Progress on the Study of Isotopic Composition in Metallic Thin Films undergone to Electrochemical Loading of Hydrogen

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SUMMARY

- **Experiments on thin films at ENEA**
  - *Film deposition*
  - *Hydrogen loading*
  - *SIMS analysis*
- **Results**
  - *Preliminary results*
  - *Further investigations*
- **Questions**
- **Conclusions**

Experiments on thin films at ENEA

- ***Reference*** and ***active*** Nickel films are deposited during the same deposition run

- The active film is loaded with H by ***electrolysis***

- Reference and electrolysed films ***isotopic composition*** is analysed by Secondary Ions Mass Spectrometry (SIMS)

to search deviations from the natural abundances (traces of nuclear processes)

FILMS DEPOSITION

Substrate

- Polyethylene substrate
- Class 1000 lab
- Chemical cleaning

⇨ *Reduction of contaminants*

Ion Beam Etching

- Strong adhesion to plastic substrate
- Surface roughness

⇨ *Good film surface status after electrolysis*

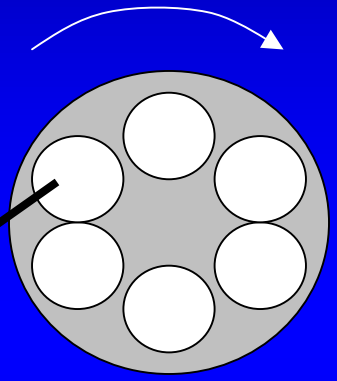
Ni Film sputtering

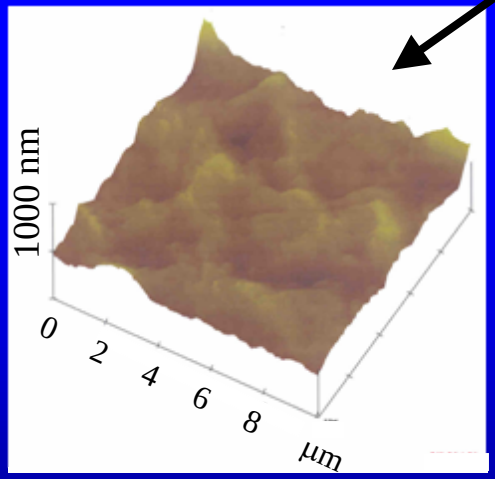
- 6 samples per runs
- 99.98% purity Ni target
- thickness 450 Å

⇨ *Identical reference and active films*

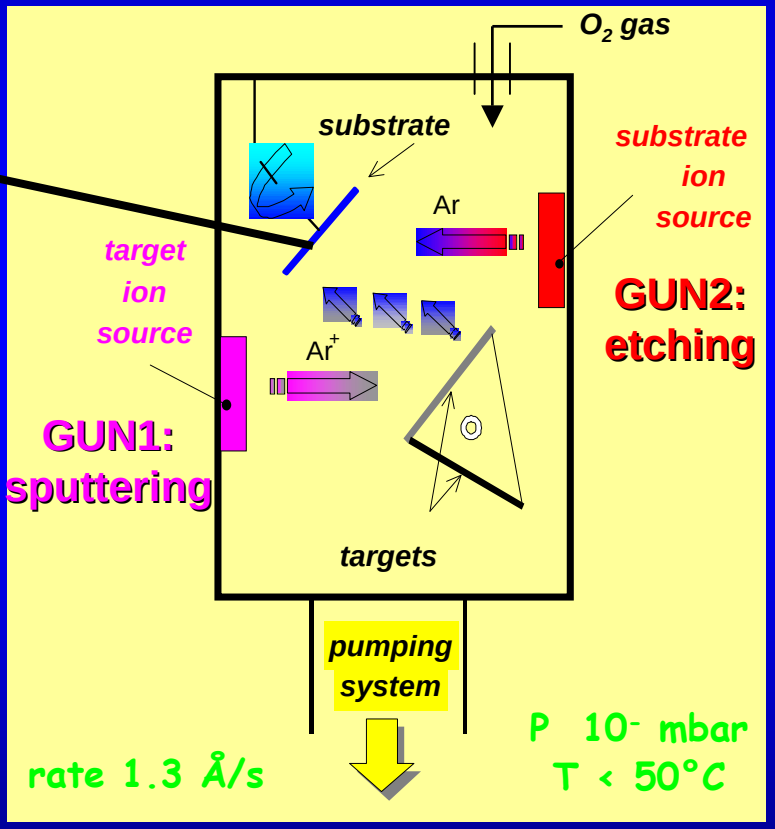
Films Deposition Details

Rotating Sample Holder
(6 identical locations)





Film Surface morphology
(by Atomic Force Microscopy)

