Best practices to simplify environmental sample analysis by ICP-MS

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Trace Elemental Analysis

The world leader in serving science

Agenda

1. Environmental analysis
   Overview and challenges
2. Best practice for the elemental analysis workflow
   Sample/standard preparation and sample introduction
3. ICP-MS instrument innovations that simplify analysis
   Hardware and software features, interference correction
4. Instrument optimization routines
   Instrument checks and routine maintenance
5. Troubleshooting tips and tricks
   Sensitivity, accuracy, precision, and carryover

- **Environmental analysis overview and challenges**

Why is elemental analysis required for the environment?

Federal, state, and local laws require the analysis of trace metals to ensure the safety of drinking water, surface and ground waters, and soils for consumption, recreation, farming, building, and urban development. Elemental analysis is also required for industrial wastes for proper disposal.

- **Federal laws and regulations**
  - Safe Drinking Water Act (SDWA)
  - National Primary and Secondary Drinking Water Regulations (NPDWR & NSDWR)
  - Clean Water Act (CWA)
  - Resource Conservation and Recovery Act (RCRA)
  - Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
  - Lead Copper Rule (LCR)
  - Unregulated Contaminant Monitoring Rule (UCMR)

U.S. EPA drinking water regulations

National Primary Drinking Water Regulations
Max Contaminant Levels (MCL)

Contaminant	MCL (mg/L)	MCLG (mg/L)
Antimony	0.006	0.006
Arsenic	0.010	0
Barium	2	2
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	1.3
Lead	0.015	0
Mercury (inorganic)	0.002	0.002
Selenium	0.05	0.05
Thallium	0.002	0.0005

National Secondary Drinking Water Regulations
Secondary Max Contaminant Levels (SMCL)

Contaminant	SMCL (mg/L)	Effects Above SMCL
Aluminium	0.05 – 0.20	Coloring of water
Chloride	250	Salty taste
Copper	1.0	Metallic taste; blue-green staining
Fluoride	2.0	Tooth discoloration
Iron	0.3	Rusty color, metallic taste, reddish/orange staining
Manganese	0.05	Black to brown color and staining; bitter metallic taste
Silver	0.10	Skin discoloration
Sulfate	250	Salty taste
Zinc	5	Metallic taste

U.S. EPA regulations

Unregulated Contaminant Monitoring Rules (UCMR)
Inorganic Contaminant Levels

Rule	Contaminant	Minimum Reporting Level (µg/L)
UCMR 3 (2012 - 2016)	Vanadium	0.2
	Molybdenum	1.0
	Cobalt	1.0
	Strontium	0.3
	Chromium (total)	0.2
	Chromium - 6	0.03
UCMR 4 (2017 - 2021)	Germanium	0.3
	Manganese	0.4
UCMR 5 (2022 - 2026)	Lithium	9.0

Lead Copper Rule

Contaminant	MCL (mg/L)	MCLG (mg/L)
Copper	1.3	1.3
Lead	0.015	0

Environmental analysis

Environmental analysis encompasses a broad range of applications throughout industry

Wastewater treatment

Environmental remediation

Agricultural testing

Drinking water compliance

Discharge monitoring

Industrial waste disposal

Environmental sample analysis

Challenges when analyzing environmental samples

- Complex sample matrices
- Variety of samples
- Regulation and compliance
- Trace and ultra-trace detection requirements
- Comprehensive QC standards and protocols
- Failed sample analyses and re-reruns
- Sample throughput
- Quick turnaround of results
- Data transfer and management
- Reporting requirements
- Traceability and documentation
- Maintenance and troubleshooting
- Training new analysts

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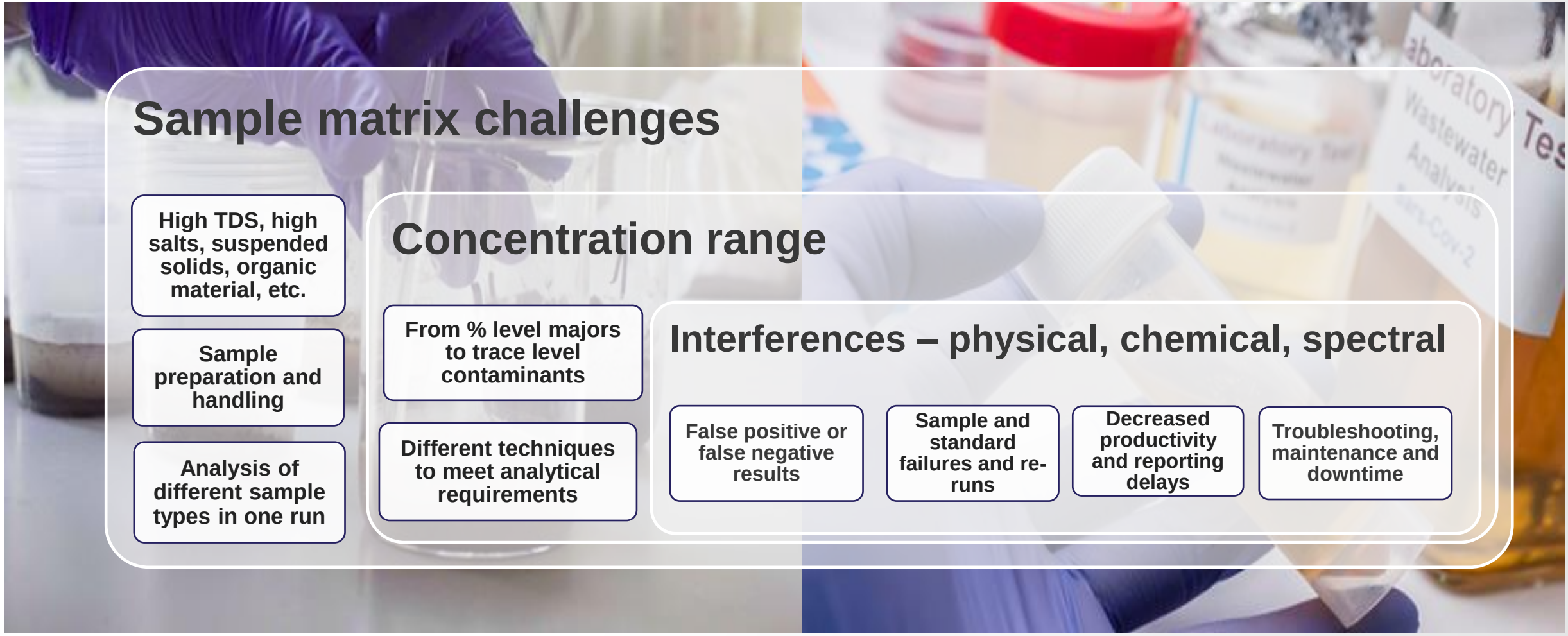
Environmental sample analysis

- ❑ Why is environmental analysis 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…**

Environmental sample analysis

Challenges related to 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

Environmental sample analysis

Regulation and compliance add another layer of challenges

- **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 or other industry methods**
  - Specific quality control protocols
  - Method validation
  - Numerous QC standards and samples analyzed prior to samples
  - Control limit criteria
- **Audit, data management, and reporting requirements**
- Documentation and traceability
- Data reporting
- Data package audit
- Onsite audit
- Data transfer to LIMS
- Data security

Addressing the challenges in environmental analysis

- **General best practices to streamline workflow**
  - Sample and standard preparation
  - Sample handling
  - Contamination prevention
  - Sample introduction automation
- **Instrument innovations**
  - Hardware design and features
  - Software features
  - Interference correction
- **Instrument optimization routines**
- **Troubleshooting and maintenance tips**
  - Troubleshoot failures due to sensitivity, accuracy, precision, and carryover

- **Best practices for the elemental analysis workflow**

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 achieving trace and ultra-trace detection required in environmental analysis

Be aware of all contamination sources.

Use clean and compatible apparatus.

Minimize handling and transfer steps.

Measure weights and volumes with accuracy.

Use high purity reagents.

Have separate sample and standard preparation areas.

Use high purity reagent water.

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 & 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

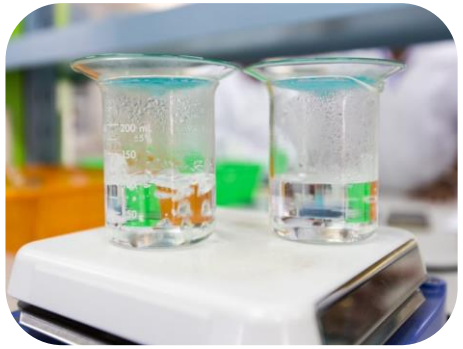
Teflon wash bottle, best for ppt level preparations

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

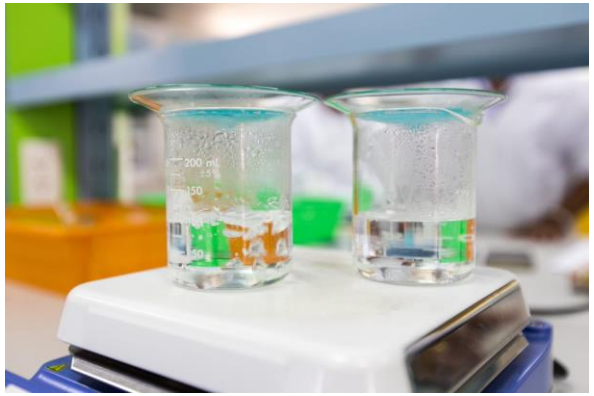
Environmental Sample
(e.g., ground/surface water, wastewater, soils, sludge)



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

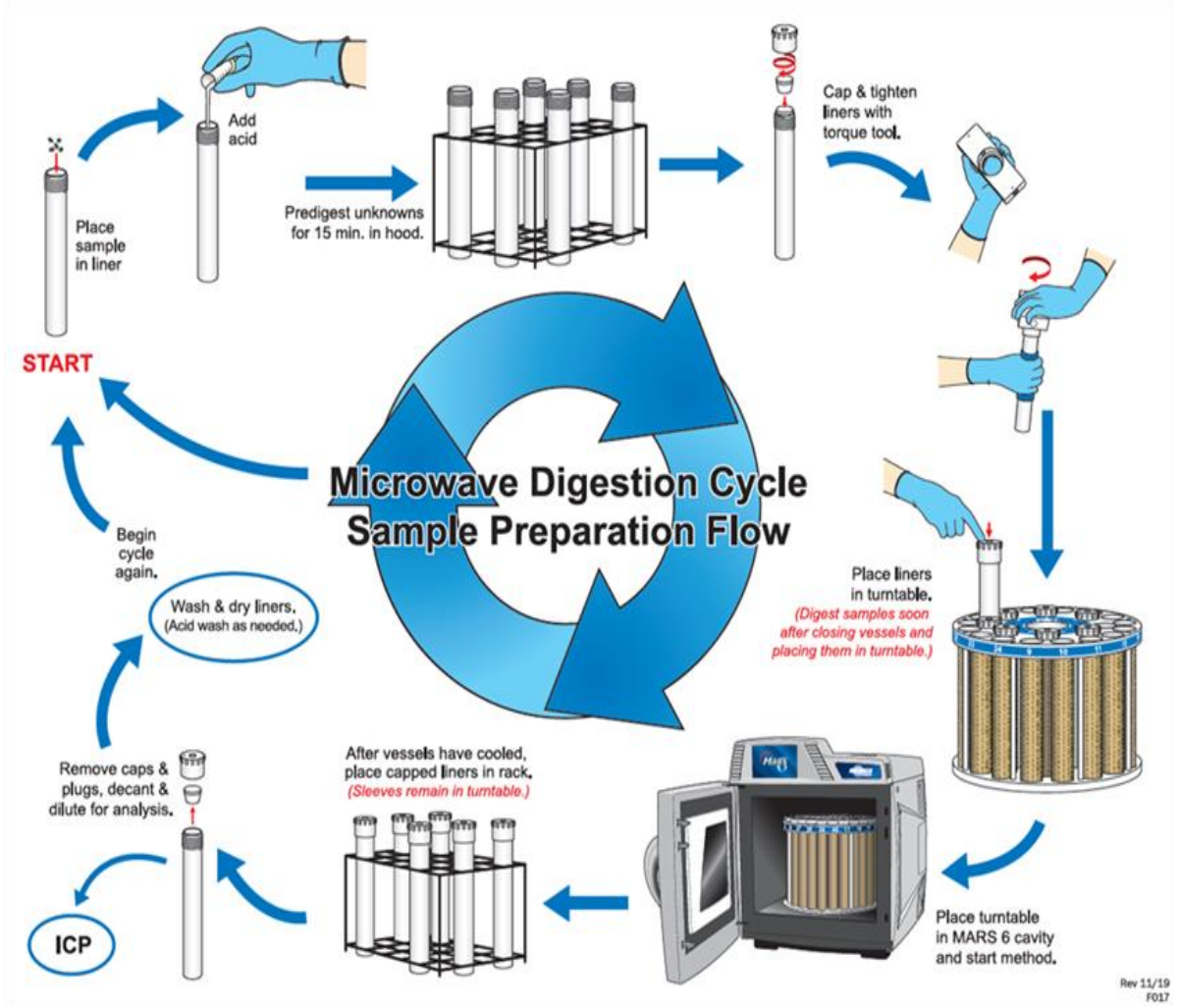
- **Long digestion time (hours)**
- Incomplete digestion
- Loss of analyte
- Exposure to atmosphere
- High reagent consumption
- Constant monitoring

