Ultra-sensitive neutron activation analysis of U, Th and K in the liquid scintillator for the JUNO experiment

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The JUNO experiment

The Jiangmen Underground Neutrino Observatory (JUNO) experiment

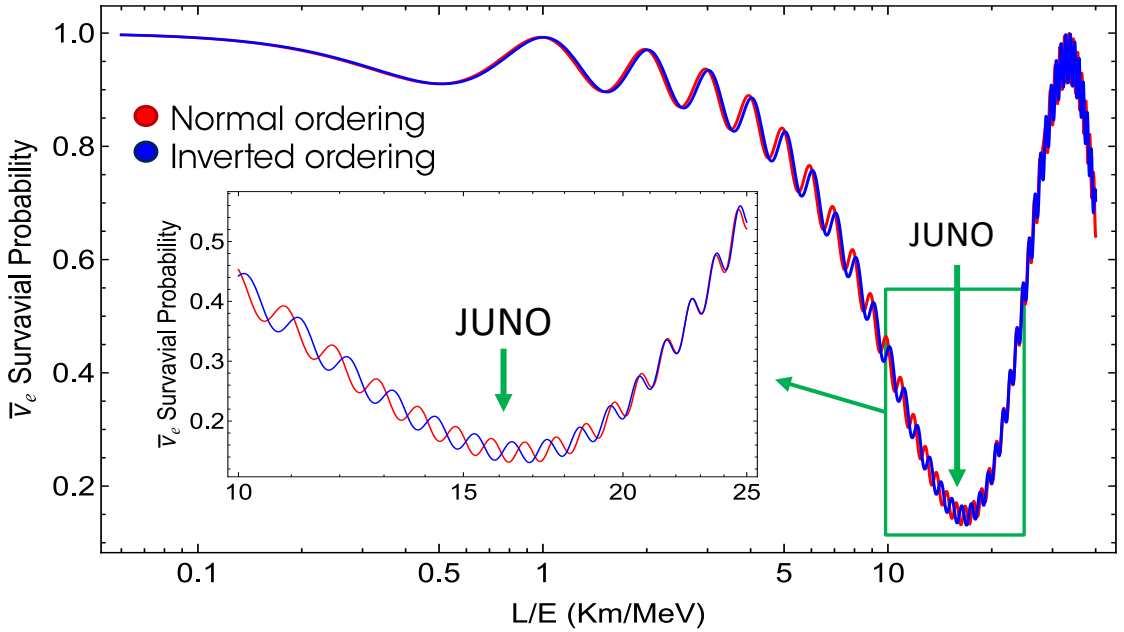
Main physics goals

- 3σ measurement of the **neutrino mass ordering** with reactor antineutrinos in 7,1 years
- Measuring **oscillation parameters** with a precision < 0.5 %
  $(sin^2\theta_{12}, \Delta m^2_{21}, \Delta m^2_{31})$

JUNO features

- The biggest LS-based neutrino detector
- Largest PMT coverage ever built
- Excellent energy resolution (2,95% @ 1 MeV)

The detector location and design are optimized for the best sensitivity to NMO



Broad physics program:

- Solar neutrinos
- Atmospheric neutrinos
- Geo-neutrinos
- Supernova neutrinos
- Proton decay
- …

