Department of Physics
Technical University Munich

INFN LNGS
Istituto Nazionale di Fisica Nucleare
Laboratori Nazionali del Gran Sasso

MAX-PLANCK-GESELLSCHAFT

Performing matrix extraction and characterization of copper samples by High Resolution Inductively Coupled Plasma Mass Spectrometry

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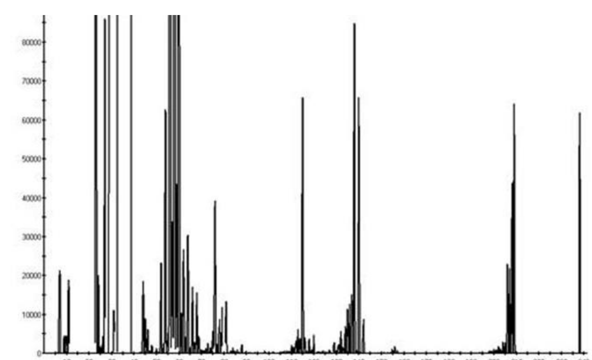
Krakow 1/10/2024

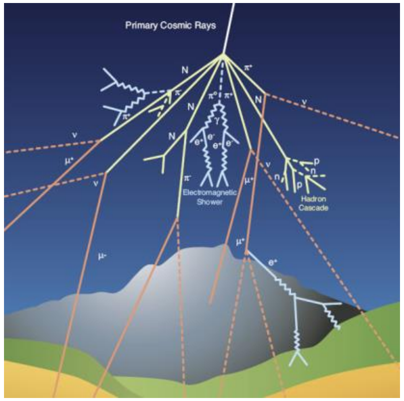


Outlook

- Use of copper in physics experiment
- Treatment of pieces
- Conditioning of extraction system
- Chemical separation of Th U
- ICP-MS characterization
- Data analysis
- Considerations

LOW BACKGROUND

- Necessary to search rare events and also regards biological response
- Improve sensitivity of astroparticle physics experiments, environment with low background radiation
- Contribute of radiopure materials
- Working in clean room ISO 6 to avoid environmental contamination



ICP-MS FACILITY AT LNGS

Agilent 7850 single quadrupole with collision cell

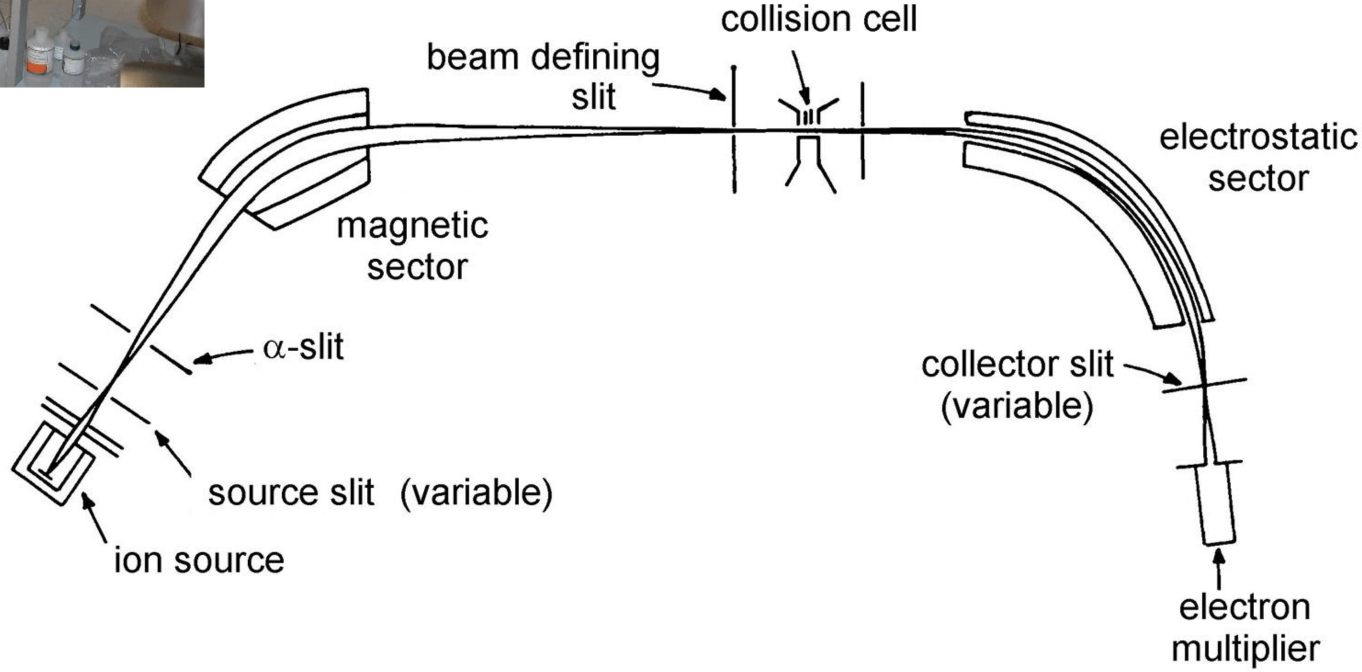
Thermo Element 2 with double focusing – inverse geometry