Digestion method

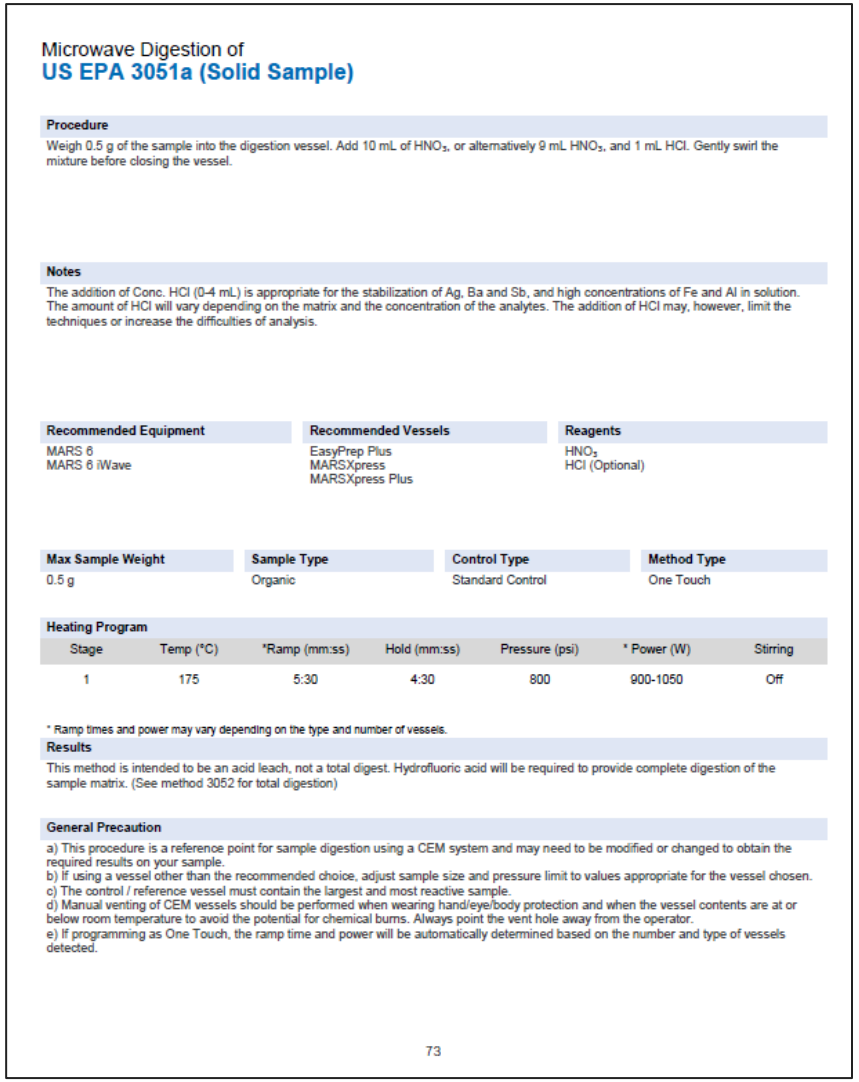
Microwave assisted acid digestion

- **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



Microwave digestion – US EPA Method 3051a



Microwave Digestion of
US EPA 3051a (Solid Sample)

Procedure

Weigh 0.5 g of the sample into the digestion vessel. Add 10 mL of HNO_3, or alternatively 9 mL HNO_3, and 1 mL HCl. Gently swirl the mixture before closing the vessel.

Notes

The addition of Conc. HCl (0-4 mL) is appropriate for the stabilization of Ag, Ba and Sb, and high concentrations of Fe and Al in solution. The amount of HCl will vary depending on the matrix and the concentration of the analytes. The addition of HCl may, however, limit the techniques or increase the difficulties of analysis.

Recommended Equipment	Recommended Vessels	Reagents
MARS 6 MARS 6 iWave	EasyPrep Plus MARSXpress MARSXpress Plus	HNO_3 HCl (Optional)

Max Sample Weight	Sample Type	Control Type	Method Type
0.5 g	Organic	Standard Control	One Touch

Heating Program

Stage	Temp (°C)	*Ramp (mm:ss)	Hold (mm:ss)	Pressure (psi)	* Power (W)	Stirring
1	175	5:30	4:30	800	900-1050	Off

* Ramp times and power may vary depending on the type and number of vessels.

Results

This method is intended to be an acid leach, not a total digest. Hydrofluoric acid will be required to provide complete digestion of the sample matrix. (See method 3052 for total digestion)

General Precaution

a) This procedure is a reference point for sample digestion using a CEM system and may need to be modified or changed to obtain the required results on your sample.
b) If using a vessel other than the recommended choice, adjust sample size and pressure limit to values appropriate for the vessel chosen.
c) The control / reference vessel must contain the largest and most reactive sample.
d) Manual venting of CEM vessels should be performed when wearing hand/eye/body protection and when the vessel contents are at or below room temperature to avoid the potential for chemical burns. Always point the vent hole away from the operator.
e) If programming as One Touch, the ramp time and power will be automatically determined based on the number and type of vessels detected.

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- Digest up to 24 solid matrix samples simultaneously
- Digestion time10 minutes
- Samples ready for analysis in under 30 minutes compared to over 2 hours with traditional hot plate/block digestion
- Use disposable liners to eliminate vessel washing

Sample introduction automation

Autosamplers and autodilution systems

Teledyne CETAC

Teledyne CETAC SDX_{HPLD} Liquid Dilution System with ASX-560 Autosampler

Elemental Scientific (ESI)

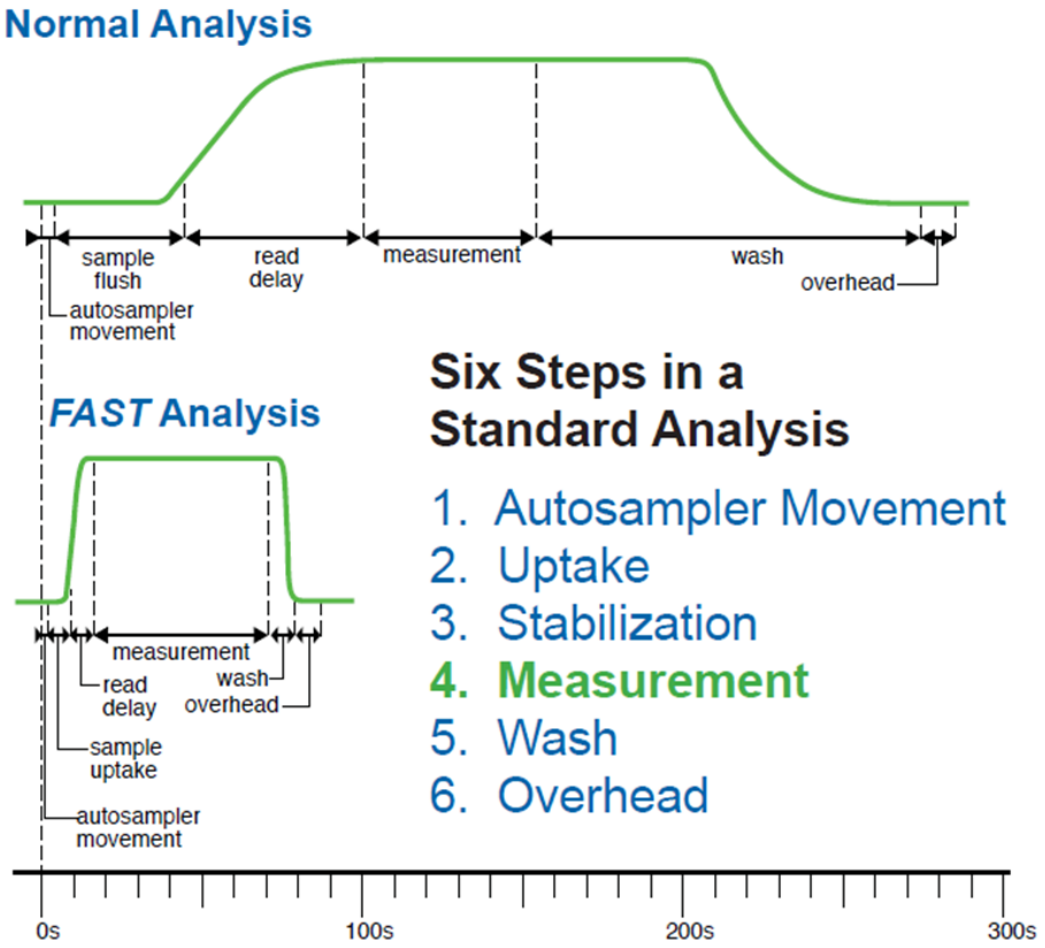
ESI SC-4 DX Autosampler

ESI prepFast Autodilution System

Autosamplers and autodilution systems

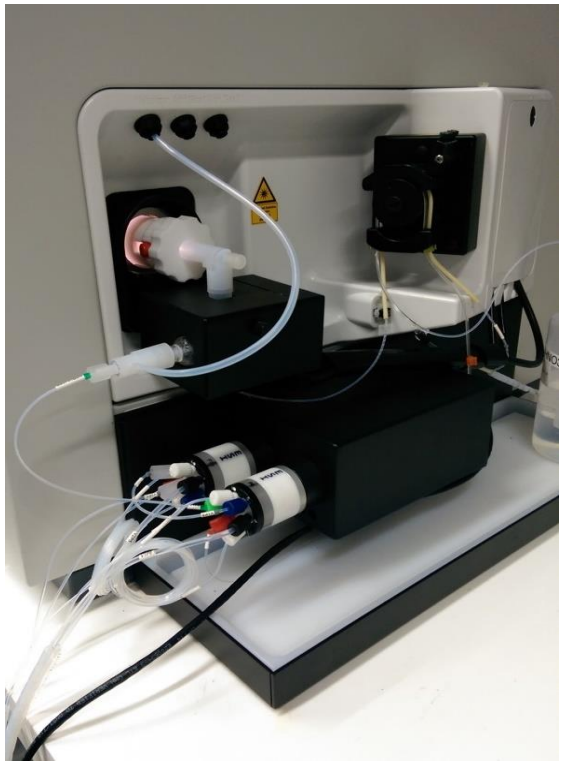
Discrete sampling valves for optimized uptake and washout

- *FAST* is a reliable, high-throughput, automated sample introduction system using a discrete sampling valve
- Speeds up total analysis time by reducing sample uptake time and rinse time between samples



ESI prep*FAST* autodilution system

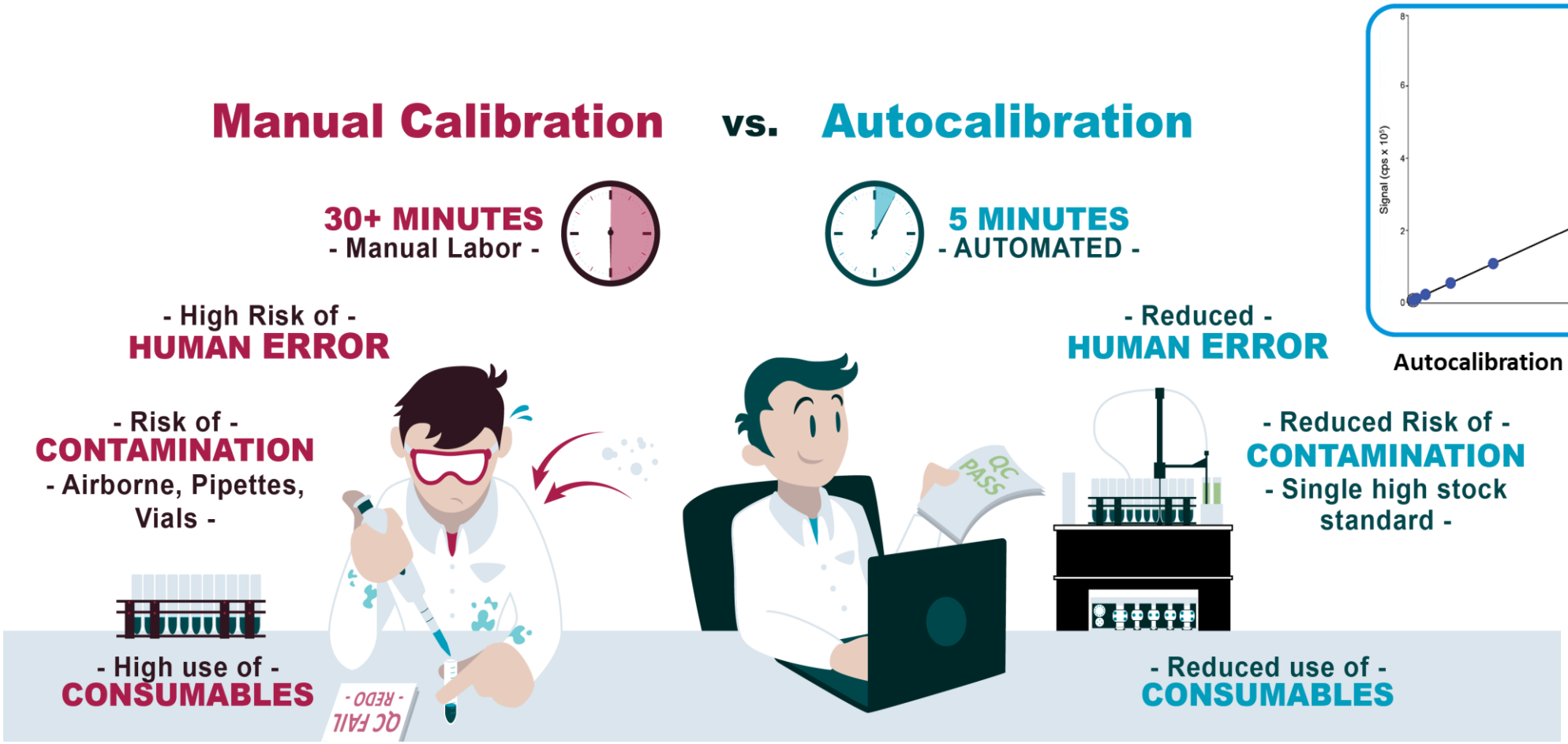
- Prep*FAST* is an inline dilution system that fully automates laboratory dilutions while providing high sample throughput
- High precision autodilution up to 400x
- Autocalibration from one or multiple stock standards
- Syringe-driven internal standard addition
- Vacuum or syringe sample loading on prep*FAST*
- Autodilution performed when Qtegra records an out-of-range analyte concentration or internal standard failure

