Best practices for the analyses of complex samples by ICP-OES and ICP-MS: Streamline workflow for accurate results

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Trace Elemental Analysis

The world leader in serving science

Elemental analysis in the petrochemical industry

- Oil and gas exploration and production
- Refining of crude oil and further processing
- Post-refining QA/QC of finished product
- Environmental analysis of wastewater and solid wastes
- Analysis of in-service chemicals

Challenges for elemental analysis

Challenges when analyzing petrochemical and environmental samples

Complex samples

- Oils, produced waters, volatile organics, refinery wastewaters, solid wastes, metallic matrices, etc.
- Complex matrices requiring further instrument and method optimization and interference removal.

High throughput and quick turn around of results

- Quick turnaround of crude oil & feedstock analysis for continuous plant operation.
- Analysis of lubricating oils as part of equipment maintenance programs.
- Environmental analysis of wastewater/solid wastes

Process and product Quality Control (QC)

- Presence of trace metals in refining can cause:
  - equipment corrosion
  - catalyst poisoning
  - engine deposition
  - compromise to product,

  hence, best MDLs and accuracy are key.

Regulation and compliance

- Analysis according to industry (ASTM) standards and US EPA methods.
- Method validation
- QA/QC protocols
- Traceability/documentation
- Data transfer and management
- Audit (data and laboratory)

How do we address these challenges?

- Why are petrochemical and environmental samples challenging?
- Where do we begin to address these challenges?
- How can we prevent these challenges?
- When do we call service or applications support?

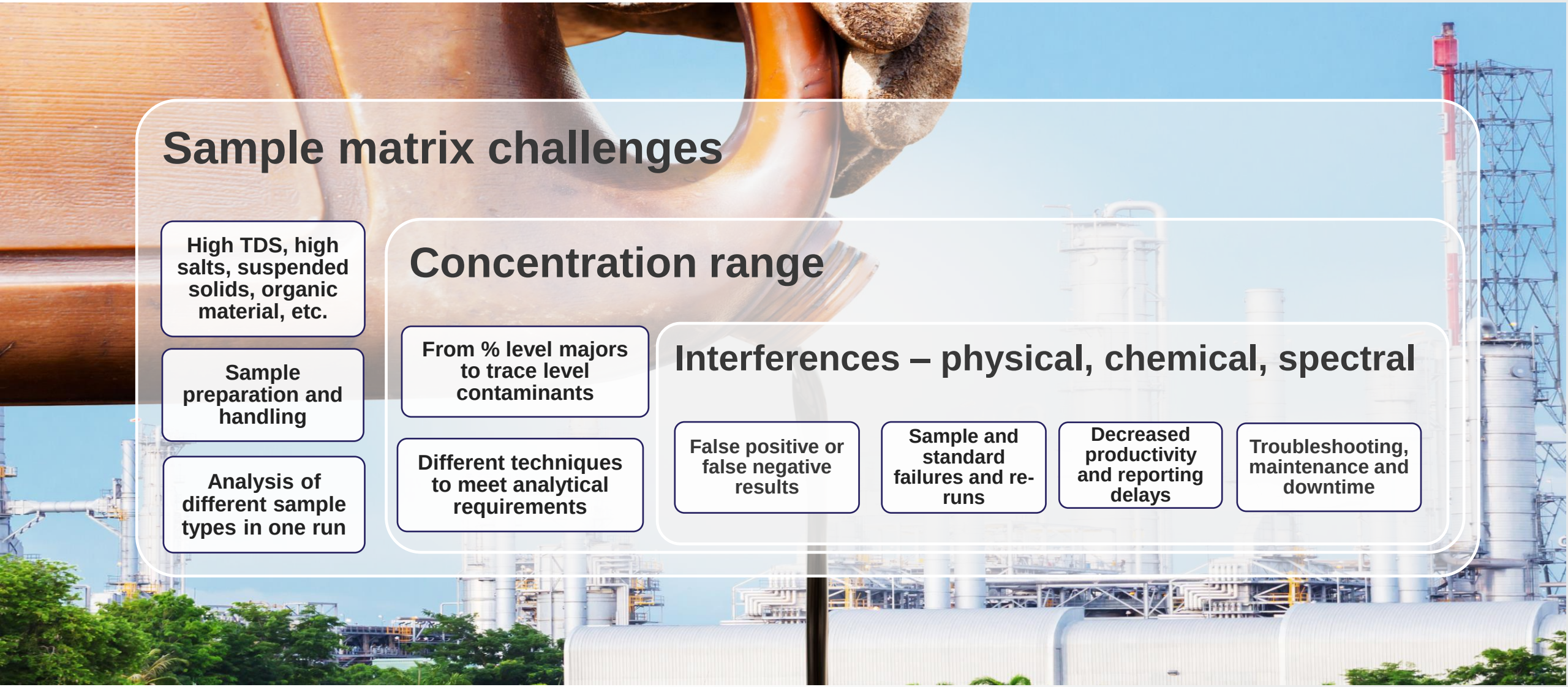
➢ **Let's start with the sample matrix…**

What are complex samples?

Complex samples for ICP-OES and ICP-MS analyses

- High Total Dissolved Solids (TDS)
  - For ICP-MS, > 0.2%, for ICP-OES > 3%
- Organic samples
  - Volatile (e.g., organic solvents)
  - Non-volatile (e.g., crude oil, lubricating oil)
- High salt (e.g., brines, seawater)
- Suspended solids/sediments
- Metals or metallic matrix
- Multi-phasic (e.g., sludge)
- High viscosity
- Hydrofluoric Acid (HF) containing
- Spectrally rich

Layers of challenges related to the sample matrix



Sample matrix challenges

- High TDS, high salts, suspended solids, organic material, etc.
- Sample preparation and handling
- Analysis of different sample types in one run

Concentration range

- From % level majors to trace level contaminants
- Different techniques to meet analytical requirements

Interferences – physical, chemical, spectral

- False positive or false negative results
- Sample and standard failures and re-runs
- Decreased productivity and reporting delays
- Troubleshooting, maintenance and downtime

Regulation, compliance, and quality standards

Regulation, compliance, and QA/AC add another layer of challenge

- **Detection limit requirements**
  - National Primary Drinking Water Regulations
  - National Secondary Drinking Water Regulations
  - Unregulated Contaminant Monitoring Rule (UCMR)
  - Different state/municipal regulations
- **Analysis according to EPA, ASTM or other industry standards**
  - Specific quality control protocols
  - Method validation
  - QC standards and samples
  - Control limit criteria
- **Audit, data management, and reporting requirements**
- Data package audit
- Onsite audit
- Data transfer to LIMS
- Data security

Addressing challenges in elemental analysis

- General best practices and tips to streamline workflow
  - Sample and standard preparation
  - Sample handling
  - Contamination prevention
- Instrument innovations
  - Hardware design
  - Software features
- Method optimization
  - Sample introduction system
  - Plasma parameters
  - Interference correction
- Troubleshooting and maintenance tips
  - Troubleshoot failures due to issues with sensitivity, accuracy, precision, and carryover

Elemental analysis workflow

Processes in the elemental analysis workflow

Standard Preparation

Standard preparation can take long

Sample Preparation

Hot plate acid digestion can take hours

Sample Dilution

Sample Introduction

Uptake and rinse times add to sample analysis

Sample Analysis

Data

Out of range samples require dilution and re-analysis

How can these processes be done more efficiently?

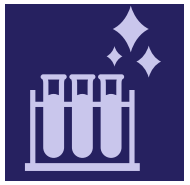
What are some best practices to ensure accuracy and quality data?

General best practices for the elemental analysis workflow

Key for obtaining the low detection limits required for environmental analysis

Be aware of all contamination sources.

Minimize handling and transfer steps.

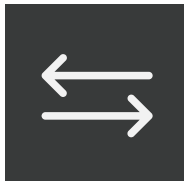


Use high purity reagents.

Use high purity reagent water.

Use clean and compatible apparatus.

Measure weights and volumes with accuracy.



Have separate sample and standard preparation areas.

Apply proper skill, be consistent, and pay attention to detail.

Tips and tricks for sample and standard preparations

Along with the general best practices, apply the following for standard and sample preparations

Apparatus

- Use plastic, avoid glass especially for ultra-trace detection limits
  - E.g., PTFE, PFA, PMP, FEP, HDPE, LDPE, PP
- Use mechanical pipettes with disposable plastic tips
- Use Class A volumetric flasks

Standards

- Use high purity, NIST traceable, ISO certified stock standards designated for ICP-MS or ICP-OES analyses
- Use multi-elements stock standards for most preparations
- Use custom standards, if possible
- Use single element standards to prepare the Internal Standard solution

Reagents

- Use ASTM Type I water (resistivity 18.2 MΩ-cm) or ultrapure water
- Use high purity (e.g., Optima™) grade concentrated acids
- Ensure water purification system delivers ASTM Type 1 water
- Ultrapure water is not Deionized water!

Tips and tricks for sample and standard preparation

Tips and tricks to ensure accurate weights and measurements

Analytical balances

- Calibrate yearly or as needed
- Check at least weekly using Class 1 standard weights and spot check daily, document all checks
- Store balances on a heavy table away from windows, heat, high traffic areas, doorways, vibration

Mechanical pipettes

- Calibrate yearly or as needed
- Check weekly by measuring increasing volumes of water on an analytical balance
- Spot check daily, document checks
- Use colorless pipette tips
- Always hold pipette upright when drawing up and dispensing liquid
- Pull up and dispense liquid slowly to avoid air bubbles and liquid from going up to pipette causing damage

Tips and tricks for sample and standard preparations

Tips and tricks to streamline sample handling and prevent contamination

Handling and transfers

- Never place pipette tip directly into container of stock standard or high purity concentrated acid as this will cause contamination.
- Pour an aliquot of stock standard and concentrated acids into disposable plastic beakers (e.g., 5 mL PP) to pipette from when preparing standard solutions.
- Use plastic (e.g., Teflon) wash bottles to store and dispense dilute acid solutions (e.g., 1% HNO_3) for preparations.
- Avoid multiple transfers by preparing calibration standard solutions in autosampler tubes. Ensure autosampler tubes are Class A, metal free, and thoroughly cleansed prior to use.

Labcon MetalFree™ centrifuge tube, Class A, made from ultra clean resins, with additive free cap

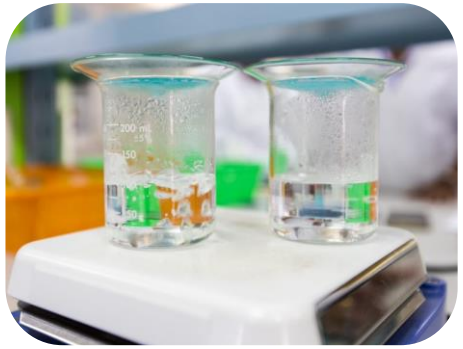
Teflon wash bottle, best for ppt level preparations

Sample preparation

Goals of an optimized sample preparation process

- To convert sample into a solution suitable for introduction to an ICP-OES or ICP-MS
- Decompose the sample matrix, completely or partially
- Complete solution and retention of analytes at measurable concentrations
- Prevent loss of analytes
- Minimize sample contamination
- Reduce digestion time to satisfy laboratory throughput and turnaround requirements

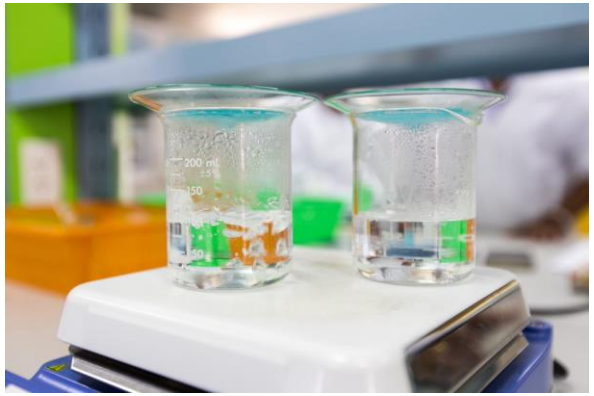
Environmental sample
(e.g., ground/surface water, wastewater, soils, sludge)



Digestion method
(hot plate, hot block, and microwave)

Digestate
(clean, colorless solution)

Digestion methods



Hot plate acid digestion

Advantages

- Simple set-up, needs minimal and common apparatus
- Uncomplicated procedures
- Higher sample weights
- High number of samples
- Low initial investment

Disadvantages

- **Long digestion time (hours)**
- Incomplete digestion
- Loss of analyte
- Exposure to contamination
- High reagent consumption
- Constant monitoring
- Numerous handling steps
- Inefficient

Hot block acid digestion

Advantages

- Reduced sample handling and transfers
- Reduced exposure to contamination
- All plastic parts, no metal
- Elimination of issues associated with use of glassware

Disadvantages

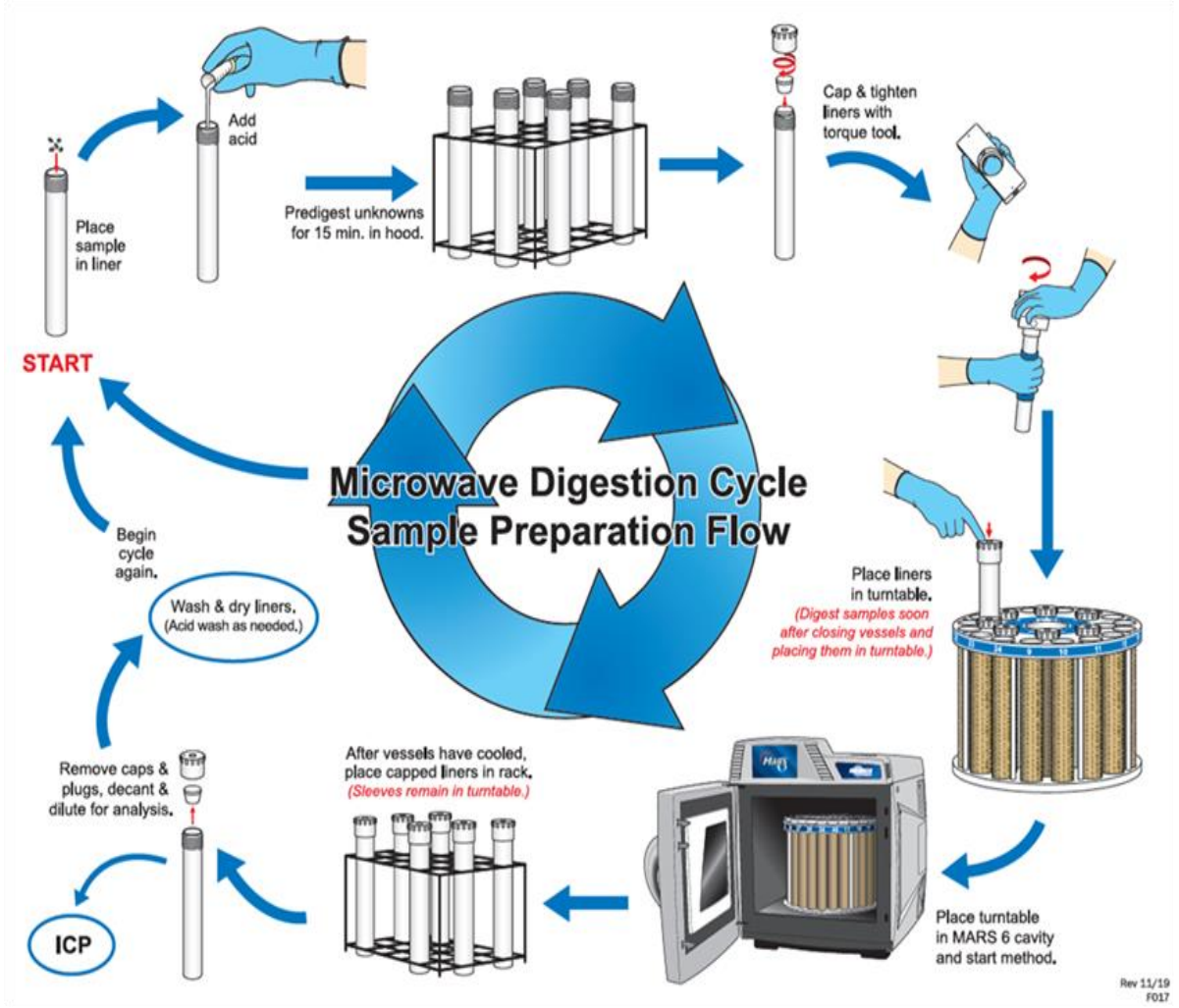
- **Long digestion time (hours)**
- Incomplete digestion
- Loss of analyte
- Exposure to atmosphere
- High reagent consumption
- Constant monitoring