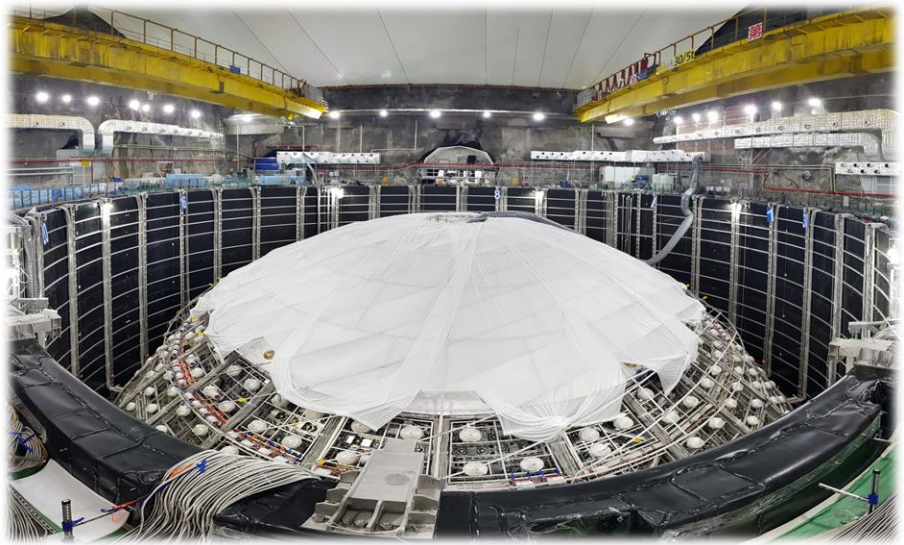
The JUNO experiment

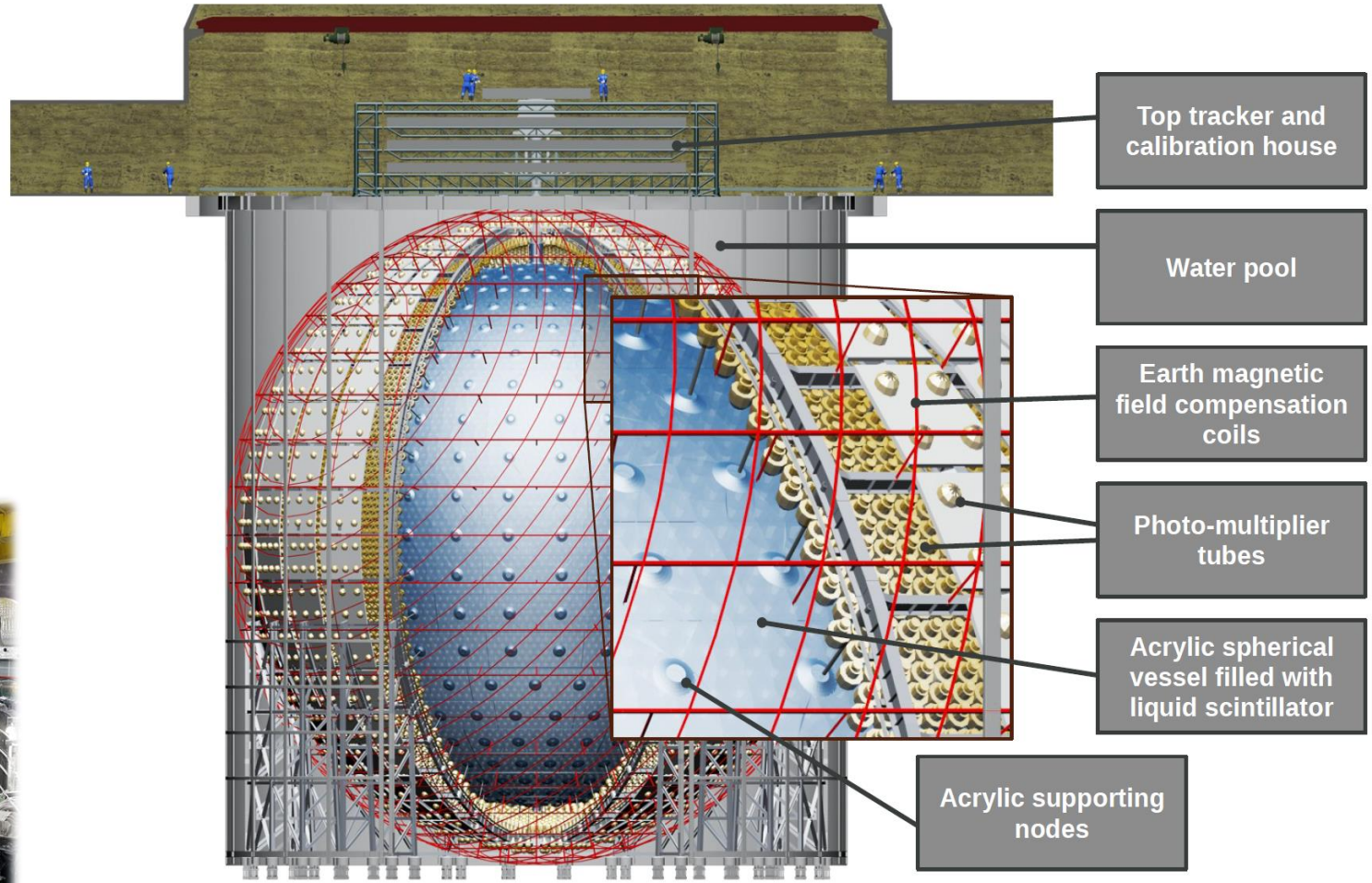
Central detector:

- 20 000 t of LS in acrylic vessel
- 17612 large PMTs (20-inch)
- 25600 small PMTs (3-inch)
- ~ 78% PMT coverage
- Earth magnetic field shielding coil

Water Cherenkov Detector (muon veto):

- 2400 20-inch PMTs
- 35 000 t ultra-pure water
- Muon detection efficiency > 99%





JUNO liquid scintillator

- JUNO liquid scintillator is composed by Linear Alkyl Benzene (LAB) + PPO (2,5 g/L) + bis-MSB (3 mg/L)
- Minimum radiopurity requirements: **U, Th < 10^{-15} g/g** (1 ppq) and **K < 10^{-16} g/g** (0,1 ppq)
- Its optical properties play a crucial role for energy resolution:
  light yield 1665 PE/MeV with attenuation length > 20 m @ 430 nm

→ **Dedicated purification system**

LAB tank

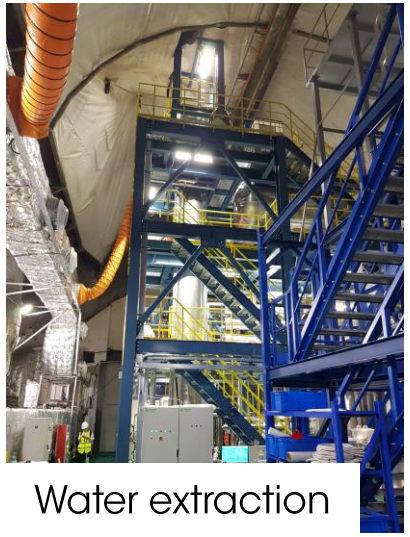
Filtration on Al_2O_3

Distillation

PPO & bis-MSB mixing

Underground

Gas stripping



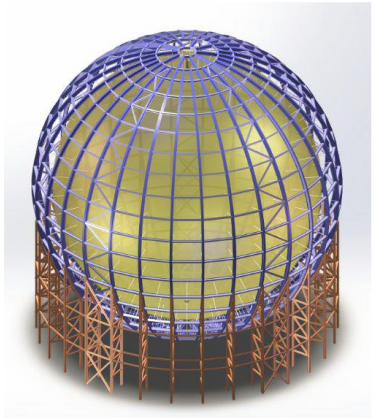
Water extraction

Validation of the radiopurity is required

85%

OSIRIS

15%



Developed technique for ultra-sensitive analysis of U and Th

U/Th measurement strategy

Liquid scintillator is the active part of the JUNO detector and has a huge mass → It is the **most critical component** for radiopurity → Requirement at **10^{-15} g/g** for U/Th and **10^{-16} g/g** for K

Very promising technique: **Neutron Activation Analysis**

Dedicated techniques and detectors must be developed to reach at least 10^{-15} g/g

$$^{A}_{Z}X + n \rightarrow {}^{A+1}_{Z}X \xrightarrow{\beta^-} {}^{A+1}_{Z+1}Y + \gamma$$

Neutron activation + HPGe γ measurement

10^{-12}g/g

β–γ coincidence detector: GeSparK

- Beta-gamma coincidence
- ^{239}Np delayed coincidence
- Cosmic muon veto

Radiochemical treatments

- Concentration of the nuclides of interest (higher equivalent sample mass)
- Removal of interfering nuclides

10^{-13}g/g - 10^{-14}g/g

$<10^{-15}$g/g

Contamination control – Importance of cleanliness

U and Th are present in rock, soil, air, human body and all common materials with different concentrations.