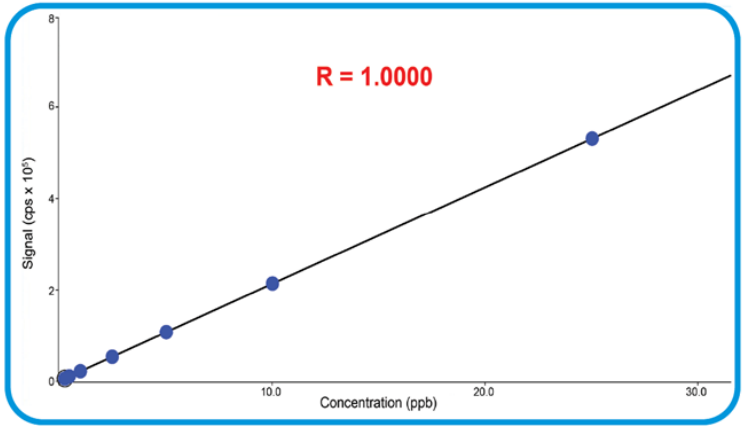


prep*FAST* valve module on an iCAP RQ and SC-2DX autosampler cart with S400V syringe pump

Autodilution system for automatic standard preparation

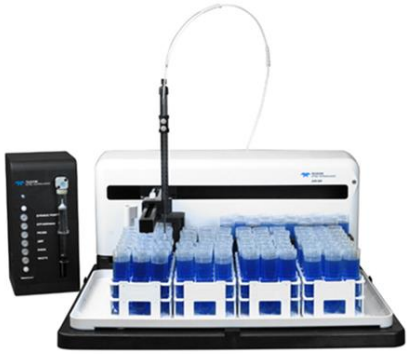
Automatic standard preparation reduces preparation time and systematic error





Autocalibration from single 50 ppb Co standard

Streamlined elemental analysis workflow



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

Faster results

Now let's discuss instrumentation

- **ICP-MS instrument innovations that simplify analysis**

Instrument solutions for environmental analysis

A portfolio of innovative instruments for simplified environmental analysis

Atomic Absorption Spectrometry (AAS)

Flame

Graphite Furnace

Flame & Graphite Furnace

Thermo Scientific™ iCE™ 3000 Series AAS

- ✓ Lower investment and complexity
- ✓ GFAA offers high sensitivity for key elements
- ✓ Flame offers fast, single element analysis

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Thermo Scientific™ PRO™ Series ICP-OES

- ✓ Fast, multi-element analysis
- ✓ Robustness for high matrix samples
- ✓ Flflexibility, performance, and ease of use

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

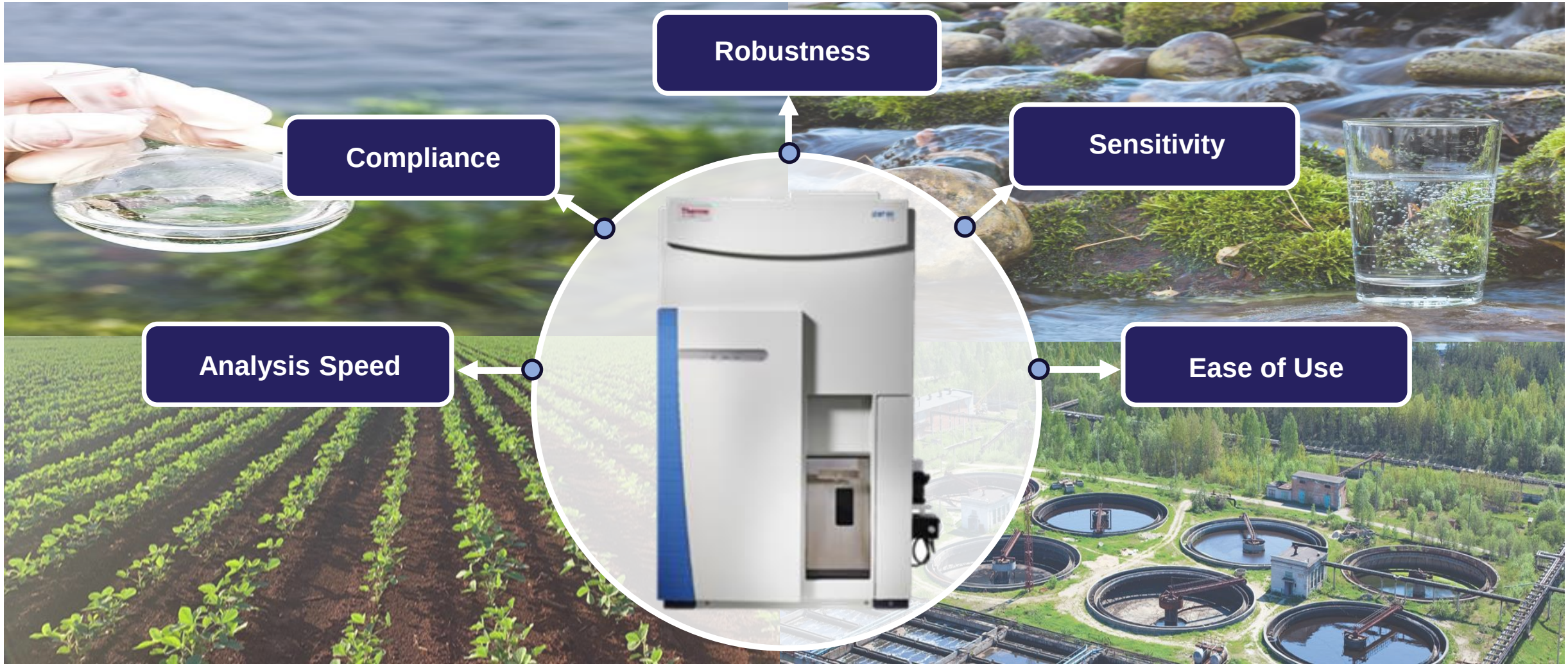
Thermo Scientific™ iCAP™ RQ ICP-MS

Thermo Scientific™ iCAP™ TQ ICP-MS

- ✓ Improved detection capability
- ✓ High sensitivity and wide dynamic range
- ✓ Removal of advanced spectral interferences
- ✓ Hyphenated techniques

Addressing challenges through instrument innovation

Thermo Scientific iCAP RQ ICP-MS



Addressing challenges through instrument innovation

Key components for performance, robustness, and ease of use

Long-life SEM detector

Zero user maintenance Collision/Reaction Cell, ion optics, and quadrupole

Right Angle Positive Ion Deflection (RAPID) Lens

iCAP RQ ICP-MS

Vertical analyzer for small footprint

Quick connect, push-fit sample introduction components

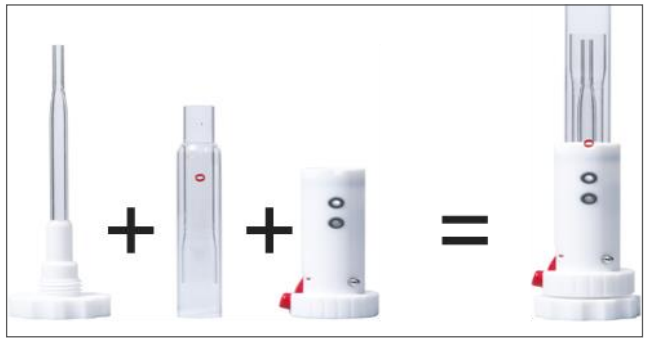
Robust interface for reliable, long-term analysis of high matrix samples

Unique interface with drop-down door

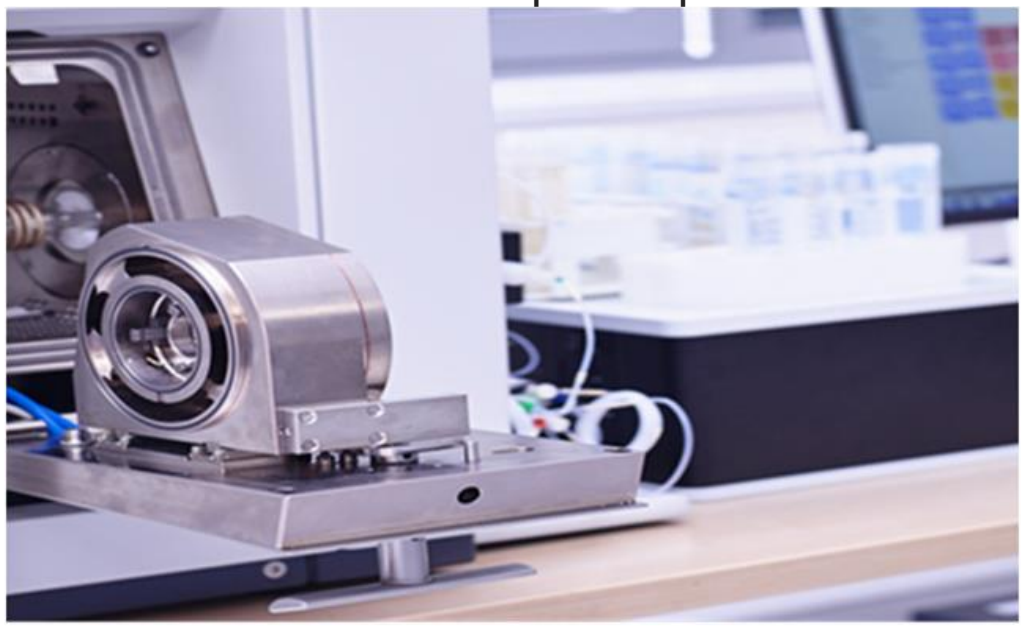
Addressing challenges through instrument innovations

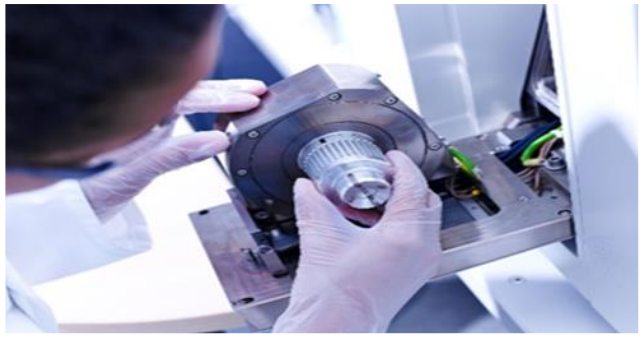
Sample introduction system and plasma interface

Quick connect sample introduction components



Plasma interface unique drop-down door





Addressing challenges through instrument innovations

Unique interface designed for maximum coverage of sensitivity and dynamic range:

			
High Sensitivity 2.8 mm	High Matrix 3.5 mm	Robust 4.5 mm	Argon Gas Dilution
Below 0.1% TDS	Up to 0.2% TDS	Up to 0.5% TDS	Above 0.5% and up to 3-4% up to 25% possible
Pure solutions	Universal, e.g. digested samples, drinking waters etc.	Waste waters, hard drinking waters	Sea water, highly saline sample types

Easily implemented through dedicated grouping and autotunes in the software

Addressing challenges through instrument innovations

High matrix samples

- Use of Argon Gas Dilution (AGD) for robust, long-term analysis of high matrix samples (e.g., sea water, brackish water, wastewater) in one analytical run sequence
  - Consistent internal standard recovery despite the changing sample matrices

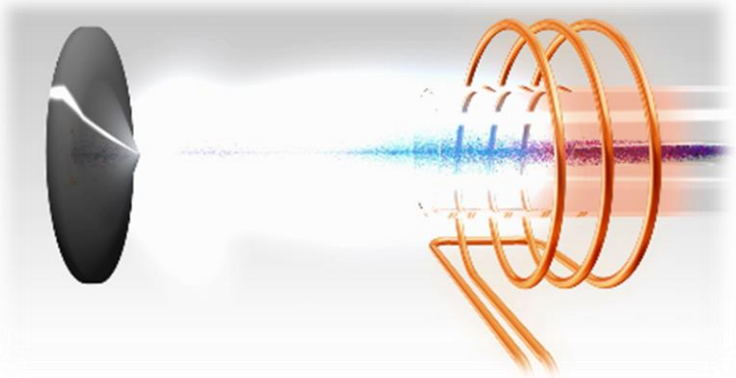
Parameter	Value
RF Power	1550W
Nebulizer Gas Flow	0.25 L·min^{-1}
Additional Gas Flow	0.65 L·min^{-1}
Interface Configuration	Nickel, High Matrix Insert
Modes	SQ-KED
Gas Flow	4.65 mL min^{-1}
CR Bias	-21 V
Q3 Bias	-18 V

Spectral Interferences in ICP-MS

Two Types of Spectral Interferences – Polyatomic and Isobaric

Where do polyatomic interferences come from?

