Re-visiting Spectral Correction in ICP-OES

2017 NEMC 8-7-2017

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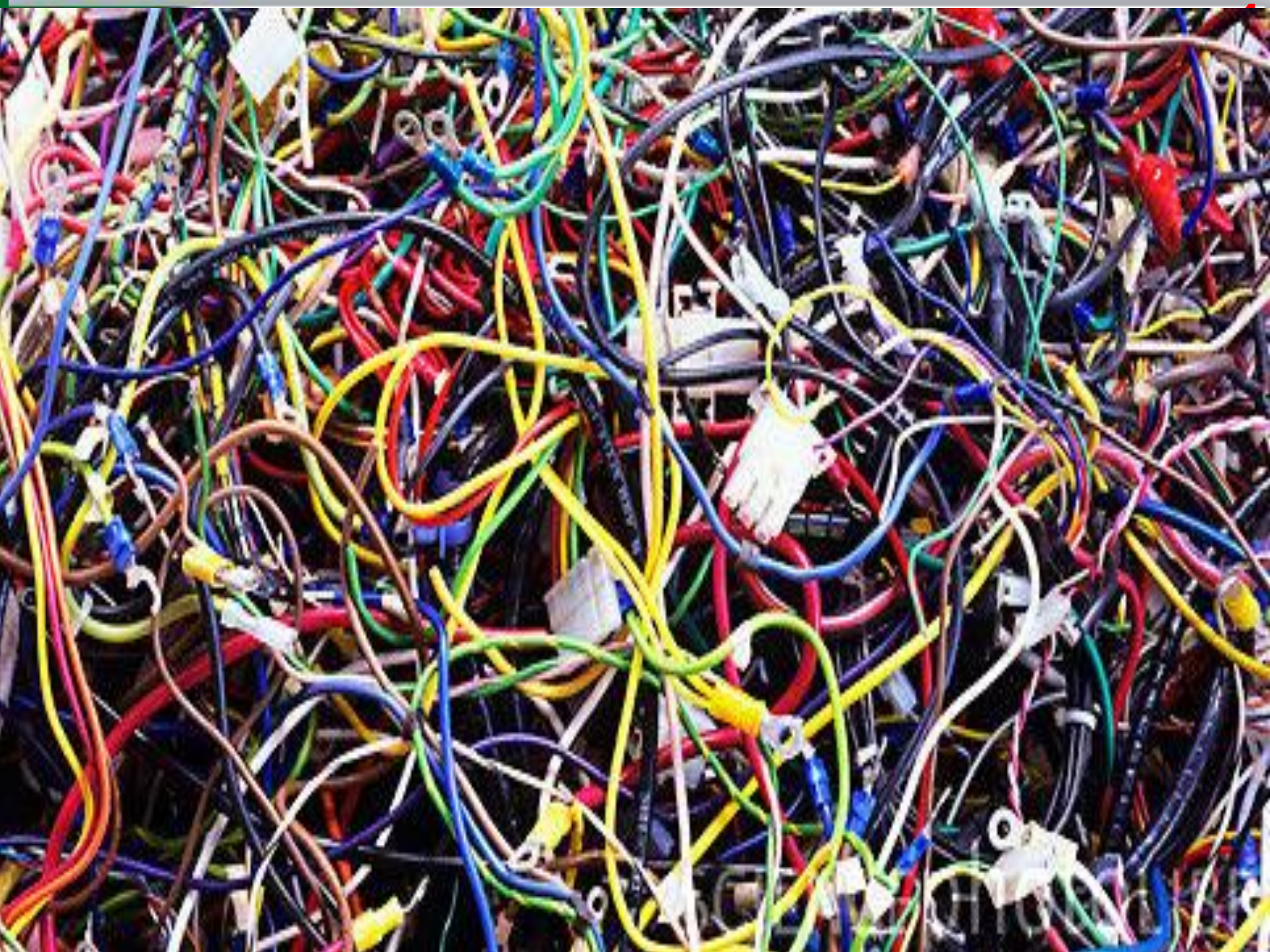
Problem Statement

- ICP-OES analysis is sold as "Plug & Play".
- **It's Not.**
- Quality training is largely unavailable.
- **TRUTH**: Critical method **detail** on interference correction non-existent or indecipherable.
- **CONSEQUENCES**: Many labs are not generating the requisite quality of ICP.

