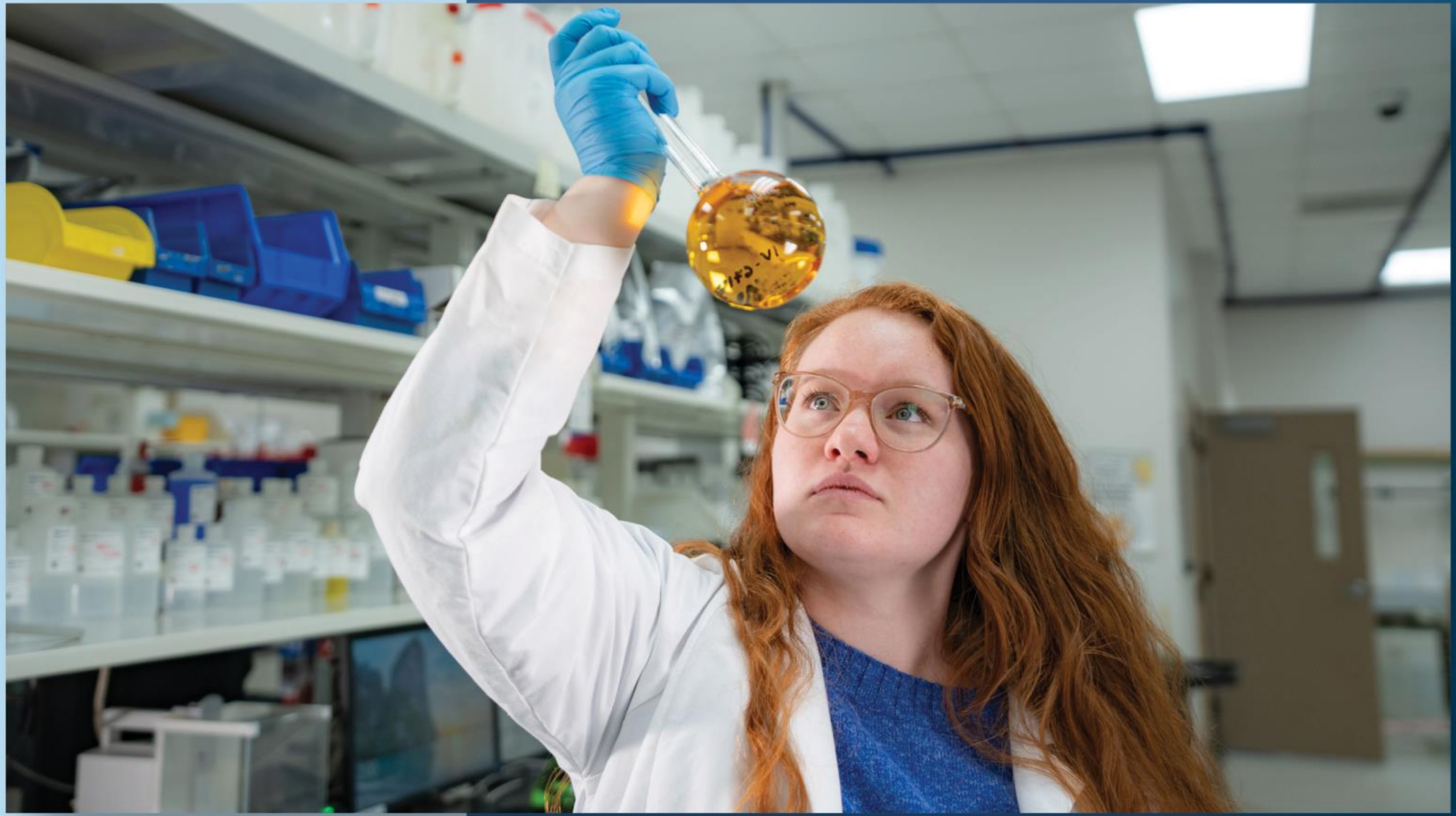

Tips for Trace Analysis by ICP-OES & ICP-MS

Mike Booth
Innovation & Applications
Development Manager

What does Inorganic Ventures do?