↓

The U-Th concentration in LAB required by JUNO are **many orders of magnitude** lower than their typical concentrations in the environment

↓

The materials, air pollution and human body are immense sources of contaminations

↓

The cleanliness of working area, the consumables and the reagents is crucial

- All the treatments are performed in an ISO 7 clean room (class 10 000). The extraction and chromatography are performed under an ISO 6 (class 1000) laminar flow hood.
- A dedicated cleaning protocol has been developed for the containers and consumables
- Use of specific container with extremely low contaminations (Teflon, PFA)
- Use of reagents with the highest purity available ("ultra pure")

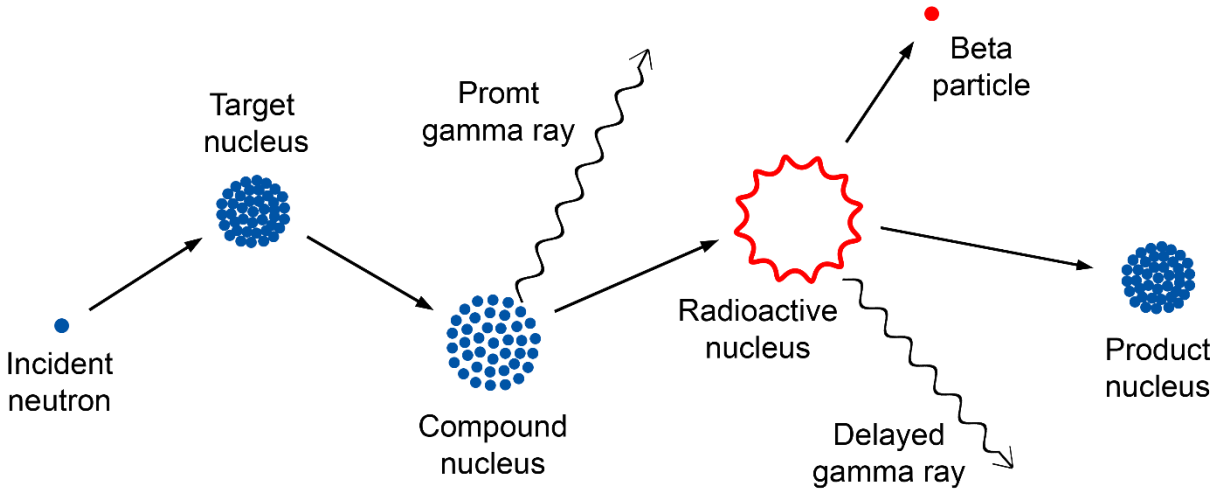
Reagents validated by ICP-MS @ LNGS

	$^{238}\mathrm{U}(g/g)$	$^{232}\mathrm{Th}(g/g)$
H_2O Milli-Q	$<0.7\cdot10^{-15}$	$<0.8\cdot10^{-15}$
H_2O Milli-Q Element	$<0.7\cdot10^{-15}$	$<0.8\cdot10^{-15}$
Ultra-pure NHO_3	$<3\cdot10^{-14}$	$<3\cdot10^{-14}$

Neutron activation technique - Introduction

Exposure of the sample to a neutron flux → Measurement of the induced gamma radioactivity → Computation of the radionuclide concentration based on the comparison with a known standard.

$$ {}^{A}_{Z}X + \mathrm{n} \rightarrow {}^{A+1}_{Z}X \xrightarrow{\beta^-} {}^{A+1}_{Z+1}Y^* \rightarrow {}^{A+1}_{Z+1}Y + \gamma $$

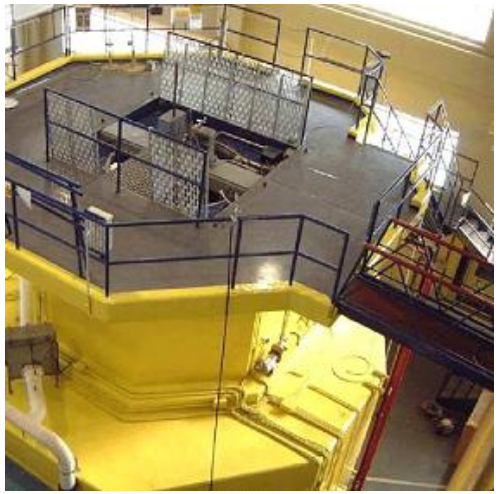


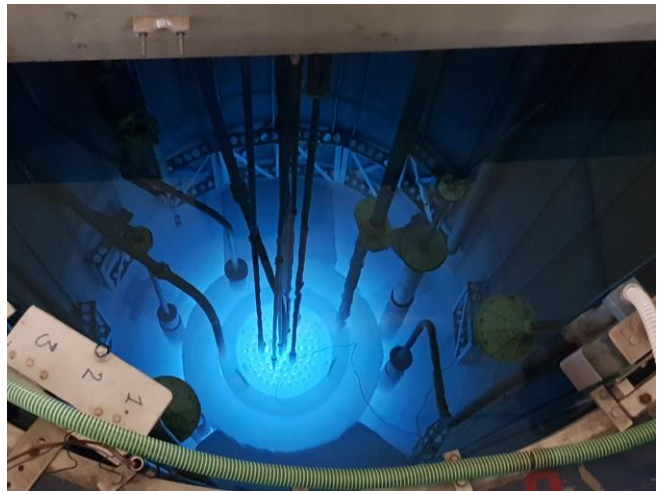
The neutron activation transform **stable or long-lived** nuclides into **shot-lived** radioactive nuclides

$$ {}^{238}U + n \rightarrow {}^{239}U \xrightarrow{\beta^- 23{,}5m} {}^{239}Np \xrightarrow{\beta^- 2{,}36d} {}^{239}Pu $$

$$ {}^{232}Th + n \rightarrow {}^{233}Th \xrightarrow{\beta^- 21{,}8m} {}^{233}Pa \xrightarrow{\beta^- 27d} {}^{233}U $$

