

# ***“Secrets for Determining Inter-element Correction Factors for ICP”***

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## **IEC Problem Statement**

- o **Methods are not much help**
- o **How to determine what interferences exist?**
  - what elements should be tested?
  - at what levels?
- o **Spectral overlap? Background correction?**
- o **How to generate correction factors (IEC)?**
- o **How to verify adequate correction?**
  - Only guidance: methods and CLP
  - “Common sense” approach
    - ▶ ICS-A.... 1<sup>o</sup> interferences
    - ▶ ICS-B... 2<sup>o</sup> interferences
    - ▶ Review both relative to a calibration blank

## Method Confusion

EPA provides the following guidance regarding evaluation of correction factors (IECs) in methods 200.7 & 6010C.

7.13.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

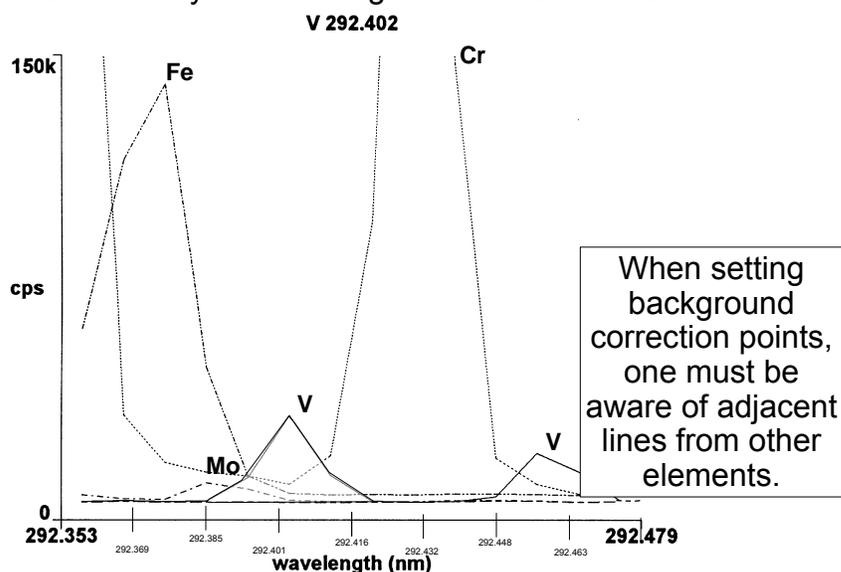


What does THAT mean???

7.13.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

## Spectral Overlap? Or background correction issue

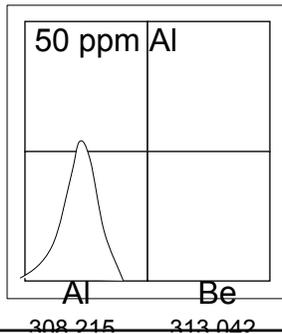
Where would you set background correction here?



## Spectral Overlap? Background Correction?

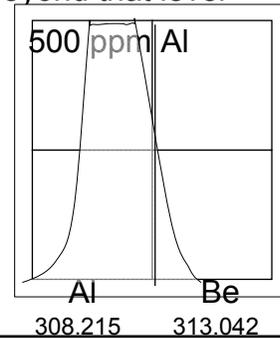
Spectral overlap occurs when either an interfering element directly shares an emission line 1 or more target elements

- There may be a level below which no significant interference occurs
- But need to consider what happens beyond that level



**Classic Spectral Overlap**

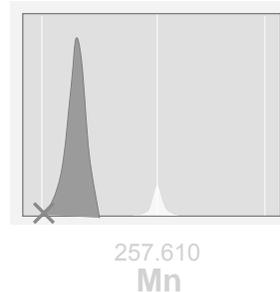
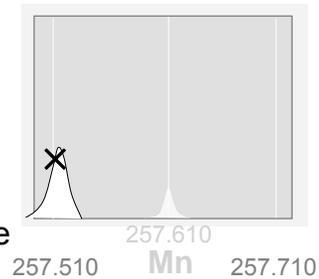
With only 50 ppm background Al, there is no impact on Be. At higher levels, however, we have a problem.



## Spectral Overlap? Background Correction?

Two situations to consider with background correction:

- (A) a relatively uncommon element has a line right on the background correction point (X). Background correction is only adequate when the element is not present.
- (B) a relatively uncommon element has a line adjacent to the background correction point (X). As concentration (and intensity) increases, there is bleed into the background correction point wavelength. Background correction MAY work below certain levels.