Ar and Air (O, N, C)



ArAr, ArO, ArN,
ArC, ArH, ArCa,
ArNa, ArK, ArMg,
ArCl, ClO, NO,
CO, CaO, NaO

Polyatomic Interferences

H_2O, Ca, Na, K, Mg, Cl

Products ← Reaction ← Reactants

- **Polyatomic interferences are formed when 2 or more isotopes combine to form species with the same m/z as the analyte ion, e.g., $^{40}Ar^{16}O \rightarrow {}^{56}Fe$; $^{40}Ar^{35}Cl \rightarrow {}^{75}As$; $^{40}Ar^{12}C \rightarrow {}^{52}Cr$**

Addressing challenges through instrument innovations

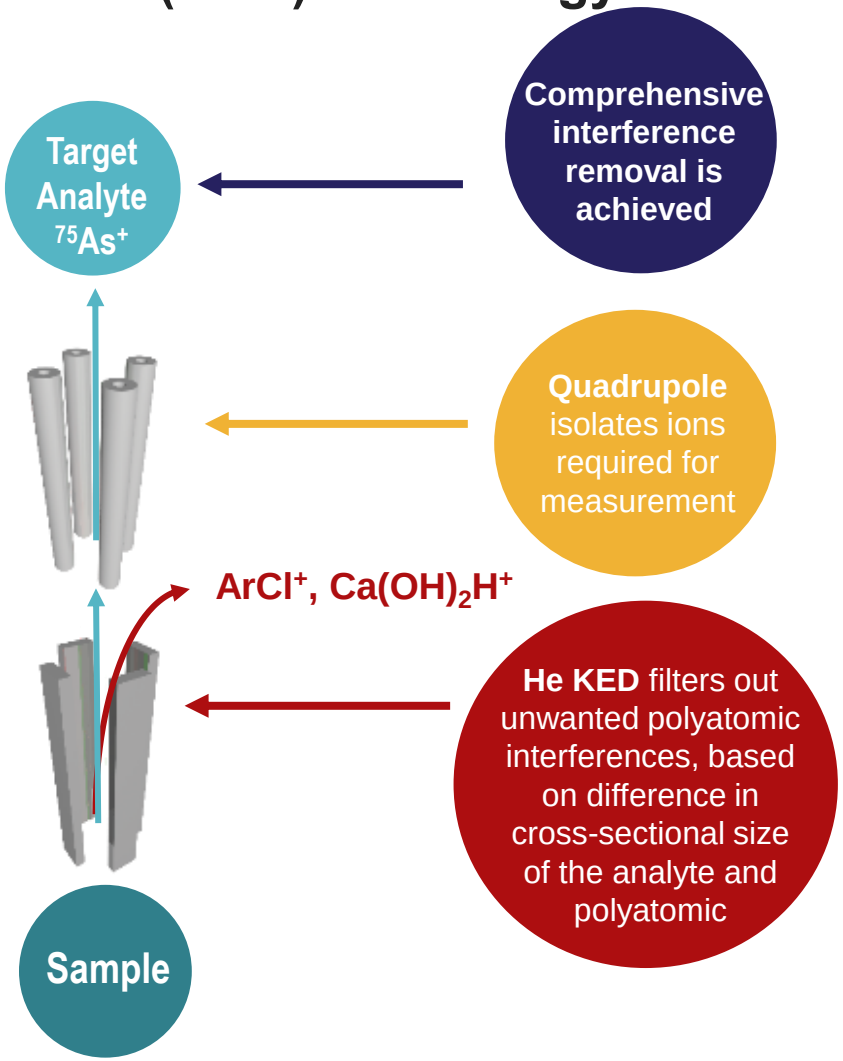
Spectral interference removal with QCell™ Collision/Reaction Cell (CRC) Technology

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

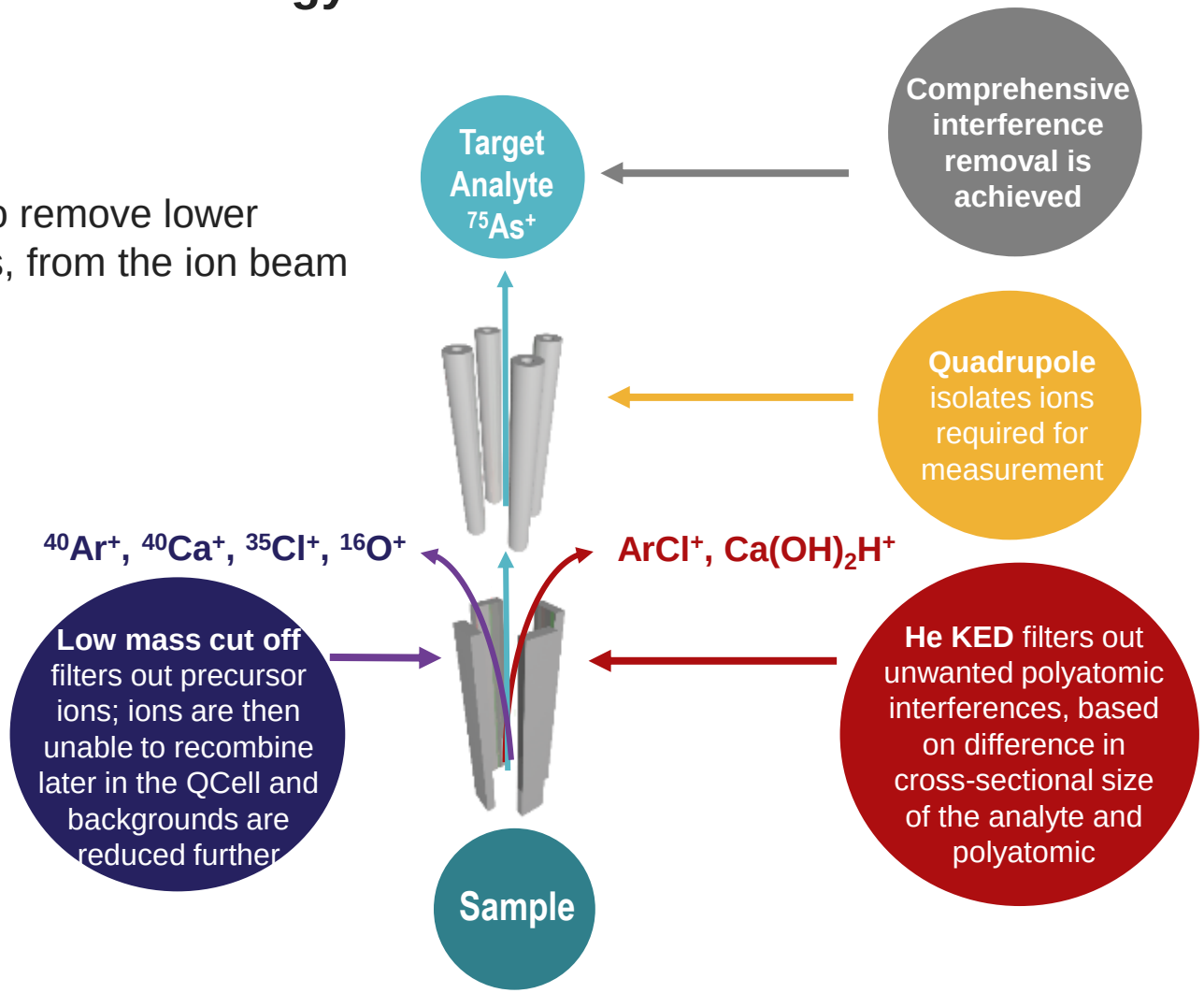
Spectral interference removal with QCell CRC technology

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



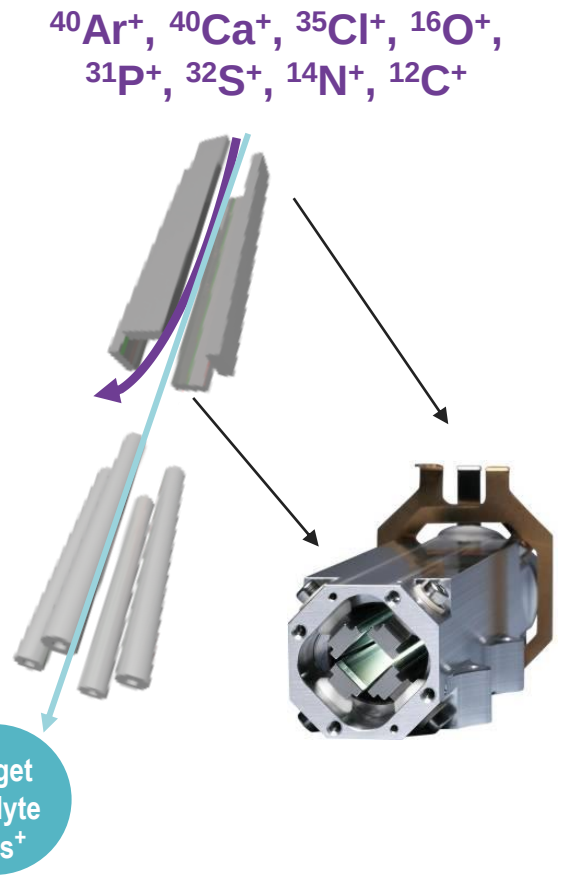
Addressing interferences with Low Mass Cutoff

Low Mass Cutoff eliminates lower mass ions from traveling through the Qcell and contributing to interferences……

Mass	Interferences	Precursors
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, N, O, S, Cl
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{31}P^{32}S$	C, N, O, Na, P, S, Cl, Ar
^{75}As	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{40}Ar^{34}SH$, $^{37}Cl^{2}H$	H, S, Cl, Ca, Ar

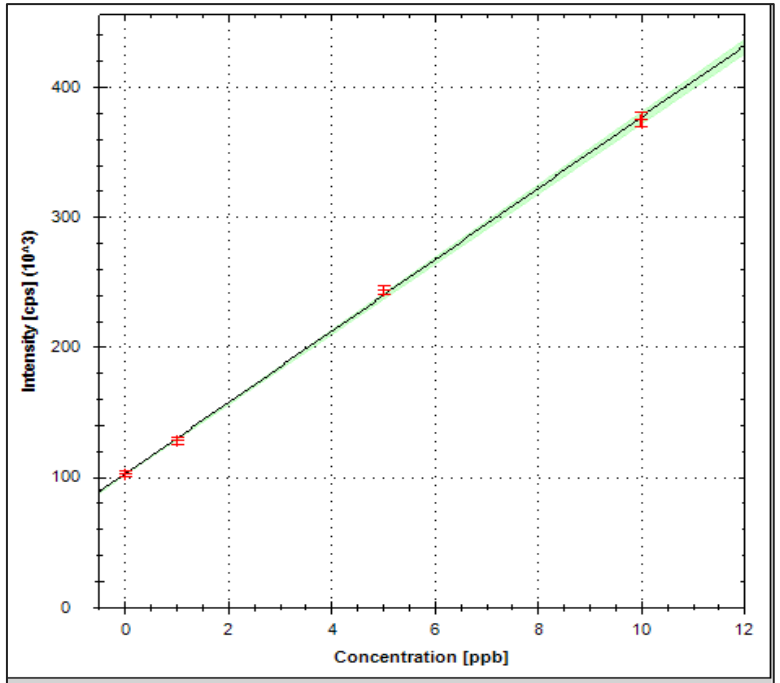
Mass	Interferences	Precursors
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, N, O, S, Cl
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{31}P^{32}S$	C, N, O, Na, P, S, Cl, Ar
^{75}As	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{40}Ar^{34}SH$, $^{37}Cl^{2}H$	H, S, Cl, Ca, Ar

….and reduces BECs further than KED alone



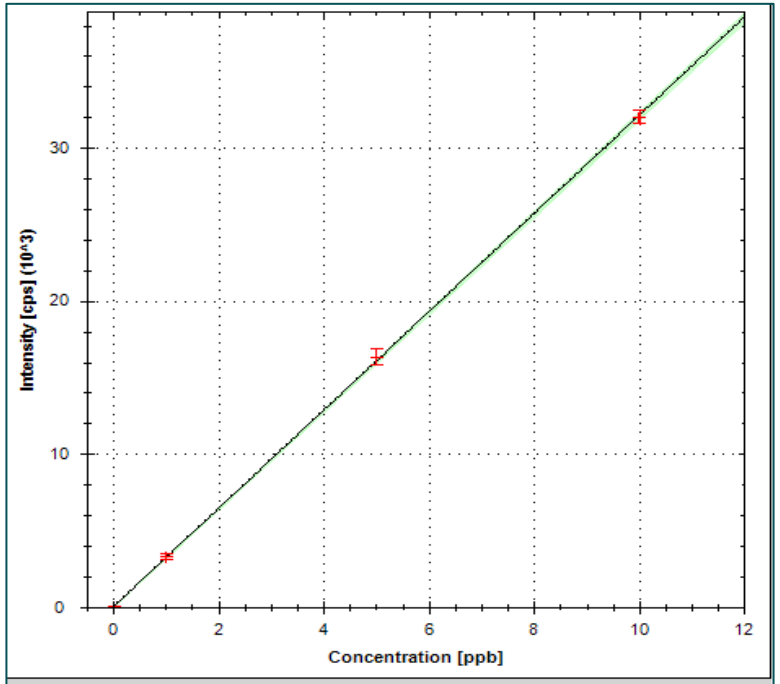
Handling interferences – KED with LMCO

Calibration curve for ^{75}As in a solution containing 1.2% v/v HCl



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	27,454.885	+/-458.243	279.809	1.019
a	102,068.772	+/-0.000	0.000	0.000
R^2	0.990			
BEC	3.718 ppb			
IDL(LOD)	0.2271 ppb			



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	3,211.981	+/-26.800	16.364	0.509
a	8.889	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.003 ppb			
IDL(LOD)	0.0041 ppb			

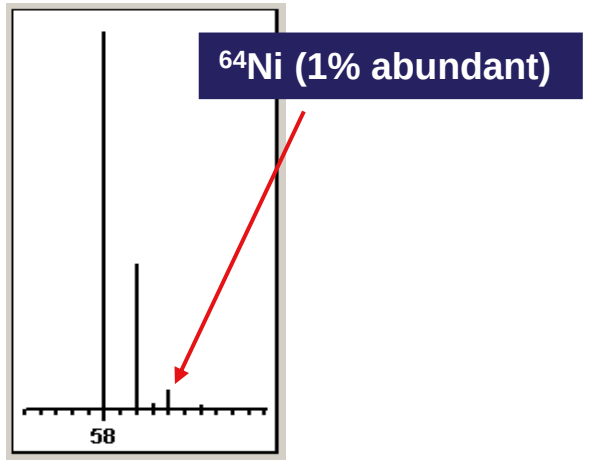
STD mode: Polyatomic interference leads to poor IDL and elevated BEC

