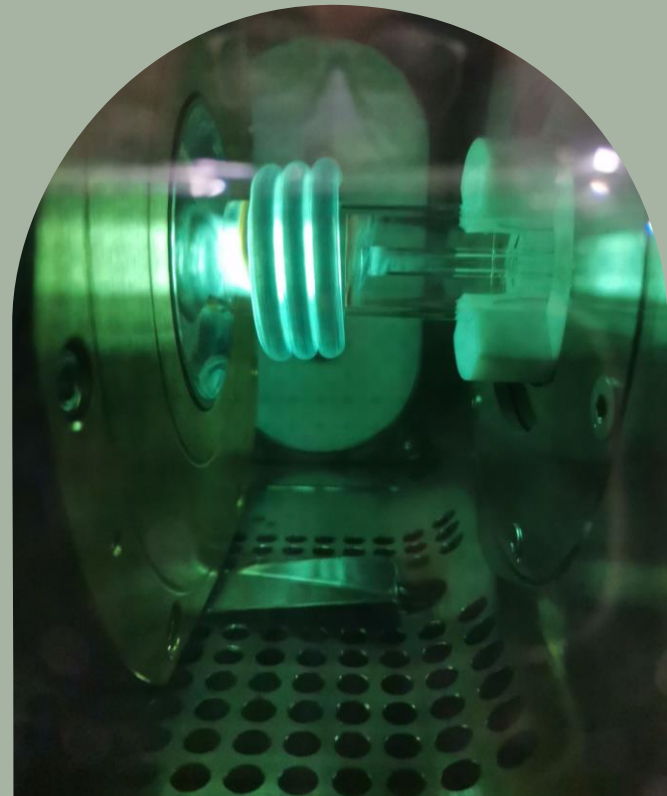


LSC

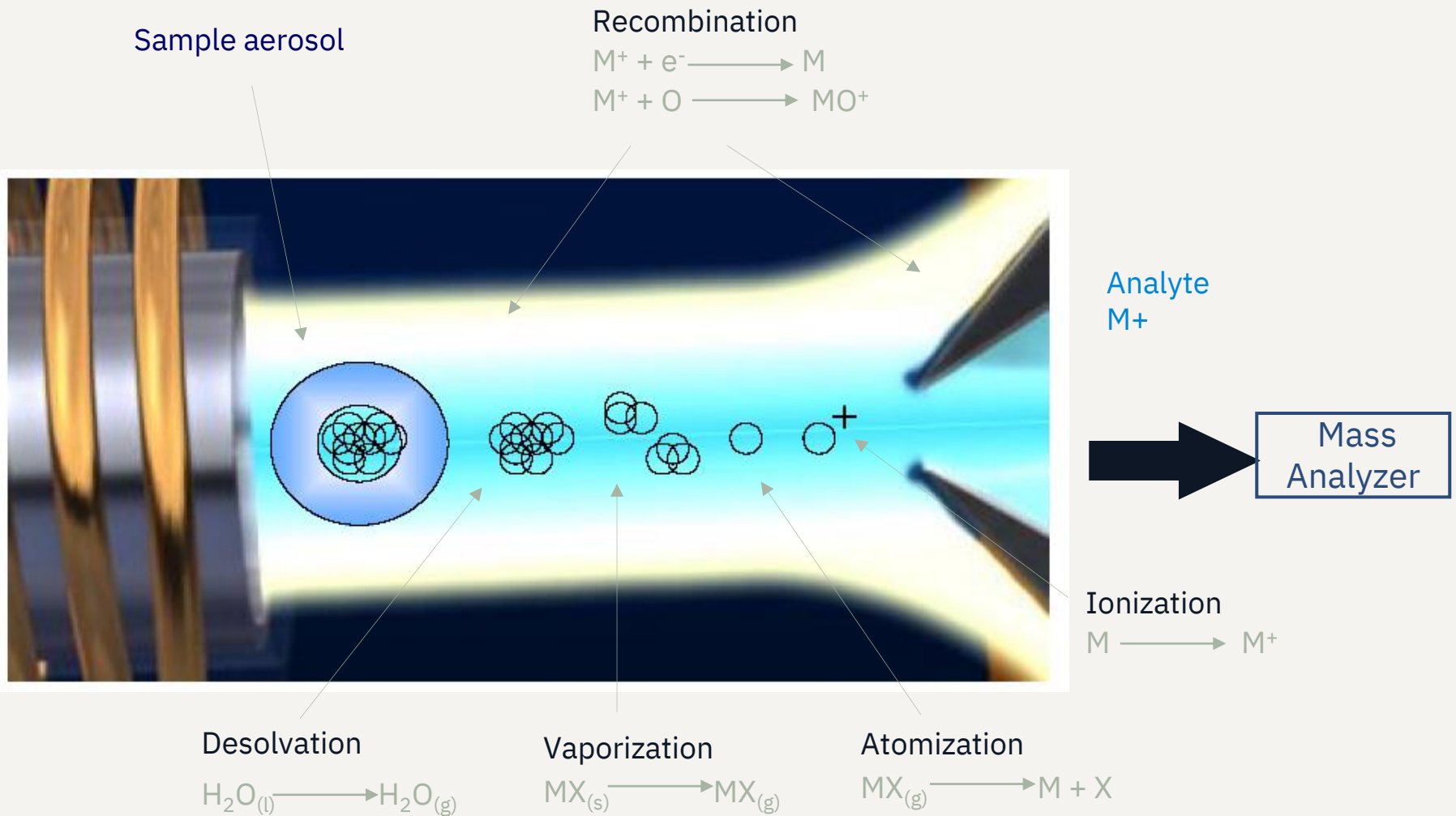


Low radioactivity measurements based on ICP-MS at LSC



INTRODUCTION

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)



ICP-MS (SQ)



- ✓ Installed at Main building Laboratory
- ✓ Thermo iCAP RQ ICP-MS (single quad).
- ✓ Sample preparation laboratory available.
- ✓ Working since 2017.

ICP-MS (SQ)



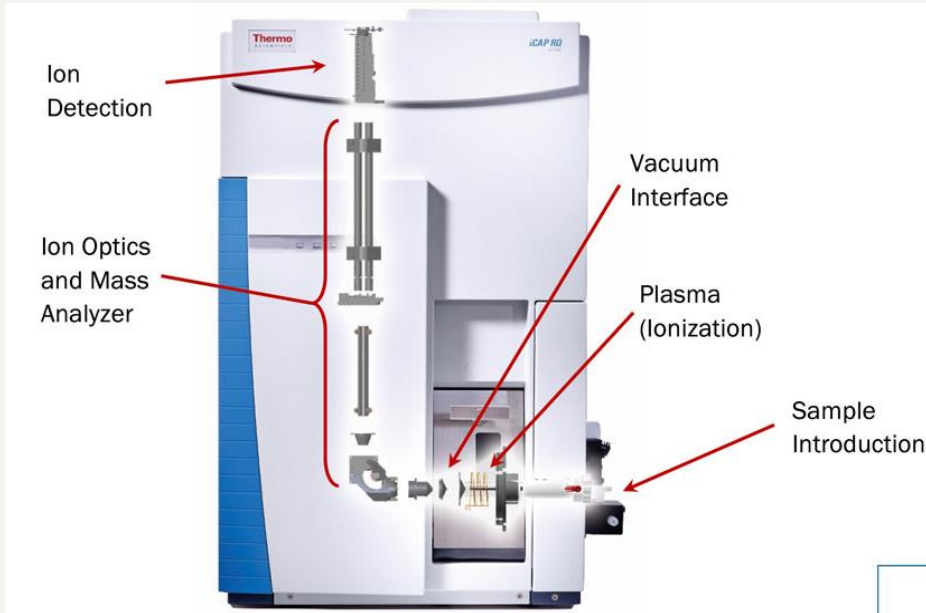
- ✓ Installed at Main building Laboratory
- ✓ Thermo iCAP RQ ICP-MS (single quad).
- ✓ Sample preparation laboratory available.
- ✓ Working since 2017.