$$ {}^{41}K + n \rightarrow {}^{42}K \xrightarrow{\beta^- 12{,}4h} {}^{42}Ca $$





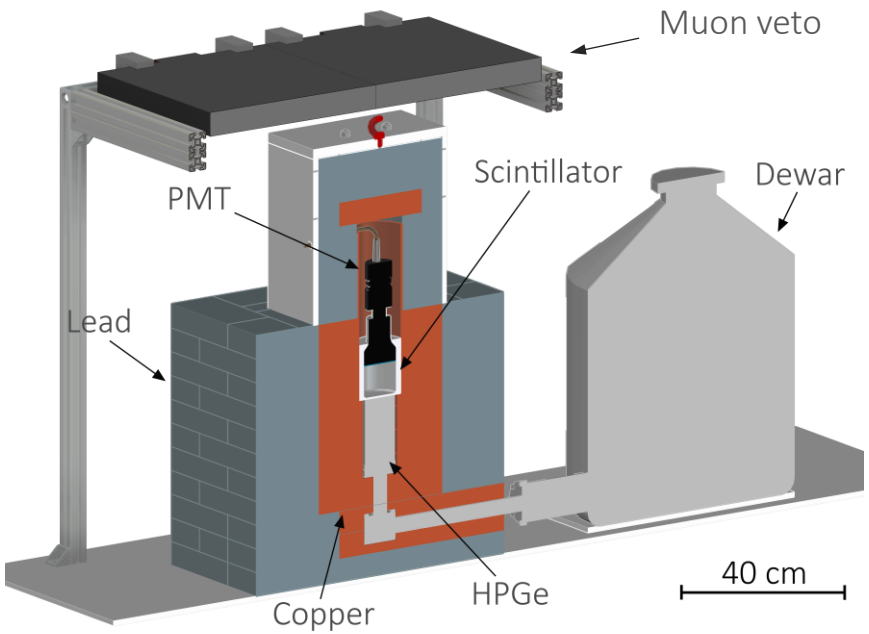
Triga Mark II research reactor (LENA – PV):

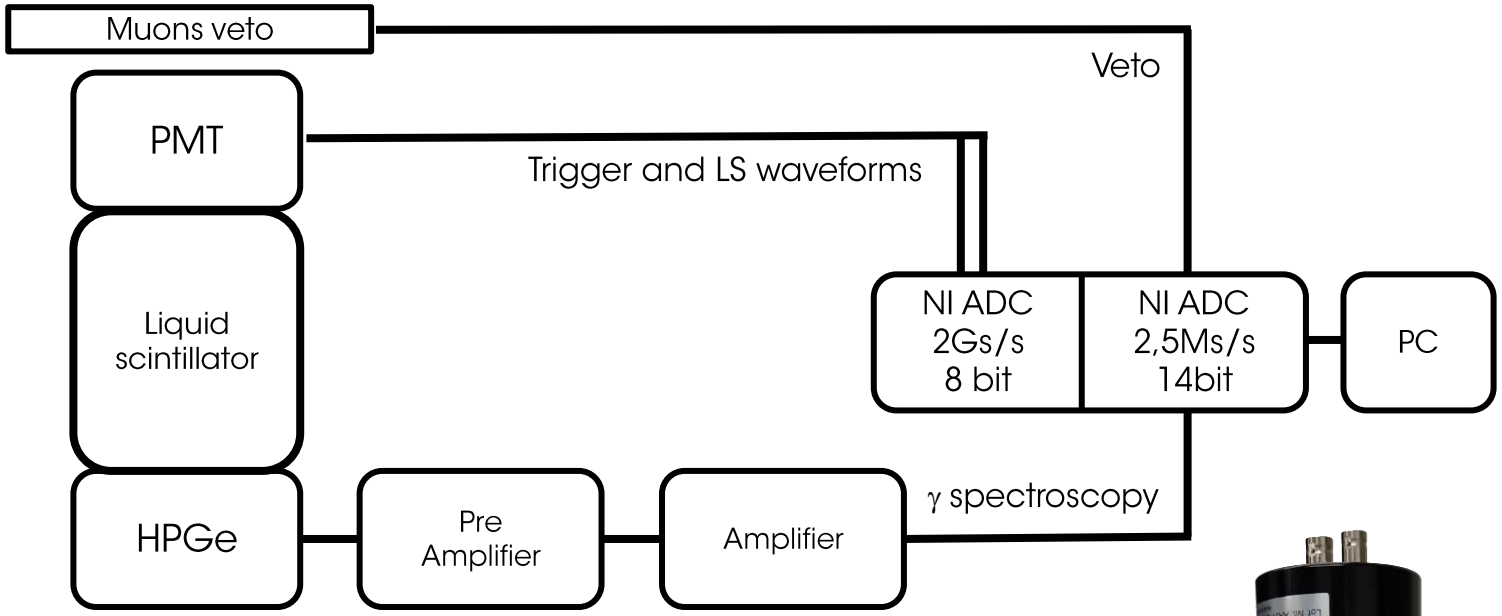
- Thermal power: 250 kW
- Thermal neutron flux in Lazy Susan channel: 10^{12} n/(s cm^2)
- Irradiation time: 6h

The GeSparK beta-gamma coincidence detector

The GeSparK is a **liquid scintillator** (LS) detector coupled to an **HPGe** detector working in time coincidence.