Digestion method

Microwave assisted acid digestion

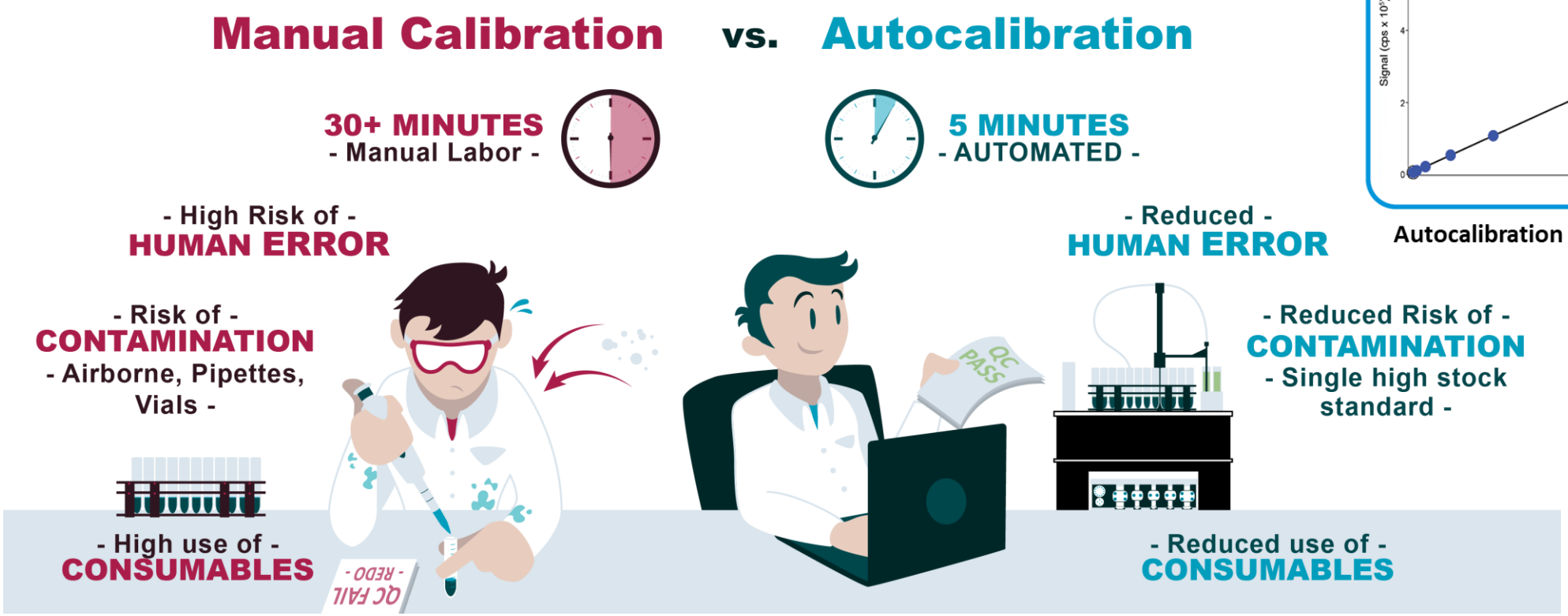
- **Advantages**
  - **Faster digestion (e.g., 20 minutes**)
  - Quality digestion
  - Reduced exposure to contamination
  - Reduced reagent consumption
  - Reduced loss of analyte
  - Overall efficiency
- **Disadvantages**
  - Higher initial investment
  - Limited number of samples
  - Ease of set-up

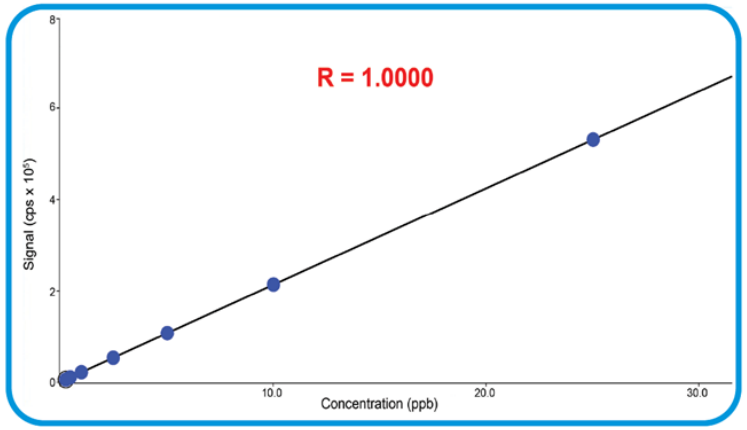
CEM Mars 6 microwave digestion system



Autodilution system for automatic standard preparation

Automatic standard preparation reduces preparation time and systematic error





Autocalibration from single 50 ppb Co standard

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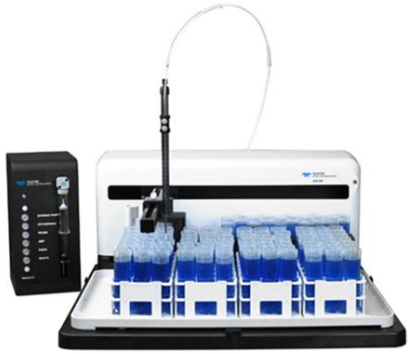
Streamlined elemental analysis workflow



Or

Faster results

Sample

Sample preparation
Microwave digestion

Streamlined sample preparation, from hours to minutes

Sample introduction automation
Autosamplers
autodilution systems

Streamlined standard preparation and faster sample analysis

Sample analysis

Now let's discuss instrumentation

Instrument innovations

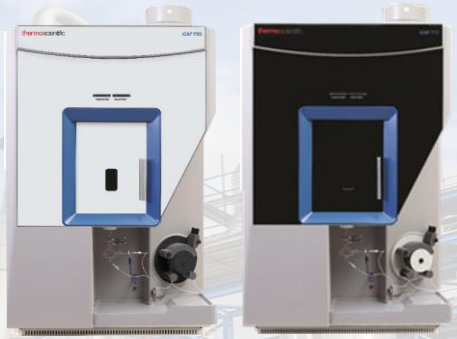
Addressing challenges through instrument innovation

Atomic Absorption Spectrometry (AAS)

Thermo Scientific™ iCE™ 3000 Series AAS

- ✓ Lower investment
- ✓ Lower level of complexity
- ✓ GFAAS - higher sensitivity
- ✓ FAAS - fast, single element analysis

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)



Thermo Scientific™ PRO™ Series ICP-OES

- ✓ Fast, multi-element analysis
- ✓ Smallest footprint of any ICP-OES
- ✓ Robustness for high matrix samples
- ✓ Flexibility, performance and ease of use

ICP Mass Spectrometry (ICP-MS)

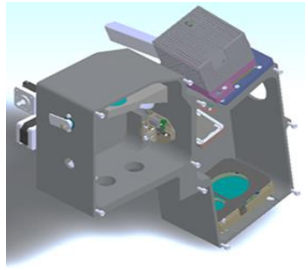
Thermo Scientific™ iCAP™ RQ ICP-MS

Thermo Scientific™ iCAP™ TQ ICP-MS

- ✓ Improved detection capability
- ✓ Wide linear dynamic range
- ✓ Advanced interference removal
- ✓ Speciation with chromatography

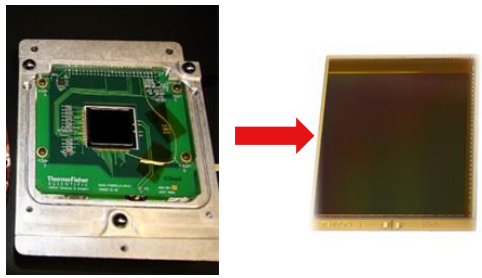
Addressing challenges through instrument innovations

iCAP PRO Series ICP-OES



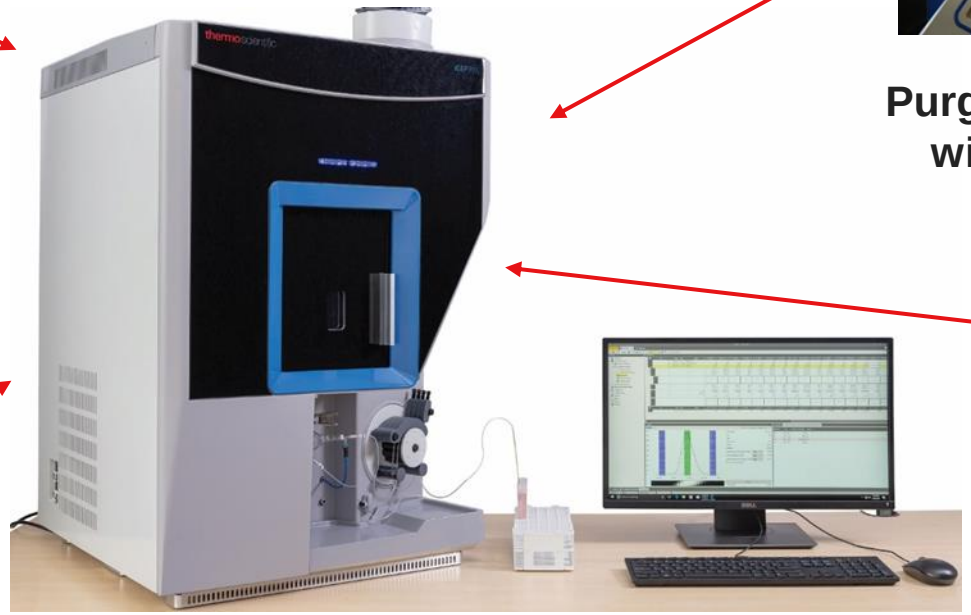
Optics designed for high sensitivity and stability

- New optical design
- Simultaneous measurement of full spectrum in one acquisition (iFR) mode
- Enhanced UV (eUV) mode



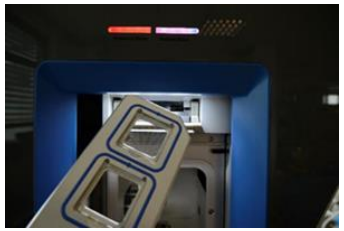
Unique CID821

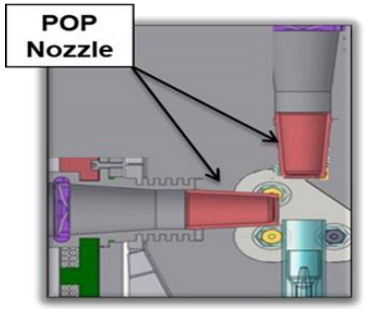
- Inherently anti-blooming
- Full frame imaging
- Order separation with over 4M pixels



Small footprint optimizes bench space

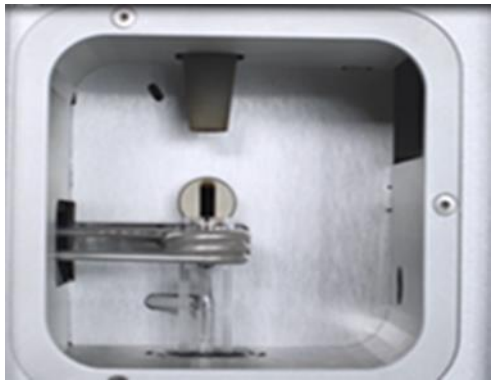
24.21 in. x 27.16 in. x 36.73 in (LWH)





Purged Optical Path (POP) nozzles and windows for enhanced robustness

- Durable ceramic cones
- New easy to remove POP window



New vertical torch designed for robustness and stability

- Optimized airflow through torch box
- Removable inner torch box

ICP-OES analysis

Why is ICP-OES the technique of choice for the analysis of high matrix samples?

- High matrix tolerance – advantage over all spectroscopy techniques
- Robustness
- Stability
- Sensitivity
- Wide linear dynamic range
- Fast, multi-element analysis
- Relatively easy to operate and maintain
- Established technique

How can high matrix samples affect analysis?

Challenges when analyzing aqueous samples

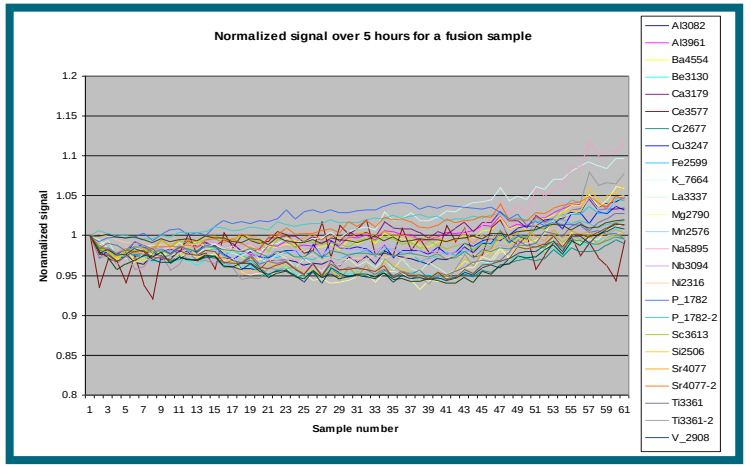
Challenges when analyzing high matrix aqueous samples (e.g., wastewater, seawater, brackish water, sludge)

- High TDS, salts, and suspended solids cause problems many problems in ICP-OES analysis

Sample introduction system	Deposits on quartz torch and center tube	More frequent sample introduction maintenance	More frequent replacement of quartz torch and center tube
Analytical run	Clogging of nebulizer and center tube	Drift in instrument performance	Failure of QCs and samples
Samples	Physical Interferences	Chemical Interferences	Suppression or Enhancement of Signal

Damaged quartz torches

EIE Effect: $Na \rightleftharpoons Na^{+} + e + e$



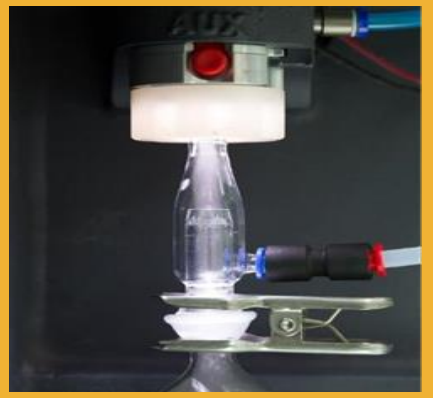
Signal Instability

Addressing challenges through method optimization

Four key areas for method optimization

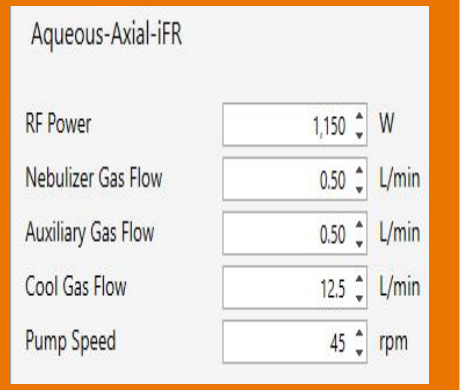
Sample introduction system

Selection of the appropriate components is key for method optimization.



