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

By DeWayne Kennedy-Parker

WI State Lab of Hygiene

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IEC Problem Statement

- Methods are not much help
- How to determine what interferences exist?
  - what elements should be tested?
  - at what levels?
- Spectral overlap? Background correction?
- How to generate correction factors (IEC)?
- How to verify adequate correction?
  - Only guidance: methods and CLP
  - “Common sense” approach
    - ICS-A….1° interferents
    - ICS-B… 2° interferents
    - 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?

When setting background correction points, one must be aware of adjacent lines from other elements.
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.

### 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

<table>
<thead>
<tr>
<th>Method</th>
<th>Test Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.7</td>
<td>17 elements</td>
</tr>
<tr>
<td>6010C</td>
<td>10 elements</td>
</tr>
<tr>
<td></td>
<td>Al, Cr, Cu, Fe, Mn, Ni, Ti, V</td>
</tr>
</tbody>
</table>

### 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?

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 mg/L: Fe</td>
</tr>
<tr>
<td></td>
<td>200 mg/L: Al</td>
</tr>
<tr>
<td></td>
<td>50 mg/L: Ba; Be; Cd; Ce; Co; Cr; Cu; Mn; Mo; Ni; Sn; SiO2; Ti; Tl; and V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>6010C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 mg/L: Al, Ca, Fe, Mg</td>
</tr>
<tr>
<td></td>
<td>200 mg/L: Cu, Mn, Ni, Ti, Cr, V</td>
</tr>
</tbody>
</table>

Is this sufficient? Does it make sense?
Identifying the need for an IEC

Fe has large and significant effect on Tl 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 Tl, As, and Se.

...while elements such as Zn do not seem to be affected
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 ≥ 100 ppm
- Spectral overlap yields positive bias
  A “negative” IEC can result where an interfering line is encountered at the background correction λ rather than the peak λ
Evaluating IECs – what the methods say

<table>
<thead>
<tr>
<th>200.7</th>
<th>6010</th>
</tr>
</thead>
<tbody>
<tr>
<td>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</td>
<td>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</td>
</tr>
</tbody>
</table>

\[
\text{Range}_x = \left[\text{INT}_x \times \text{CF}_x \right] / 10
\]

7.13.4 If the apparent analyte concentration ([AA]), after subtraction of the calibration blank (CB) is outside of this "Range", then a 10% or greater change in the CF has occurred

\[
\text{If } [\text{AA}_x] - \text{CB} > \pm \text{Range}_x \text{...expect a 10%...or greater... change in CF}
\]

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 interferents 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: ± 20% of the true value for each interferent
- ICS-AB: ± 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 ≠ GOOD quality

± 20% is pretty forgiving at 250-500 ppm levels

But ± 20% for target analytes means:

± 100-200 ppb for all analytes (in earlier SOWs)

Which means ± 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

ICS-A+ (aka ICS-AB)

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

VS.

ICS-B  Secondary interferents only

Consider substituting an evaluation step

ICB  No analytes of interest

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 ± 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 ± 5% of true value
   All unspiked target analytes should be within ± 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 ± 10% of true value
   All unspiked target analytes should be within ± 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 ± 10% of true value
   At 3 x LOQ, target analyte recovery should be ± LOD
Conclusions

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- Generating correction factors
- Verifying adequate correction
  - Only guidance: methods and CLP
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