Inorganic Ventures is a manufacturer of inorganic Certified Reference Materials (CRMs) commonly referred to as a "standards", "chemical standards" or "calibration standards".

- Elemental Standards
  - High Purity Single Element
  - Custom Blends
- pH Standards
- Conductivity Standards
- Titrants
- Reagents

2 Day Turn-Around-Time on Stock Products!
10 Day Turn-Around-Tine on Custom Products!

01

Top Topics for Today:

- **Environmental Contamination**
  It is critical to be as contaminant free as possible for accurate trace analysis work.
- Solution Matrix
- Washout Issues
- Uncertainty of Measurements

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

Container Selection

More In-Depth

Values are the ng of impurity per 125mL bottle.

*** We've seen it on occasion.**

LDPE

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

Leaching Observations

- Un-leached bottles do contain some metallic impurities
- After high temperature leaching, impurities are significantly reduced.
- Allowing hot solution to mix within the bottles significantly reduced the amount of impurity left behind
- Chemical dishwashers deposited significant amounts of metallic impurities onto the bottle walls.
  - Chemical dishwashers contain stainless steel parts.

How Do We Leach Bottles?

- Pre-make 1-5% HNO_3
- Does not need to be highest purity acid

- Stand the bottles upright using automation

- Fill the bottles completely and cap them

How Do We Leach Bottles?

- Allow bottles to sit for at least 7 days at room temp (20°C)
  - Or 4 days at 50°C

- Empty out the bottles and rinse at least 3Xs with DI H_2O

- Clean bottle for general purpose use
  - Ex. trace analysis

Environmental Contamination

- Classed clean rooms help prevent particle contamination
- Several criteria to consider to class a clean room
  - Air changes per minute
  - Filter efficiency (ULPAs or HEPAs)
  - Ceiling type / ceiling panel material
  - Light fixture type
  - Wall and floor material
  - Air return location
  - Assessed by counting # of particles of specified size

Classed Clean Room Summary

Criteria	Class 10 ISO4	Class 100 ISO5	Class 1,000 ISO6	Class 10,000 ISO7	Class 100,000 ISO8
Air changes/min	8-10	5-8	3	1	0.33
Filter Coverage	90-100%	60-70%	20-30%	7-15%	4-5%
Filter Efficiency	99.9997%	99.997%	99.997%	99.997%	99.97%
Ceiling Type	Al T-bar grid	Al T-bar grid	Al T-bar grid	Conventional T-bar grid	Conventional T-bar grid
Light Fixture Type	Tear Drop or flow thru	Tear Drop or 2'x4' cleanroom fixture	2'x4' cleanroom fixture	2'x4' cleanroom fixture	2'x4' standard fixture
Air Returns	Raised Floor or center	Low wall on long axis	Low wall on perimeter	Low wall	Low wall or ceiling

Reagent Purity

- Clean Acids (HNO_3, HCl, HF, 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

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02

Top Topics for Today:

- Environmental Contamination
- **Solution Matrix**
  Will your sample and standards be stable for your analysis?
- Washout Issues
- Uncertainty of Measurements

Solution Matrix

- Most elements are stable using only HNO_3
- Some elements require HF for stability
  - HF stability often revolves around plastic surfaces
  - Some elements will precipitate in the presence of HF
- Some elements require HCl for stability
  - Only a few elements have issues in the presence of HCl
- Bromide/Iodide require basic matrices for stability
  - Some other elements are stable in base without HNO_3/HF

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Solution Matrix – HNO_3/HF

Not Checked by ICP	HF Elements
HF "thieves"	Avoid HF

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		

Solution Matrix - HCl

Not Checked by ICP	HCl Elements
Can work w/o HF	Avoid HCl

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

Solution Matrix -
$TEA/NH_4OH/H_2O$

Not Checked by ICP

Basic Elements

Can work w/o HNO_3/HF, but must be basic

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

Multi-Element Compatibility

(How many elements can be combined at 1,000 ppm?)