Agilent 8900 triple quadrupole
Cetal laser ablation

OCTOBER – NOVEMBER 2024

Schematic mass spectrometers

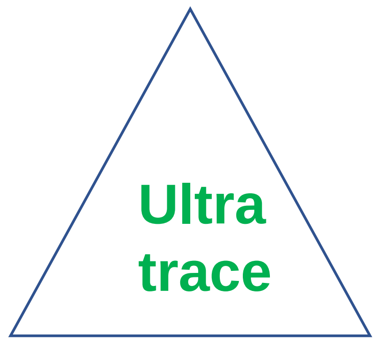
Element 2 Thermo Fisher Scientific



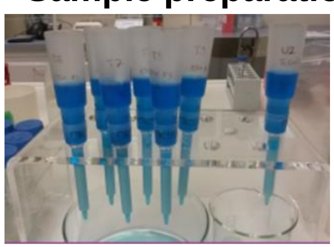
LOW RESOLUTION
MEDIUM RESOLUTION
HIGH RESOLUTION

«triangle» of ultra-trace

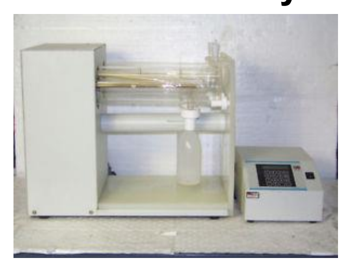
Instrumentation



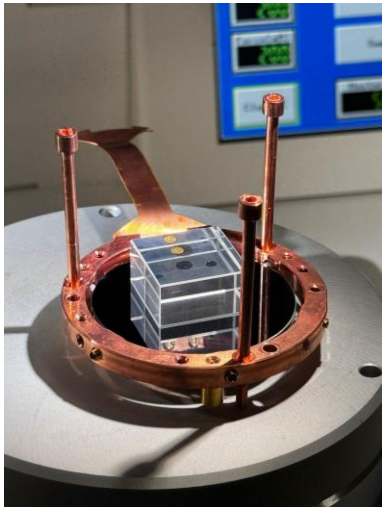
Sample preparation

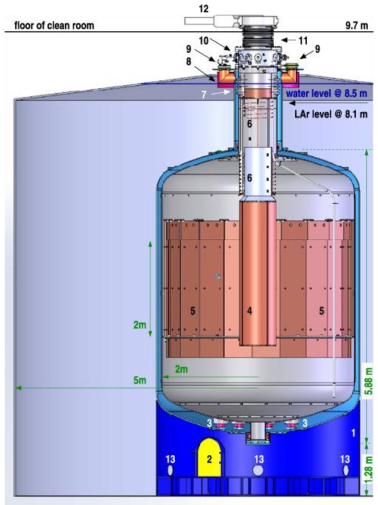


“Clean chemistry”