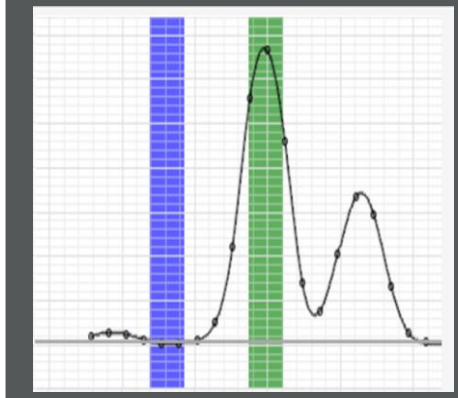
Accessories

Accessories available to improve sample handling, robustness and stability.



Operating parameters

Set up operating parameters based on sample matrix and productivity requirements.



Interference correction

Apply the appropriate correction techniques for physical , chemical and spectral interferences.

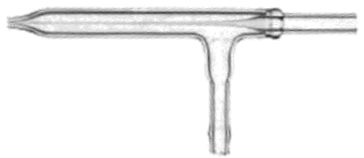
Sample matrix is a major consideration for optimization

Method optimization – sample introduction system component selection

Aqueous samples

Low solids < 3%

- Concentric glass nebulizer
- Glass Cyclonic spray chamber



High solids

> 3%

- Parallel path nebulizer (e.g., PEEK Burgener Mira Mist)
- Cyclonic chamber
- Argon humidifier

> 15%

- Parallel path or high solids nebulizers (e.g., Aerosalt)
- Baffled cyclonic spray chamber
- Sheath gas
- Large bore injector (e.g., 2.0 mm)

For enhanced robustness when running high solid samples for long periods, use a Ceramic D-torch and Sheath Gas

HF Containing

- HF resistant nebulizer (e.g.,Teflon Burgener Mira Mist)
- PFA spray chamber
- Alumina injector

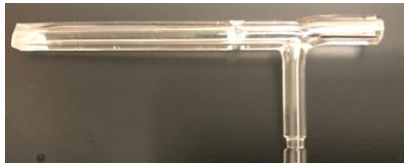
Method optimization – sample introduction system component selection

Organic samples

e.g., Kerosene, Xylene, MIBK, Toluene

Non-volatile

- V-groove nebulizer
- Baffled cyclonic spray chamber
- Small bore (1 mm ID) center tube
- Chemical resistant pump tubing



Ceramic D-torch for analysis of non-volatile organic samples, e.g., lubricating oils, for long periods

Use compatible peristaltic pump tubing!

Volatile

e.g., Petrol, Benzene, Hexane, Naphtha

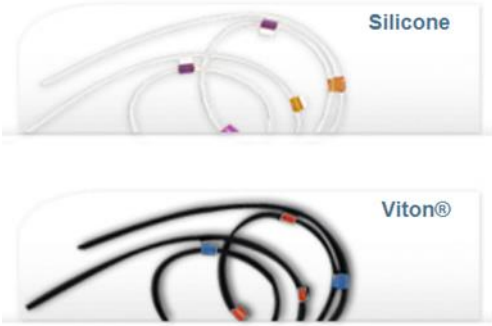
- V-groove nebulizer
- Small bore (1 mm ID) center tube
- Chemical resistant pump tubing
- Temperature controlled (cooled) spray chamber

Temperature controlled spray chamber using the **Glass Expansion IsoMist™** (operating range -10°C to 60°C) and the new **Glass Expansion IsoMist XR™** (extended range, from -25°C to 80°C)

Sample introduction components - tips and tricks

Peristaltic pump tubing

- Always use material compatible with the sample solution
- Chemical resistance charts for peristaltic pump tubing are available for reference
- **Types of material**
  - PVC – standard for aqueous samples, dilute acids
  - Viton® - concentrated acids or aggressive samples
  - Solvent Flex – volatile and non-volatile organic solvents
  - Santoprene™ - medium to high concentrated acids, some organic solvents



unity lab services
by Thermo Fisher Scientific

Chemical Resistance Chart

Legend
X = **Satisfactory**
O = **Use only after testing**
U = **Unsatisfactory**
- = **No data available**

Important note on service life, temperature, compatibility and chemical resistance:
The data provided in the tables are advisory values and not guaranteed. In all cases customers should conduct tests to ensure compatability with their chemicals and processes.

We recommend:
Place the tubing in the medium to be used for a period of 48 hours. After this time, examine the tubing for signs of swelling, softening or hardening. A judgement can then be made as to the likely suitability of the tubing.

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Acetaldehyde	U	X	U	X	X
Acetates (low mol. wt.)	U	O	U	X	X
Acetic acid (<5%)	X	X	X	X	X
Acetic acid (>5%)	X	U	O	X	X
Acetic anhydride	O	O	U	X	U
Acetone	U	X	U	U	U
Acetyl bromide	U	-	-	X	-
Acetyl chloride	U	-	-	X	-
Air	X	X	X	X	X
Alcohols	X	X	X	X	-
Aliphatic hydrocarbons	X	O	U	U	-
Aluminium chloride	X	O	X	X	-
Aluminium sulfate	X	X	X	X	X
Alums	X	-	X	X	-

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Benzaldehyde	U	U	U	U	X
Benzene	O	U	X	U	U
Benzene sulfonic acid	O	-	X	X	-
Benzoic acid	X	O	X	U	U
Benzyl alcohol	X	-	X	U	X
Bleaching liquors	X	O	X	X	X
Boric acid	X	X	X	X	X
Bromine	X	U	X	X	U
Butane	O	U	X	U	U
Butanol	X	O	X	-	-
Butyl acetate	U	-	U	U	U
Butyric acid	U	-	O	X	X
Calcium salts	X	O	X	X	X

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Ethyl bromide	U	-	X	X	-
Ethyl chloride	U	U	X	X	U
Ethylamine	U	-	U	X	-
Ethylene chlorohydrin	U	U	X	X	U
Ethylene di-chloride	U	U	X	X	U
Ethylene glycol	X	X	X	X	X
Fatty acids	O	O	X	X	-
Ferric chloride	X	O	X	X	-
Ferric sulfate	X	O	X	X	X
Ferrous chloride	X	O	X	X	
Ferrous sulfate	X	O	X	X	-
Fluoborate salts	X	-	-	X	X
Fluoboric acid	X	-	-	X	

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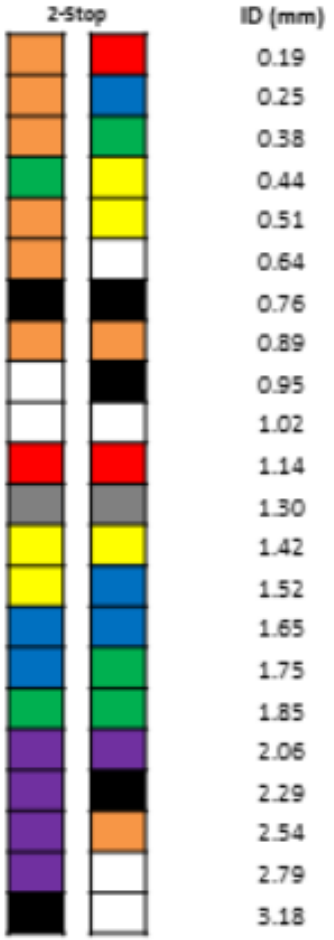
Sample introduction components - tips and tricks

Pump tubing

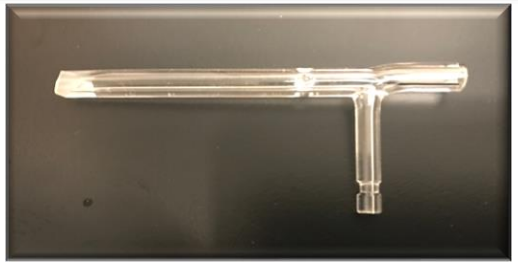
- **Pump tube size and selection**
  - Ensure that the correct size of pump tube is being used.
  - Ensure that the pump tube for the drain is larger than the sample tube.
  - Ensure that the correct type is being used for the matrix being analyzed.

- **Pump tube maintenance**
  - Ensure that the pump tube is not stretched or has flat spots.
  - Do not put unneeded pressure on the tube by over tightening.
  - Replace the tubing if any leaks or defects are observed.
  - Replace the tubing frequently; poor stability is due to defective pump tubing



Sample introduction components - tips and tricks

Nebulizer types

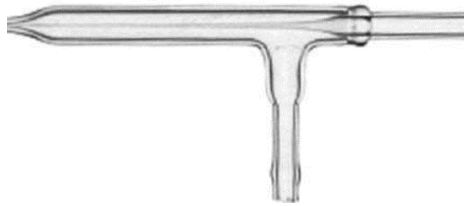


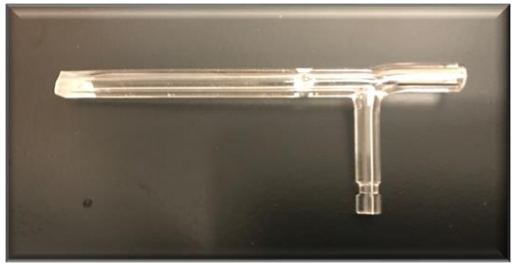
Type	Sample type	Precision	Sensitivity	TDS tolerance	HF compatibility	Organics compatibility
Concentric (glass)	Environmental - food - beverage	Best	Best	Moderate	Not compatible	Low Tolerance
V-Groove (glass)	Organics - high solids	Moderate	Moderate	Best	Not compatible	Best
Aerosalt (glass)	Seawater - high solids	Good	Best	Best	Not compatible	Low Tolerance
Burgener Mira Mist (PEEK)	Variety of matrices - limited organics	Good	Good	Good	Best	Moderate tolerance

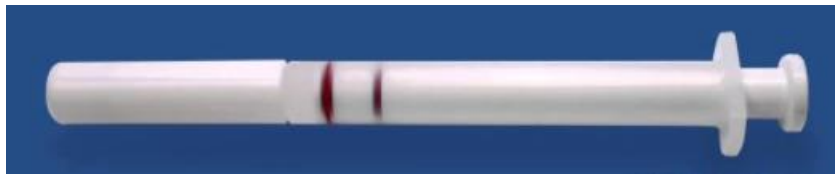
Sample introduction components - tips and tricks

Nebulizer

- **Maintaining the nebulizer**
  - Examine the nebulizer to ensure it is clean of particulates.
  - Examine the nebulizer for any damage.
  - To remove deposits on the nebulizer soak in a dilute acid solution.
    - The strength of the acid will vary depending on the deposit.
    - Typically, a solution of 2%-5% HNO_3 is utilized for soaking.
      - Concentrated acid or Aqua Regia could be used if needed.
    - Soak the nebulizer until the deposit has dissolved.
    - Rinse with DI Water until all acid solution is removed.
  - For blockages that will not dissolve, the Eluo Nebulizer Cleaning Tool is available from Glass Expansion – Part # 70-ELUO (Glass Nebulizers Only)
- **Do not use a wire or ultra sonic bath to clean**







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Sample introduction components - tips and tricks

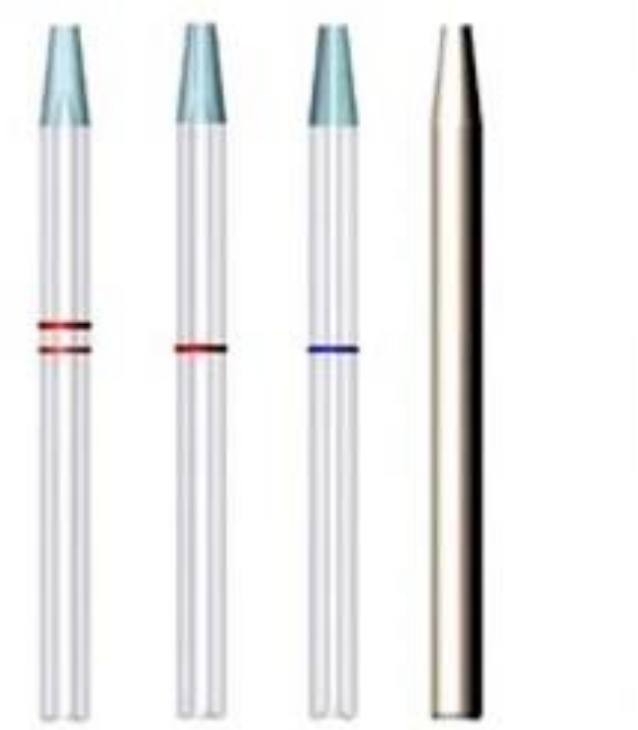
Spray chamber

Type	Sample Type	Precision	Sensitivity	TDS Tolerance	HF Compatibility	Organics Compatibility
Single Pass Cyclonic	Aqueous	Best	Best	Good	Not Compatible	Good
Double Pass Cyclonic	High TDS - Organic Solvent	Good	Good	Best	Not Compatible	Best
Inert Single Pass Cyclonic	HF Matrices	Good	Good	Good	Best	Best

Sample introduction components - tips and tricks

Injector

Using a different size injector/center tube alters the characteristics of the sample

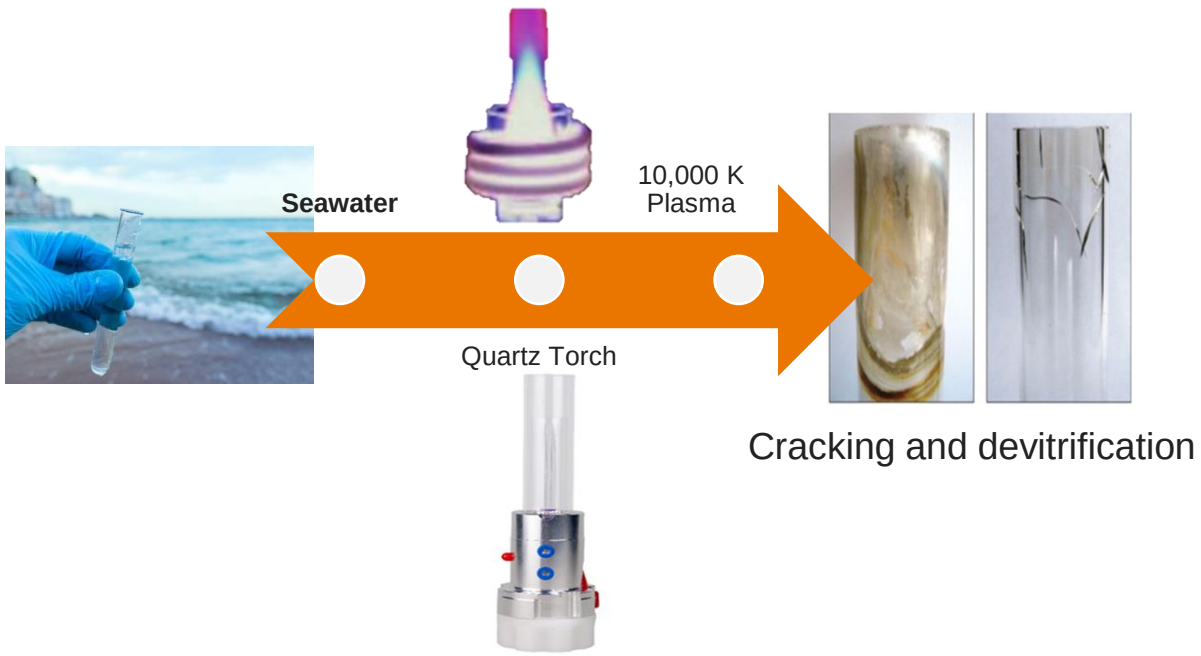


Injector options	Usage
1.0 mm quartz (double red ring)	Organic solvent analysis
1.5 mm quartz (single red ring)	Aqueous samples
2.0 mm quartz (single blue ring)	High TDS/salts/solid samples
2.0 mm ceramic	HF containing samples

