WEBINAR

Improving ICP Calibration:

A TROUBLESHOOTING SESSION

THURSDAY, JANUARY 7
9:00–10:00AM EST

SPEAKERS:

Lesley Owens, PhD
Manager,
Technical Support

Michael Booth
Director,
Quality Control

Outline

- **Design**
- **Handling CRMs/Working Solutions**
- **Troubleshooting**

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- **Design**
- Handling CRMs/Working Solutions
- Troubleshooting

Inorganic Ventures Certified Reference Materials (CRMs)

Stocks and Customs - ~57,000 approved solutions in our database

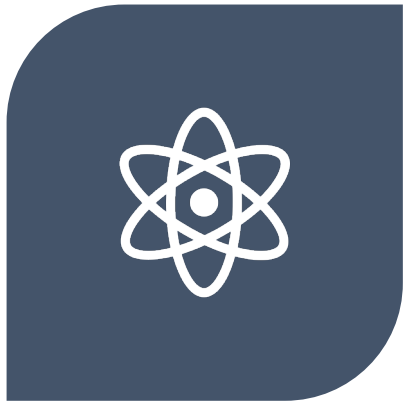
- Single and multi-analyte solutions of varying complexity
- Analytes are certified and traceable to NIST (very few exceptions)
- Method of certification might vary by product line, product, or intended use

Options for Calibration Standards

1. Ready-To-Use
2. Make Your Own from commercially-available stock(s)

	Ready-To-Use Custom	Customer-Preparation of Stock
Advantages	Training not required	Greater flexibility
	Simplifies inventory	More volume per $
	Less waste	Lower cost (stock products)
	Audit compliant (less risk)	
	Accuracy (?)	
Disadvantages	Less flexibility	Training required
	Less volume per $	Increased regulatory burden
	Higher cost (customs products)	More waste (expiring standards)

Key Considerations for Standard Design



ELEMENTS

CONTAINER

MATRIX

Elemental Concerns

- K & Si – gel formation at concentrations > 200 ppm
- Pt & Cs – precipitation of $Cs_2(PtCl_6)$
- Re & Cs – precipitation at concentrations > 2500 ppm

Elemental Concerns Continued

- Cr(VI) & Pb/Ba/Tl – precipitation as chromates
- Hg/Pd & C (and sources) – reduction to metallic forms
- Geochemical twins – consider ratios of these elements
  - Zr and Hf
  - Nb and Ta
  - Mo and W

Container Concerns

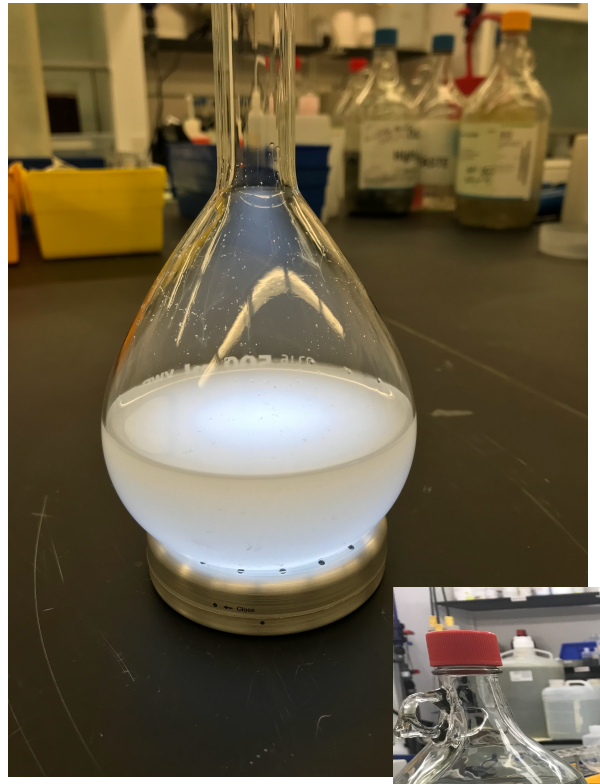
LDPE

- Preferred due to its cleanliness and chemical compatibility.
- Specially leached LDPE is used for low-level HEPA blends (≤ 100 ppb).

Borosilicate glass

- Used for solutions containing ≤ 200 ppm Hg and/or < 10 ppm Pd in HNO_3 matrices
- Not compatible with HF matrices due to attack of glass
- Not recommended for solutions containing Na, Al, B, Ba, Ca, K, Fe, Ni, Zn, Sr, and/or Zr

Matrix Concerns



HNO_3

- Avoid Sb(tartaric) @ > 2% v/v HNO_3
- As + Bi + Pb @ 1000 ppm requires 15% v/v HNO_3
- Au cannot be blended in HNO_3 only

HCl

- Os – HCl ONLY!
- Ag – photosensitive; avoid traces of Cl
- Avoid Tl (I)

HF

- Avoid rare earths, Group 2As, Th, and Cr (III)

PPB Stability Study

Web Series
Sample Preparation Guide

Trace Analysis Guide

ICP Operations Guide Download

Technical Guides
USP 232 and ICH Q3D – Element Stability in ICP Standards - NEW

General observations regarding USP 232

Elemental Analysis of Zeolites

Pure Chlorite Standard Developed

Mercury Chemical Stability

Silver Chemical Stability

Part-Per-Billion Stability Study

By Paul Gaines, Ph.D.

The purpose of this study was to determine the stability of elements at the ppb level in low density polyethylene (LDPE) bottles. The stability of metals at the ppb level in this container material was of consequential concern. In work reported previously, it was found that LDPE is the cleanest container material (see Container Material Properties for details) for trace metals solutions.

