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Removal of Long-Lived Radon Daughters From Surfaces

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Low Radioactivity Techniques 2022, 14-17 June 2022, South Dakota Mines / SURF, USA

Outline

- Introduction
- Analysis of surfaces
- Cleaning of surfaces
- Summary

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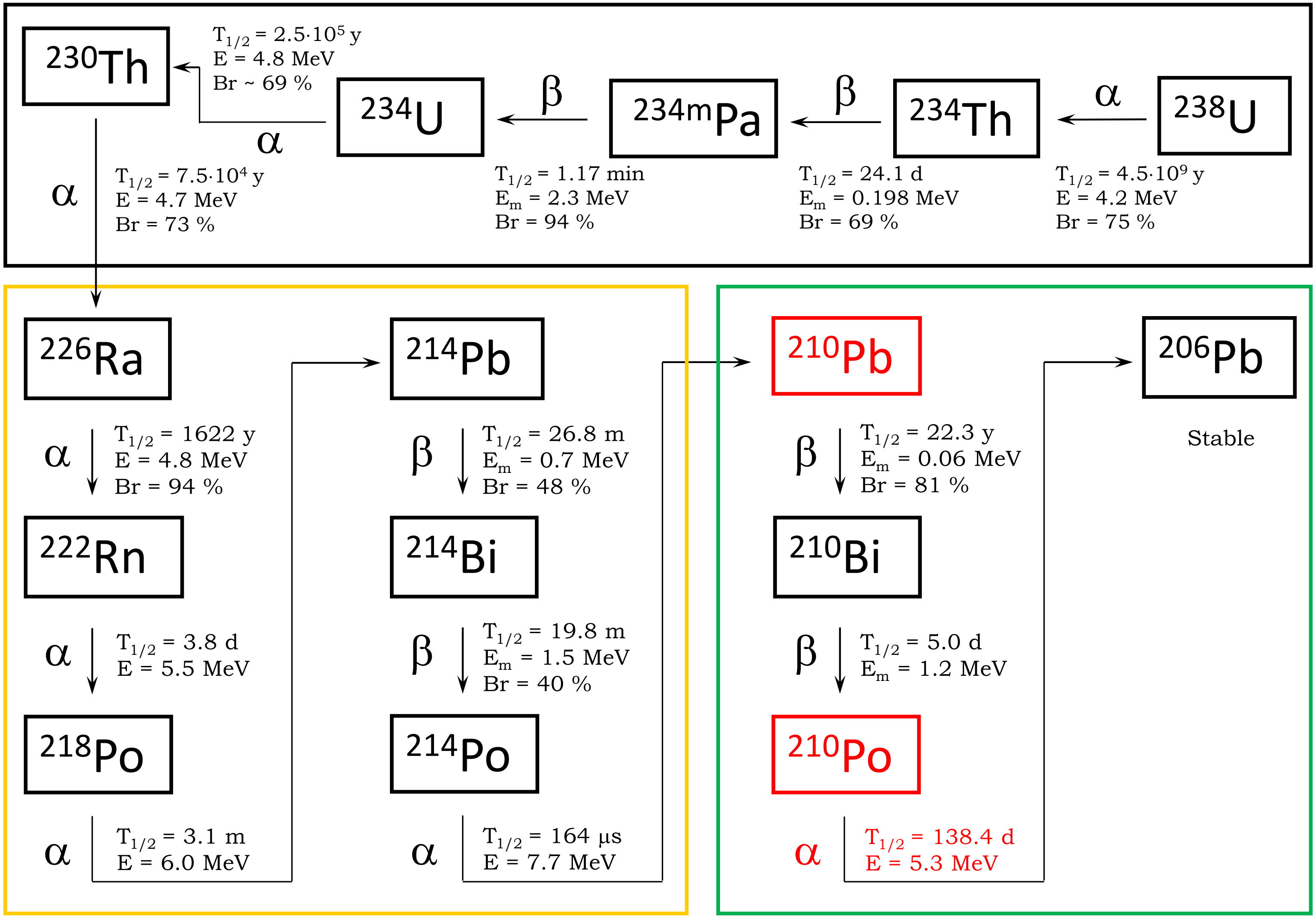
^{238}U decay chain



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Large surface alpha spectrometer

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- Surface and bulk alphas registered
- Low background, large surface alpha spectrometer
- Ar used as counting gas (3.5 l/min)
- Sample size: 43 cm × 43 cm / 30 cm diam. disc, a few mm thick
- PSD + veto guard (discrimination of background events)

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LOW RADIOACTIVITY TECHNIQUES
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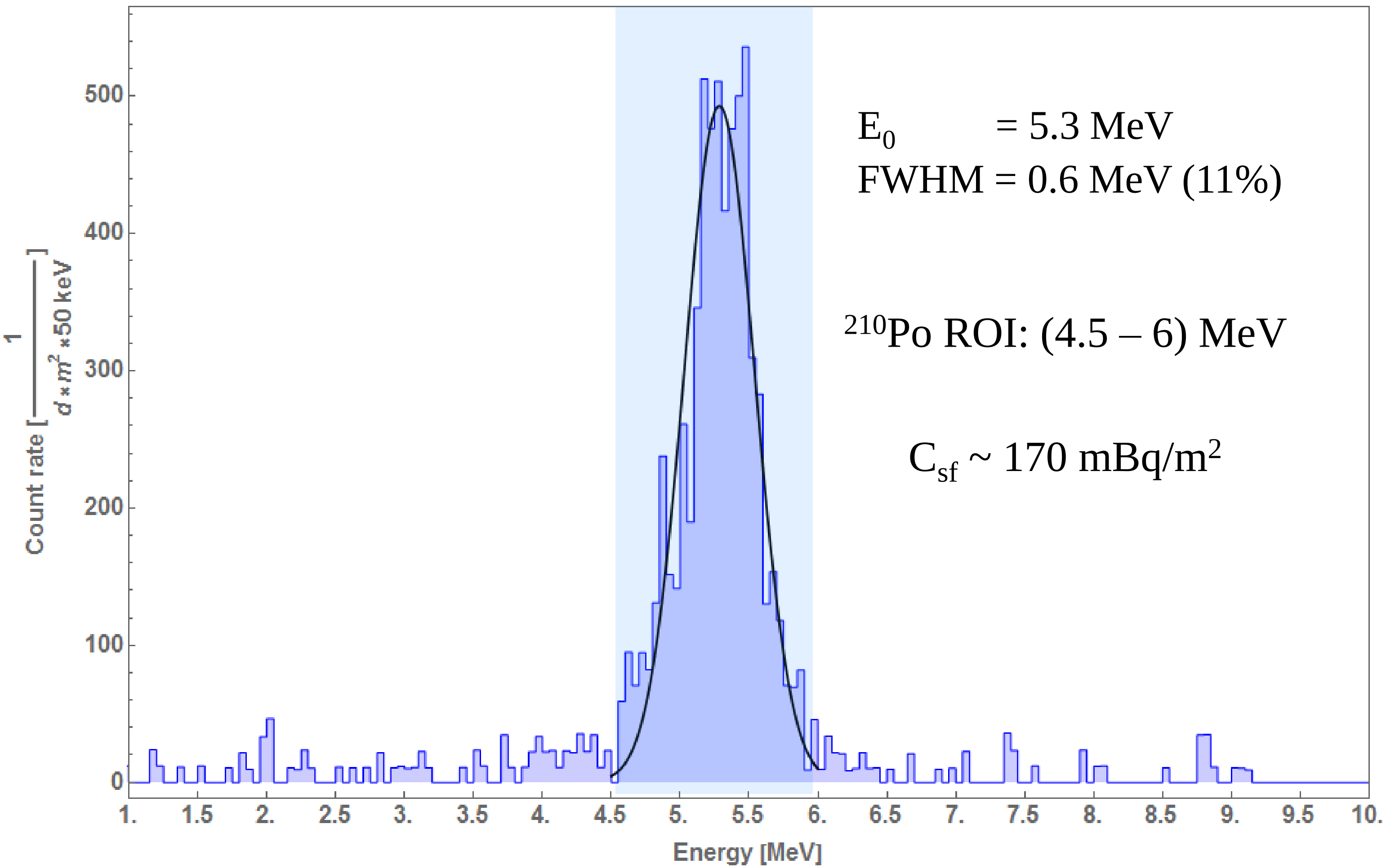
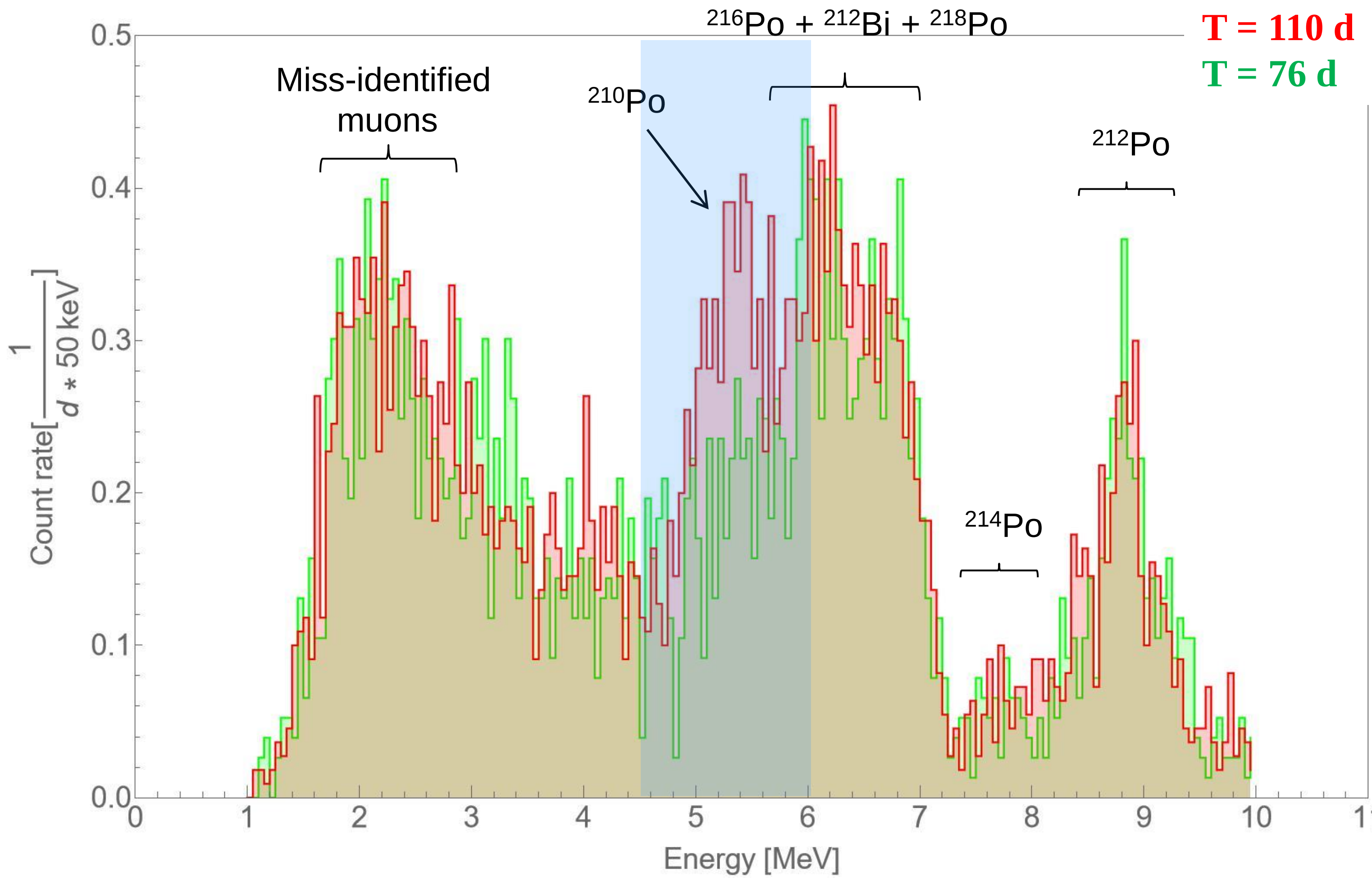
^{210}Po energy spectrum