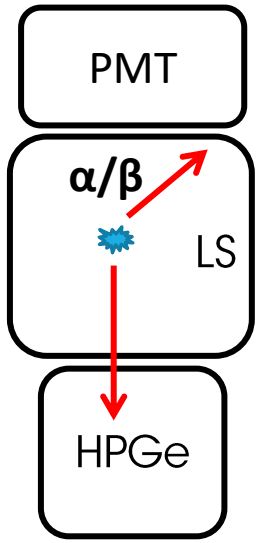
- LS: High efficiency and high time resolution
- HPGe: Very high energy resolution





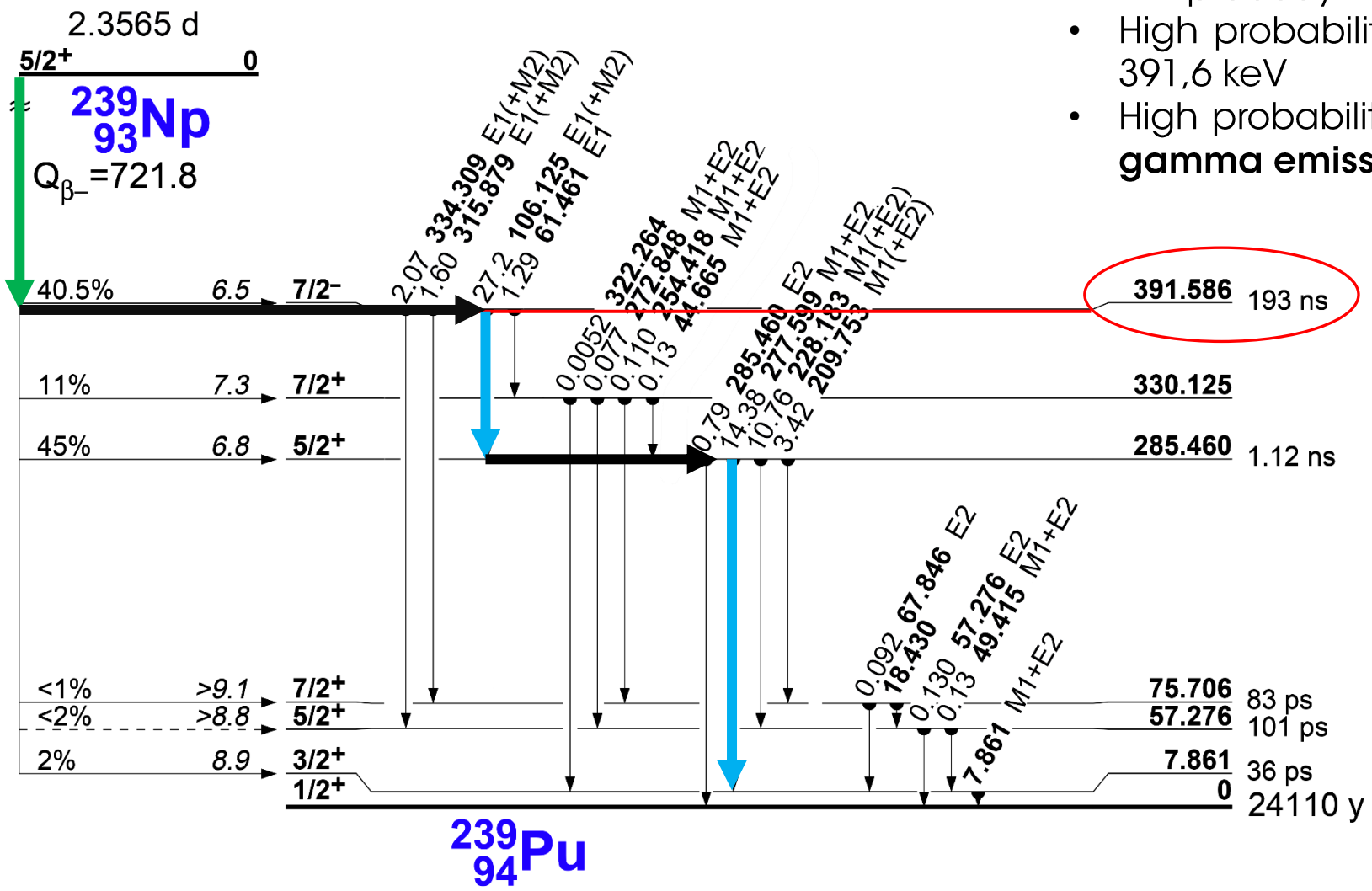
Time coincidence:

- Drastic random **background reduction**
- Analysis of **delayed coincidence** events (see next slide)



Delayed coincidence technique for ^{238}U measurement – Theory

$$^{238}U + n \rightarrow {}^{239}U \xrightarrow{\beta^- \ 23{,}5m} {}^{239}Np \xrightarrow{\beta^- \ 2{,}36d} {}^{239}Pu$$



- Many **internal conversion transitions** are present in ^{239}Np decay
- High probability to populate the metastable state at 391,6 keV
- High probability that its deexcitation is followed by a **gamma emission + IC transition.**

- β → γ → IC
- β → IC → γ

The γ and IC transitions following the beta decay are **delayed** by the lifetime of the metastable state

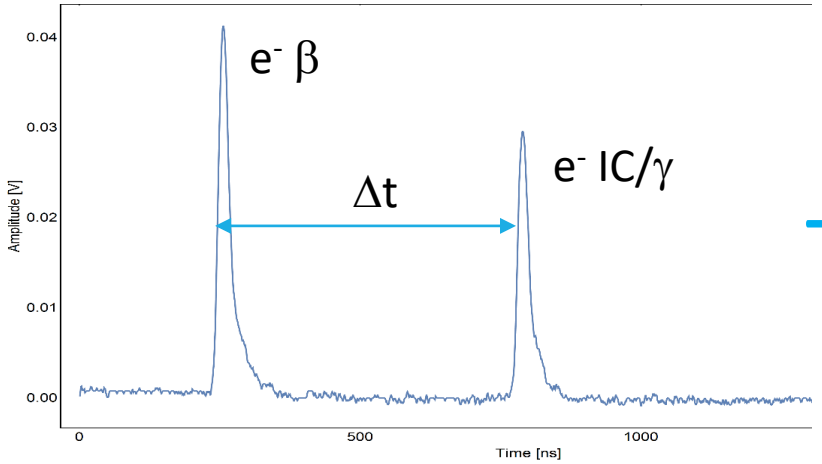
IC electrons and β electrons produce similar signals in LS.