Sample introduction components - tips and tricks

Enhanced Matrix Tolerance (EMT) quartz torch

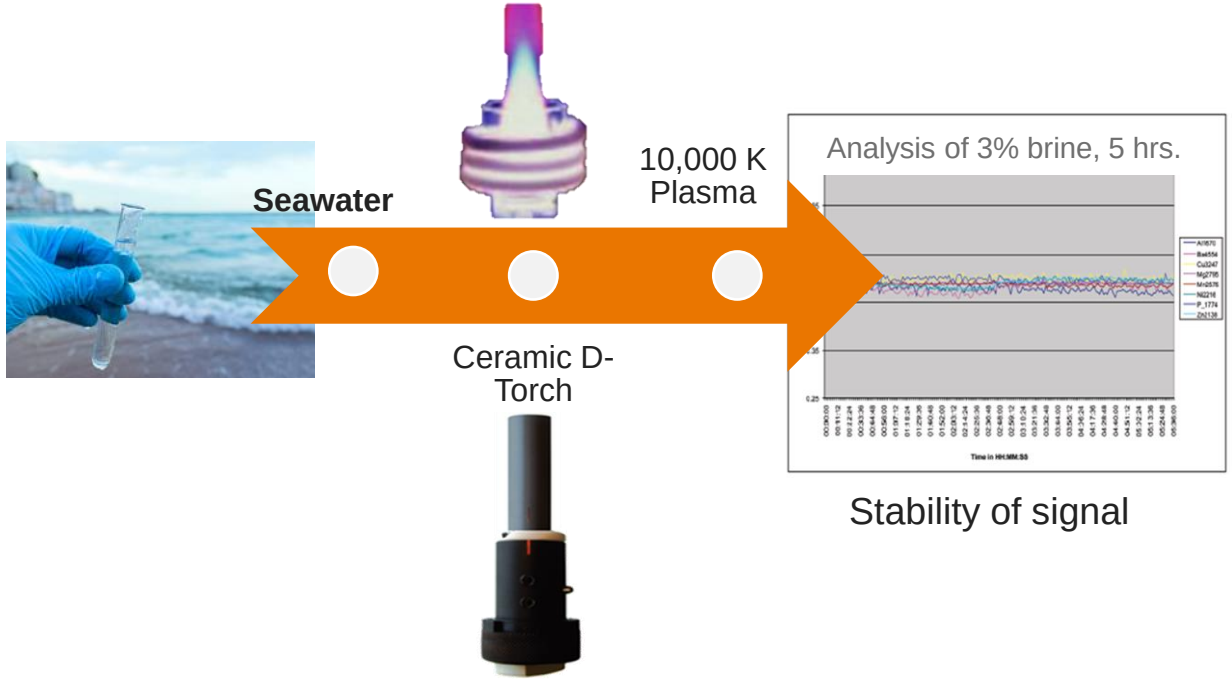
- Made from Quartz, a crystalline form of SiO_2, ideal for most aqueous samples, dilute acids
- Limitation:
  - With continuous analysis of high matrix samples (e.g., sea water) quartz can devitrify/crack leading to signal instability, failed samples/QC and more maintenance



Cracking and devitrification

Ceramic demountable torch (D-torch)

- Made from Sialon (silicon nitride), a highly durable material, heat and chemical resistant material
- Alumina intermediate tube for excellent chemical and temperature resistance
- Use for high matrix samples (e.g., brines, sea water, fusions, lubricating oils, etc.,)



Stability of signal

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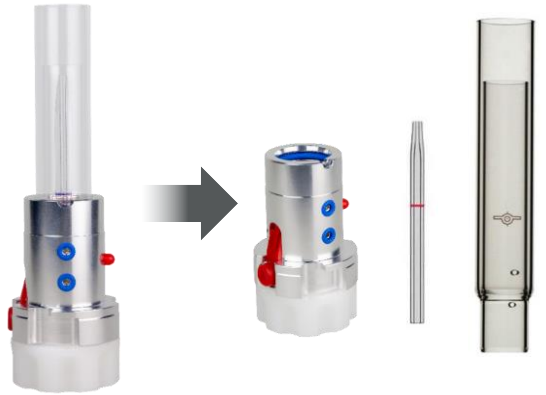
Sample introduction components - tips and tricks

Torch

- **To clean the torch**
  - Shut down the system.
  - Inspect the O-rings in the metal torch mount (three internal and two external). Replace them, if any wear or damage is visible.
  - Soak the torch in a dilute analytical-grade surfactant for five minutes to remove salt deposits.
  - To remove metallic deposits from the tip, separate the torch quartz section, immerse the tip of the torch in acid. A mixture of nitric and hydrochloric acid similar to aqua regia is suitable.
  - Rinse the torch with deionized water. Place it in a drying oven at 95 °C until it is dry. Rinsing with a volatile, zero residue, organic solvent (propanol is suitable) aids drying.
- **To clean the torch of carbon deposits**
  - Place the torch in a muffle furnace and heat it to 750 °C.
  - Open the door of the furnace to admit air for a few seconds.
  - Close the door. Let the temperature return to 750 °C.
  - Repeat step 1 to step 3 two or three times until the carbon is burned off
  - Switch off the muffle furnace. Let it cool without opening the door. This takes several hours.



Plasma interface – tips and tricks

Inner torch box

- **If high matrices like brines are analyzed over prolonged periods of time, deposits can form on the inside of the inner torch box. This inner torch can be removed and cleaned.**
- **To clean the Inner Torch Box**
  - **Shut down the system.**
  - **Open the torch box door and remove the torch from the torch box.**
  - **Remove the axial POP cone from the torch box (if applicable).**
  - **Loosen the three screws on the rim of the inner torch box facing to you and take out the inner torch box. Do not loose the screws inside the torch box.**
  - **You can now also remove and clean the radial POP cone, if necessary.**
  - **Soak the torch box in a dilute analytical-grade surfactant for five minutes to remove salt deposits.**
  - **Rinse the torch box with deionized water. Place it in a drying oven at 95 °C until it is dry. Rinsing with a volatile, zero residue, organic solvent (propanol is suitable) aids drying.**
  - **Re-install the inner torch box by reversing the steps above.**

Sample introduction components - tips and tricks

Pre-configured kits simplify the selection of sample introduction components

Aqueous Kit

- Cyclonic spray chamber
- Concentric nebulizer
- 1.5 mm injector (Duo), 2.0 mm injector (radial)
- EMT torch and holder, Ball joint and clip

HF Kit

- PFA cyclonic spray chamber
- MiraMist concentric nebulizer
- 2.0 mm alumina injector
- EMT torch and holder
- Ball joint and clip

High Solids Kit

- Baffled cyclonic spray chamber
- Aerosalt concentric nebulizer
- 2.0 mm injector
- EMT torch and holder
- Ball joint and clip
- Option: Argon humidifier

Volatile Organics Kit

- Baffled cyclonic spray chamber
- V-groove concentric nebulizer
- 1.0 mm injector, EMT torch and holder
- Ball joint and clip
- Option: IsoMist Spray Chamber

Organics Kit

- Baffled cyclonic spray chamber
- V-groove concentric nebulizer
- 1.0 mm injector, EMT torch and holder
- Ball joint and clip

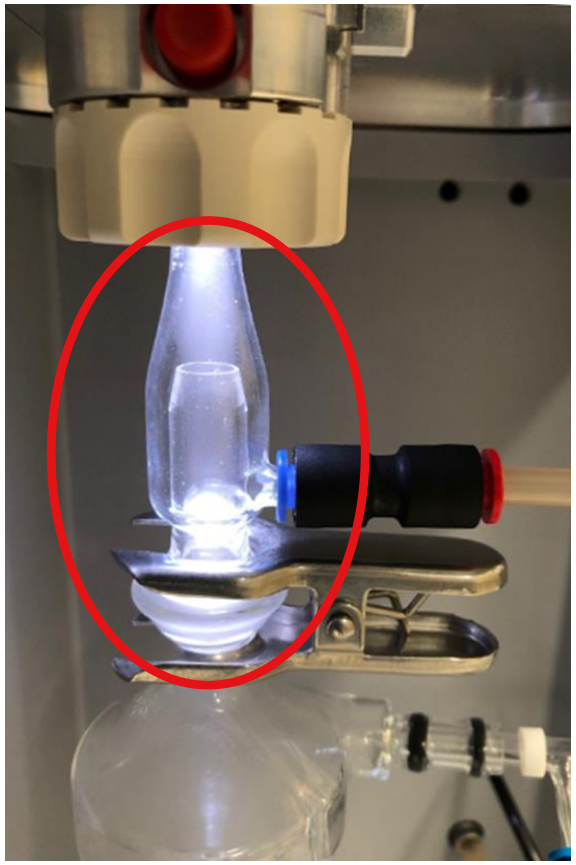
Note: Peristaltic pump tubing not included

Method optimization - accessories

Sheath gas adaptor – accessory for enhanced robustness and stability

- A Sheath Gas is a constant flow of argon that envelopes the sample aerosol tangentially to
  - prevent contact with the injector
  - reduce sample deposition in the injector
- The Sheath Gas is introduced between the spray chamber and torch with the Sheath Gas Adaptor
- Benefits of a Sheath Gas
  - Enables higher tolerance of TDS
  - Less sample dilution, hence improved MDLs
  - Improvement in stability for the long-term analysis of high solid samples (e.g., sea water)
  - Reduced need for extended rinse time between samples

Sheath Gas Off



Sheath Gas On

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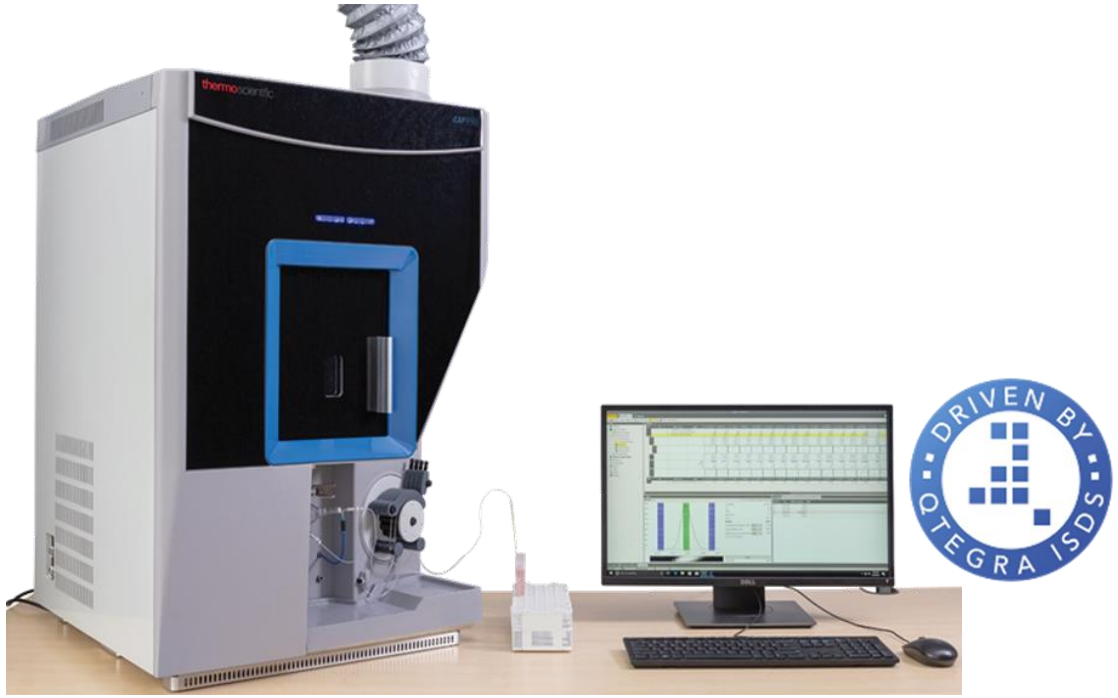
Method optimization – operating parameters

Operating parameters set-up through instrument software

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software

- **Benefits of the Qtegra ISDS Software:**
  - Intuitive, streamline workflow platform
  - Plug-ins for fast autosamplers and autodilution systems
  - A range of new software features (e.g., Plasma TV, auto tunes, modes, etc.) added for ease of use
  - 21 CFR Part 11 compliance tool set
  - Same software platform as Thermo Scientific ICP-MS instruments for easy cross-training

