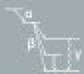


Surface Cleaning Techniques

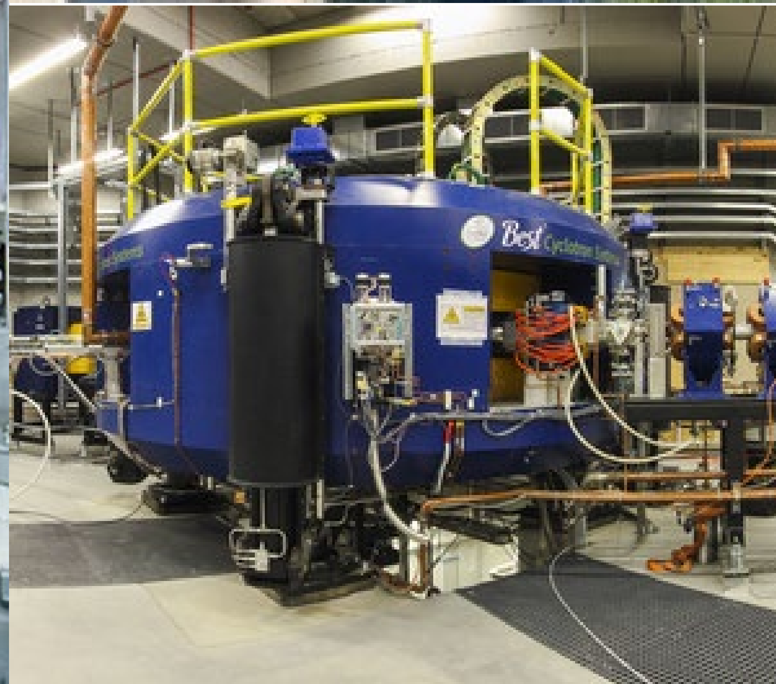
The Experience of LNL Surface Treatments Team in the framework of CUORE-CUPID and Darkside Collaborations

Oscar Azzolini

INFN-LNL

INFN Laboratori Nazionali di Legnaro

INFN
LNL



Surface Contamination vs Bulk Contamination

- ✓ Wrong Exposure
- ✓ Wrong Machining
- ✓ Wrong Manipulation

Protocols of
Cleaning,
Manipulation,
Transport,
Storing

PROBLEM SOLVED!

- ✓ Wrong Production

INFN-LNL for CUORE Collaboration

The Ultra-Cleaning Protocol (TECM: Tumling + Electropolishing + Chemical etching+ Magnetron sputteting) consists of 58 different steps

The total number of Copper components (frames, pillars, etc.) cleaned is around 8100

The Ultra-Cleaning Protocol for CUORE copper components

Optical Inspection → Tumbling → Electro polishing → Chemical Etching → Plasma Cleaning → Delivery

- Tumbling: Media check; Tumblers maintaining
- Electro polishing / Chemical Etching: Chemical purchase; Chemicals storage; Wasting exhaust chemicals; Wasting exhaust rinsing water
- Plasma Cleaning: Pump maintaining; Ar cylinder storage; Vacuum system maintaince

	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
h/day					
D=	6	5	8	8	8
R=	8	8	8	8	5
K=	0	0	8	0	8
A=	1	3	5	3	4

De Biasi (D), Rampazzo (R), Keppel (K), Azzolini (A)

