

Determination of Th and U contaminants based on ICP-MS combined with different pretreatment approaches at IHEP

Yayun Ding

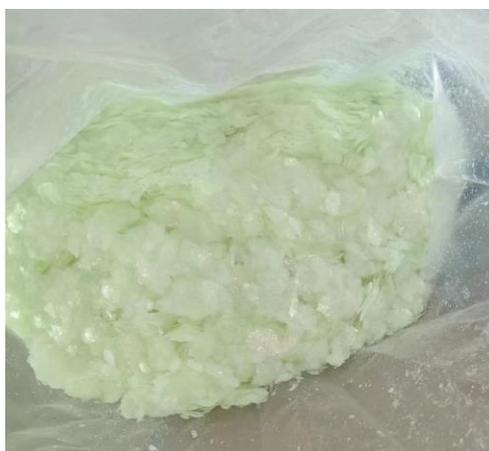
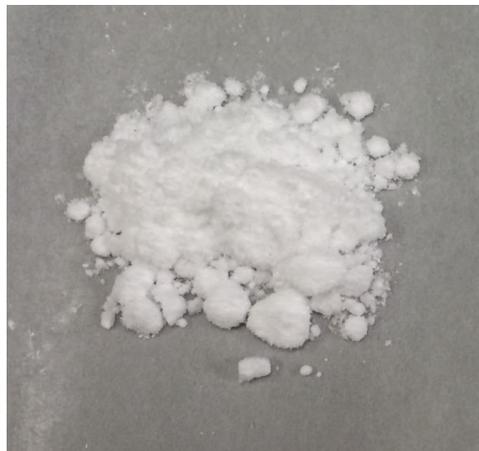
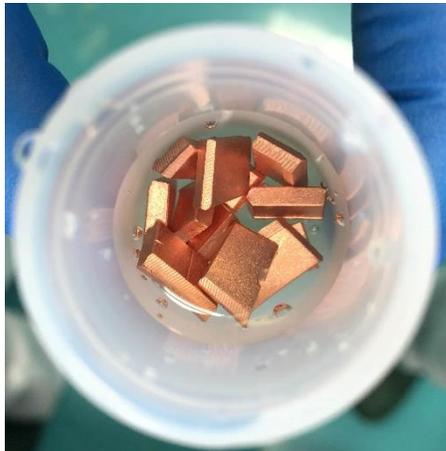
Mengchao Liu, Fei Liu, Yuanxia Li, Jie Zhao, Liangjian Wen

IHEP, CAS, Workshop on Low BG Technologies, Jan. 2024



Outlines

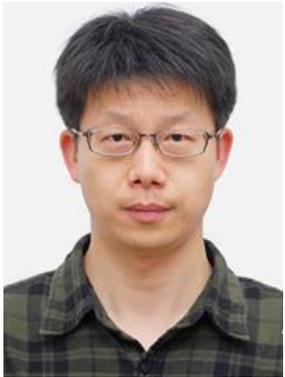
- A brief blurb about the low radioactivity assay group at IHEP
- Introduction of our works
 - Measurements of ^{238}U (and ^{232}Th) in copper to sub-ppt level
 - Measurements of Th and U in PPO to 10^{-14} g/g level
 - ...
- Short summary for low background measurement





The low radioactivity assay group at IHEP

- IHEP has the experience on ICP-MS for nearly 20 years, mainly focused on biological and environmental samples
- The assay on ultralow background materials has been initiated from 2016
- A new low radioactivity assay group at IHEP has been formed and grown, collaborating with nEXO and JUNO experiments
- Group members:



Liangjian Wen
Professor
Group Leader



Yayun Ding
Assoc. Prof.



Jie Zhao
Assoc. Prof.



Jinquan Dong
Senior
Technician



Mengchao Liu
Technician



Yuanxia Li
Technician



Fei Liu
Technician

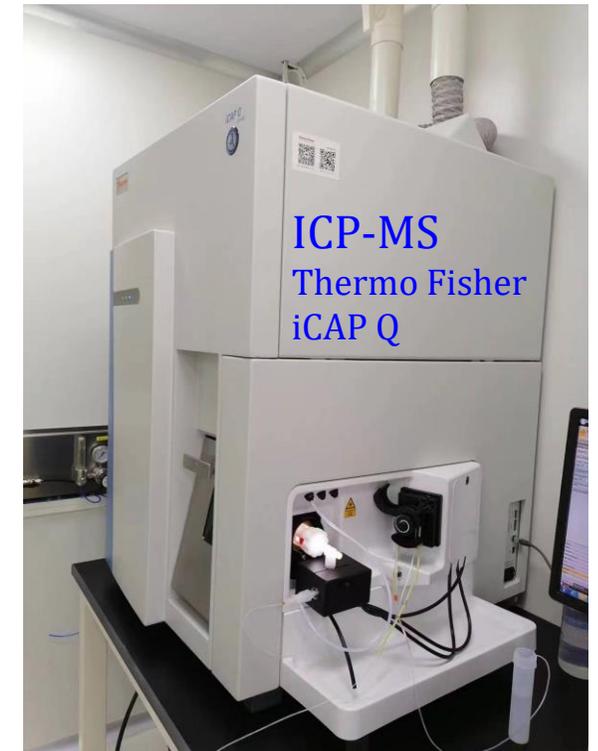


Nan Wang
Technician



The low radioactivity assay group at IHEP

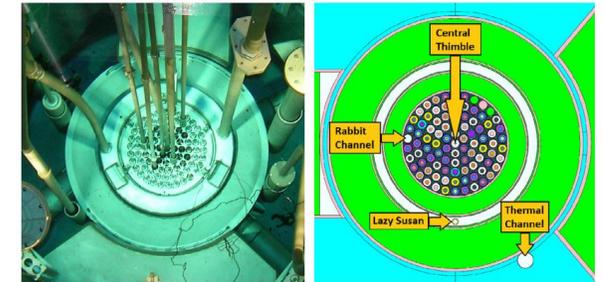
- **Goals:** to measure radio-impurities in different detector materials for ultra low background physics researches, such as neutrino-less double beta decay, precise oscillation parameters of neutrinos, dark matter...
- Facilities and instruments





Why ICP-MS?

- The highly sensitive methodologies known to date
 - High-purity germanium detector (HPGe)
 - Non-destructive measuring technique
 - Typical sensitivity: ppb (10^{-9} g/g) or sub-ppb level for ^{238}U and ^{232}Th
 - Higher sensitivity requires days or even weeks of running, hard to reach 10 ppt level
 - Neutron activation analysis (NAA)
 - Higher sensitivity
 - Need reactors for activation
 - Inductively coupled plasma mass spectrometry (ICP-MS)
 - A fast and sensitive elemental analysis technique
 - Almost all the naturally occurring elements and many non-natural, radiogenic elements
 - High sensitivity: sub-ppt levels for many elements
 - Typically used to analyze samples that are liquids
 - Samples need to be pretreated



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	H																		He	1
2	Li	Be								B	C	N	O	F	Ne					2
3	Na	Mg								Al	Si	P	S	Cl	Ar					3
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		4
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		5
6	Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		6
7	Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Ff	Uup	Lv	Uus	Uuo		7
	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				



Sample preparation techniques for ICP-MS

- Clean solutions are very important for obtaining accurate results from ICP-MS
 - Diluted acid solution, HNO_3 is the ideal choice
 - Total dissolved salts (TDS) $<0.2\%$
 -
- Sample preparation techniques for ICP-MS
 - Dilution, simple but effective as long as the interested elements are detectable
 - **Acid extraction**, matrix effect and extraction efficiency
 - **Digestion**, wet digestion and dry ashing
 - Ion exchange, cation exchange and anion exchange
 - Enzymolysis, for biological samples
 -



