Fundamentals of Trace Impurity Analysis by ICP-OES

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INORGANIC VENTURES

Key Topics

- Defining our Goals
- Basic Sample Preparation Concerns
- Standards for Trace Metals Analysis
  - Stability
  - Compatibility Concerns
- ICP-OES Testing Strategies
  - Calibration Techniques
  - Interference Considerations
  - Detection Limits

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Overall Goals for a TMI Analysis

(Trace Metallic Impurity)

- ✓Measuring what's not supposed to be present
- ✓Ignoring what is expected to be in solution
- ✓Eliminating sources of contamination
- ✓Defining instrument detection limits (DLs)
- ✓Defining real-world DLs of the sample
- ✓Identifying interferences & method contamination
- ✓Confirming observations by second methods
  - If possible

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Sources of Contamination

- Containers
- Pipet Tips
- Weigh Boats
- Clean Air
- Reagents
- Digestion Methods

Container Selection

- **LDPE**, HDPE, PTFE, PFA, PP, Borosilicate Glass
  - Plastic made from virgin polyethylene is critical
- Sample tubes vs. **bottles**
- **Leach containers with dilute HNO_3 (1-5% v/v)**
- **High temperature leaching is more effective (50°C)**

PP?

PP

HDPE

PTFE

Boro Glass

Containers: More in-depth

Element	LDPE	HDPE	PP	PTFE	Boro
Al	2	*	87		8750
Ba					5000
B					9400
Ca		28	*	25	2800
Fe		150		95	125
Mg	6	11	575	15	125
K				16	3600
Na	42	63	42	90	27500
Zn					125

Values are the ng of impurity per 125mL bottle.

* We've seen it on occasion.

LDPE

- The good news, precious metals never show up in container materials.

Other Sources of Contamination

- Pipet Tips
  - Same contamination concerns as with sample tubes
  - Leaching tips if effective
  - Sterilized tips are for biologicals, not inorganic metals
- Weigh Boats
  - Notorious for dust contamination
  - Colored boats will have metallic contamination
    - Virgin or “natural” material is critical
  - May have surface calcium contamination

Reagent Purity

- Clean Acids (HNO_3, HCl, etc.)
- Clean Bases (TEA, NH_4OH, etc.)
- Clean DI Water (ASTM Type 1, 18MΩ)
- Particle Filtration (0.3µm or smaller)
- Use of reagent blanks
  - Critical for blank subtraction to determine true real-world sample impurity levels and detection limits

Digestion Methods

- How does this all tie in?
  - Open-air digestions
    - Clean air more critical
  - Microwave assisted digestions
    - Tubes are typically reused
    - Was everything cleaned properly?
  - Reagent/Method Blanks essential for proper assessment of TMI in a sample

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Standards for Trace Metals Analysis

- Standards for trace impurity testing can be fairly low – less than 10ppm
- The lower the concentration, generally the more elements you can put together
- Certain physical and chemical stability limitations exist
- Certain elements have compatibility issues depending on acid matrix

Stability

- Physical stability issues include:
  - Transpiration – Loss of H_2O through the walls of the bottle
  - Evaporation – Loss of H_2O through the bottle cap threads
  - Temperature – Change in density due to temperature
- Ways to minimize these issues include:
  - Resealing aluminized bags over your standards (heat seal)
  - Place standards in fridge for long term storage
  - Properly tighten caps (overtightening is just as bad)
  - Remove density from the equation (convert to w/w and weigh aliquots)

Precious Metals-Specific Stability

- Chemical stability issues involving HCl include:
  - Ag with HCl (Silver Chloride Precipitate, Photosensitive)
  - Tl^{+1} with HCl (Needs a Tl^{+3} starting material such as Tl_2O_3)
  - Pt with Cs (Can form Cs_2PtCl_6 precipitate)
  - Re with Cs (Can also form a precipitate like Pt)
  - Os with HNO_3 can cause insoluble oxides or OsO_4 to form
  - Au must have HCl for long term stability
  - Low level Pd must have HCl for long term stability
  - Hg and Pd in HNO_3 in LDPE can be lost to the bottle walls
    - Borosilicate glass is okay
    - Hg and Pd in HCl is okay in LDPE

Compatibility Concerns

- Regarding pure standards:
  - Most elements are okay in HNO_3 only
  - Some elements need/prefer HCl
  - Some elements need/prefer HF

HNO_3 HCl HF

Preferred Acid (if other than HNO_3 only)

H																He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Not Checked by ICP