ICP-MS/MS (QQQ)

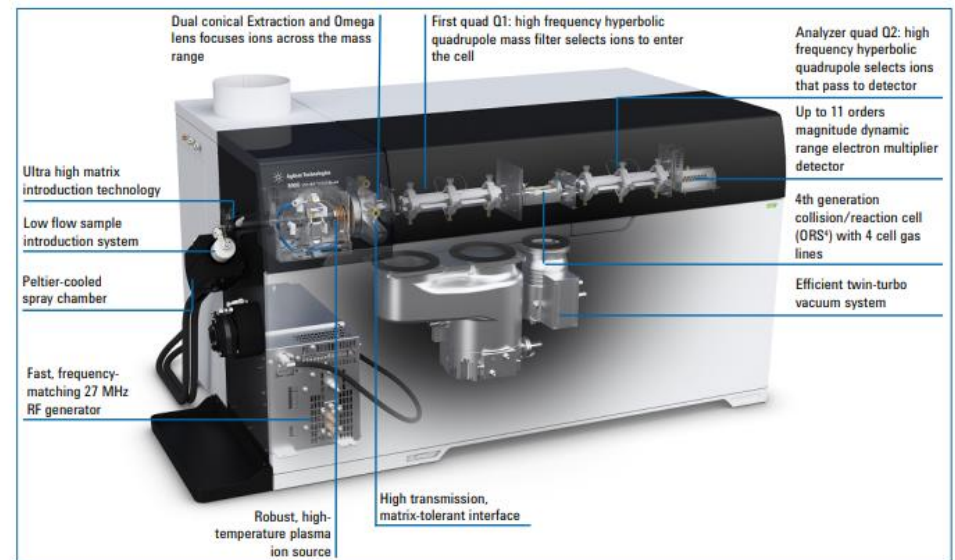
- ✓ Underground Clean Room ISO6 class
- ✓ ICP-QQQ Agilent 8900 + Autosampler Cetac 560.
- ✓ Sample preparation equipment available in ISO7 Clean Room
- ✓ **Installed since 2023**
- ✓ He and $\text{NH}_3:\text{He}$ (10:90): collision/reaction cell gases. O_2 (Also available soon).



ICP-MS (SQ) vs ICP-MS/MS (QQQ)

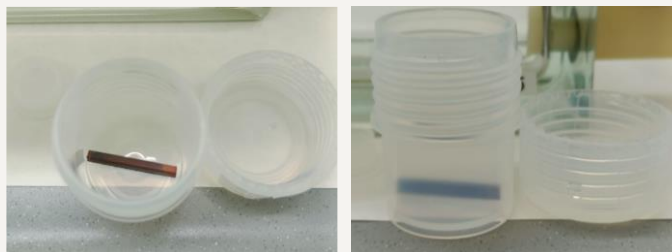


Thermo Fisher Scientific®

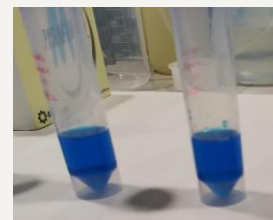


Agilent Technologies®

Copper matrix: U and Th determination



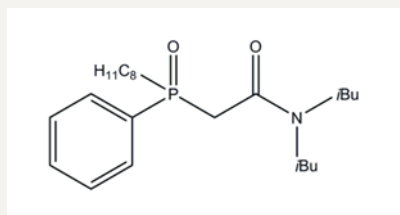
Copper sample: Etching procedure



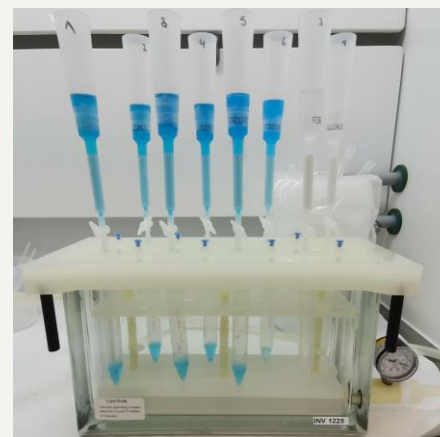
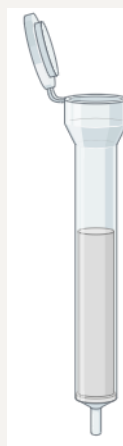
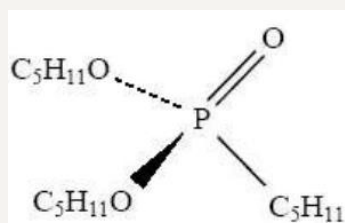
Etched Copper

U and Th isolation/preconcentration – Chromatographic resin cartridge

TRU Resin [®] Triskem

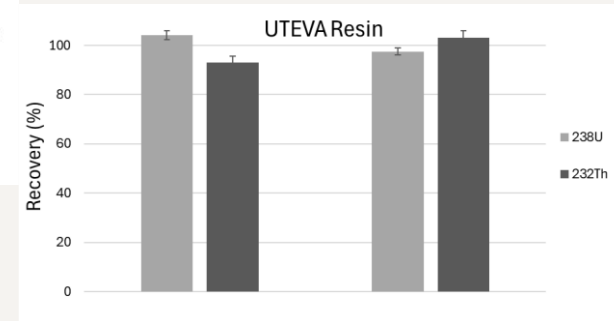
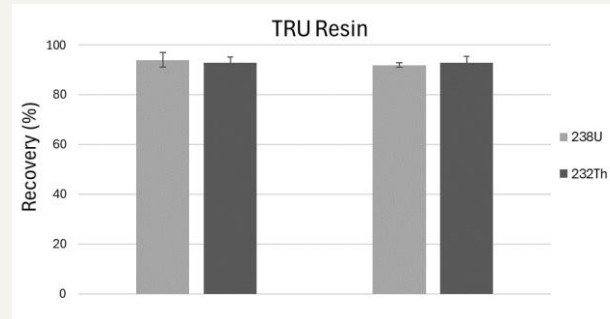
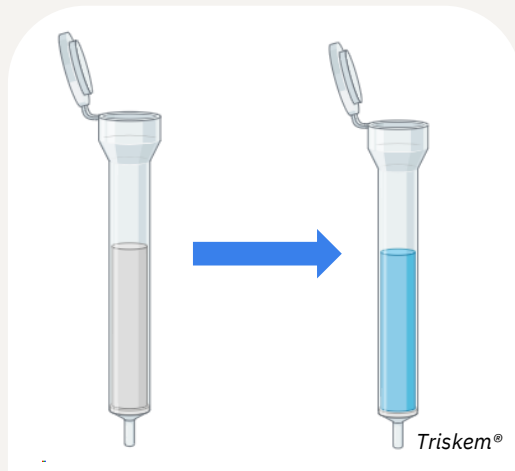


UTEVA RESIN [®] Triskem



Copper matrix: U and Th determination

U and Th isolation/preconcentration UTEVA/TRU RESIN



STEPS:

- Cleaning resin cartridges: **TRU**: Ammonium oxalate.