Electrolytic Tough Pitch (ETP) Copper with surface ^{210}Po (air-born)



Background spectrum



- Tray covered with **OFCu** / **OFCu cleaned at Legnaro** → significant reduction of background below 5.3 MeV w.r.t. original steel tray
- Surface ROI: **(46.5 ± 1.6)** / **(34.8 ± 1.5)** cpd/m^2 → **DL ~ 7.5 cpd/m^2 ~ 0.1 mBq/m^2**
- Above 5.3 MeV background dominated by ^{220}Rn/^{222}Rn daughters (residual emanation from the detector components), and around 2 MeV by miss-identification of muons

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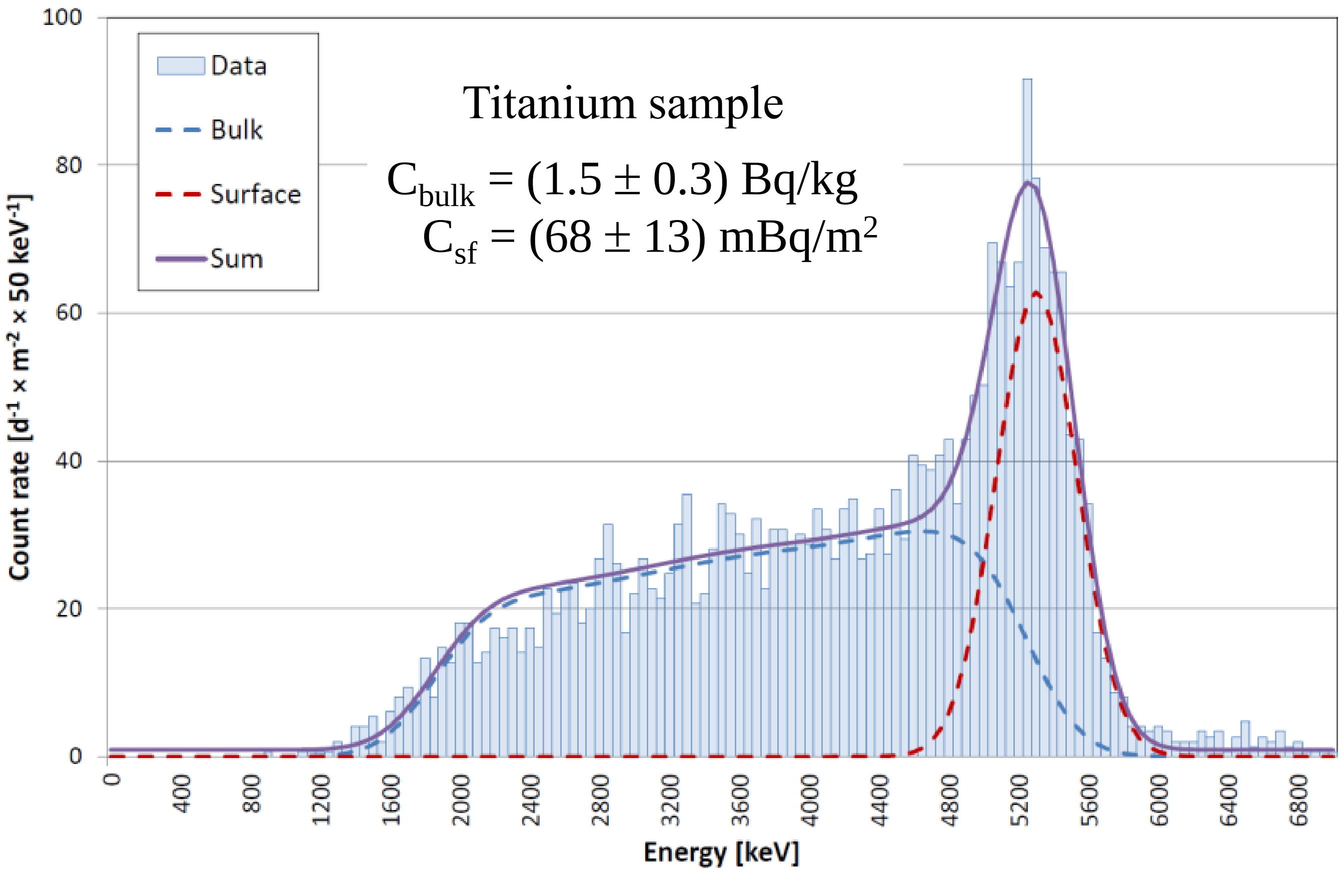
Analysis method

- First measurements of ^{210}Po in/on metals **(App. Rad. Isot. 126 (2017) 165 – 167)**
- MC used to de-convolute contributions form ^{210}Po in the bulk material and on the surface
- Sensitivities: $C_{bulk} \leq 50$ mBq/kg, $C_{sf} \leq 0.1$ mBq/m^2



Analysis of surfaces / bulk

Sample	^{210}Po surface specific activity [mBq/m^2]	^{210}Po bulk specific activity [mBq/kg]	Remarks
Fire copper	320 ± 20	9 600 ± 800 (10 000 ± 600)	XIA Rad-chem.
ETP copper	170 ± 30	75 ± 20	Not cleaned
OFHC copper	< 0.5	54 ± 18	After cleaning
Electroformed Cu (LSC)	< 1	< 51 (20 ± 4)	XIA Rad-chem.
High purity Ti	143 ± 21 68 ± 13 / 27 ± 4	1500 ± 300 **1 400 / 1 300 ± 200** (1 800 ± 200)	Not cleaned Cleaned (2017/2022) Rad-chem. (2019)
Stainless Steel 1.4301	< 0.5 5 ± 2	80 ± 20	Surface protected Surface not protected
Teflon	--	< 46	DS-50
3M ESR film	< 0.4	--	

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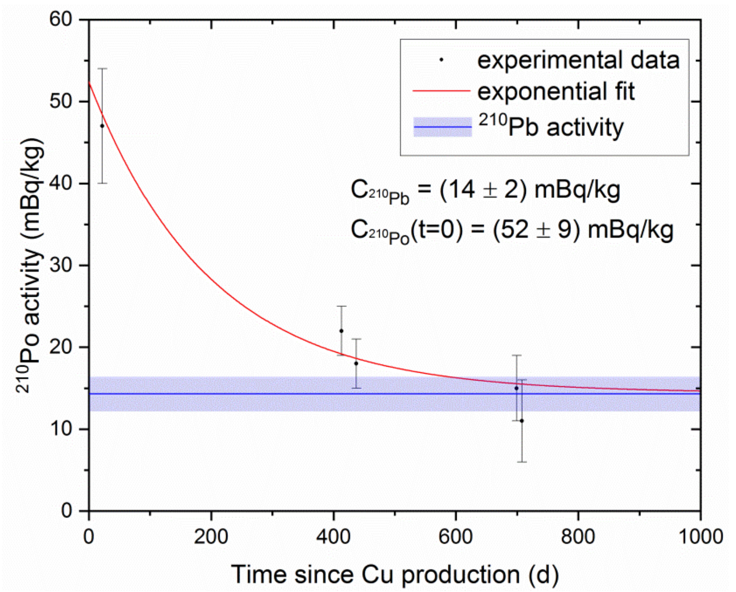
Radiochemical separation of ^{210}Po

- Dissolution of a sample, adding tracer (^{209}Po)
- Separation of Po from the matrix by an ion exchange chromatography
- Source preparation: spontaneous deposition of Po on a silver disc
- Determination of ^{210}Po/^{209}Po activities using a low background alpha spectrometer
- **Time sequence of ^{210}Po measurements → determination of ^{210}Pb; DL ~single mBq/kg**