Use of copper



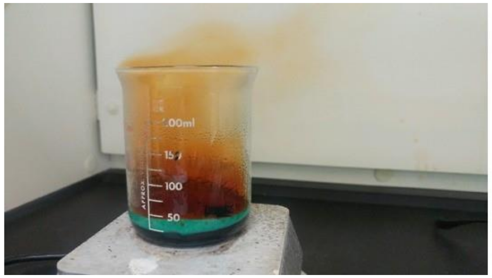


- Copper is widely used due to its thermal properties and conductivity
- Best properties can be reached by electrofotming

Operations - 1

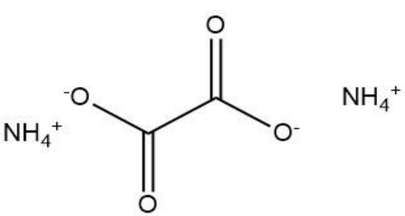
- Different sampling of internal and external surface of copper cake
- Rinse of samples with different washing solutions (acid soap to eliminate surface impurities)
- Estimation of Cu mass to dissolve in each etching

$$Cu_{(s)} + HNO_{3\,(aq)} \rightarrow Cu(NO_3)_{2\,(aq)} + NO_{2\,(g)} + H_2O_{(l)}$$



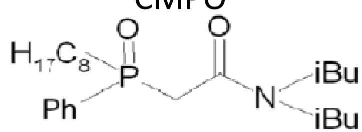
Operations - 2

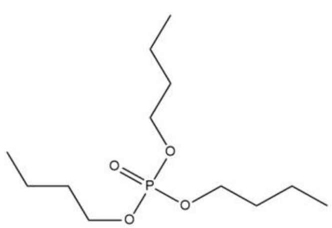
- Concentration of solution
- Conditioning of TRU columns with $HNO_3/(NH_4)_2C_2O_4$
- Optimization of alternating washing cycles
- Blank's subtraction of each columns to perform quantification analysis