Hours: 8 9 10 11 12 13 14 15 16 17 18 19 20

pre cleaning, tumbling: D D D D D D ... D D

electropolishing: R R R R R R R R / D D D R R R R R R R R, A A A

chemical etching: D D D D D D D D R R R R R, R R R

electropolishing: D D D R R R R R R R R, A A A

chemical etching: D D D D D D, R R R R R

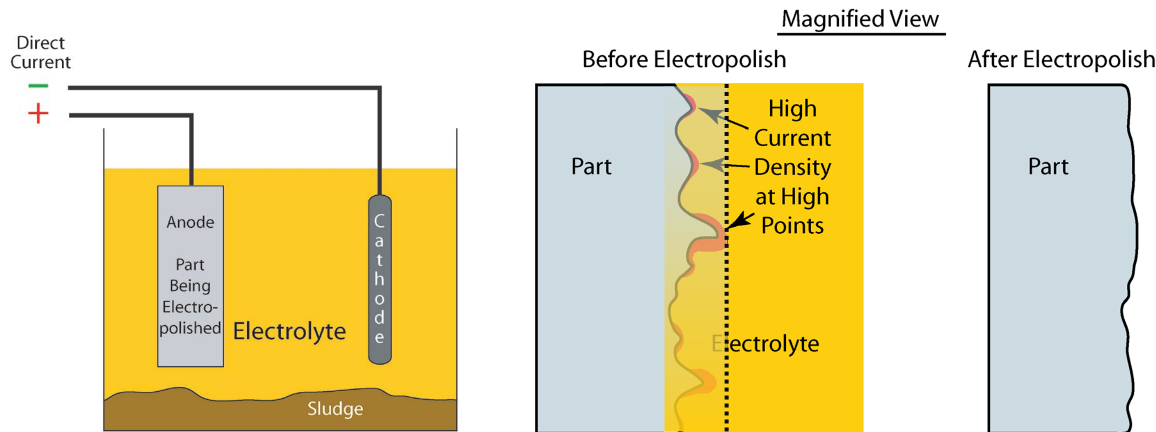
plasma: A ... K K K K K K K K, A A A A

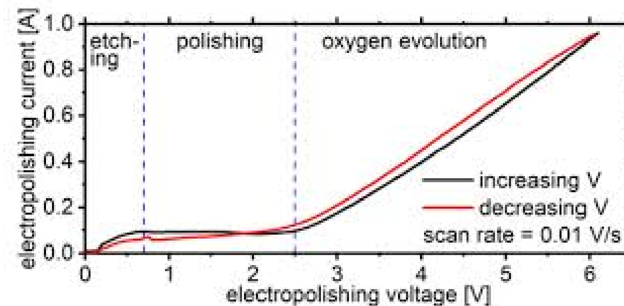
plasma: A ... K K K K K K K K, A A A A

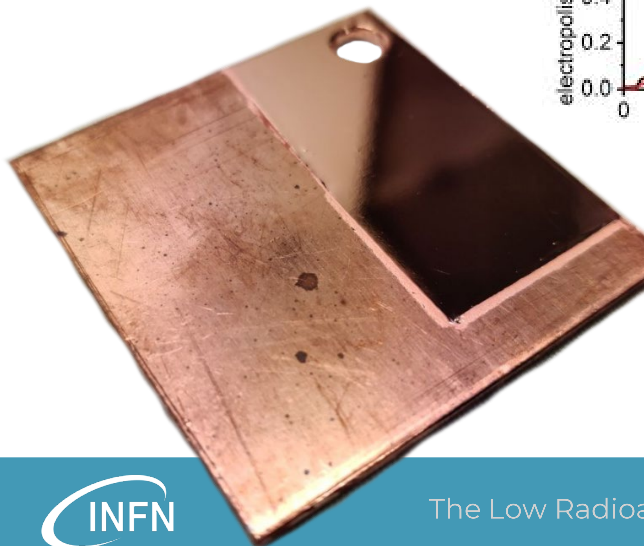
Mechanical Polishing: Tumbling

(Al_2O_3 powder in epoxy resin matrix)
Thickness removed: 1um

EP Process and Setup





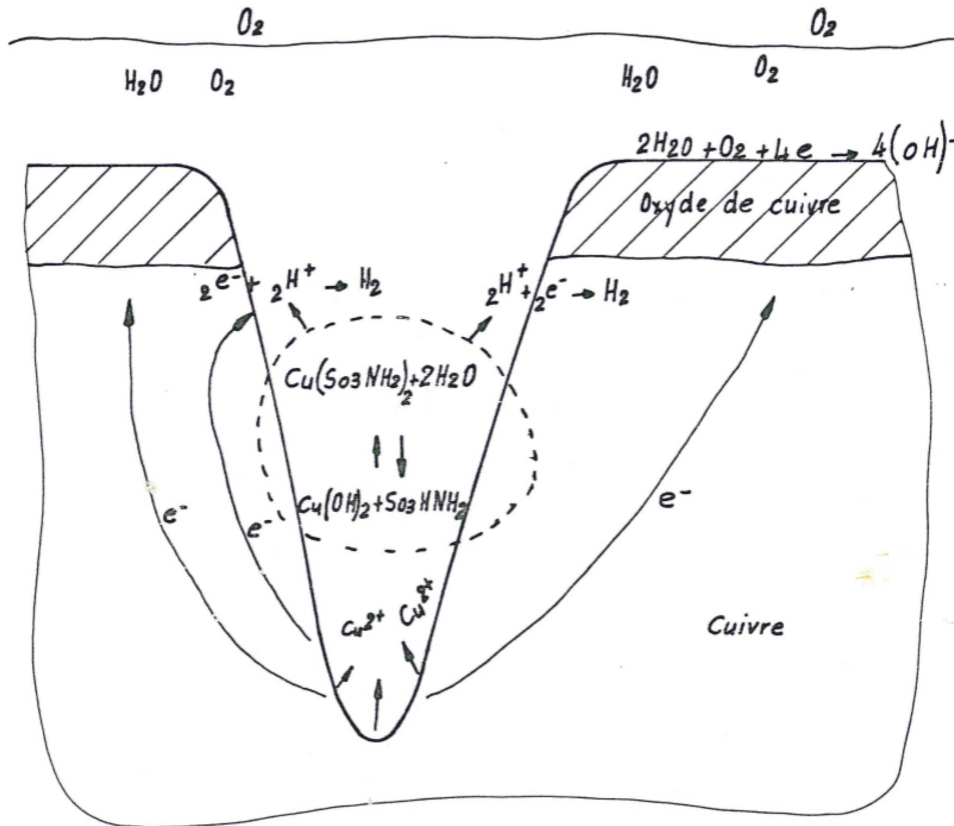


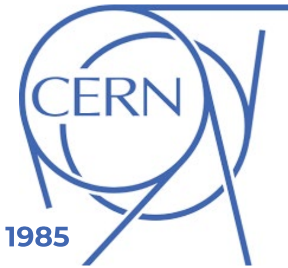
Procedure:

1. The Teflon® protections are fixed to the copper pieces (to protect sensible zones, i.e. threads, holes, etc.);
2. The copper components are connected to the positive terminal of a DC power supply;
3. The cathode is connected to the negative terminal of a DC power supply;
4. The tank is filled with electrochemical solution (**99% butanol – 85% phosphoric acid in 2:3 volumetric ratio**) through a pumping system;
5. The copper components are submerged in the electrochemical bath;
6. The specific electropolishing voltage is applied (plateau of the electropolishing curve);
7. The stirring of the EP solution is applied if necessary;
8. The charge [e] required to **remove from 5 to 100 µm of thickness** is calculated to determine the process time;
9. The copper components are extracted from the electropolishing bath, maintaining the cathode voltage applied, to prevent 210Po re-deposition;

The Electropolishing
dedicated EP system

Chemical Etching: SUBU5



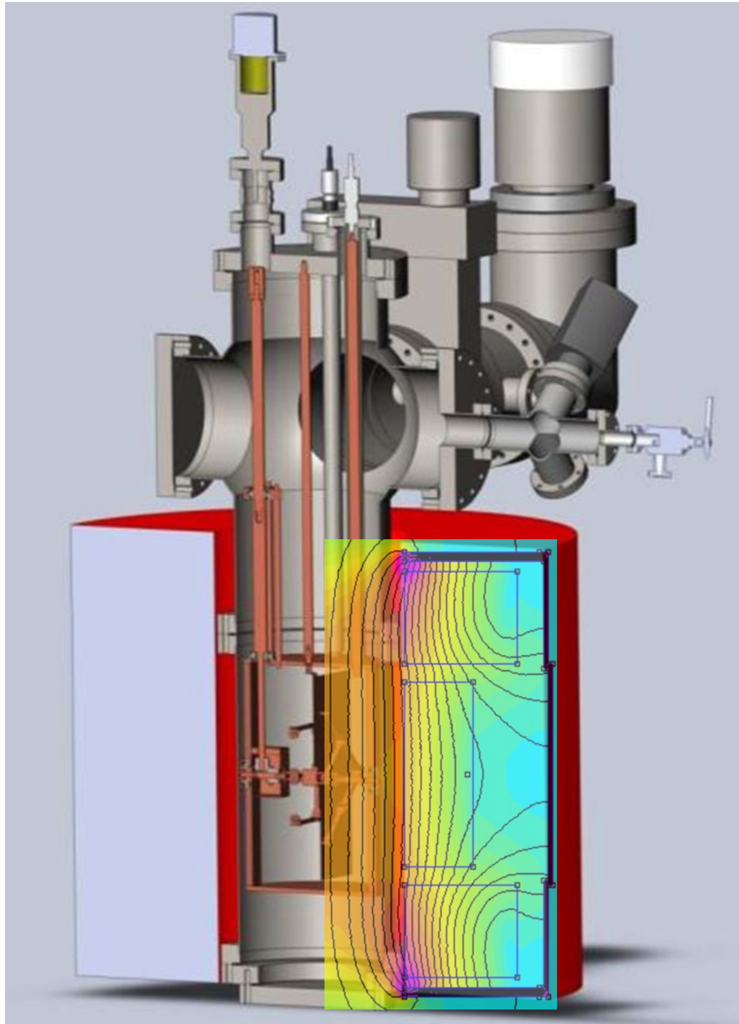


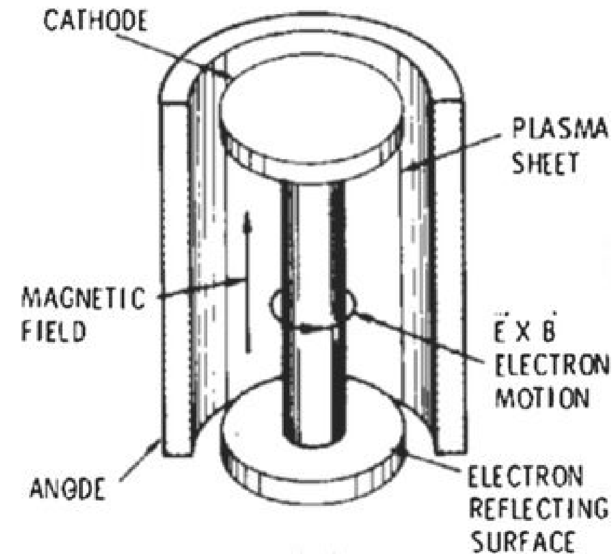
Internal Report 1985

Procedure:
1.The deionized water is heated at (72±2) °C;
2.The SUBU solution is prepared first introducing the salts (sulfamic acid 5g/l and ammonium citrate 1g/l) and then, the liquids (30% hydrogen peroxide 50ml/l and 99% butanol 50ml/l) maintaining the final temperature in the range (72±2) °C;
3.The solution is stirred to mix all the elements of the recipe;
4.The copper components are placed inside SUBU solution for 5 minutes;
5.The sulfamic acid solution is prepared in a container of 15 [L] with a concentration of [10g/L] to perform the passivation of the copper surface after SUBU;
6.Immediately after the SUBU process, the copper pieces are passivated submerging the components in sulfamic acid bath for 5 minutes;

