Radiopurity of Surfaces – Removal of long-lived ^{222}Rn daughters from metals

G. Zuzel, M. Grab, T. Mróz, K. Pelczar, M. Wójcik

Institute of Physics Jagiellonian University, Cracow, Poland

Low Radioactivity Techniques 2019, 19-24 May 2019, Canfranc, Spain

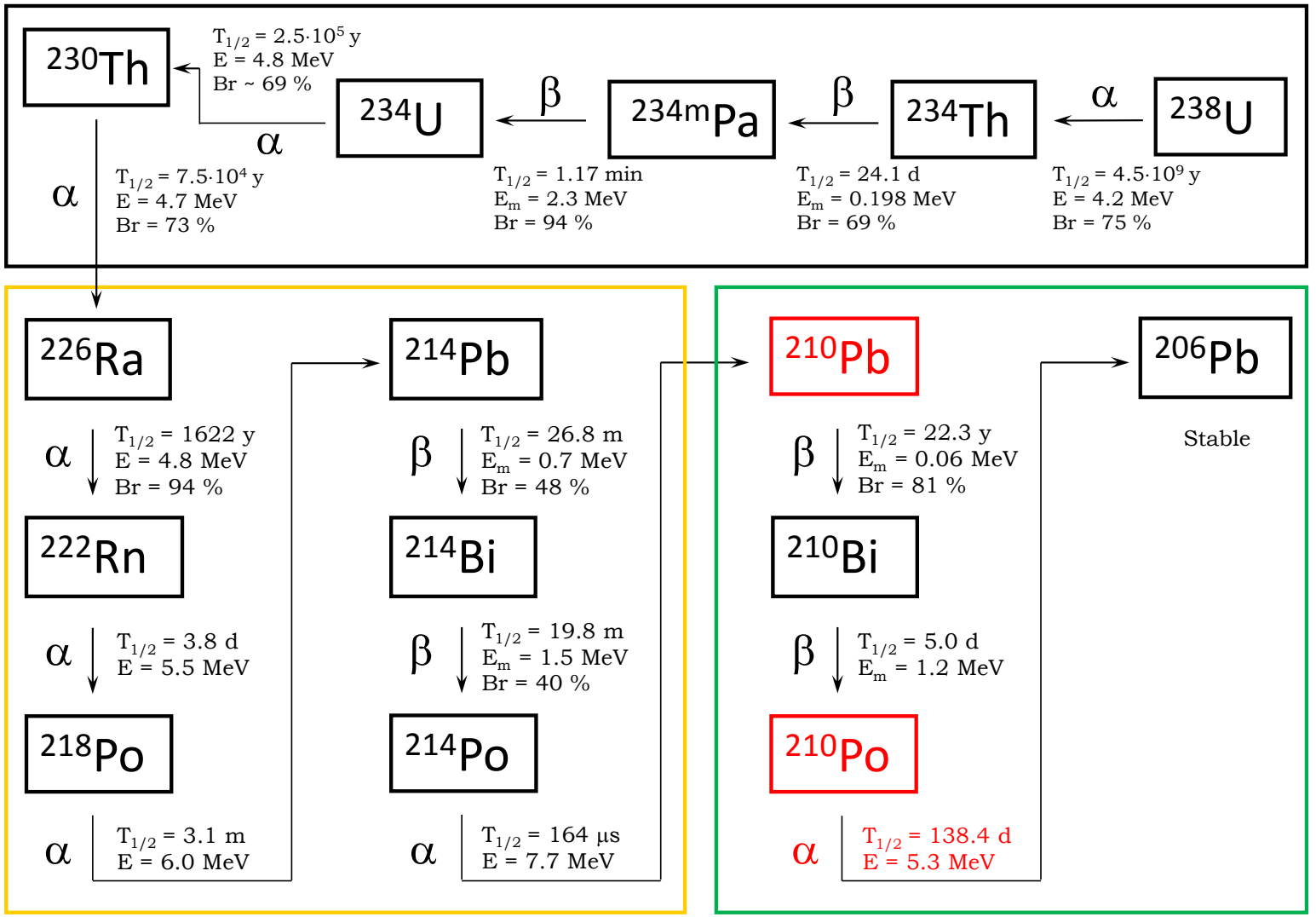
Outline

- Introduction – motivation
- High-activity case – study of artificially contaminated samples
- Low-activity case – study of naturally contaminated samples
- Summary

^{238}U decay chain

- Introduction
- High-act. case
- Low-act. case
- Summary

ICP-MS / LA ICP-MS



^{222}Rn emanation

α/β spectroscopy

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 25% - HPGe detector with an active and a passive shield