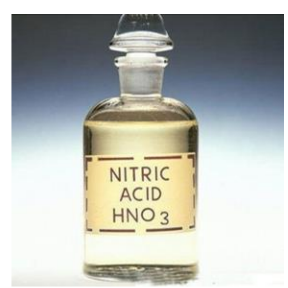
Ammonium oxalate

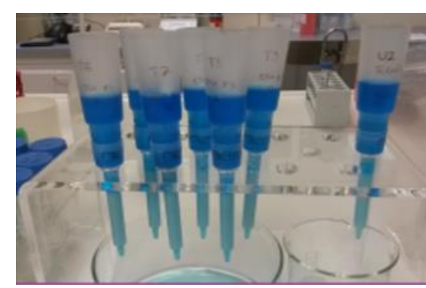
CMPO





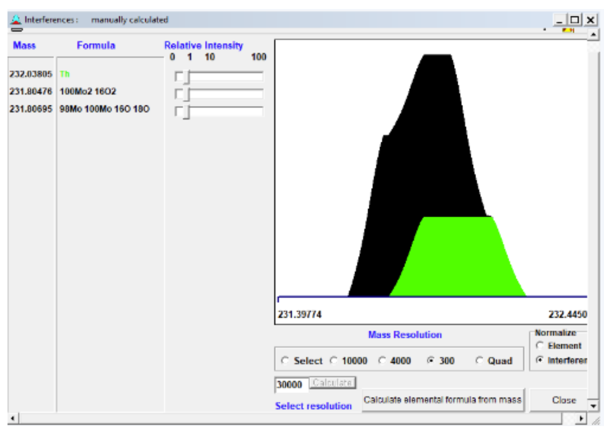
TBP

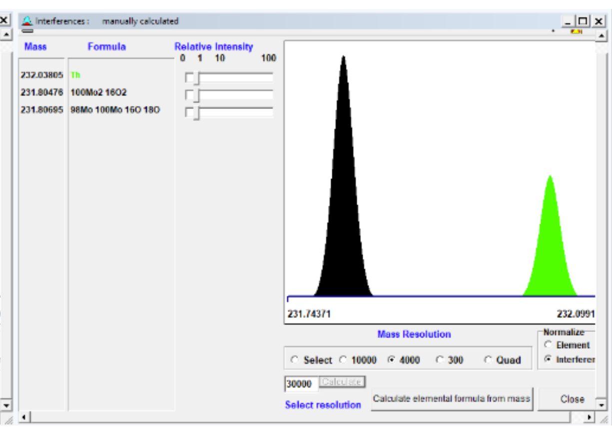




Characterization by and HR-ICP-MS

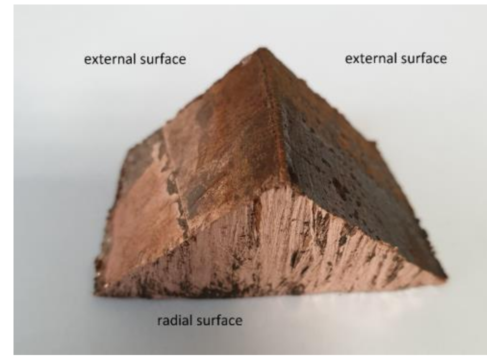
- Matrix extraction to eliminate copper
- Reduce of interferences
- Use of low and medium resolution
- Spike addition to estimate efficiency

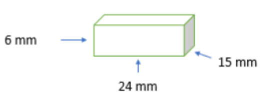




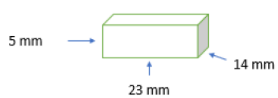
External - 1

Sample "Cu K_1"	Weight [g]	Sample treatment	Cu dissolved [g]
Starting	17.12		
After Etching n 1	14.59	4 mL H_2O + 8 mL HNO_3	2.53
After Etching n 2	11.90	4 mL H_2O + 8 mL HNO_3	2.69
After Etching n 3	9.37	4 mL H_2O + 8 mL HNO_3	2.53
After Etching n 4	6.88	4 mL H_2O + 8 mL HNO_3	2.49
After Etching n 5	4.08	4 mL H_2O + 8 mL HNO_3	2.80
After Etching n 6	1.49	4 mL H_2O + 8 mL HNO_3	1.31
After Etching n 7	0.01	4 mL H_2O + 8 mL HNO_3	1.48

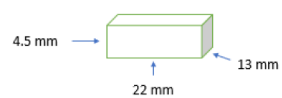




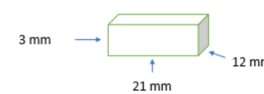
original dimension



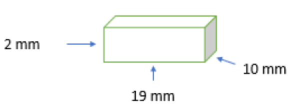
after 1st etching (surface removed 0.28 mm)



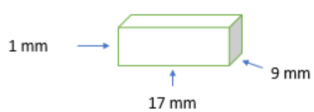
after 2nd etching (surface removed 0.34 mm)



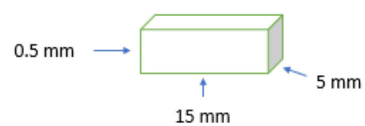
after 3rd etching (surface removed 0.40 mm)



after 4th etching (surface removed 0.56 mm)



after 5th etching (surface removed 0.86 mm)