Chemical Reactions:
Complex formation: Cu(NH2SO3)2 + 2H2O ↔ Cu(OH)2 + 2NH3SO3
Copper dissolution: Cu+2NH3SO3 ↔ Cu(NH2SO3)2 + H2
Copper Passivation: 2 Cu + O2 → 2 CuO

Plasma Cleaning: Magnetron Sputtering

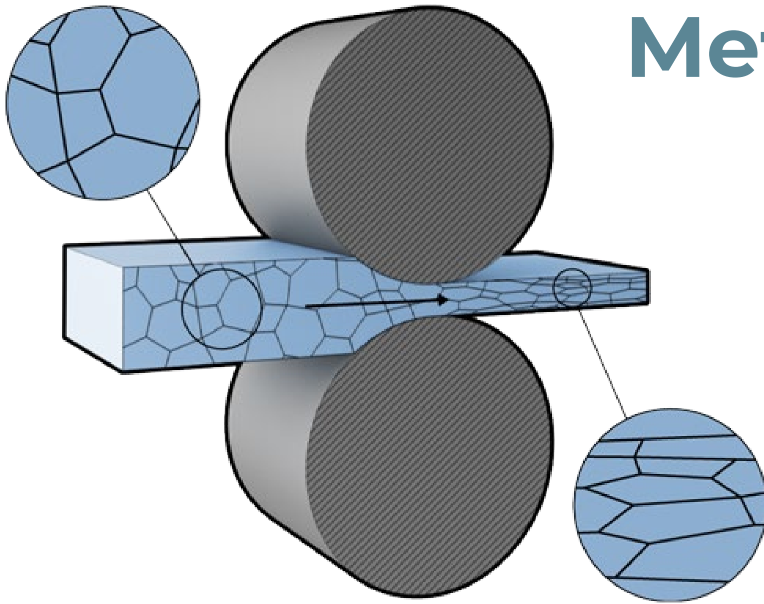


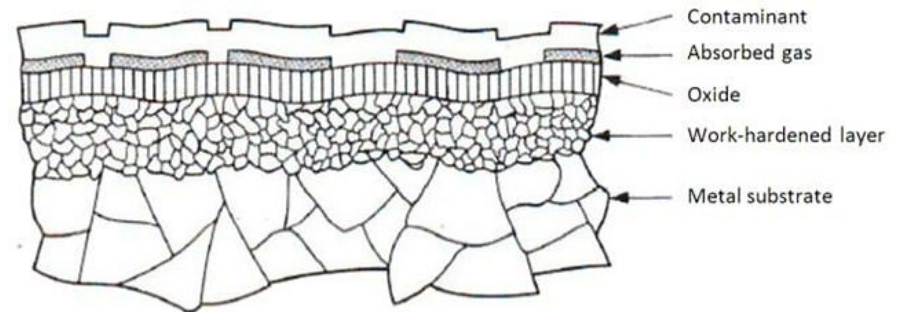


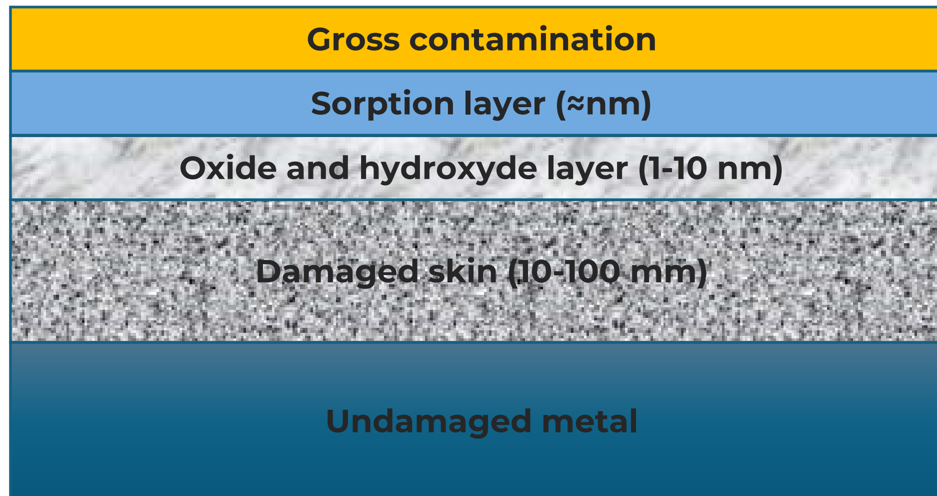
Procedure:

1. Base pressure: **10^{-8} mbar** after 24h Backing
2. Working pressure: **$8 \cdot 10^{-3}$mbar** inert Ar gas
3. Process DC power: **200W** for 15min
4. Thickness removed: **less than 1um**

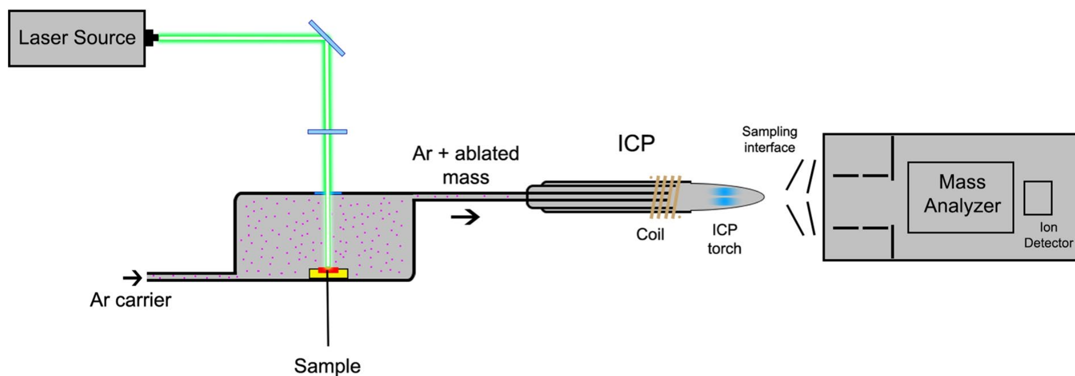
Metal Sheets Production (Cold Rolling)

