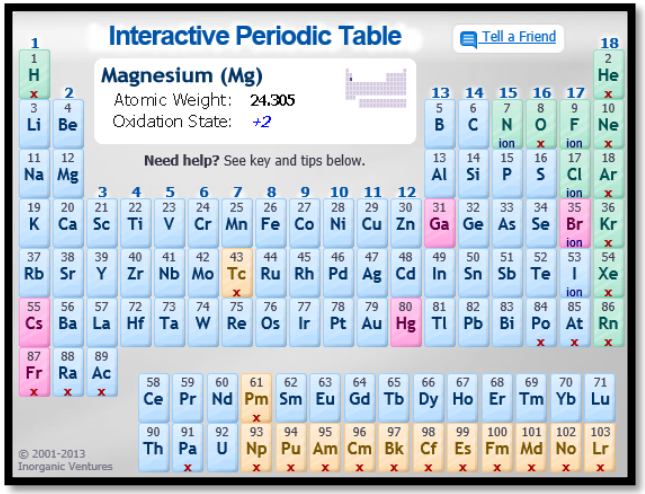
An in-depth look at trace metallic impurity determination by ICP-OES



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Key Points

- What is a 6020 Interference Check Solution (6020ICS)?
- What kinds of impurities matter most?
- Can I trust the number the instrument shows?
- What major interferences can I expect on ICP-OES?
- How do I interpret the spectra?

EPA Method 6020A

- Used for the determination of trace elements in water samples/wastes by ICP-MS
- Requires the use of an internal standard
  - (^{6}Li, Sc, Y, Rh, In, Tb, Ho, Bi, substitutions allowed)
- Requires the assessment of interferences
  - Includes isobaric, molecular, doubly-charged, physical, and memory interferences
  - Corrections can be made if validated
- Recommends a specific solution to use as an ICS

6020ICS-9A

(Synthetic matrix for water samples)

Element	ppm	Element	ppm
Al	1000	Mg	1000
C	2000	Mo	20
Ca	3000	Na	2500
Cl	21215	P	1000
Fe	2500	S	1000
K	1000	Ti	20
*User performs a 10x dilution			

6020ICS-9B

(Spike solution)

Element	ppm	Element	ppm
Ag	5	Mn	20
As	10	Ni	20
Cd	10	Se	10
Co	20	V	20
Cr	20	Zn	10
Cu	20		
*User performs a 10x dilution			

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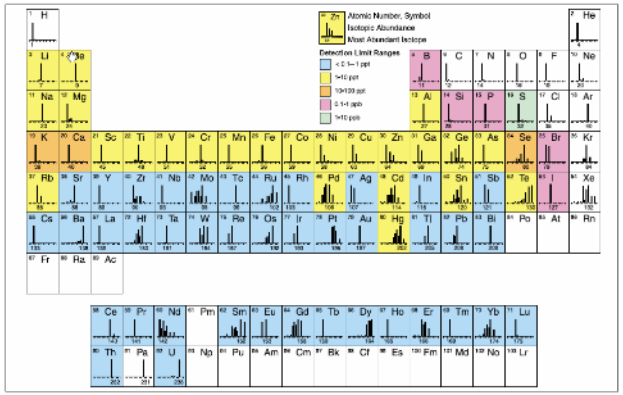

Which Elements Matter?

- Solution B elements matter most. (Major mass interference corrections are based on these elements)
- **All elements** not contained in solution A matter to some degree.
- Other elements not listed could matter depending on an analyst's specific circumstances.
- Each lab sets its own reporting limits.

6020ICS-9B

Element	ppm	Element	ppm
Ag	5	Mn	20
As	10	Ni	20
Cd	10	Se	10
Co	20	V	20
Cr	20	Zn	10
Cu	20		
*User performs a 10x dilution			

Major Sources of Contamination

Solution B Element	Potential Contamination Source from Solution A
As	**Fe**
Co	**Fe**
Cr	Al, **Fe**, C, Ca, Mg
Cu	**Fe**, Mg, K
Mn	Al, C, **Fe**, Mg
Ni	**Fe**, Mg
Zn	Al, C, Ca, Mg, P, K, Na

- Also need to worry about…
  - Deionized H_2O
  - Trace metals grade HNO_3
  - Transfer materials used
    - Weigh boats
    - Pipet tips
    - Pump tubing
  - Bottle material
    - Bulk containers
    - Acid leached bottles
  - Dust particles