FNP Team

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

FNP Team

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

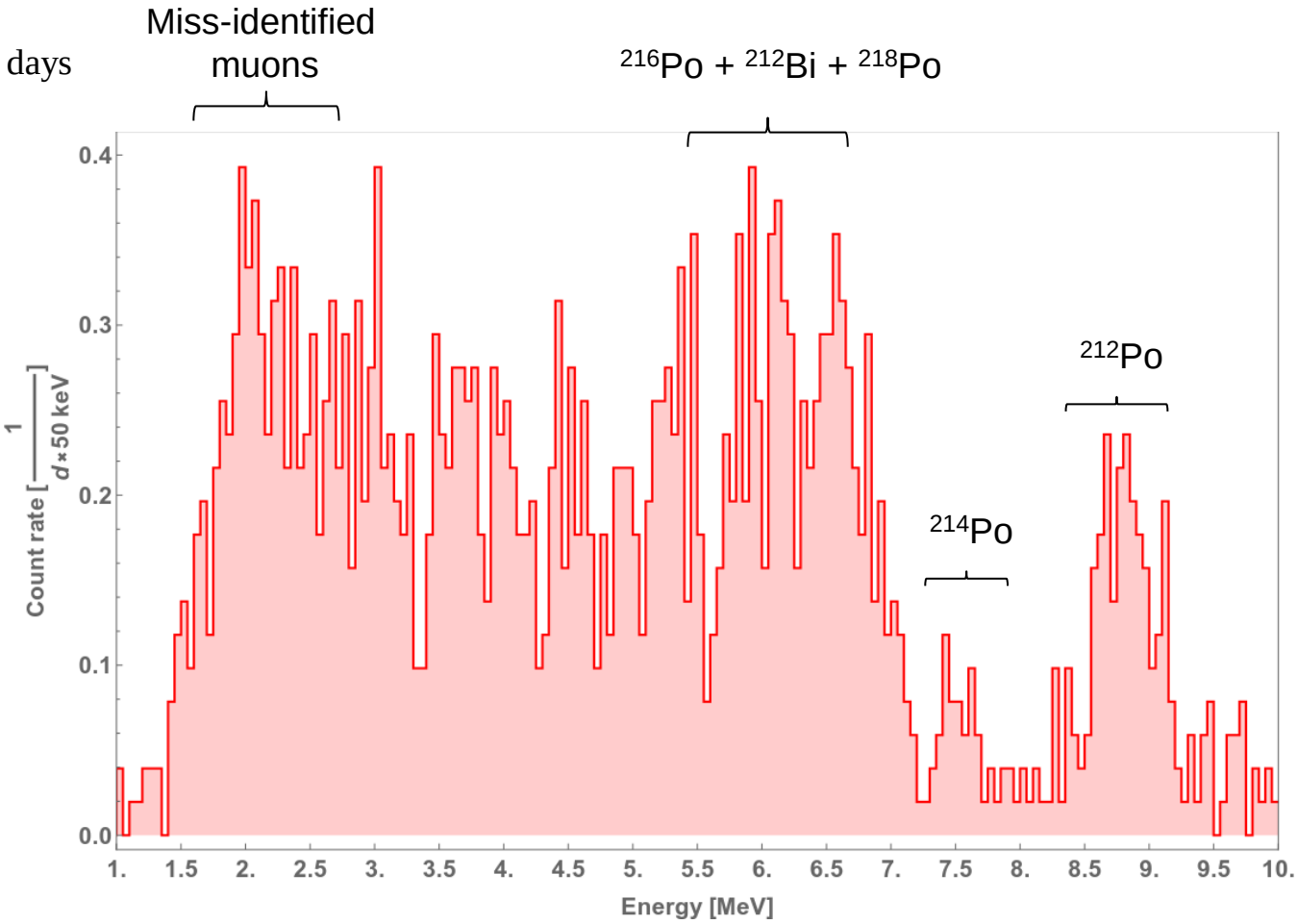
FNP Team

Low-activity case

- Only ^{210}Po studied
- Low background, large surface (LBS) alpha spectrometer
- Ar used as counting gas (3.5 l/min)
- Sample size: 43×43 cm^2 / 30 cm diam. disc, a few mm thick
- PSD + veto guard (discrimination of background events)

Background spectrum

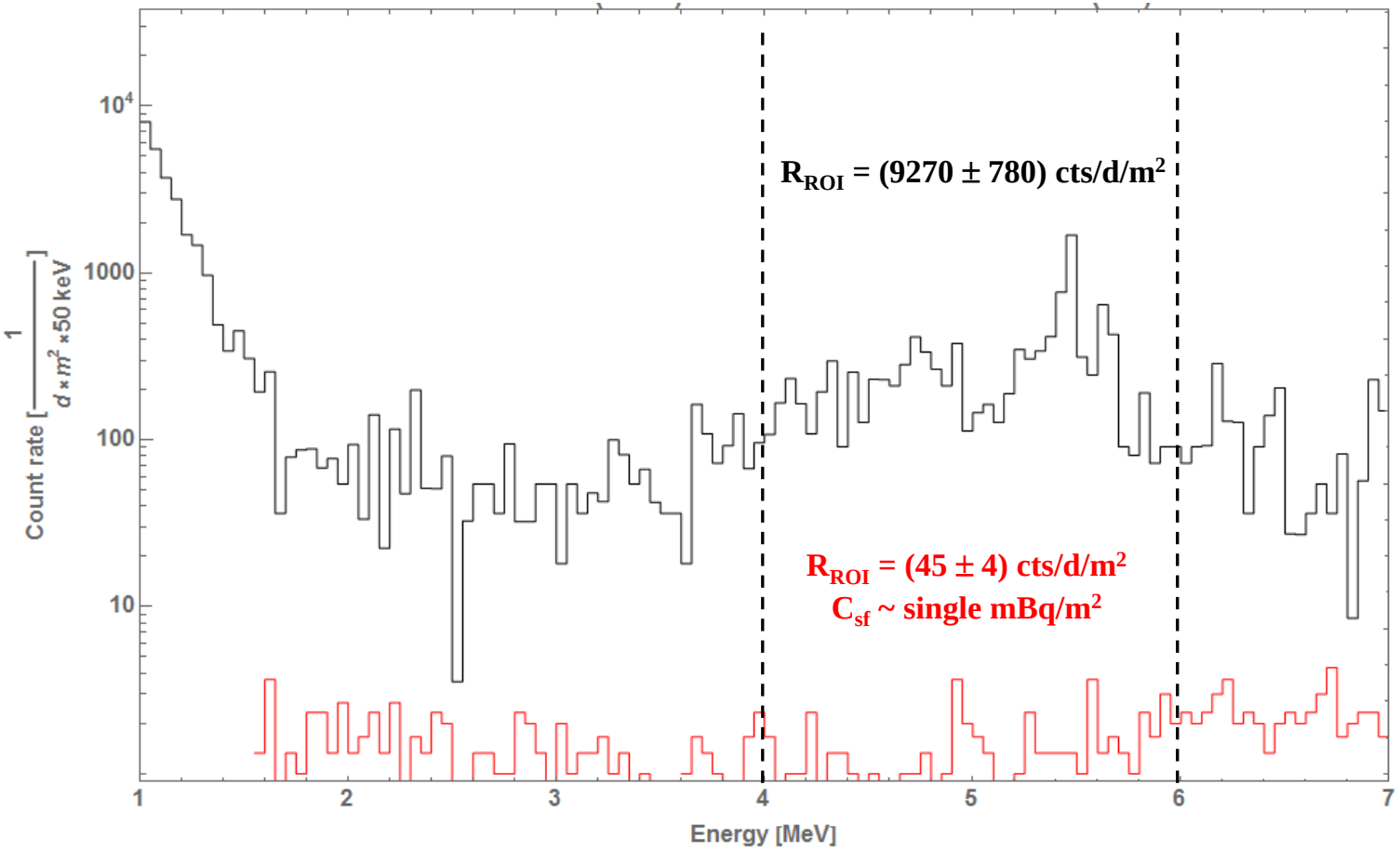
T = 51 days



- Drawer covered with OFCu → significant reduction of background below 5.3 MeV w.r.t. steel tray
- 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
- Count rate in the energy range of (1.5 – 6.0) MeV: 130 cts/d/m^2