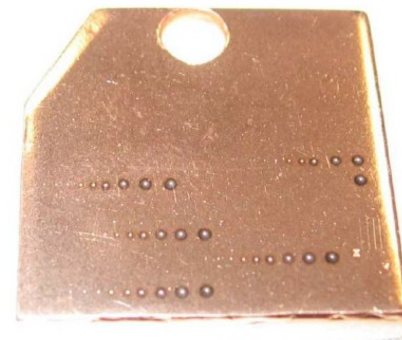


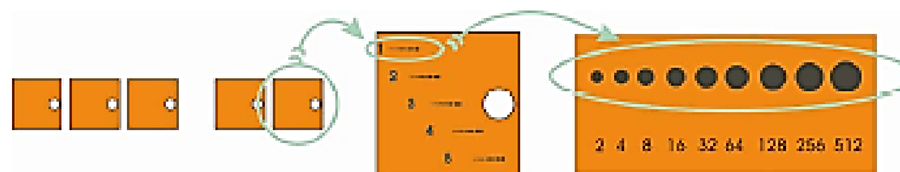


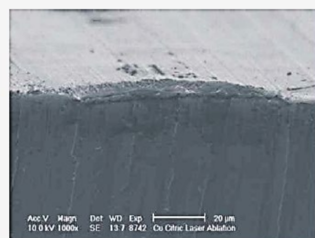


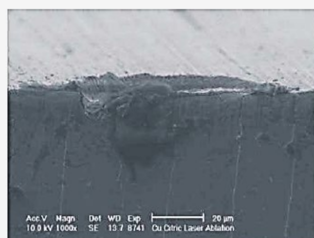
Laser Ablation-ICP-MS Depth Analysis

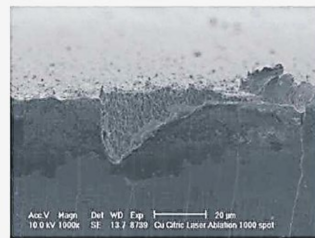


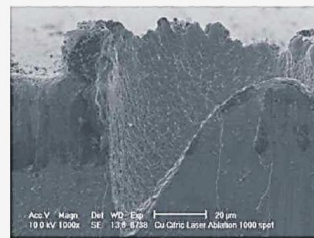





64 spot; 8,8 J/cm²; circa 3,3 µm

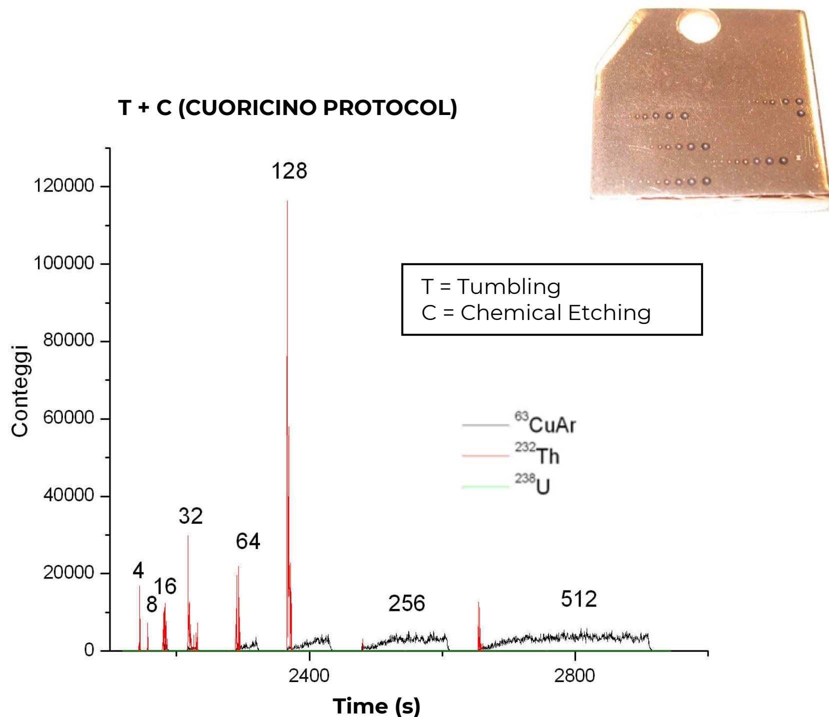

128 spot; 9 J/cm²; circa 4 µm

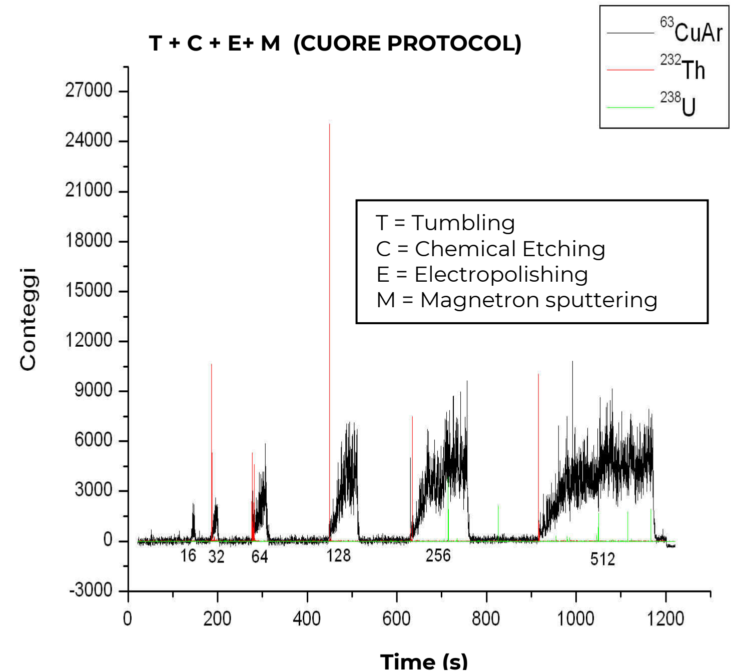

256 spot; 9 J/cm²; 16,4 µm

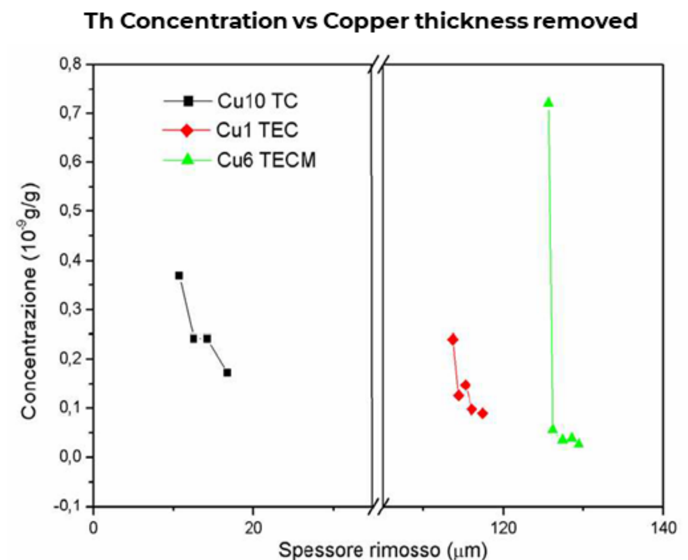

512 spot; 9 J/cm²; 63,1 µm

Spots ($9J/cm^2$)	Depth (um)
64	3,3
128	4
236	16,4
512	63,1

Laser Ablation-ICP-MS
Depth Analysis

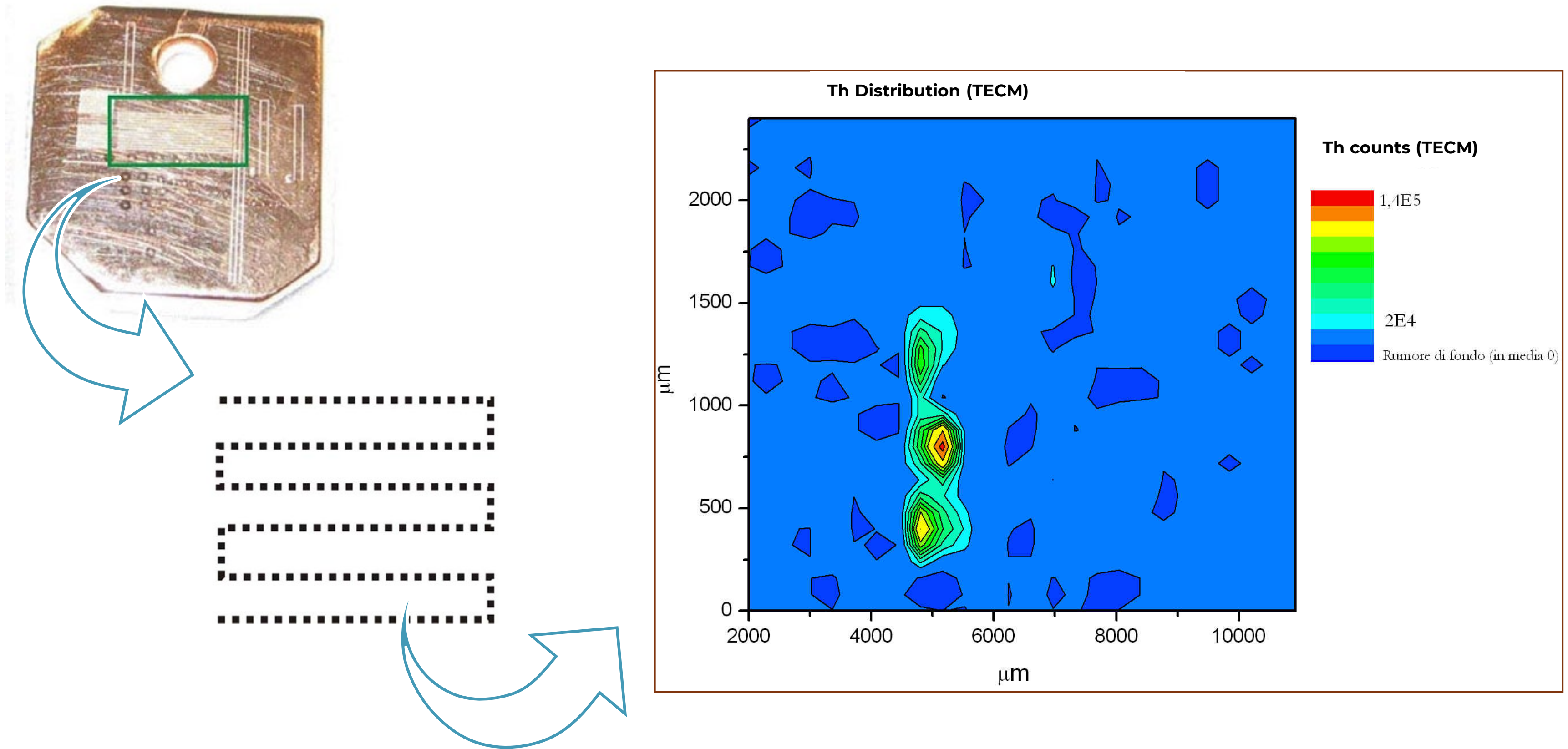