Bold? How can we say that?

- Repetitive problems with interference correction in lab audits.
- …despite 3 intensive training workshops developed and presented 2003-2014.
- Round robin "challenge" in 2005 and 2014.
- Recent results are encouraging, but there is still work to be done.
- **…and we only trained WI labs.**

How do we address this nationally?



What does this even mean?

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Round Robins – Lessons Learned

2005 Challenge PT Round Robin

GPA: 1.48

D+

- 9 labs; 25 elements
- Evaluated vs. standard PT criteria
- Lab performances …graded…were:

  3**F**'s 1**D** 3**C**'s 1**B** 1**A**

22% B or better

- Mean: 65%; Median: 67% ; Range: 47-95%
- < 70% pass: Ag, As, Ba, Be, Cu, Mo, Ni, Sb, Tl

2014 Challenge PT Round Robin

GPA: 2.80
B⁻

- 18 labs; 27 analytes tested
- Evaluated using standard PT criteria
- Lab performances …graded…were:

  0**F**'s 3**D**'s 4**C**'s 4**B**'s 7**A**'s

61% B or better

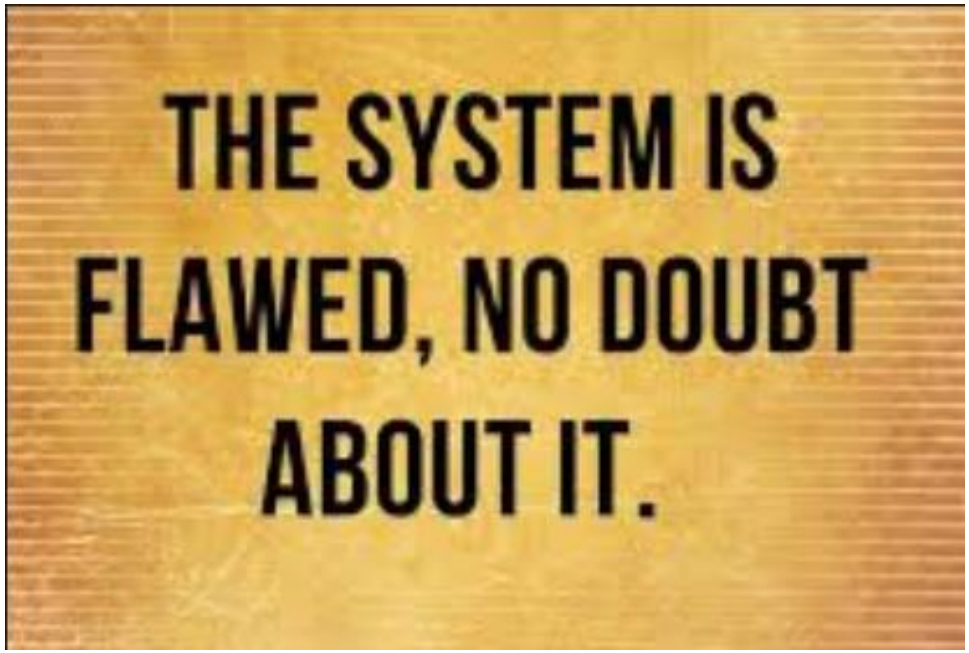
- Mean: 83%; median: 81.3%; Range: 61-100%
- < 70% pass rate for Al, Be, P, Sb, Tl, V, Zn

Why is performance still a challenge?

- *[No time to cover this]* Background correction point selection remains a problem. Defaults don't cut it.

- And even though we included previous interferents, labs still stumbled.
- Thus….spectral interferences are still not being properly identified or corrected.

Designing a defensible spectral interference correction & evaluation protocol.



ICS-AB…Can we talk?