HP Cu to be used as a shielding material for a HPGe spectrometer

Isotope	Specific activity [mBq/kg]	Comments	
^{238}U	< 0.012	< 1 ppt U, 90 % C.L.	ICP-MS
^{232}Th	< 0.004	< 1 ppt Th, 90 % C.L.	ICP-MS
^{235}U	< 0.069	90 % C.L.	HPGe
^{40}K	< 0.14	90 % C.L.	HPGe
^{60}Co	$(14 \pm 4) \cdot 10^{-3}$		HPGe
^{234}Th	< 4.2	Upper ^{238}U sub-chain, 90 % C.L.	HPGe
^{234m}Pa	< 0.45	Upper ^{238}U sub-chain, 90 % C.L.	HPGe
^{228}Th	< 0.041	90 % C.L.	HPGe
^{228}Ra	< 0.027	90 % C.L.	HPGe
^{226}Ra	$(29 \pm 8) \cdot 10^{-3}$	Clear disequilibrium between the middle and the bottom ^{238}U sub-chain	HPGe
^{210}Pb	14 ± 2		Po

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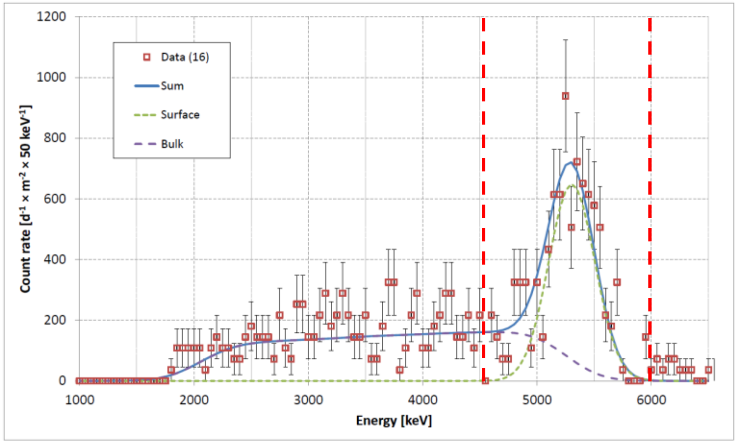
Cleaning of surfaces

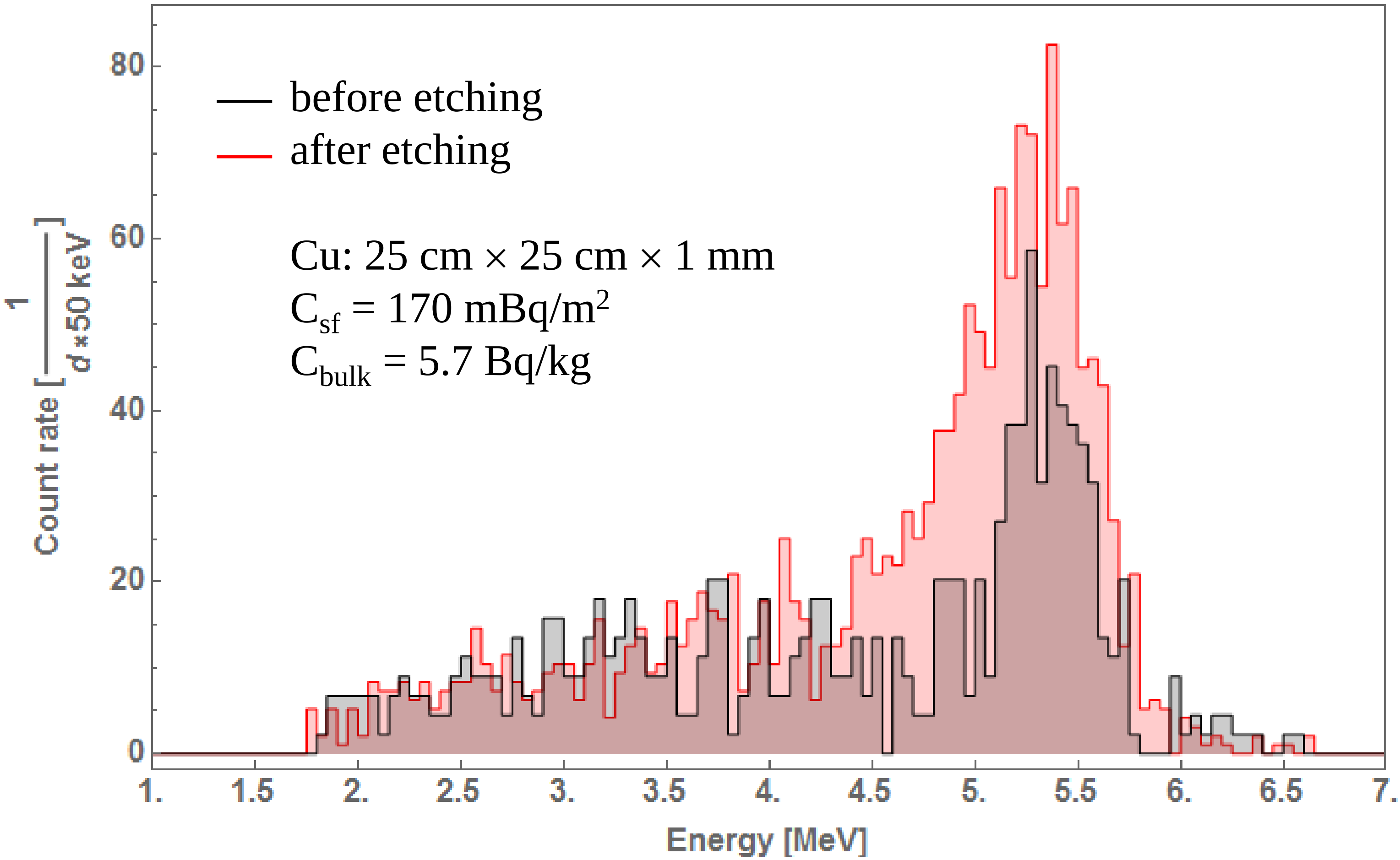
- Only ^{210}Po investigated
- Samples: sheets 43 cm × 43 cm × 1 mm (optimized for the XIA detector)
- „Natural” contamination usually low → samples contaminated with ^{210}Po by placing them in a ^{222}Rn source
- Activity of deposited ^{210}Po measured before and after the treatment → determination of the activity reduction factor
- Various surfaces (copper, stainless steel, Ti, HPGe) and methods (etching, electro-polishing, combined techniques) tested



Etching of Copper

Widely used procedure:

Etching 5 min in (1% H_2SO_4 + 3% H_2O_2), 5 min passivation in 1% citric acid



Cu sample with high bulk ^{210}Po content

Some ^{210}Po removed from the bulk (~28 mBq) re-deposited on the surface

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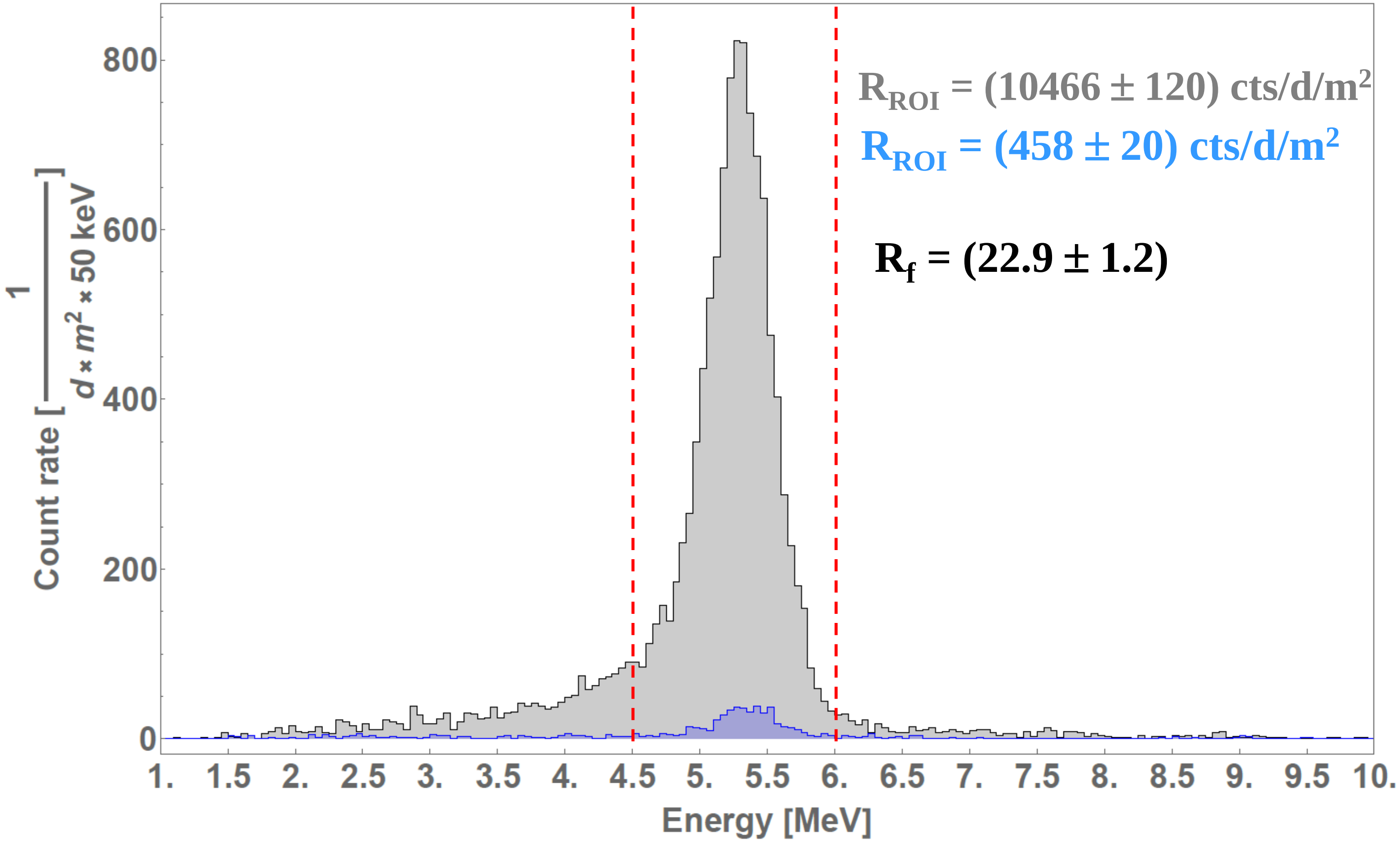
Etching of Copper

