Ultra-trace Th and U Measurements in Metals with Inductively Coupled Plasma Mass Spectrometry（ICP-MS）

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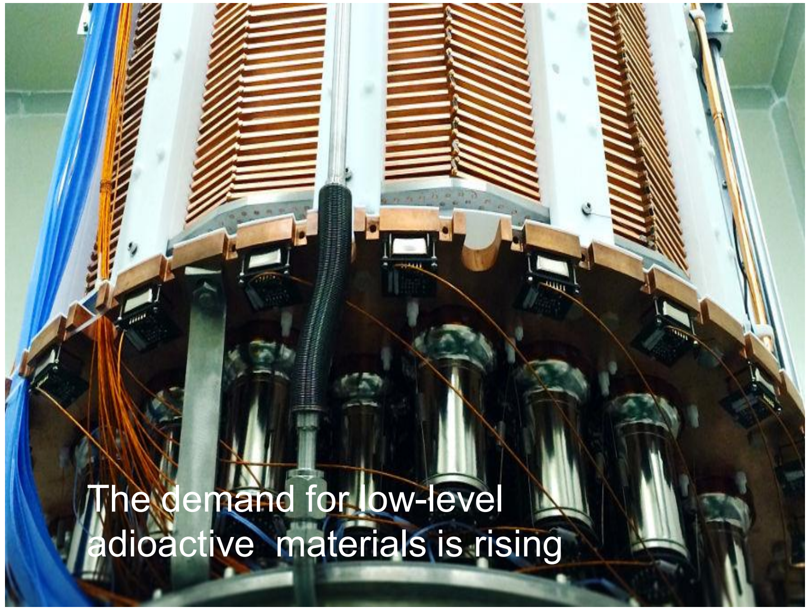
Contents

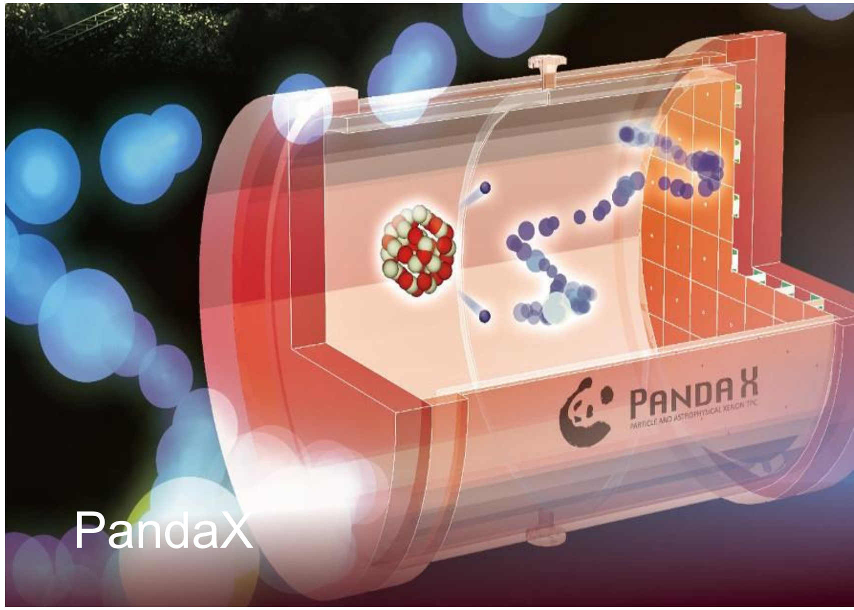
1 Lab Capabilities & Why ICP-MS

2 Th and U analyze by ICP-MS

3 Summary

1.1 Rare event & Radioactive background





The measurement, screening, and manufacturing of radio-pure materials have always been key tasks in rare event experiments

1.2 Why ICP-MS?

Critical Need: Sub-ppb Th/U screening for detector materials

Nuclear Activation Analysis (NAA)

- *Scarce neutron reactor access,* cumbersome handling, long time

γ-Spectrometry

- Insufficient sensitivity below ppb levels, long counting time

ICP-MS

⚡**Multi-element Capability:** Simultaneous analysis

⚡ **Unmatched Sensitivity:** Sub-ppt detection limits.

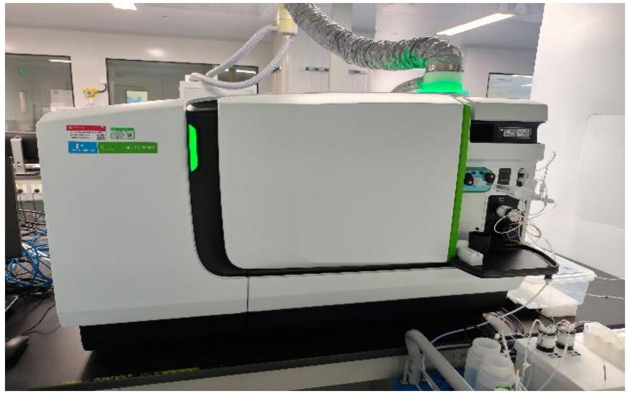
⚡ **Rapid Analysis:** Minutes per sample

1.3 Our Infrastructure: Scale and Precision

ICP-MS Platform & 200 m² Ultra-Clean Lab

Thermo fisher iCAP Q ICP-MS

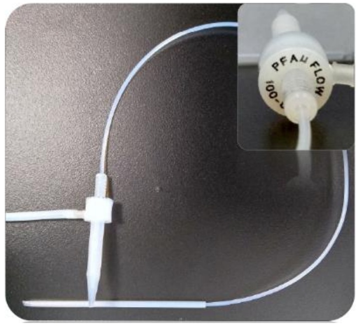
PE-NexION2000G ICP-MS



PE-NexION5000G ICP-MS

Clean room

Clean bench



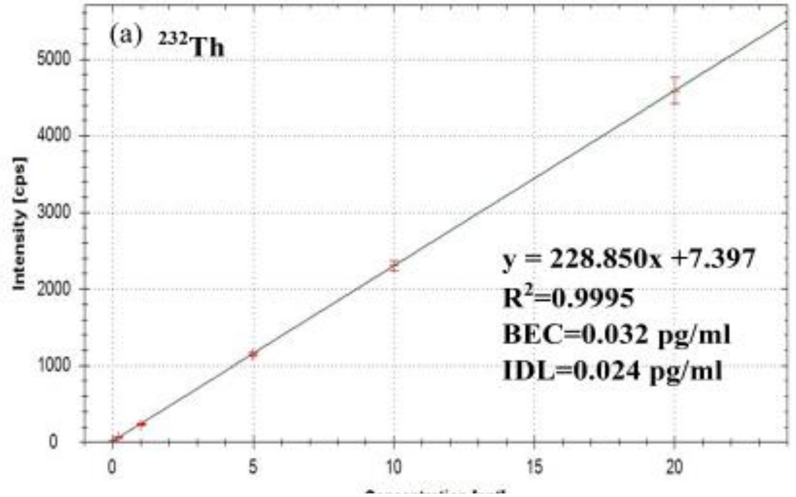
PFA nebulizer

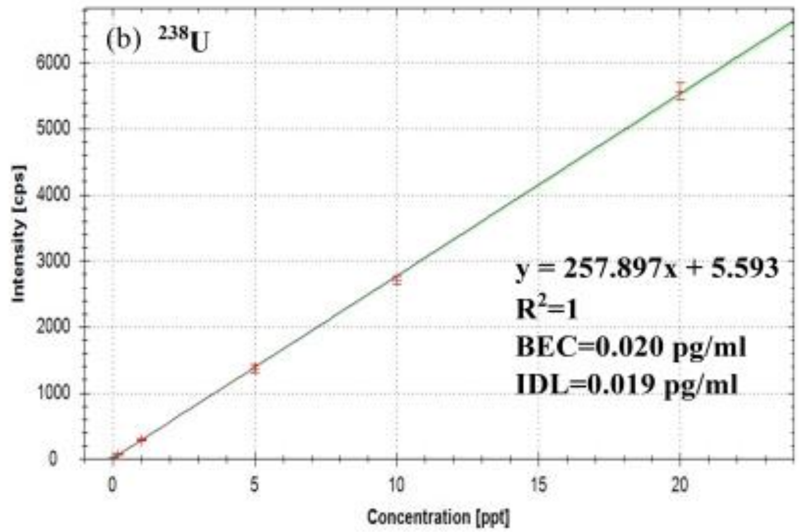
PFA chamber

1.3 Our Infrastructure: Scale and Precision

Key Performance: Thermo fisher iCAP Q ICP-MS

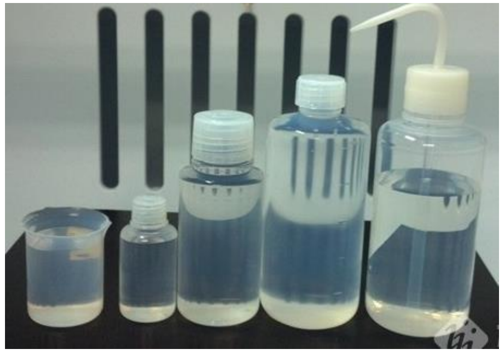
Parameters	Value
RF power	1550W
Sampling depth	7.5 mm
Sampling gas flow	0.72 L min−1
Auxiliary gas flow	0.80 L min−1
Coolant gas flow	13 L min−1
Signal sensitivity	^{7}Li≥50,000 cps/ppb ^{59}Co≥100,000 cps/ppb ^{115}In≥220,000 cps/ppb ^{238}U≥300,000 cps/ppb
Instrument detection limits	^{232}Th: 0.024 pg/mL ^{238}U: 0.019 pg/mL