Experimental Design

1. A blend of 65 elements from Inorganic Ventures / IV Labs' **CMS-SET** was prepared at the 0, 2, 10, and 100 ppb concentration level in 1 % (v/v) HNO_3 at the start of the study.
2. The set consists of the following:
   - CMS-1 - 10 µg/mL Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, U, Yb, Y in 3.5 % HNO_3
   - CMS-2 - 10 µg/mL Au, Ir, Pd, Pt, Re, Rh, Ru, and Te in 3.5 % HCl
   - CMS-3 - 10 µg/mL Ge, Hf, Mo, Nb, Ta, Sn, Ti, W, and Zr in 3.5 % HNO_3 tr. HF

Outline

- Design
- **Handling & Storage**
- Troubleshooting

Making your own standards

- We recommend using a calibrated balance for aliquots as opposed to a pipette; pipettes can have issues with air bubbles and viscous solutions.
- Leaching with 1-5% HNO_3 is recommended for cleaning bottles for ICP work.
- Usage periods for working solutions can vary based on the analyte concentrations, matrix, container materials and storage environment.
- Generally not recommended that working solutions be held for longer than one year.
- Pseudo-stability study can be used to establish expiration date for calibration standards

Container Materials

- LDPE is cleaner
- Borosilicate bottles are used for certain chemical stability considerations.

Container Material	Impurities found, ng/125mL Bottle
LDPE	~50
HDPE	~250
PP	~700
PTFE	~240
Borosilicate	~57500

Volumes/Concentrations

- Our certified Bulk Concentrates also present volume-based limitations.
- Concentrates can range from 1000ppm to 120,000ppm, most are in the 40,000-60,000ppm range.
- This limits the number of analytes we can fit into a solution at concentrations >1000ppm.
- As the analyte concentrations decrease, we can fit more analytes into solution.

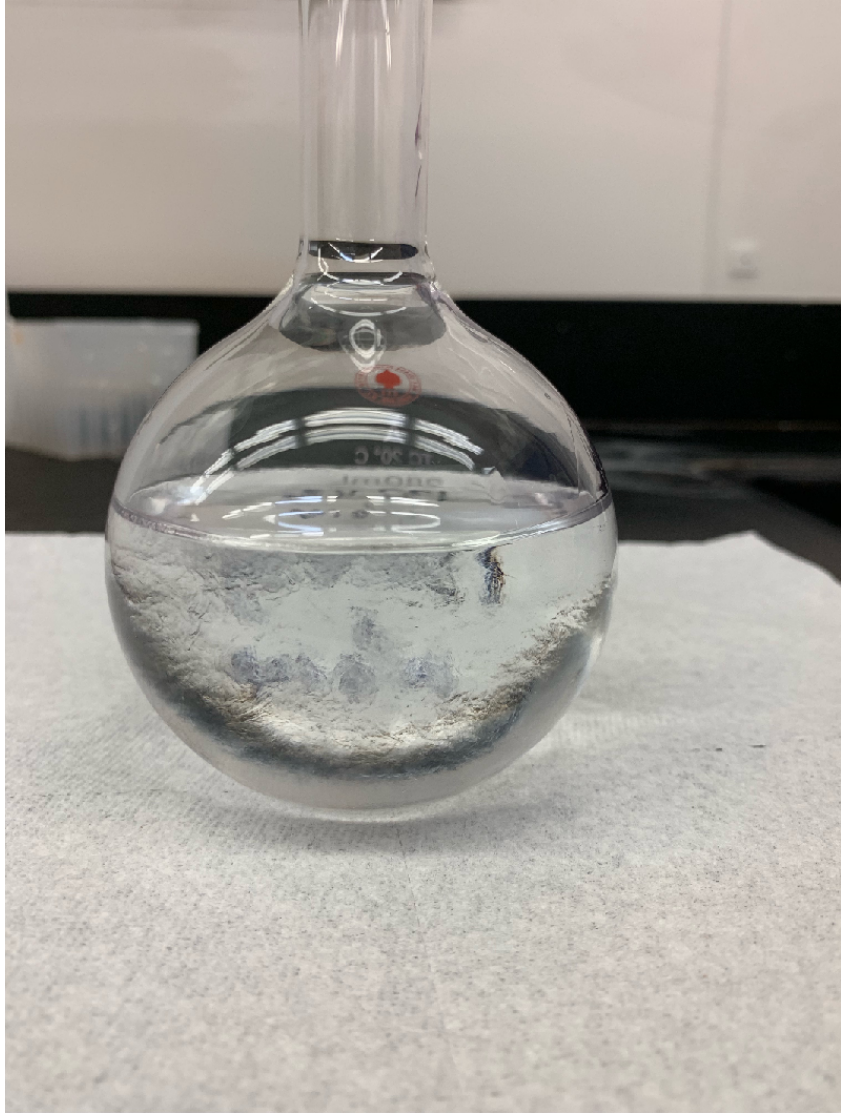
For solutions with all elements at:

- 10,000ppm: generally no more than 5 analytes
- 1,000ppm: 25-30 analytes
- 100ppm: ~50 analytes
- 10ppm: >70 analytes

Order of Additions

Very important when combining elements that have compatibility issues.