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

Introduction
High-act. case
Low-act. case
Summary

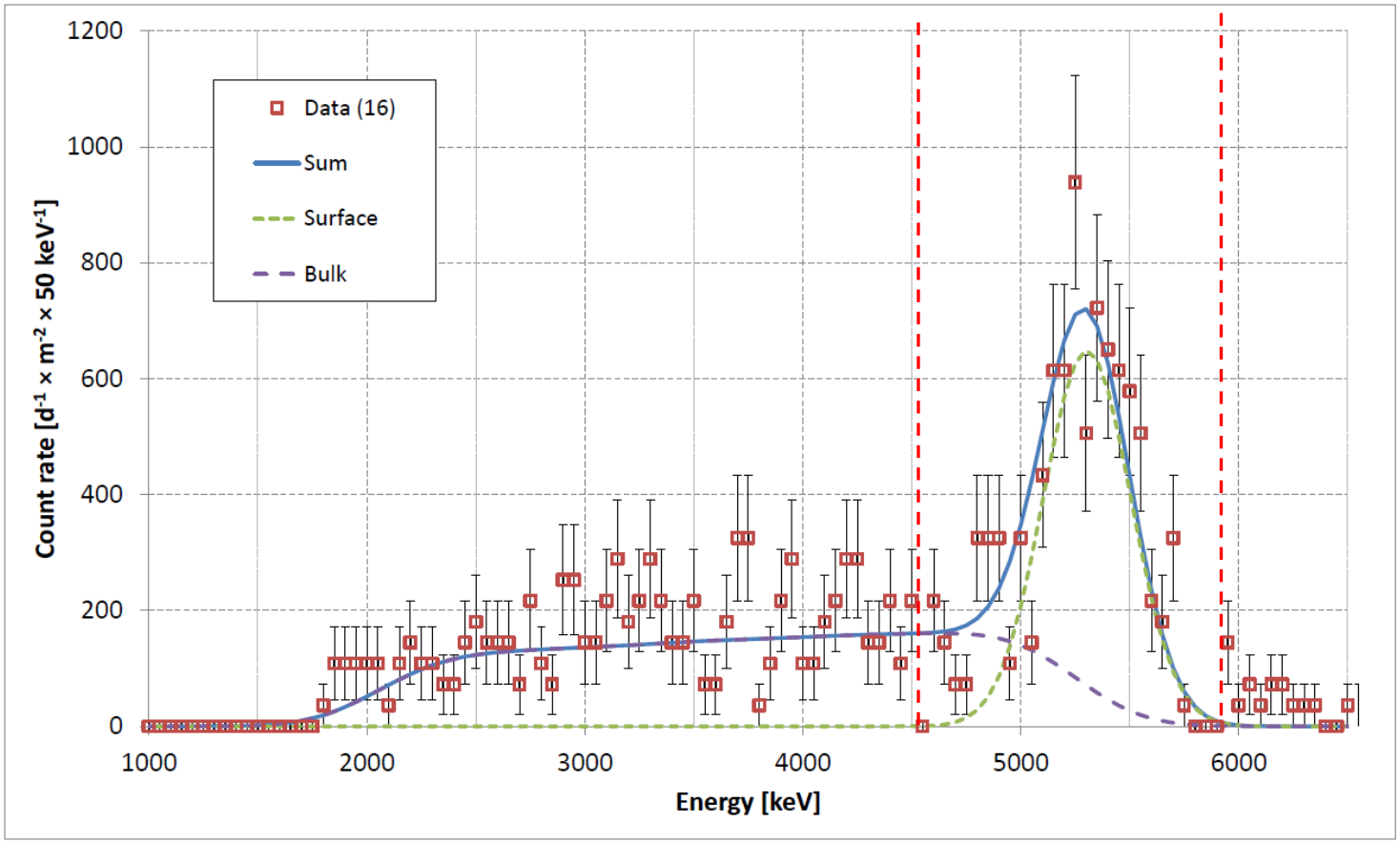
FNP Team

Analysis method

MC used to de-convolute contributions form ^{210}Po in the bulk material and on the surface, sensitivities: $C_{bulk} \leq 50$ mBq/kg, $C_{sf} \leq 1$ mBq/m^2

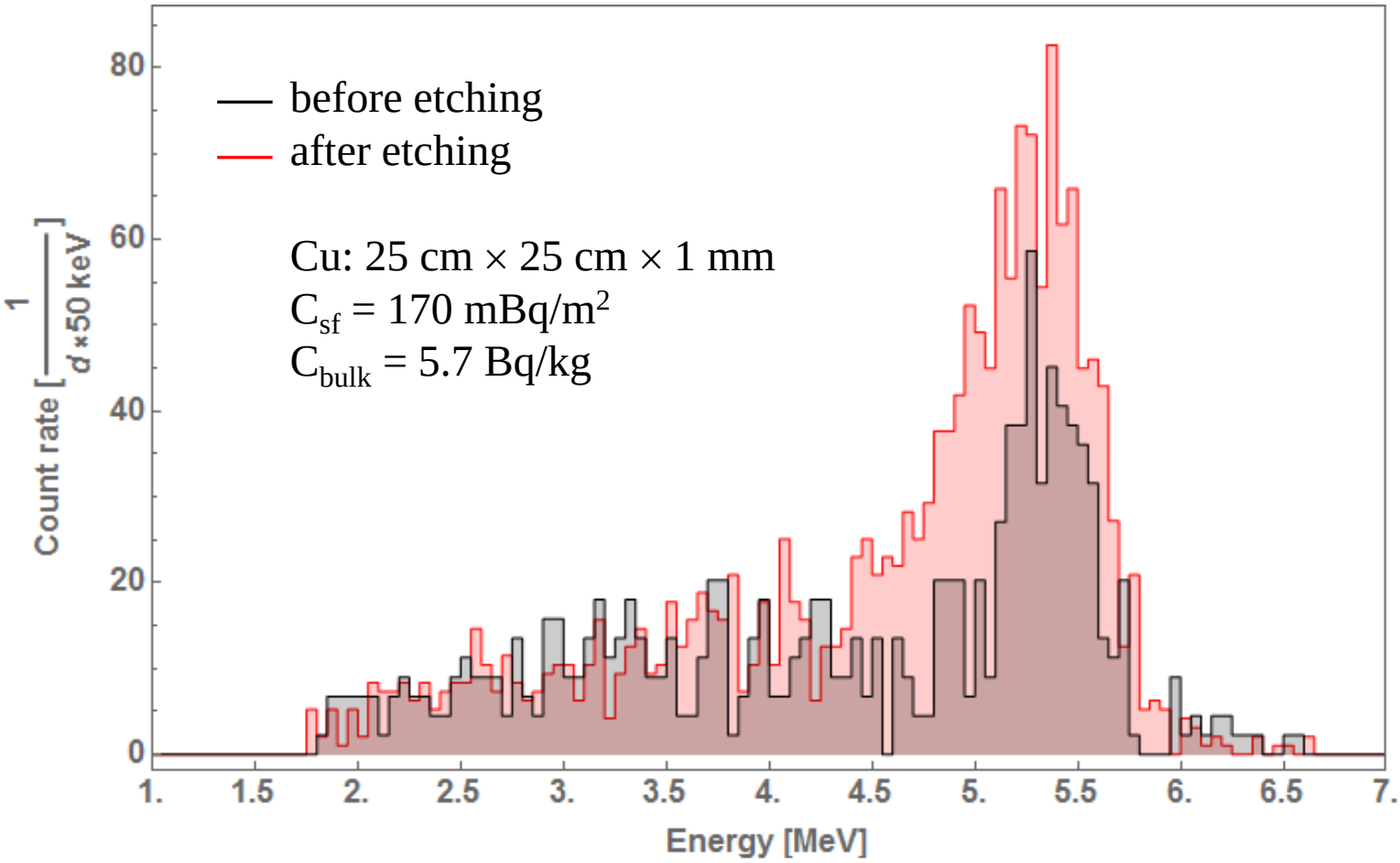
Cu sample: $C_{bulk} = (5.7 \pm 1.1)$ Bq/kg