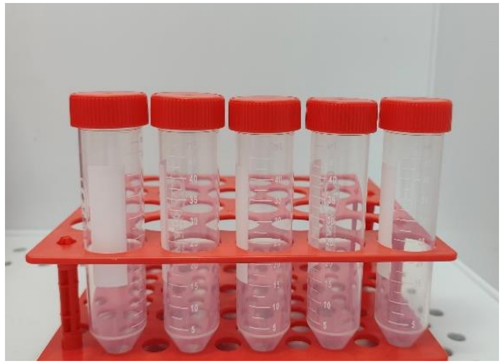


1.3 Our Infrastructure: Scale and Precision

Purity is Paramount: Stringent control is fundamental




PFA and FEP container




PP and PET container

PFA, PP, and PET containers are submerged in 5% (v/v) nitric acid for 24 hours. The concentrations of ^{232}Th and ^{238}U in 5% nitric acid were analyzed by ICP-MS

Label	^{232}Th [ppt]	^{238}U [ppt]
PET	0.15±0.13	0.06±0.06
PFA	0.16±0.04	0.06±0.05
PP (un-wash)	0.19±0.05	0.08±0.04
PP (washed)	0.14±0.08	0.08±0.07

*Results do not exclude reagent background and instrument blanks

Contents

1 Lab and Instruments

2 Th and U analyze with ICP-MS

3 summary

2. Th and U analyze with ICP-MS

Our work focuses on three pillars:

1 ICP-MS Method development

- Direct ICP-MS quantitative method;
- UTEVA extraction-ICP-MS

2 Cross-comparisons of ICP-MS and γ-HPGe

- ICP-MS v.s. γ-HPGe
- Agreement & difference

3 Application: Material screening

- Rapidly measurement of Th and U
- Impurities

2.1 Sample Preparation

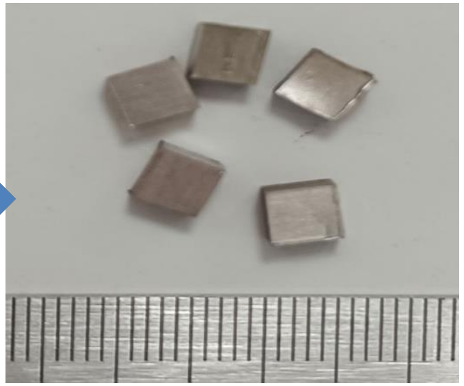
Step:1 Step:2 Step:3

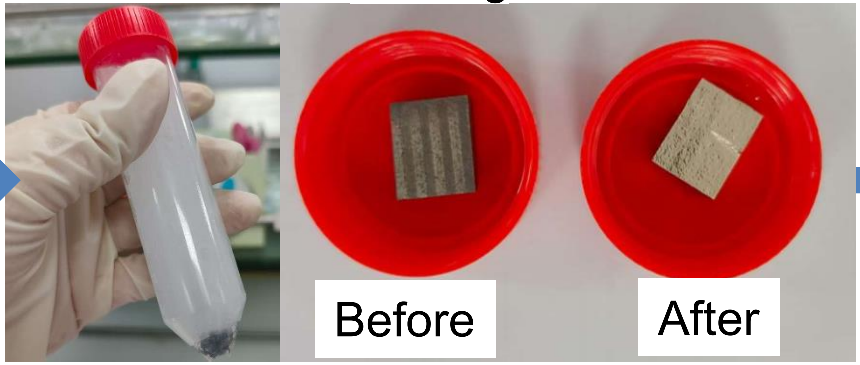
Samples → Cutting& **Cleaning** → Acid etching → **Decomposition** → ICP-MS

1. Cut into small blocks. Ultrasonic bath in acetone

2. Chemical Decontamination: Immersion in acid; Ultrapure Water Rinsing

3. Dry and digestion





2.2 Sample decomposition

Materials	Method	Reagent	Temperature
Stainless steel	ICP-MS γ-HPGe	aqua regia ($HCl:HNO_3$=3:1)	105°C
Ti	ICP-MS γ-HPGe	H_2O+ HCl+ HF	70°C.
Fe	ICP-MS	50%(v/v) aqua regia solution	105℃
Al	ICP-MS	$H_2O+HCl+H_2O_2$	
Zn	ICP-MS	H_2O+HNO_3	
Mg	ICP-MS	H_2O+HNO_3	
Cu	ICP-MS	H_2O+HNO_3	
Al2O3	ICP-MS	H_2SO_4	240℃
……..			

2.3 Direct detection with ICP-MS

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For Sub-ppb Th/U and simpler matrices

- Direct analysis after 1,000× dilution (TDS≤0.1%)

  - ⚡ He-KED mode → suppresses polyatomic interferences
  - ⚡ ^{103}Rh internal standard → corrects instrument drift
  - ⚡ **Method detection limits(MDL)**: <0.1 ppb for Th/U
  - ⚡ **Accuracy**: 90-115% spike recovery (validated by standard addition)

2.3 Direct detection with ICP-MS

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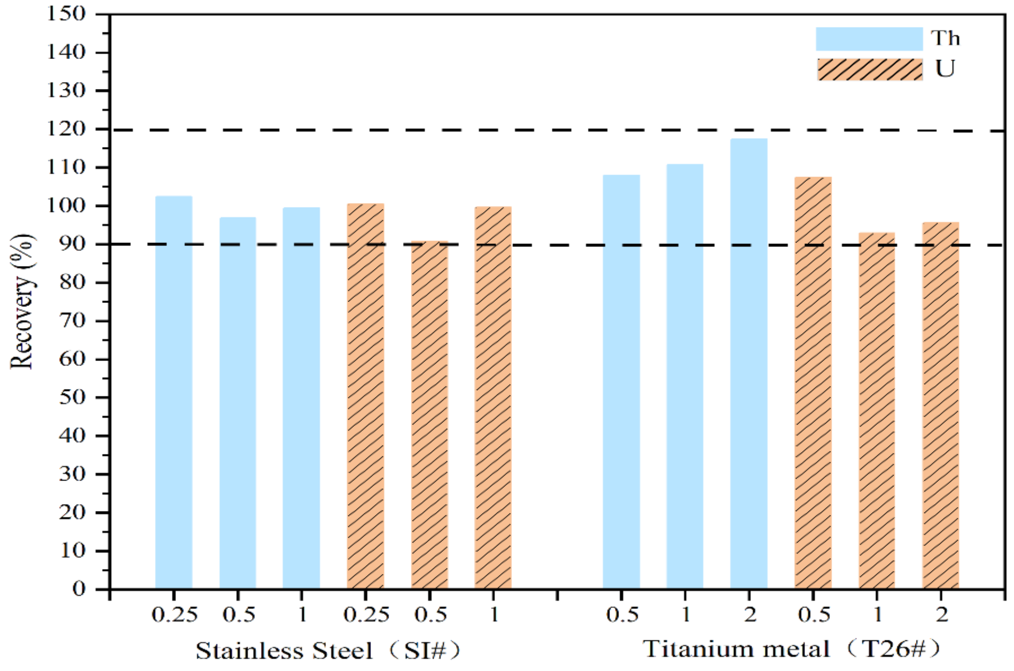
For Sub-ppb Th/U and simpler matrices

The method detection limits for Ti, stainless steel, and Fe. The values of MDL were determined using the procedural blanks of sample digestion.