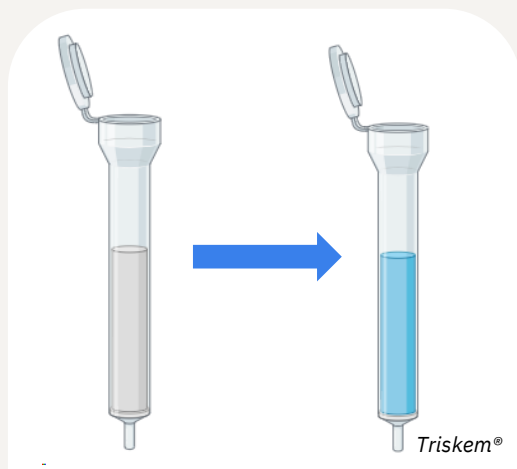
UTEVA: 4M HNO_3

- Blank procedure quantification → ICP-MS
- Sample loading: Etched copper
- Remove copper matrix: HNO_3
- Elution U and Th: **TRU**: Ammonium oxalate.

UTEVA: diluted HNO_3

Copper matrix: U and Th determination

U and Th isolation/preconcentration UTEVA/TRU RESIN



TRU Resin:

LODs copper sample:

^{232}Th : 20 ± 1 pg / g copper

^{238}U : 11 ± 1 pg / g copper

UTEVA Resin:

LODs copper sample:

^{232}Th : 0.43 ± 0.02 pg / g copper

^{238}U : 0.21 ± 0.01 pg / g copper

**Determined ICP-MS (SQ)*

STEPS:

- Cleaning resin cartridges: **TRU:** Ammonium oxalate.

UTEVA: 4M HNO_3

- Blank procedure quantification → ICP-MS

- Sample loading: Etched copper

- Remove copper matrix: HNO_3

- Elution U and Th: **TRU:** Ammonium oxalate.

UTEVA: diluted HNO_3

- **Matrix removal (reducing matrix effects)**

- **Reduce possible interferences.**

- **Some analyte preconcentration**

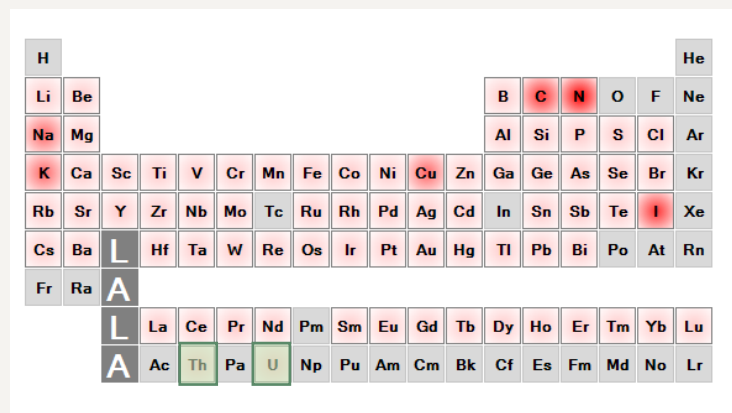
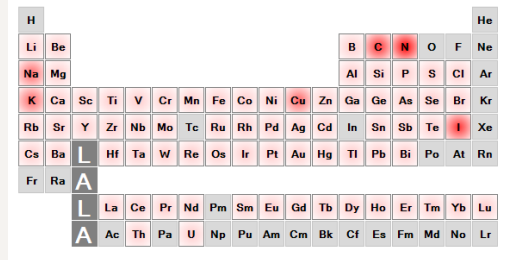
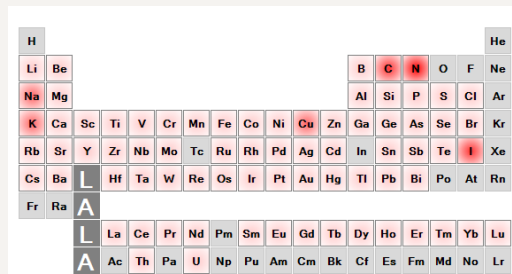
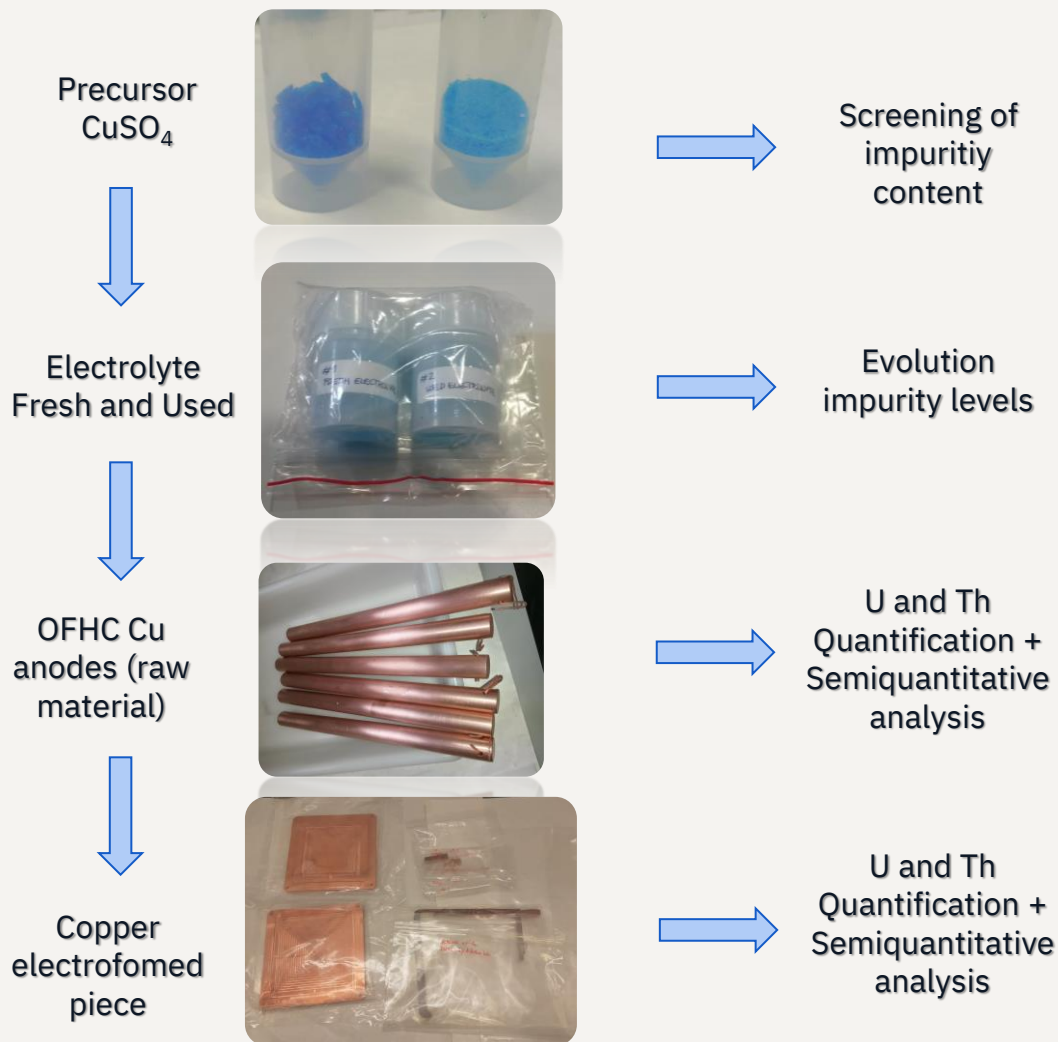
- **Time consuming → Automatization**

- **Contamination risk during the isolation procedure → Increasing background signals**

**AUTOMATIZATION
SYSTEM COMING
SOON**

Quality Control CES at LSC

Control of the Whole Electroforming process: Collaboration S. Borjabad (CES LSC)



K Determination NaI crystals - Challenges

Natural isotopic abundance

^{36}Ar (0.34%)

^{38}Ar (0.06%)

^{39}K (93.26%)

$^{38}\text{Ar}^1\text{H}^+$

^{40}K (0.012%)


^{40}Ar (99.6%)

^{41}K (6.73%)

$^{40}\text{Ar}^1\text{H}^+$

**Isobaric
interferences**

**Polyatomic
interferences**

- 
- **ISOBARIC INTERFERENCES** $^{40}\text{Ar} \rightarrow ^{40}\text{K}$
 - **POLYATOMIC INTERFERENCES** ^{39}K
 - **MATRIX EFFECTS:** NaI matrix solution \rightarrow impact on ICP response factor.