$C_{sf} = (170 \pm 13)$ mBq/m^2



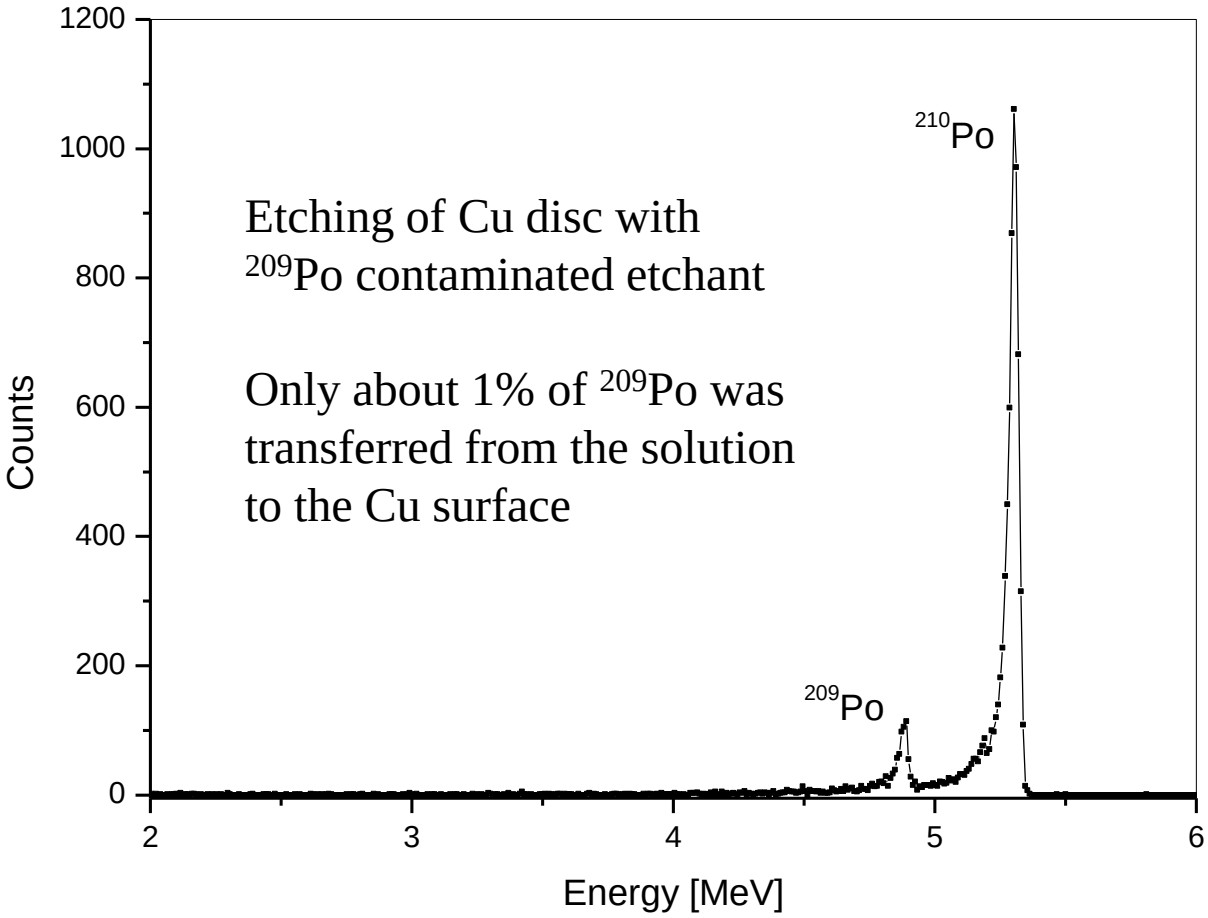
Etching of Cu

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

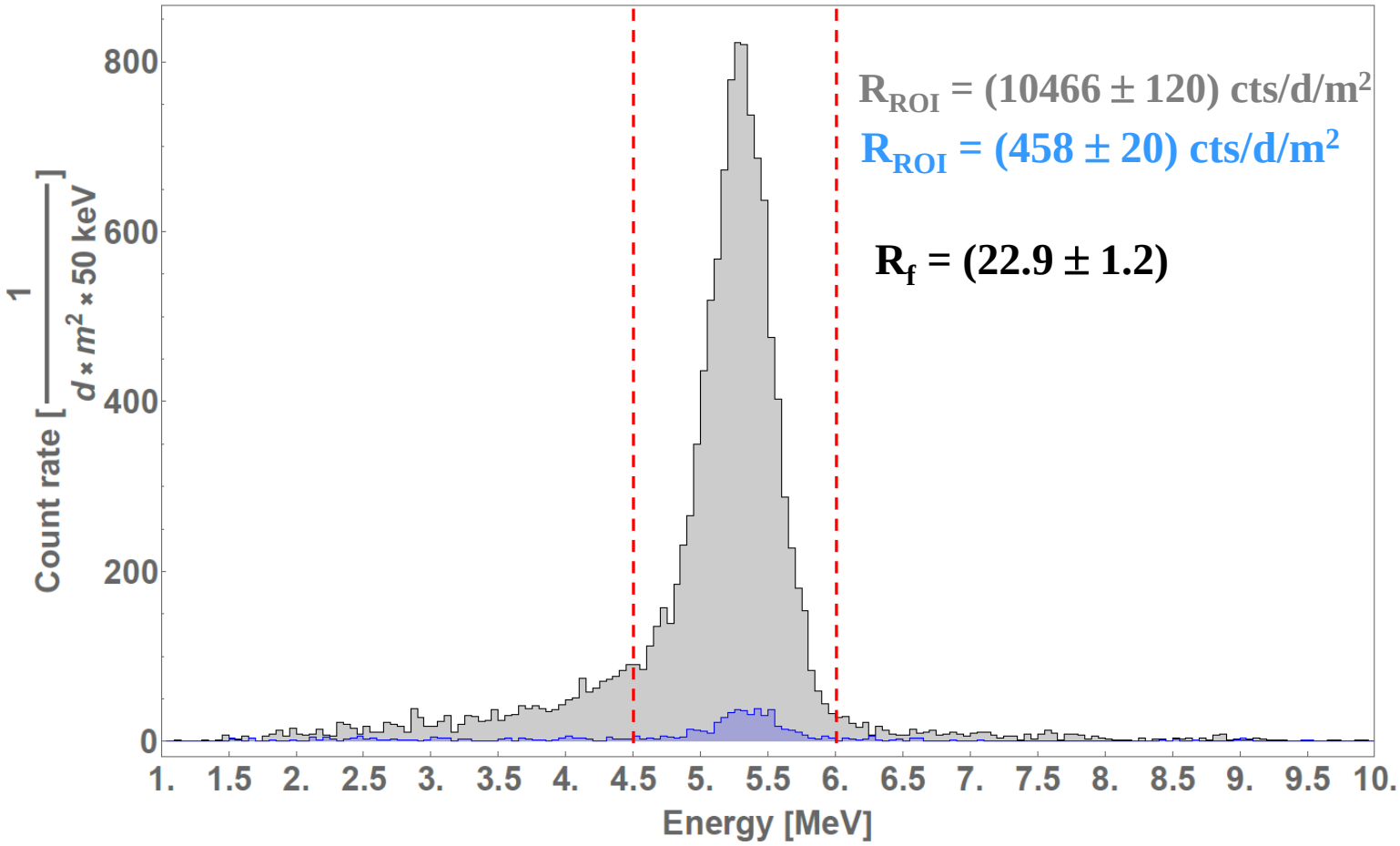
Autodeposition of Po



Autodeposition of Po during etching – „local" process

Reducing time of single etch

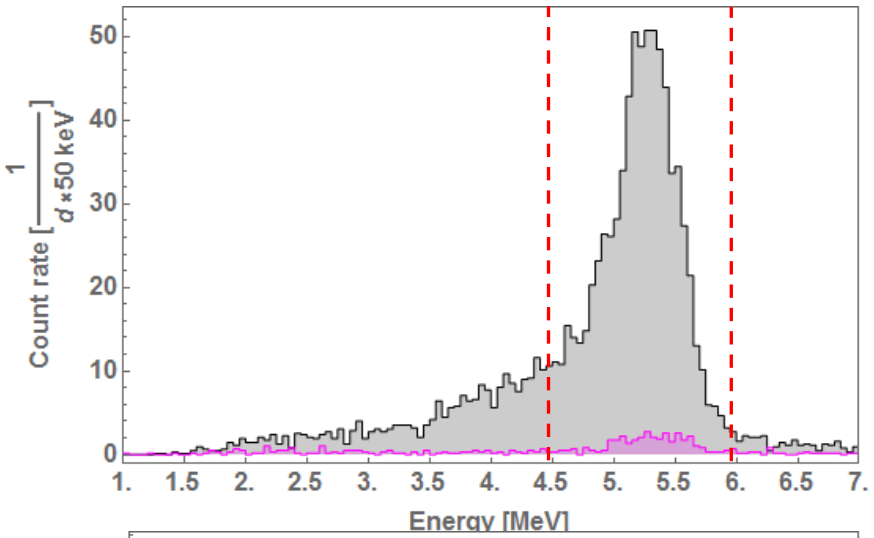
- Etching procedure: 5 x 1 min wash with a mixture of 1% H_2SO_4 + 3% H_2O_2
- Passivation with 1% citric acid (5 min)
- Washing in high-purity deionized water (18 MΩ×cm)