Sample	^{232}Th	^{238}U
Ti	9×10^{-11}g/g (0.36 mBq/kg)	4×10^{-11}g/g (0.5 mBq/kg)
Stainless	5×10^{-11}g/g (0.2 mBq/kg)	5×10^{-11}g/g (0.6 mBq/kg)
Fe	6×10^{-11}g/g (0.28 mBq/kg)	5×10^{-11}g/g (0.71mBq/kg)
Cu	5×10^{-11}g/g (0.2 mBq/kg)	5×10^{-11}g/g (0.6 mBq/kg)

Spike recovery：90-115%



ICP-MS vs. Gamma Spectrometry

1. Materials: Titanium & Stainless Steel
2. Methodology:
   - ⚡ ICP-MS: Direct ^{232}Th/^{238}U quantification (SJTU)
   - ⚡ γ-HPGe: Measured at CJPL (China Jinping Underground Lab)

     Target nuclides:

     Th-chain: $^{232}\mathrm{Th} \xrightarrow{\alpha} {}^{228}\mathrm{Ra} \cdots \rightarrow {}^{228}\mathrm{Ac}/{}^{228}\mathrm{Th}$

     U-chain: $^{238}\mathrm{U} \rightarrow {}^{226}\mathrm{Ra} \rightarrow {}^{222}\mathrm{Rn}$

2.4 Cross-comparisons of ICP-MS and γ-HPGe

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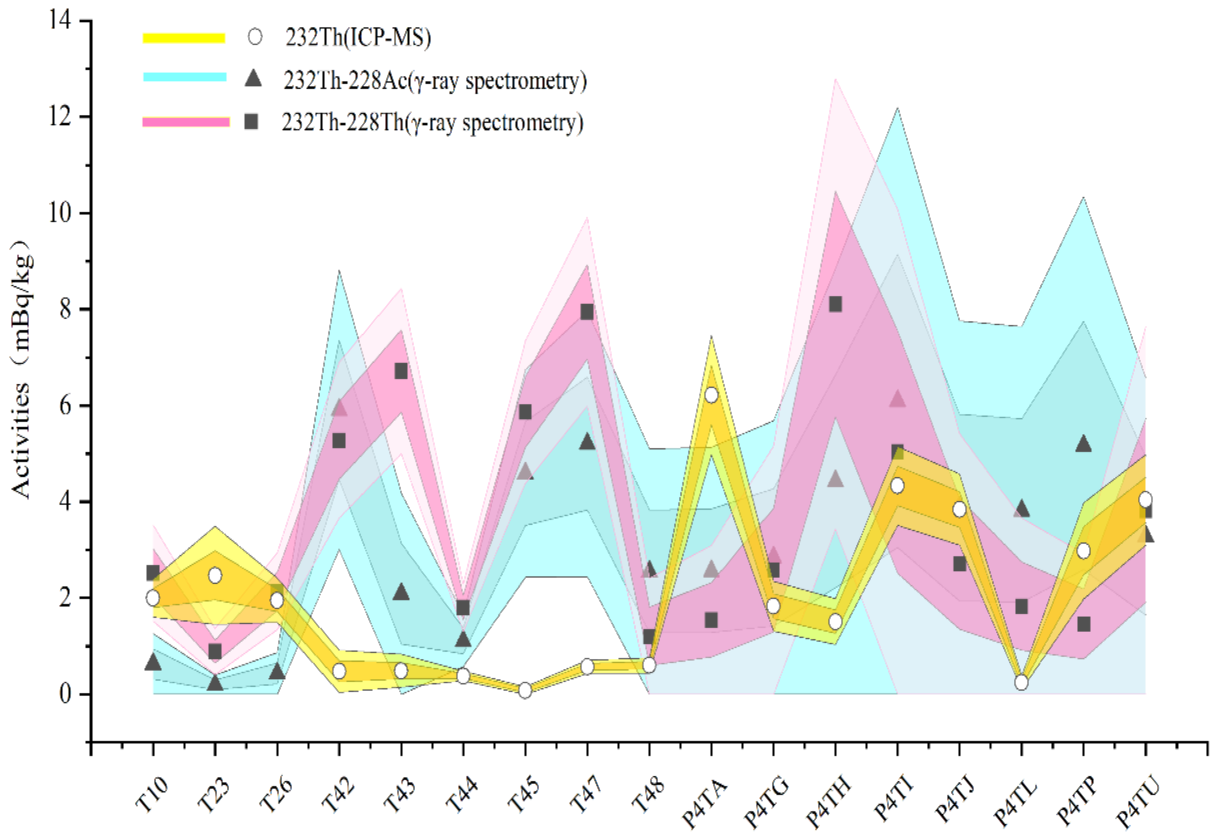
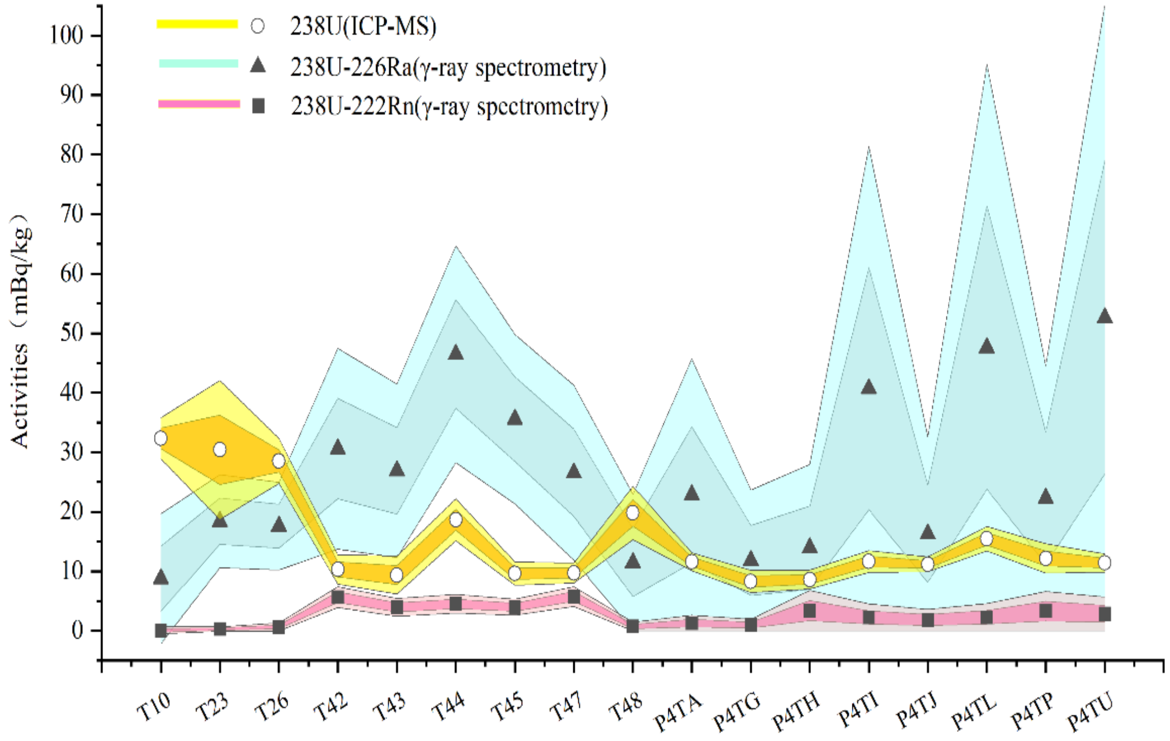
γ-HPGe ICP-MS

Name	^{232}Th-^{228}Ac	^{232}Th-^{228}Th	^{238}U-^{226}Ra	^{238}U-^{222}Rn	^{232}Th	^{238}U
T10 (Ti)	<1.26	2.52±0.50	<17.7	<0.55	2.00±0.20	32.32±1.74
T23(Ti)	<0.40	0.89±0.24	18.4±3.9	<0.59	2.47±0.51	30.40±5.85
T26(Ti)	<0.78	1.03±0.32	20.6±44.83	<0.40	1.95±0.23	28.54±1.88
T42(Ti)	5.91±1.45	5.28±0.81	30.59±8.44	5.65±0.87	0.48±0.22	10.30±1.25
T43(Ti)	<4.18	6.72±0.86	26.87±7.29	3.94±0.74	0.49±0.17	9.35±1.60
T44(Ti)	1.11±0.27	1.80±0.25	9.551±2.86	0.83±0.19	0.38±0.05	18.65±1.75
T45(Ti)	4.59±1.08	5.87±0.74	35.55±7.13	3.96±0.68	<0.36	9.61±0.98
T47(Ti)	5.21±1.38	7.95±0.98	26.56±7.33	5.77±0.83	0.57±0.07	9.71±0.84
T48(Ti)	<5.10	<2.41	<22.8	<1.48	0.60±0.08	19.80±2.23
P4TA(SS)	<5.13	<3.09	<45.70	<2.60	6.22±0.62	11.59±0.76
P4TG(SS)	<5.69	<5.16	<23.64	<1.92	1.83±0.26	8.29±0.93
P4TH(SS)	<8.85	8.11±2.34	<27.97	<6.78	1.51±0.24	8.62±0.79
P4TI(SS)	<12.20	<10.07	<81.37	<4.51	4.33±0.41	11.64±0.93
P4TJ(SS)	<7.76	<5.42	<32.56	<3.63	3.84±0.37	11.16±0.62
P4TL(SS)	<7.64	<3.66	<95.20	<4.56	0.24±0.07	15.44±1.03
P4TP(SS)	<10.34	<2.92	<44.55	<6.60	2.98±0.50	12.15±1.24
P4TU(SS)	<6.57	<7.65	<105.29	<5.71	4.04±0.47	11.39±0.77

2.4 Cross-comparisons of ICP-MS and γ-HPGe

Comparison of ICP-MS and γ-HPGe results for Th & U, within 1σ and 2σ uncertainty ranges