## Determining Interferences - what to test for

**200.7: Specifies testing of 17 elements**

**6010C: Specifies testing of 10 elements**

The only elements these 2 methods agree on to test are:  
Al, Cr, Cu, Fe, Mn, Ni, Ti, V

**3120B: No guidance**

200.7 (4.1.4) & 6010C (4.1.2):

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

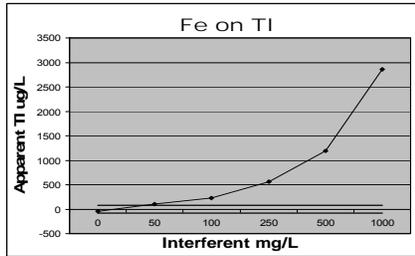
## Determining Interferences - what levels to test?

200.7    300 mg/L: Fe  
          200 mg/L: Al  
          50 mg/L: Ba; Be; Cd; Ce; Co; Cr; Cu; Mn;  
                    Mo; Ni; Sn; SiO<sub>2</sub>; Ti; Tl; and V

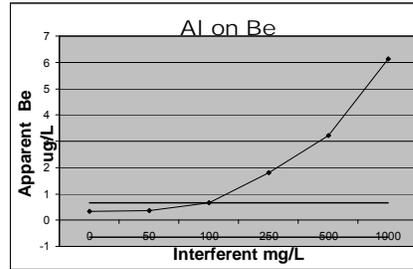
6010C    **1000mg/L:** Al, Ca, Fe, Mg  
          **200 mg/L:** Cu, Mn, Ni, Ti, Cr, V

Is this sufficient? Does it make sense?

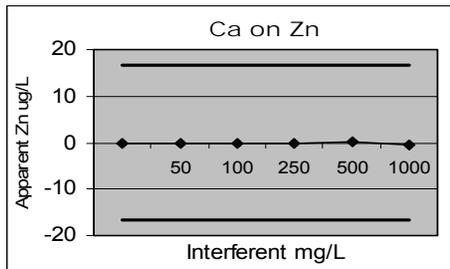
# Identifying the need for an IEC



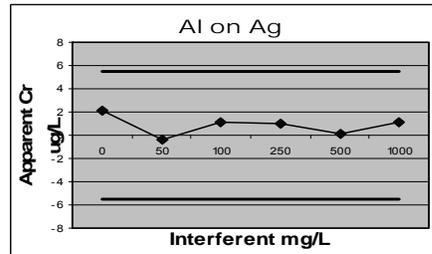
Fe has large and significant effect on TI above 100 ppm



Al has small but significant effect on Be over 100 ppm

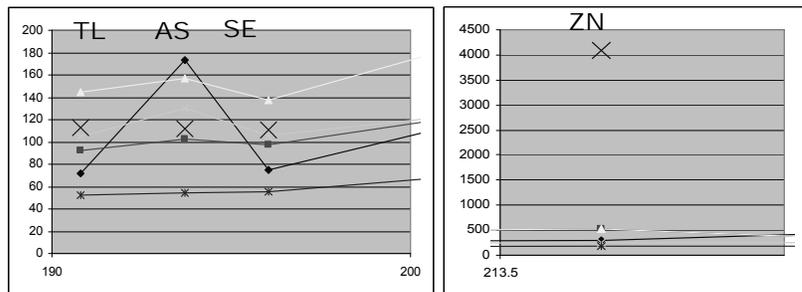


Ca shows no effect on Zn and Al shows no effect on Ag



# Determining Interferences

The signal intensity of major interferents (ICS-A) at 500 ppm on target analytes at a concentration equal to their LOQ



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

...while elements such as Zn do not seem to be affected

- ◆ AL
- FE
- ▲ CA
- × MG
- \* NA
- × Target Analytes

## SLH Procedure for Generating IECs

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

## Inter-element Correction Factors Summary

- One approach does not fit all labs/situations
- Use at least one concentration level
  - Best information obtained from multiple concentration levels
- Method recommended 100 mg/L level is not high enough for major cations
- Best overall correction obtained from average CF over multiple levels OR average of replicates at one level.
- One level probably appropriate for 2° interferents
- Watch for carryover when analyzing  $\geq 100$  ppm
- Spectral overlap yields positive bias
  - A “negative” IEC can result where an interfering line is encountered at the background correction  $\lambda$  rather than the peak  $\lambda$ .