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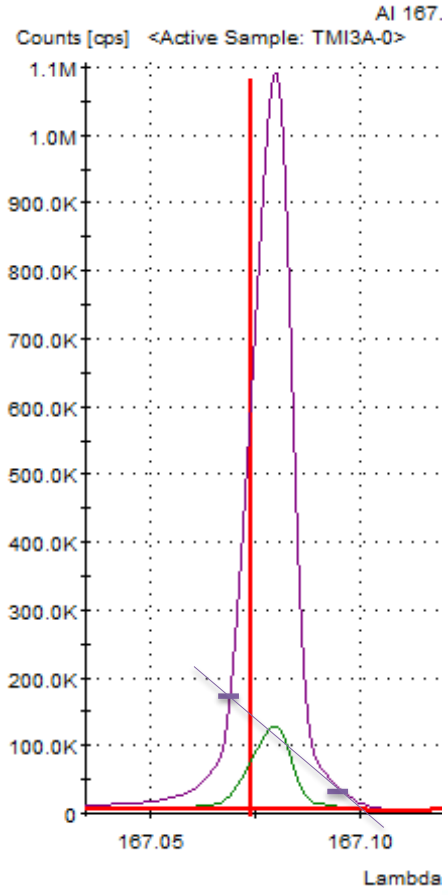
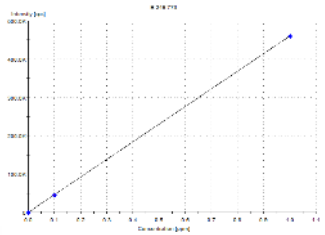
Can I trust the number?

- The short answer is **no**.
- Usually, the initial instrument number is inaccurate for solutions with complex matrices.
- Peak shifting could occur
- Background points may not be correct
- Elevated background signal may hide peaks or may not be the true baseline
- Spectroscopic interferences may directly affect the analytical line of interest
  - Run single element standards to confirm



More Considerations

- For calibration curves…
  - Standards should be matrix matched with the sample
  - Ionization buffers may help with signal depression present in high matrix samples
  - Internal standard correction factors could be too extreme
- Standard addition method is best for accuracy
  - Cannot identify interference issues without visual inspection of the spectra
  - May have trouble identifying the true zero point for a trace amount of impurity