K Determination NaI crystals - Challenges

Natural isotopic abundance

³⁶Ar (0.34%)

³⁸Ar (0.06%)

³⁹K (93.26%)

³⁸Ar¹H⁺

⁴⁰K (0.012%)

⁴⁰Ar (99.6%)

⁴¹K (6.73%)

⁴⁰Ar¹H⁺

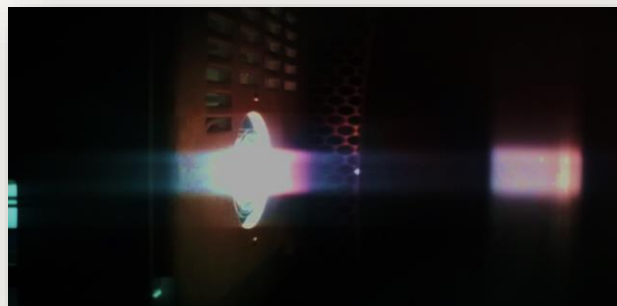
Isobaric interferences

Polyatomic interferences

- **ISOBARIC INTERFERENCES** ⁴⁰Ar → ⁴⁰K
- **POLYATOMIC INTERFERENCES** ³⁹K
- **MATRIX EFFECTS:** NaI matrix solution → impact on ICP response factor.

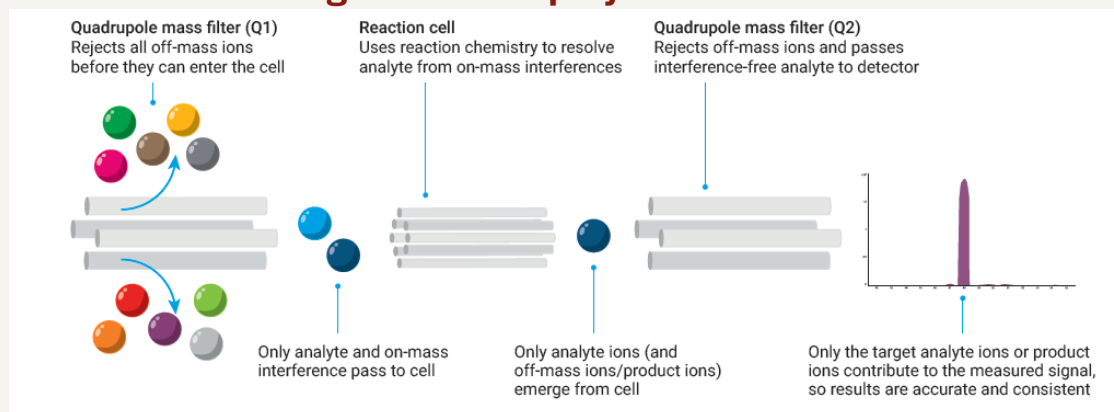


**Cool plasma conditions:
reduce Ar ionization**



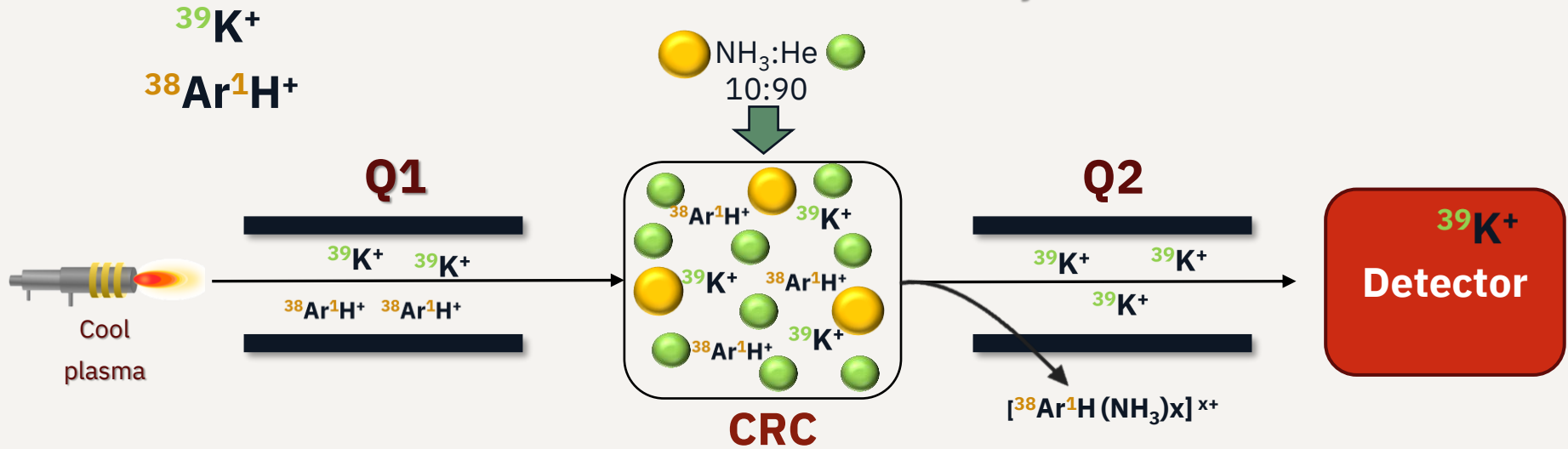
Power reduction from 1500 W to 600-800W

Reaction gas: remove polyatomic interferences



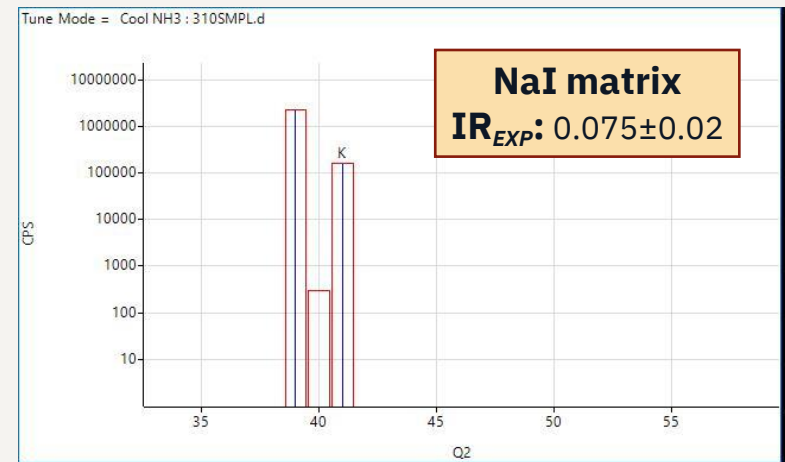
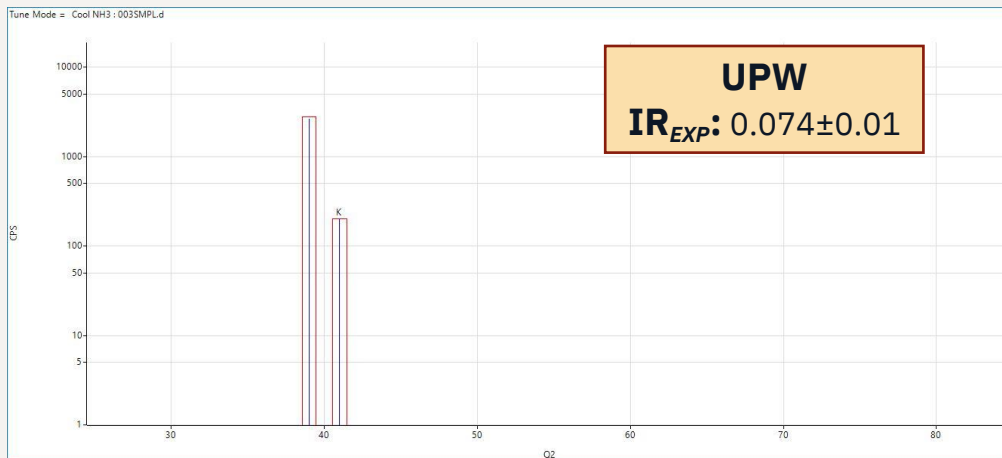