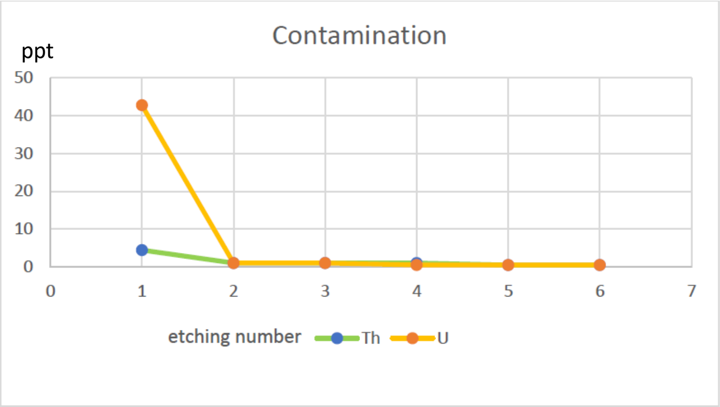


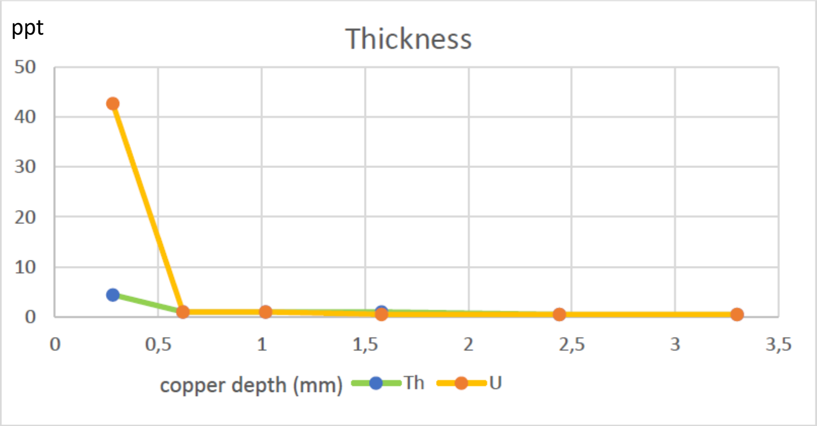
after 6th etching (surface removed 0.88 mm)

etching 7th consumed rest of material

External - 2

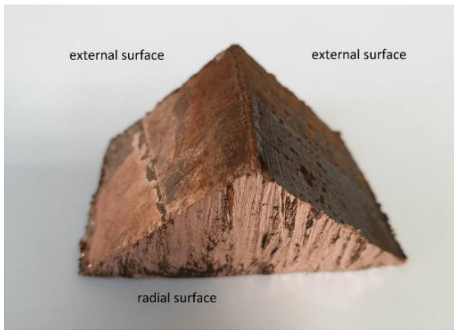
Contamination sample Cu K_A						
	Etching 1	Etching 2	Etching 3	Etching 4	Etching 5	Etching 6
	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]
Th	4.44 ± 1.33	< 1	< 1	< 0.5	< 0.4	< 0.4
U	42.73 ± 12.82	< 1	< 0.5	< 0.5	< 0.5	< 0.5



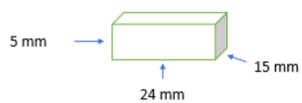


- Contaminations are on surface
- Clear decrease of impurities after 1st etching
- Acceptable values are reached by removal of 0.5 – 0.7 mm

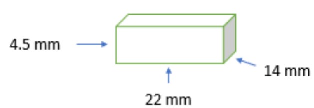
Internal - 1



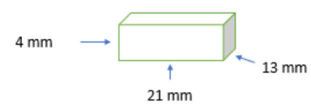
Sample "Cu K_A"	Weight [g]	Sample treatment	Cu dissolved [g]
Starting	16.17		
After Etching n 1	13.67	4 mL H_2O + 8 mL HNO_3	2.50
After Etching n 2	11.04	4 mL H_2O + 8 mL HNO_3	2.63
After Etching n 3	8.41	4 mL H_2O + 8 mL HNO_3	2.63
After Etching n 4	5.73	4 mL H_2O + 8 mL HNO_3	2.68
After Etching n 5	3.09	4 mL H_2O + 8 mL HNO_3	2.64
After Etching n 6	0.71	4 mL H_2O + 8 mL HNO_3	2.38
After Etching n 7	0.01	4 mL H_2O + 8 mL HNO_3	0.7