Co-precipitation approach to measure amount of ^{238}U in copper to sub-ppt level using ICP-MS, Y.Y. Ding et al., NIM A, 941 (2019) 162335

- Motivation: to screen copper, a widely used detector shielding material, for EXO
- Cu can be dissolved in acid, then measured by ICP-MS after dilution (TDS<0.2%)
 - 1ppt U in Cu \rightarrow ~ 0.0007 ppt U when $[\text{Cu}(\text{NO}_3)_2]=0.2\%$
- A customized approach was developed to separate U in copper
 - When dissolved in HNO_3 , soluble $\text{Cu}(\text{NO}_3)_2$ as well as other nitrates formed
 - When adding small amount of ammonia water, Cu^{2+} and other metal ion precipitate
 - When adding excess ammonia, other metal ion precipitates remain unchanged but copper precipitate dissolved because of the formation of soluble copper ammonia complex



- Precipitate can be filtered, hence separation of U and copper is realized
- Dissolve precipitate using acid for ICP-MS measurement

Conventional
precipitation
method

Cr (III), Co (III), Ni, Zn, Ag and Pt group can also form ammonia complex



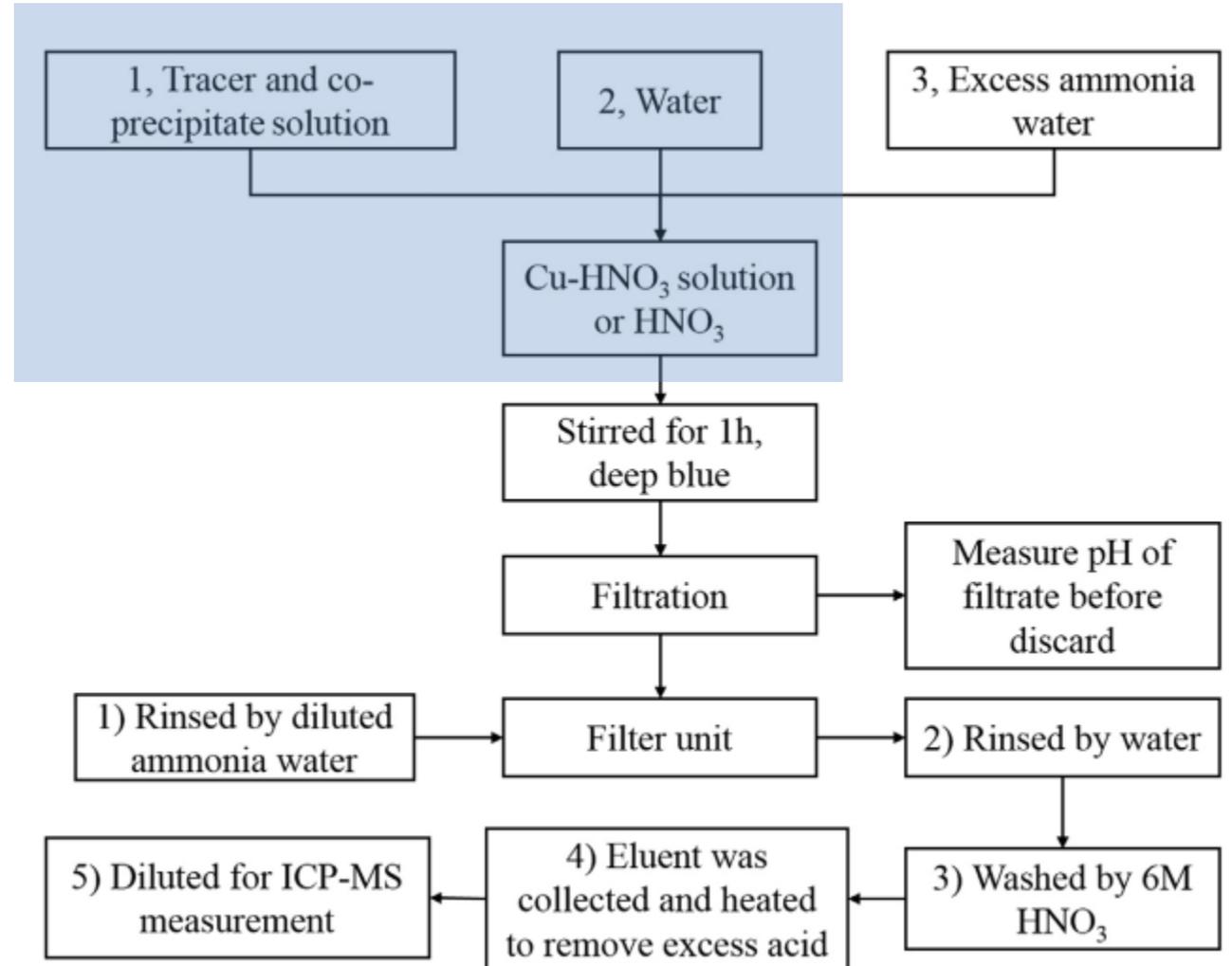
Choice of co-precipitator/carrier

- Necessity of co-precipitator
 - [^{238}U] is at ppb level: ^{238}U recovery efficiency $>90\%$
 - [^{238}U] is at ppt level: ^{238}U recovery efficiency ~ 0
- } Conventional precipitation method
- Co-precipitator: precipitates simultaneously under the conditions employed in order to increase the recovery of the elements of interest
 - Choice of co-precipitator: FeCl_3 , ZrCl_4
 - ^{233}U recovery efficiency for blanks :
 - $71\% \pm 4\%$ with ZrCl_4 as co-precipitator
 - $48\% \pm 2\%$ with FeCl_3 as co-precipitator
 - Zr was chosen, and the concentration was optimized by experiments



Flowchart of pre-treatment process

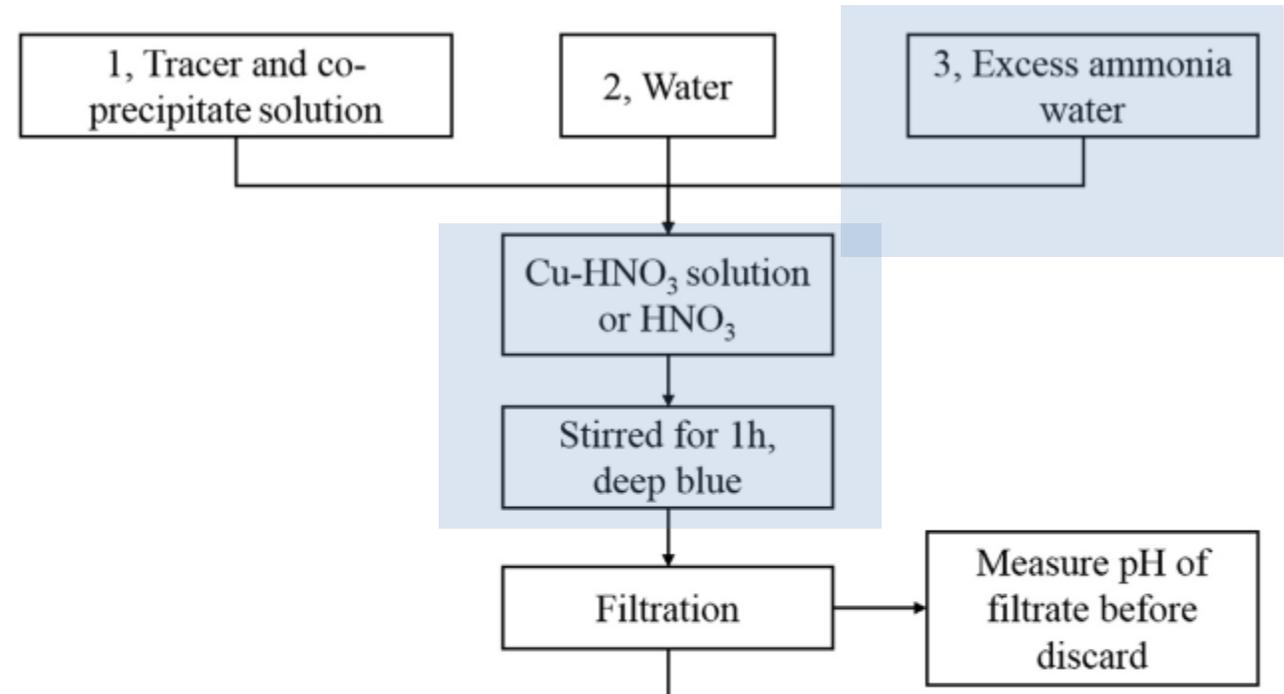
- Step 1: ~30 g Cu-HNO₃ solution (~3g Cu) was spiked with ²³³U, then co-precipitator was added