KED mode: Polyatomic interference removed - IDL below 5 ppt

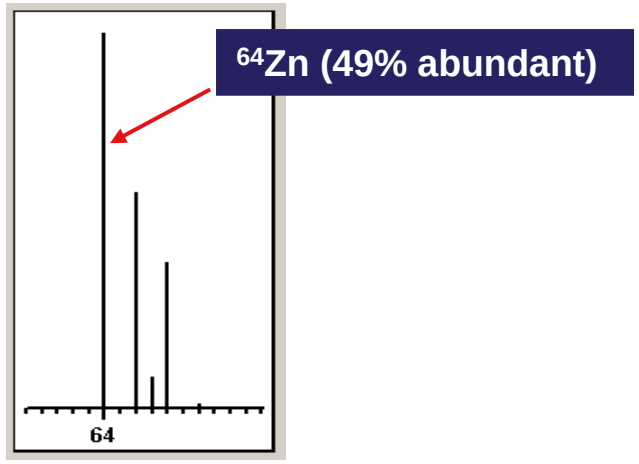
Interferences in ICP-MS

Advanced spectral interferences

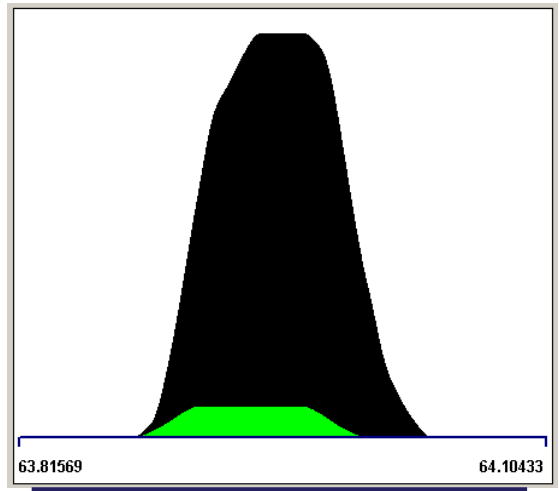
- **Isobaric Interference**
  - occurs when two elements have isotopes with the same nominal mass
    - E.g., ^{58}Fe and ^{58}Ni; ^{204}Pb and ^{204}Hg, ^{40}Ca and ^{40}Ar
- **Doubly charged ion interferences**
  - formed from elements having a 2nd ionization potential lower than the ionization potential of argon (15.8 eV)
  - Appear at half the parent isotope mass
  - 150Nd2+ on 75As+, 156Gd2+ on 78Se+



Isotopic pattern for Ni



Isotopic pattern for Zn



Isobaric Interference

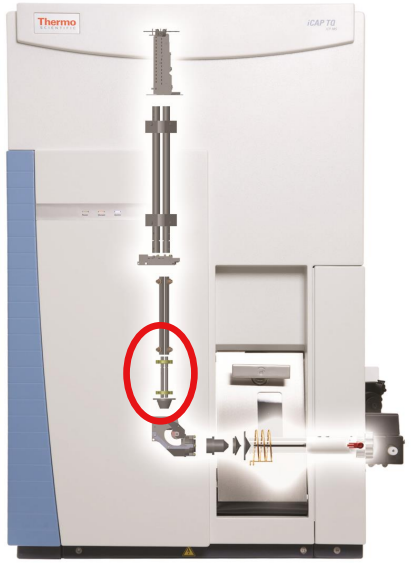
Advanced interference removal

Thermo Scientific™ iCAP™ Qnova Series ICP-MS

iCAP RQ ICP-MS

1 or 2 mass flow controllers with optimized flow rates

Innovative QCell™ Collision/Reaction Cell Technology



iCAP TQ ICP-MS

Built-in safety for handling reactive gases

4 mass flow controllers with optimized flow rates

Additional quadrupole for superior interference removal

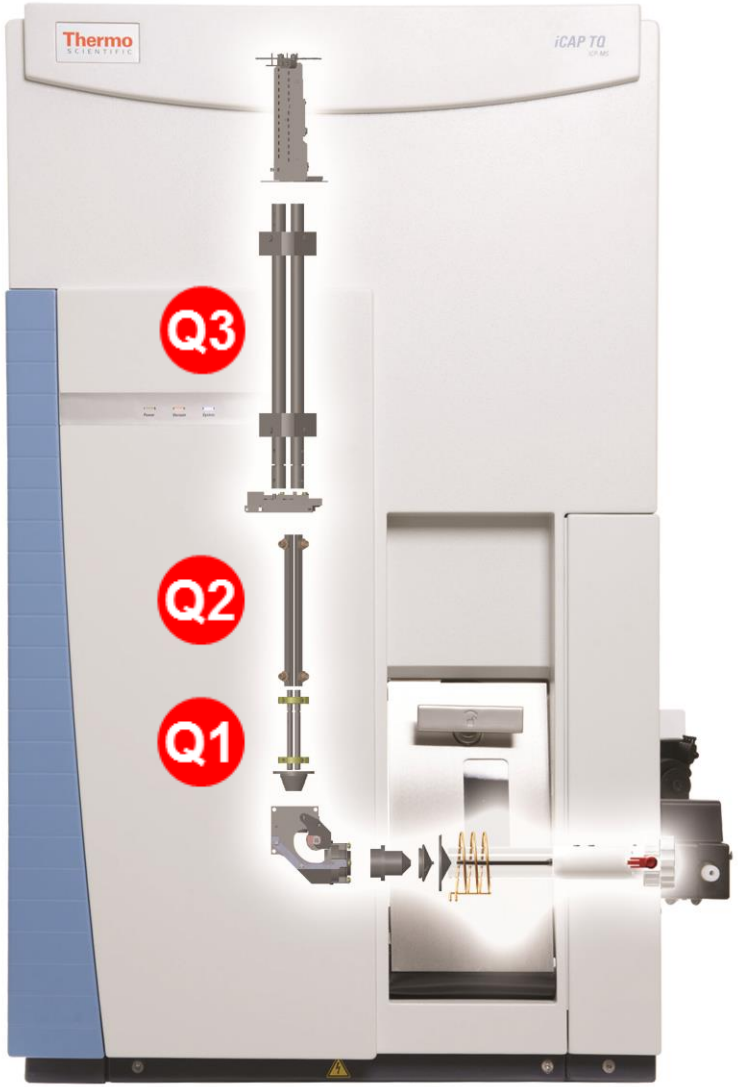
Single Quadrupole (SQ) ICP-MS

- ✓ Effective removal of polyatomic interferences with QCell technology using KED with LMCO

Triple Quadrupole (TQ) ICP-MS

- ✓ Effective removal of polyatomic interferences with Qcell technology using KED with LMCO
- ✓ **Advaned interference removal of isobaric and doubly charged ion interferences**

Triple quadrupole ICP-MS



Q1 First mass filtering quadrupole situated axially in front of a second quadrupole

Q2 Second quadrupole acting as a collision/reaction cell (CRC)

Q3 Third off-axis mass filtering quadrupole for mass analysis.

$$R \propto N = \frac{fl}{v_z}$$

R = Mass resolving power
N = Number of RF cycles experienced by the ion
f = RF frequency
l = Quadrupole length
v_z = Initial ion velocity along quadrupole axis

Voo et al., J. Vac. Sci. Technol. A, 1997, 15 (4)

- ✓ **Q1 isolates analyte and interferences that affect accurate measurement**
- ✓ **High Sensitivity (iMS) or High Resolution (1amu) as required by the application**

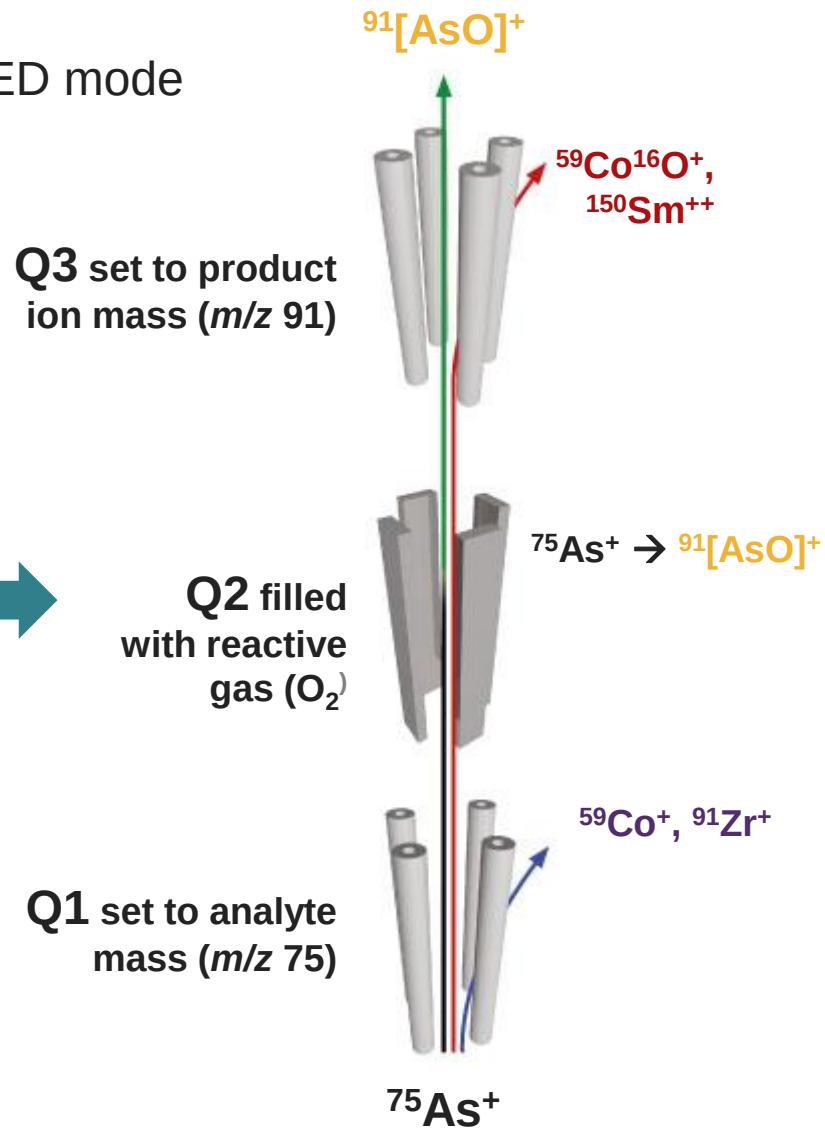
How does triple quadrupole ICP-MS work?

- Polyatomic Interferences – removed by single quadrupole ICP-MS using KED mode

Element	Interference	How to Remove
^{75}As	$^{40}Ar^{35}Cl^{+}$	KED
$^{78,80}Se$	$^{40}Ar^{38}Ar^{+}$; $^{40}Ar^{40}Ar^{+}$	KED, H_2
^{51}V	$^{35}Cl^{16}O^{+}$	KED

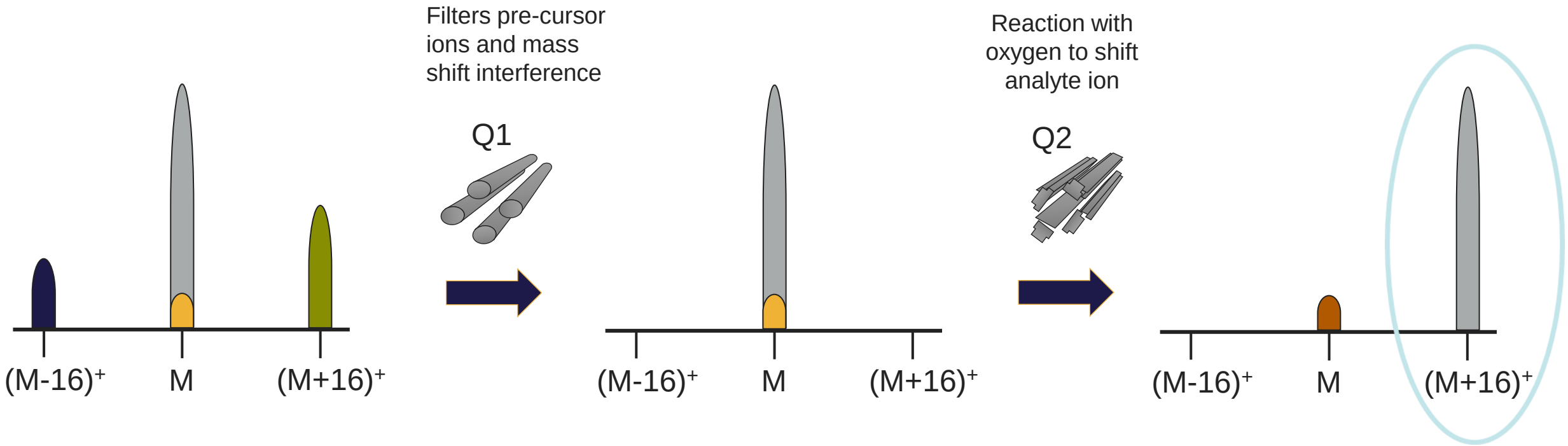
- Other Interferences – isobaric, doubly charged, high levels of polyatomics, removedd by triple quadrupole ICP-MS

Element	Interference	How to Remove
^{75}As	$^{150}Sm^{2+}$, $^{59}Co^{16}O^{+}$	O_2, mass shift of As
$^{78,80}Se$	$^{156, 160}Gd^{2+}$	O_2, mass shift of Se
^{111}Cd	$^{95}Mo^{16}O^{+}$	O_2, H_2, on mass
^{31}P, ^{32}S	$^{14}N^{16}O^{1}H^{+}$; $^{16}O^{16}O^{+}$	O_2, mass shift of P, S