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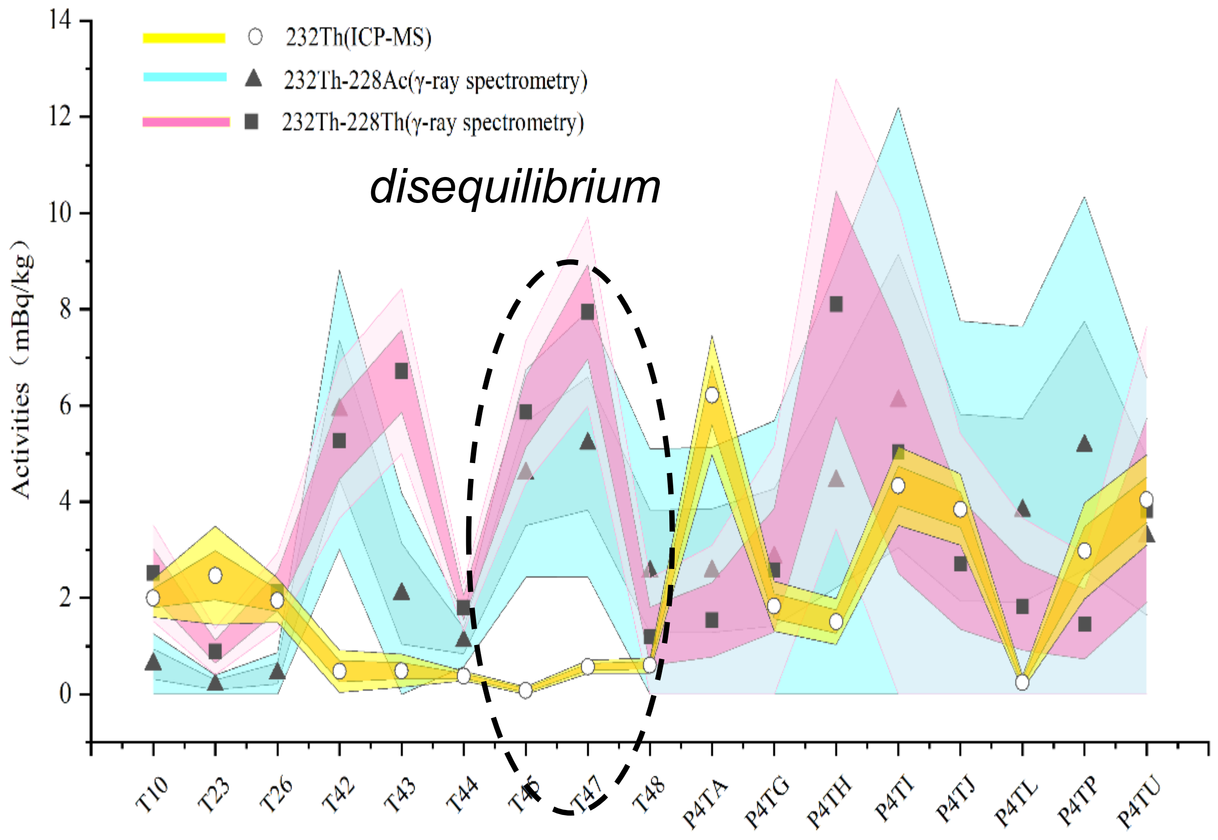
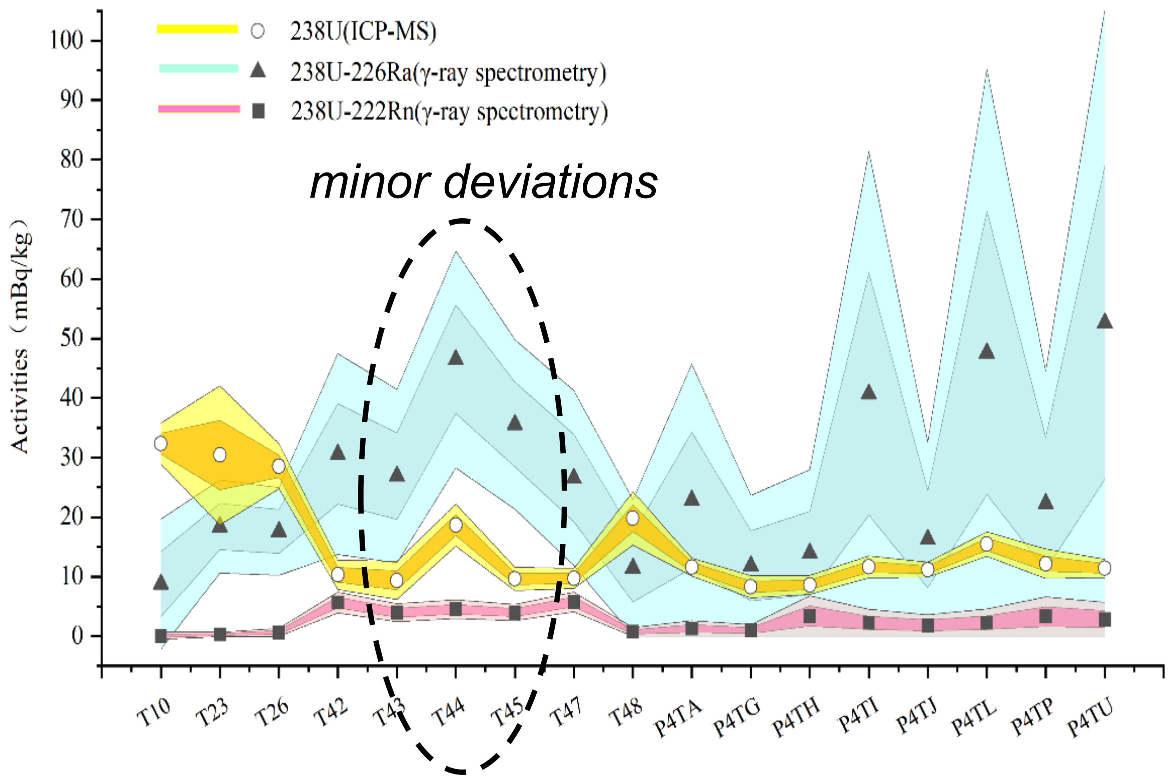