Flowchart of pre-treatment process

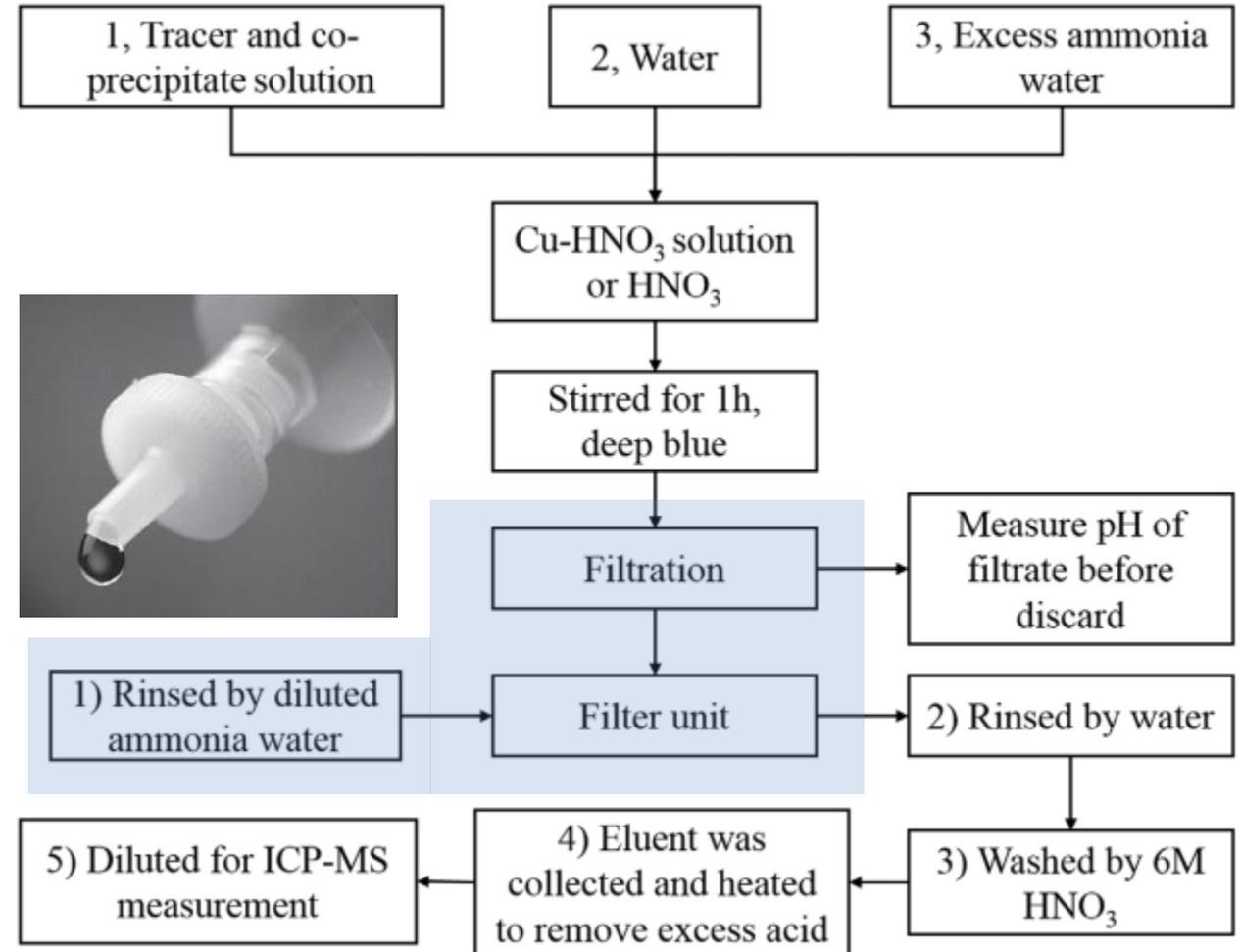
- Step 2: Add excess $\text{NH}_3 \cdot \text{H}_2\text{O}$ into the mixture under agitation
 - $\text{Cu}(\text{OH})_2$ was formed in the beginning; then $[\text{Cu}(\text{NH}_3)_4]^{2+}$ were formed, Cu-precipitate disappeared gradually
 - While U, Zr and other metal impurities are precipitates





Flowchart of pre-treatment process

- Step 3: Filter the mixture using syringe-operated filter units
 - The filter unit need to be rinsed by ammonia water to decrease the lost of U caused by pH change
 - A small device was designed and made to relieve technicians from heavy work