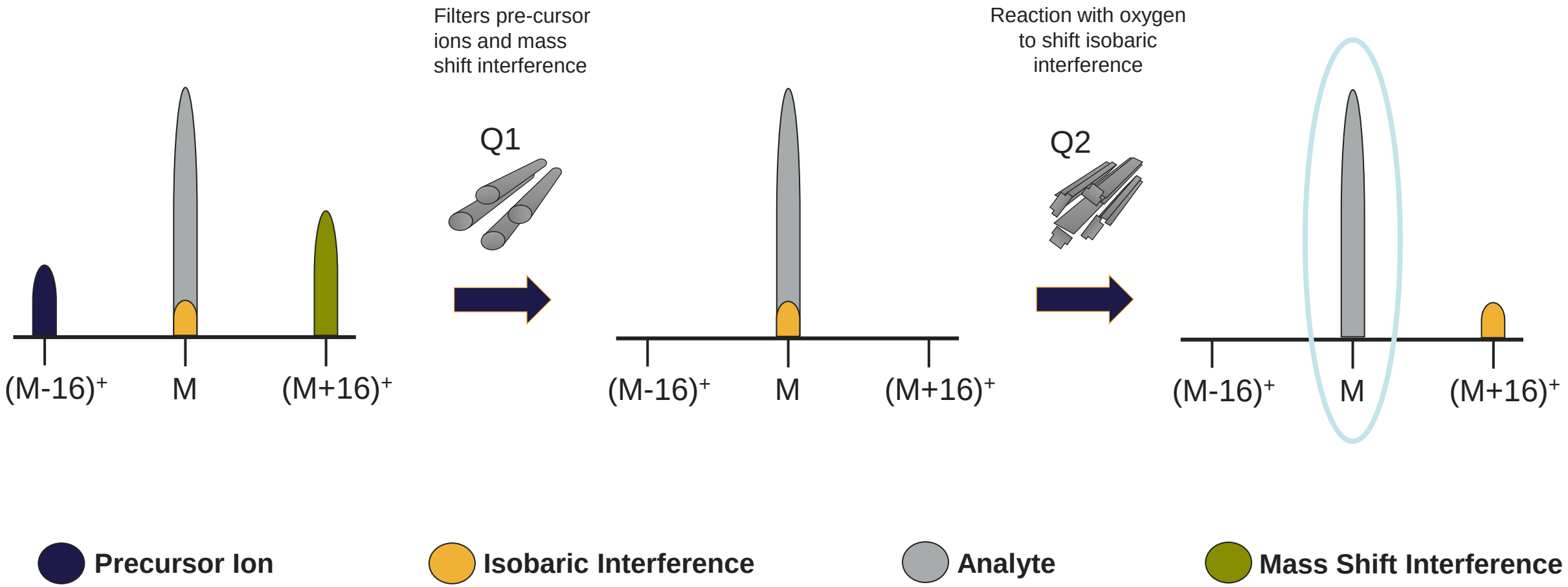
Mass shift mode with oxygen

- Use reaction gas to selectively shift the analyte to a higher mass
- Measure the analyte isotope **at its new, higher mass**



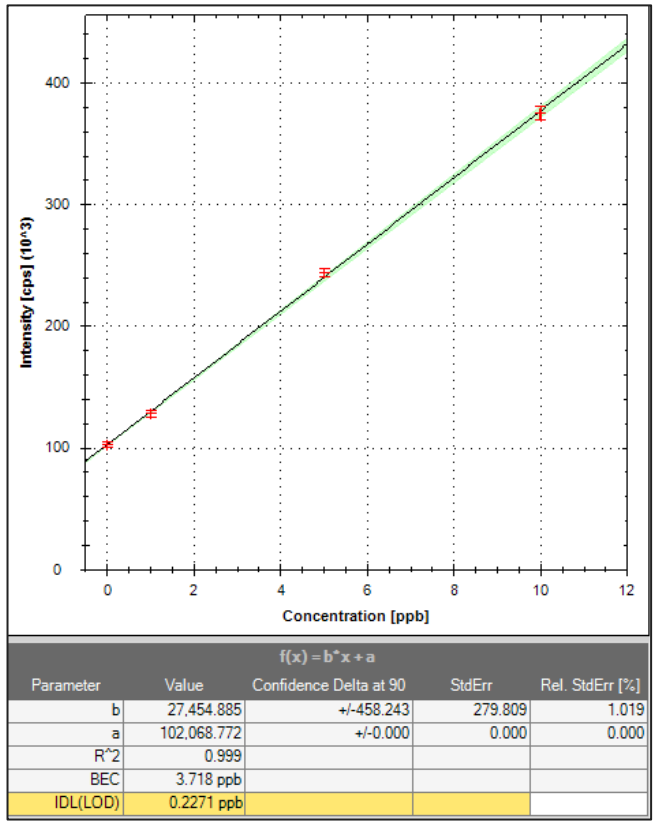
On mass mode with oxygen

- Use reaction gas to selectively shift the interference to a higher mass
- Measure the analyte isotope **at its original mass**



Triple quadrupole reactions – interference removal

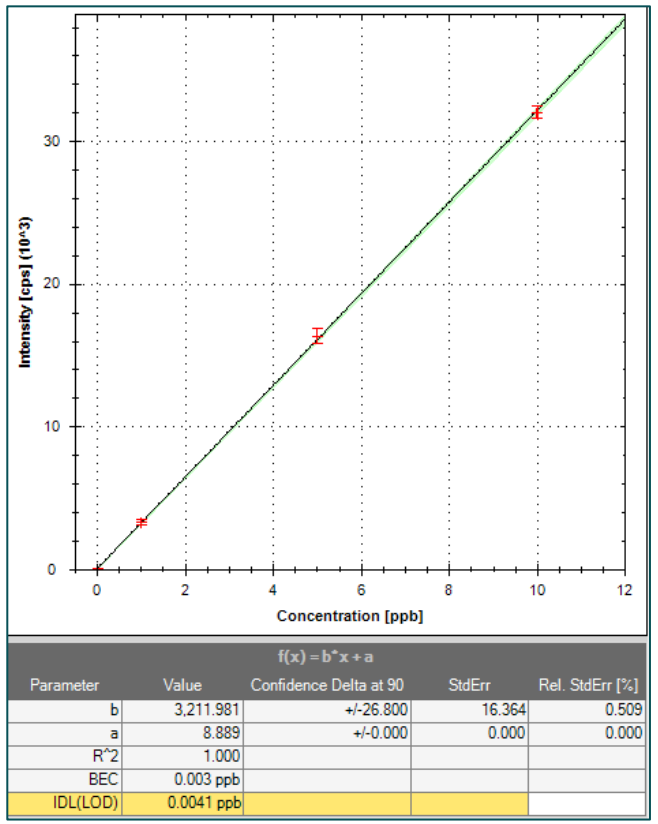
Calibration curve for ^{75}As in a solution containing 1.2% v/v HCl



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	27,454.885	+/-458.243	279.809	1.019
a	102,068.772	+/-0.000	0.000	0.000
R^2	0.999			
BEC	3.718 ppb			
IDL(LOD)	0.2271 ppb			

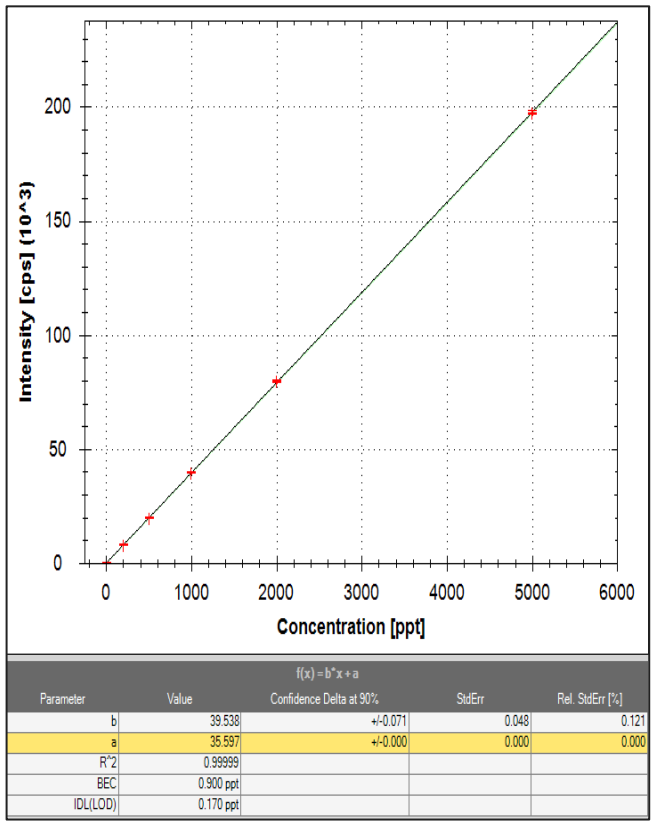
STD mode:
IDL = 227 ppt
BEC = 3,718 ppt



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	3,211.981	+/-26.800	16.364	0.509
a	8.889	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.003 ppb			
IDL(LOD)	0.0041 ppb			

KED mode:
IDL = 4.1 ppt (55x better)
BEC = 3.0 ppt (1240x better)



f(x) = b*x + a

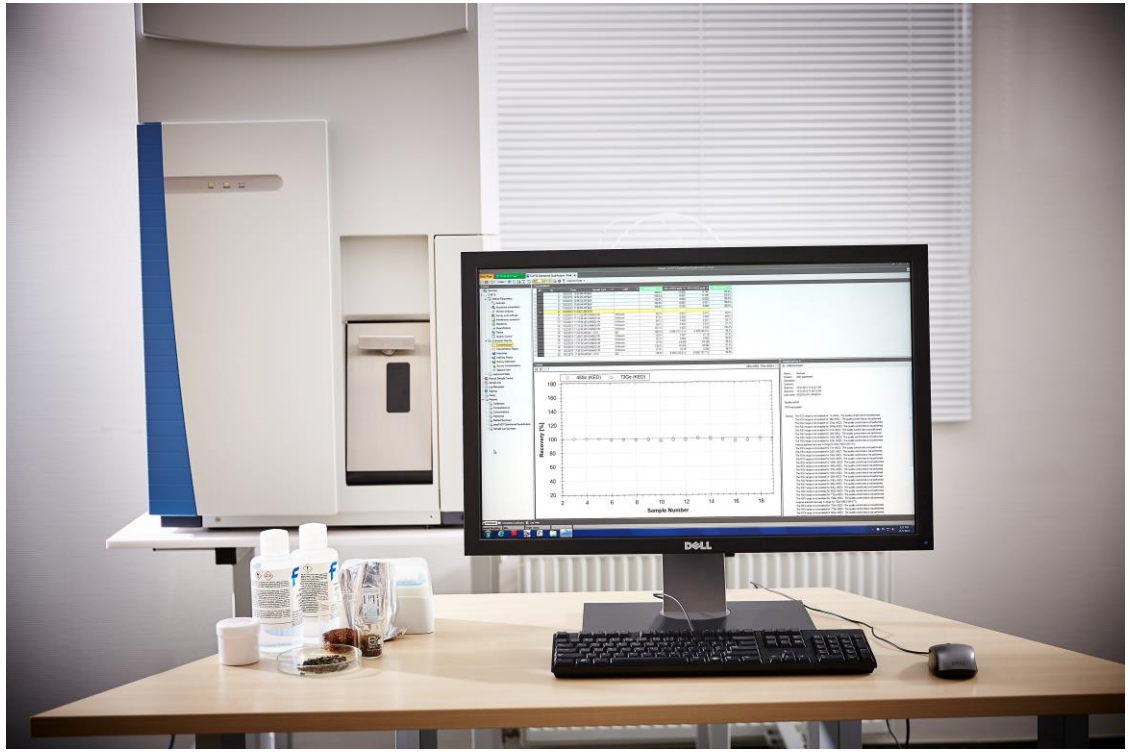
Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	39.538	+/-0.071	0.048	0.121
a	35.597	+/-0.000	0.000	0.000
R^2	0.99999			
BEC	0.900 ppt			
IDL(LOD)	0.170 ppt			

TQ-O_2 mode:
IDL = 0.17 ppt (1340x better)
BEC = 0.90 ppt (4130x better)

Simplified method development with a streamline workflow software

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

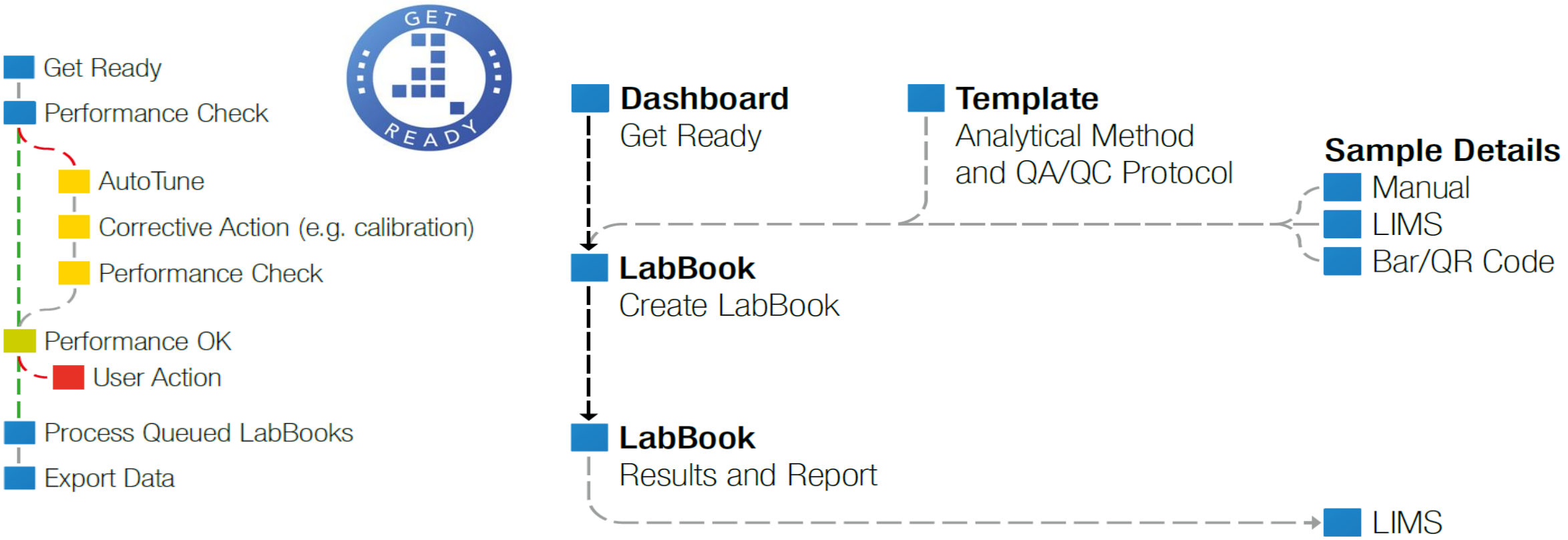
- Intuitive, streamline workflow platform
- A range of new features added for ease of use
- Built-in QC features for Method 200.8 and 6020B
- Same leading **21 CFR Part 11** compliance capabilities
- **Common across Thermo Scientific ICP-OES and ICP-MS instruments**