Reducing time of a single etch:

- Etching procedure: 5 x 1 min (40 s) wash with a mixture of 1% H_2SO_4 + 3% H_2O_2
- Passivation with 1% citric acid (5 min)
- Washing in high-purity deionized water (18 MΩ×cm)



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Etching of Copper

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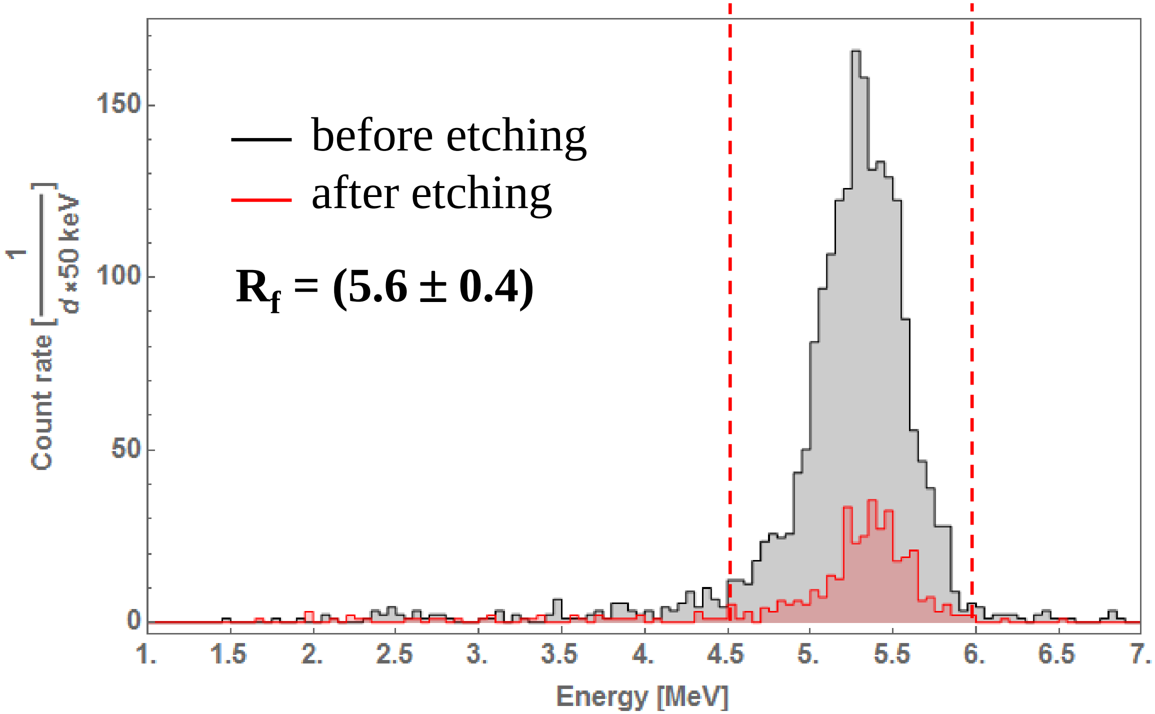
Etching in nitric acid

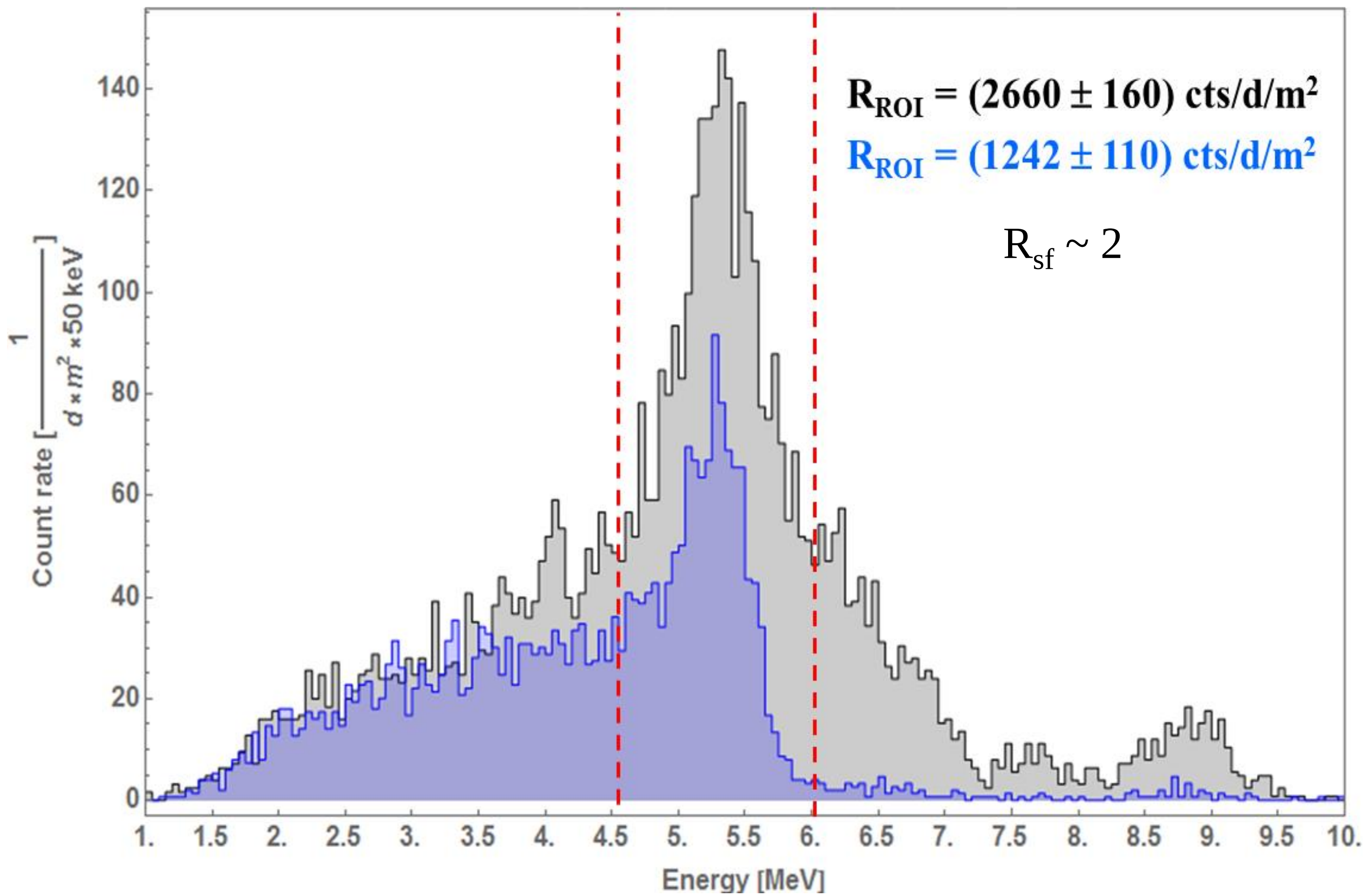
- Etching procedure: 1 run for 1 min in a mixture of 15% HNO_3 + 2% H_2O_2
- Passivation with 1% citric acid



Step	Conc. of HNO_3 [%]	Conc. of H_2O_2 [%]	^{210}Po reduction
1	15	2	5.6 ± 0.4
2	15	4	2.3 ± 0.3
3	15	7	5.0 ± 0.4

Etching of Titanium

- Ti, High Purity, Gr2
- Etching procedure: 1 run for 5 min in a mixture of 5% HF + 10% HNO_3



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Electro-polishing of Copper

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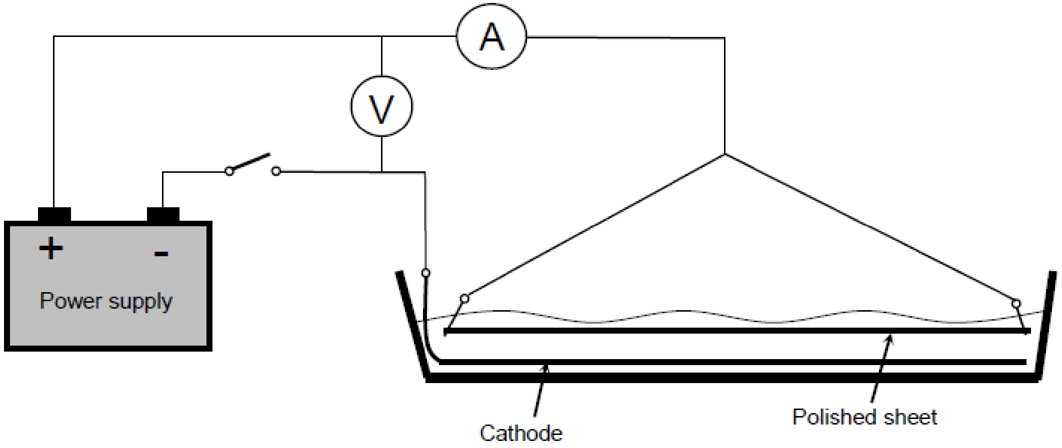