HF

HCl

Specific Acid Compatibility Concerns

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

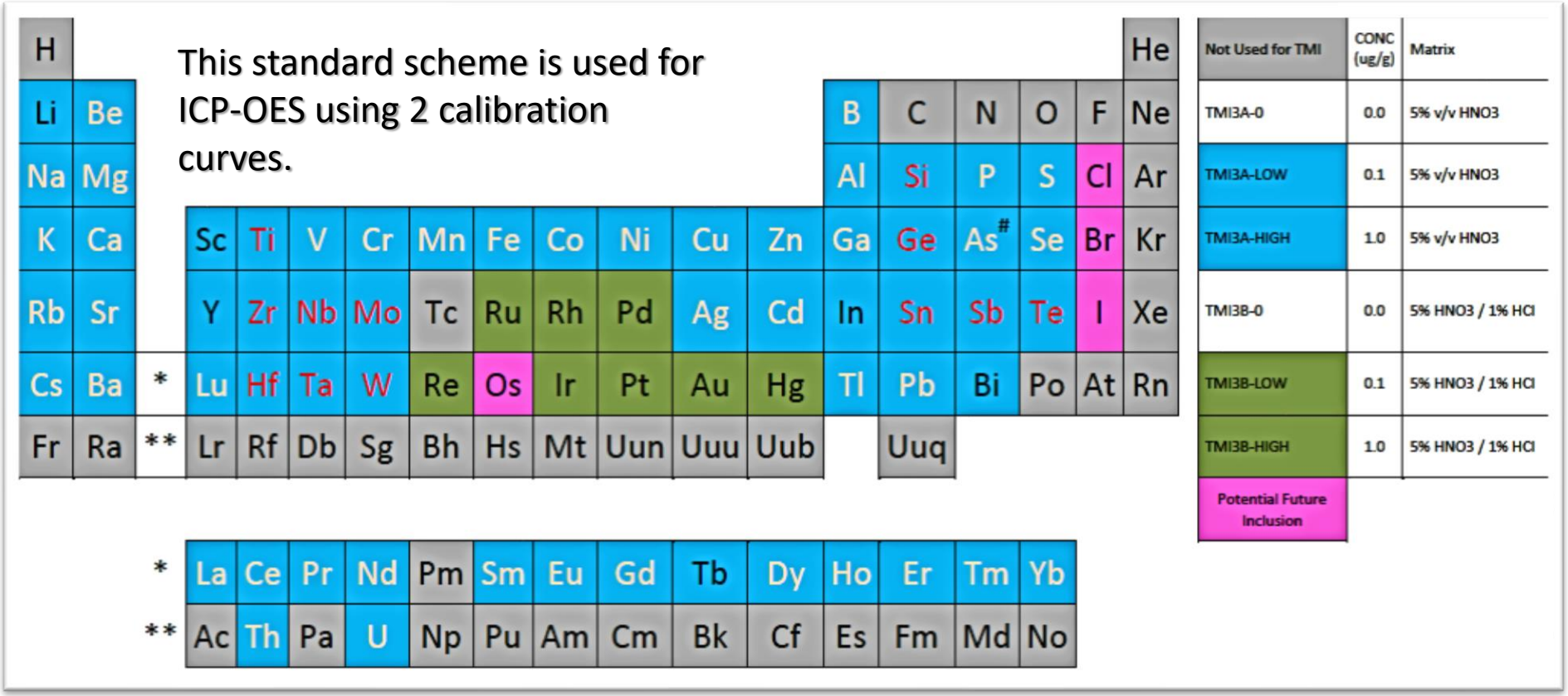
Not Checked by ICP

Avoid HF

Avoid HCl

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Periodic Table of TMI-OES Standards



Set 1 contains silver, so it does not have any HCl present

Both sets contain As to allow for evaluation on 228.812nm (Major Cd Interference)

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Calibration Techniques

- Calibration Curves
  - Easier to automate using instrument software
  - Requires careful inspection of spectra to check for:
    - Spectral Interferences
    - Background Correction Points
  - Can use an internal standard to correct for intro system and plasma based effects
    - This makes matrix matching less critical
    - Must choose an appropriate element absent from sample and free of interferences
  - ICP signal response is generally linear

Calibration Techniques

- Standard Additions
  - Much more accurate since matrices are matched
  - Requires there to be a clear flat background for an appropriate “zero” calculation
  - Again, requires careful inspection of spectra to check for:
    - Spectral Interferences
    - Background Correction Points
  - Generally does not employ the use of an internal standard
  - Instrument software usually does not allow for this method, almost always requires offline spreadsheet work
  - Multi-element additions can be tricky

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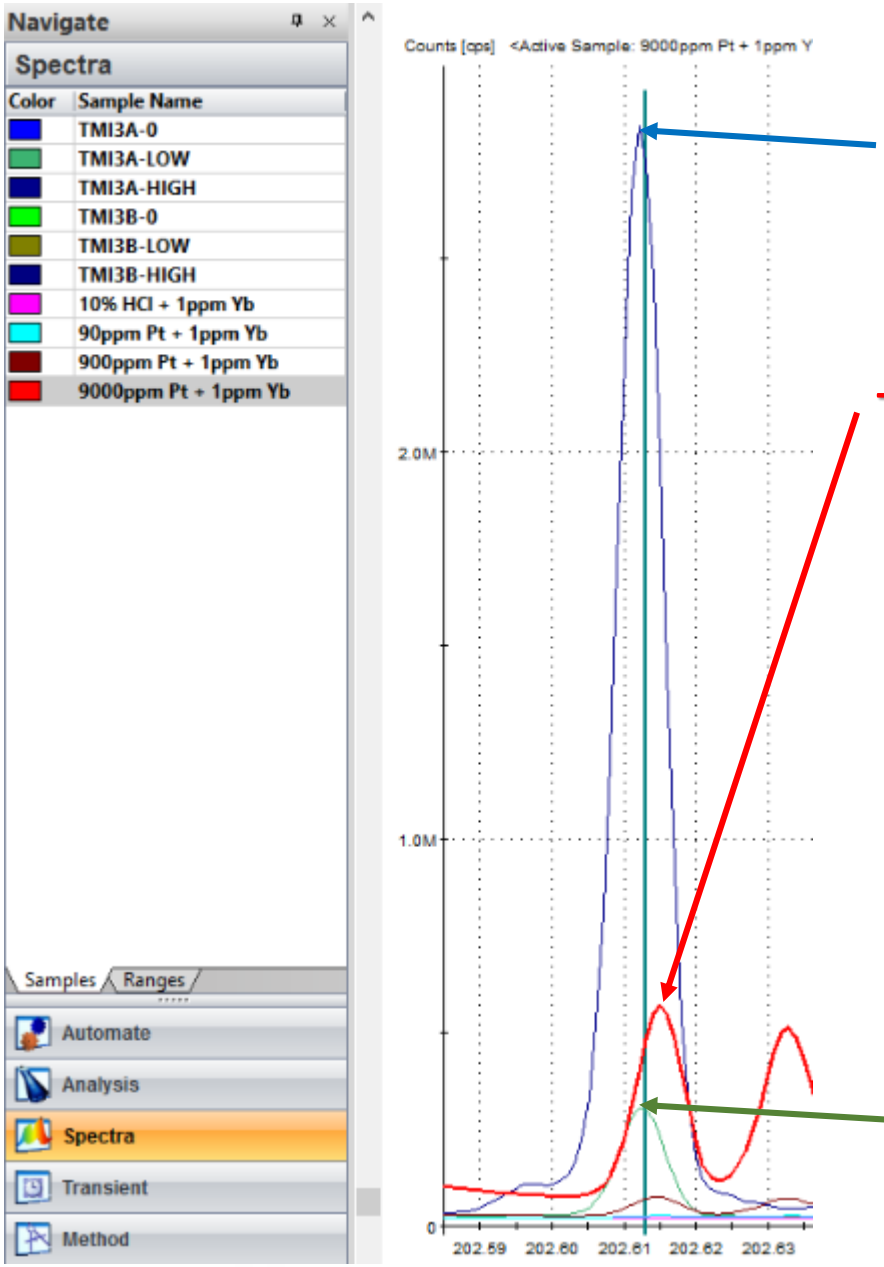
Interference Considerations