Signal from a scanning line of holes. The CuAr (black) signal is proportional to the number of spots for the single hole. Note how the Th (red) signal is only present in the first few seconds of acquisition while U is present at higher depth.

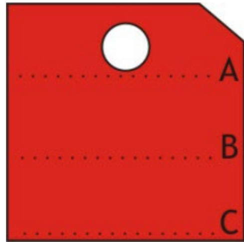
Laser Ablation-ICP-MS **Mapping Analysis**



A two-dimensional scan of 7000 x 2400 µm with a resolution of 100 x 200 µm and spots **Ø = 80 µm** was carried out on the T+C+E+M sample in order to create a two-dimensional map of the distribution of contaminants on the surface

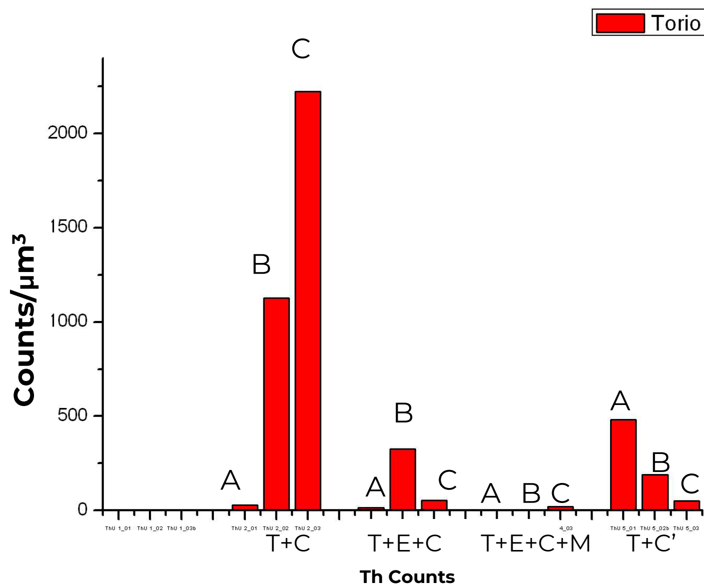
G. keppel, Surface Treatments for low background experiments, TACT2019

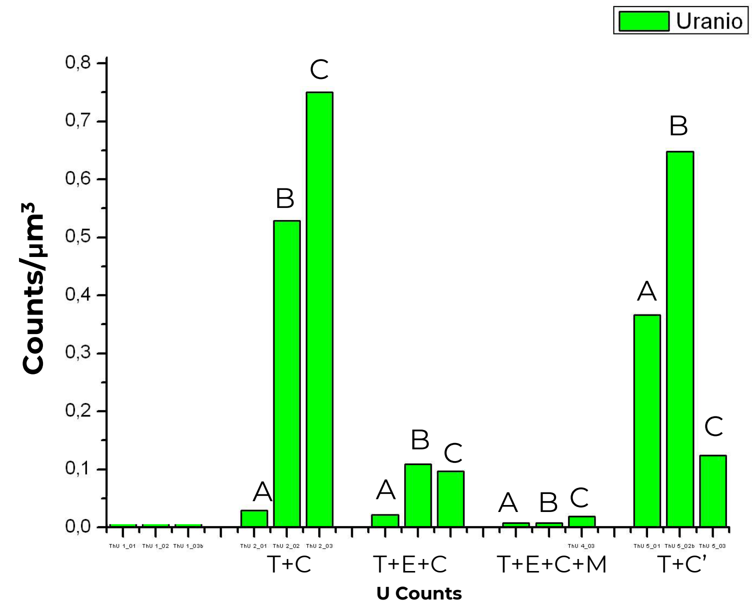
Laser Ablation-ICP-MS Machining Analysis



Series of scans taken to correlate the machining processing and residual surface contaminants.