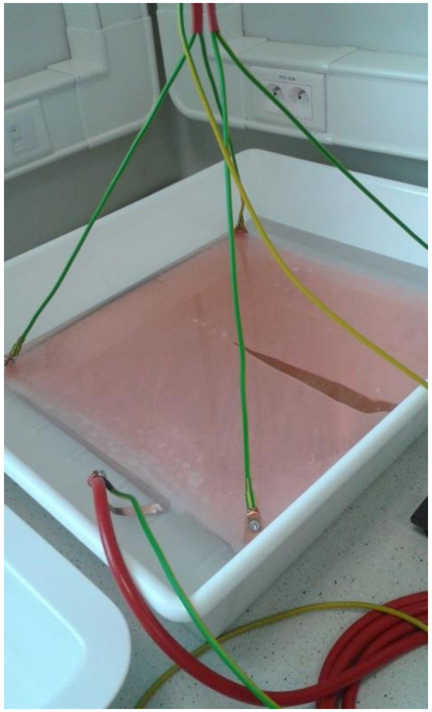

Electro-polishing of Copper

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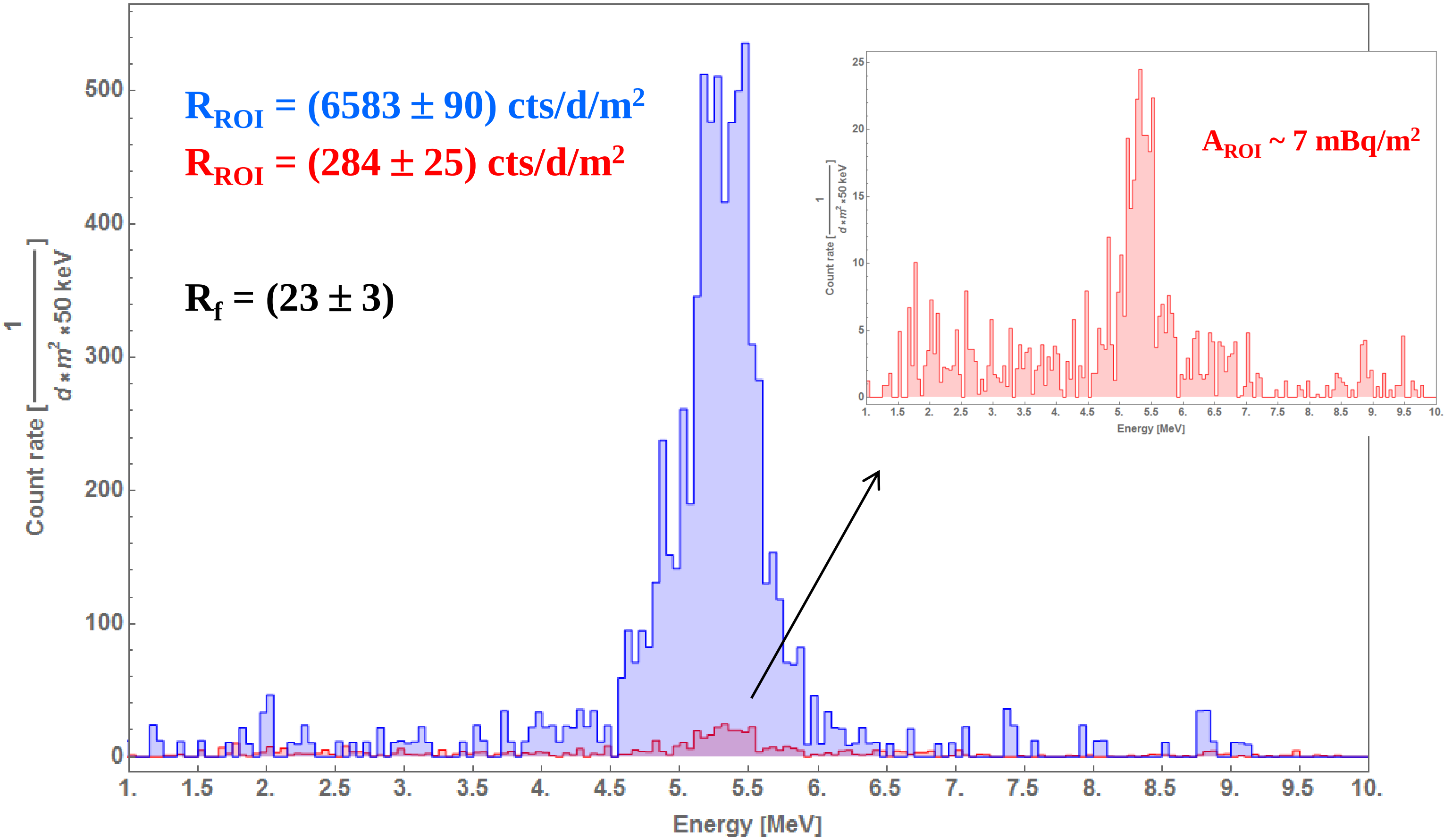
ETP copper (z4), 43 cm x 43 cm x 0.1 cm,



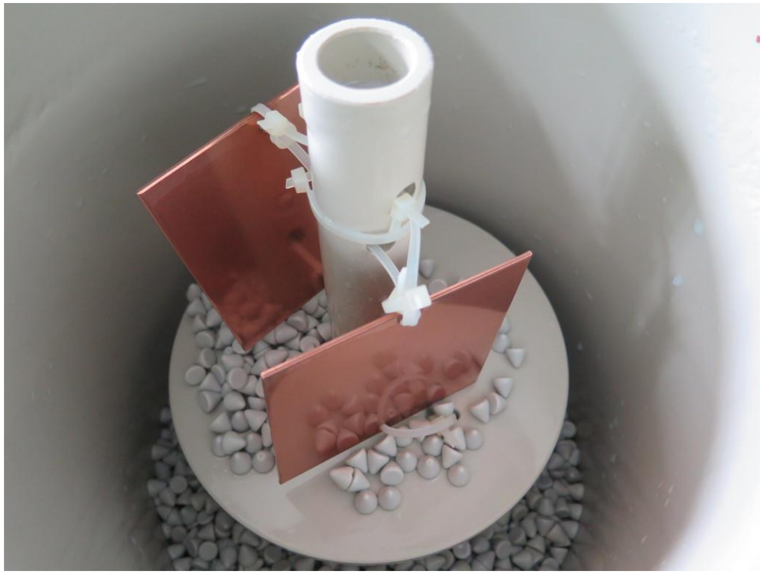
- Polishing mixture: 95% H_3PO_4 + 1% 1-butanol
- Polishing conditions: 2.5 A/dm^2, 3 V, 20 min, distance between plates: 2 cm, room temperature

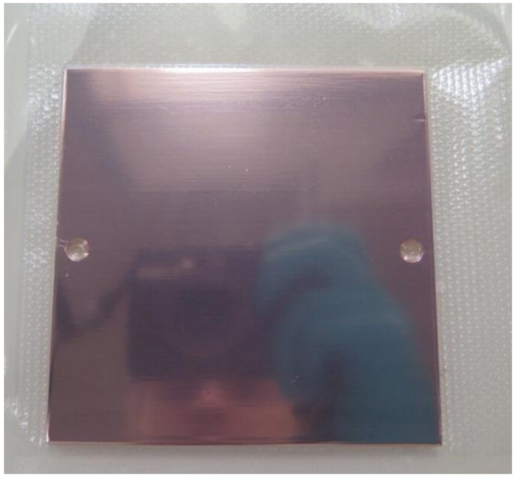
DS Copper Cleaning Protocol

INFN Legnaro

Combination of mechanical and chemical cleaning:

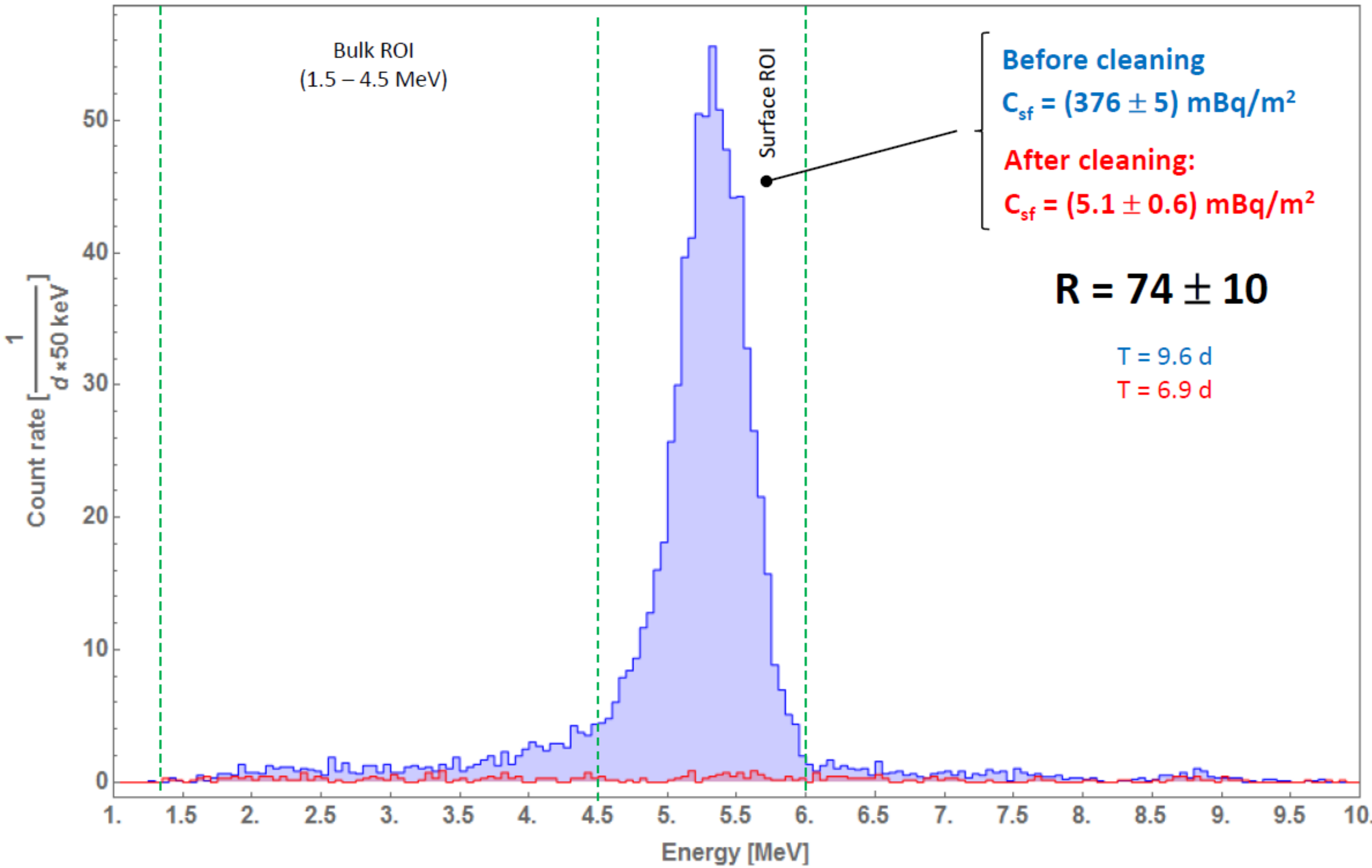
- Tumbling (~1 μm)
- Electro-polishing (10-100 μm)
- Etching (~5 μm)