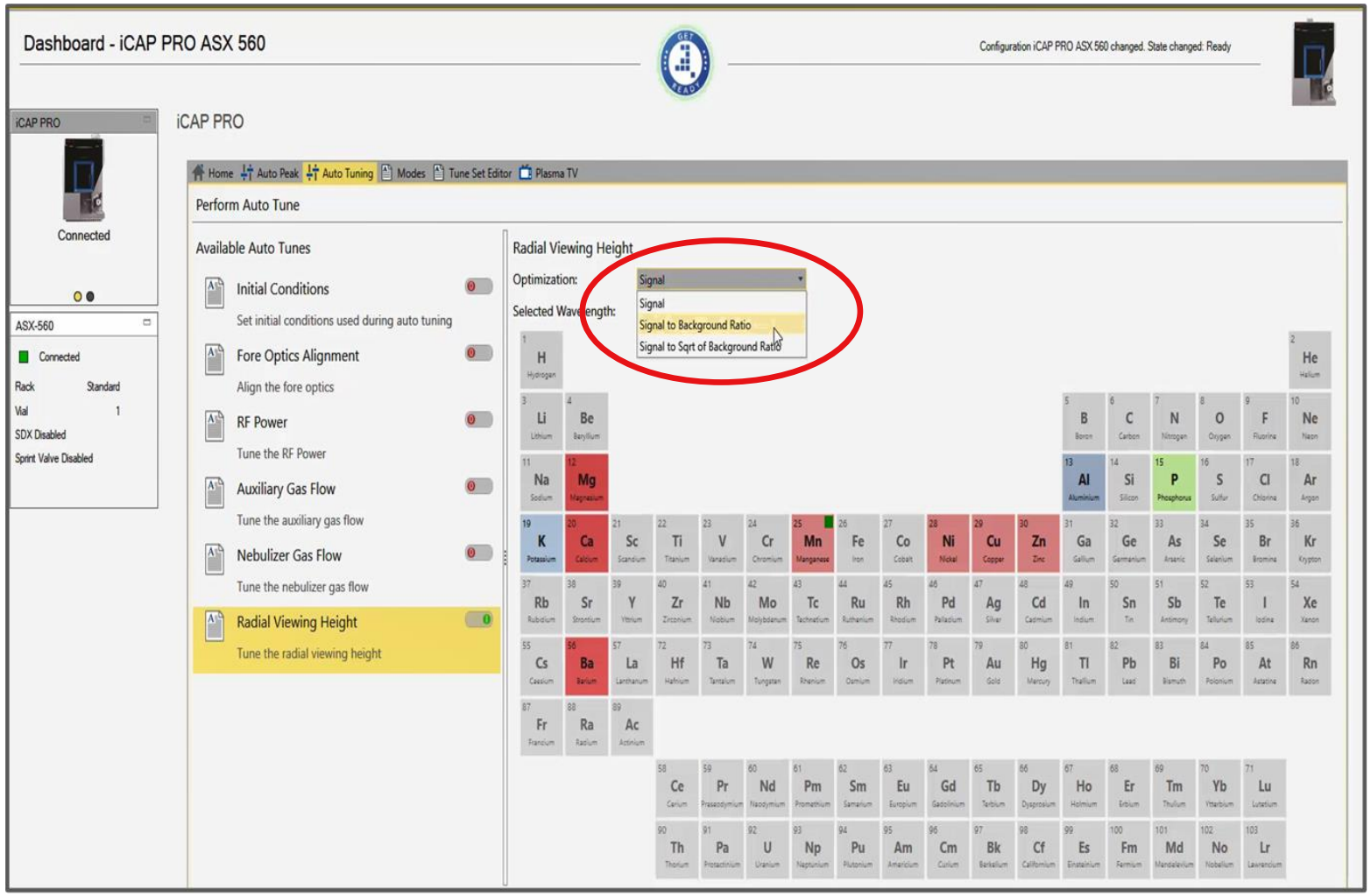


Method Optimization – operating parameters

New AutoTune feature for automatic optimization of operating parameters

- **Auto Tune**

- Optimizing operating parameters can be done automatically using the Auto Tune feature within the Qtegra ISDS software.
- Operating parameters (e.g., nebulizer gas flow, radial view height) can be automatically tuned based on signal, signal to background or signal to square root of background.
- A multi-element test solution for auto tuning is included.



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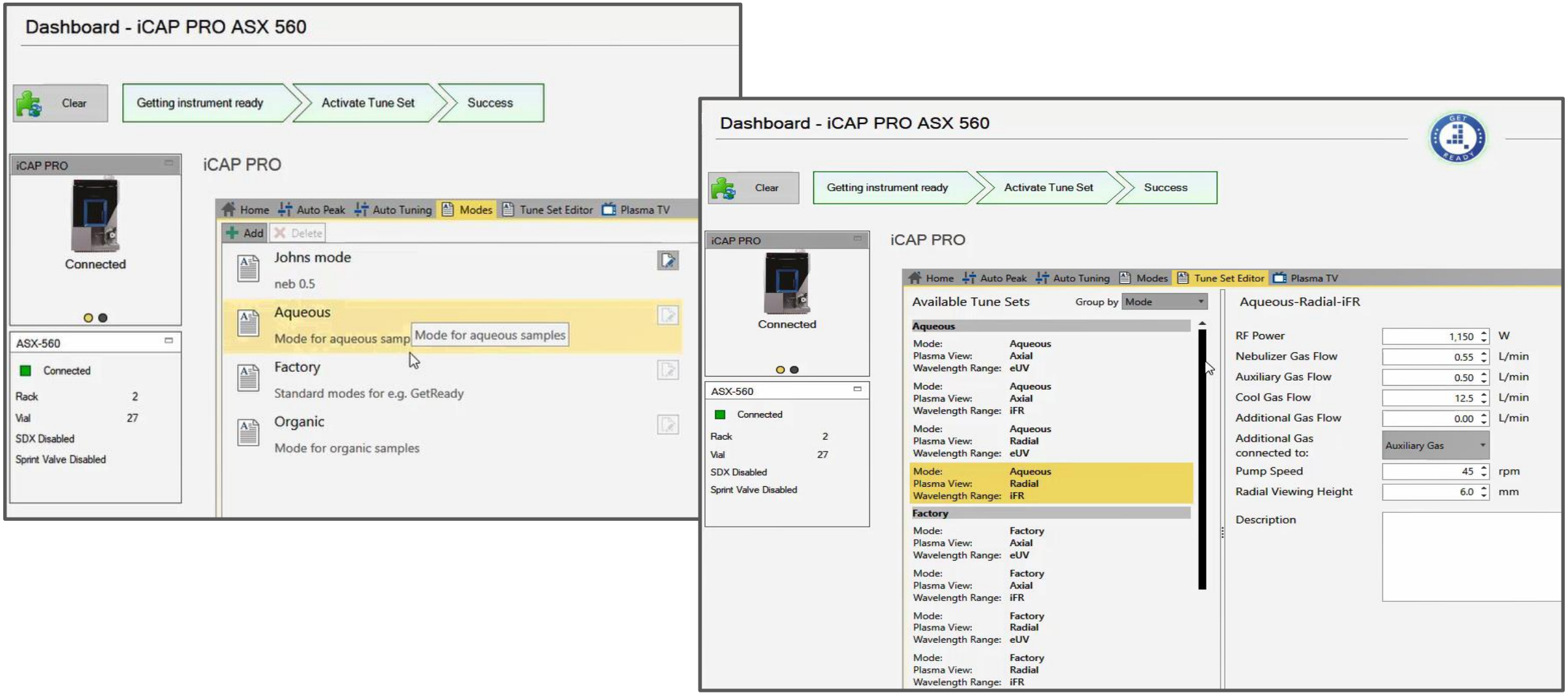
Method optimization – operating parameters

Built-in and customizable modes for aqueous and organic samples for easy method development



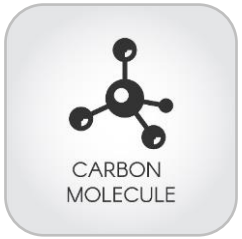
Method optimization – addressing interferences

What are the interferences in ICP-OES Analysis?

Three types of interferences

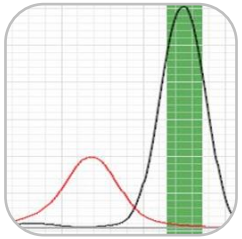
Physical interferences

Difference in physical properties in samples and standards affecting sample transport and nebulization efficiency. They are multiplicative and not specific to a wavelength.



Chemical interference

Difference in the way sample and calibration standards react in the plasma during vaporization, atomization and ionization.



Spectral interference

Characterized by an overlap of a constituent wavelength on the analyte wavelength. Also includes background signal interferences.

Method optimization – physical interferences

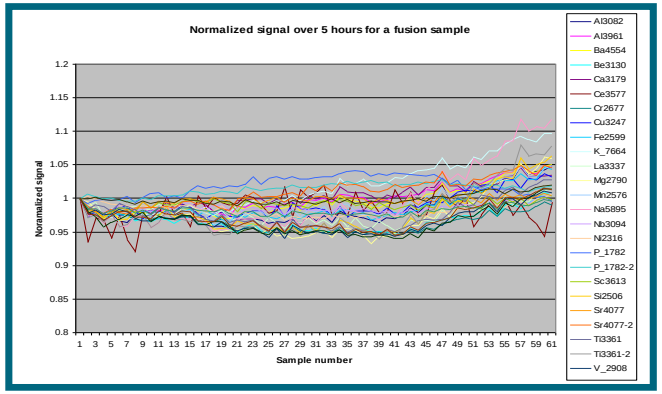
Addressing physical interferences

Cause

- High TDS, suspended solids, high salts, viscosity, density, volatility, etc.

Effect

- Suppression or enhancement of signal
- Instability of signal, drift during analysis
- Sample and standard failures
- More frequent maintenance



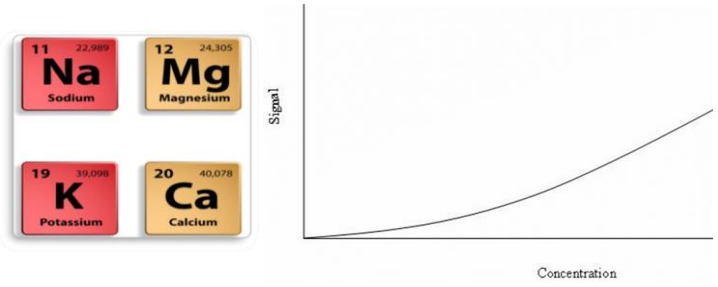
Solution

- Dilution – preferred solution
- Matrix Matching – samples and calibration standards
- Internal Standardization – online (preferred) or manual addition of internal standard
- Optimize sample introduction and operating parameters
- Method of Standard Additions – least preferred solution

Method optimization – chemical interferences

Addressing chemical interferences

Easily Ionized Element Effect (EIE)



$Na \rightleftharpoons Na^+ + e^- + e^-$ (Na, Ca, Mg, K)

- High concentration of Grp. I & II elements, excess electrons shifting equilibrium in the plasma
- **Effect:** Enhancement of atomic lines
- Solutions: radial viewing, ionization buffer (e.g., Cs, LiCl, etc.), dilution

Molecular formation

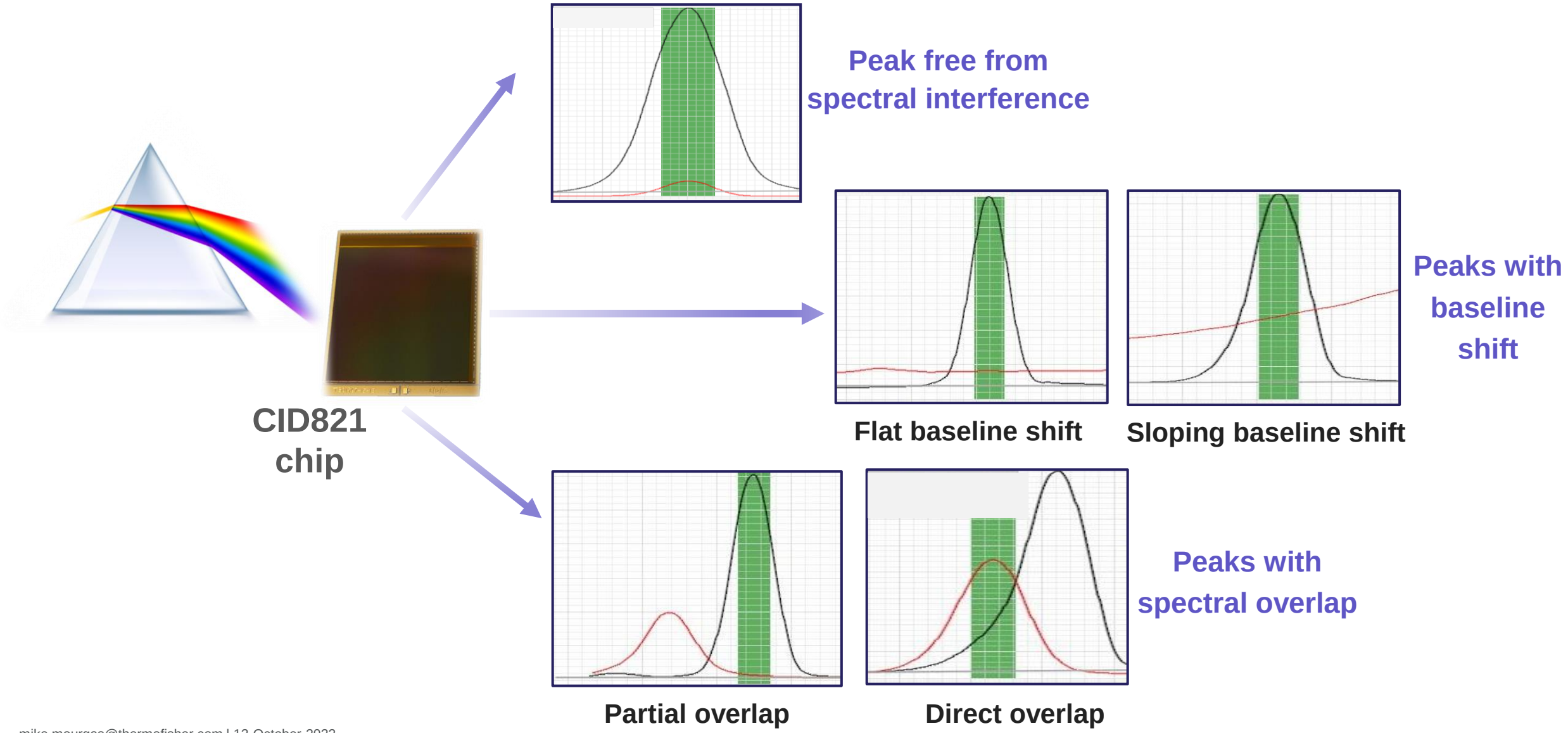
- Caused by molecular emissions in the plasma interfering with the analyte wavelength
- **Effect**
  - Elevated background
  - Spectral interferences
    - e.g., emission from carbon-containing molecules interferes with the Na 589.592 nm line
- Solutions: radial viewing, proper Background Point placement, dilution

Plasma loading

- Increased consumption of plasma energy needed to break-up high matrices (e.g., TCLP extracts) causing insufficient energy to excite low concentration or high ionization potential analytes
- **Effect**
  - Suppression of ionic wavelengths
  - Low sensitivity for key elements (e.g., As, P, S) and atomic wavelengths
- Solutions: dilution, robust plasma conditions (e.g., higher power setting, higher plasma gas flow, etc.)