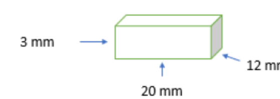
original dimension



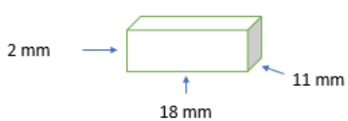
after 1st etching (surface removed 0.30 mm)



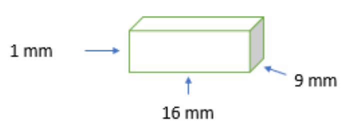
after 2nd etching (surface removed 0.35 mm)



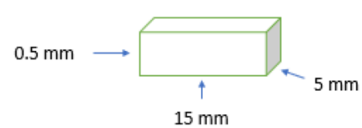
after 3rd etching (surface removed 0.43 mm)



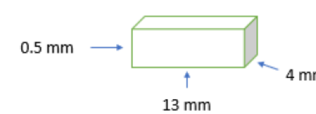
after 4th etching (surface removed 0.59 mm)



after 5th etching (surface removed 0.86 mm)



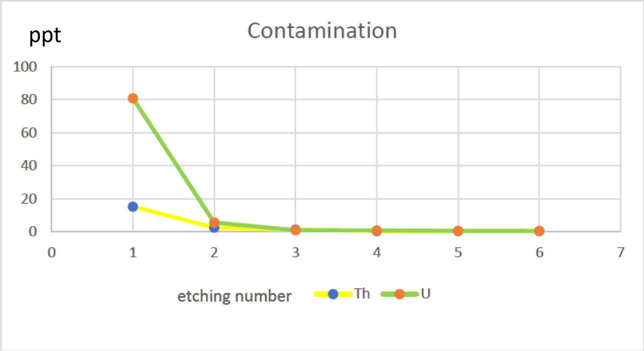
after 6th etching (surface removed 2.23mm)

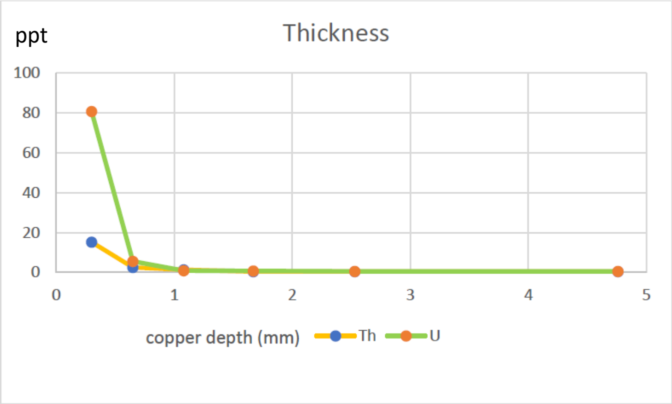


etching 7th consumed rest of material

Internal - 2

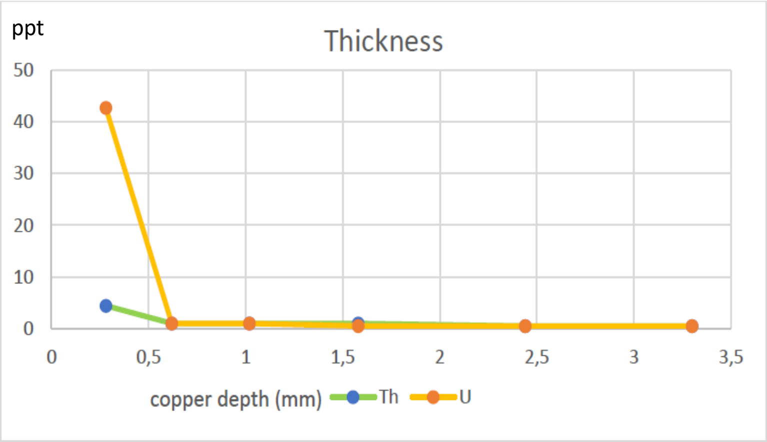
Contamination sample Cu K_A						
	Etching 1	**Etching 2**	**Etching 3**	**Etching 4**	**Etching 5**	**Etching 6**
	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]	[pg * g^{-1}]
Th	15.24 ± 4.57	2.50 ± 0.75	1.35 ± 0.41	< 0.5	< 0.4	< 0.4
U	80.85 ± 24.26	5.60 ± 1.68	0.87 ± 0.26	0.78 ± 0.23	0.59 ± 0.18	< 0.5