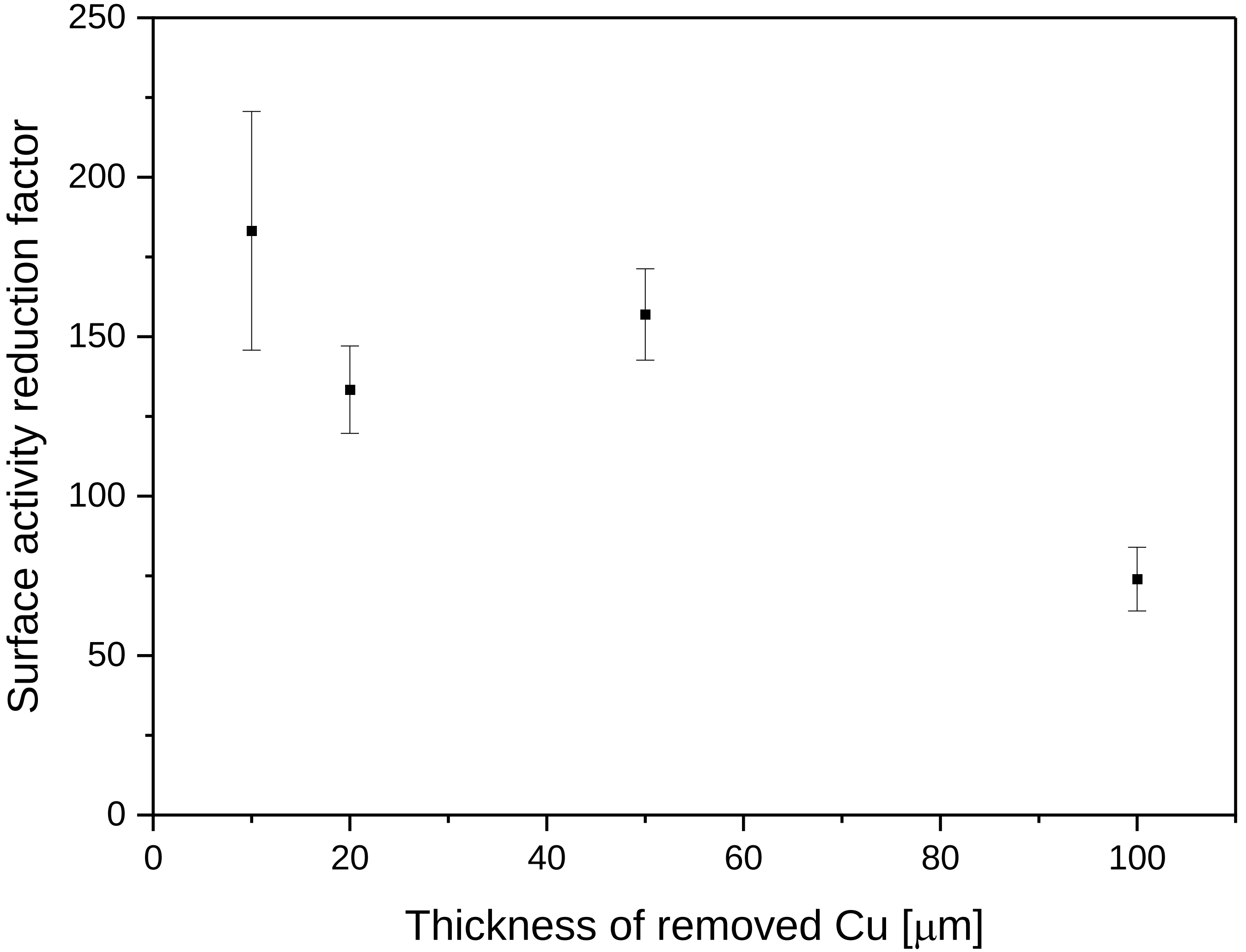
DS Copper Cleaning Protocol

Full procedure applied to contaminated samples: 100 μm Cu removed



DS Copper Cleaning Protocol

^{210}Po activity reduction factors vs. amount of removed Cu



Preventing (re-)contamination

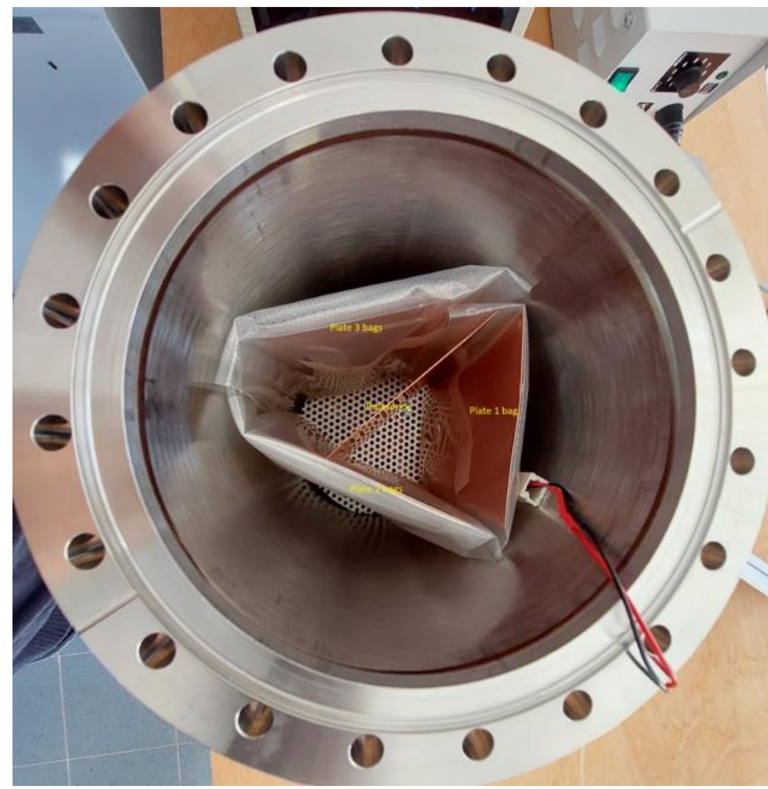
How to protect materials from recontamination with ^{222}Rn daughters during storage and transportation ?

→ Identification of materials with negligible Rn permeability

→ Testing foil made out of triple layers: PE/PA/PE.

(J. Busto)

- 4 Cu plates, 20 cm × 20 cm, cleaned at Legnaro and measured to verify their cleanliness
- Plates sealed in nylon bags (various number of layers applied) and placed in a ^{222}Rn-rich atmosphere (~0.4 MBq/m^3) for 7 months. One naked plate used as a reference
- Activity of deposited ^{210}Po on Cu measured with the XIA detector