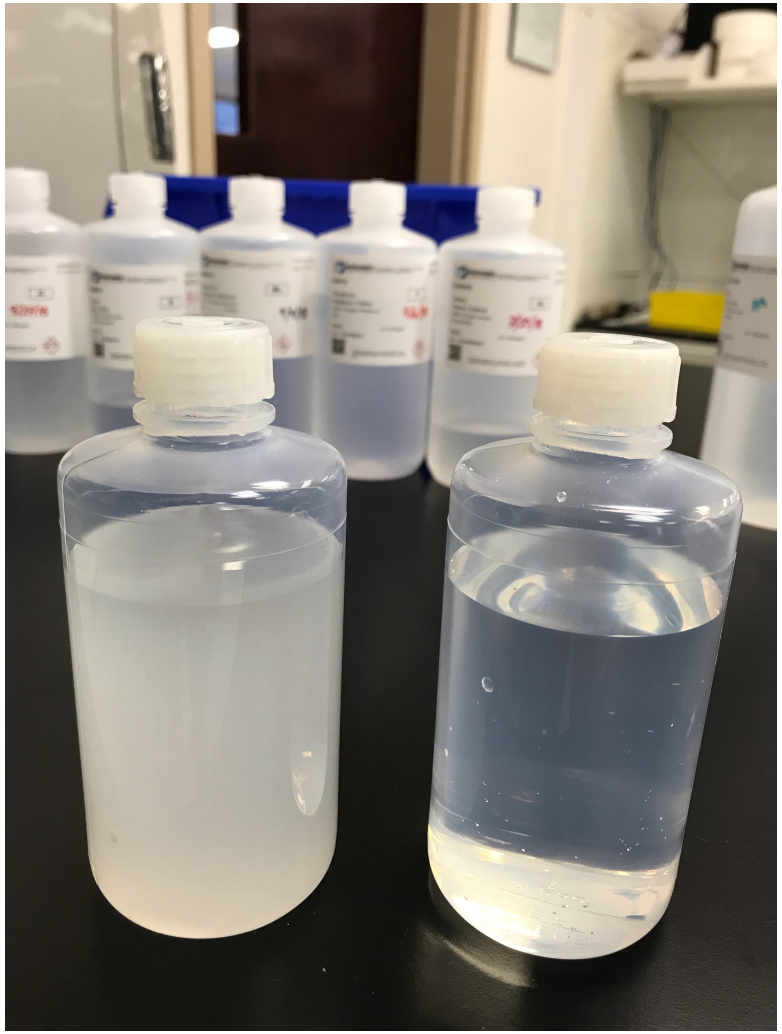
- Generally, add DI water and required acid for the matrix first in a 2:1 water to acid ratio.
- Add aliquots for analytes, swirling after each addition. Dilute to volume/weight with water when all aliquots have been added.
- Swirling helps to avoid concentrated elements from encountering “pockets” of localized acid or other elements.



Order of Additions

Several compatibility issues have been conquered through improved order of addition, including:

- Os with high HNO_3-bearing analytes
- Group 2A elements/REEs in HF matrices

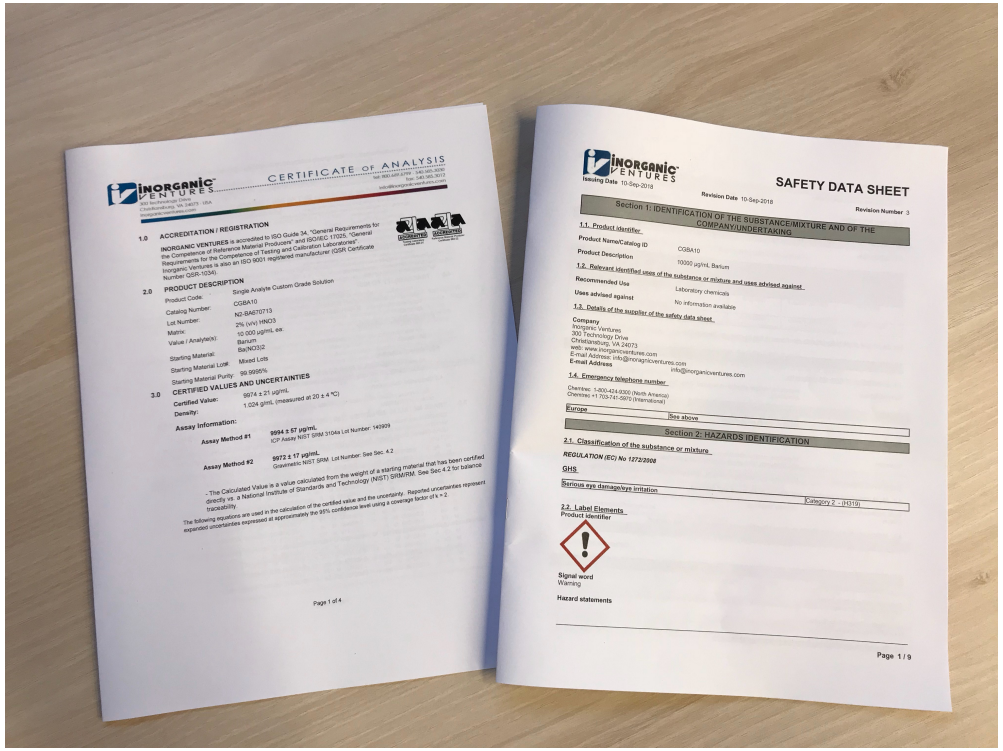


Precipitation of CaF_2

Handling CRMs and Working Solutions

Always refer to your Certificate of Analysis, but generally speaking:

- Store at room temperature (20 °C) or below
- Never pipet directly from the Stock bottle
- Never pour back into the Stock bottle
- Avoid storing in direct sunlight
- Keep cap secured when not in use
- Always consult the Safety Data Sheet



Transpiration

- Transpiration occurs when water vapor escapes from the bottle through the cap and walls; as more water is lost, analyte concentrations increase.
- IV uses Transpiration Control Technology (TCT) to effectively stop transpiration, allows for longer periods of validity.

What affects transpiration?