A: drill hole
B: centre of the sample (rolling)
C: edge of the sample cutted





G. keppel, Surface Treatments for low background experiments, TACT2019

Protocol Results

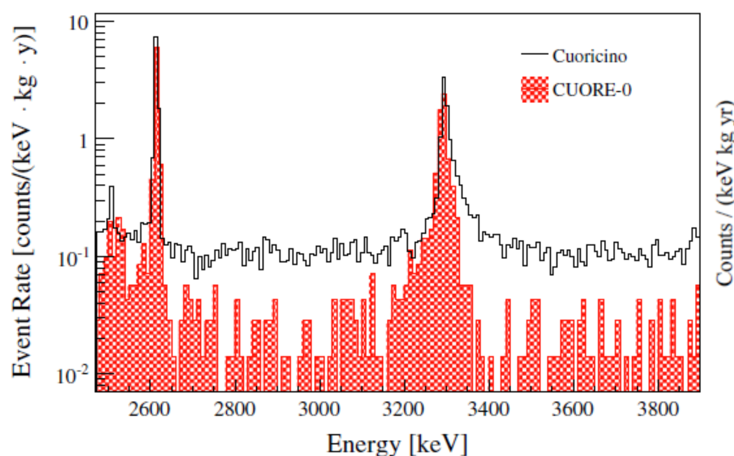
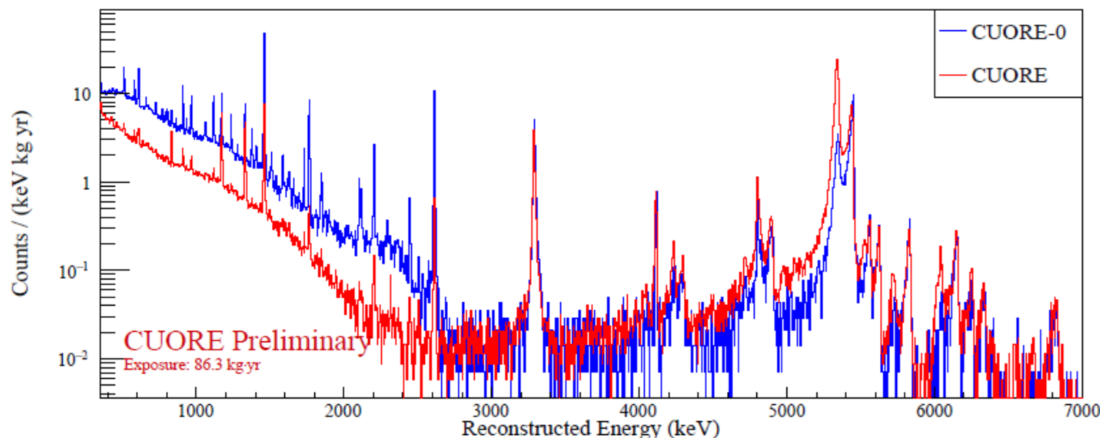


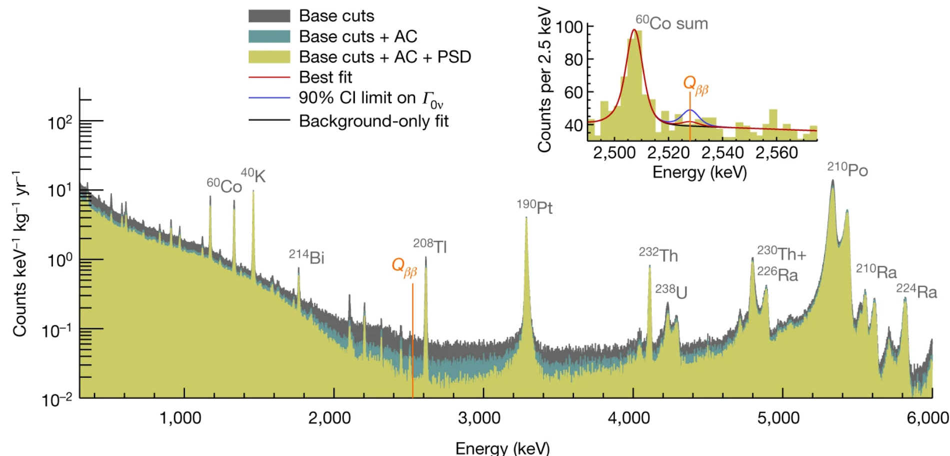
Fig. 4 Background spectrum of CUORE-0 (*red* with shades) and Cuoricino (*black*) in the region dominated by degraded α particles. The figure shows reduction of the flat background caused by degraded α particles in the energy region of [2.7–3.1] and [3.4 – 3.9] MeV

Background rate in the ROI is (0.058±0.004) counts/(keV·kg·yr) with an **improvement of factor 3** respect previous experiment

D.R. Artusa et al., Eur.Phys.J. C74 (2014) 2956



CUORE: the preliminary background rate in the ROI is **0.014±0.002 counts/(keV·kg·yr)**
CUORE-0: background rate in the ROI is **0.058±0.004 counts/(keV·kg·yr)**



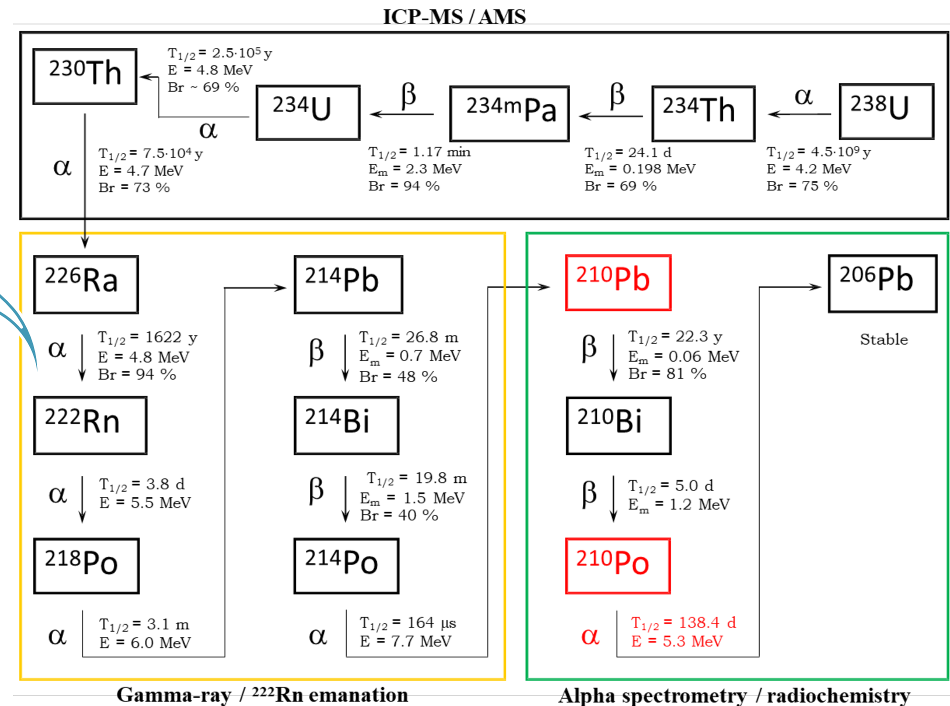
Search for Majorana neutrinos exploiting millikelvin cryogenics with CUORE, The CUORE Collaboration, *Nature* **volume 604**, pages53–58 (2022)