- You should always examine spectra
  - Check for proper background corrections
  - Make sure the peaks are centered
  - Some instrument software packages don't always do what you think they do (quick manual calculation checks are not that complicated)
- If you need to determine the source of an interference:
  - Run single element standards to confirm
  - Check blanks after samples (memory interferences)

Zn 202.613nm

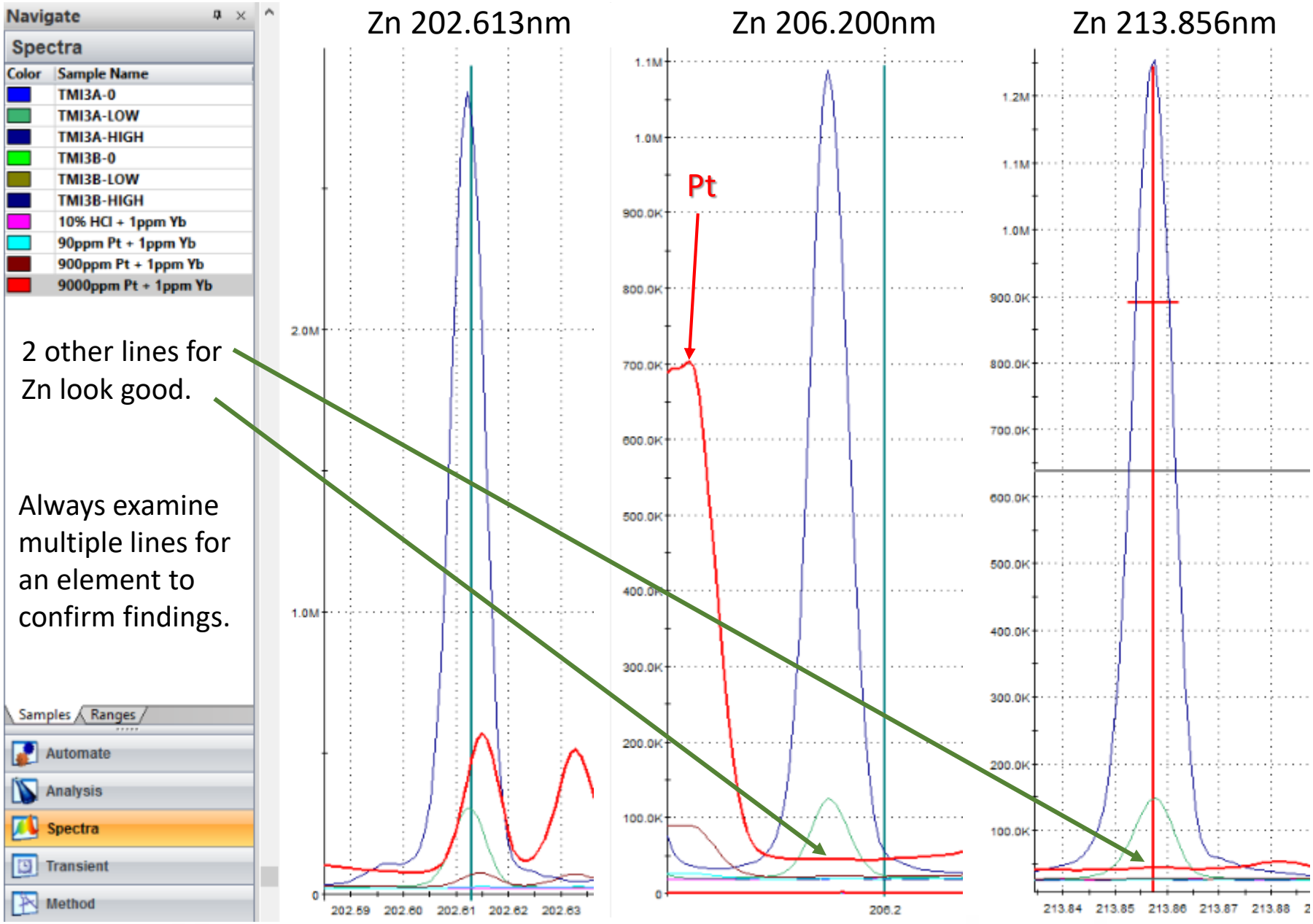


1ppm Zn

This is not Zn. How do we know?