## Evaluating IECs – what the methods say

200.7		6010	
7.13.4	If correction is operating properly, the determined target analyte concentrations from analysis of SICs A thru Q should fall within a concentration range bracketing the CB	4.1.8	If correction routine is operating properly, the determined target analyte concentrations from each SIC should fall within a concentration range bracketing the CB
7.13.4	$Range_x = [INT_x] \times CF_x / 10$	4.1.8	$Range_x = [INT_x] \times CF_x / 10$
7.13.4	If the apparent analyte concentration ([AA]), <u>after subtraction of the calibration blank</u> (CB) is outside of this "Range", then a 10% or greater change in the CF has occurred	4.1.8	If the apparent analyte concentration ([AA]), <u>after subtraction of the calibration blank</u> (CB) is outside of this "Range", then a 10% or greater change in the CF has occurred
7.13.4	If $[AA_x] - CB > \pm Range_x$ ... expect a 10%...or greater... change in CF	4.1.8	If $[AA_x] - CB > \pm Range_x$ ... expect a 10%...or greater... change in CF

**OK....so there's no crystal clear guidance on how to verify adequacy of correction factors...**

## Evaluating IEC Data

Review IEC Data against some evaluation criteria  
When does an *apparent* interference warrant correction?

While it is never *clearly* stated in EPA methods, it would seem appropriate to base corrections on LODs:  
*If an apparent analyte concentration (i.e. interference) exceeds the analyte's LOD, it would result in a false positive*

### **Optimal approach...for major cations(Al, Ca, Fe, Mg)**

- Test a series of increasing concentrations of each
- Plot apparent analyte (ug/L) vs. interferent (mg/L)
- Add plot lines of + LOD and -LOD
- Identify those needing an IEC vs. BGC concerns

## IECs - CLP approach

### Designed 2-part “Interference Check Standard (ICS)”

- ICS-A = 4 major interferences only (Al, Ca, Fe, Mg)
- ICS-AB = ICS-A + 0.5-1.0 ppm of each target analyte

### Analytes in the ICSA and ICS-AB shall fall within the greater of:

- ICS-A:  $\pm 20\%$  of the true value for each interferent
- ICS-AB:  $\pm 20\%$  of the true value: for each interferent and target analyte

### If the results of either the ICSA or ICS-AB do not fall within the control limits,

- Stop analytical sequence
- correct problem
- recalibrate
- re-analyze all samples since last compliant ICS-A

## CLP Procedure drawbacks

“Known and documented” quality  $\neq$  GOOD quality

$\pm 20\%$  is pretty forgiving at 250-500 ppm levels

**But  $\pm 20\%$  for target analytes means:**

*$\pm 100-200$  ppb for all analytes (in earlier SOWs)*

*Which means  $\pm 10-20$  detection limits for most analytes*

## Devising an Appropriate ICS

### Take what we have (CLP) and update it

ICS-A

Major interferent  
analytes only

This  
is critical

### Add a simple, but overlooked evaluation step

ICB

No analytes of  
interest

### Consider substituting an evaluation step

ICS-A+  
(aka ICS-AB)

REPLACE: ICS-AB:  
Major interferents  
spiked with all  
analytes

VS.

ICS-B

WITH: ICS-B  
Secondary  
interferents only

### Re-evaluate acceptance criteria (QA)

### Re-think analytical frequency

## To ICS-AB or not to ICS-AB

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

## ICS Recommendations: How do we know our IECs are working?

### 1. Analyze & Evaluate Initial Calibration Blank (ICB)

All target analytes should be within  $\pm$  LOD

### 2. Analyze & Evaluate an ICS-A standard

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

**Use levels = 99% level of expected concentration**

May use different ICS-A levels for different matrices

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

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

**Interferents should be within  $\pm$  5% of true value**

**All unspiked target analytes should be within  $\pm$  LOD**

Optimally, checks should be made with each run  
(Methods allow weekly if control is demonstrated)

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

### 3. Analyze & Evaluate an ICS-B standard

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

Use levels = 99% level of expected concentration

Suggest 10-50 ppm for each

**Interferents should be within  $\pm$  10% of true value**

**All unspiked target analytes should be within  $\pm$  LOD.**

If you REALLY want to continue using ICS-AB...

ICS-A+ / B+ = Interferents at typical ICS-A level

Spike all target analytes as well

Design target analyte spike levels to detect bias near LOD

Suggest 3 x LOQ for each analyte

**All analytes should be within  $\pm$  10% of true value**

**At 3 x LOQ, target analyte recovery should be  $\pm$  LOD**

## Conclusions

- o Methods are not much help
- o Determining what Interferences exist
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- o Generating correction factors
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