INFN-LNL for Darkside Materials WG

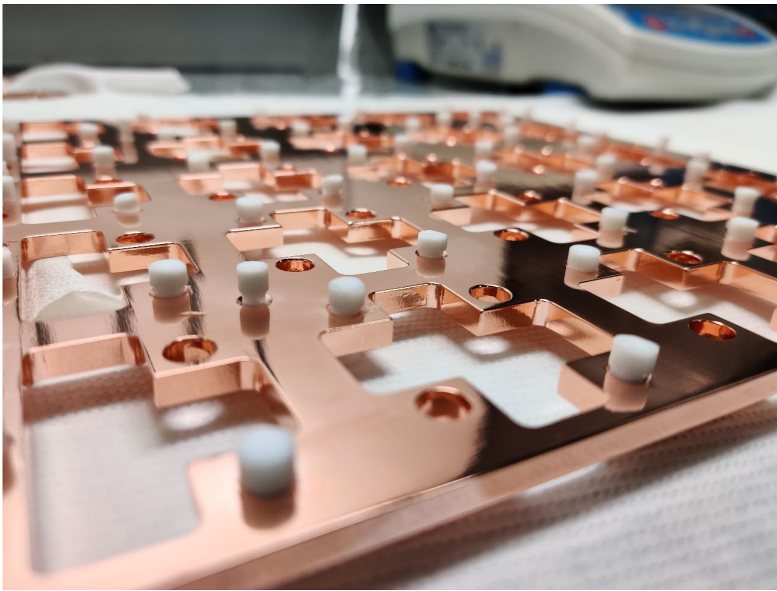
TEC Protocol

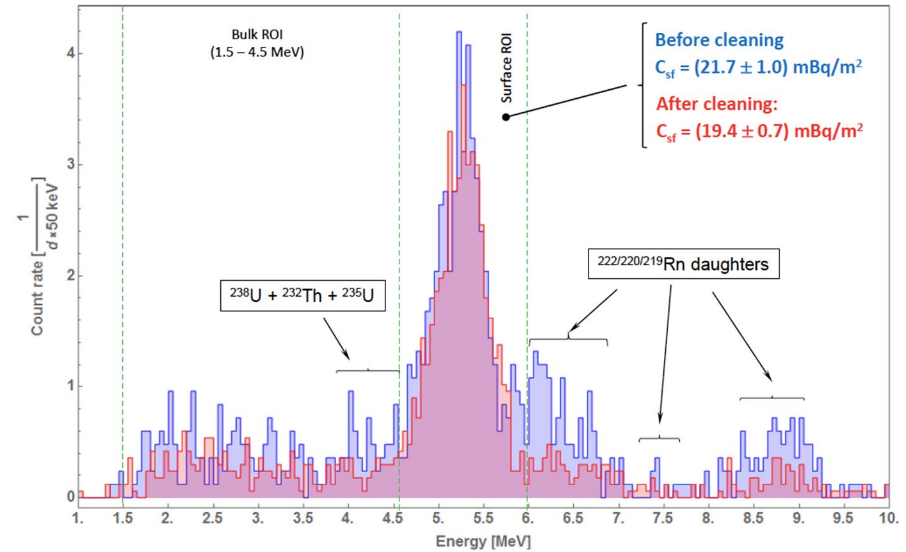
The decay products of radon can collect electrostatically on dust particles in the air.

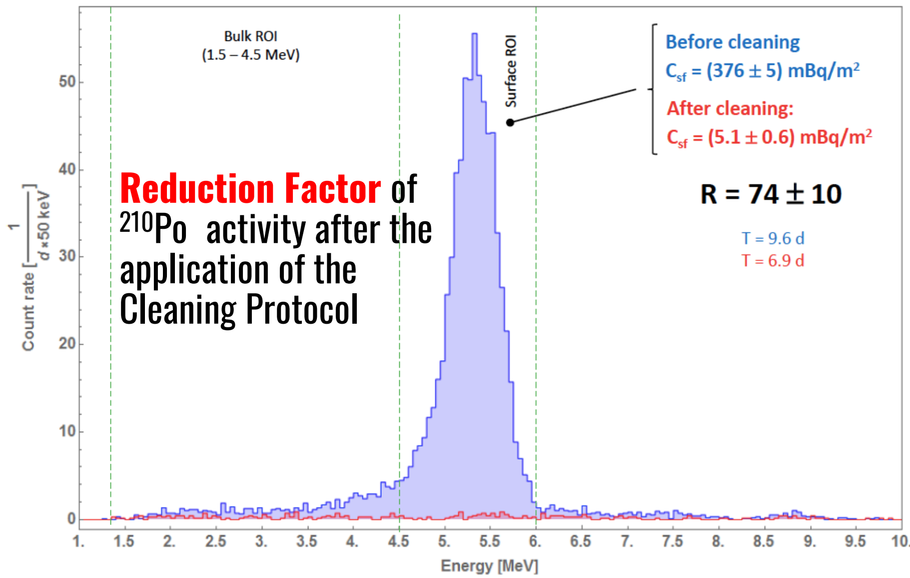
^{238}U decay chain



Copper Cleaning Protocol for DarkSide Experiment





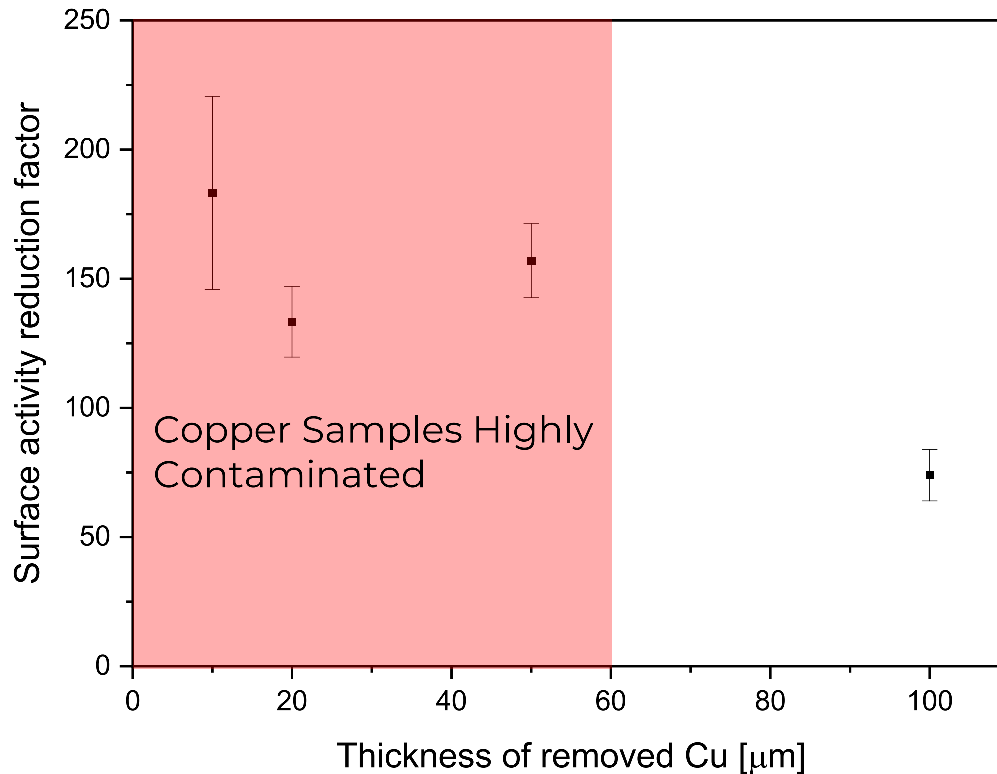


Reduction Factor of ^{210}Po activity after the application of the Cleaning Protocol