↓

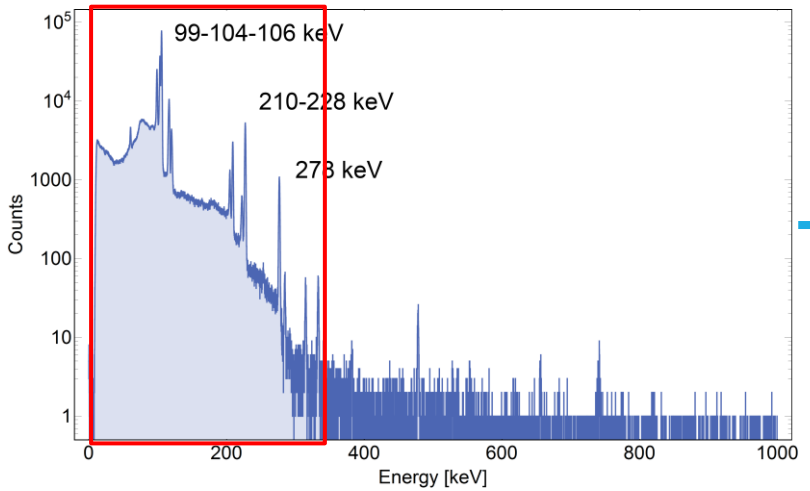
It is possible to measure the **time distance between β and IC**

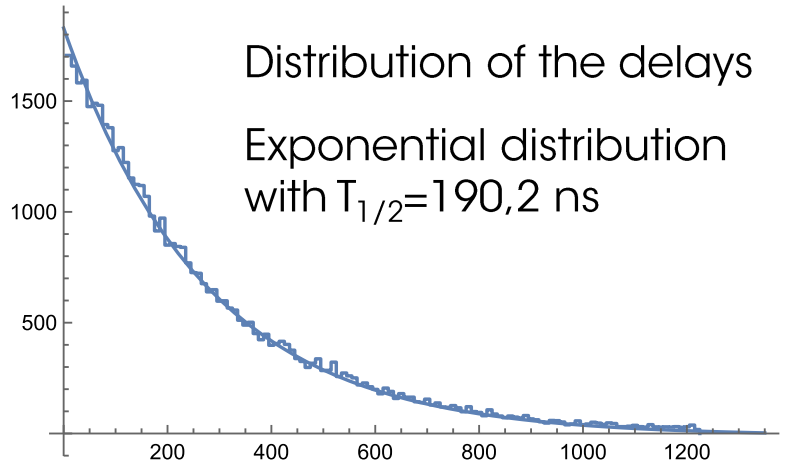
Delayed coincidence technique for ^{238}U measurement – Signals and data analysis

Delayed events in the LS



HPGe coincidence spectrum





Distribution of the delays

Exponential distribution with $T_{1/2}$=190,2 ns

A very strong marker is associated to this transition:
2 electron signals in short time window + 1 gamma → A drastic background reduction can be obtained! → Triple coincidence

Delayed events in the LS in coincidence with a γ-ray in HPGe detector → Sample → Signal events computed by **maximizing the likelihood function** of the **combined distribution signal + background** for the *c* parameter

$$\mathcal{D} = c \cdot \frac{\frac{1}{\tau} e^{-\frac{t}{\tau}}}{\int_0^{\Delta t} \frac{1}{\tau} e^{-\frac{t}{\tau}} dt} + (1 - c) \cdot \frac{1}{\Delta t}$$

Radiochemical treatments – Introduction and motivations

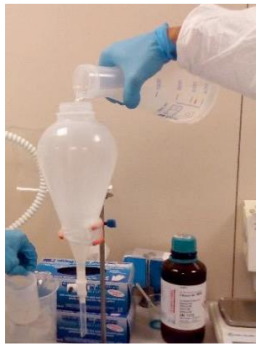
Despite the combination of neutron activation, GeSparK detector, and delayed coincidence technique (for U), the sensitivity is limited by:

- **Low sample mass**
- **Measurement background (interfering nuclides)**

Objective: **increase mass sample at constant background**

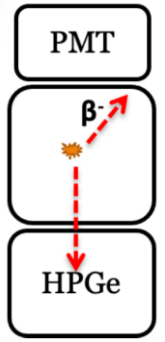
Cleaning protocol (Pre-Irradiation) → Any manipulation or treatment of the sample could introduce contaminations before irradiation

Radiochemical Treatments (Pre-Irradiation) → **Removing interferences** and **concentrating** the sample



Sample irradiation → Transforming long-life nuclides $^{238}U/^{232}Th$ into the radioactive short-life $^{239}Np/^{233}Pa$ nuclides.

Radiochemical Treatments (Post-Irradiation) → **Removing interferences**



β/γ measurements → We developed a new detector suitable to β/γ **coincidence** measurements on liquid irradiated samples

Radiochemical treatments – Treatments description

Liquid – liquid extraction

Why

Transfer U-Th from the LAB to an aqueous solution to use the chromatography resins

Principle

Exploits the different affinity of U-Th ions to a polar acid aqueous solution with respect an apolar organic compound (LAB)

How

1. Vigorous mixing of LAB and acid aqueous solution (HNO_3 5M)
2. Separate the two immiscible phases with the separatory funnel

Repeat the two steps 3 times

Extraction chromatography

Why

Allow the concentration of U-Th and the selective reduction of interfering nuclides

Principle

Exploits the different affinity of U-Th or Np-Pa ions to resins with respect to all other nuclides