- Bottle size – transpiration occurs faster in smaller bottle sizes
- Volume level – transpiration increases as the fill level in a given bottle decreases
- Temperature – transpiration rates increase with higher temperatures
- Torque – capping bottles too loosely or tightly can cause higher transpiration rates

Outline

- Design
- Handling CRMs/Working Solutions
- **Troubleshooting**

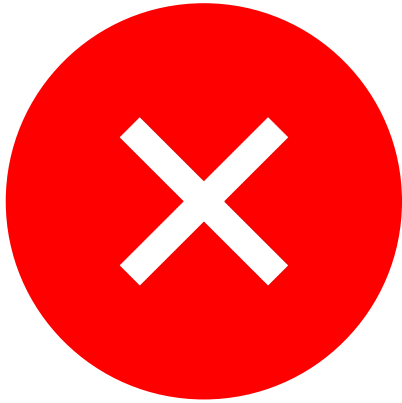
Types of Errors

NO RESULT

LOW RESULT

HIGH RESULT

No Results



Potential Causes

- Leak
- Clogging
- Plasma extinguished

Potential Solutions

- Check Sample Introduction System
  - Pump Tubing
  - Nebulizer
  - Pump/syringe delivery
  - Gas flow(s)
  - Spray Chamber
- Retune
- Perform daily maintenance
- PM

Instrument Tuning

ICP-OES

- **High Intensity**
  - Torch Alignment
  - Confirm Gas Flows
- **Low RSDs**
  - Confirm Method Timings
  - Check Intro System Connections
  - Confirm Gas Flows

ICP-MS

- **High Intensity**
  - Torch Alignment
  - Confirm Gas Flows
  - Lens Tuning
- **Low RSDs**
  - Confirm Method Timings
  - Check Intro System Connections
  - Confirm Gas Flows
- **Low Oxides**
  - Nebulizer Gas Flow
  - Spray Chamber Temperature
- **Low Doubly Charged Species**
  - Lens Tuning

ICP-MS Instrument Tuning

Auto-Tuning

- The Auto-Tune will usually work best to tune the instrument for the entire mass range.
- Depending on your instrument software this can be done as part of the start up routine.

Manual Tuning

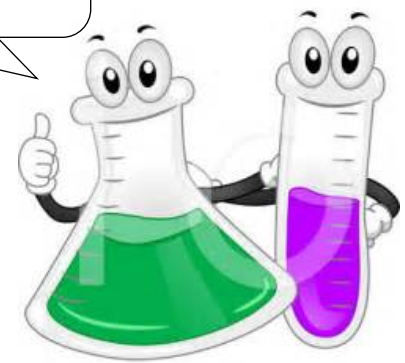
- This can be done much more quickly than the auto-tune once you are familiar with your instrument.
- You can tune for specific mass ranges.

Remember: You only have to tune to meet *your* performance checks

IV Recommended Maintenance Schedule

The manufacturer's instrument manual should have a recommended maintenance schedule

Necessary maintenance will vary based on instrument make, model, and sample matrix



Daily

ICP-OES
- Clean Interface
- Clean/Replace Torch
- Clean Spray Chamber
- Clean Nebulizer
- Replace Peristaltic Pump Tubing
- Inspect Tubing Connections
- Acquire Performance Report
- Inspect Other Intro System Parts

ICP-MS
- Inspect Cones
- Inspect Torch
- Inspect Spray Chamber
- Inspect Nebulizer
- Inspect/Replace Peristaltic Pump Tubing
- Inspect Tubing Connections
- Acquire Performance Report
- Inspect Other Intro System Parts

Weekly

ICP-OES
- Perform Wavelength Calibration
- Inspect All Tubing

ICP-MS
- Clean Cones
- Clean/Replace Torch
- Clean Spray Chamber
- Clean Nebulizer
- Perform Mass Calibration
- Inspect All Tubing

Monthly

ICP-OES
- Replace All Tubing
- Check Filters and Chiller

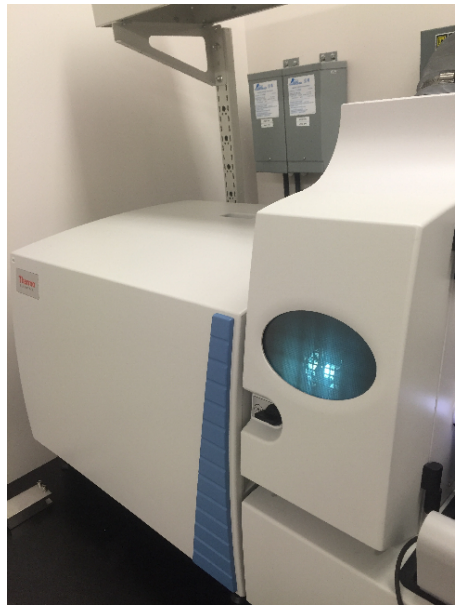
ICP-MS
- Replace All Tubing
- Check Filters and Chiller
- Check Vacuum Pump

Instrument Operation

Issues with tuning and/or calibration standards can affect operations in the ICP-OES/ICP-MS

- Low/no counts during tuning or normal operation
- Plasma getting extinguished
- Clogging in the introduction system

Bottom line: if you see issues during normal procedures, double check your tuning/calibration solutions



Low Results

Potential Causes

- Mixing
- Stability

Potential Solutions

- Remix calibration solution
- Assess stability of working solution

Mixing

- Proper mixing ensures a homogenous working solution
- Mixing by inversion is recommended
- Improper mixing could result in inconsistent results; most commonly all analytes are low if a solution is not properly mixed.

Stability Assessment

Fresh prep vs Aged prep

When ran head-to-head are your results statistically similar?