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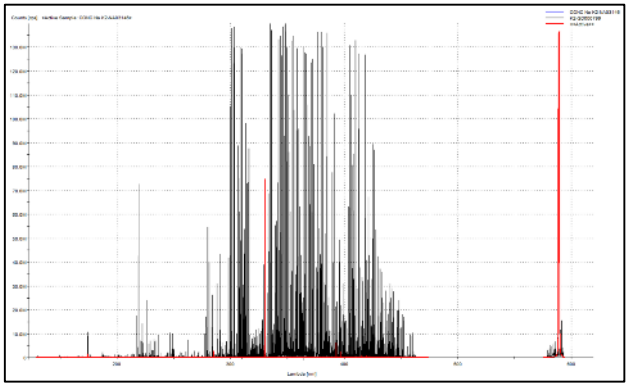
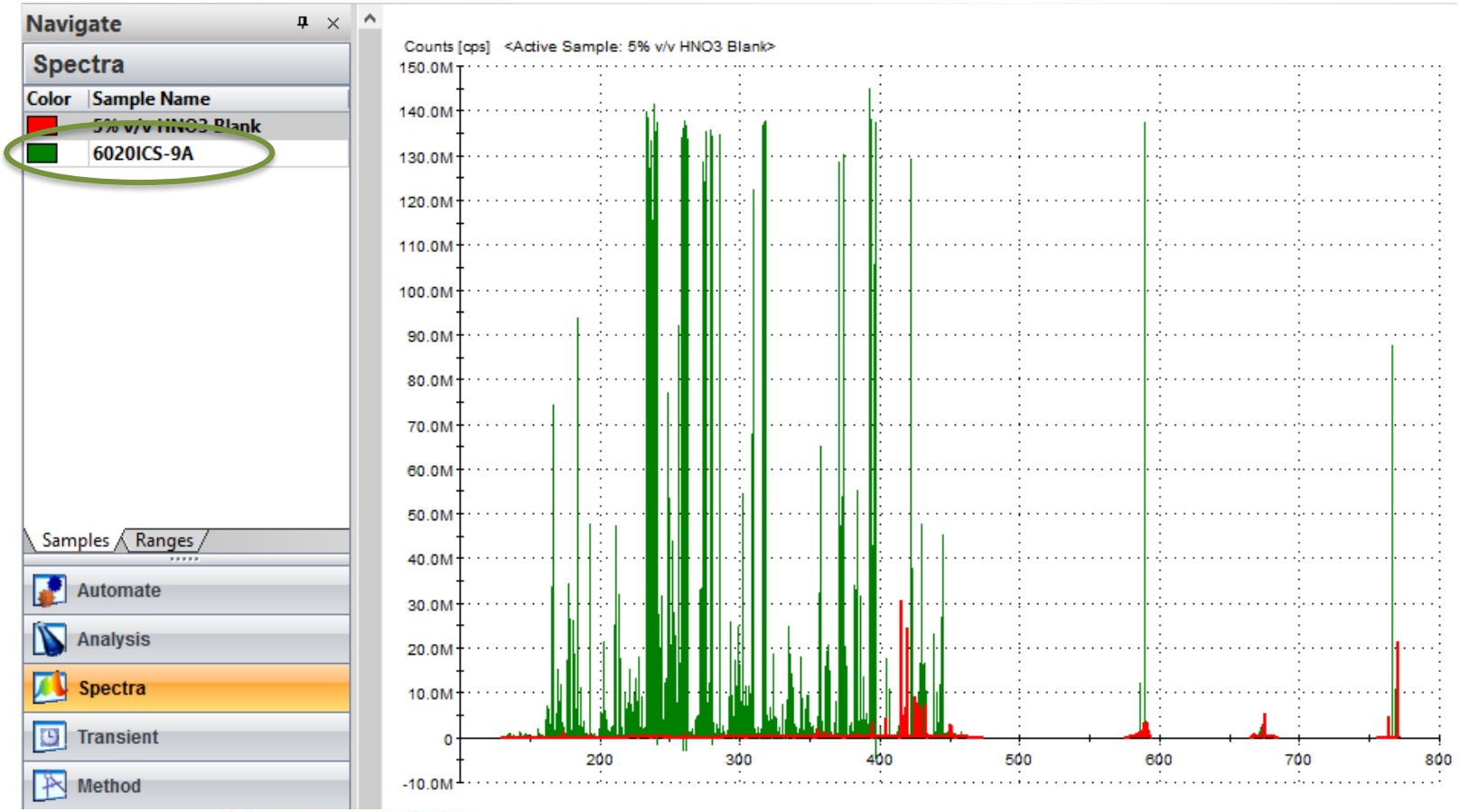
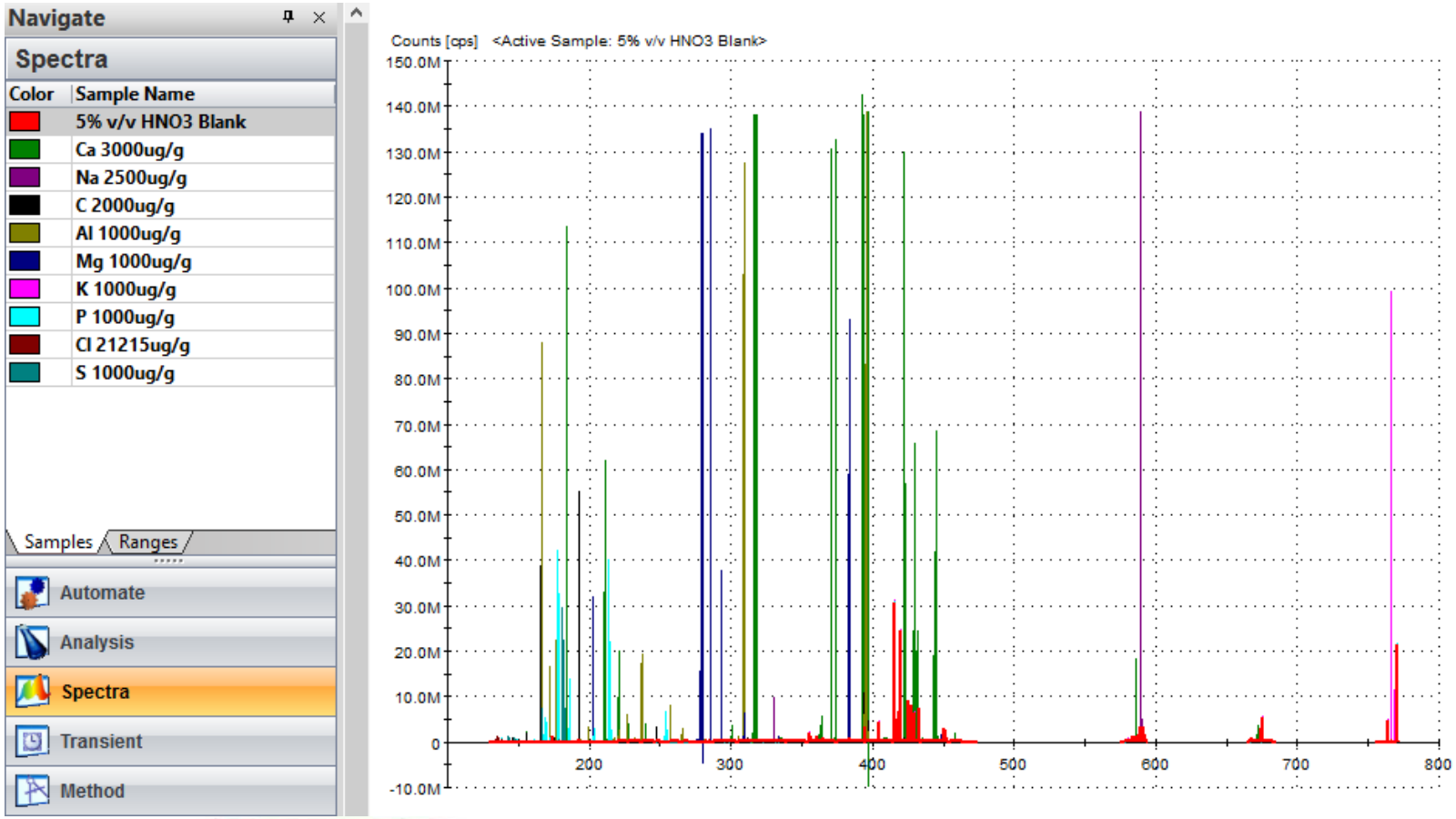