Method optimization – spectral interferences

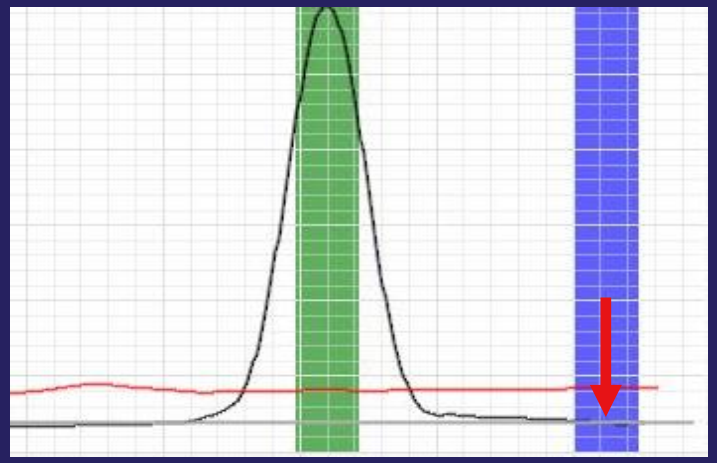
Types of spectral interferences



Method optimization – spectral interferences

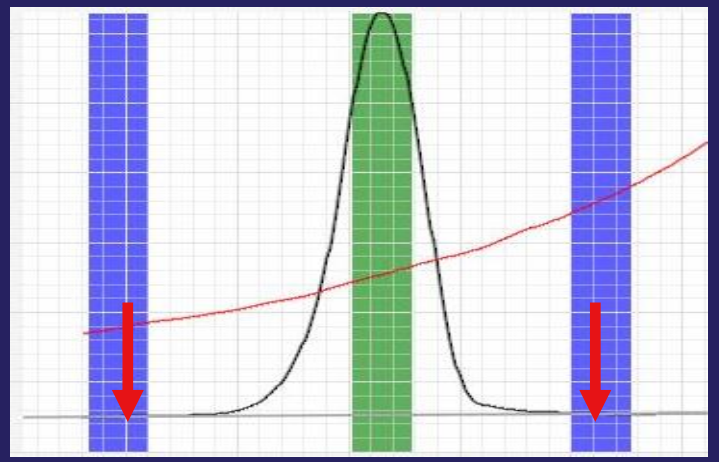
Addressing spectral interferences through background correction points

- Spectral interferences can be corrected by:
  - Applying Background Points
  - Interelement Correction Factors (IECs)



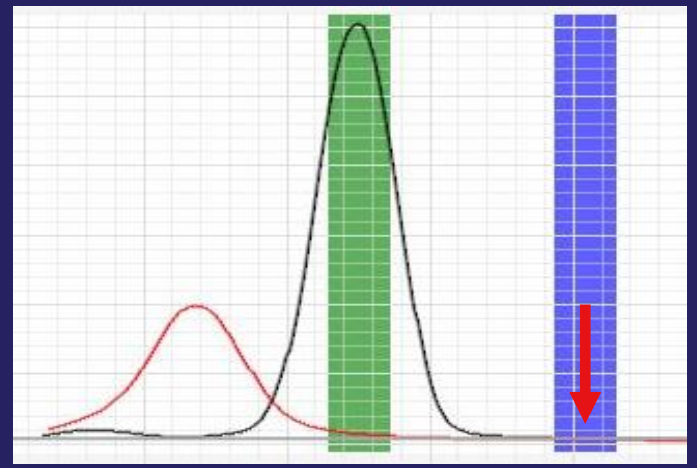
Flat Baseline Shift

- Place background point on the side of the peak with no interference



Sloping Baseline Shift

- Always use two background points on both sides of the peak



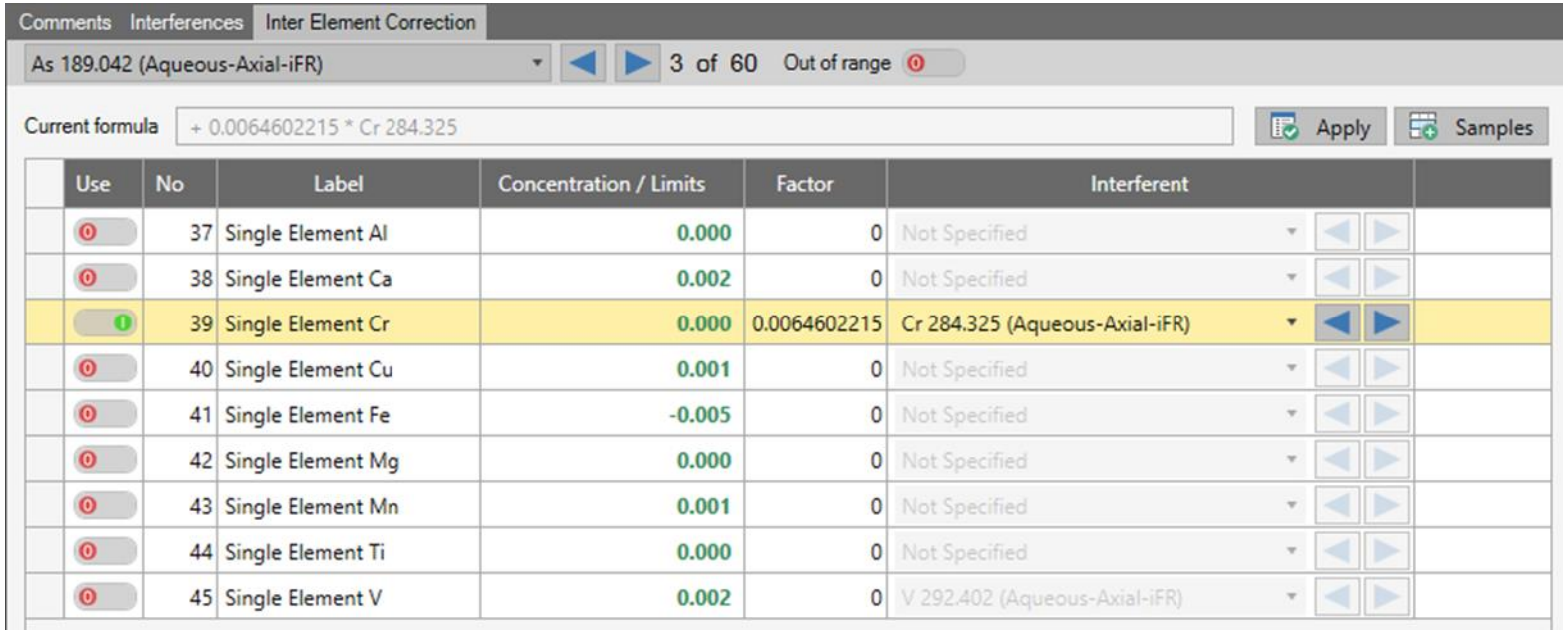
Spectral Overlap

- Place background point on side of the peak with no interference
- Use alternative wavelength, if possible
- Apply Interelement Correction Factor

Applying Interelement Correction Factors (IECs)

IEC feature within the Qtegra ISDS software

- Inter-Element Correction (IEC) corrects for direct spectral interferences (overlaps), these can be defined in the Qtegra ISDS software
- An IEC is a ratio correction factor that is applied to all samples
- In the Qtegra ISDS software, just select the interferent in the LabBook, the software will then calculate the correction factor based on measurements of single element solutions



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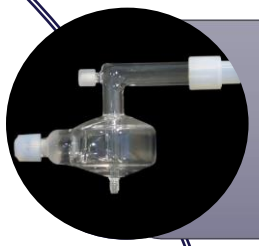
Addressing challenges through instrument innovations

Key ICP-MS features to overcome challenges in sample analysis

Addressing challenges through instrument innovation

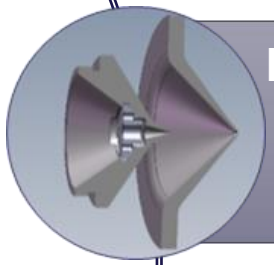
Components that deliver performance, ease of use, and robustness

iCAP RQ ICP-MS



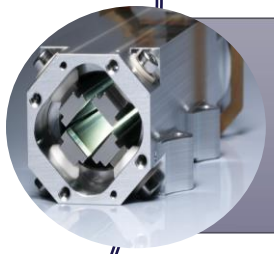
Sample introduction system

- Quick connect torch with automatic gas connection
- Push fit nebulizer, low volume spray chamber, etc.



Plasma Interface

- Unique drop-down door for easy access to sample and skimmer cones
- Exchangeable skimmer cone inserts for enhanced matrix tolerance or high sensitivity



Collision/Reaction Cell

- Kinetic Energy Discrimination (KED) with Low Mass Cut-off (LMCO)
- Triple quadrupole technology for advanced interference removal

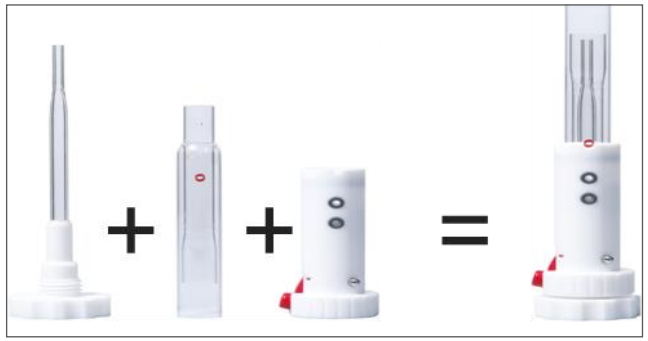
Software

- Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software designed for ease of use and streamlined workflow

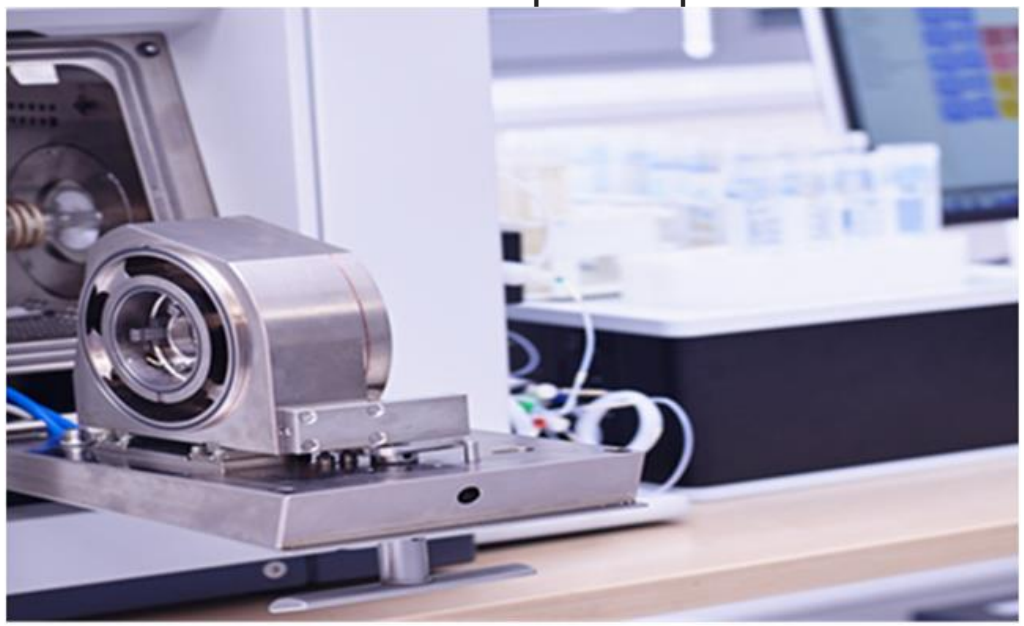
Addressing challenges through instrument innovations

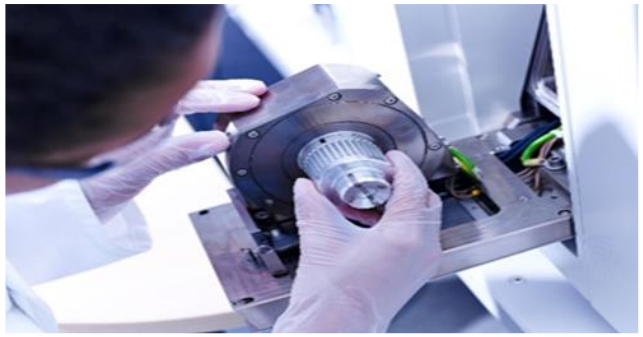
Sample introduction system and plasma interface

Quick connect sample introduction components



Plasma interface unique drop-down door





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Addressing challenges through instrument innovations

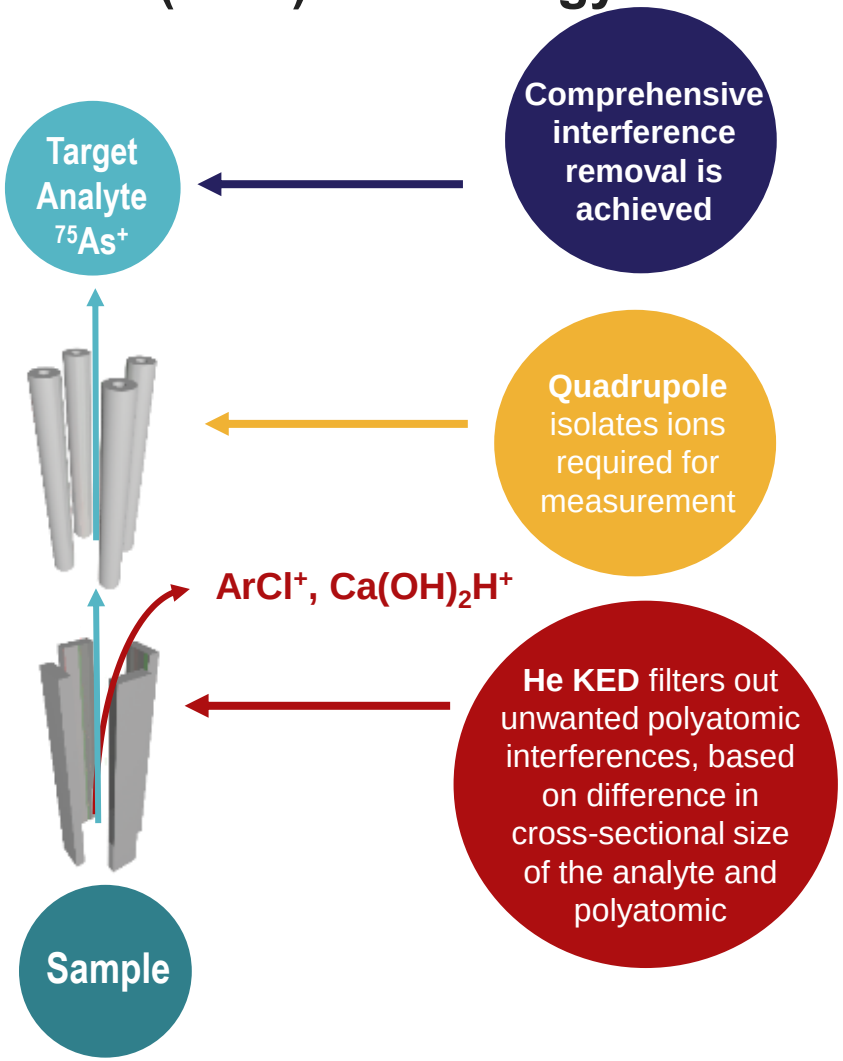
Spectral interference removal with QCell™ Collision/Reaction Cell (CRC) Technology

Kinetic Energy Discrimination (KED)

- Single mode interference removal with He KED
- Method development is simplified as He KED eliminates interferences for most applications