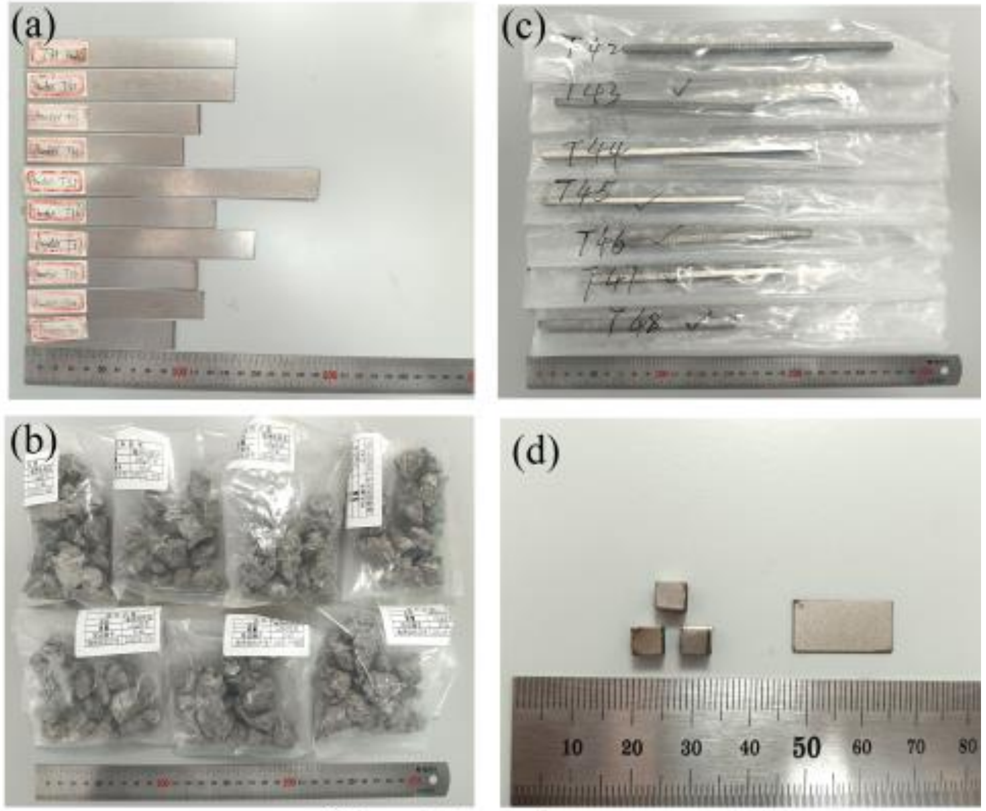


Likely disruptions in secular equilibrium during metallurgical processing

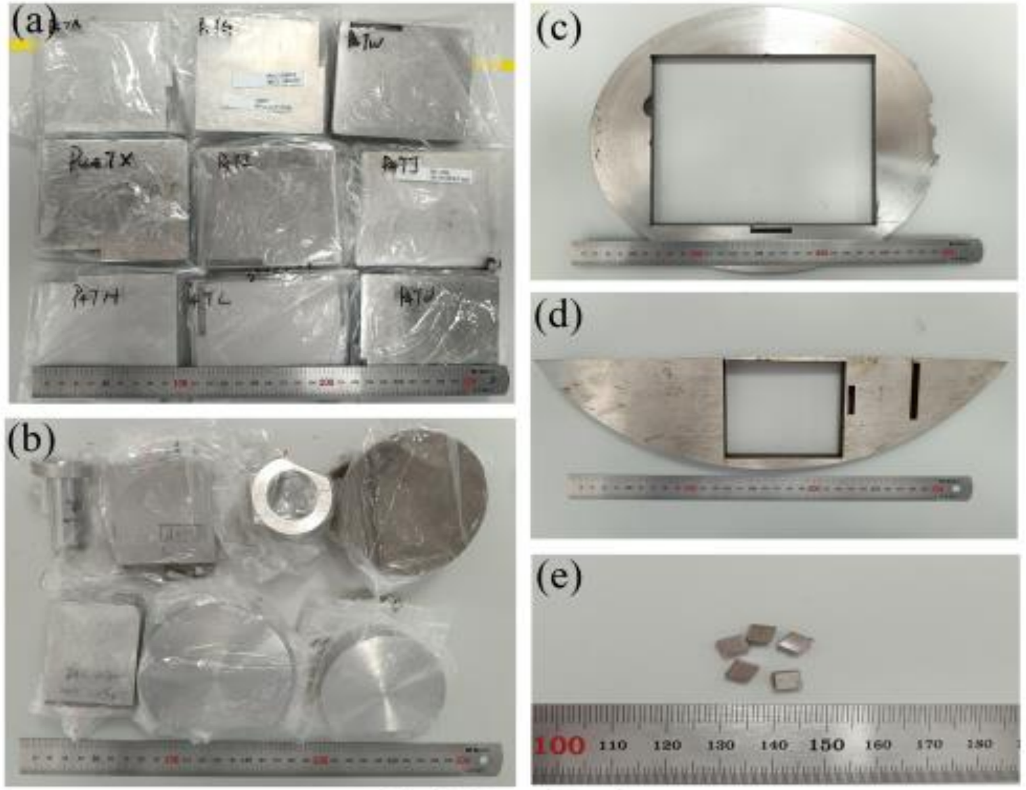
2.5 Material Screening Application

Direct-ICP-MS analysis

- The SS samples are from Panda X-Ⅱ and Panda X-4T vessel
- The Ti metal and Ti sponge samples are from Panda X pre-research.