- The
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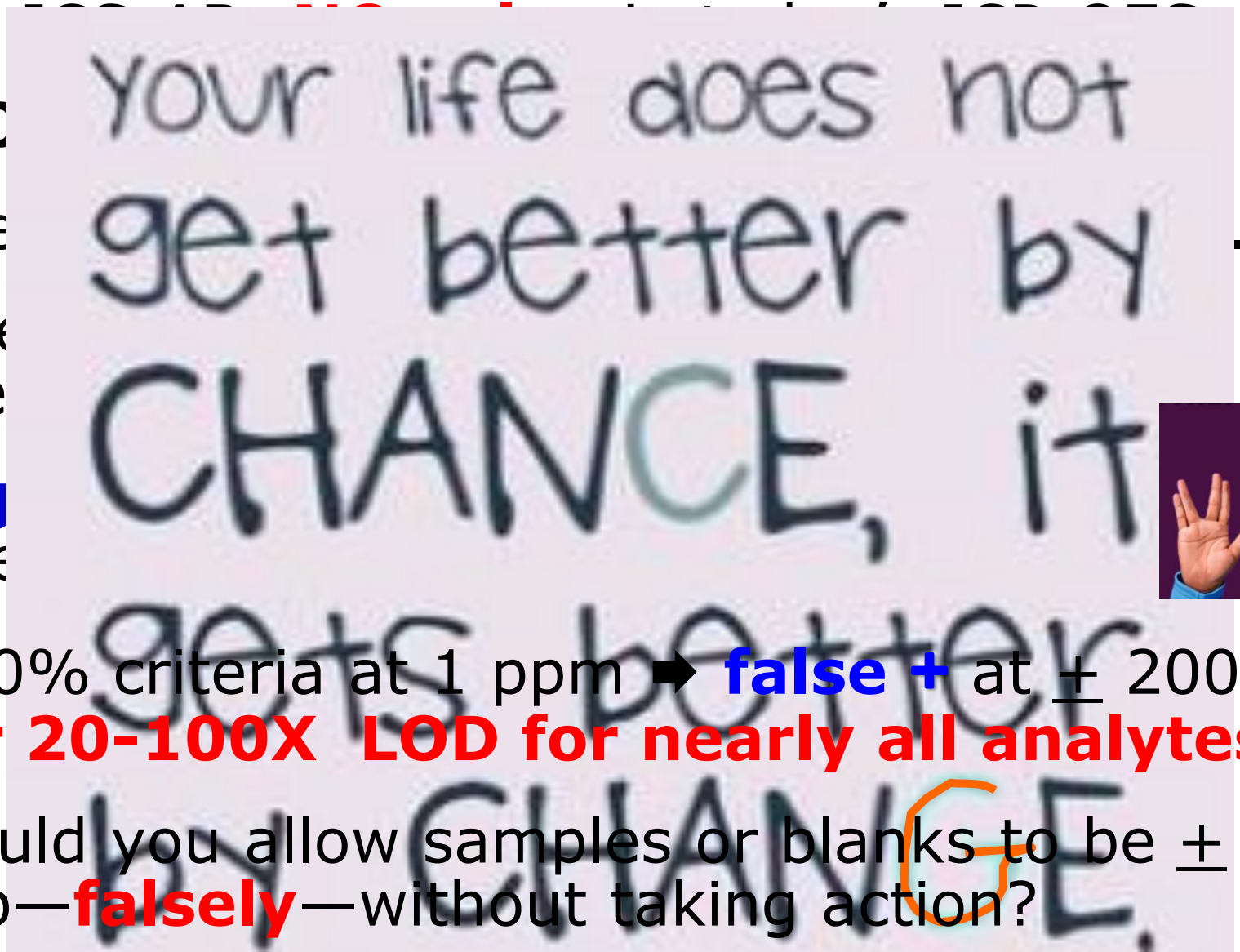
- ±20% criteria at 1 ppm ➡ **false +** at ± 200 ppb **(or 20-100X LOD for nearly all analytes.)**
- Would you allow samples or blanks to be ± 200 ppb—**falsely**—without taking action?



± 200 ppb?

I don't think so!

How about for lead in drinking water?