15% HNO_3 | + 3% HF

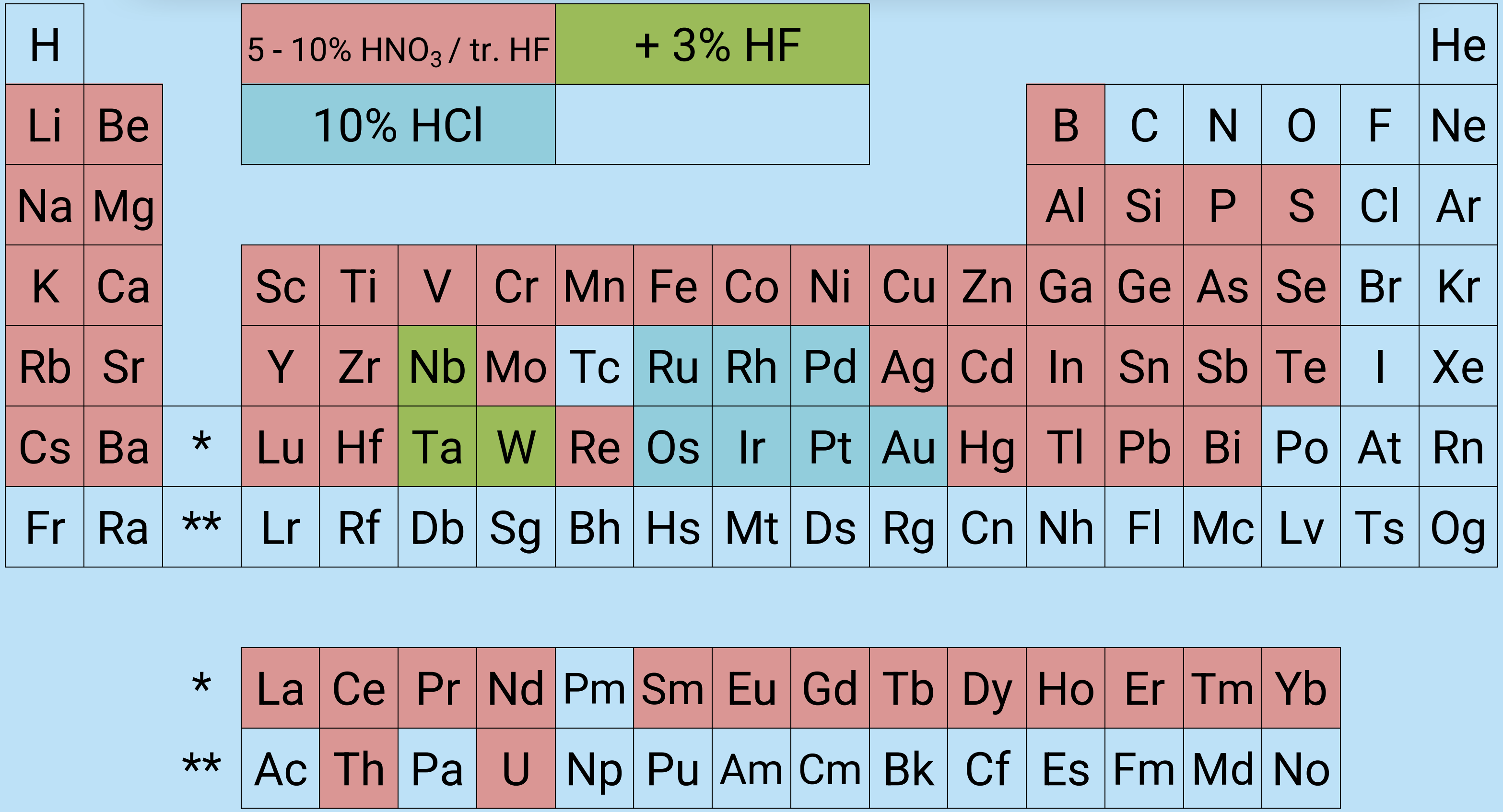
10% HCl

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

Multi-Element Compatibility

(How many elements can be combined at 100 ppm?)



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Multi-Element Compatibility

(How many elements can be combined at 10 ppm?)