K Determination NaI crystals



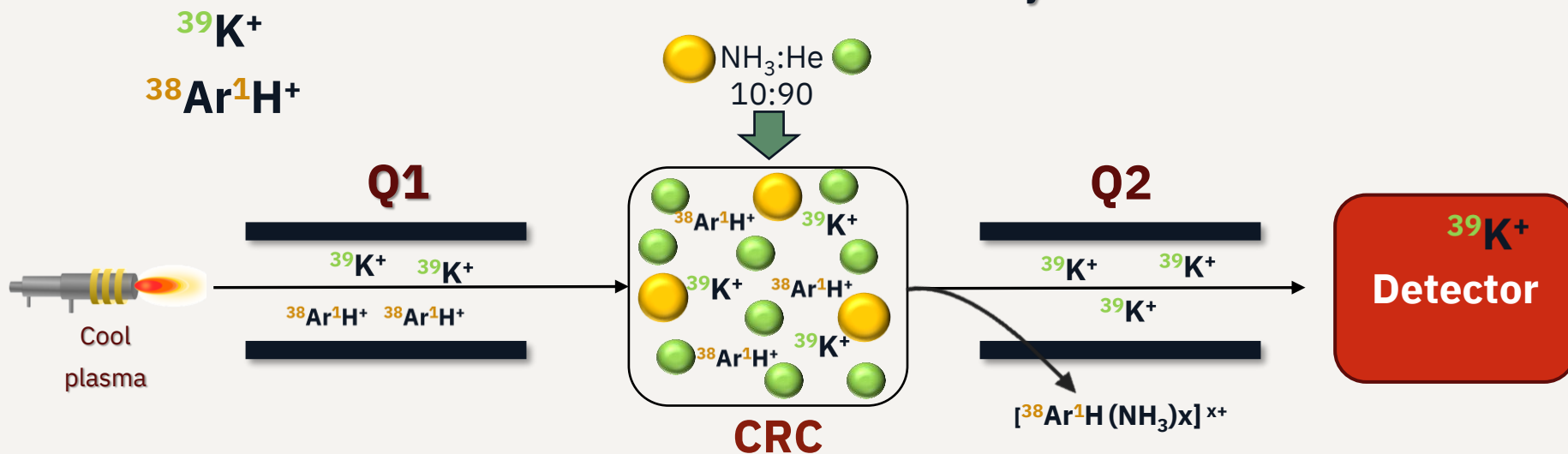
Isotopic Ratio: $IR = \frac{^{41}K}{^{39}K}$ Calculated in UPW and NaI sample matrix

$IR_{Theo}: 0.072$



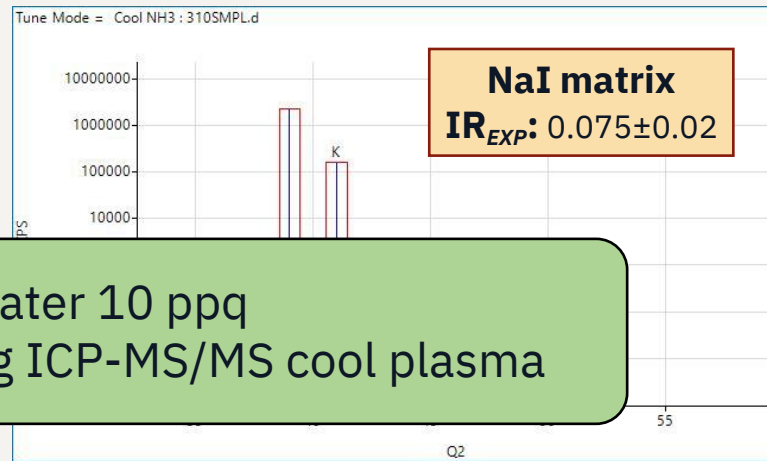
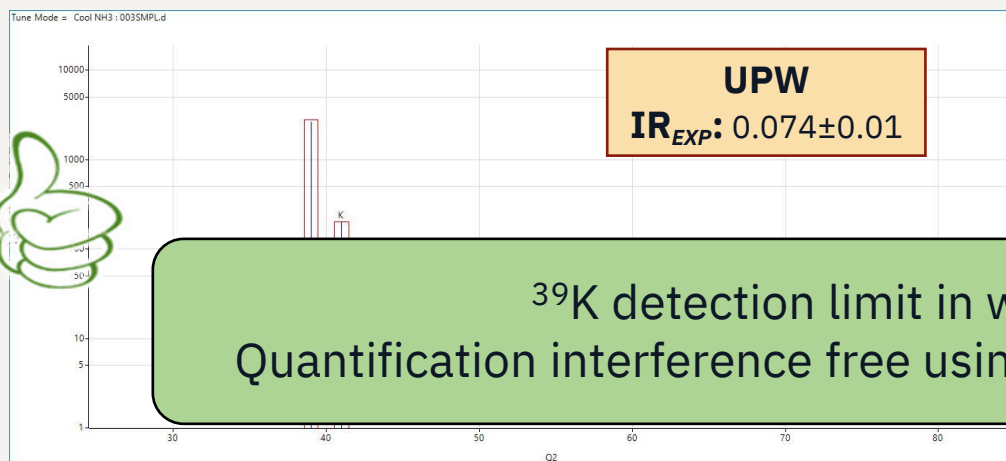