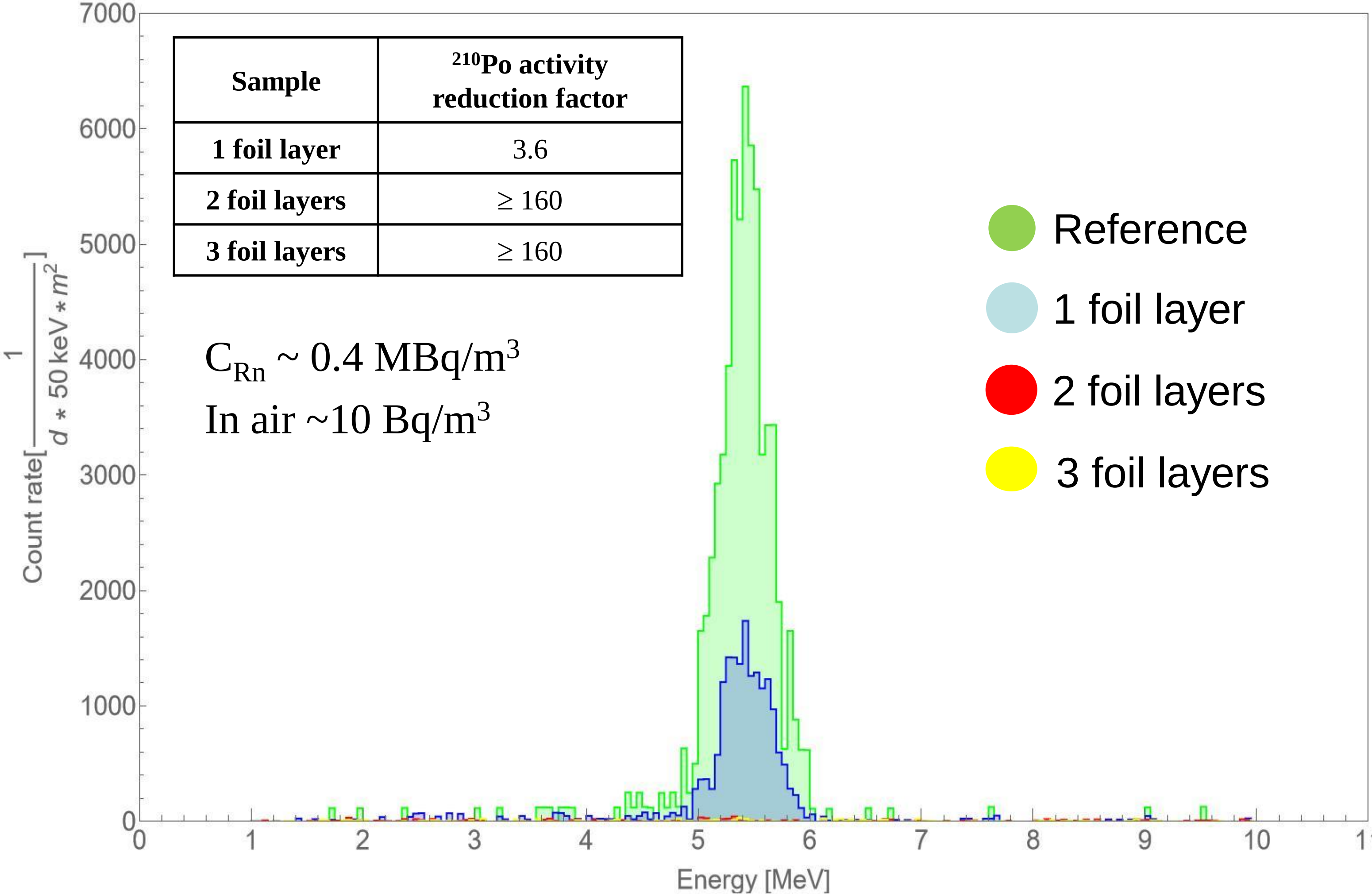


Preventing (re-)contamination

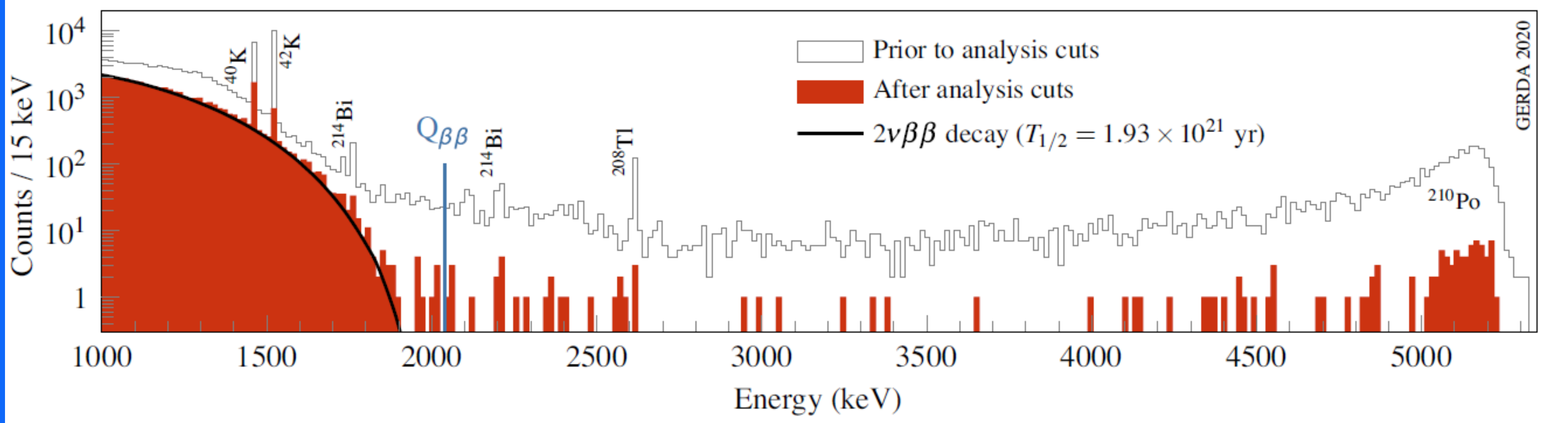
Sample	^{210}Po activity reduction factor
1 foil layer	3.6
2 foil layers	≥ 160
3 foil layers	≥ 160

C_{Rn} ~ 0.4 MBq/m^3

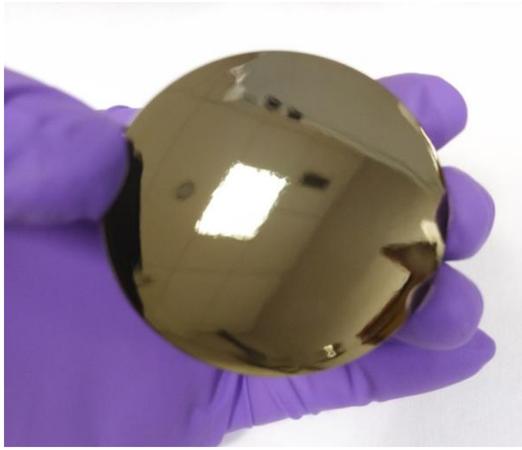
In air ~10 Bq/m^3



Removal of Rn daughters from HPGe



- Raw / passivated / B-implanted (like p^+ contact) HPGe surfaces were exposed to a strong ^{222}Rn source (~14.5 kBq) for 245 d (B-implanted for 68 d)
- ^{210}Pb and ^{210}Po accumulated on HPGe surfaces was measured with low-background gamma and alpha spectrometer, respectively.
- Exposed discs were washed in hot methanol (B-implanted) and etched (passivated HPGe) in CP4



5 cm diameter passivated HPGe disc

Removal of Rn daughters from HPGe

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Raw / passivated HPGe surfaces exposed for 245 d (1.8 × $T_{1/2}$ (^{210}Po))

	^{210}Pb rate [cpd]	^{210}Po rate [cpd]	^{210}Pb sp. act. [mBq/cm^2]	^{210}Po sp. act. [mBq/cm^2]	Pb / Po
Raw HPGe	3468 ± 61	28934 ± 573	120 ± 2	45 ± 1	2.7 (2.5)
Passivated HPGe	4549 ± 75	44859 ± 655	158 ± 3	70 ± 1	2.6 (2.5)

B-implanted HPGe surface exposed for 68 d (0.5 × $T_{1/2}$ (^{210}Po))

	^{210}Pb rate [cpd]	^{210}Po rate [cpd]	^{210}Pb sp. act. [mBq/cm^2]	^{210}Po sp. act. [mBq/cm^2]	Pb / Po
Implanted HPGe	1551 ± 31	4340 ± 78	51 ± 1	6.7 ± 0.1	7.6 (8.8)

Removal of Rn daughters from HPGe

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Discs processed 5 min in hot (~65 ^{o}C) methanol

	Initial rates [cpd]		Rates after 1st cleaning [cpd]		Rates 2nd cleaning [cpd]		Activity reduction factors $R_{0\text{->}2}$	
	^{210}Pb	^{210}Po	^{210}Pb	^{210}Po	^{210}Pb	^{210}Po	^{210}Pb	^{210}Po
Raw HPGe	59 ± 10	28934 ± 573	74 ± 8	32801 ± 937	--	--	**0.8 ± 0.2**	**0.88 ± 0.04**
Passivated HPGe	126 ± 15	44859 ± 655	97 ± 10	32839 ± 937	108 ± 10	--	**1.2 ± 0.2**	**1.37 ± 0.04**
Implanted HPGe	1551 ± 31	4340 ± 78	1527 ± 28	3371 ± 185	--	3001 ± 75 3130 ± 37*	**1.01± 0.03**	**1.39 ± 0.03**

*) Disc washed 5 times for 30 sec., every time in fresh/hot methanol

Discs etched 90 s in CP4

	Initial rates [cpd]		Rates after cleaning [cpd]		Activity reduction factors $R_{0\text{->}2}$	
	^{210}Pb	^{210}Po	^{210}Pb	^{210}Po	^{210}Pb	^{210}Po
Raw HPGe	3468 ± 61	32801 ± 937	< 4.5	< 14	**> 770**	**> 2 300**
Passivated HPGe	4549 ± 75	32839 ± 937	< 15	< 14	**> 303**	**> 2300**

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Summary

- Developed and tested etching / electro-polishing procedures remove effectively ^{210}Pb, ^{210}Bi and ^{210}Po from metal surfaces, the effect seems to be material- and surface finish dependent. „Static" etching did not affect ^{210}Po on copper
- ^{210}Po (^{210}Pb) surface and bulk specific activities for various materials have been investigated with sensitivities down to 0.5 mBq/m2 and 40 mBq/kg (? mBq/kg for the radiochemical method), respectively
- Clean surfaces may be effectively protected against recontamination with ^{222}Rn daughters by appropriate packing materials
- ^{210}Po and ^{210}Pb are effectively removed by etching (CP4) form HPGe bare and passivated surfaces. p^+ contact-like surface cannot be cleaned with hot methanol
- How to avoid ^{210}Po? $\rightarrow$ handling of the detectors/critical components in the Rn-free atmosphere (Rn-free clean rooms)