5 - 10% HNO_3 / tr. HF

10% HCl

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
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*	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

Multi-Element Compatibility

(How many elements can be combined at 10 ppm?)

H			10% HCl / tr. HF				$(Cs,Rb)_2PtCl_6$											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

03

Top Topics for Today:

- Environmental Contamination
- Solution Matrix
- **Washout Issues**
  Poor washout can lead to inaccurate results. How do your blanks look?
- Uncertainty of Measurements

Causes for Washout Issues

- Solution matrix (HNO_3/HCl/HF/NH_4OH)
  - Could be from commercially available standards
  - Could be from specific sample preparation protocols
- Specific elemental affinity toward different types of plastics (Pump tubing, HF-resistant intro system)
- Spray chamber design (Single-pass, double-pass)
- Rinse protocols using the wrong acids/bases
- Allowing for the appropriate amount of time to rinse

Problem Elements

Not Checked by ICP	Elements with washout issues

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

Common Rinse Solutions

HNO_3

- 5-10% on an OES
- 1-2% on a MS

RBS-25

- 2.5% on an OES
- Not Recommended on MS due to high Sodium

HCl

- 5-10% on an OES
- 1-2% on a MS

H_2O

- Can be effective enough for Na, K, Ca, etc.

Rinse Solutions with HF

HNO_3

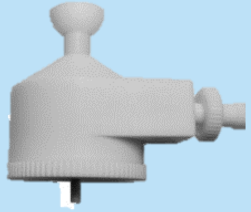
- 5-10% on an OES
- 1-2% on a MS

HF

- 0.1-2% on an OES
- 0.05-0.5% on a MS

- If using borosilicate glass nebulizer and spray chamber
  - ***Limit HF*** to a max of 0.2%
  - B and Si results will be unreliable

- If using HF Resistant nebulizer and spray chamber
  - Limit HF to a max of 3%



Specialty Rinse Solutions

- **NH_4OH**
  - 1-5% for OES or MS
  - Use for B, Br, I, Hg
- **HCl / Thiourea**
  - 1-10% HCl
  - 0.5% Thiourea
  - Use for Hg, Au, Os
- **HCl / Hydroxylamine·HCl**
  - 10% HCl
  - 0.5% $NH_2OH \cdot HCl$
  - Use for Os

Washout Study Results

Washout Times Comparison				
	Time to Washout (s)			
Rinse Solution	**Au 208.209 nm**	**Bi 223.061 nm**	**Hg 184.950 nm**	**Os 225.585**
10% HNO3	50	30	175	170
10% HCl	40	80	45	100
5% HNO3 / 5% HCl	70	170	110	120
1% NH4OH	60	60	130	60
10% HCl / 0.5% HydroxylamineHCl	50	80	50	75
ICP-TRUE-RINSE	35	25	35	30

ICP-TRUE-RINSE decreased washout time for all four elements in the study.

Troubleshooting Washout Issues

- Identify the elements that give you trouble
- Experiment with different rinse solutions
- *Keep up with routine instrument maintenance*
- Identify specific causes for washout issues
- Develop methods that include effective rinse strategies and only the elements you require

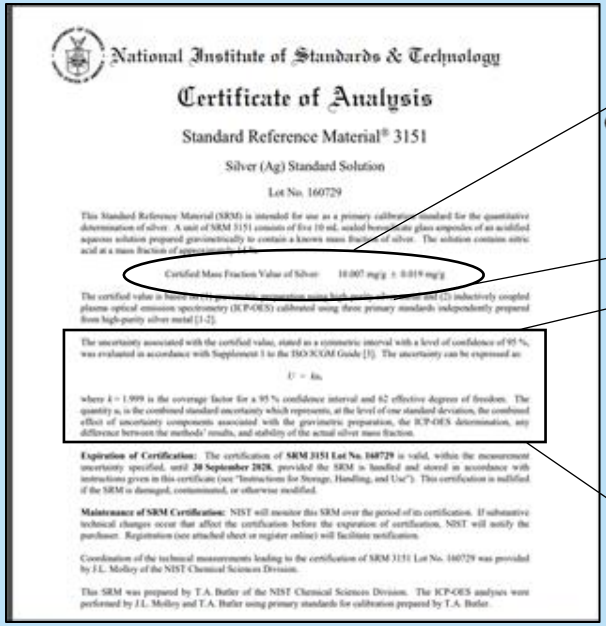
04

Top Topics for Today:

- Environmental Contamination
- Solution Matrix
- Washout Issues
- **Uncertainty of Measurements**
  What is a reasonable uncertainty for your analysis, and can you take any steps to improve it?