Full Spectra View of 6020ICS-9A



All Major Elements Except Fe



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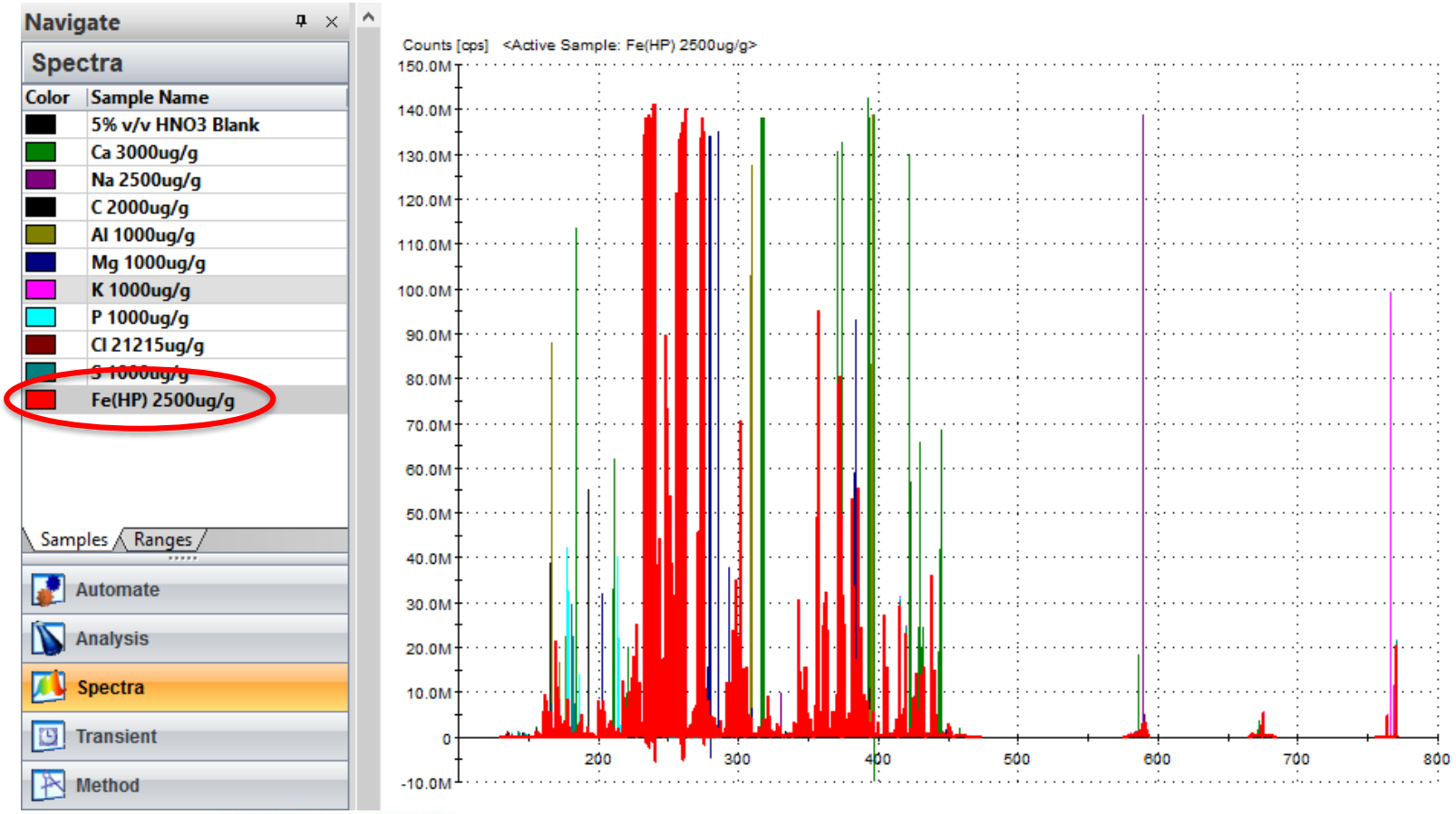
All Elements With Fe