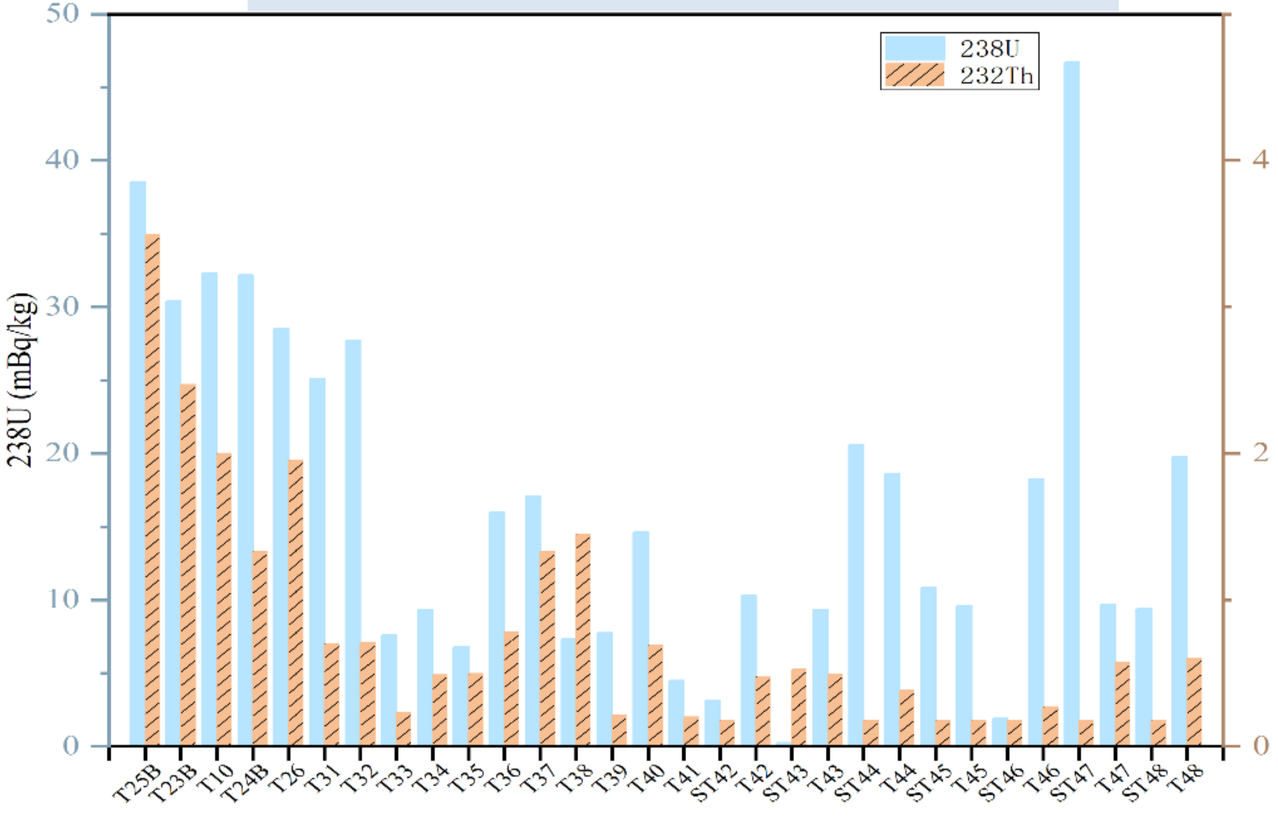
Ti metals and sponges



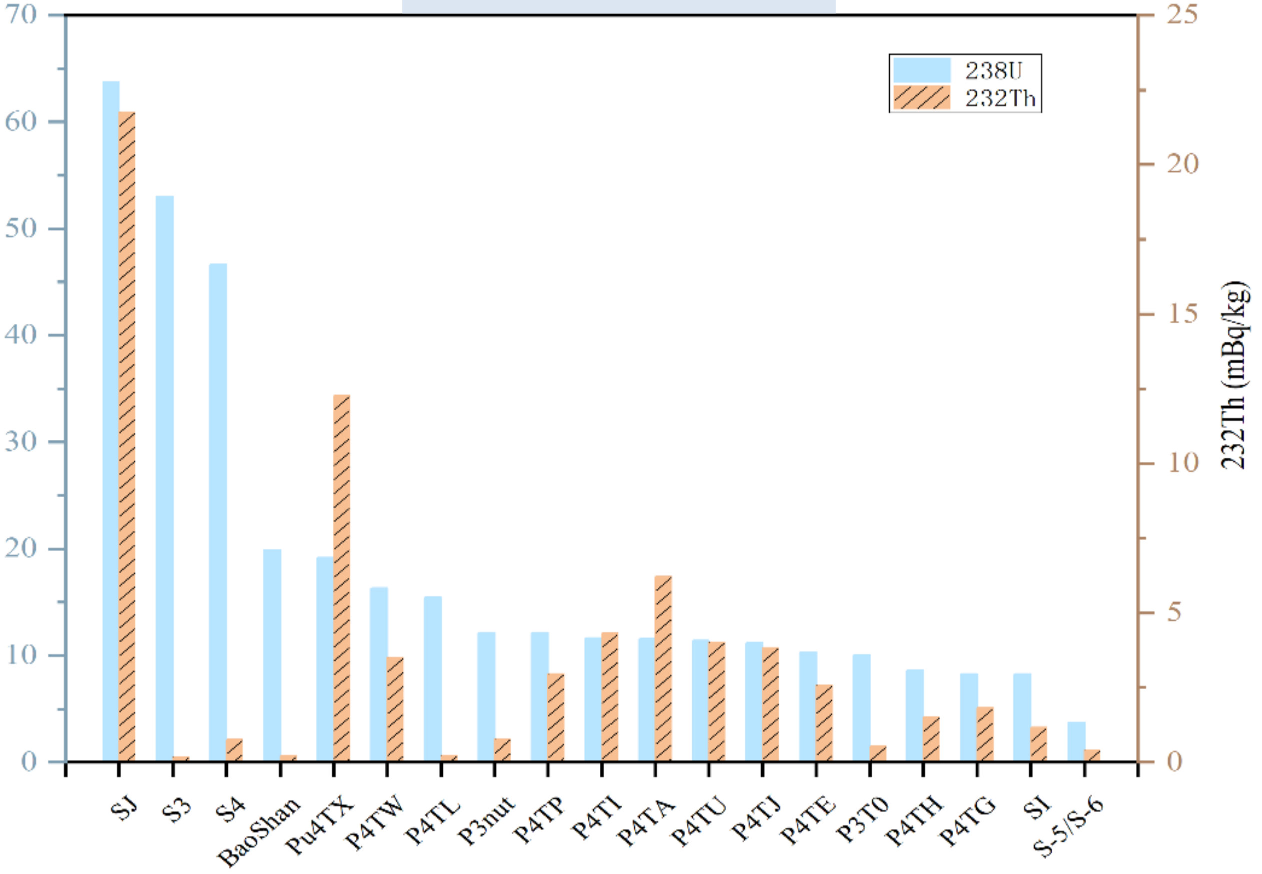
Stainless Steels

2.5 Material Screening Application

Ti metal and sponge samples



Stainless steel

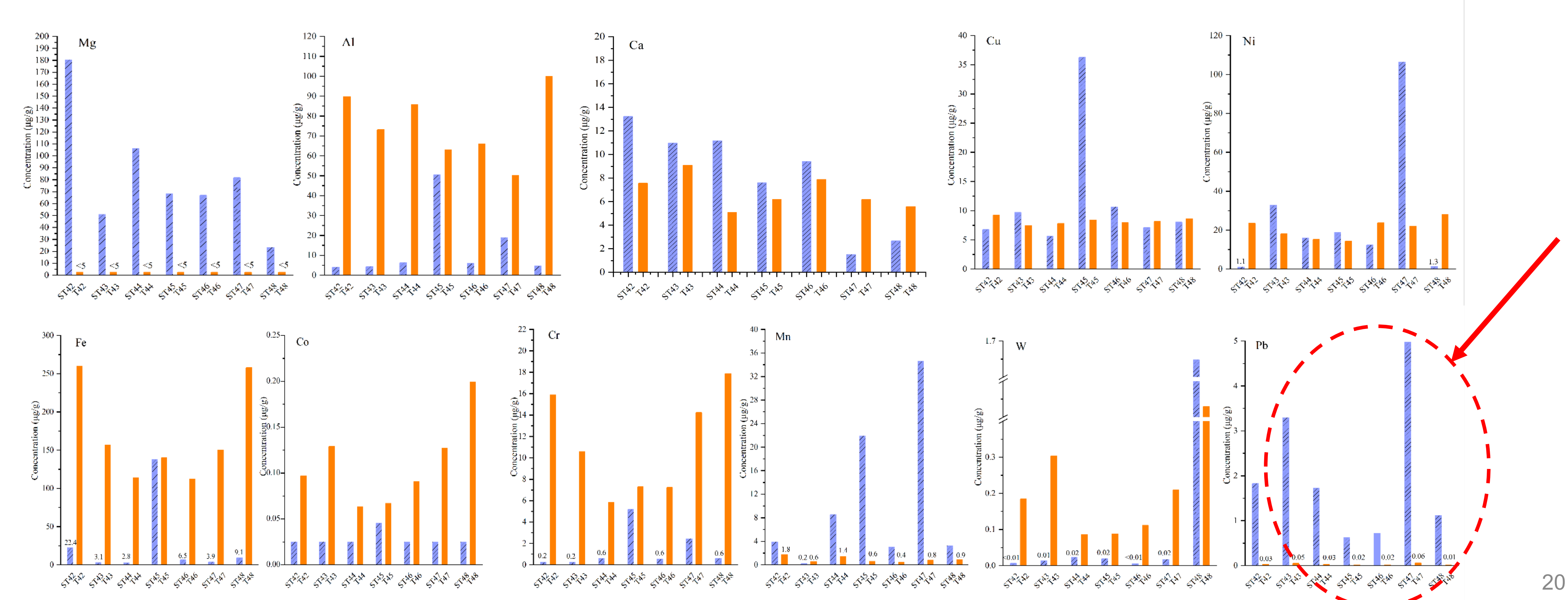


- The Activity ***Th : ND-21.27 mBq/kg U : 3.72- 63.74 mBq/kg***
- Concentration ***U > Th***

2.5 Material Screening Application

Smelting 's dual role:

- Purification: Efficiently removes volatile Mg, Mn, and Pb
- Contamination: introduces Cr, Fe , W from furnace background



2.6 UTEVA Extraction-ICP-MS

Need for UTEVA - Cu Limitation

Quantifying Th/U in high-purity copper confronts two fundamental limits:

1. **Ultra-trace detection demands**:
   - ⚠ Direct ICP-MS MDLs stall at **~50 ppt**
   - ⚠ Rare-event experiments require **< 1 ppt**
2. **Matrix-induced suppression**:
   - ⚠ Cu^{2+} causes **signal suppression**
   - ⚠ Clogs sampler/skimmer cones at **>0.2% TDS**

→ Forced dilution *sacrifices analyte* sensitivity

Solution: Chemical separation via extraction

2.6 UTEVA Extraction-ICP-MS

Why UTEVA for Th/U Separation?

Specific selectivity

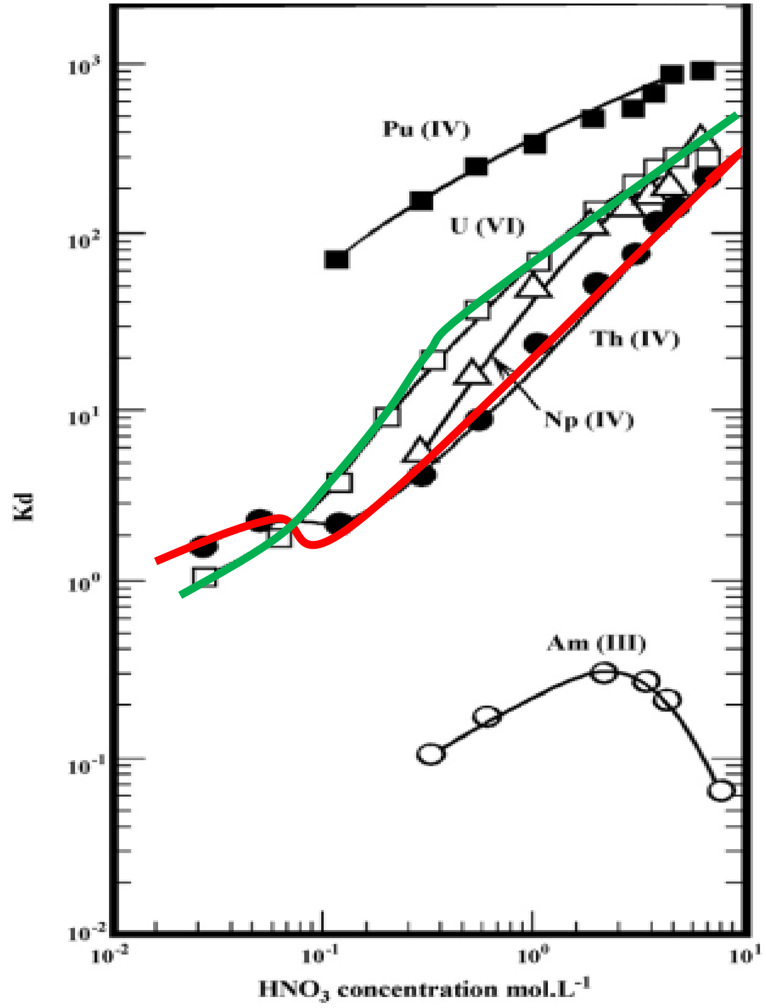
- Excellent Th(IV) & U(VI) adsorption: high affinity for Th^{4+} and UO_2^{2+} .

  Synchronous >90% recovery for both Th and U

- *Single-column simplicity:* Significantly reduces processing time
- Matrix tolerance : Allows most matrix ions (e.g. Fe,Al,Ca) to flow through.