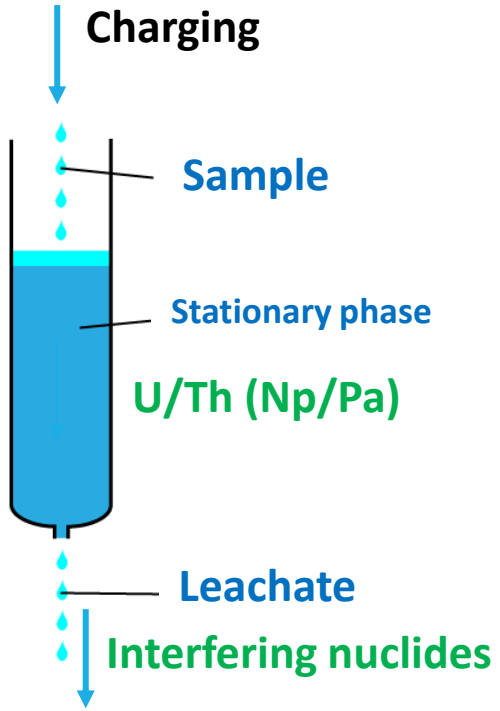
How

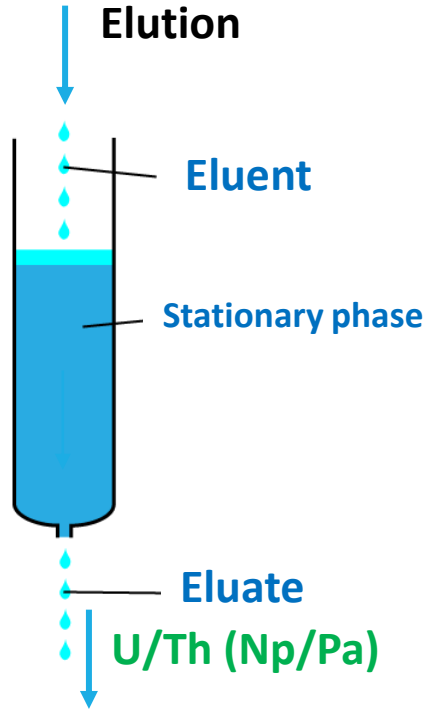
Next slide…

Radiochemical treatments – Extraction chromatography description

Procedure

1. **Washing**: clean the new resin
2. **Conditioning**: prepare the resin to accept the sample
3. **Charging**: nuclides of interest in the sample are absorbed by the resin
4. **Washing**: remove residues of interfering nuclides
5. **Elution**: nuclides of interest are released by the resin





Pre-irradiation: U-TEVA (U/Th)
- Reduce the sample volume
- Remove interfering nuclides

Post-irradiation: TEVA (Np/Pa)
- Remove activated interfering nuclides

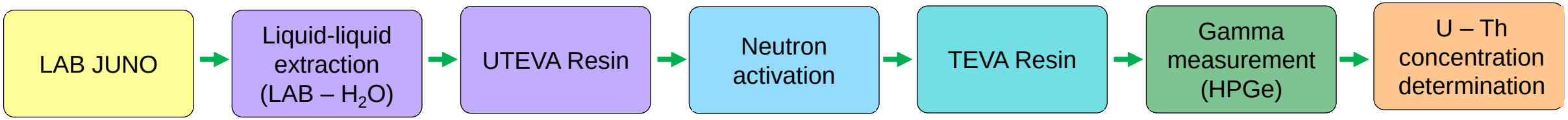
Different resins require different operating condition:
- Concentration and composition of the solutions
- Redox potential (Np-Pa)

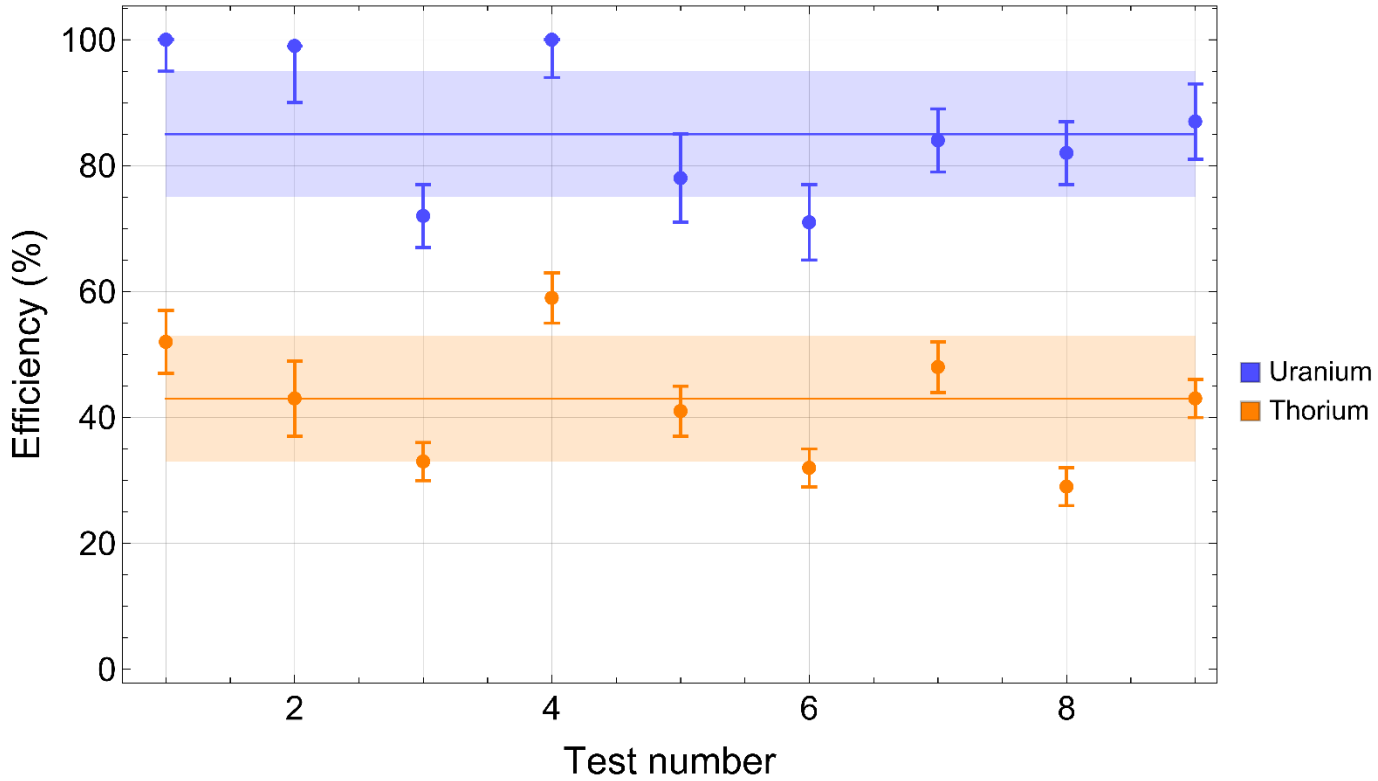
The affinity of the resin is different based on the acid concentration of the solutions