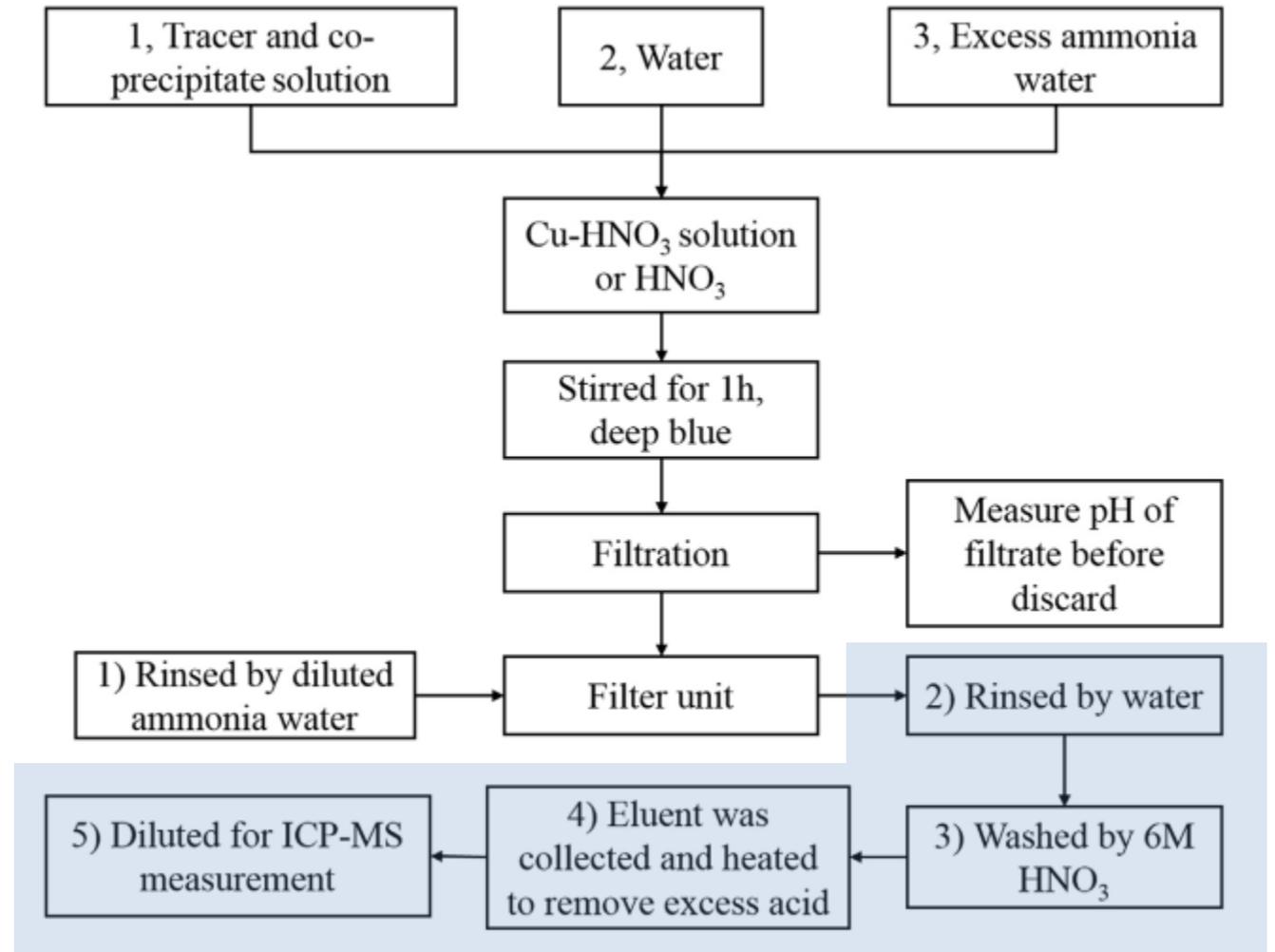
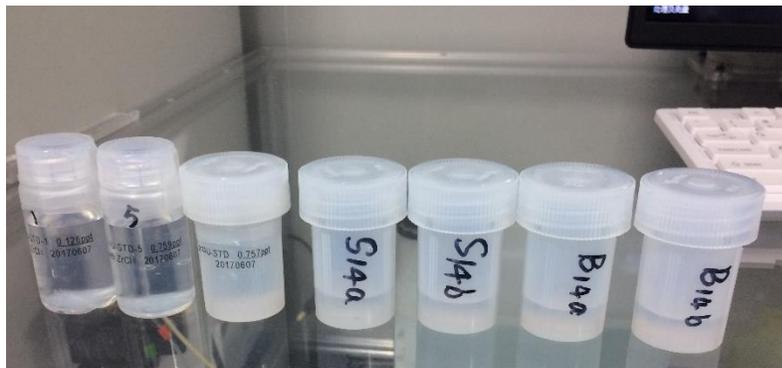




Flowchart of pre-treatment process

- Step 4

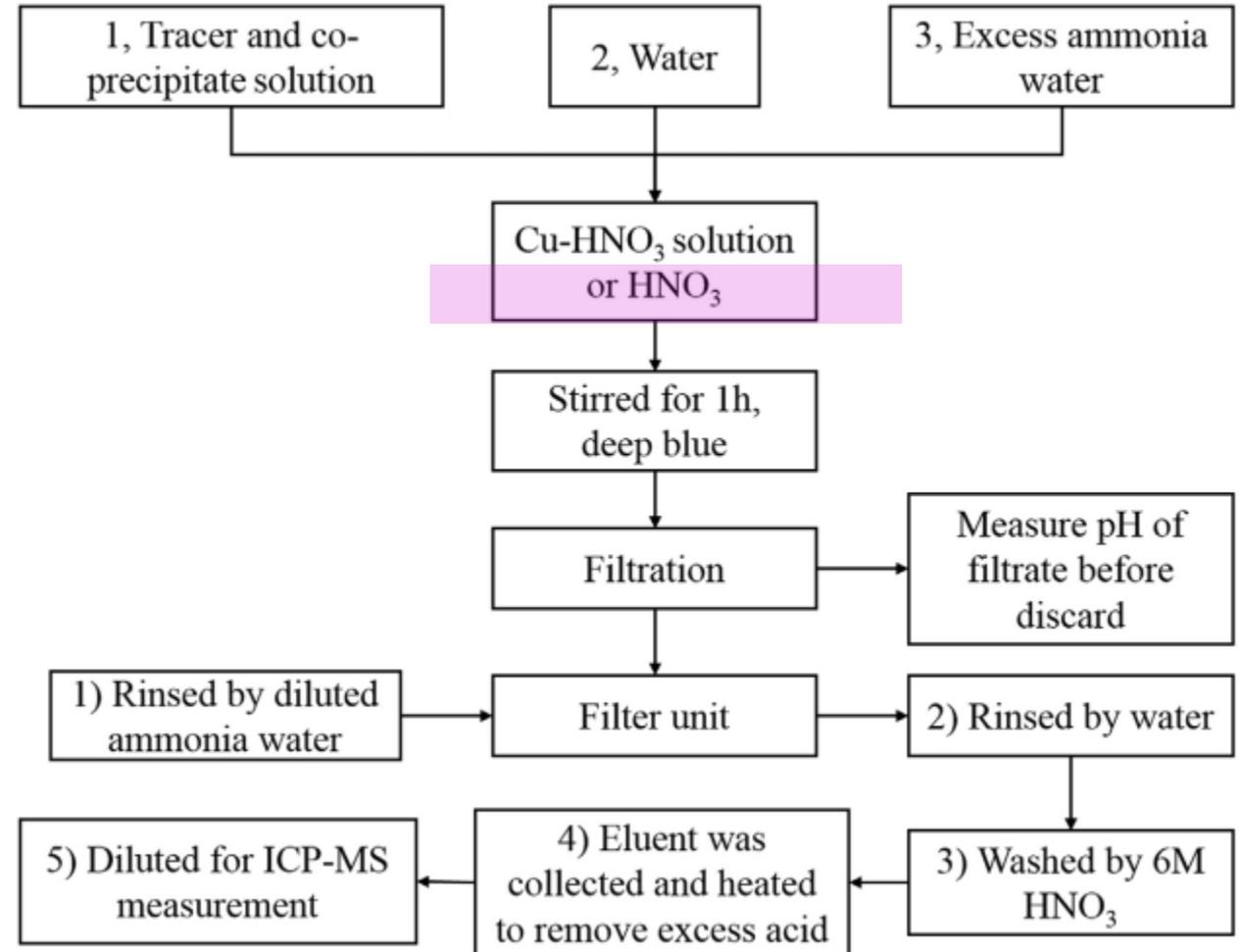
- Precipitate in filter units can be washed out using HNO_3
- Eluant was collected for ICP-MS measurements after suitable treatments





Flowchart of pre-treatment process

- **Blanks** are always necessary
 - To determine the background introduced by reagents, labware, environment
 - For method detection limit





ICP-MS measurement: Interferences

- Spectral interference
 - Isobaric interference
 - For ^{238}U and ^{233}U measurements, the isobaric interference can be ignored since there is no isobar for these two isotopes
 - Polyatomic interference
 - Measured and estimated. The polyatomic interference on ^{233}U and ^{238}U measurements for both blanks and Cu-samples are less than 0.01 ppt. Can be ignored if the U in copper is at the 0.1~1 ppt level
- Non-mass spectroscopic interference
 - Physical interference, the most critical one in this work is **the matrix effect**
 - TDS in blanks or Cu-samples were <0.1% by mass, can be ignored for ordinary analysis, but should be considered in low background analysis
 - Internal standard method (e.g. standard addition method)
 - Isotope dilution method
 - Argon gas dilution
 - Chemical separation method
 - ...