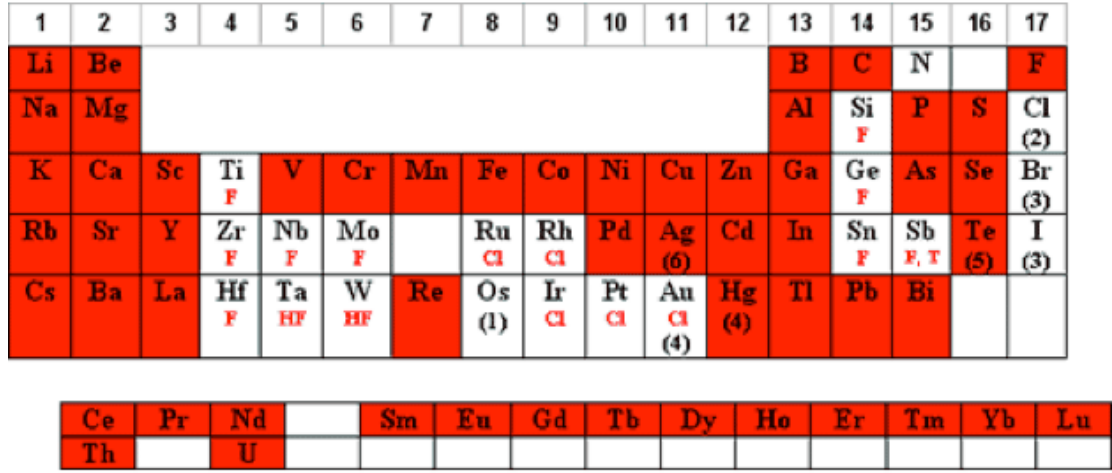
How to use info to assign expiration for working solutions?

Matrix Considerations

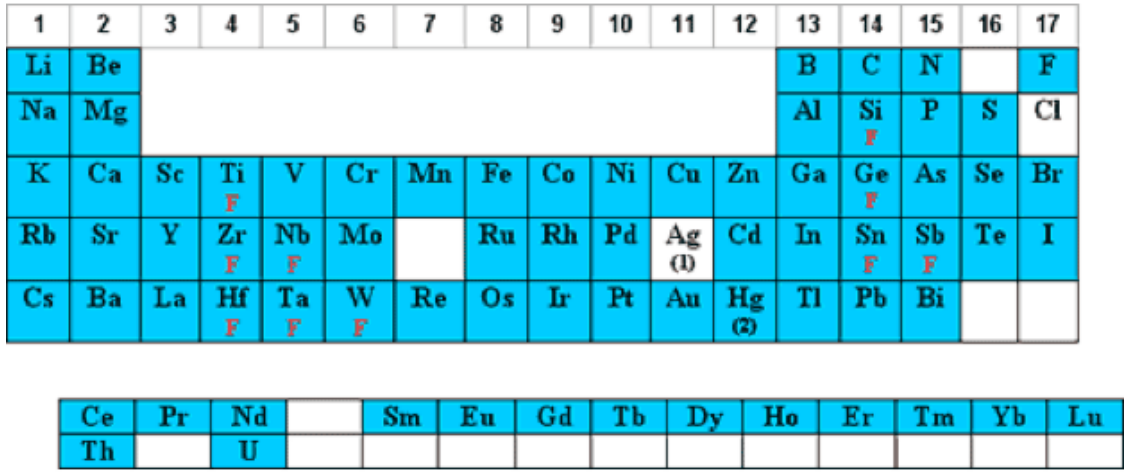
Vast majority of our standards are stabilized in either HNO_3 or HCl.

Notes:

- Avoid Sb(tartaric) in >2% v/v HNO_3 (degradation of tartaric acid)
- As/Bi with Pb at concentrations at or above 1000ppm need 15% v/v HNO_3
- Os – HCl only! (OsO_4 formation)
- Ag can photoreduce in the presence of trace Cl^-
- Avoid Tl^+ in HCl matrices (use Tl^{3+})



Elements stable in HNO_3



Elements stable in HCl

Matrix Considerations

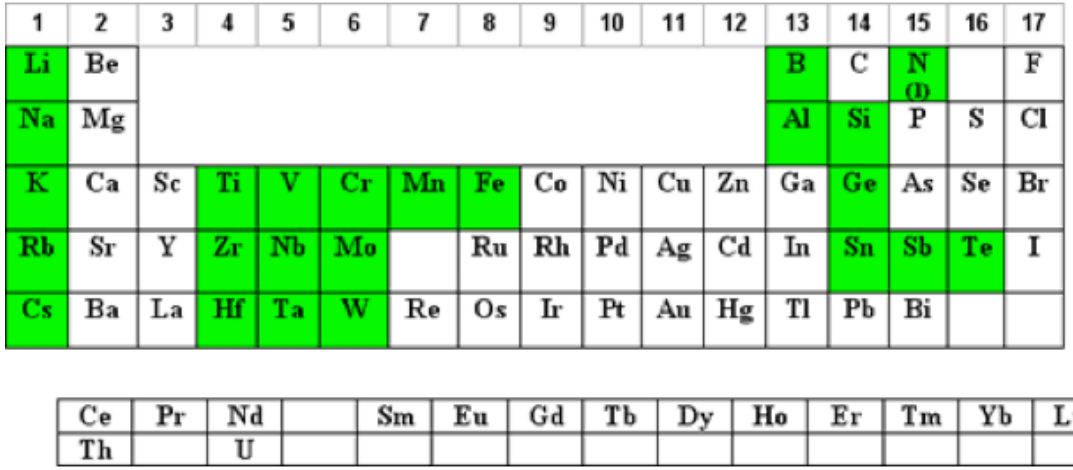
What about HF?

Certain elements require some minimum amount of HF for stability.

Extremely useful in dissolutions/digestions.