Same Processes but in a Wrong way

Copper Cleaning Protocol for DarkSide Experiment

^{210}Po vs Thickness of copper removed



^{210}Po Reduction factor removing 100-50-20-10μm we obtained similar results with XIA analysis

Innovative Treatments for Delicate Surfaces

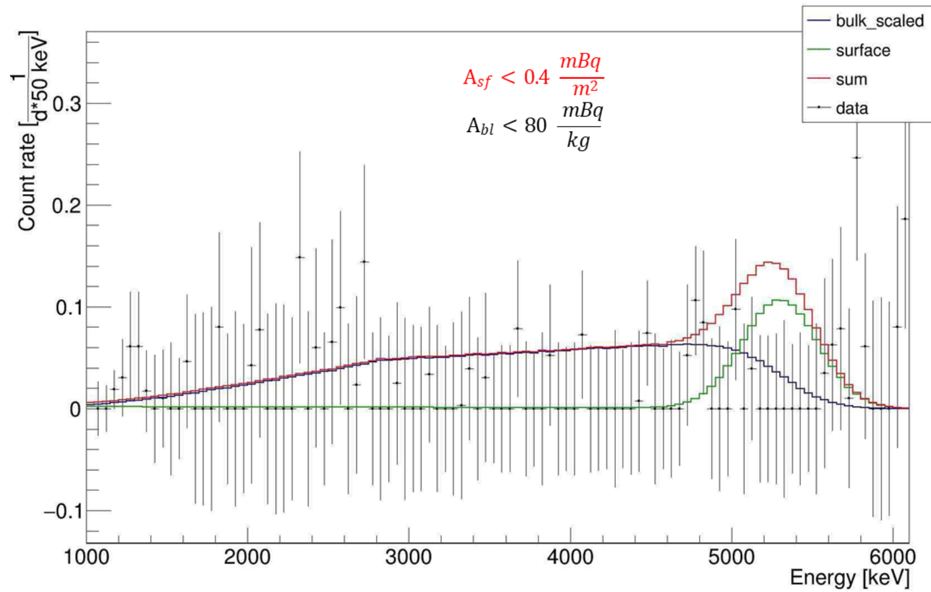
ESR Reflector Foil

Scalable Technique

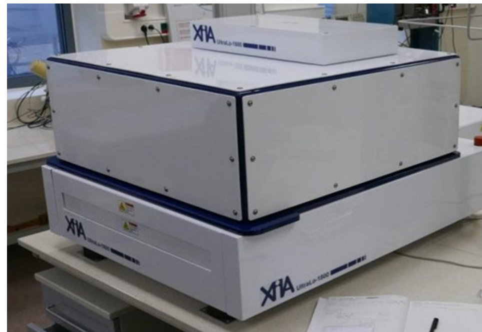
Atmospheric Plasma

Vacuum Plasma

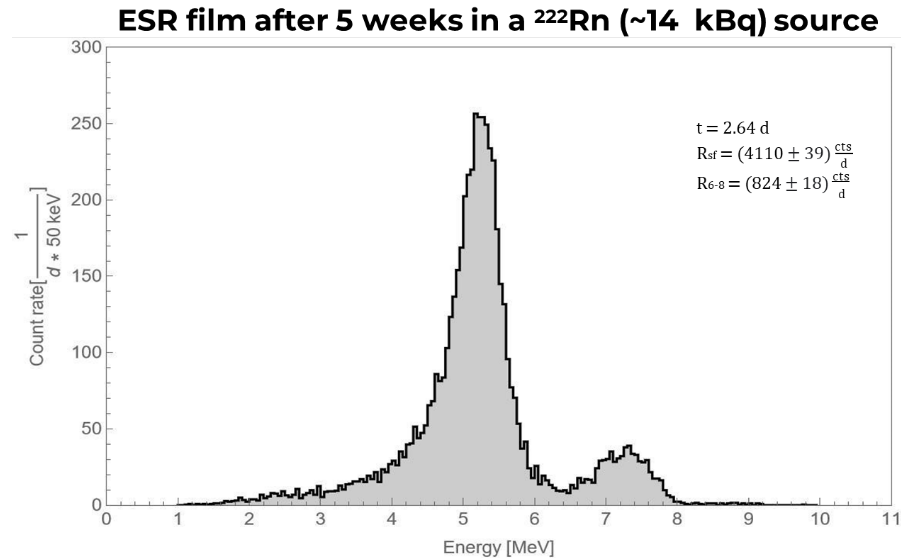
Innovative Treatments for Delicate Surfaces



Detection limit of the XIA



ESR film after 5 weeks in a ^{222}Rn (~14 kBq) source



Conventional Methods vs Plasma Cleaning

Results obtained for ESR 1 and ESR 2 sample

	^{210}Pb	
Cleaning method	Reduction factor ESR 1	Reduction factor ESR 2
Isopropanol	1.1 ± 0.1	1.4 ± 0.1
EDTA + 2% H_2O_2	1.5 ± 0.1	1.4 ± 0.1
HCl	1.0 ± 0.1	1.0 ± 0.1
HNO_3	1.1 ± 0.1	1.1 ± 0.1
Citric acid	0.8 ± 0.1	1.1 ± 0.1
EDTA	1.1 ± 0.1	0.8 ± 0.1
Acetic acid	1.0 ± 0.1	1.0 ± 0.1
MeOH	1.1 ± 0.1	1.1 ± 0.1

Results obtained for ESR 5: ^{210}Pb removal

Cleaning method	Before cleaning [cpd]	After cleaning [cpd]	Reduction factor
EDTA + 2% H_2O_2 (first cleaning)	811 ± 25	508 ± 27	1.6 ± 0.1
EDTA + 2% H_2O_2 (second cleaning)	508 ± 27	456 ± 24	1.1 ± 0.1
EDTA + 2% H_2O_2 (third cleaning)	456 ± 24	449 ± 19	1.0 ± 0.1
Total reduction	811 ± 25	449 ± 19	**1.8 ± 0.1**

^{210}Pb removal test (plasma)

Sample	Cleaning method	Reference (t_0) [Bq]	T [d]	Before cleaning (t_1) [Bq]	After cleaning [Bq]	Reduction factor
ESR 3	Vacuum Plasma	26.6 ± 1.5	22 ± 5	26.6 ± 1.5	6.2 ± 0.3	**4.3 ± 0.3**
ESR 4	Atmospheric Plasma (H)	20.5 ± 1.3	84 ± 5	20.4 ± 1.3	17.1 ± 0.7	**1.2 ± 0.1**
ESR 4	Atmoshperic Plasma (V)	17.1 ± 0.7	34 ± 5	17.1 ± 0.7	18.0 ± 0.7	**0.95 ± 0.05**
ESR 6	Vacuum Plasma	46.5 ± 1.1	23 ± 5	46.4 ± 1.1	8.2 ± 0.4	**5.6 ± 0.3**

Conclusions:

Problems of Surface Contamination?

Yes We can Help You!!

THANK YOU
FOR YOUR ATTENTION