Matrix effect

- **Isotope dilution method** (short for IDM) for the quantification of U
 - A known amount of standard (isotopically enriched form of the analyte, ^{233}U in this work) was added to the sample
 - Analyte (^{238}U) and standard (^{233}U) are in the same matrix, the matrix effect significantly suppressed
 - If the isotopes are mixed homogeneously, their ratio is expected not to change during the entire analytical procedure (sample preparation, analyte separation, and enrichment)
 - The ratio of ^{238}U to ^{233}U can be obtained by ICP-MS, the concentration of ^{238}U can be calculated

$$R = (n_{238} + n'_{238}) / n'_{233}$$

measured ratio
of ^{238}U to ^{233}U
by ICP-MS

^{238}U NOT
originated from
tracer solution

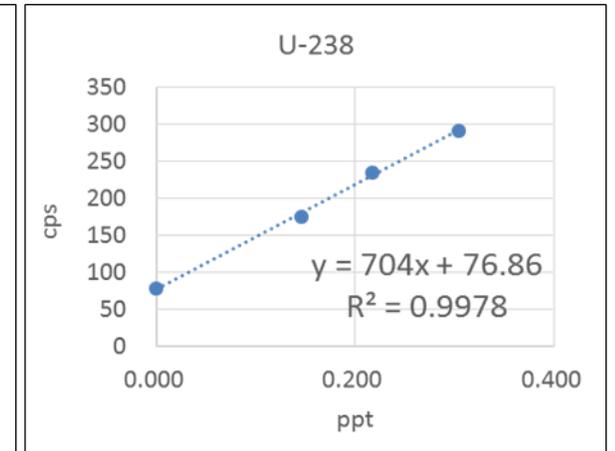
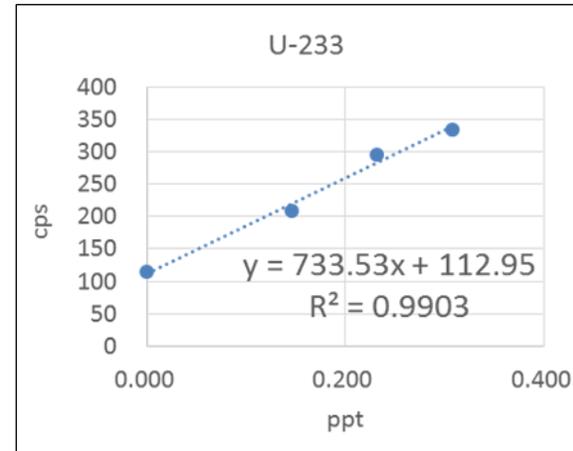
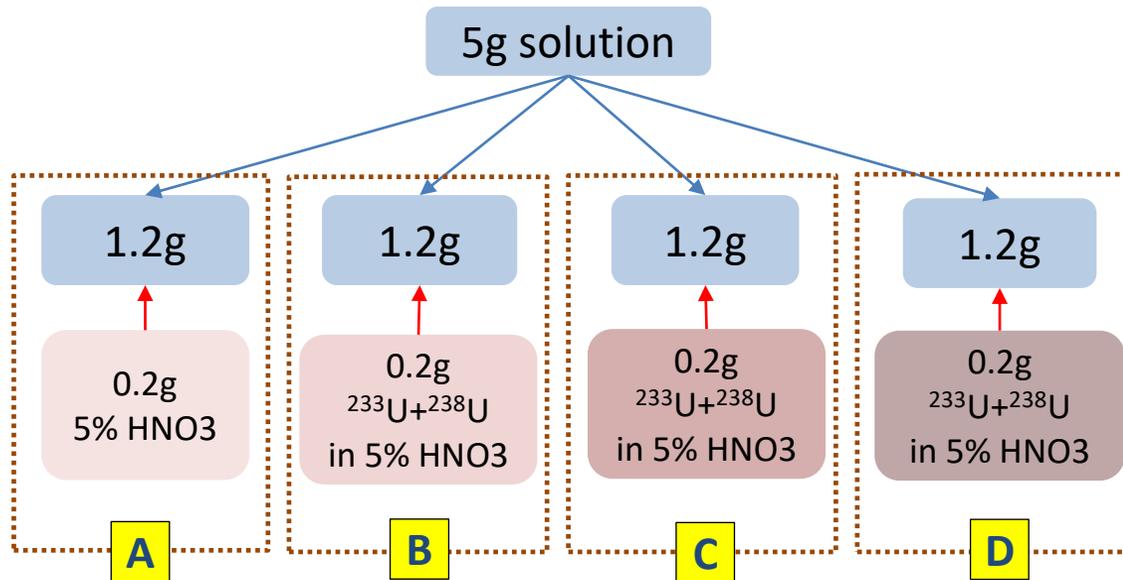
^{238}U or ^{233}U
originated from
tracer solution,
known amount

- The ^{233}U recovery efficiency cannot be obtained



Matrix effect

- The standard addition method (short for SAM) was also applied for quantification of U
 - Suppress the matrix effect by matrix matching



[U] in solution A = intercept / slope

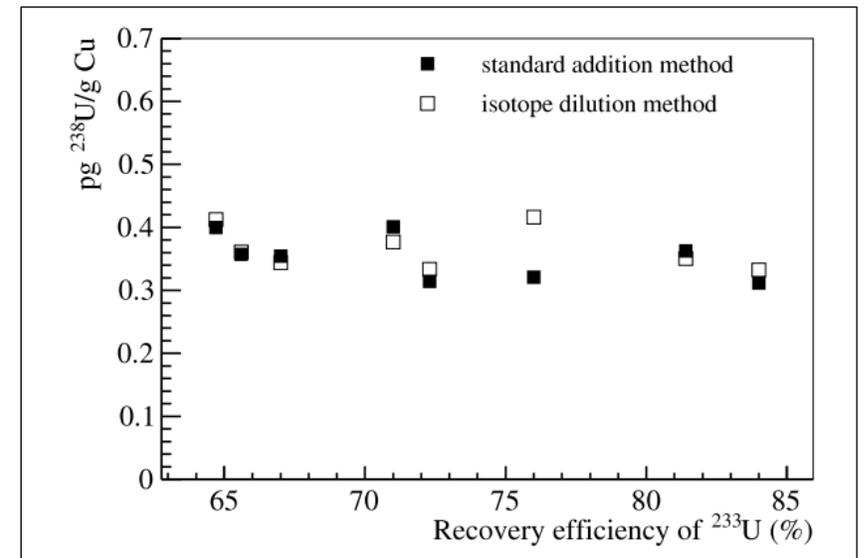
- Concentration of ^{233}U and ^{238}U were obtained
- Recovery efficiency of ^{233}U and MDL of ^{238}U



Method detection Limit (MDL)

- MDL for ^{238}U in copper was obtained by measuring eight reduplicative blanks
 - MDL is calculated as $2.998 \cdot \text{SD}$ (standard deviation)
 - Two quantitative methods (SAM and IDM) were used to cross-check each other
 - ^{233}U recovery efficiencies obtained by SAM are listed
- A MDL of ~ 0.1 ppt is consistently achievable for the two different quantitative methods
- Measured ^{238}U vs. the different ^{233}U recovery efficiencies, no obvious dependency was found, indicating the robustness of the pre-treatment and analysis