Notes:

- Rare earth elements, Group 2A elements and Th tend to precipitate out of solution as fluorides (concentration dependent).
- Elements such as Al, As, Bi, P can help mitigate this (to an extent) by tying up excess F^- ions in solution.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N (d)		F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

Elements requiring or stable in HF

High Results

Potential Causes

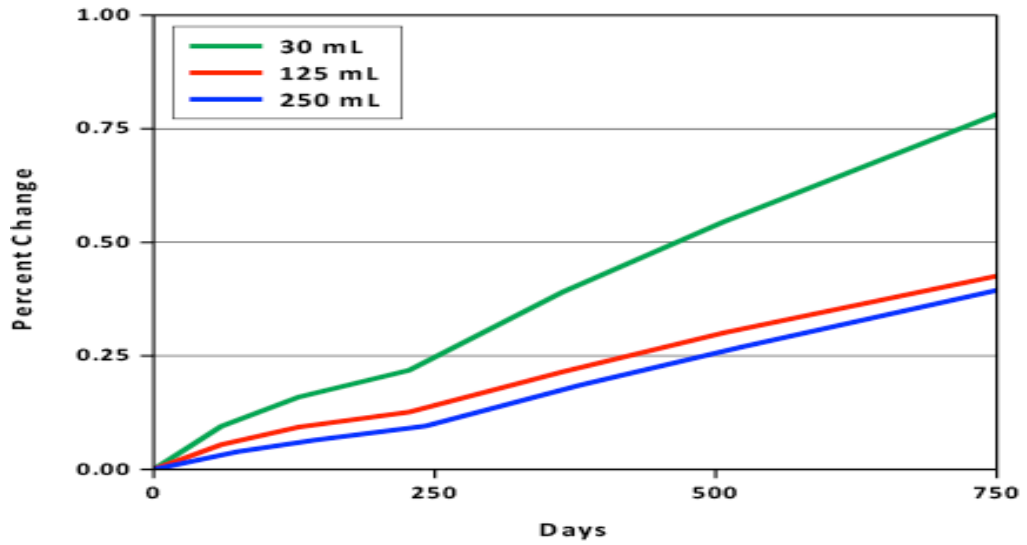
- Transpiration
- Interference
- Washout Issues

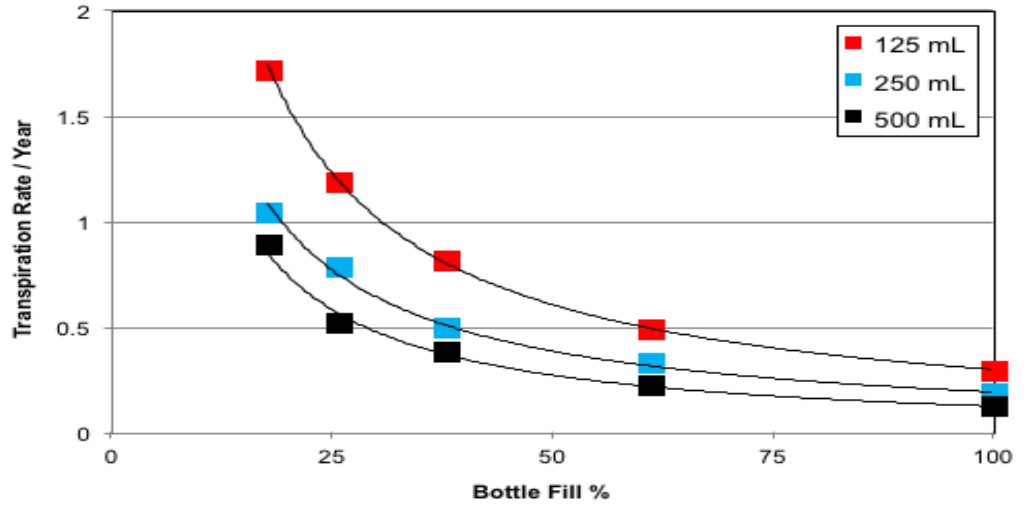
Potential Solutions

- Store according to manufacturer's recommendations
- Understand sample/standard composition
- Spray chamber temperature

Transpiration

- Bottle size – transpiration occurs faster in smaller bottle sizes
- Container materials – Glass and HDPE have lower transpiration rates than LDPE
- Volume level – transpiration increases as the fill level in a given bottle decreases