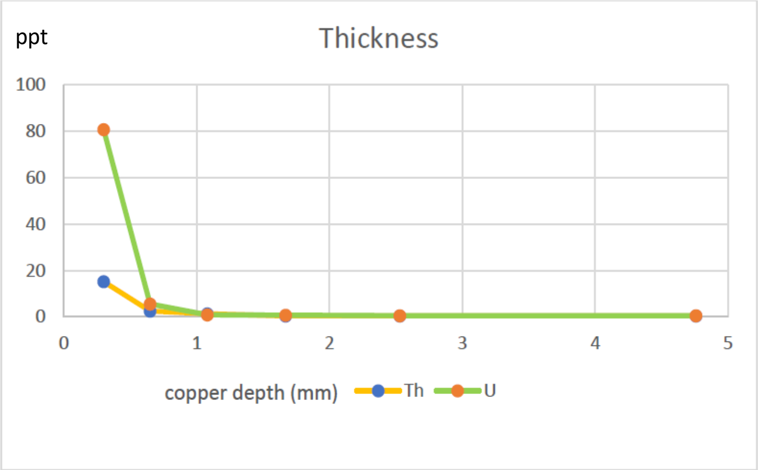
- Contaminations are on surface
- Clear decrease of impurities after 1st etching
- Acceptable values are reached by removal of 0.5 – 0.7 mm

Internal vs External



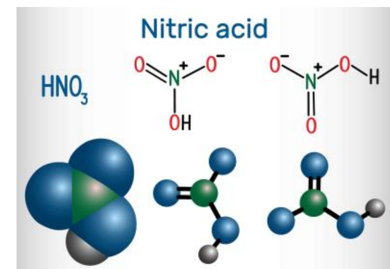
- Similar behaviour for external and internal surface
- Contaminations coming from melting

- Contaminations are on surface
- Clear decrease of impurities after 1st etching
- Acceptable values are reached by removal of 0.5 – 0.7 mm



Kokille - 1

- Container where copper is poured after melting
- Carbonaceous compound
- Thermal heating carried out by 10% HNO_3



Kokille - 2

Sample	Th	U
	$ng*g^{-1}$	$ng*g^{-1}$
Surface of Kokille "probe 10"	143 ± 40	61 ± 18

- Concentration of Th and U on surface
- Diffusion of impurities into Cu
- Th and U remains in 0.5 mm from walls of kokille

- Sensitive difference between copper and kokille
- High temperature needed for melting process doesn't contimante copper

Conclusions

- Low detection limits have been reached in Cu samples by study carried out on column resins, material mass, loaded volumes, selection of ammoium oxalate solution
- Washing columns has been improved through alternate rinse cycles
- Development of new acquisition method has been improved quantification of results and determination of detection limits
- Preliminary sample treatment was fundamental to perform ICP-MS measurements to avoid risk of contamination
- Next characterizions performed by laser ablation system

Acknowledgements

- Gran Sasso National Laboratories
- LNGS Chemistry Service
- COSINUS LEGEND CRESST, collaborations
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- Aurubis
- Italian Chemical Society
- Young Italian Spectrometrists

Thanks to

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Istituto Nazionale di Fisica Nucleare
Laboratori Nazionali del Gran Sasso
Servizio di Chimica e Impianti Chimici

TUM
Department of Physics
Technical University Munich

MAX-PLANCK-GESELLSCHAFT

Thank you all for your attention

LEGEND
Large Enriched
Germanium Experiment
for Neutrinoless ββ Decay

COSINUS

CRESST
Cryogenic **Rare Event Search**
with Superconducting Thermometers