K Determination NaI crystals



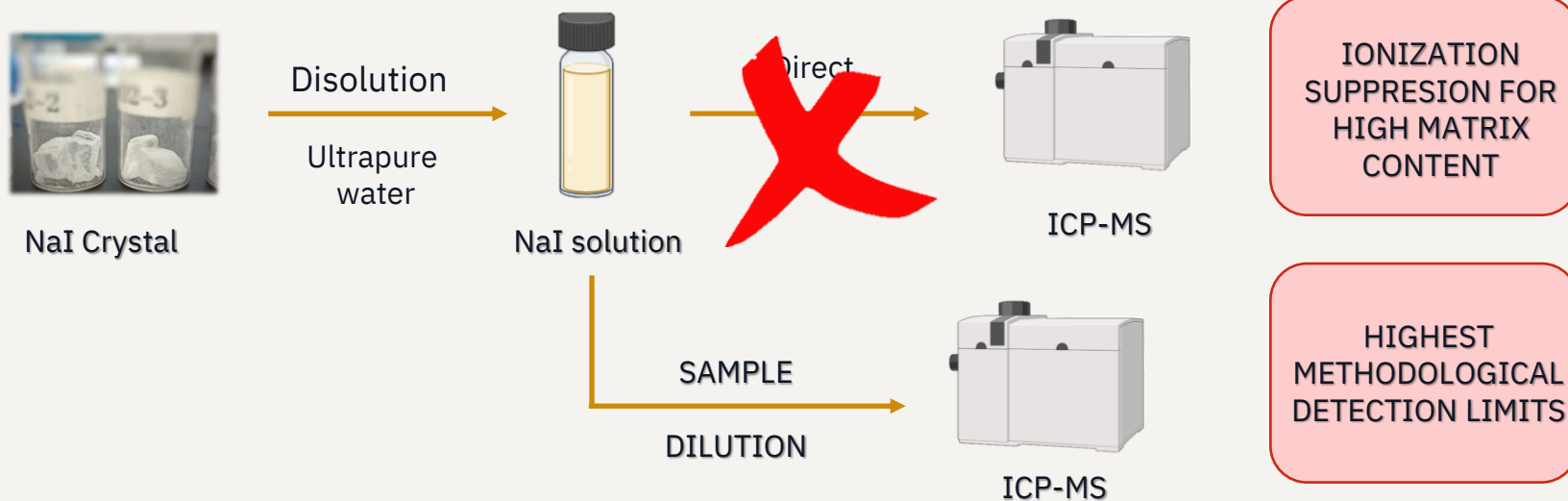
Isotopic Ratio: IR $\frac{^{41}\text{K}}{^{39}\text{K}}$ **Calculated in UPW and NaI sample matrix**

IR_{Theo}: 0.072

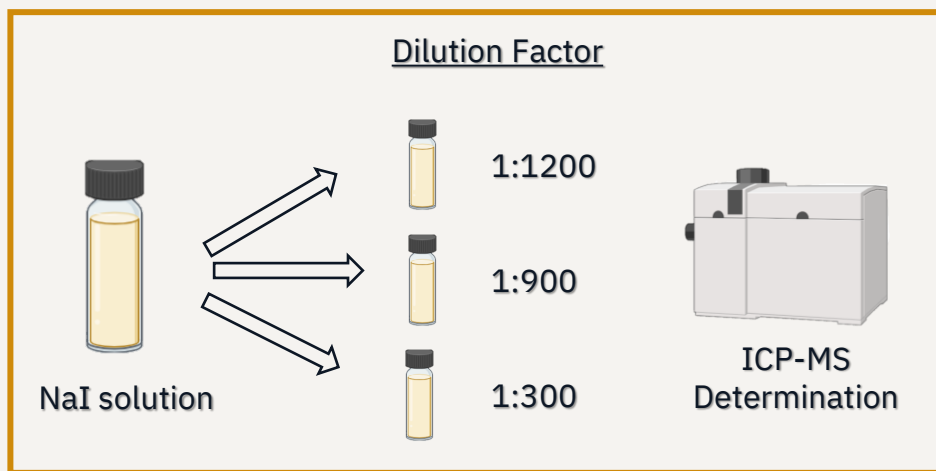
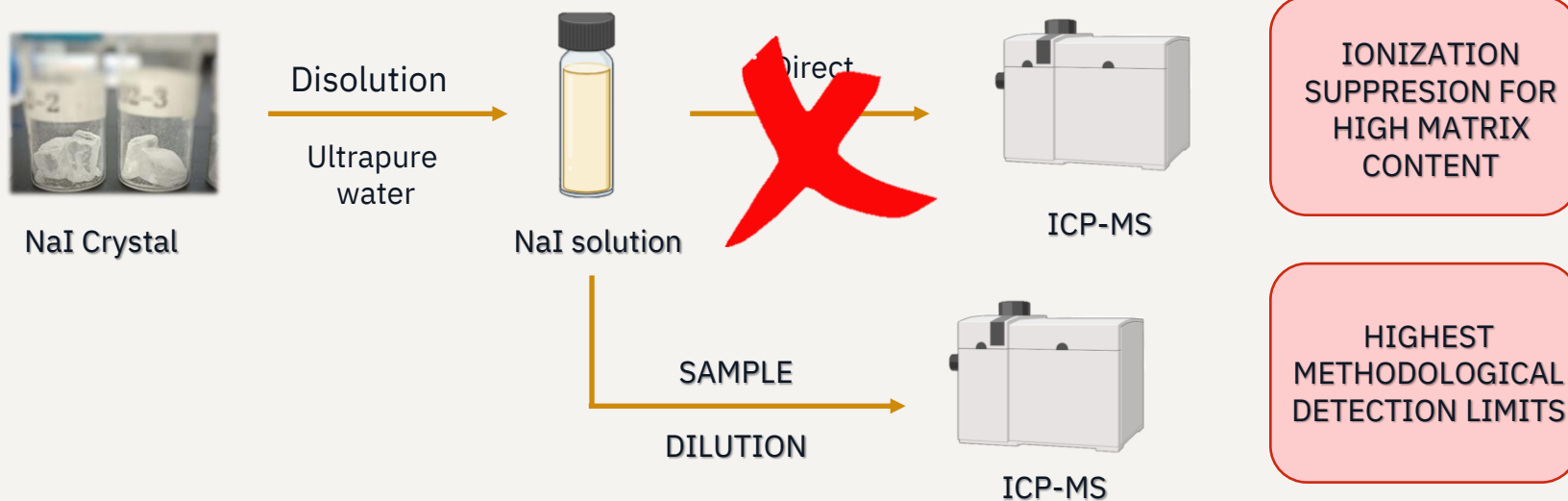