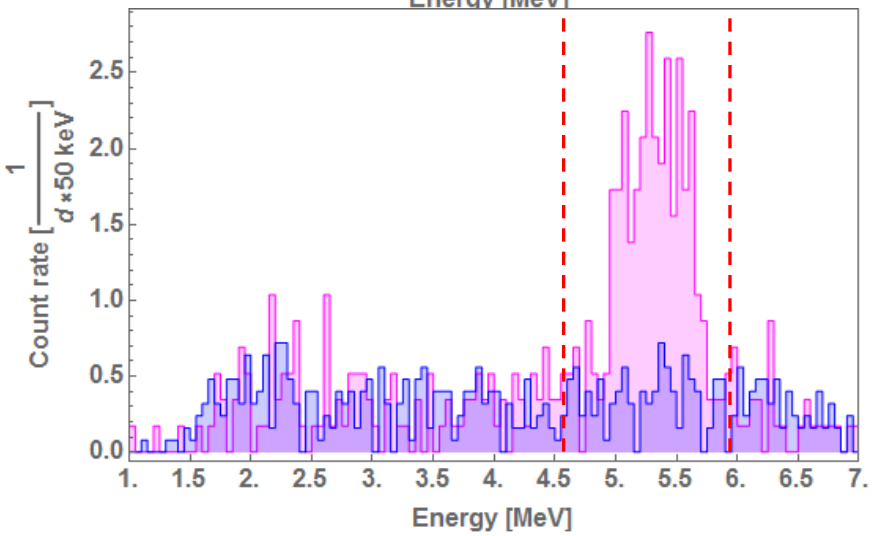
FNP Team

Reducing time of single etch

- Etching procedure: 1 / 2 runs for 40 sec in a mixture of 1% H_2SO_4 + 3% H_2O_2
- Passivation with 1% citric acid



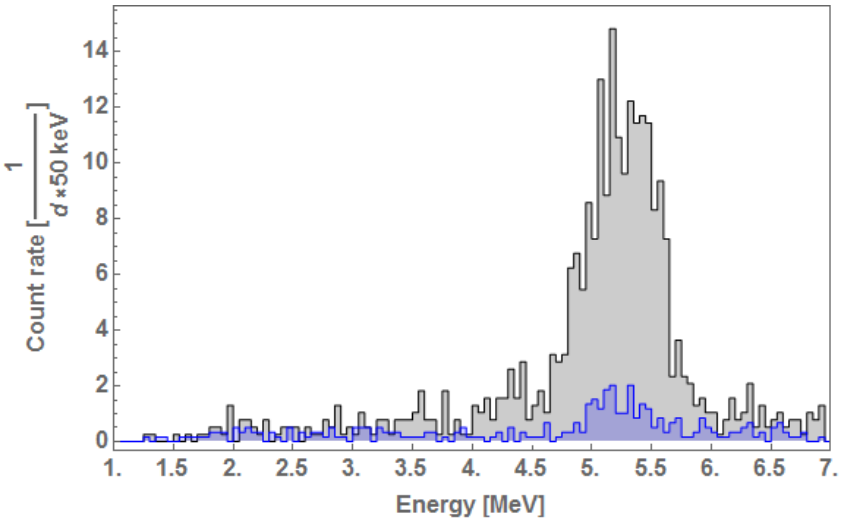
$R_1 = 20.1 \pm 1.7$



$R_2 \geq 3.6$

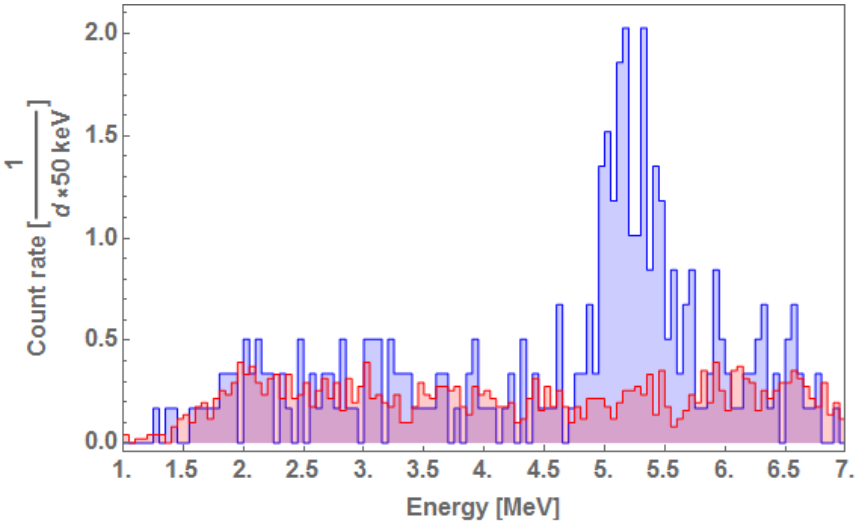
Electroformed copper (LSC)

- Etching procedure: 2 x 4 runs for 40 sec in a mixture of 1% H_2SO_4 + 3% H_2O_2
- Passivation with 1% citric acid