Standards of Comparison

- How low can you go in terms of uncertainty?
  - Review the uncertainties of your CRMs for a baseline


National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3151

Silver (Ag) Standard Solution

Lot No. 160729

Certified Mass Fraction Value of Silver: 10.007 mg/g ± 0.019 mg/g

The uncertainty associated with the certified value, stated as a symmetric interval with a level of confidence of 95 %, was evaluated in accordance with Supplement 1 to the ISO/JCGM Guide [3]. The uncertainty can be expressed as:

$$U = ku_c$$

where $k = 1.999$ is the coverage factor for a 95 % confidence interval and 62 effective degrees of freedom. The quantity u_c is the combined standard uncertainty which represents, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES determination, any difference between the methods' results, and stability of the actual silver mass fraction.

Sample Preparation

- Sample Preparation by weight is superior to preparation by volume.
- Example: Sample Aliquot Volume vs Weight

Preparation by Volume	Preparation by Weight		
1mL Aliquot Calibrated Electronic Pipettor	1g Aliquot 4-place Analytical Balance	1g Aliquot 3-place Analytical Balance	1g Aliquot 2-place Analytical Balance
0.3% Relative Error	0.03% Relative Error	0.2% Relative Error	1.5% Relative Error

Sample Preparation Best Practices

- Operate in units of weight/weight (Ex. µg/g) if possible
- If you must work in units of weight/volume (Ex. µg/mL) use densities to convert to weight/weight units
    1. Perform your analysis in weight/weight
    2. Convert your results back to weight/volume using your densities
    3. Remember to track the uncertainty from density measurements also

Instrumentation

Sample Intro System and Instrument Sampling Method

- This is one of the most important factors to achieve excellent results
- Double check tubing connections frequently
- This includes uptake times, stabilization delays and other settings like integration time

Matrix Matching

- Different matrices will demonstrate different nebulization efficiencies
- Density and TDS (Total Dissolved Solids) seem to have the largest impact on nebulization efficiency

Interferences

- It is important to know as much about your sample as possible
- Keep in mind contaminants that may have been introduced during sampling and/or storage
- Be mindful of interferences that may be present in your calibration curve but not present in your sample

Limits of Detection

MDL Review: Construct your calibration curve and run a series of method blanks.

$$\text{Method Detection Limit} = t \times Standard\ Deviation\ of\ Method\ Blanks \times Dilution\ Factor$$

To lower your MDL, focus on measurement sensitivity, precision, and dilution factor.

Sensitivity: Higher sensitivity improves signal-to-noise, reducing variability in blank measurements and lowering the MDL.
Precision: If you can increase precision your standard deviation should be lower.
Dilution Factor: Selecting the right dilution factor is critical.

Too low and the total dissolved solids/matrix concentrations can cause issues. Too high and you do not have enough analyte to detect.

Conclusions & Resources

- **Largest contributors to uncertainty**
  - Uncertainty of the standard of comparison
  - Measurements of small weights or volumes
  - RSDs

Resources

- GUM, Guide to the Expression of Uncertainty in Measurement
- VIM, International Vocabulary of Metrology
- EURACHEM Guide, Available from www.eurachem.org.
- Joint Committee for Guides in Metrology (JCGM)

  http://www.iso.org/sites/JCGM/JCGM-introduction.htm

Questions?

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RESOURCES

Questions?

- **Mike Booth**
  - mbooth@inorganicventures.com
- **Thomas Kozikowski**
  - tkozikowski@inorganicventures.com