**^{39}K detection limit in water 10 ppq
Quantification interference free using ICP-MS/MS cool plasma**

K Determination NaI crystals

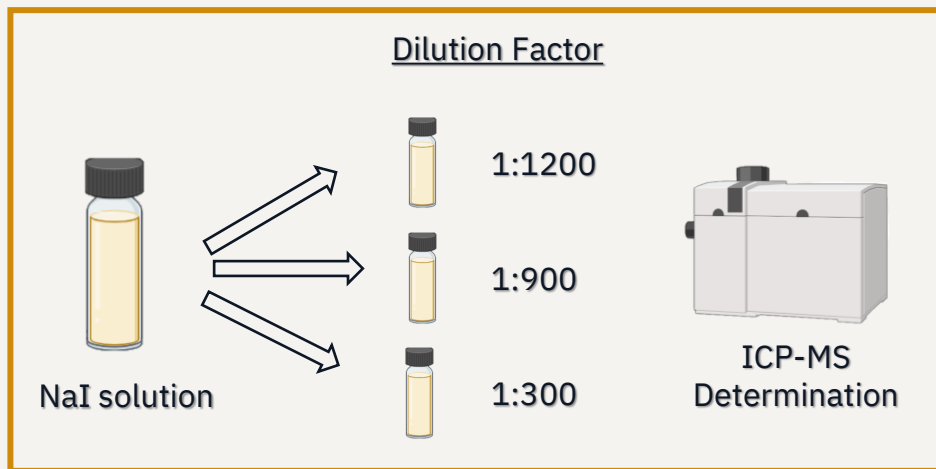
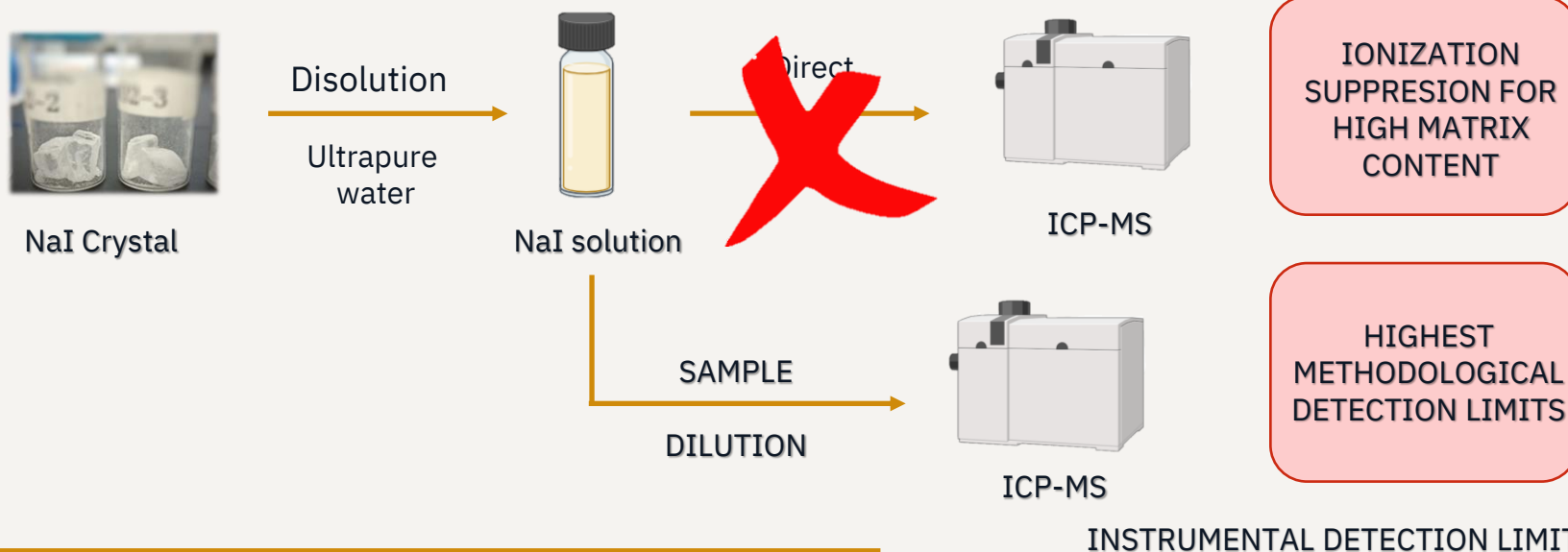


K Determination NaI crystals



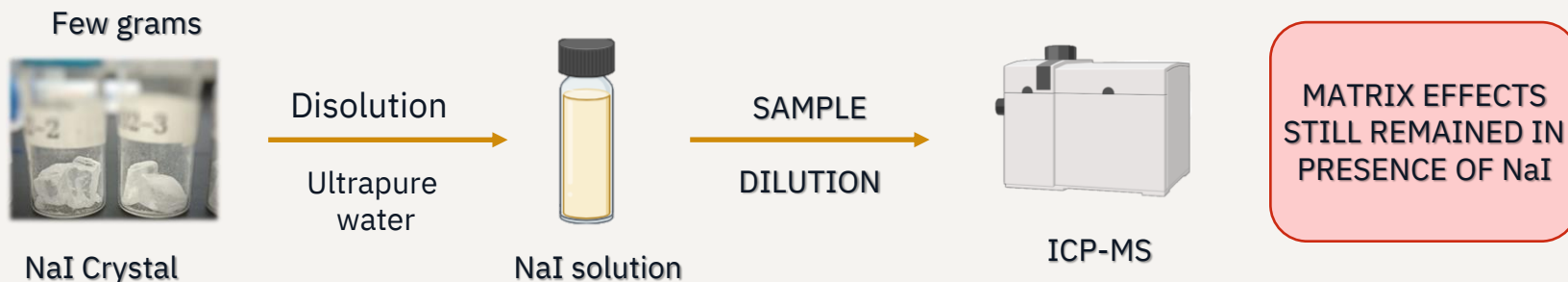
Compromise between Dilution Factor and Reduction en Sensitivity (NaI content)

K Determination NaI crystals

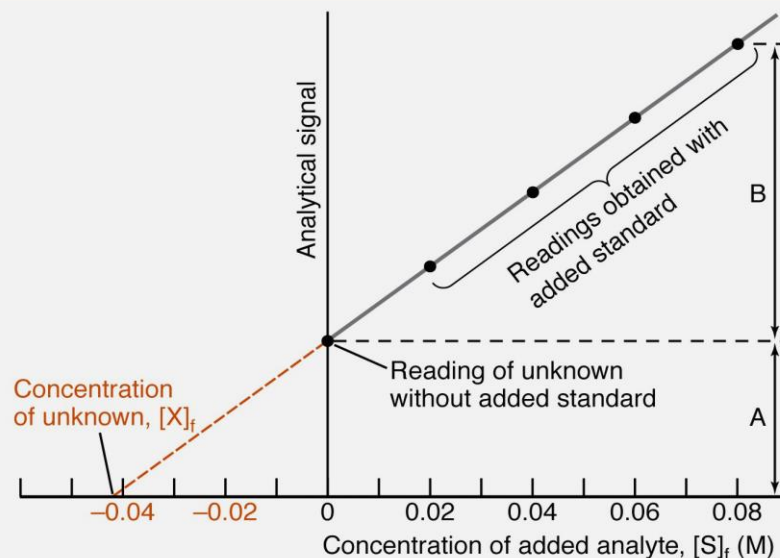
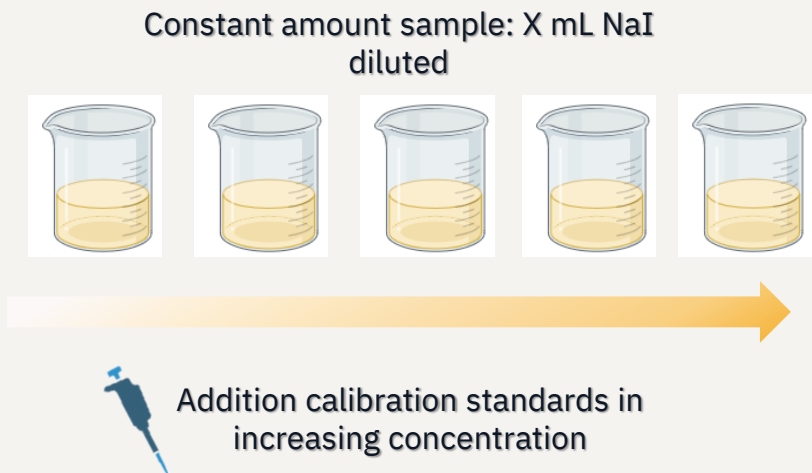


DILUTION FACTOR NaI	³⁹ K RESPONSE FACTOR ICP (CPS/ppb)	Detection limit ³⁹ K in solid NaI crystal (ppb)
1:1200	77100	8
1:300	46000	4