Quadrupole set to filter out exact mass of target analyte

QCell in collision mode with pure He uses energy discrimination



With QCell, KED is complemented by a second active mechanism…

Addressing challenges through instrument innovations

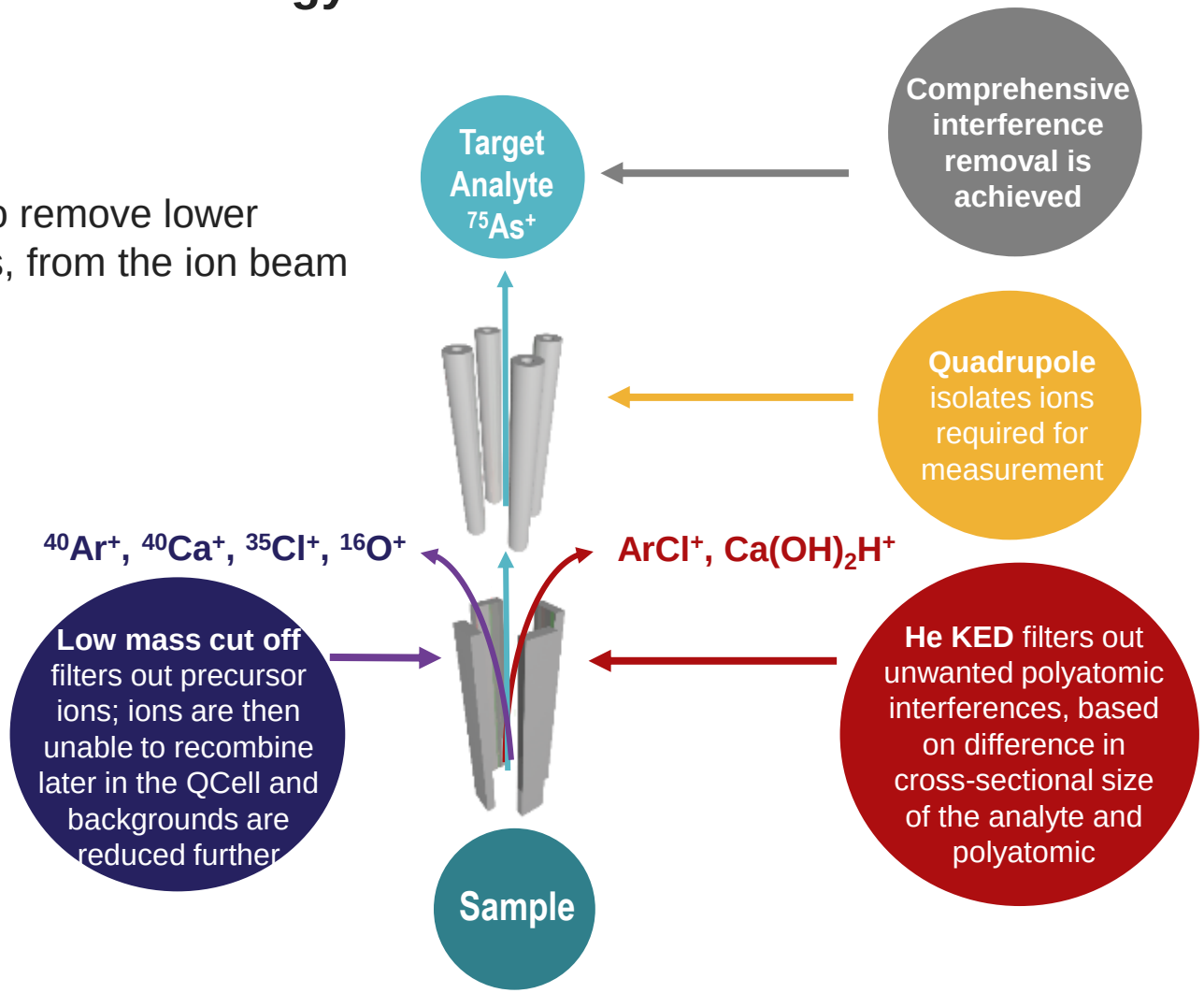
Spectral interference removal with QCell CRC technology

Kinetic Energy Discrimination (KED) plus Low Mass Cutoff (LMCO)

- A unique characteristic of flatapoles, used in QCell, to remove lower mass precursor ions, that can form new interferences, from the ion beam

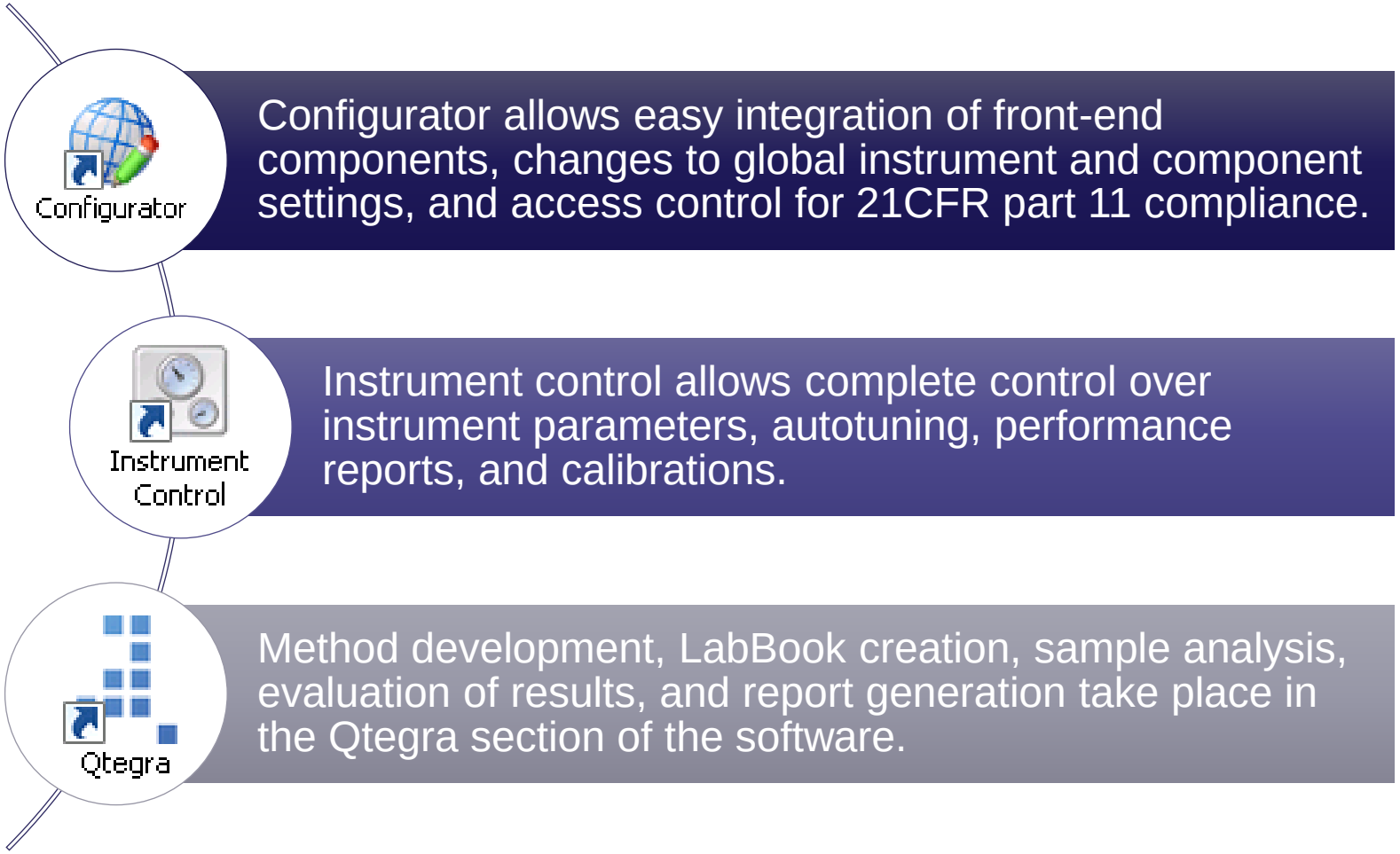
Quadrupole set to filter out exact mass of target analyte

QCell in collision mode with pure He uses energy discrimination

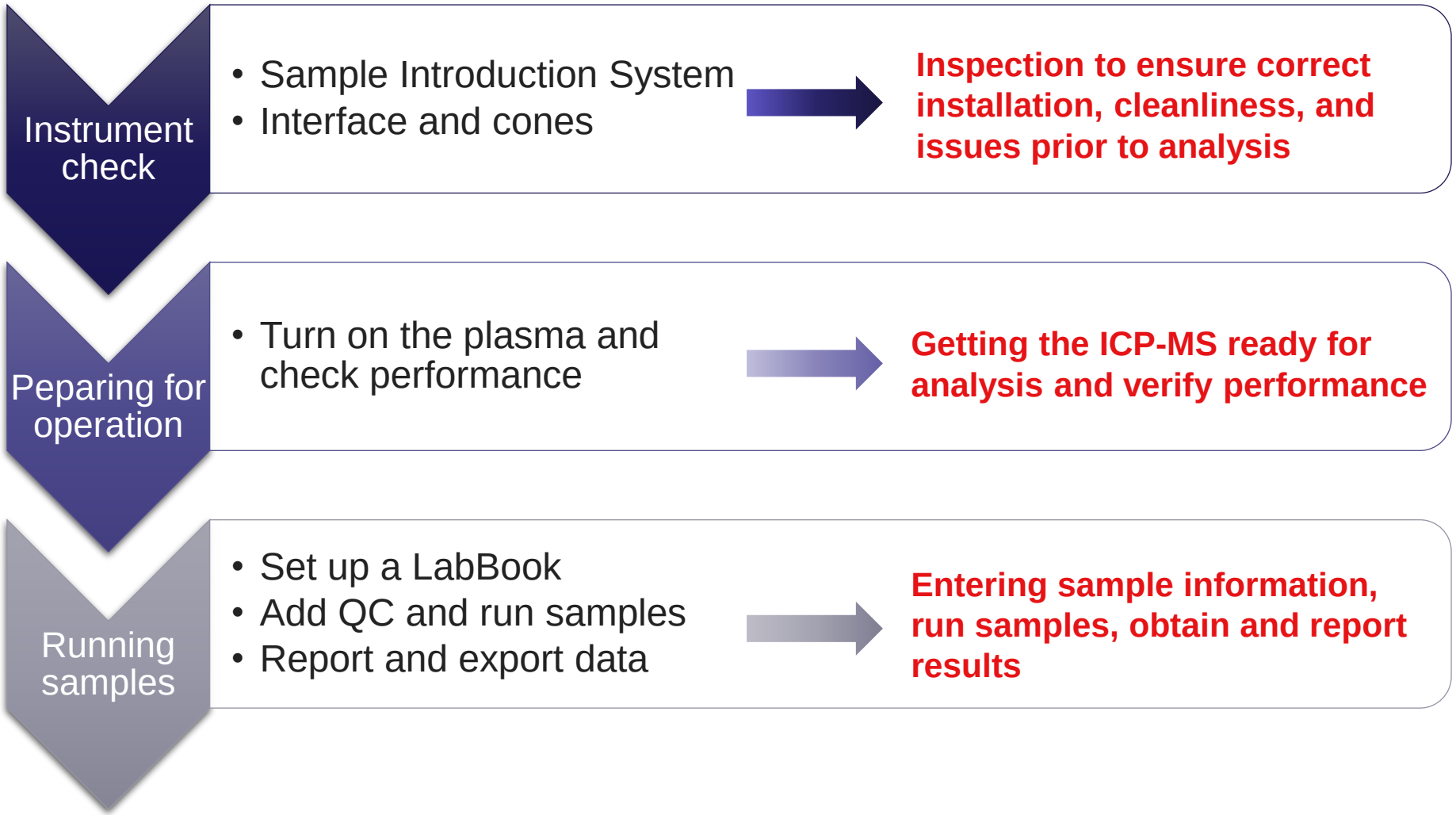


Thermo Scientific Qtegra ISDS software

Three sections of the Qtegra ISDS software



Typical ICP-MS analysis workflow



Instrument checks – sample introduction system

Instrument checks

- Sample Introduction System

Torch assembly

- Inspect injector/center tube and torch for matrix build up, blockages, cracks, fractures, and devitrification
  - ➢ these defects will affect sensitivity, precision, accuracy, and cause drift throughout the analysis

iCAP RQ ICP-MS torch assembly

- **TIP:** Always have a spare torch assembly, clean and ready to use

Sample introduction system – torch assembly

Torch assembly - 2 types of torches available for ICP-MS analysis

Quartz torch

- Comes standard with the iCAP RQ ICP-MS
- Good for most aqueous applications consisting of dilute acid solutions
- Quartz has a high coefficient of linear expansion
- Disadvantages
  - Devitrification
  - Poor tolerance to high matrix
  - Not compatible with HF
  - Maintenance and replacement

Ceramic PLUS torch

- PLUS – **P**erformance, **L**ifetime, **U**ltraclean **S**pectrum
- Made from high purity and high-performance ceramic material
- Identical geometry as the standard quartz torch
- Benefits
  - Decrease in background for Si
  - Resistant to HF
  - Improved robustness for high matrix samples
  - Less maintenance and less frequent replacement

Quartz torch | Ceramic torch

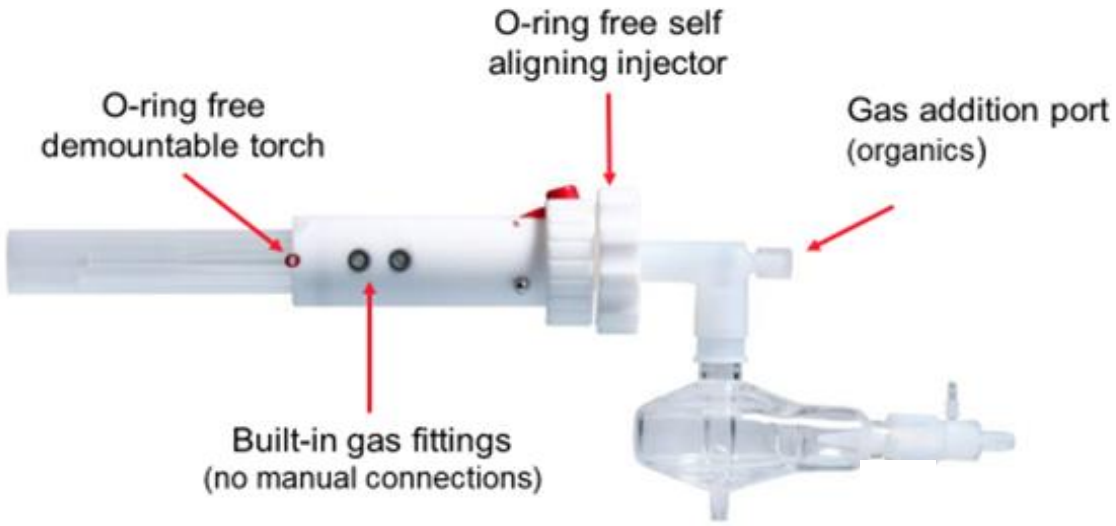
Instrument checks – sample introduction system

Instrument checks

- Sample introduction system

Check the spray chamber

- There should be no droplets inside the spray chamber
  - ➢ Droplets and condensation along the walls of the spray chamber cause signal instability



Baffled cyclonic spray chamber

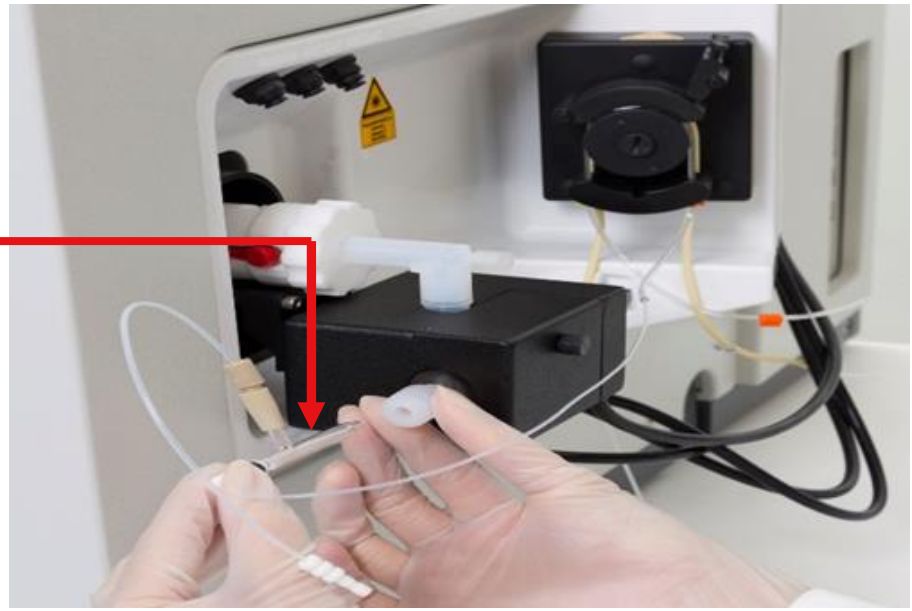
Instrument checks – sample introduction system