Streamline workflow software

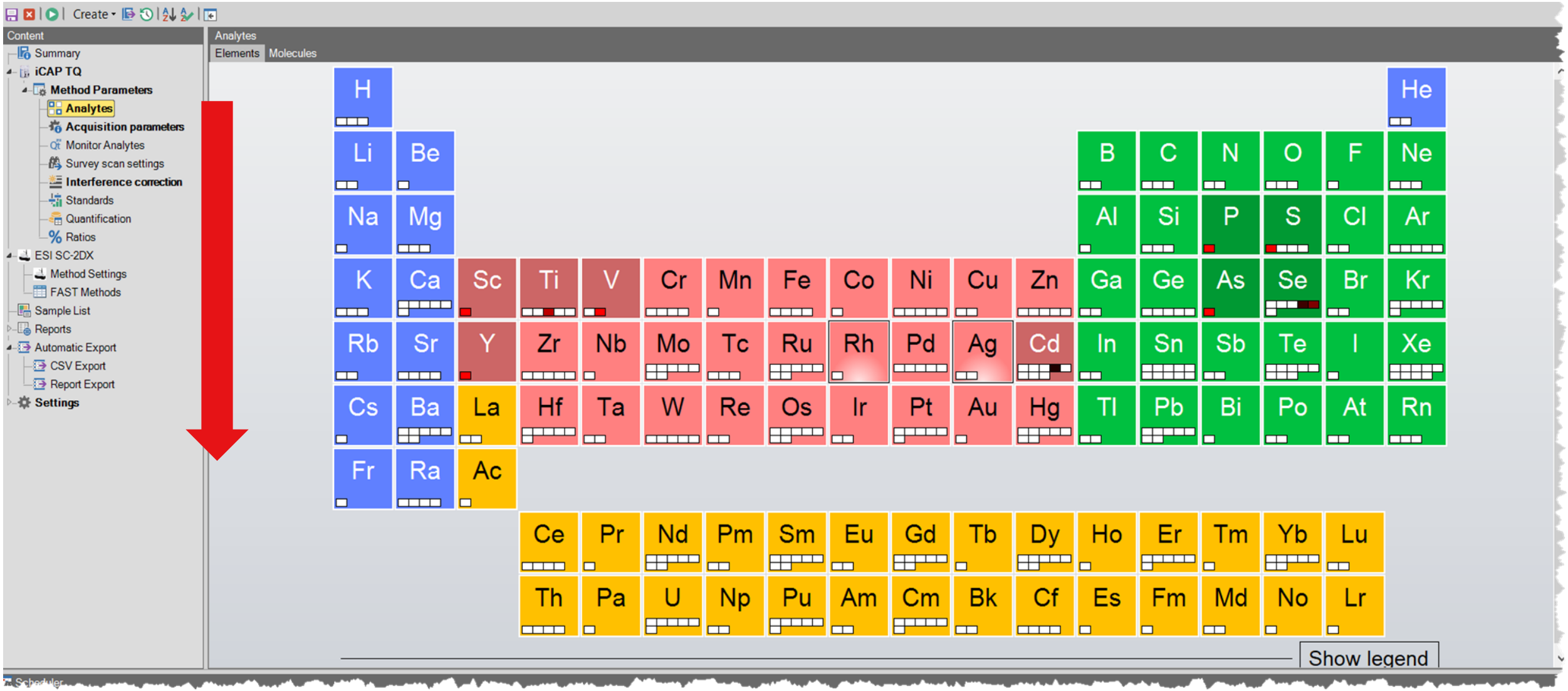
Qtegra ISDS Software

- From Simple Workflows to Quality Results
- Easy to use, yet contains features for flexibility in method development



Streamline workflow software

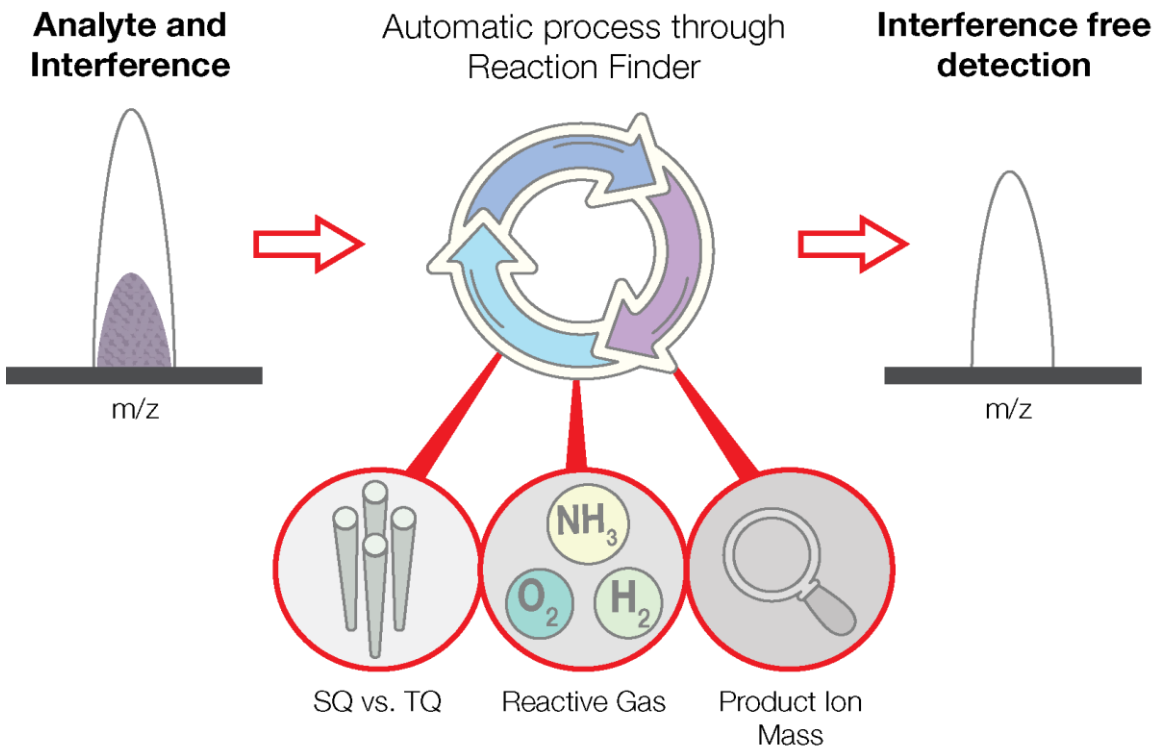
Intuitive method development from starting from the top moving down



Simplified method development for triple quadrupole ICP-MS

- Triple quadrupole ICP-MS offers multiple interference modes for accurate analysis of your sample
- Problem: When faced with the measurement of a sample where interferences are expected, which is the best measurement mode???

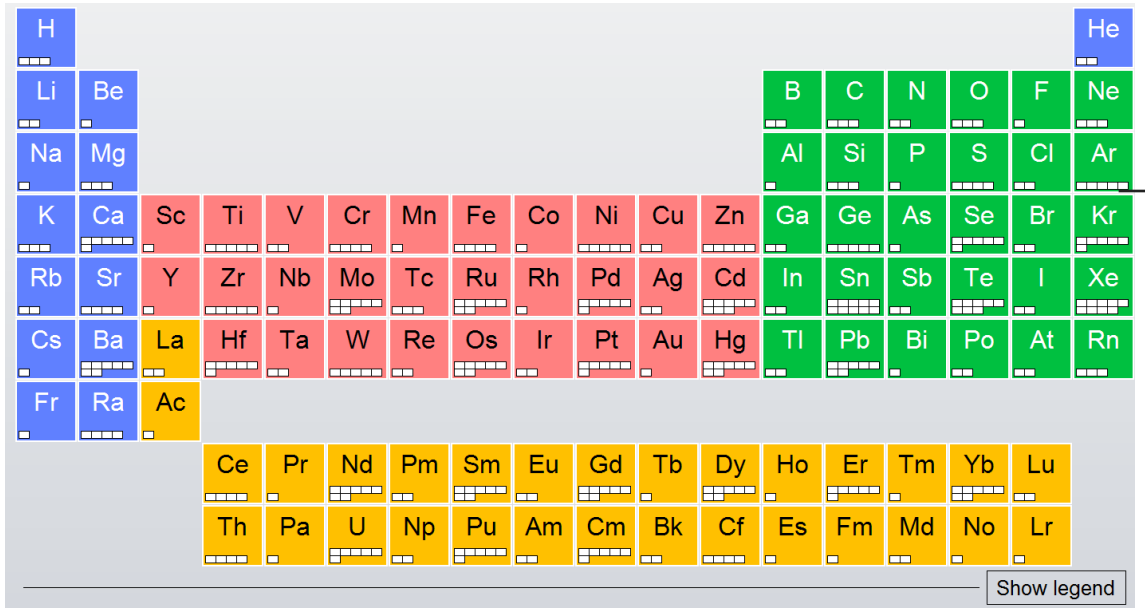
  - Which analyte isotope?
  - Which gas? None, He, reactive gas?
  - Which product ion?

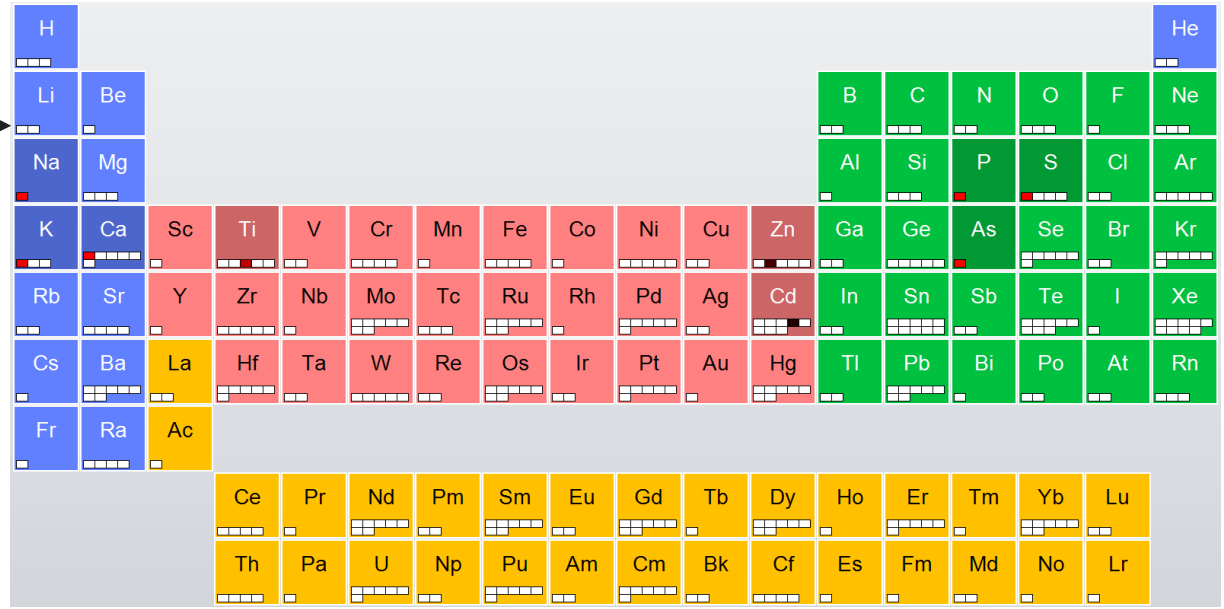


Reaction Finder method development assistant

How does it work?

Select the element/isotope of interest with a single click





How Does Reaction Finder Method Development Assistant Work?