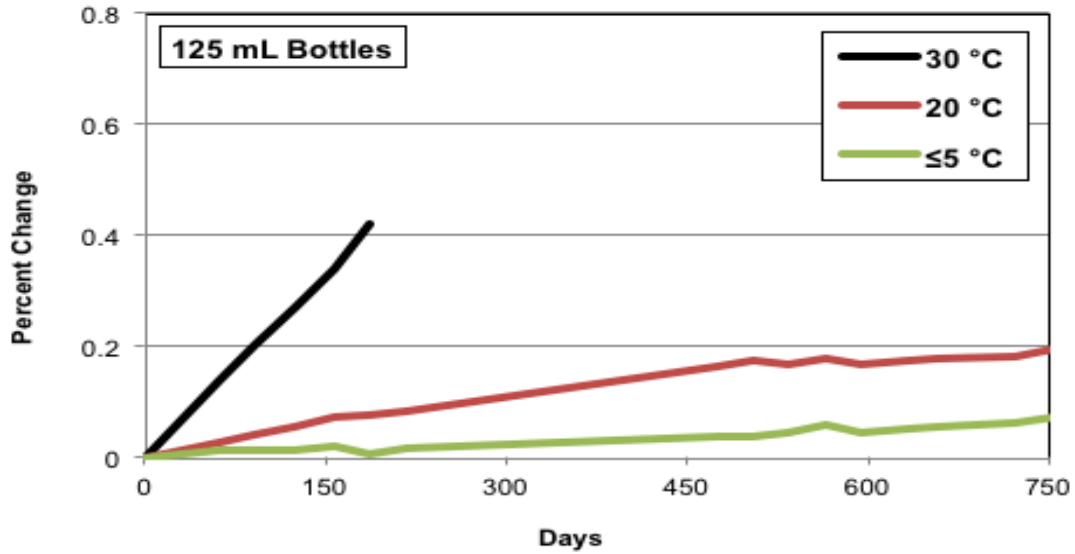


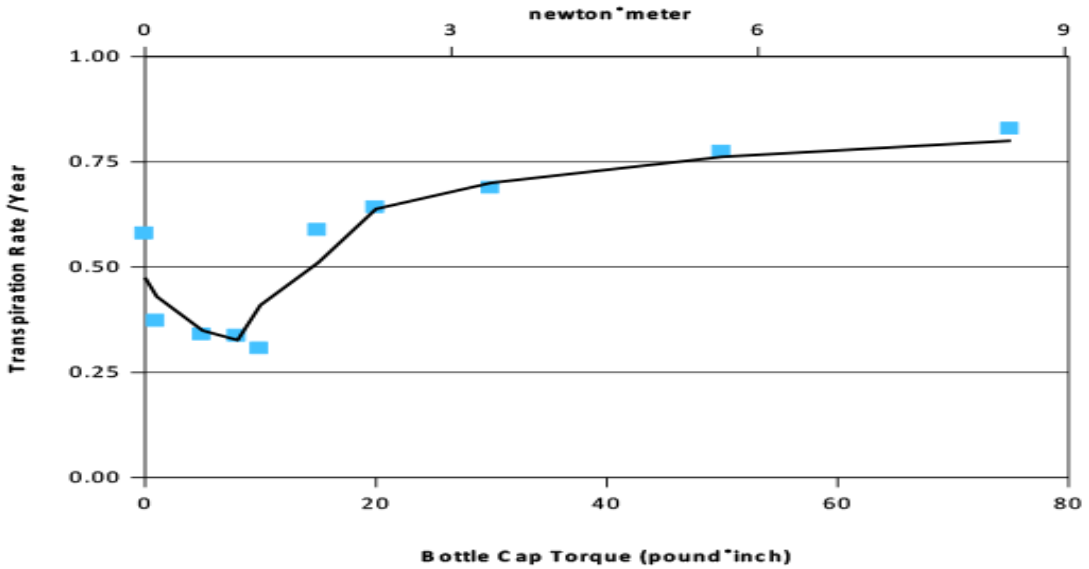


Transpiration

- Temperature – transpiration rates increase with higher temperatures

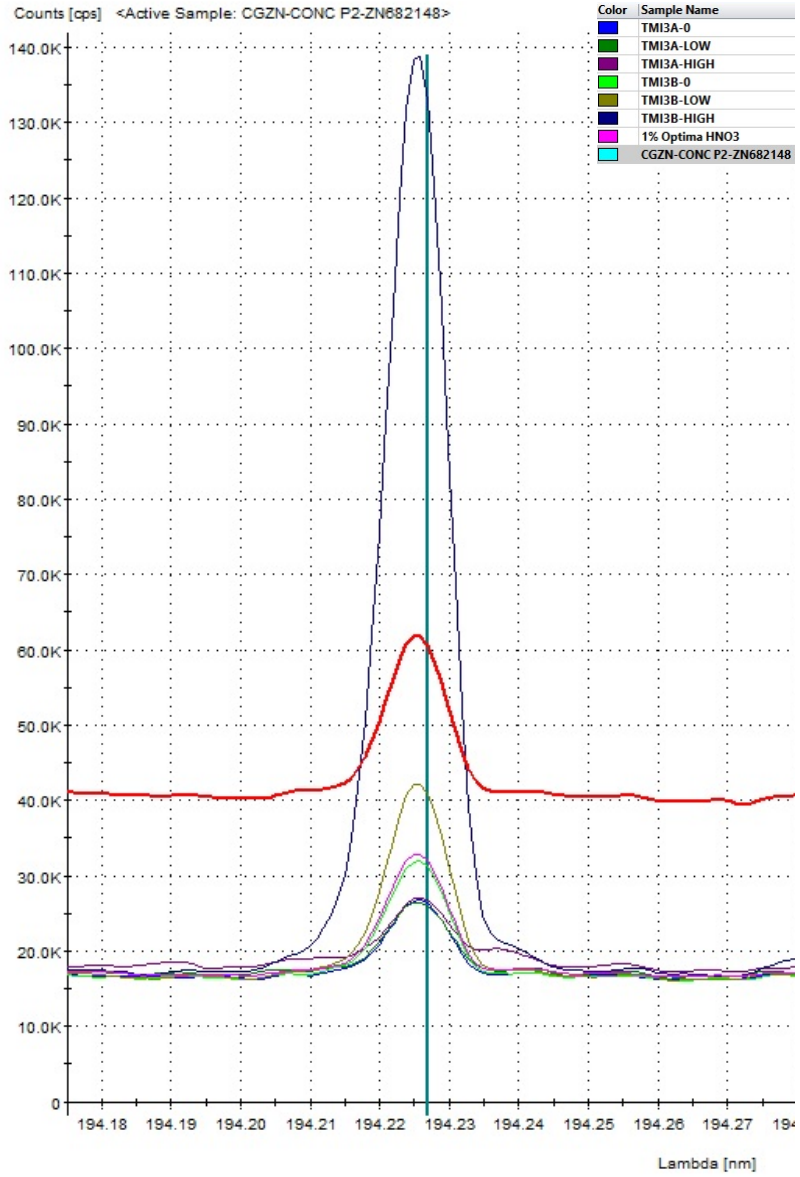
- Torque – capping bottles too loosely or tightly can cause higher transpiration rates





Confirming Results

- Most methods prescribe some avenue for confirming calibrations
  - 2nd source check solution
  - Use of RMs to verify proper performance
- Standard addition can assist with confirming interferences.
- **Checking the raw spectra/counts can aid in troubleshooting any inconsistent/unexpected results.**



Additional Handling Info

- Be mindful of the environment in which standards are stored
- Solution in low-volume bottles will transpire faster than it will in full bottles
- If standards are stored frozen, wait for bottle to reach room temperature before shaking/mixing to ensure homogeneity
- Color changes over time are often a result of changes in oxidation state, normally do not affect ICP standards
- Some compatibility issues can be avoided through improved order of addition

