS).

Biosolids issues- **Ce** 500 ppm, **P** 700 ppm **Fe** 750 ppm
IEC changes required for 10 elements

High levels of Y in RE100 (less so in RE300)
Y used as internal standards (IS) to adjust element data.
Bias in IS will result in biased results.

500 ppm Ce required huge IECs for **Nd** and **Pr**

"Synergistic" interferences: Compound 1 affects Arsenic, but Compound 2 interferes (high bias) w/ compound 1 (e.g. **Pr**)

But
now what?

Communication - WWTP role

When you send biosolids samples to a contract lab, you need to:

- TELL the lab if you use(d) RE100 or RE300
- ASK if they plan to use ICP (or GFAA or ICP/MS)
- Verify that they understand and correct for interferences due to REE
- If results for Arsenic appear to be biased high, verify that the lab applied corrections for REEs.
- The lab should understand. If they do not, you may want to consider using a different lab.

Communication – Lab role

When you receive biosolids samples:

- ASK if any phosphorus-complexing chemicals were used (and which)…*or if the facility received flow/solids from a plant that did.*

If RE100 or RE300 were used

- Review pre-RE100/300 data (if you have it)
- Review historical levels & dosage rate vs. flow
- Arsenic: Use the 193.696 nm line vs. 188.979 nm
- Use only a single background correction point
- Ensure proper corrections are in place
- Create a special ICS to assess effectiveness of IECs

Conclusions

RE100/RE300 DO effectively remove phosphorus.

These products DO pose challenges for ICP & ICP/MS

But…. The challenges can be overcome …

…as long as you know to address them

GFAA= slow (8 elements= 8 runs)

ICP =faster/ less matrix interferences than GFAA

ICP/MS, while a viable option, is overkill

… **like hunting squirrels with an elephant gun**

It ain't over 'till....

- Just last week….
- Facility "X" exceeded the Se standard for its 3rd QTR biosolids: 116 mg/kg
- QTR 1 was 8.1 mg/kg; QTR 2 was 12 mg/kg. Our data collected 2.5 wks earlier also indicated 8.2.
- The only thing that changed in QTR 3 was a pilot test using RE-300. Hmmmm…

This was a team effort!

Neo Materials
Pam Cornish

WWTP Facilities
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Tim Hayden (Juneau WWTP)
Kevin Freber (Watertown Water/Wastewater Utilities)
Dennis Wolf (Sussex WWTP)
Ben Propson (Kewaskum)

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