ICS Evaluation Criteria

We submit that an ICS standard is no different than an ICV…
Thus ± 20% is too broad

Devising an Appropriate ICS

Compare ICS-A to the ICB

…for "unspiked" analytes…

	LOD	ICB Blank Avg	ICS-A *	
Al	0.013	0.2974	49.14	LOD too low?
Ba	0.001	-0.0001	0.2967	+300 ppb! IEC!
Zn	0.007	0.0037	- 0.0175	Possible IEC

* ICS-A = Al 50 ppm + Fe 20 ppm

Compare ICS-B to the ICB

For "unspiked" analytes…

	LOD	ICB 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

12 Step Program for a more scientifically sound interference correction system

Interference correction 12 points

1. IECs are not mandatory

A lab could make the case that no correction is required for their samples, but they would **have to prove it**. **IEC ≠ ICS**

2. Special case: Interference-free samples.

Lab solely analyzes finished purified water. Both 200.7 & 6010D (*particularly unequivocal*) indicate that even when no interference correction is used, **lab is obligated to "prove" that no correction is needed**.

Interference correction 12 points

3. Correction specific to configuration

If you change torch, or adjust the plasma, nebulizer, or spray chamber then IECs need to be at least verified.

4. Size & resolution do not matter

Focal length & enhanced resolution can minimize –but not eliminate – interference.

Only true high resolution ICP will work

Interference correction 12 points

5. Defensibility limited to levels tested.

- ICS standards contains element "X" at 10 ppm
- $\therefore$ 10 ppm = limit at which correction from "X" has been defensibly verified.
- If "X" is found at 20 ppm all bets are off.

6. Protection is only as good as ICS.

- If not tested, can't prove it doesn't interfere.
- Cerium factor. Rare earths not so rare!
- Make use of wavelength finder software.
- ICS standards provide defensibility.

Interference correction 12 points

7. Too many cooks spoil the broth and too many interferents produce chaos.

Creating a chef's salad of all possible interferents in one mix is simply not a viable solution.
Can it work? Maybe. Advisable? No.

Methods 200.7 and 6010 encourage a list of 5 or 6 (6010) calibration mixes.
Why would that be?

If calibration is difficult when analyzing a single mix, how could that possibly work for verifying lack of interference? *It doesn't.*

Interference correction 12 points

8. Interferents should be recovered as well as in an ICV.

Ancient CLP protocol for evaluation of ICS-A and *(gulp!)* ICS-AB is ± 20% of true value. That's broader criteria than any PT sample! At those levels, we should expect ± 5%....or 475 to 525 ppm for a 500 ppm standard. **That's not only reasonable, it's appropriate.**

9. Please...no more ICS-AB

There is need for an ICS-A.

Also a need for an ICS-B (+ ICS-C?,D?,E?).

But absolutely no need for an ICS-AB.

Interference correction 12 points

10. What's NOT present is more important.

The concentration of any analyte which is NOT present in an ICS should be the same as that in an initial calibration blank (ICB). Overly negative concentrations are just as telling as positive ones.

11. Acceptance criteria cannot exceed the LOQ for un-spiked analytes.

While --in theory-- establishing criteria for unspiked analytes in an ICS should be $\pm$ LOD, in practice that may not be realistic.

Limits the LOQ to 3X LOD

Interference correction 12 points

12. Do it daily for best results.

Run your series of ICS solutions (*because by now you should see that one ICS solution just will not cut it for 99% of labs*) daily for best effect. The validity and defensibility of each's days analyses depend on your ability to document on each day that interferences are under control.

Purchasing ICS-AB solutions just doesn't make sense… and as **Judge Judy says, "If it doesn't make sense, it isn't right"!**

ICP Conclusions

- **Understanding ICP becoming a lost art.**

Control spectral interferences.

- Cannot control what isn't identified.
- ICS evaluation protocol is 30+ yrs old!
- Evaluation of interference correction needs a whole new approach.
- Requires sound scientific protocols.
- Background correction is a component.

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WISCONSIN DEPT. OF NATURAL RESOURCES

Thanks also to the following for their contributions:
Wisconsin State Lab of Hygiene: DeWayne Kennedy-Parker, Kevin Kaufman, Roger Schultz
Wisconsin DNR (retired, State Lab of Hygiene): George Bowman
Retired: Chuck Wibby, PT & Metals guru, founder of Wibby Environmental