Troubleshooting Checklist

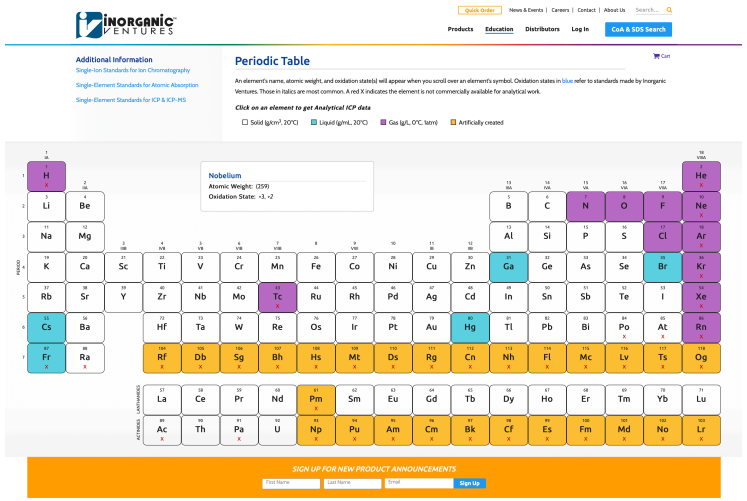
- **Review the stability rules** – any obvious oversights?
- **Use clean and proper container materials** – a proper risk assessment can save time and resources.
- **Properly mix working standards** – inversion is key!
- **Amend the order of addition** – element-specific instability can be overcome.

Troubleshooting Checklist

- **Contact the CRM provider for guidance** – can provide insight on Stock solution preparation
- **Working stability program** – running freshly prepared working standards against stored working standards can validate preparations/holding times
- **Double-check any calculations involved** – human error
- **Verify instrument performance**

Technical Support – Available to Everyone

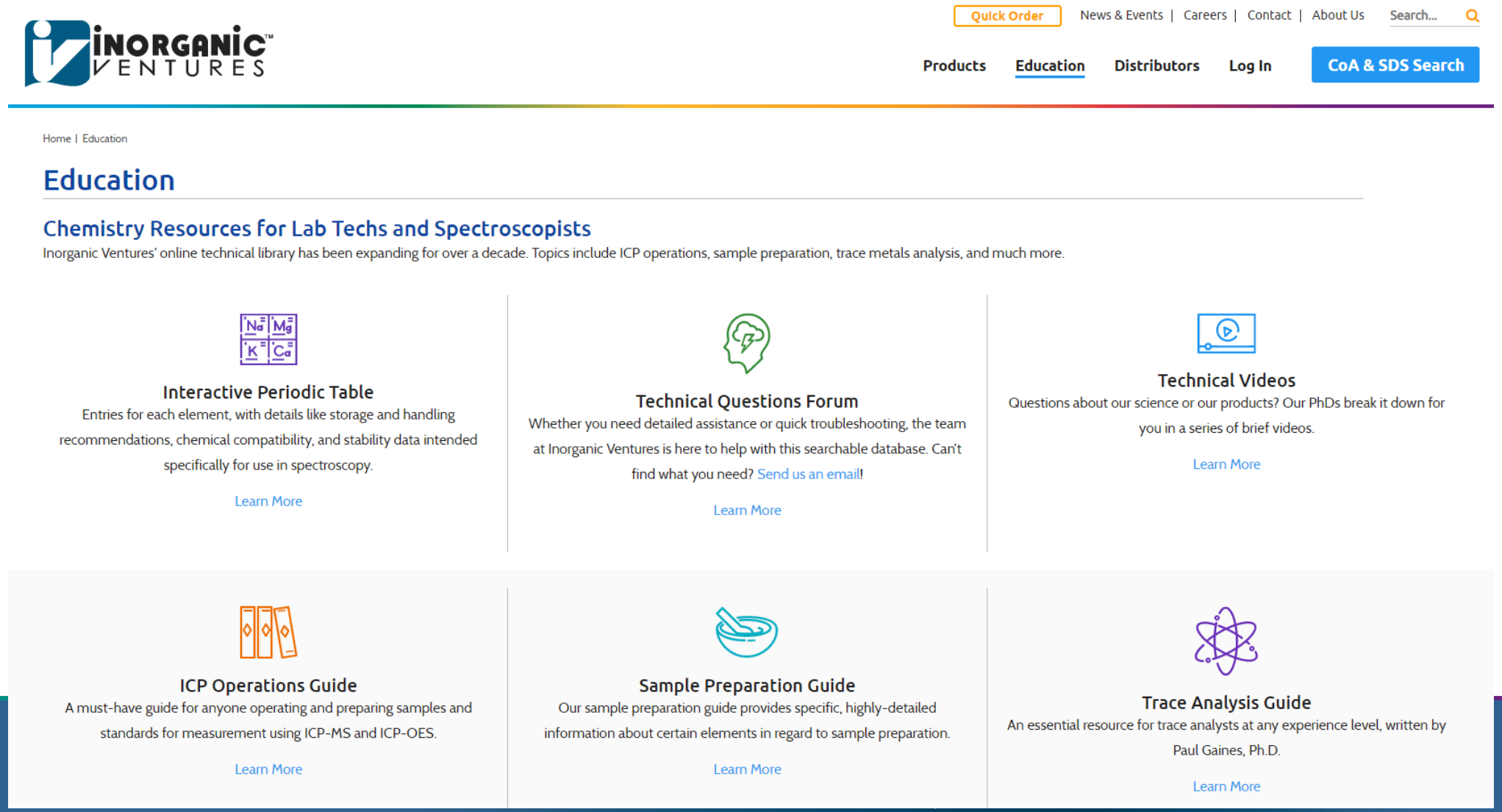
Online Resources at inorganicventures.com



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.**

Resources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Interactive Periodic Table
Entries for each element, with details like storage and handling recommendations, chemical compatibility, and stability data intended specifically for use in spectroscopy.
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An essential resource for trace analysts at any experience level, written by Paul Gaines, Ph.D.
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Resources

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