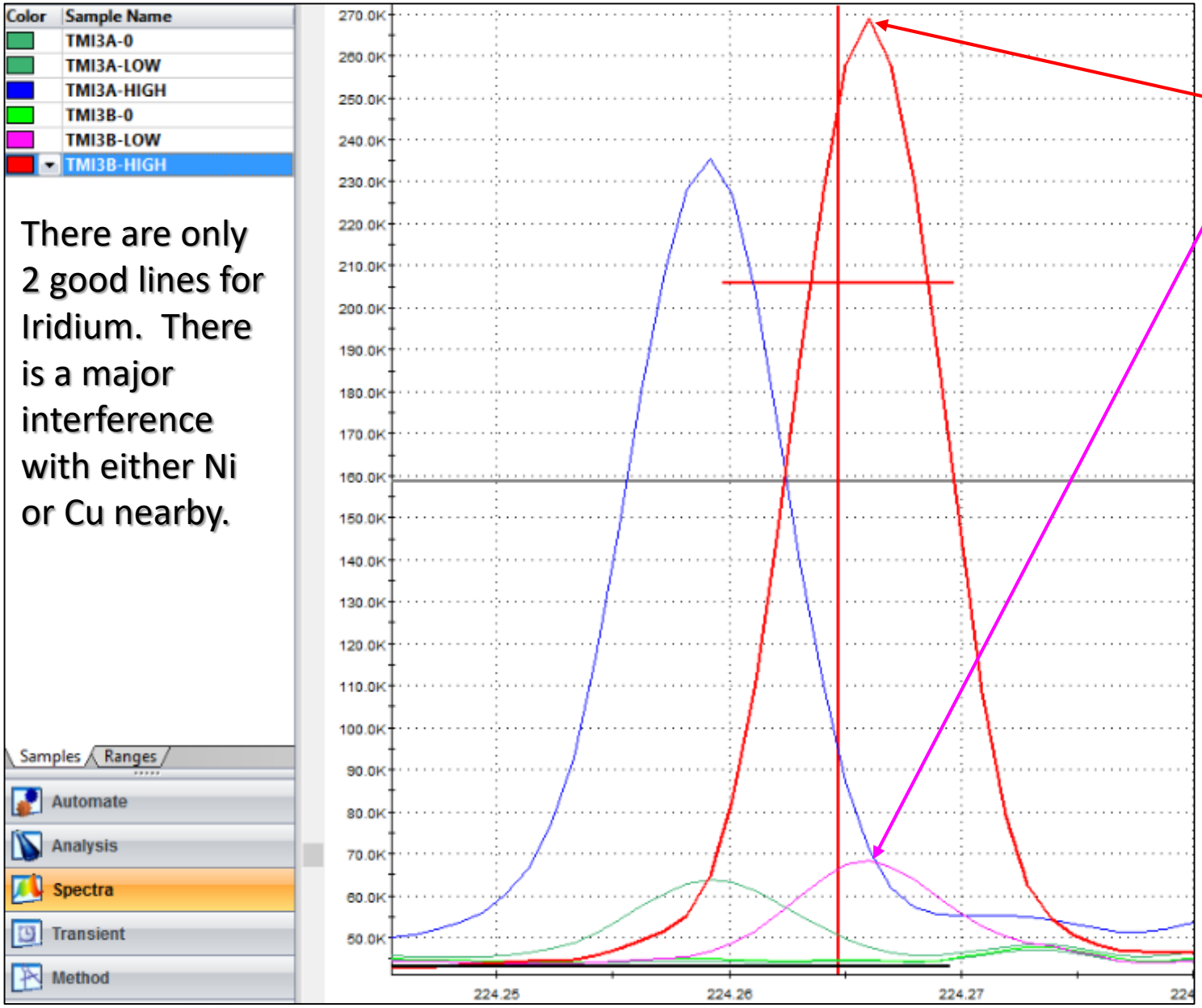
- The peak is not centered on the single-element standard.
- There really isn't anything else that can be assumed by looking at this line.
- What do the other OES Zn lines look like?