Measurement of the recovery efficiency

Efficiency of the radiochemical treatments for U-Th

The effectiveness of the radiochemical treatments have been studied by using **spiked LAB samples**



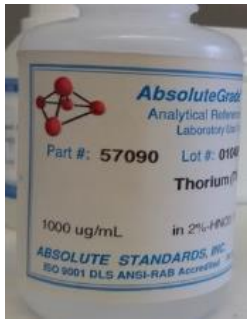


STDs containing a known amount of the element are used as **tracers**

^{238}U Recovery Efficiency:
(86 ± 12)%

^{232}Th Recovery Efficiency:
(43 ± 10)%

Interfering nuclide reduction:
~100 %



Potassium procedure

LAB-LS Radiopurity – ^{40}K

Procedure for ^{40}K measurement: direct NAA measurement without radiochemical treatments

LAB irradiation → **HPGe measurement**

Reduce the risk to contaminate the sample

Measurement with high efficiency HPGe

K is a very common element: there is a high probability to contaminate the sample

↓

Multiple measure must be performed

Limitation:

The sensitivity is strongly limited by the mass sample (tens of g) → ~ few ppq

Blank measurements and sensitivity

Blank measurements and sensitivity

Blank NAA measurements for U/Th:
5 M ultrapure nitric acid treated with the complete radiochemical procedure

Sample mass (g)	^{238}U concentration (ppq)	^{238}U mass (pg)
46.5	14 ± 5	0.67 ± 0.23
48.33	3,7 ± 2,5	0.18 ± 0,12
Elution without sample		0,34 ± 0,15

Constant amount of U and Th are recovered → The contamination comes from the resin

To better estimate the resin background with high statistics we measured 30 blank samples with ICP-MS at LNGS (*Courtesy of S. Nisi*)

Mean resin contribution to background:

^{238}U: (0,29 ± 0,17) pg

^{232}Th: (0,21 ± 0,13) pg

Blank samples for potassium:
Irradiation of ultrapure water in PFA vials

Blank sample mass (g)	^{40}K concentration (ppq)
25.34	< 1.3
26.04	< 1.7

Current sensitivities on U, Th and K

Nuclide	Sensitivity @ 95 % CL	Limiting factor
^{238}U	< 0,7 ppq @ 500 mL < 0,4 ppq @ 1 L	Resin background
^{232}Th	< 1,6 ppq @ 1 L	Sample mass, resin and detector background
^{40}K	< 0,7 ppq @ 126 g	Sample mass

Measurement results during the purification plant commissioning

LAB-LS measurement results during first plants commissioning

Raw LAB → Alumina plant → Distillation plant → Mixing plant → Pipes to underground → Water extraction plant → Steam stripping plant → OSIRIS → FOC system (pipes + tanks)

Steam stripping plant → LS after stripping plant → LS room tank

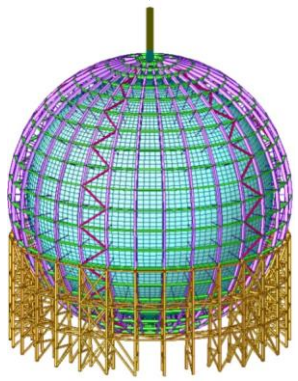
Raw LAB
U: < 5 ppq
Th: < 16 ppq
K: < 3 ppq

Al_2O_3 LAB
U: < 6 ppq
Th: < 11 ppq
K: < 3 ppq

Distilled LAB
U: < 0,7 ppq
Th: < 9,5 ppq
K: < 1,7 ppq

U: < 0,8 ppq
Th: < 8,2 ppq
K: < 0,7 ppq

spilling point for measurement



- Different sensitivities due to different sample masses, measurement times and measurements during technique development
- Radiopurity validation is still ongoing
  -> new validation during the joint commissioning

Summary

Summary

- JUNO is a neutrino observatory with unprecedented features and a rich physics program in particle and astroparticle physics
- Very demanding requirements for radiopurity of the LS: **U, Th < 10^{-15} g/g** and **K < 10^{-16} g/g.**
- Dedicated measurement technique has been developed by combining **NAA**, **β–γ coincidence detector** and **radiochemical treatments**

^{238}U and ^{232}Th procedures

- The efficiency and background of the process are well understood
- Reached **< 0,4 ppq** sensitivity for **^{238}U** and **< 1,6 ppq** for **^{232}Th**

^{40}K procedure

- With the direct NAA we reached **< 0,7 ppq** sensitivity

LAB-LS measurement results

- No evidence of U, Th and K contamination in all sample
- Best current **^{238}U** limits on the distilled LAB and LS after stripping plant **<0.7/0.8 ppq**
- No evidence of **^{232}Th** contaminations in all samples up to **<8 ppq**
- No evidence of **^{40}K** contaminations in all samples and LS after stripping plant **<0,7 ppq**

Thank you for your attention

Backup slides

Improving background (and sensitivity)

Since contamination is not caused by the acid but by the resin, a **new cleaning process might reduce the background contamination**

→ New **UTEVA** resin **cleaning process** tested

UTEVA resin protocol for extraction chromatography

1.	50 mL cleaning	0.02M HNO_3
2.	10 mL conditioning	5M HNO_3
3.	50 mL cleaning	0.02M HNO_3
4.	15 mL conditioning	5M HNO_3
5.	Sample loading	
6.	15 mL elution	0.02M HNO_3

LAB-LS measurement results during first plants commissioning (Table)

Measured sample	^{238}U (ppq)	^{232}Th (ppq)	Mass (g)	^{40}K (ppq)	Mass (g)
LAB - RAW	< 11	< 33	373	< 5	21,79
	< 5	< 16	761	< 3	43,55
LAB – Al2O3	< 6	< 11	680	< 3	36,70
				< 3	42,60
LAB – Distilled	< 0,7	< 9,5	394	< 2,5	21,79
				< 1,7	21,79
LS – After stripping plant	< 0,8	< 8,2	370	< 1,7	21,51
				<0,7	126,0

Limits at 95% CL