Blank no.	Meas. by SAM (ppt)	Meas. by IDM (ppt)	$\epsilon(^{233}\text{U})$
1	0.3206	0.4162	76.0%
2	0.4010	0.3768	71.0%
3	0.3543	0.3438	67.0%
4	0.3116	0.3325	84.0%
5	0.3623	0.3505	81.0%
6	0.3143	0.3333	72.3%
7	0.3572	0.3608	65.6%
8	0.4001	0.4125	64.7%
Average	0.3527	0.3658	72.2%
SD	0.0356	0.0333	–
MDL	0.107	0.099	–





Method detection limit: ^{232}Th

- Determination of Th in copper is also required, but we are short of ^{229}Th at that time
- MDL and recovery efficiency were measured and calculated when ^{229}Th finally arrived
- It's a pity the data are too later for publication

Black No.	Meas. By SAM (ppt)	Meas. By IDM (ppt)	ϵ (^{229}Th)
1	0.3487	0.4373	86.5%
2	0.3311	0.4216	94.1%
3	0.3259	0.3895	81.2%
4	0.3011	0.3635	83.4%
5	0.2537	0.3389	74.7%
6	0.2902	0.3896	60.2%
7	0.3802	0.3748	81.6%
8	0.3019	0.3785	95.6%
Average	0.3166	0.3867	82.3%
SD	0.0387	0.0312	-
MDL	0.116	0.094	-

Practical applications of the approach

- Th and U in many copper samples from different universities or institutes were measured and are measuring in our lab using the approach

- Structural part of the detector
- Th and U was determined to be ~ppt
- Higher radon release rate for machined copper

Question: Is the surface Contaminated?



	$^{232}\text{Th}/\text{ppt}$	$^{238}\text{U}/\text{ppt}$
Surface	0.44 ± 0.11	1.92 ± 0.08
Inside	0.23 ± 0.04	0.43 ± 0.05

- **Conclusion:** The surface of the copper is contaminated after machining.



Measuring Th and U contaminants in PPO to 10^{-14} g/g level via acid extraction

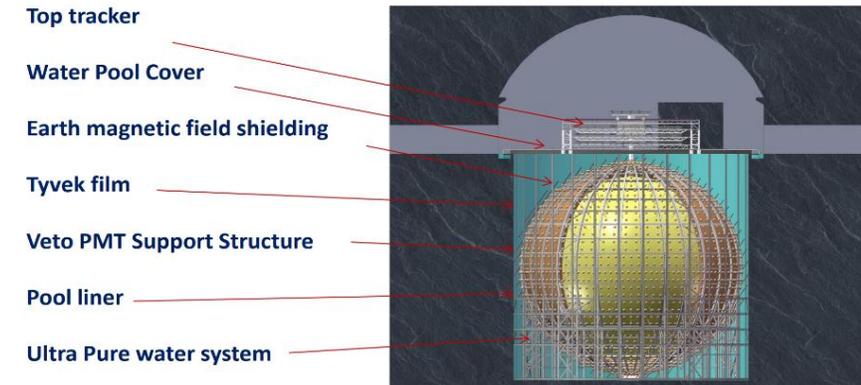
Mengchao Liu, et al, NIM A 1041 (2022) 167323

- Motivation:

- The Jiangmen Underground Neutrino Observatory (JUNO) : determine neutrino mass hierarchy and precisely measure oscillation parameters
- Radiopurity is a fundamental aspect for JUNO



- JUNO central detector will be filled with 20 kton LS
- JUNO LS recipe
 - **2.5g/L PPO** (2,2-diphenyl oxazole)
 - 1~3mg/L bis-MSB(1,4-bis(2-methylstyryl)benzene)
 - LAB (linear alkyl benzene)



- 60 t PPO is needed, one of the main sources of radio-impurities
- To develop a reliable and precise measuring approach for PPO QA/QC (Th and U)



Measuring Th and U contaminants in PPO to 10^{-14} g/g level via acid extraction

- Minimal requirement of JUNO PPO: **0.34ppt** for ^{238}U or ^{232}Th
 - Minimal requirement of JUNO LS radiopurity: 10^{-15} g/g of ^{238}U or ^{232}Th
 - 20 kt LS, 2.5g/L PPO and 1~3mg/L bis-MSB in LAB
- MDL with 99% confidence level in the approach
 - **0.033** ppt for ^{232}Th in PPO
 - **0.040** ppt for ^{238}U in PPO
- Can be applied for QA/QC of PPO

Table 3

Measurements of eight blanks. The average \bar{X} , standard deviation S_b and method detection limit MDL_b for ^{232}Th and ^{238}U were calculated.

Blank No.	pg ^{232}Th /g PPO	pg ^{238}U /g PPO
1	0.030	0.031
2	0.024	0.034
3	0.027	0.034
4	0.029	0.035
5	0.028	0.030
6	0.028	0.034
7	0.025	0.030
8	0.027	0.036
\bar{X}	0.027	0.033
S	0.002	0.002
MDL_b	0.033	0.040



Acid Extraction

- Pre-treatment method: acid extraction
 - Typical liquid–liquid extraction: organic phase and aqueous phase

PPO, a white solid with the melting range of 76~78°C

Dissolved in organic solvent

Liquid state under high temperature

Acid solution, HNO₃



Advantages

- No extra organic solvent, lower background
- Higher extraction efficiency under higher temperature
- Highest PPO concentration, smallest volume