0.1ppm Zn

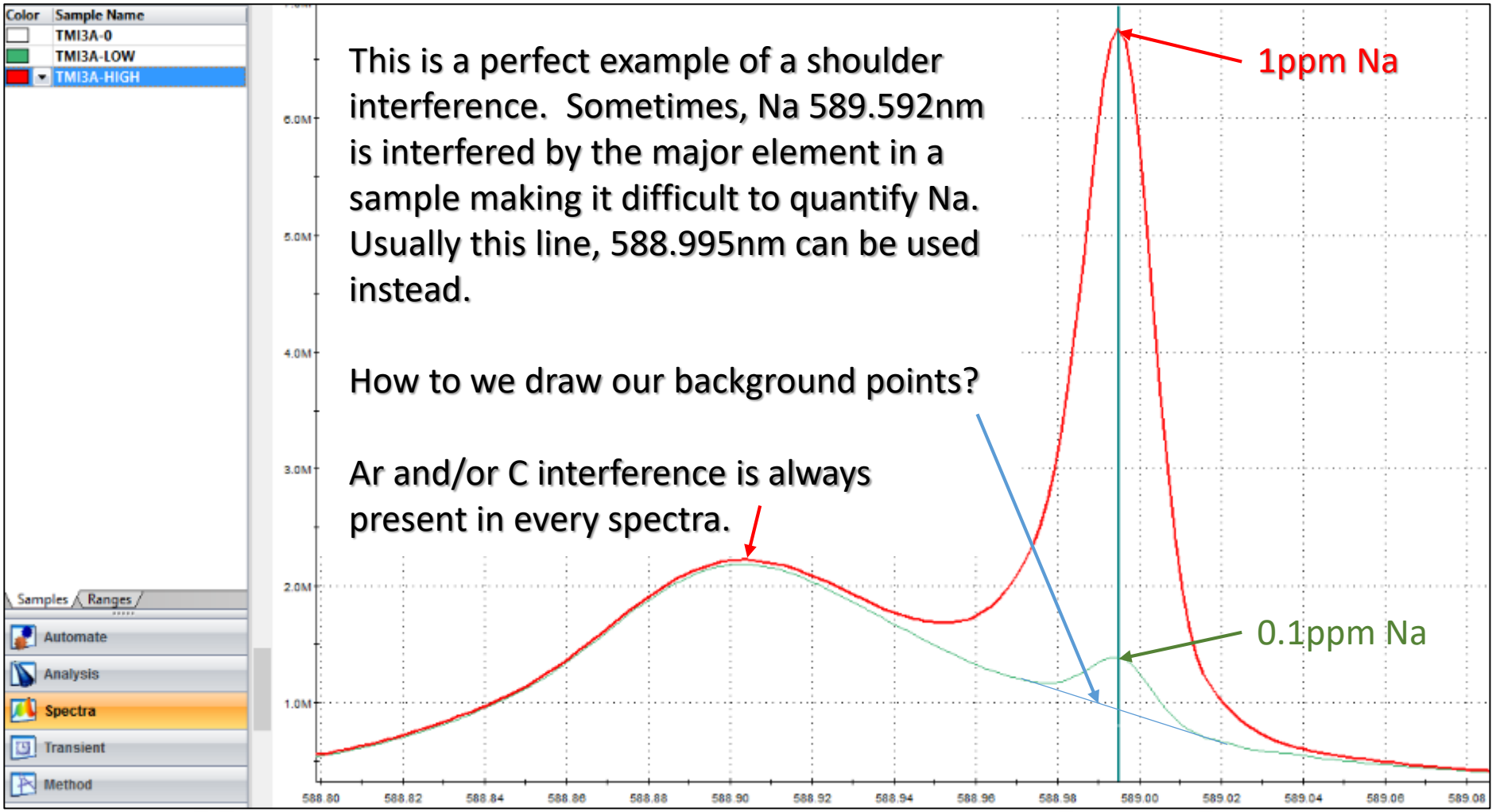

Navigate
Spectra
Color
Sample Name
TMI3A-0
TMI3A-LOW
TMI3A-HIGH
TMI3B-0
TMI3B-LOW
TMI3B-HIGH
10% HCl + 1ppm Yb
90ppm Pt + 1ppm Yb
900ppm Pt + 1ppm Yb
9000ppm Pt + 1ppm Yb
Zn 202.613nm
Zn 206.200nm
Zn 213.856nm
Pt
2 other lines for Zn look good.
Always examine multiple lines for an element to confirm findings.
Samples
Ranges
Automate
Analysis
Spectra
Transient
Method
2.0M
1.0M
0
1.1M
1.0M
900.0K
800.0K
700.0K
600.0K
500.0K
400.0K
300.0K
200.0K
100.0K
0
1.2M
1.1M
1.0M
900.0K
800.0K
700.0K
600.0K
500.0K