- Reaction Finder loads a list of corresponding default optimum settings from a stored database

Optimum analysis mode

High cell gas flow for intense interference removal

Normal = Intelligent Mass Selection (iMS) for Q1
High = 1 amu for Q1

Most sensitive isotope available

Identifier	Q3 Analyte	SQ / TQ	CR Gas Flow	CR Gas	Dwell time (s)	Channels	Spacing (u)	Q1 resolution	Q3 resolution
9Be (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	High	Normal
23Na (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	High
39K (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
48Ti | 48Ti.14N4.1H10 (S-TQ-NH3)	48Ti.14N4.1H10	TQ	Normal	NH_3	0.1	1	0.1	Normal	Normal
52Cr | 52Cr.16O (S-TQ-O2)	52Cr.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
59Co (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
75As | 75As.16O (S-TQ-O2)	75As.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
80Se | 80Se.16O (S-TQ-O2)	80Se.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
111Cd | 111Cd (S-TQ-iO2)	111Cd (110.904u) (de	TQ	High	O_2	0.1	1	0.1	Normal	Normal
138Ba | 138Ba.16O (S-TQ-O2)	138Ba.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
205Tl (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
208Pb (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal

Best Q3 mass (on mass or mass shift)

Best Q2 cell gas

Select high resolution if you want to extend linear range

iMS ensures ***complete interference removal*** while ***maximizing sensitivity***

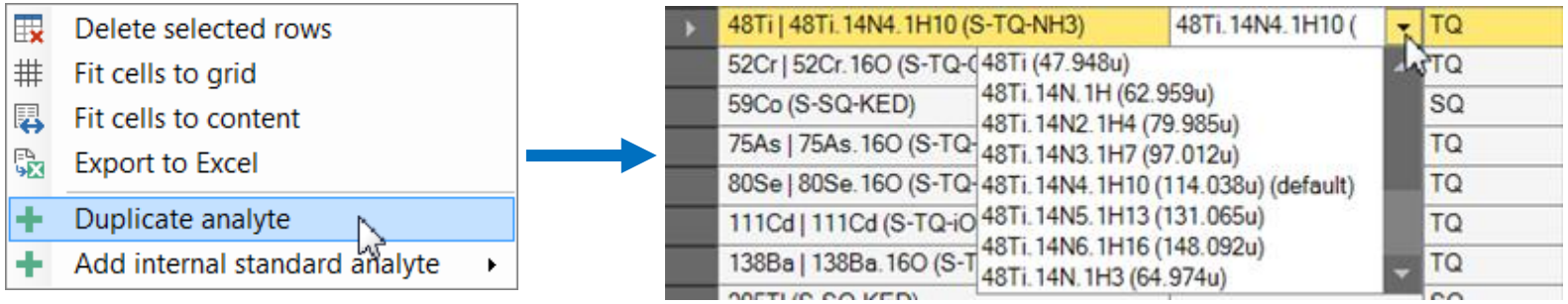
Reaction Finder method development assistant

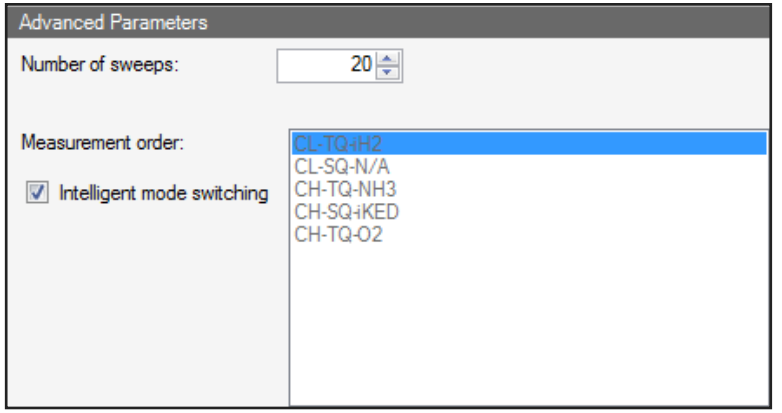
Flexibility and easy method set up

Identifier	Q3 Analyte	SQ / TQ	CR Gas Flow	CR Gas	Dwell time (s)	Channels	Spacing (u)	Q1 resolution	Q3 resolution
9Be (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	High	Normal
23Na (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	High
39K (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
48Ti | 48Ti.14N4.1H10 (S-TQ-NH3)	48Ti.14N4.1H10	TQ	Normal	NH_3	0.1	1	0.1	Normal	Normal
[illegible]	[illegible]	TQ	Normal	[illegible]	0.1	1	0.1	Normal	Normal
59Co (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
75As | 75As.16O (S-TQ-O2)	75As.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
80Se | 80Se.16O (S-TQ-O2)	80Se.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
111Cd | 111Cd (S-TQ-iO2)	111Cd (110.904u) (de	TQ	High	O_2	0.1	1	0.1	Normal	Normal
138Ba | 138Ba.16O (S-TQ-O2)	138Ba.16O	TQ	Normal	O_2	0.1	1	0.1	Normal	Normal
205Tl (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
208Pb (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal
111Cd (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1	Normal	Normal

- Flexibility to modify settings or add modes for key elements
  - Add other modes for method development
  - Choose another gas or product ion (list automatically displayed)

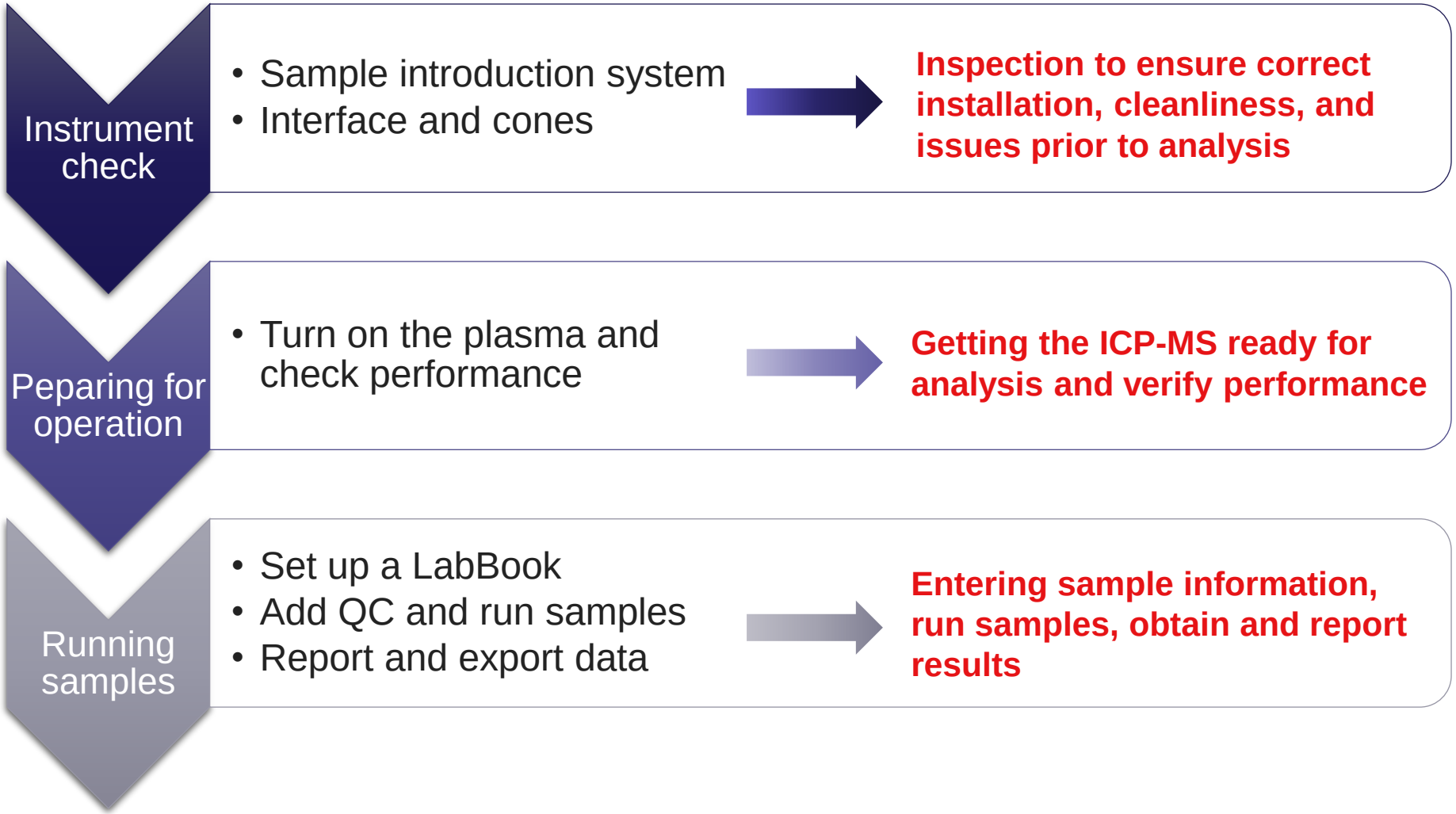
Intelligent Mode switching chooses the most optimal analysis order for each run





- **Instrument optimization routines and troubleshooting tips and tricks**

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

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

iCAP RQ/TQ ICP-MS torch assembly

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, **Ul**traclean **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

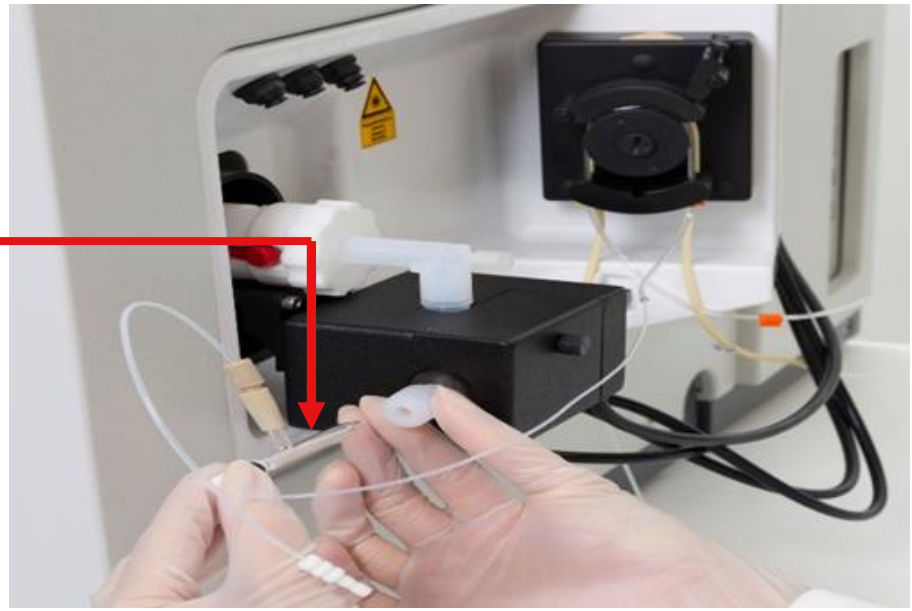
Instrument checks – sample introduction system

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 the appropriate type of nebulizer is used for the application

		
Glass concentric micro mist nebulizer	**PFA-ST nebulizer**	**Burgener Mira 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	• All PFA construction, chemical resistant • Self-aspirating • 400 µL/min flowrate • High transport efficiency, high sensitivity • Resistant to clogging and breakage	• 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

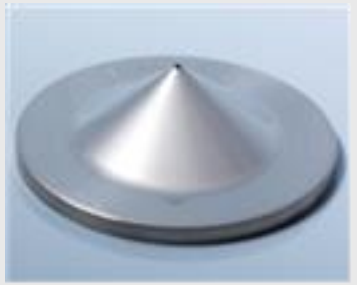
- Interface and sample and skimmer cones

- 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

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

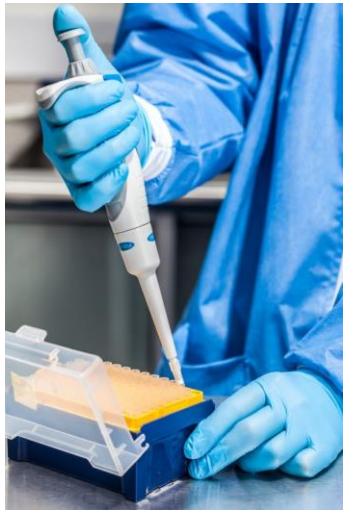
Contamination issues are shown by high blanks and sample or standard recoveries. Carryover is characterized by high standard blanks (CCB) and decreasing sample replicates resulting to high % RSD.

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 to simplify environmental sample analysis

Streamlining workflow helps to obtain fast, accurate results and quality data



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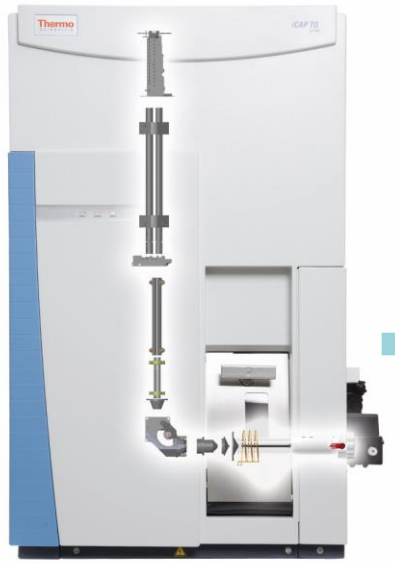

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Savings in time and resources and quality data

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

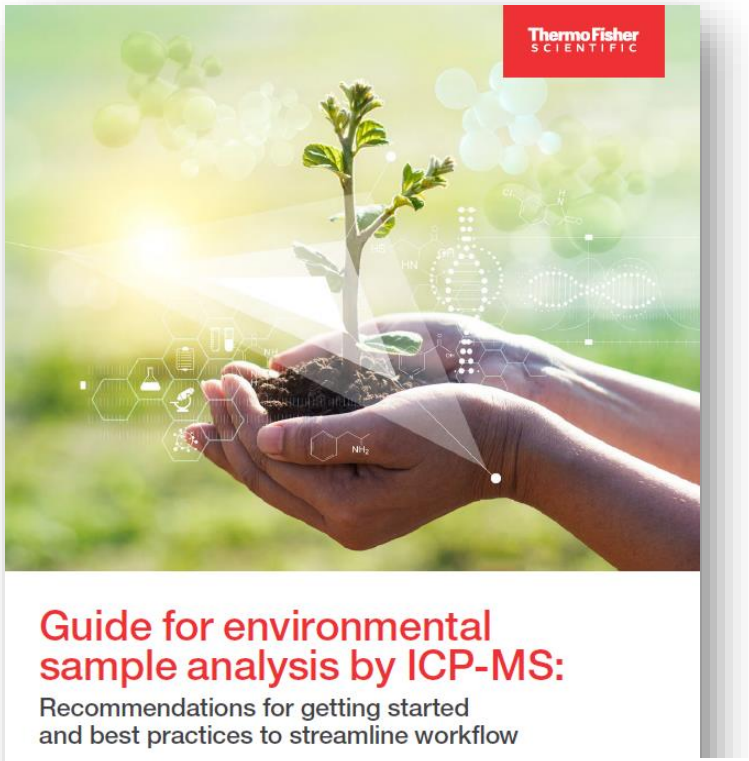
New resource

Guide for environmental sample analysis by ICP-MS

If your laboratory is

- Experiencing analytical challenges, inaccurate results, & 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
- Recommended pre-calibration routines and instrument inspections
- General instrument maintenance and troubleshooting tips and tricks

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Thank you