High-level Elements of Concern

- Fe and other 1st row transition metals
- “HF” elements such as W, Zr, Mo
- All of the rare-earth elements
- Uranium is by far the worst
- Very important to run clean single element standards to verify the source of interferences
  - Utilize a lines library for guidance

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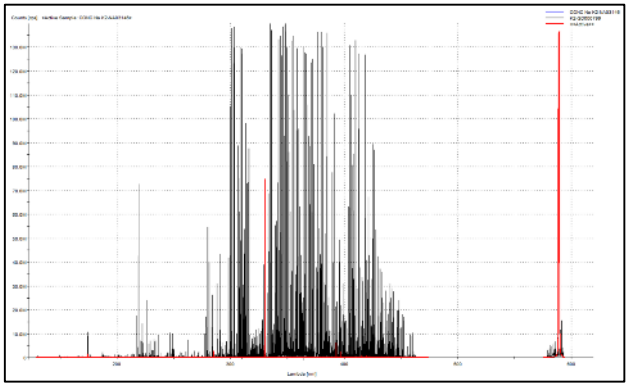
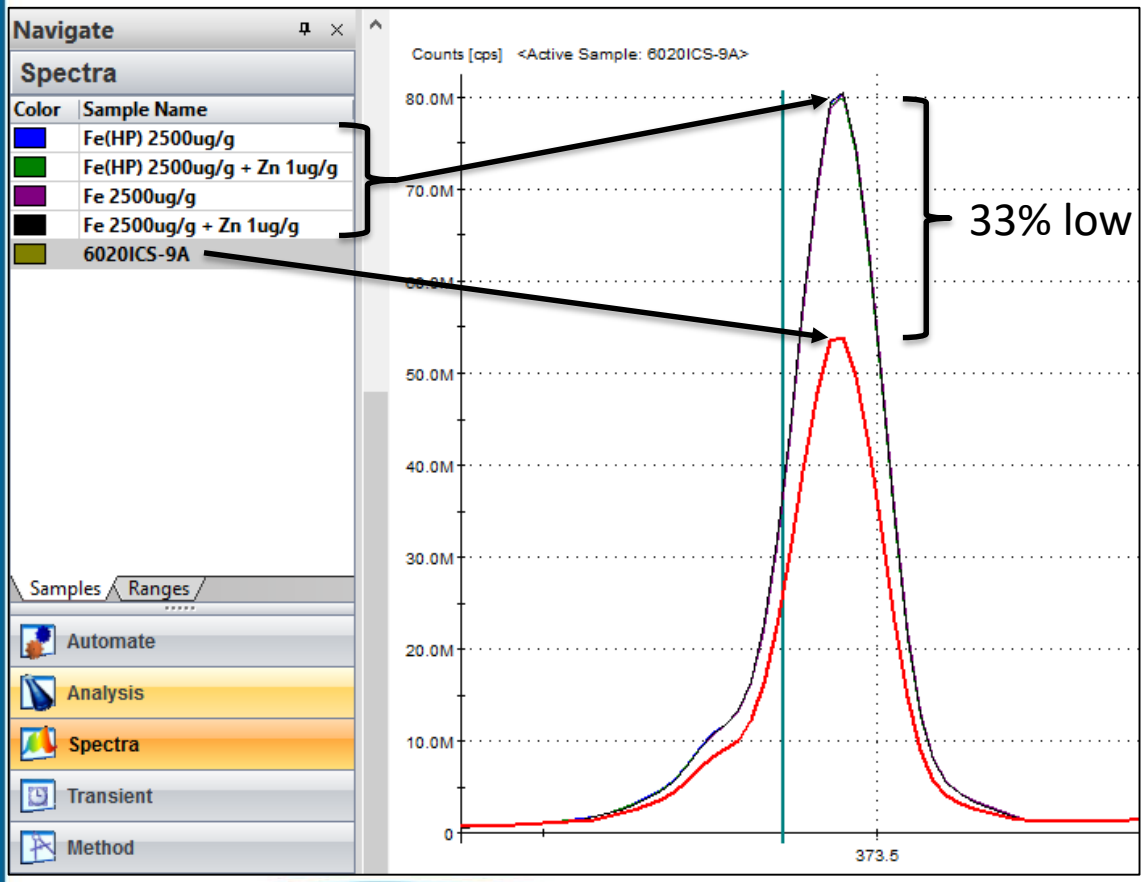