400.0K
300.0K
200.0K
100.0K
202.59
202.60
202.61
202.62
202.63
206.2
213.84
213.85
213.86
213.87
213.88

Types of Interferences

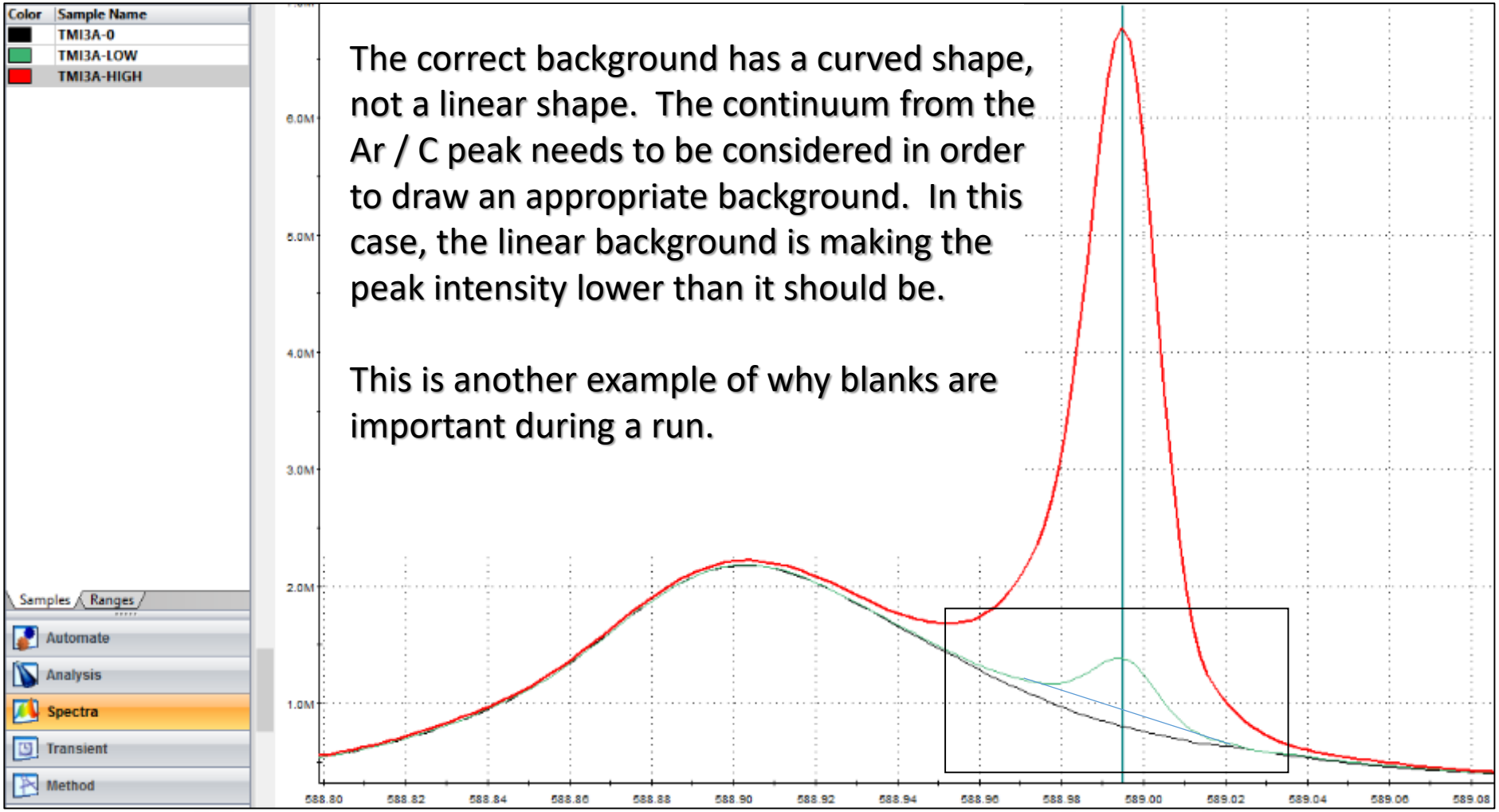
- Complete spectral overlap
  - Must be confirmed using single element standards
  - Some instrument software suites allow for subtraction
- Shoulder interferences
  - Are not too complicated to correct
  - Must use a curve background correction instead of linear
- Memory interferences
  - Can cause trouble if running multiple samples
  - Different rinse strategies can help speed up washout