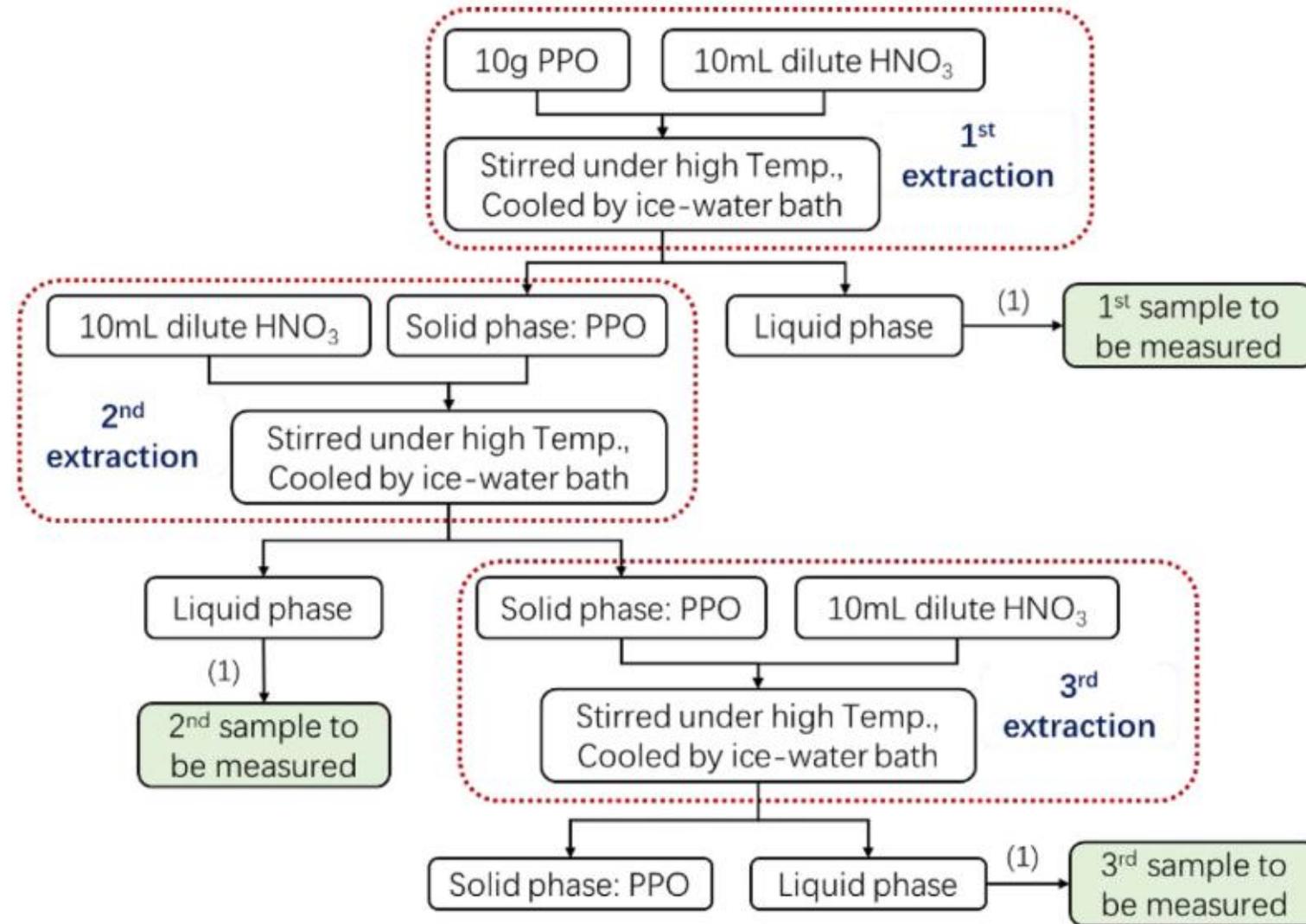


Fig. 1. Flowchart of the PPO pre-treatment. For the step “(1)”: the liquid phase was heated to remove the excess acid, then diluted with 5% HNO₃ to ~5 g amount, finally filtered using the syringe-driven filter with a pore size of 0.2 μm.



Optimization of Pre-treatment parameters

- Optimization of nitric acid concentration
 - At least 90% Th and 85% U in PPO are not water-soluble
 - Insoluble Th and U compounds react with nitric acid to become acid-soluble species followed by transferring to acid phase

Table 2

Impact of the nitric acid concentrations on the PPO measurements. The PPO samples A, B and C were from different suppliers, and their measured Th and U contents were blank-subtracted.

PPO sample	Aqueous phase	Measured ^{232}Th in PPO/ppt	Measured ^{238}U in PPO/ppt
PPO #A	H ₂ O	0.4 ± 0.2	0.32 ± 0.02
	5% HNO ₃	5.0 ± 0.8	2.1 ± 0.2
PPO #B	5% HNO ₃	2.4 ± 0.4	1.2 ± 0.2
	10% HNO ₃	2.5 ± 0.7	1.2 ± 0.1
PPO #C	5% HNO ₃	94.1 ± 8.6	27.5 ± 1.3
	30% HNO ₃	50.9 ± 4.5	12.8 ± 1.7

- Violent oxidation reaction
- PPO turned yellow and acid phase became yellowish-green
- Acid phase contains too much PPO

Matrix effect?

Interference analysis for ICP-MS measurements

- Matrix effect
 - $TDS \leq 0.2\%$, can be ignored in this assay
 - Small amount of PPO may stay in the acid phase and influence the signal of ICP-MS
- Evaluation of Matrix effect
 - Acid phase after extraction, marked as M, was separated and used for the evaluation
 - M was diluted by 20, 12, 6, 3 and 1.5 times separately with 5% HNO_3 , and the diluted solutions were marked as M_1 , M_2 , M_3 , M_4 and M_5 , respectively
 - Fig. 2 shows the measured cps versus the relative Th and U concentrations
 - The data points agreed perfectly with the linear fit, indicating negligible matrix effect
- Negligible matrix effect, standard curve method can be applied for quantification

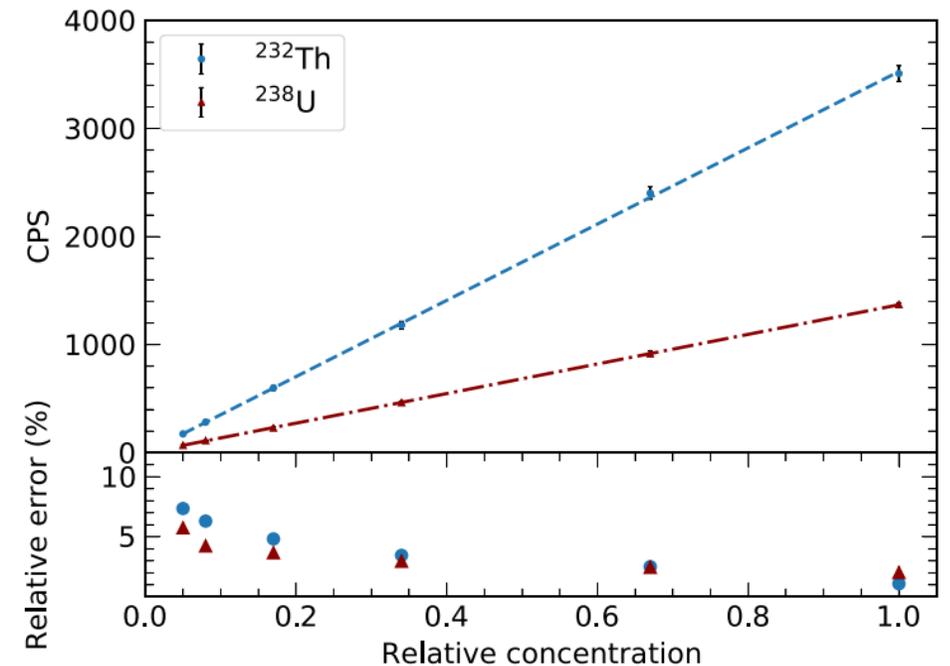


Fig. 2. The measured counts per second with ICP-MS versus the concentrations of solutions M, M_1 to M_5 , where the concentrations are normalized with that of the undiluted solution M. The blue dashed line and red dot-dashed line are linear fits. The bottom panel shows the relative error of each measured point.



Q: Has all the Th and U been extracted from PPO?

- Inherent question for the acid extraction
 - Many chemical species of Th and U, can they all react with 5% HNO₃ to form acid-soluble species? If not, what is the extraction efficiency?
- Best way to answer this question: a standard PPO sample with known amount of Th and U, the species of Th and U should be the same as that of the PPO samples to be determined
- What we do:
 - Recoveries of tracers (²²⁹Th and ²³³U) to evaluate the effectiveness of the three-stage extraction strategy
 - **Cross-check** using other methods with different measuring principles
 - Estimation of acid extraction efficiency

Q: Has all the Th and U been extracted from PPO?