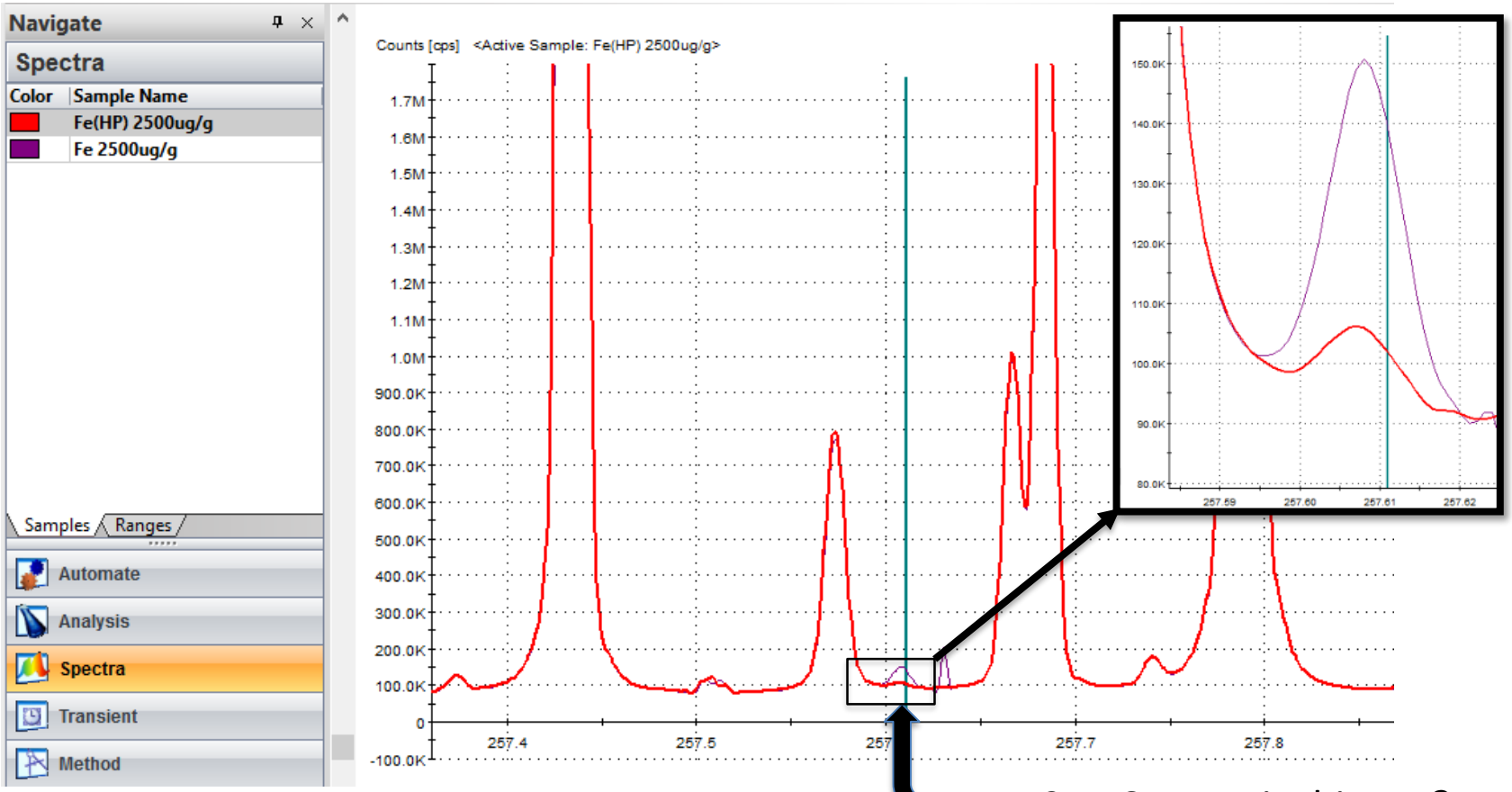
Example of Signal Quenching



- Good indication of signal quenching
- Consider using internal standard or ionization buffer

- All 5 samples contain the same amount of Fe.
- 1st 4 only contain Fe and low level Zn.
- 6020ICS-9A contains several other high matrix elements.

Is this Mn, or is it Fe?



Importance of 2nd Methods

- In this case, the spectral line is in fact Mn.
- A second source standard with differing impurity levels helped with interference determination.
  - In this case second source starting materials were used, Fe powder and Fe pieces
  - There was a clear difference in signal between the high purity Fe powder vs the lower purity Fe pieces.
- ICP-MS also supported the presence of Mn.
- How much Mn is there?