$C_{sf\_in} = (25 \pm 2)$ mBq/m^2

$R_1 = (8.1 \pm 1.0)$

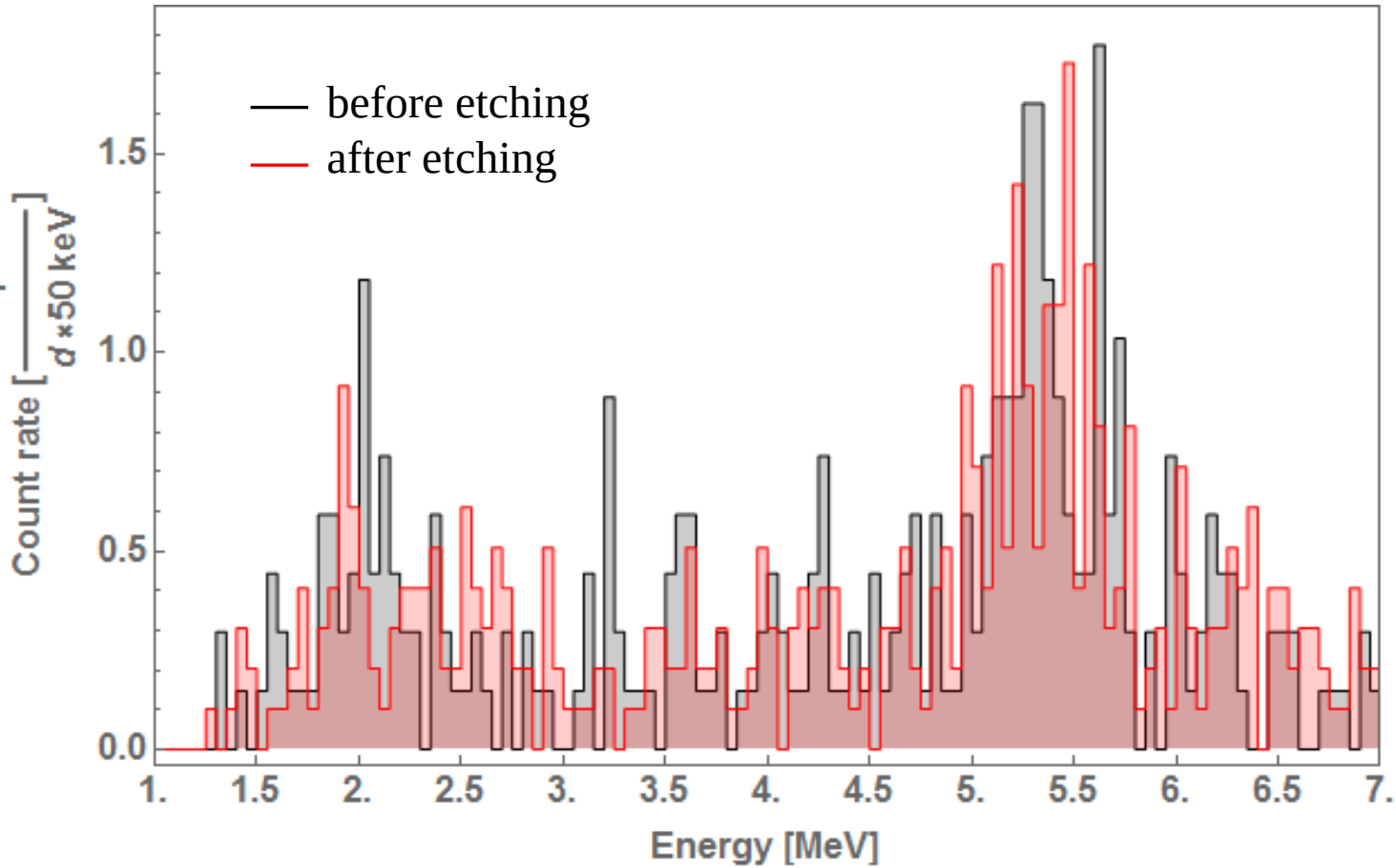


$R_2 \geq 3$

$C_{sf\_fin} < 1$ mBq/m^2

Increasing H_2O_2 concentration

- Etching procedure: 1 run for 40 sec in a mixture of 1% H_2SO_4 + **10% H_2O_2**
- Passivation with 1% citric acid



Surface covered with copper oxide

No effect on ^{210}Po

Increasing H_2SO_4 and H_2O_2

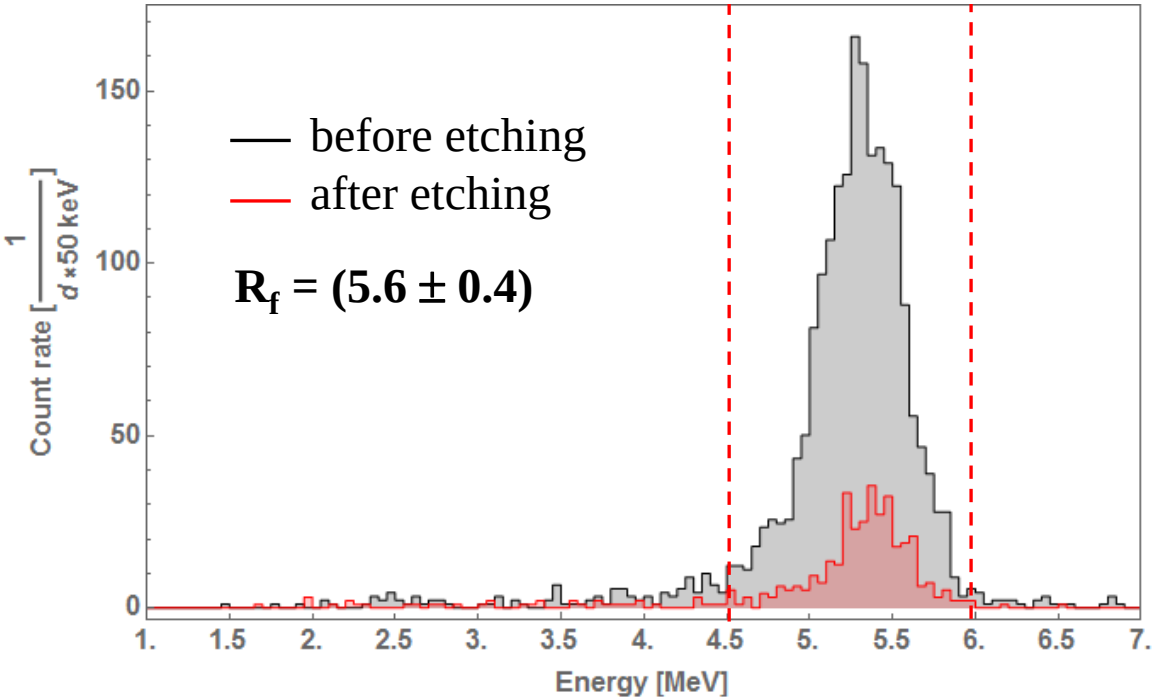
- Etching procedure: 40 sec in a mixture of 5% H_2SO_4 + 10% H_2O_2
- Passivation with 1% citric acid (5 min)
- Washing in high-purity deionized water (18 MΩ×cm)

Step	^{210}Po surface spec. activity [mBq/m^2]	^{210}Po reduction factor
0	365 ± 55	
1	139 ± 21	2.6 ± 0.7
2	74 ± 15	1.9 ± 0.6
3		
1-2		4.9 ± 1.7