Color
Sample Name
TMI3A-0
TMI3A-LOW
TMI3A-HIGH
TMI3B-0
TMI3B-LOW
TMI3B-HIGH
There are only 2 good lines for Iridium. There is a major interference with either Ni or Cu nearby.
Samples
Ranges
Automate
Analysis
Spectra
Transient
Method
270.0K
260.0K
250.0K
240.0K
230.0K
220.0K
210.0K
200.0K
190.0K
180.0K
170.0K
160.0K
150.0K
140.0K
130.0K
120.0K
110.0K
100.0K
90.0K
80.0K
70.0K
60.0K
50.0K
224.25
224.26
224.27
Ir 224.268nm
1ppm Ir
0.1ppm Ir
This is an example of partial spectral overlap.

Shoulder Interferences



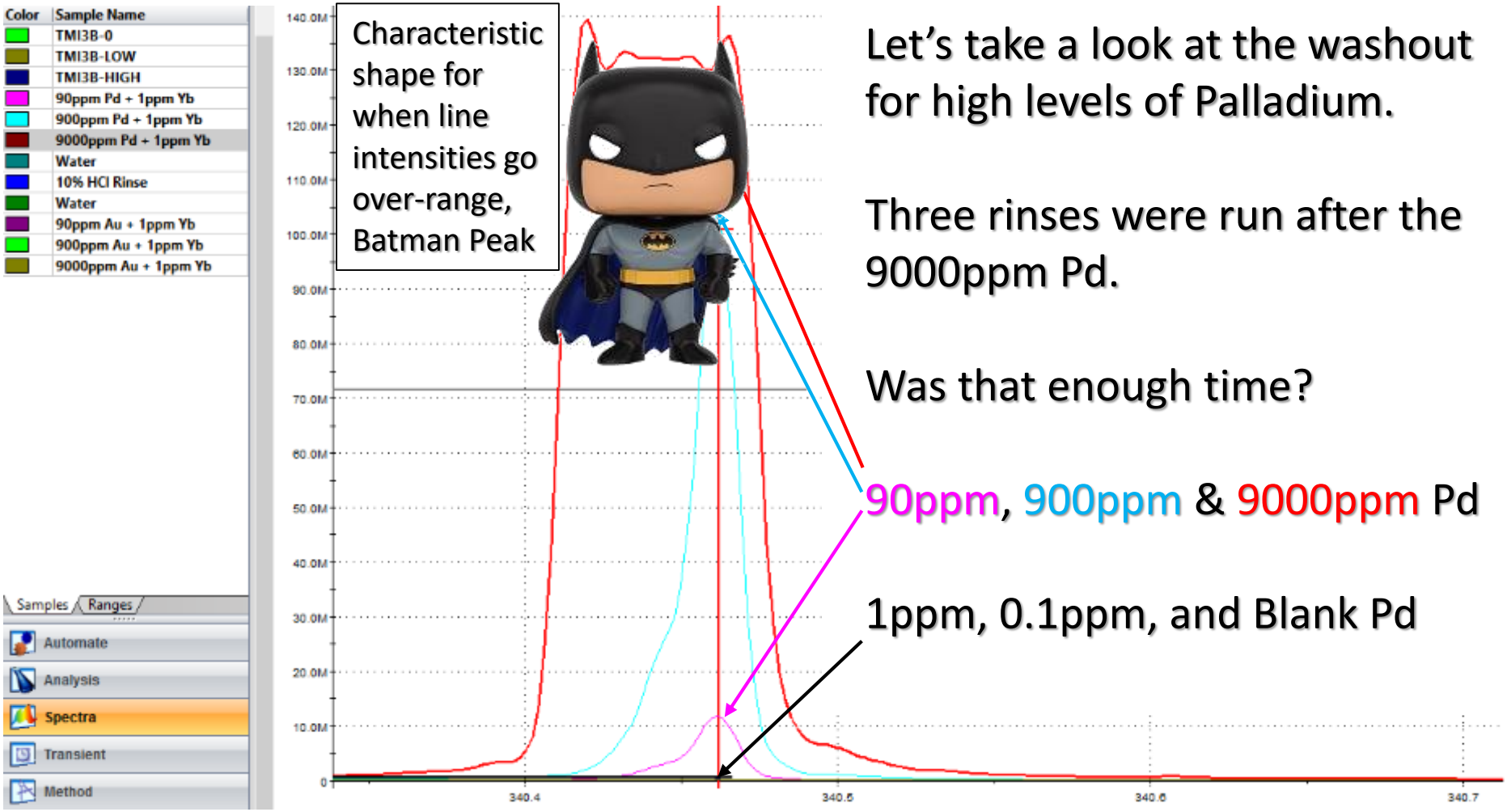
Shoulder Interferences



The correct background has a curved shape, not a linear shape. The continuum from the Ar / C peak needs to be considered in order to draw an appropriate background. In this case, the linear background is making the peak intensity lower than it should be.

This is another example of why blanks are important during a run.

Memory Interferences



Let's take a look at the washout for high levels of Palladium.

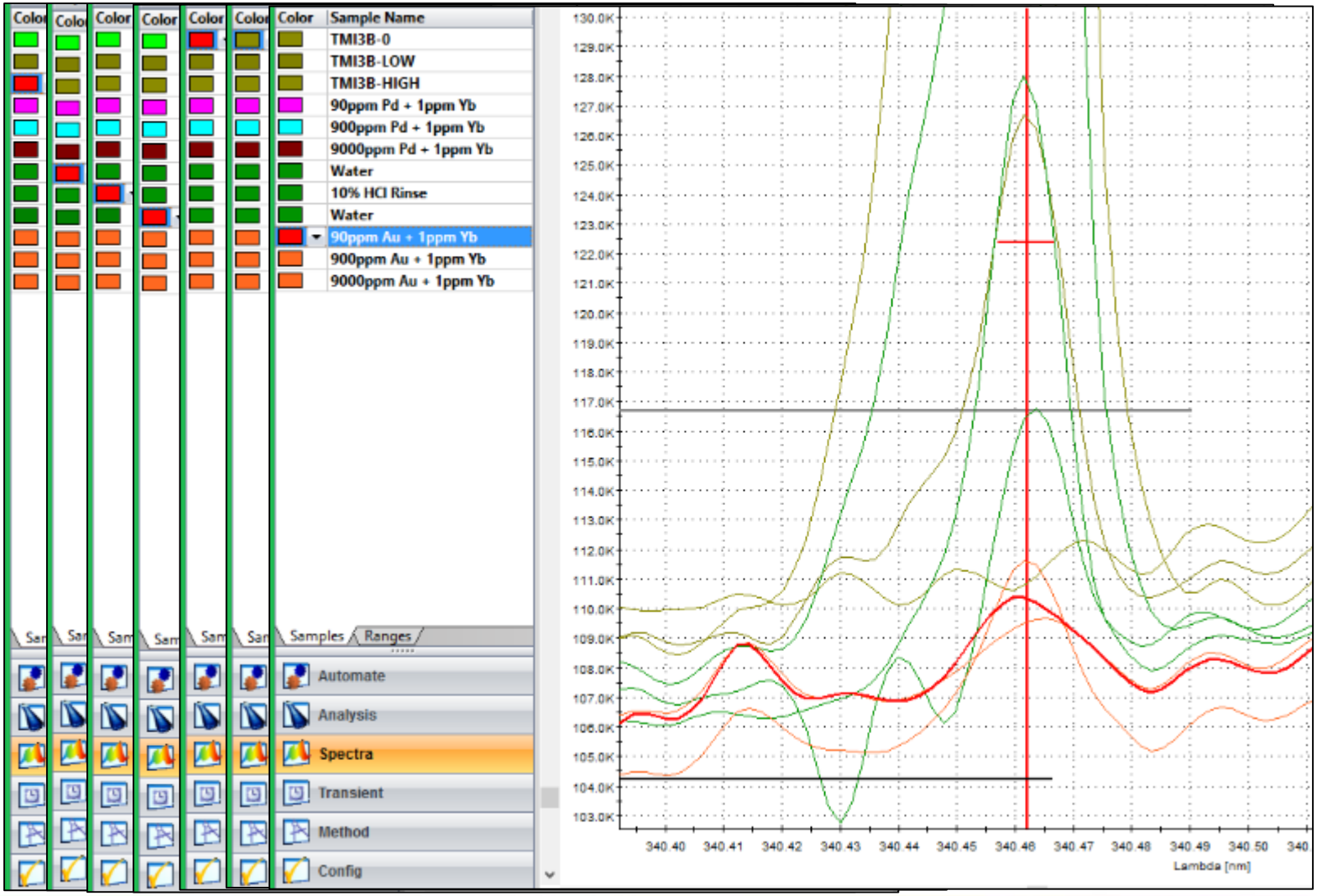
Three rinses were run after the 9000ppm Pd.

Was that enough time?