ICP-OES

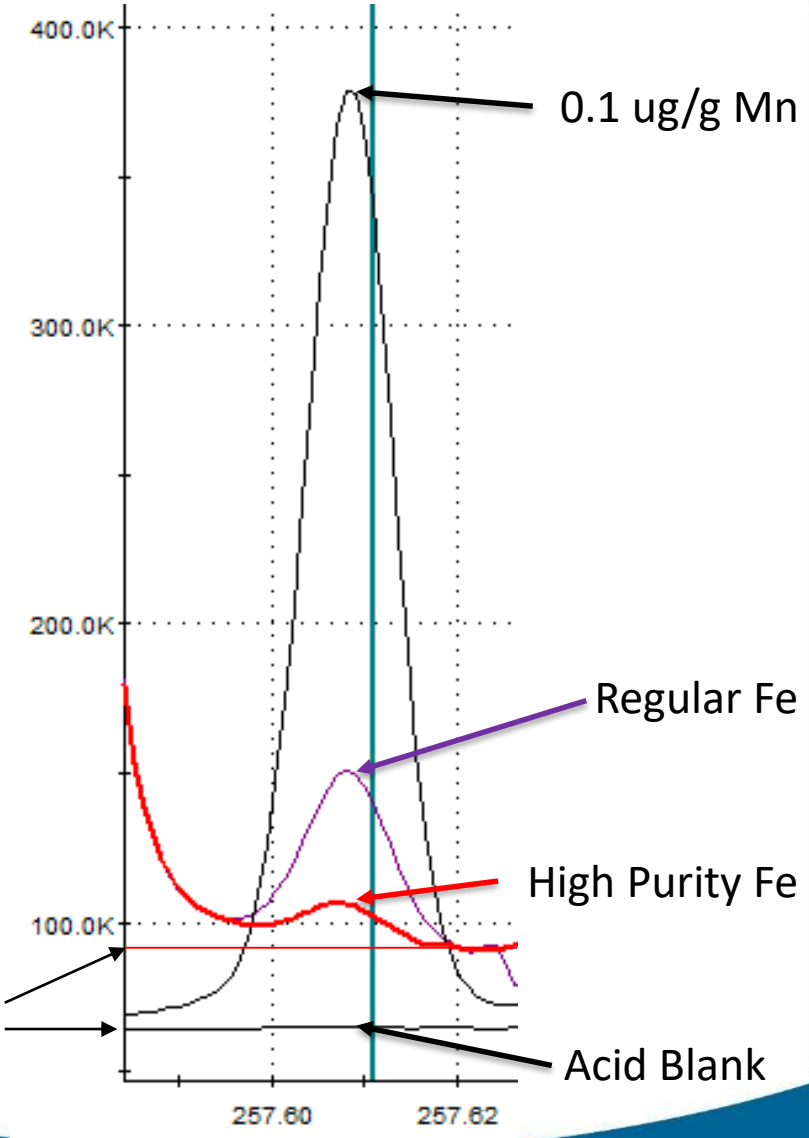
ICP-MS

Intensity readings for ICP-OES Calibration Curve:
0.1 ug/g Mn is 312,010 cps
Regular Fe is 60,370 cps to the red BG (19ppb)
Regular Fe is 84,860 cps to the black BG (27ppb)
HiPur Fe is 15,740 cps to the red BG (5ppb)
HiPur Fe is 40,295 cps to the black BG (13ppb)

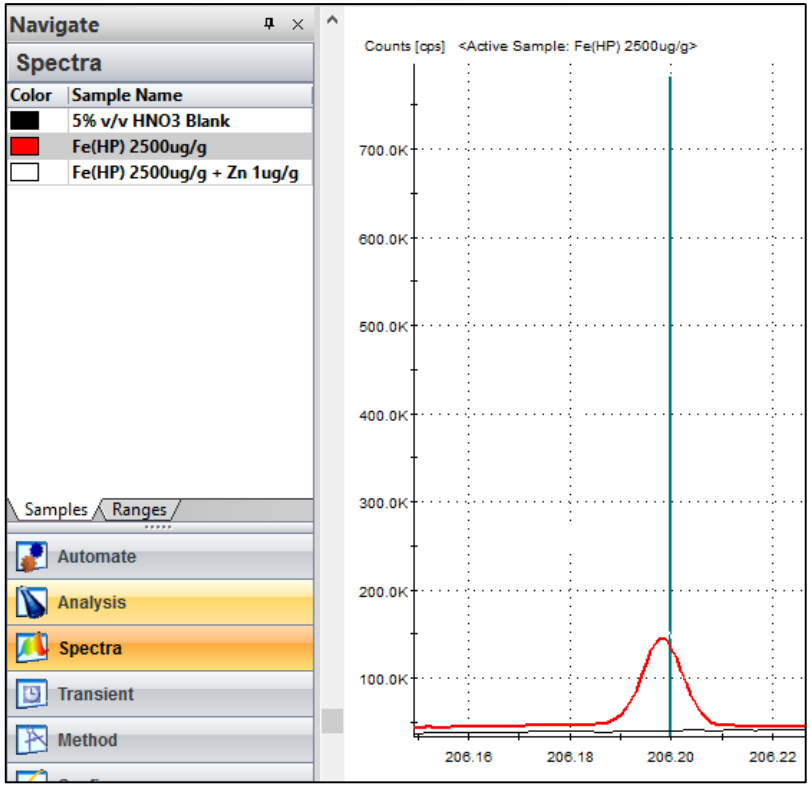
With ICP-MS standard additions method:
Regular Fe contains 36ppb Mn
High Purity Fe contains 9ppb Mn
(Known interference on mass $^{55}Mn^{+}$ with $^{54}FeH^{+}$)

Standard additions method by ICP-OES is probably best.
Would correct for signal quenching and help resolve the elevated background questions.