FNP Team

Etching in nitric acid

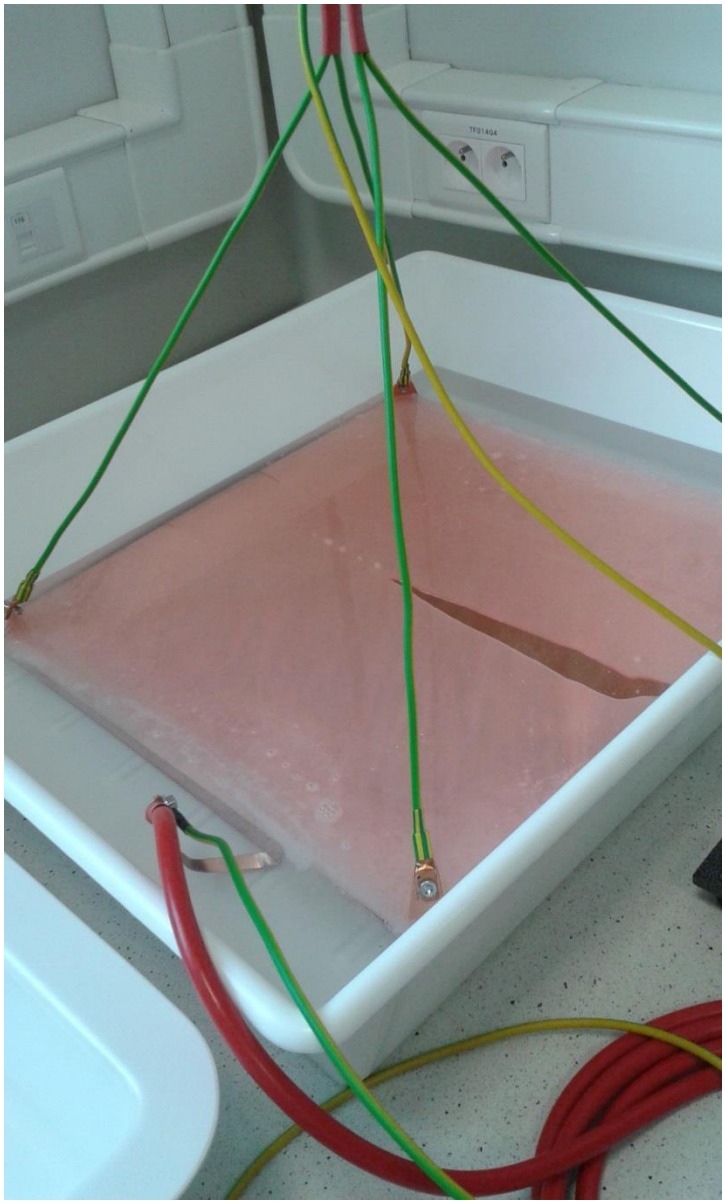
- Etching procedure: 1 run for 1 min in a mixture of 15% HNO_3 + 2% H_2O_2
- Passivation with 1% citric acid

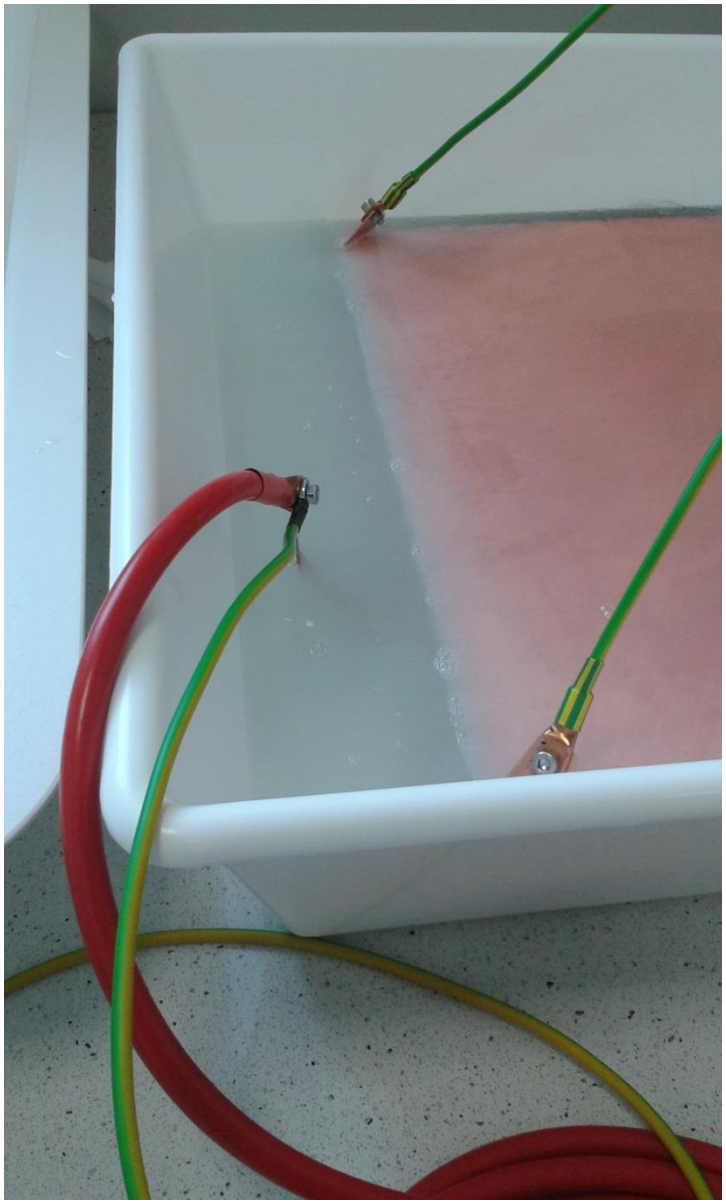


Step	Conc. of HNO_3 [%]	Conc. of H_2O_2 [%]	^{210}Po reduction
1	15	2	5.6 ± 0.4
2	15	4	2.3 ± 0.3
3	15	7	5.0 ± 0.4