90ppm, 900ppm & 9000ppm Pd

1ppm, 0.1ppm, and Blank Pd

Memory Interferences



Memory Interferences

- 3 Rinses (as samples) did not fully washout Pd
  - Rinses never went to baseline according to initial blank
- Now there is a peak in the subsequent Au standards
  - We are not confident that Pd is present due to potential memory interferences
  - We should rerun Au on a clean system OR
  - We should confirm results by ICP-MS

Washout Recommendations

- Water by itself works for certain elements.
- 5-10% HCl works well for most of the precious metals
- Adding thiourea can help with Au and Hg
- Hydroxylamine hydrochloride helps with Os
- When in a crunch for time, change out the peri-pump tubing.
  - The PVC material tends to be the worst offender for memory interferences.
- Glass systems should work well for precious metals
- HF-resistant systems can have trouble with Hg in HNO_3

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Defining Detection Limits

- Limit of Detection (LOD)
  - Defined as 3 times the standard deviation of the blank
  - Can be calculated using
    - peak to peak noise or extrapolation to zero on a calibration curve
    - Calibration curve should have 3 concentration zones (low,mid,high) approximately 10x difference in concentration, (ex. 0.1ppm, 1ppm, 10ppm)

Defining Detection Limits

- Limit of Quantification (LOQ)
  - Defined as 10 times the standard deviation of the blank
  - Calculated using the same values used for LODs
  - LOQs will have an uncertainty of approximately 30% at the 95% confidence level
  - Most impurities found in clean standards are below LOQ, which is one reason why we don't "certify" trace levels of impurity

Defining Detection Limits

- Detection limit values are run-specific on an ICP
  - Defined by the background signal noise of a blank
  - Depend on the standards used
  - Depend on instrument conditions
  - As an instrument ages, the detection limit values will raise over time
  - You will never have the same levels attainable at the time of instrument setup with a brand new ICP

Real World Detection Limits

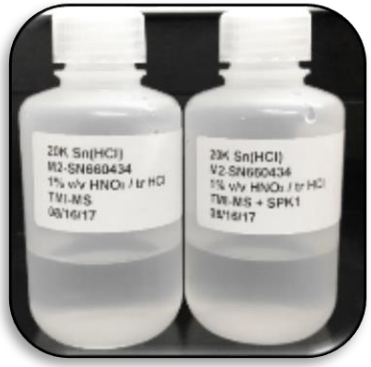
- Must use dilution factors to translate back to starting material
- Most samples must be diluted in order to run at levels that will keep the ICP running
  - High Na, K, Cs can shut the plasma off
  - High total dissolved solids (TDS) can clog the nebulizer
  - Greater than 2000ppm TDS on MS will make internal lenses dirty (requires a service call to clean)

Real World Detection Limits

99.93µg/g Sn ← 17,738µg/g Sn ← 1,000,000µg/g Sn

Found 452pg/g Pb → Found 80.23ng/g Pb → Found 4,523ng/g Pb

DL 1pg/g DL 0.18ng/g DL 10ng/g Pb



Dilution of sample acceptable for ICP-MS Testing

Sn dissolved in HCl and H_2O OK on ICP-OES

Sn Shot Starting Material

ICP-OES Detection Limits

Emission Line	LOD (ppb)	LOQ (ppb)	Major Problems?
Au 242.795	6	20	Pt overlap
Au 267.595	23	75	Ta, Nb, or Co?
Ir 212.681	12	40	Pt shoulder
Ir 224.268	18	60	
Pd 324.270, 340.458	26-30	85-100	
Pt 214.423, 191.170	27-36	90-120	
Rh 343.489	26	85	Pt shoulder
Rh 233.477	12	40	
Ru 240.272	6	20	Pt shoulder
Ru 267.876	11	35	Cr, Zr, and Pt shoulder
Ag 328.068, 338.289	5-9	15-30	
Re 221.426	8	25	Pt
Re 227.525	15	50	Sr
Os 225.585, 228.226	13-14	45-46	

These detection limits are based on peak to peak noise and a 100ppb calibration standard.

9000ppm Pt, Au, Pd were evaluated for interferences.

ICP-MS Detection Limits

Mass	LOD (ppb)	LOQ (ppb)	Major Interference
^{99,101}Ru	0.1	0.3	
^{103}Rh	0.1	0.3	
^{105,108}Pd	0.1-0.2	0.3-0.6	^{108}Cd
^{107,109}Ag	0.1-0.2	0.3-0.6	
^{185,187}Re	0.1	0.3	^{187}Os
^{188,189}Os	0.1	0.3	
^{191,193}Ir	0.1	0.3	
^{194,194}Pt	0.1	0.3	
^{197}Au	0.3	0.9	

These detection limits are based on the standard deviation of 3 blank readings and a 4ppb spike standard.

100ppm Pt, Au, Pd were run by standard additions

Results shown are multiplied by 90 to show DLs & LOQs with respect to a 9000ppm solution of each element, Pt, Au, Pd.

Instrument Comparison

Element	ICP-MS LOQ (ppb)	ICP-OES LOQ (ppb)
Ru	0.3	20-35
Rh	0.3	40-85
Pd	0.3-0.6	85-100
Ag	0.3-0.6	15-30
Re	0.3	25-50
Os	0.3	45-46
Ir	0.3	40-60
Pt	0.3	90-120
Au	0.9	20-75

Even though sample run on the ICP-MS was diluted 100X, DLs and LOQs were 2 orders of magnitude better.

ICP-MS uses less sample for testing (larger dilution with better results).

ICP-MS has less interferences for precious metal elements.

ICP-OES has better % RSDs.

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Summary

- Plan out your testing strategy & sample prep
- Eliminate sources for issues
- Choose standards wisely
- Flesh out the details for your ICP analysis
  - Calibration technique
  - Examine your spectra!
  - Interference determination and elimination
  - Detection limit comparisons

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.