- Recoveries of tracers (^{229}Th and ^{233}U)
 - Nearly 100% recovery efficiencies of ^{229}Th and ^{233}U were obtained in both the spiked PPO samples and blanks
 - Both extraction fractions and recoveries indicated that three-stage extraction was sufficient to extract all acid-soluble Th and U species

Still don't know whether there are non-acid-soluble Th and U species in PPO

Table 4

Calculations of the total recovery efficiency (ξ), the extraction fraction (η_i), extraction efficiencies ($\epsilon_{a.e.}^i$) of spiked ^{229}Th and ^{233}U in PPO at the i th extraction stage, where m_i is the measured amount of isotopes with blank subtracted and M is the known amount of added isotopes. The values in the parentheses are standard deviations of the seven duplicate PPO samples.

ith Extr.	$\eta_i = m_i / \Sigma m_i$ (%)		$\epsilon_{a.e.}^i$ (%) ^a	
	^{229}Th	^{233}U	^{229}Th	^{233}U
1	97.1 (0.5)	95.3 (0.5)	97.1 (0.5)	95.3 (0.5)
2	2.8 (0.4)	4.4 (0.4)	95.4 (2.9)	94.9 (1.1)
3	0.2 (0.1)	0.2 (0.1)	–	–
Total	$\xi = \Sigma m_i / M$			
Recovery	102.0 (1.4)	101.5 (3.0)		

^a $\epsilon_{a.e.}^1 = m_1 / \Sigma m_i$, $\epsilon_{a.e.}^2 = m_2 / (m_2 + m_3)$.

Extraction fraction

Extraction efficiency



Cross check

- Direct evidence to prove whether Th & U in PPO are fully recovered by acid extraction
- **Vaporization approach:**
 - PPO was heated and vaporized in the quartz crucible until nothing visible left; the crucible was washed with 35% HNO₃; treated for ICP-MS measuring

	Acid extraction approach (ppt)	Vaporization approach (ppt)
²³² Th	56.9 ± 6.8	52.5 ± 2.0
²³⁸ U	28.7 ± 3.9	26.4 ± 8.3

- Data from Daya Bay anti-neutrino experiment: no difference in magnitude
- NAA results from INFN:
 - Sensitivity of NAA: 0.x ppt for ²³²Th or ²³⁸U
 - PPO sample with ~1 ppt Th and ~2 ppt U measured simultaneously: no difference
 - PPO sample: ~0.1ppt using acid extraction approach, lower than detection limit of NAA

Estimation of acid extraction efficiency and fraction

Table 5

Extraction fraction (η_i) and extraction efficiency ($\epsilon_{a.e.}^i$) of ^{232}Th and ^{238}U in PPO in the i th extraction stage, respectively. The Th and U contents in PPO are categorized into three groups according to the Th and U concentrations, i.e., (0, 1) ppt, [1, 10] ppt and [10, 100] ppt, respectively. N_s is the number of samples and the values in the parentheses are the errors (standard deviations) in each group. The efficiency and error values are rounded to 1% precision due to relative large uncertainties.

^{232}Th (ppt)		∈(0, 1)	∈[1, 10)	∈[10, 100)	
N_s		4	12	6	
$\eta_i = \frac{m_i}{\sum m_i}$ (%)	1st	85 (3)	88 (3)	88 (6)	Extraction fraction of Th
	2nd	10 (2)	8 (2)	9 (4)	
	3rd	4 (1)	3 (1)	<1	
$\epsilon_{a.e.}^i$ (%) ^a	1st	85 (3)	88 (3)	88 (6)	Extraction efficiency of Th
	2nd	69 (9)	73 (6)	70 (6)	
^{238}U (ppt)		∈(0, 1)	∈[1, 10)	∈[10, 100)	
N_s		4	12	8	
$\eta_i = \frac{m_i}{\sum m_i}$ (%)	1st	90 (3)	91 (3)	93 (3)	Extraction fraction of U
	2nd	7 (2)	7 (2)	6 (2)	
	3rd	3 (1)	2 (1)	2 (2)	
$\epsilon_{a.e.}^i$ (%) ^a	1st	90 (3)	91 (3)	93 (3)	Extraction efficiency of U
	2nd	72 (7)	81 (7)	79 (6)	

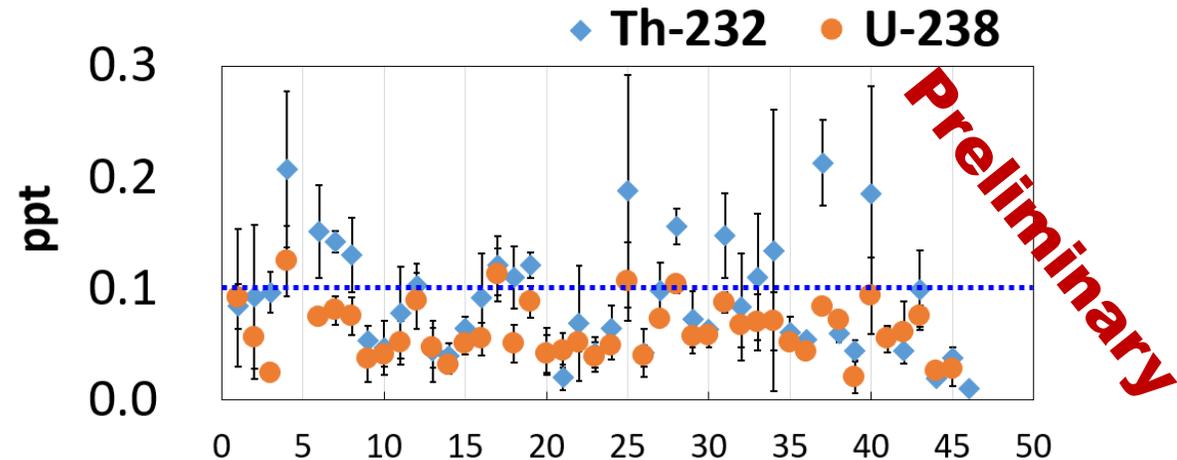
^a $\epsilon_{a.e.}^1 = m_1 / \sum m_i$, $\epsilon_{a.e.}^2 = m_2 / (m_2 + m_3)$.

- The approach will also be applied to monitor PPO samples from different purification steps before real production, which may contain different amount of Th and U (even sub-ppb level)
- **Does the efficiency depend on the Th or U concentration in PPO?**
 - The answer is No
 - The extraction fractions and efficiencies were relatively stable in a wide range of Th and U concentrations in PPO
- The approach is reliable, stable and sensitive for the quality testing of JUNO PPO



Practical application: JUNO PPO

- Production of 60 t high-quality PPO for JUNO started since Jul. 2021
- Each production batch was checked at IHEP for optical properties and content of radio-impurities



- The reliable and precise measurement of the Th and U in PPO as well as the corporation with the manufacturer help to decrease the Th and U in JUNO PPO down to ~ 0.1 ppt, which meets the minimal requirements (0.34 ppt) of JUNO LS with further purification



Other low background measurements

- Radio-impurities in wavelength shifter (bis-MSB) of JUNO LS: dry ashing and acid extraction
- Radio-impurities in acrylic, material for building JUNO center detector
 - C. Cao, et al., A practical approach of high precision U and Th concentration measurement in acrylic, NIM A 1004 (2021) 165377
- Radio-impurities LS master solution, LS, water, dust... for JUNO
- Radio-impurities in silicon wafer, capacitors, ...for nEXO
-



How to perform low back ground measurement (ICP-MS)?

- **Clean environment:** clean room, routine maintenance and monitoring are necessary
- **Clean Instruments:** not contaminated, maintenance and monitoring
- **Clean labware:**
 - Made of suitable materials that can be cleaned to certain level, such as PFA
 - A standard cleaning procedure; checked by ICP-MS before use
- **Clean reagents:**
 - Ultra-pure water, high-purity HNO_3 , ... (purification if necessary)
- **Sample preparation techniques (for ICP-MS)**
 - Separation and enrichment
 - Familiar with the chemical and physical properties of the components of the objects to be determined
- **ICP-MS measurement:** routine maintenance and checking during measuring
- **Evaluation of the whole approach:** interferences, MDL, recovery, reliability,....
- **Training for the operators:** safety training, chemical training, experimental details



Thank you for your attention!