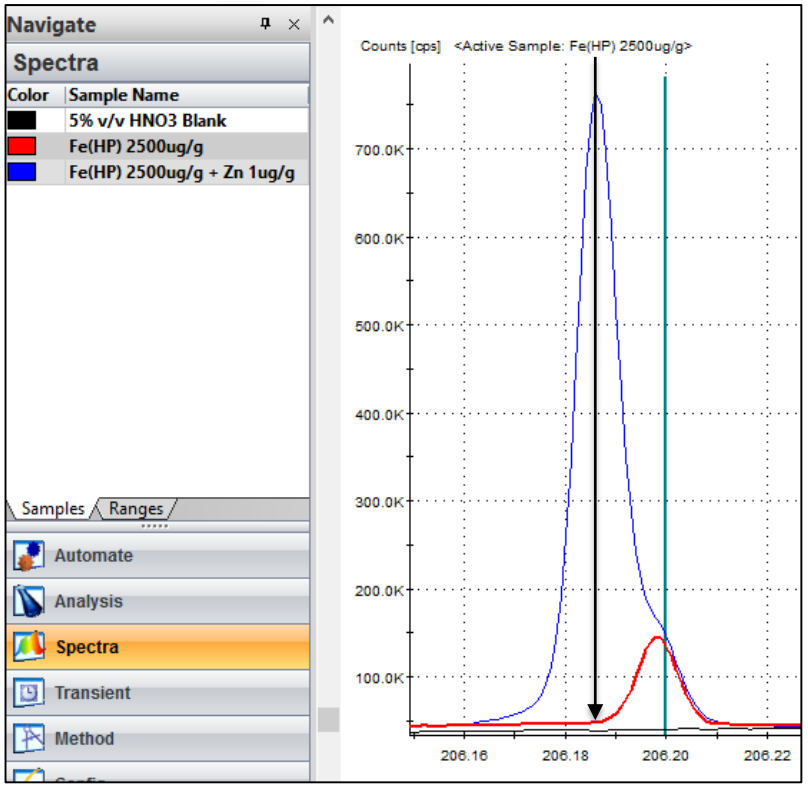
Which background is correct?



Is this Zn, or is it Fe?



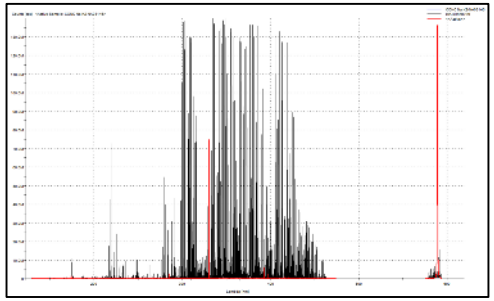
Zn 206.200nm? Or is this an Fe interference?



- It's Fe! The Zn 206.200nm line is not properly centered. There is actually no Zn present in this sample.

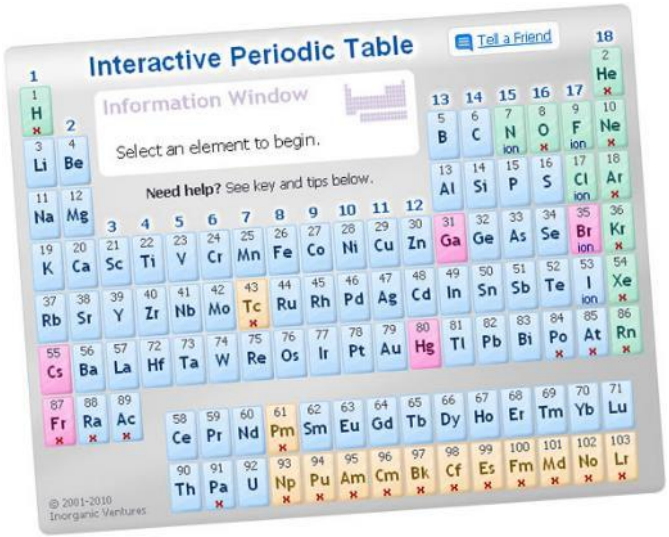
Key Advice for ICP-OES

- Always look at the spectra
  - Pay attention to the background points
  - Make sure the peak is centered
- Use a lines library for guidance
- Verify lines by running single element standards
- Use multiple lines or 2nd methods to confirm results



Technical Support – Available to Everyone

Online Resources at inorganicventures.com



Customers can visit our website's Tech Center, which includes:

- Interactive Periodic Table
- Sample Preparation Guide
- **Trace Analysis Guide**
- ICP Operations Guide
- Expert Advice
- And much, much more.