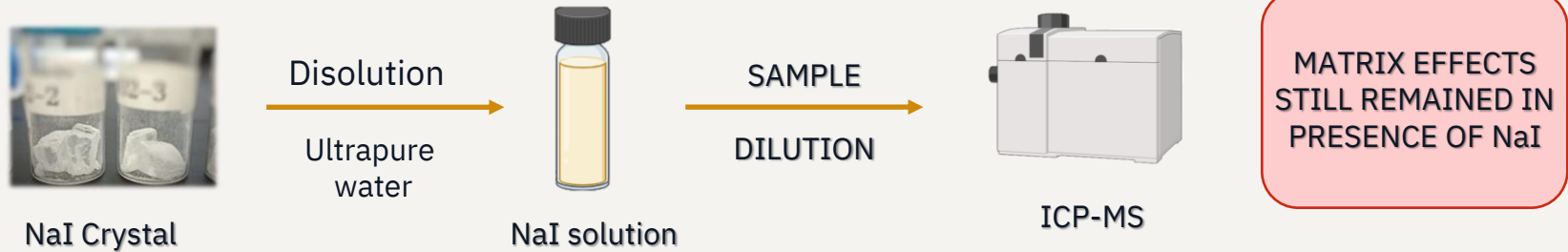
K Determination NaI crystals



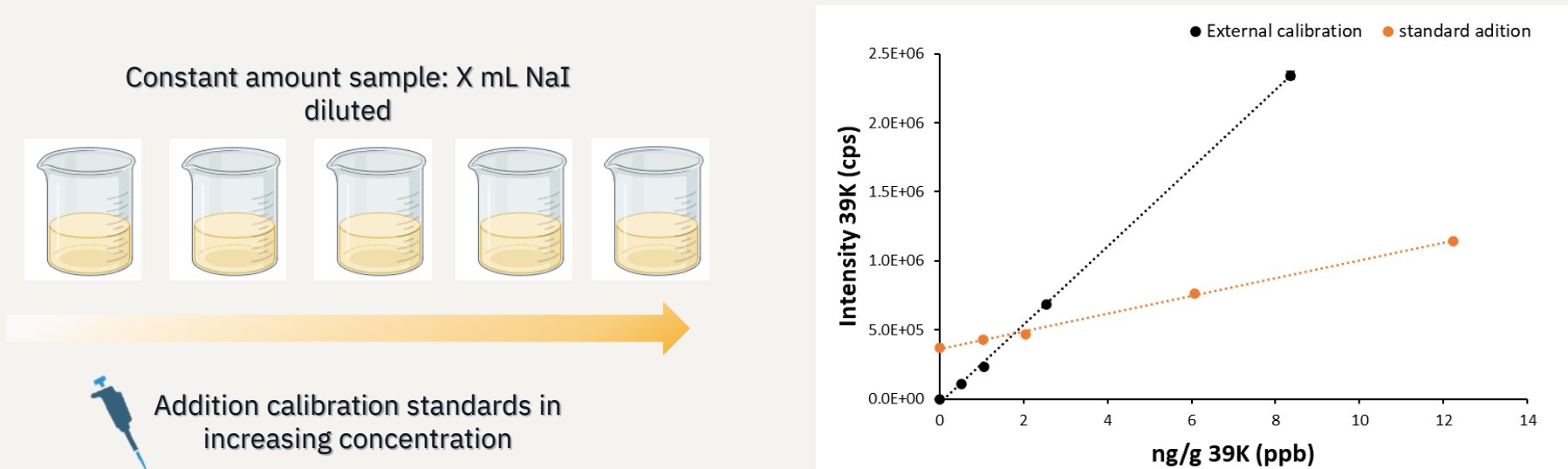
STANDARD ADITION CALIBRATION STRATEGY



K Determination NaI crystals



STANDARD ADITION CALIBRATION STRATEGY



Determination NaI crystals



H																				He
Li	Be										B	C	N	O	F	Ne				
Na	Mg										Al	Si	P	S	Cl	Ar				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	A																		
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

Direct analysis

Measured after evaporation

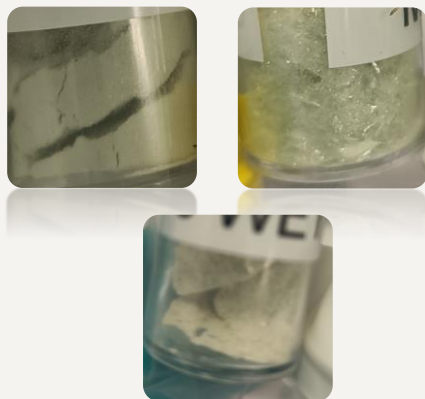
Memory effects of Tl Formation of TlI

↓

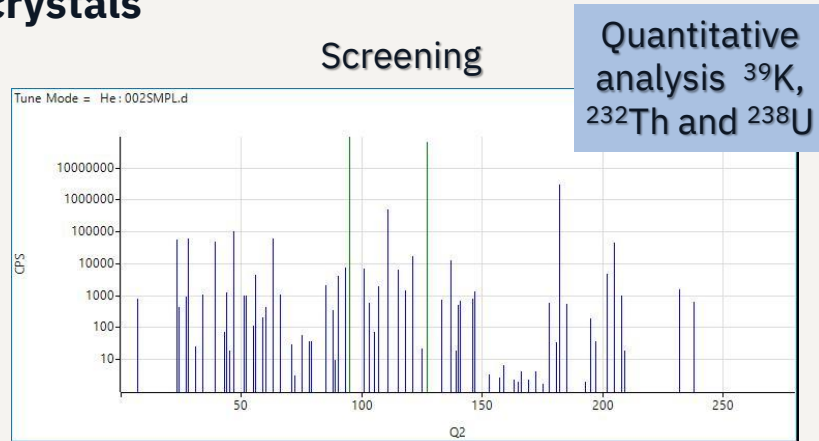
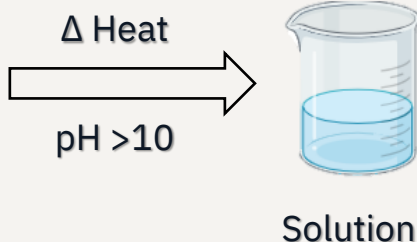
**Evaporation I₂
No Tl memory effects detected**

Other type of samples analyzed

Mo-based salts and crystals



Mo-based salts



Plastic samples: PTFE , HDPE



HDPE samples



Ashing procedure: Pt crucibles

- Cleaning Pt crucibles
- Ashing process: plastic samples
- Ashes Reconstitution: acidic media
- ICP-MS: quantitative analysis ^{232}Th , ^{238}U

HDPE Recovery:

^{238}U : $104 \pm 2\%$
 ^{232}Th : $99 \pm 2\%$

PTFE Recovery:

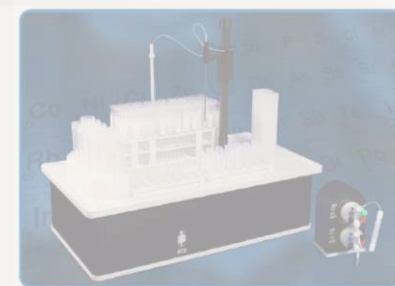
^{238}U < 60%
 ^{232}Th < 60%

Still in progress

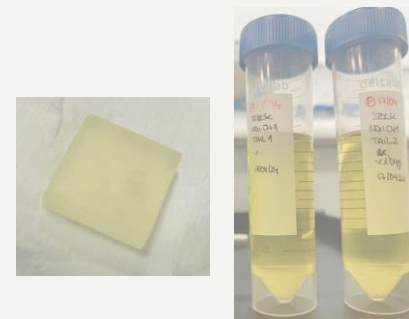
Summary and Future Steps



- The ICP-MS service of the LSC has been improved with the installation of a **new ICP-MS/MS in the Underground Clean Room**.
- Progress has been made in the development of new methods for the quantification **of U and Th in copper samples**. Further improvement → **AUTOMATIZATION SAMPLE PREP**.
- **QA of electroforming procedure** is being carried out in collaboration with LSC CES: precursors → copper pieces.
- A method for the determination of **K in NaI crystals** (in the presence of Tl doping) using cold plasma and MS/MS technology has been successfully implemented.
- Other matrices have been analyzed (Mo-based crystals, plastics) → Screening and Quantitative analysis.



Elemental Scientific®



Laboratorio Subterráneo Canfranc



THANK YOU