Backup

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High-activity case

Isotope	Activity reduction factors after etching/electropolishing			
			Germanium	
	Copper	Stainless steel	NPGe	HPGe
^{210}Pb	50 / 300	100 / 400	100 / –	700 / –
^{210}Bi	50 / 300	100 / 800	400 / –	800 / –
^{210}Po	1 / 400	20 / 700	1000 / –	100 / –

Copper

- etching: 5 min in (1% H_2SO_4 + 3% H_2O_2) and 5 min in 1% citric acid
- electro-polishing: 85 % H_3PO_4 + 5 % 1-butanol ($C_4H_{10}O$)

Stainless steel:

- etching: (20 % HNO_3 + 1.7 % HF) and 15 % HNO_3
- electro-polishing: 40 % H_3PO_4 + 40 % H_2SO_4 + 3 % CrO_3

Germanium:

- etching: CP4 solution (45.45 ml HNO_3 + 27.27 ml HF + 27.27 ml CH_3COOH + 0.5 ml Br for 100 ml solvent) done by Canberra-France in Lingolsheim in cooperation with MPP Munich

NIM A 676 (2012) 140
NIM A 676 (2012) 149

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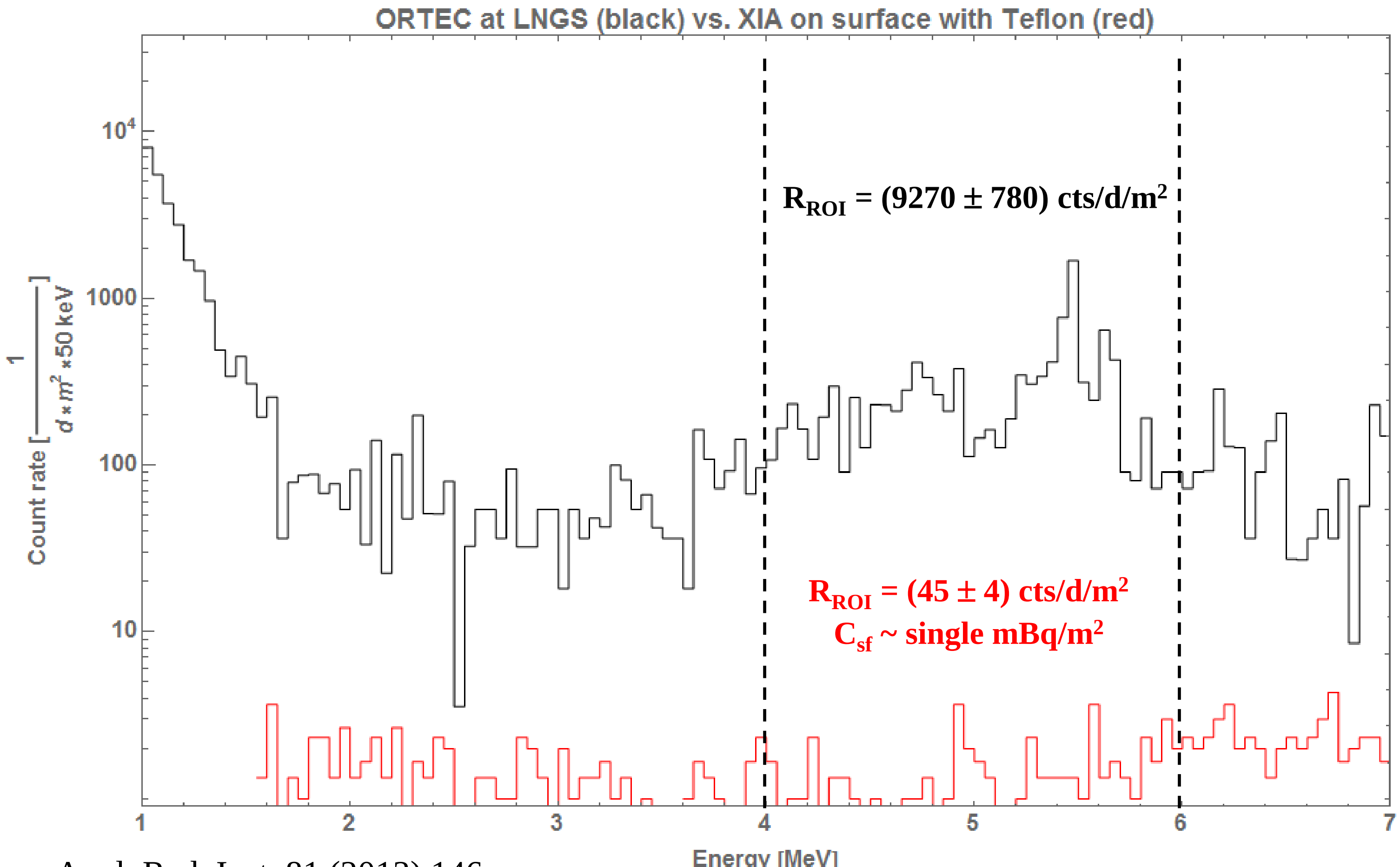
High-activity case

- Samples in a form of discs with 50 mm diameter
- To increase the sensitivity samples were artificially loaded with ^{210}Pb, ^{210}Bi and ^{210}Po: placed in a strong ^{222}Rn source for several months (^{210}Po specific activities of ~100 Bq/m^2)
- Screening of ^{210}Po with an alpha spectrometer 50 mm Si-detector, bcg ~2 α/d (1-10 MeV) sensitivity ~20 mBq/m^2 (100 mBq/kg, ^{210}Po)
- Screening of ^{210}Bi with a beta spectrometer 2×50 mm Si(Li)-detectors, bcg ~0.18/0.40 cpm sensitivity ~10 Bq/kg (^{210}Bi)
- Screening of ^{210}Pb (46.6 keV line) with a gamma spectrometer 16 % - HPGe detector with an active and a passive shield

Background spectrum

Low background ORTEC α detector (40 mm diameter) at LNGS vs. LBS spectrometer: **factor ~200 improvement**.



- Appl. Rad. Isot. 81 (2013) 146
- https://doi.org/10.1016/j.apradiso.2017.01.030

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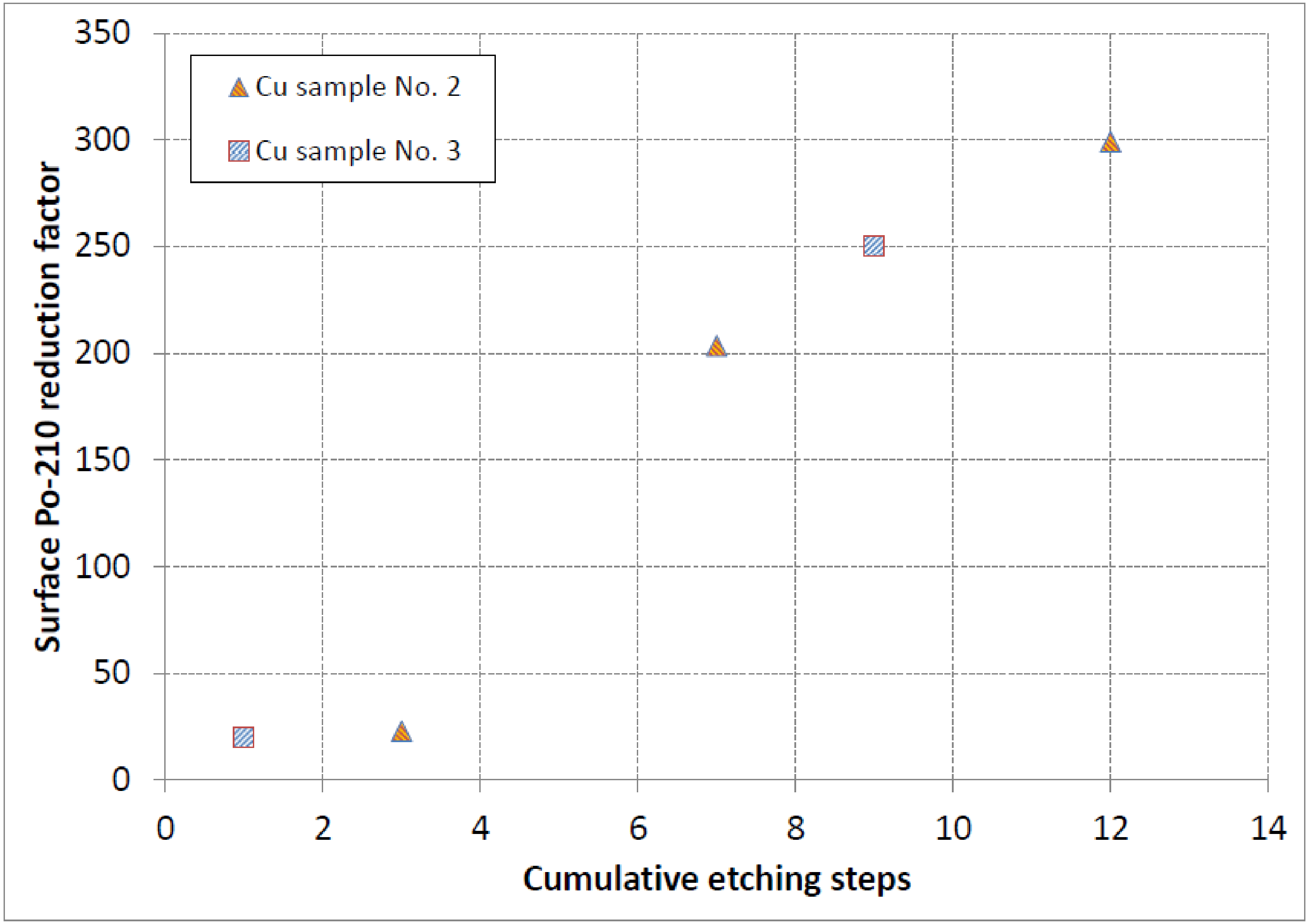
„Dynamic” etching



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