Resin	Target Elements	Th Recovery	Process Steps	Suitability
TRU	Am^{3+}/Cm^{3+}	< 60%	Multi-step	❌
TEVA	U^{4+} ; Th^{4+}	70-90%	2 columns	△
UTEVA	Th^{4+}/U^{4+}	99±2%	Single column	✅

UTEVA Mechanism & Optimized Workflow



UTEVA Kd vs. HNO3 concentration

E Philip HOW et al /Anal Chm Acta 266 (1992) 25-37

Separation scheme for Th & U

U,Th, Cu
5M HNO3

Load ↓ **0.25g/mL Cu**

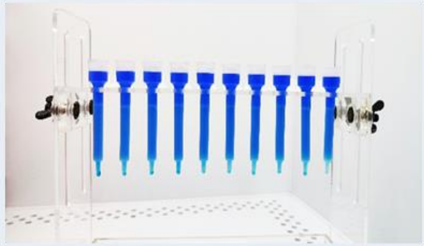
UTEVA Resin

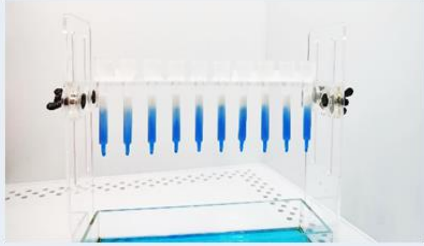
Rinse → 5M HNO3 ➡ Cu

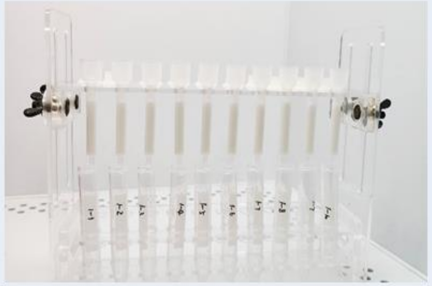
Elute → 0.1M HNO3+oxalic acid ➡ Th U

↓ **Analyze**

ICP-MS

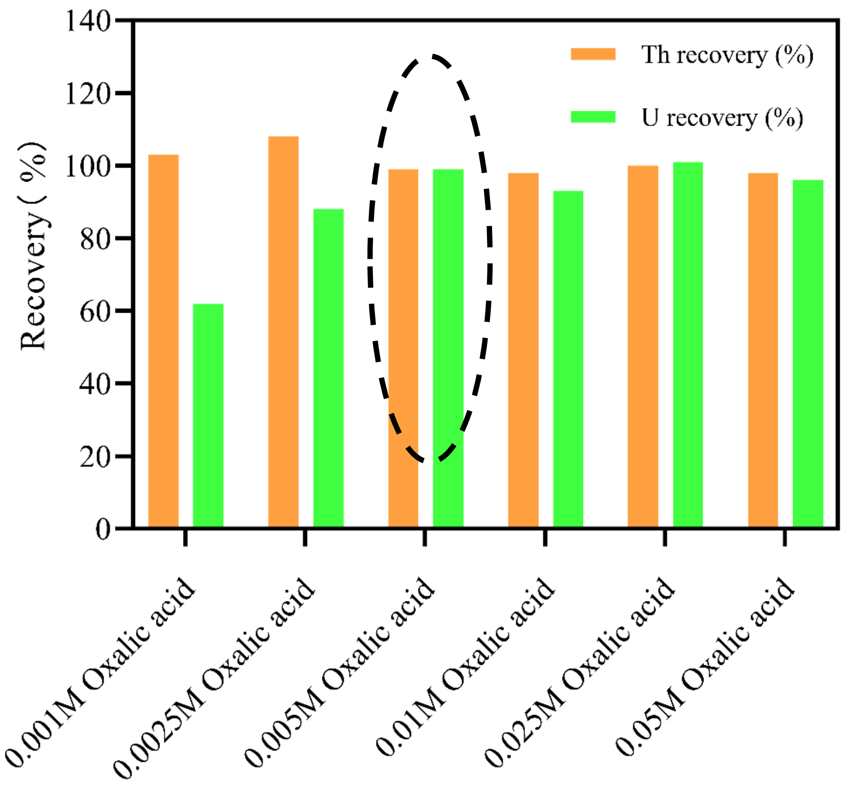






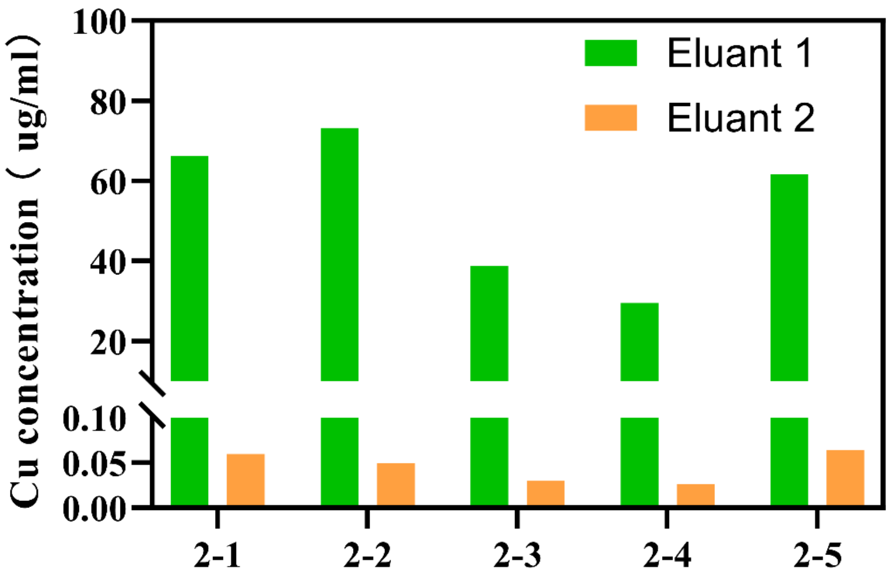
Critical Parameters Refined

Eluent Composition



0.005M Oxalic Acid in 0.1M HNO_3

Copper removal efficiency

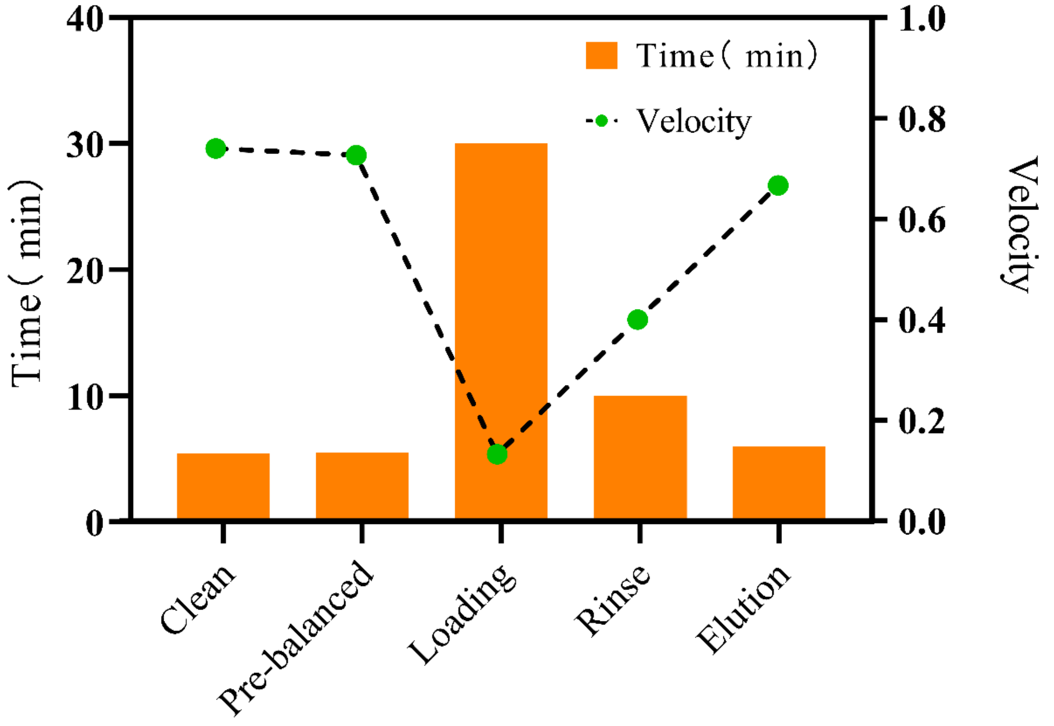


Cu concentration:

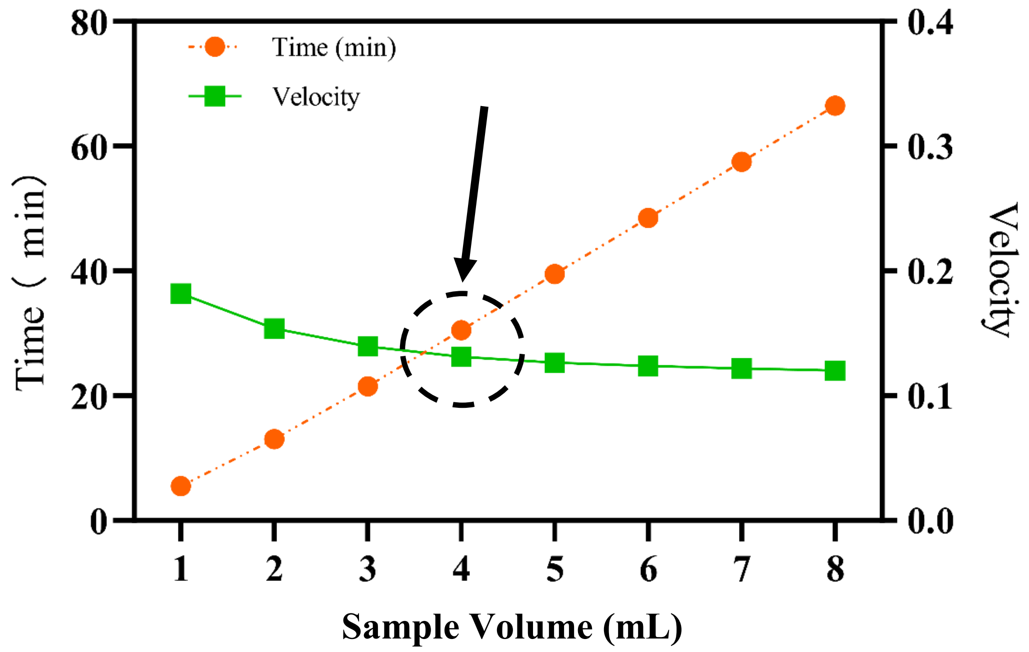
250,000 ppm → ~ 50 ppm 99.98% reduction

Critical Parameters Refined

Sample flow rate and extraction time



Sample volume and extraction time



2.6 UTEVA Extraction-ICP-MS

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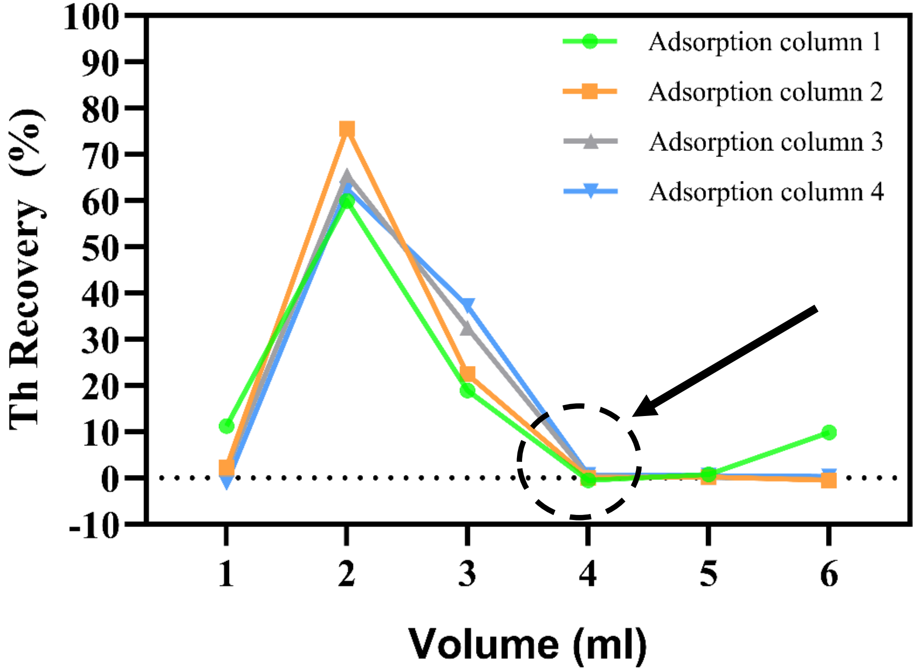
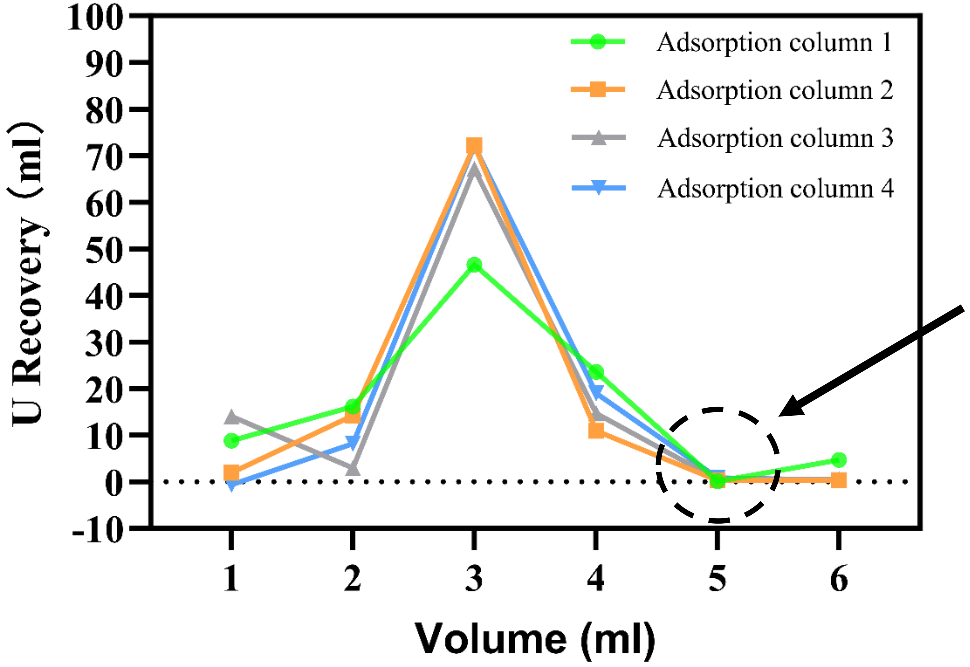
Elution Profile & Collection Strategy

Elution behaviors of Th



Elution behaviors of U



UTEVA method performance meets ultra-trace analysis demands

- MDL: Th 0.12 ppt, U 0.14ppt;
- Accuracy: 95-107% spike recovery (standard addition validated)

Label	^{232}Th Recovery (%)	^{238}U Recovery (%)
Cu+5ppt Th U	100.84	100.14
Cu+10ppt Th U	97.63	99.31
Cu+20ppt Th U	106.17	100.58
Cu+40ppt Th U	102.42	95.49
Cu+60ppt Th U	107.0	98.8

Contents

1 Labs and Instruments

2 Th and U analyze by ICP-MS

3 **Summary**

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In our work:

1 Developed methods

- direct-ICP-MS: several tens ppt MDLs
- UTEVA extraction: sub-ppt MDLs

2 Cross-validation

- Good agreement between ICP-MS and γ-HPGe *within 2σ uncertainty bounds*
- Disequilibrium

3 Material screening

- Levels of Th and U
- Effectiveness of smelting for Pb removal

Instrumental Analysis Center of SJTU

Instrument Units

- Electron Microscopy & Imaging Unit
- Surface & Properties Analysis Unit
- Spectrometry & Spectroscopy Unit
- Cryo-Electron Microscopy Unit
- The Element Analysis Unit


Cryoelectron microscope


X-ray microscope


Time of flight secondary ion mass spectrometer


700MHz NMR


Ion mobility mass spectrometer


Raman image-scanning electron microscope

Contact Us: https://iac.sjtu.edu.cn iac_office@sjtu.edu.cn

Instrumental Analysis Center of SJTU

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The Element Analysis Unit

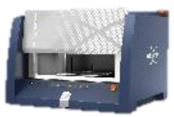
- **ppt~100% Quantitative Analysis System**

ICP

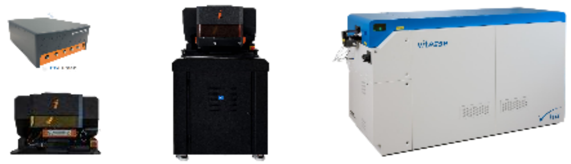
ICP-MS

WD-XRF

- **In-situ/Imaging Elemental Analysis System**



μ-XRF



LA-ICP-TOFMS / LA-LIBS

- **Elemental Ion State, Form, Single Nanoparticle/Single Cell Analysis System**

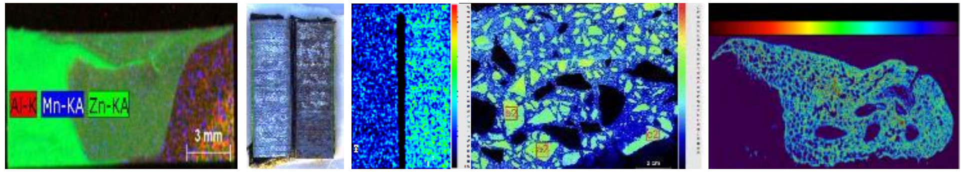
IC

SP/SC-ICPMS

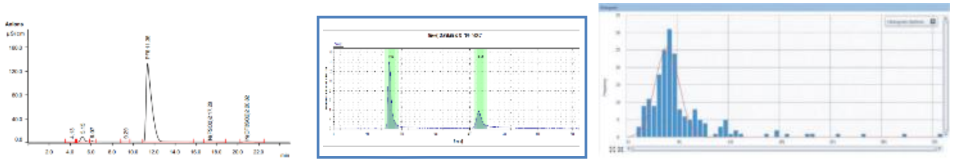
EA

- **Typical Analytical Capabilities**

Material Composition Analysis, Chemical Substance Structural Verification, Agricultural and Forestry Soil Analysis, Metallomics Analysis



Material Elemental Distribution, Corrosion Element Analysis, Archaeological Building Material Analysis, Heavy Metal Distribution in Biological Tissues



Analysis of Lithium Multiple Forms, Analysis of Trivalent and Pentavalent

Contact Us: https://iac.sjtu.edu.cn iac_office@sjtu.edu.cn

Thank you!

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