Instrument checks

- Sample introduction system

Nebulizer

- Inspect the nebulizer for deposits at the tip or any damage
- Ensure that the nebulizer is clean and that there are no blockages
  - Deposits and blockages restrict aerosol formation decreasing sensitivity, causing signal drift, and affecting accuracy and precision



Instrument checks – sample introduction system

Instrument checks

- Sample introduction system

Nebulizer

- Ensure that the appropriate type of nebulizer is used for the application

Glass concentric micro mist nebulizer
• Low flow, borosilicate glass, self-aspirating, concentric design, 400 µL/min flowrate • High sensitivity, good for most applications • Can tolerate up to 1% TDS • Comes standard with iCAP RQ ICP-MS

PFA-ST nebulizer
• All PFA construction, chemical resistant • Self-aspirating • 400 µL/min flowrate • High transport efficiency, high sensitivity • Resistant to clogging and breakage

Burgener Mira Mist nebulizer
• PEEK construction, resist most chemicals • Parallel Path design, 0.4 – 0.2 mL/min • Best balance between sensitivity and matrix tolerance • Not self-aspirating

Instrument checks – sample introduction system

Instrument checks

- Sample introduction system

Autosamplers and autodilution systems

- Inspect the autosampler lines and autosampler probe
  - ➢ Obstructions will cause longer uptake times and poor stability resulting to precision issues
- Ensure that the samples are loaded according to the method
  - ➢ Samples must be in the correct location and on the correct rack
- Remove autosampler caps, tops, and any covering from the samples
- Remove any items that will interfere with the movement of the sample probe
- Check the sample probe depth and ensure it is above any precipitate/solids that have settled
- Inspect autosampler wash station pump tubing for wear and tear

✓ Tip: Use an autosampler cover to prevent dust or dirt from depositing onto samples

Instrument checks – interface and cones

Instrument checks

- Interface and sample and skimmer cones

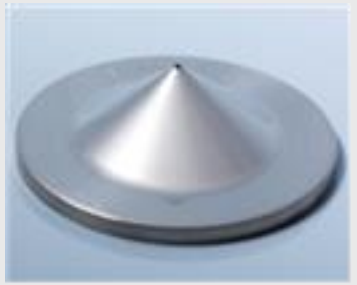
- The ICP-MS interface is the point where sample ions are transferred into the mass spectrometer
- Cones can be prone to build up of sample matrix
- Inspect sample and skimmer cones prior to analysis for blockage and wear around the orifices
- Ensure that the appropriate skimmer cone insert is placed at the back of the skimmer cone

		
Robust 4.5 mm	High matrix 3.5 mm	High Sensitivity 2.8 mm

mike.mourgas@thermofisher.com | 12-October-2022

Maintenance, tips, and tricks for sample and skimmer cones

- Reminder! New cones and cones that have been thoroughly cleaned must be conditioned prior to use. Condition cones by:
  - aspirating a solution of 500 ppm calcium in 2% HNO_3 and 0.5% HCl for 1 hour
  - aspirating the highest matrix sample for 1 hour followed by the blank solution
- Clean cones if blockage and damage to the orifices are visible and if performance issues (e.g., increased background, memory effects, signa drift, poor precision) remain after troubleshooting sample introduction system (e.g., torch, nebulizer).
- Cones should not be cleaned aggressively or more often than necessary. Clean cones by:
  - Sonicating with reagent water for 5 -10 minutes. This should be adequate to clean and restore performance. Conditioning is not necessary as coating of oxides should still be intact.
  - If performance issues persist or for tough deposits, sonicate in 2% Citranox or 2% nitric acid for 5 - 10 minutes. Rinse cones and allow to air dry. Condition cones prior to analysis.
- Handle both cones with care, especially the skimmer cone as the tip is more delicate.
- If tips are chipped or the orifices are enlarged, replace cones as soon as possible.



Sample cone

Skimmer cone

Routine maintenance

When does the peristaltic pump tubing need to be replaced?

Intensities

No	Date / Time	Label	7Li	59Co	115In	238U
38	9/3/2019 4:06:25 PM	<Identifier>	353,995	376,923	319,111	384,184
39	9/3/2019 4:07:20 PM	<Identifier>	400,960	439,965	364,775	454,618
40	9/3/2019 4:08:40 PM	<Identifier>	386,138	412,953	342,489	417,645
		1	410,788.1	440,256.5	368,845.4	444,588.5
		2	389,443.0	413,674.8	337,935.3	416,452.5
		3	358,183.4	384,926.6	320,684.9	391,895.2
		Mean:	**386,138.1**	**412,952.6**	**342,488.5**	**417,645.4**
		RSD [%]:	6.9	6.7	7.1	6.3
		SD:	26,457.6	27,672.0	24,400.9	26,366.9

No	Date / Time	Label	7Li	59Co	115In	238U
41	9/3/2019 4:09:37 PM	<Identifier>	421,115	444,523	379,697	454,945
42	9/3/2019 4:13:45 PM	<Identifier>	7,165	1,104	371	115
43	9/3/2019 4:14:41 PM	<Identifier>	6,993	906	270	3
44	9/3/2019 4:15:59 PM	<Identifier>	6,973	880	273	1
46	9/3/2019 4:27:54 PM	<Identifier>	321,208	337,602	280,372	343,619
47	9/3/2019 4:28:51 PM	<Identifier>	316,370	330,756	274,959	338,767

Maintenance, tips, and tricks for the torch assembly

- Clean the quartz torch by:
  - Soaking the ends of the torch up to where matrix has deposited in acid solutions (e.g., 5% nitric acid and 2% HCl) for at least 30 minutes or a few hours for persistent deposits.
  - Rinse thoroughly with reagent water and allow to air dry completely.
- Do not sonicate the torch and injector or use a wire brush or scraping tools to remove deposits.
- Do not touch torch and injector with bare hands. Always wear gloves when handling torch and injector to prevent oil and moisture from contaminating/damaging the surface.
- Ensure that the argon flow rates are optimized for the application and set prior to plasma ignition. Incorrect settings may cause damage, such as melting of the torch.
- After analysis, rinse the torch by running the blank solution followed by reagent water for a few minutes to prevent formation of matrix/salts inside the injector.

Maintenance, tips, and tricks for concentric glass nebulizers

- Proactively prevent nebulizer blockage by:
  - filtering particulates/suspended solids in the samples prior to analysis
  - covering samples using an autosampler enclosure especially for long runs
- Clean the nebulizer by:
  - Soaking in acid solutions (e.g.,10% nitric acid or aqua regia)
  - For heavy deposits, soak the nebulizer for several hours in more concentrated acid (e.g., 20% HNO_3) solution and rinse thoroughly with reagent water
- Do not sonicate or insert a wire through the tip of the nebulizer to remove blockage!
- Do not touch the delicate tip of the nebulizer and do not handle aggressively, store in its original packaging when not in use.
- Monitor the nebulizer back pressure to detect blockages. Record back pressure daily to track upward or downward trends.
- After analysis, rinse the nebulizer by running the blank solution followed by reagent water for a few minutes to prevent sales, sample matrix, etc., from forming inside the capillary. Allow the nebulizer to run dry.
- Disconnect the sample line to prevent liquid from being drawn up to the nebulizer when not in operation.

Concentric Glass Nebulizer

Maintenance, tips, and tricks for the cyclonic spray chamber

- Clean the spray chamber by:
  - Soaking in acid solutions (e.g., 5% HNO_3 and 2% HCl) for a few hours or overnight for persistent contamination.
  - Rinse with reagent water and allow to air dry completely.
- Do not touch spray chamber with bare hands and do not use a wire brush for cleaning.
- Clean new spray chambers following the same procedure. Although the spray chamber is new, there may be dust or dirt settled inside.
- For samples containing HF, always use a PFA spray chamber.
- After analysis, rinse the spray chamber by running the blank solution followed by reagent water for several minutes to prevent sample deposits from forming inside the spray chamber when the solvent dries out.

Dirty Spray Chamber

Clean Spray Chamber

Troubleshooting tips and tricks

Troubleshoot issues with sensitivity, precision, accuracy, and contamination/carry over

Sensitivity

Sensitivity issues are typically characterized by decrease or increase of signal and failure of continuing calibration standard (CCV) recoveries.

To Troubleshoot **Check the following:**

- Nebulizer or injector blockage
- Sample and skimmer cone orifices for blockage/damage
- Use of nebulizer appropriate for sample matrix
- Dirty spray chamber
- Operating parameters, nebulizer and gas flows, power setting and pump speed
- Interferences and appropriate correction applied
- Old/expired calibration standards
- Analysis of second source standard for reference

Precision

Precision issues are typically characterized by high % RSD between sample replicates.

To Troubleshoot **Check the following:**

- Worn peristaltic pump tubing
- Nebulizer or injector blockage
- Use of nebulizer appropriate for the sample matrix
- Dirty spray chamber
- Sufficient sample uptake time
- Sufficient rinse time between samples
- Operating parameters, gas flows, pump speed
- Use of the appropriate rinse solution for sample matrix

Troubleshooting Tips and Tricks

Troubleshoot issues with sensitivity, precision, accuracy, carryover and contamination

Accuracy

Accuracy issues are typically characterized by poor sample recoveries, failures in the analysis of CRMs and second source standards.

To Troubleshoot **Check the following:**

- Nebulizer or injector blockage
- Use of nebulizer appropriate for sample matrix
- Dirty spray chamber
- Operating parameters, nebulizer and gas flows, power setting and pump speed
- Sufficient uptake time for sample matrix
- Interferences and appropriate correction applied
- Use of appropriate Internal Standard
- Old/expired calibration standards

Contamination and Carryover

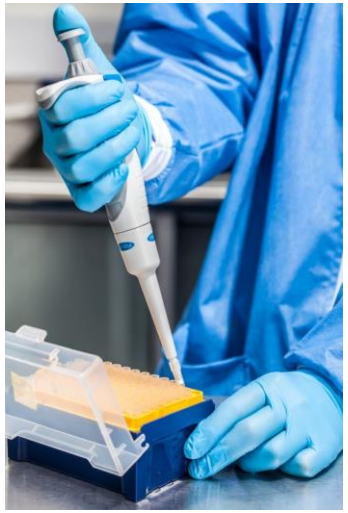
Contamination issues are shown by high blanks and sample or standard recoveries. Carryover is characterized by high standard blanks (CCB) and decreasing sample replicates resulting to high % RSD.

To Troubleshoot **Check the following:**

- Sufficient rinse time for sample matrix
- Appropriate rinse solution for sample matrix
- Dirty spray chamber
- Contaminated DI water supply and acids, use trace metal or higher-grade acid if possible
- For “sticky” elements (e.g., Hg, Mo, Sb), use longer rinse times. For Hg, use Au to help rinse out Hg.
- Clean work bench/environment free of dust and dirt

Best practices for the analysis of complex samples

Streamlining workflow helps to obtain faster results and ensure accurate results and data quality



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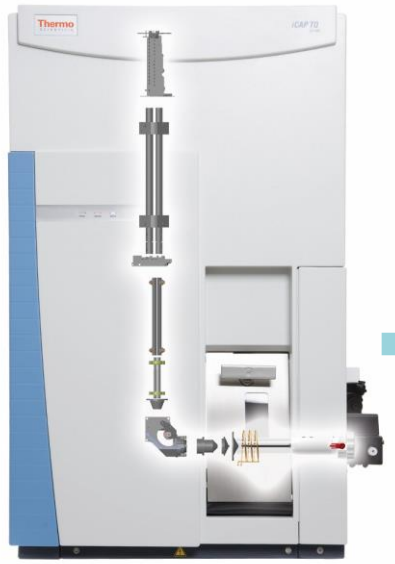

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GET READY

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Savings in time and resources and quality results

Best Practices
Sample/Standard Preparation and Handling

Microwave Digestion
Fast sample digestion

Sample Introduction Automation
Autosampler and autodilution

Instrument Innovations
iCAP PRO ICP-OES and iCAP RQ ICP-MS

Streamlined Workflow Software
Qtegra ISDS Software

New resource

Guide for environmental sample analysis by ICP-MS

If your laboratory is

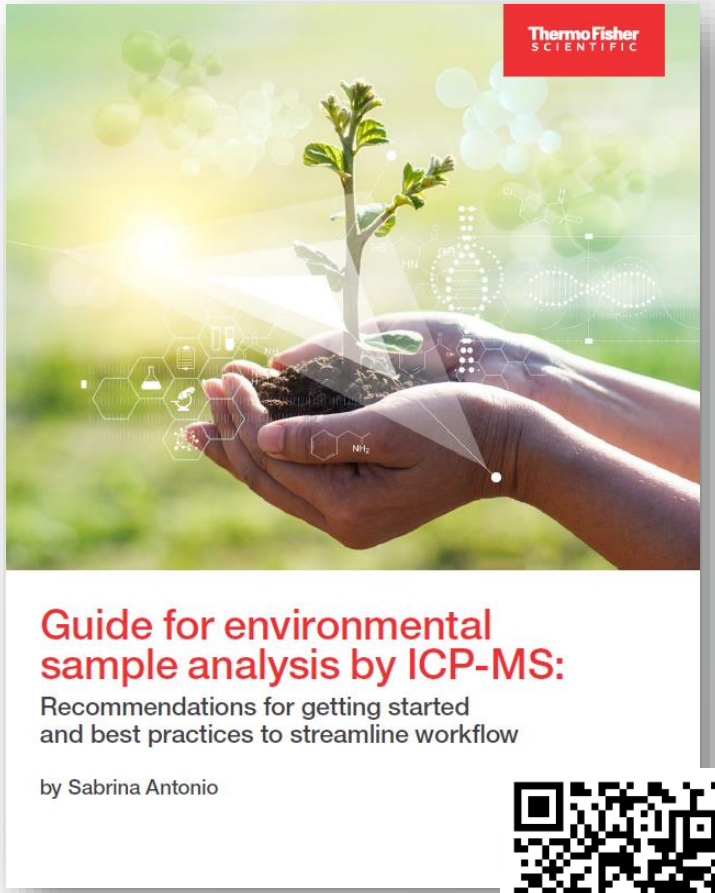
- experiencing analytical challenges, inaccurate results, and sample reruns
- seeking to streamline current methodologies and workflows
- starting up or preparing for environmental sample analysis by ICP-MS

our eBook, ***"Guide for Environmental Sample Analysis by ICP-MS: Recommendations for Getting Started and Best Practices to Streamline Workflow,"*** serves as a helpful resource

Topics include:

- considerations and tips for selecting laboratory apparatus, equipment, reagents, and standard solutions
- best practices for the entire elemental analysis workflow
- best practices and tips to streamline sample and standard preparations
- recommended pre-calibration routines and instrument inspections
- general instrument maintenance and troubleshooting tips and tricks

https://www.thermofisher.com/us/en/home/global/forms/industrial/environmental-sample-analysis-by-icp-ms-ebook.html



Visit this page or scan the QR code to download the eBook

Thank you!

Questions?

mike.mourgas@thermofisher.com | 12-October-2022