FNP Team

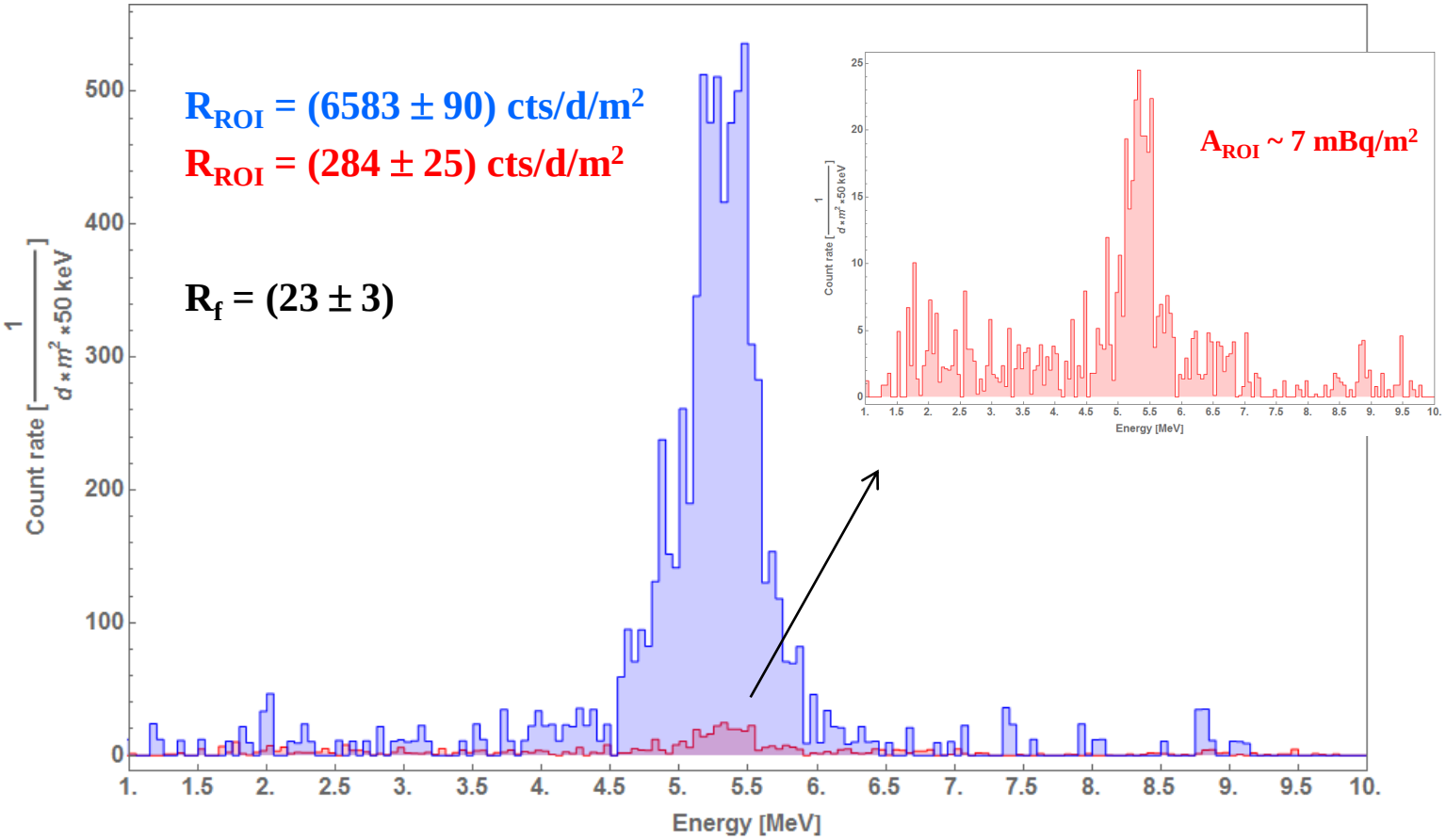
Electro-polishing





Electro-polishing of copper

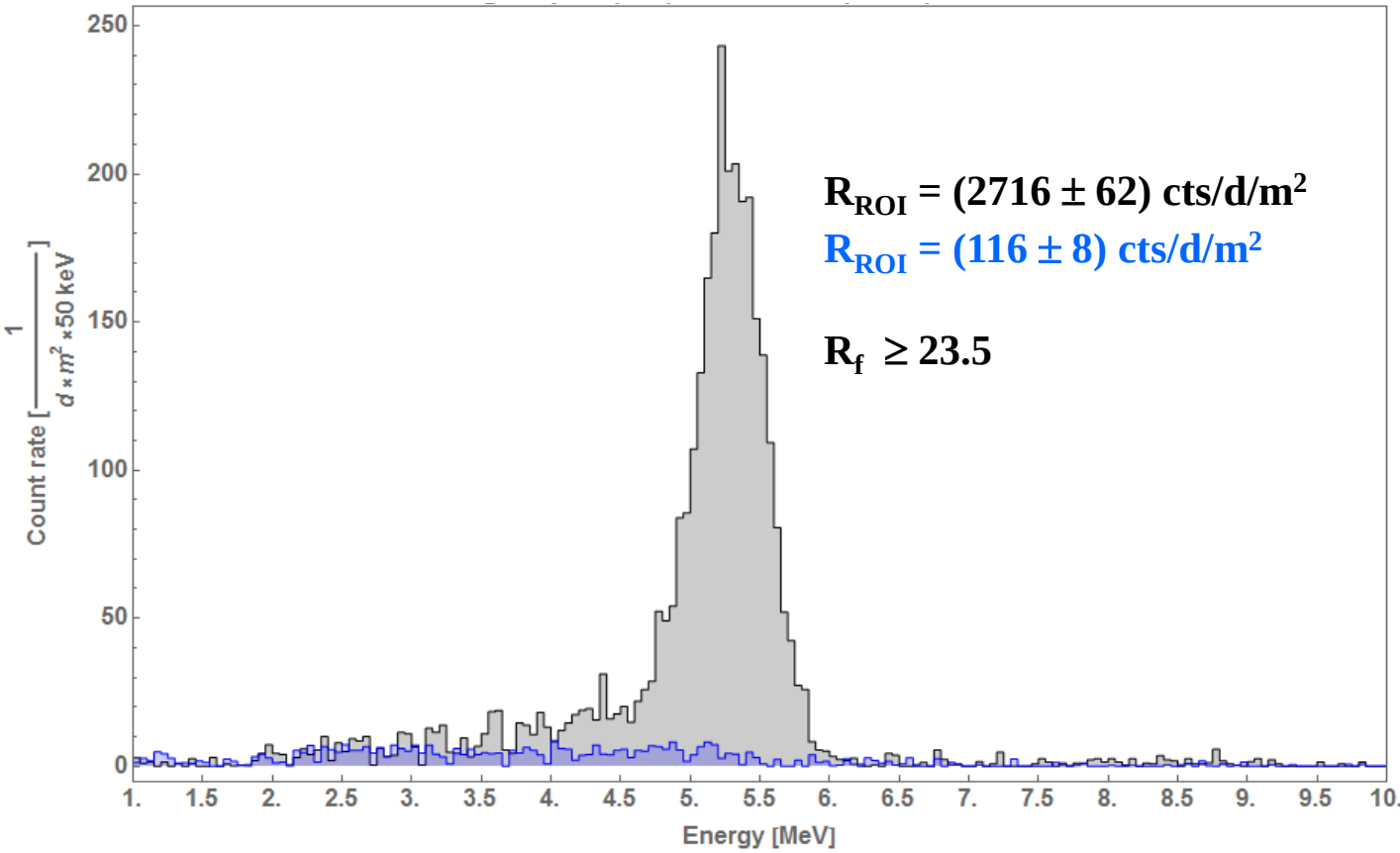
ETP copper (z4), 43 cm x 43 cm x 0.1 cm,



- Polishing mixture: 95% H_3PO_4 + 1% 1-butanol
- Polishing conditions: 2.5 A/dm², 3 V, 20 min, distance between plates: 2 cm, room temperature

Electro-polishing of stainless steel

SS 1.4301 (304), 43 cm x 43 cm x 0.1 cm,



- Polishing mixture: 1:1 of 95% H_2SO_4 and 85% H_3PO_4
- Washing: 5 min in 15% HNO_3 and later in HP water
- Polishing conditions: 2.5 A/dm^2, 2 V, 25 min, distance between plates: 2 cm, T ~ 50 ^{o}C

Summary

- Etching/electro-polishing removes ^{210}Pb, ^{210}Bi and ^{210}Po from metal surfaces, the effect seems to be material- and surface finish dependent. Long etching did not affect ^{210}Po on copper due to re-deposition of Po
- Multi-stage etching with H_2SO_4 or HNO_3 with short (< 1 min) steps removes ^{210}Po from copper, 8 – 10 steps are sufficient to obtain practically ^{210}Po-free surface (bulk starts to dominate)
- At the level of mBq/m^2 proper etching/electro-polishing does not contaminate surfaces with ^{210}Po
- Other methods under investigations (combination of tumbling, electro-polishing and etching)
- Surfaces of copper and stainless steel protected against ^{222}Rn (air) do not show indications of ^{210}Po down to mBq/m^2
- How to avoid ^{210}Po? → handling of the components in ^{222}Rn-free atmosphere (^{222}Rn-free clean room)

FNP Team