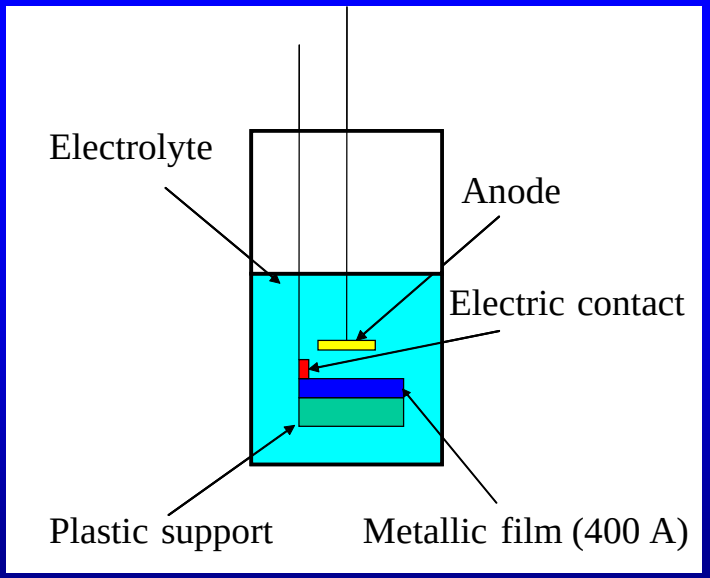


Dual Ion beam Sputtering plant

HYDROGEN LOADING

- Pure Polyethylene (Kartell)
- Pure Pt (99.98) wire
- Light water (18MΩ) $LiSO_4$ solution
- 3-40 hours
- Current = 5 - 190 mA
- Voltage = 3 – 7 V

Photo of the electrodes



Electrolytic Cell

SIMS analysis

- SIMS technique
- Isotopic shift measurements
- Depth profile
- Active & reference in the same analysis conditions

Secondary Ion Mass Spectrometry (SIMS)

- Very suitable technique to reveal small traces of surface elements or compounds (not quantitative)
- Very accurate measurements of isotopic ratio
- Dynamic SIMS allows depth profile of elements/compounds concentration

Leybold SSM200-Mass Spectrometer Module

Leybold IQE 12/38 ion source and Balzers Quadrupole Mass Analyzers with ion optics

- **Primary beam**

  heavy ions [Ar^+], spot $\varnothing \approx$ 2mm, I≈0.5-2 μA, E=1-5 KeV, 45°
- **Emergent particles:** Positive and negative ions
- **Mass range:** m/e≥1 [0-511 a.m.u.]
- **Resolution:** 0.5 a.m.u.
- **Sensitivity:** 10^{12} at/cm^2 (0.1% of 1 atomic monolayer)

SIMS Equipment

Leybold SSM200-Mass Spectrometer Module
at ENEA Frascati Lab. (Italy)

Reference and electrolyzed films are loaded together into the analysis chamber and positioned at 180 ° on a cylindrical support and analyzed in series under the same SIMS conditions.

Previous results (ICCF9)

Neutron Activation Analysis (NAA- ENEA Casaccia, Italy) of Nickel thin films indicates evidence of ***isotopic shift*** on ***Ag*** contaminant.

	Ni1b	**Ni2b**
Ag107	<0,019	<0,034
Ag109	0.025	0.06
Shift Ag%	29.37	47.39

Our SIMS signals on Ag masses are too low to obtain useful information on the isotopic shift

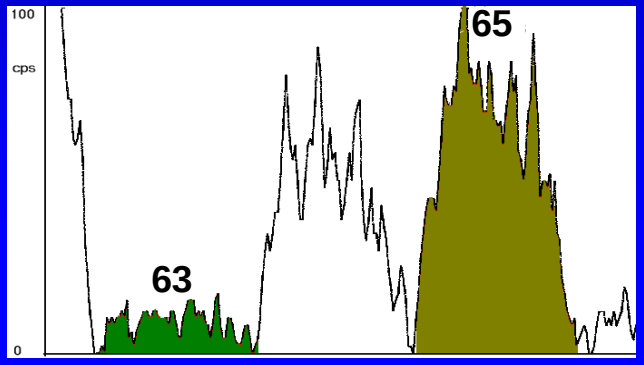
Preliminary Results

SIMS analysis on Ni thin films indicates an apparent isotopic shift on the 63/65 Cu masses *(Cu has these only two isotopes!)*

Electrolysed film:

The Cu^{63}/Cu^{65} isotopic ratio strongly differs from the natural value (2.25):

$$Cu^{63}/Cu^{65} \cong 0.12 \pm 0.1$$

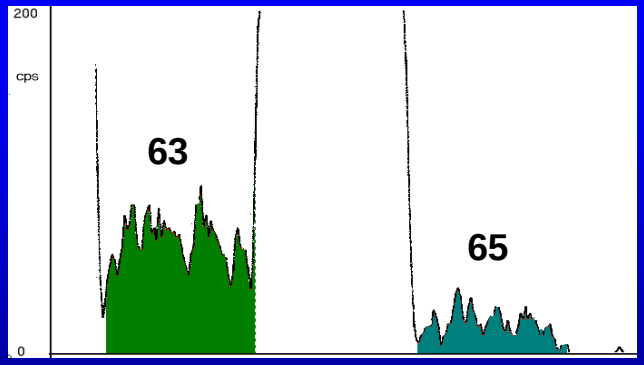


SIMS spectrum of electrolysed film

Reference film:

The Cu^{63}/Cu^{65} isotopic ratio respects the natural value

$$Cu^{63}/Cu^{65} \cong 3.3 \pm 1$$



SIMS spectrum of reference film

the tuning of the instrumentation was checked by moving the argon beam on the stainless steal sample-holder where the Cu isotopic composition was always the natural one.

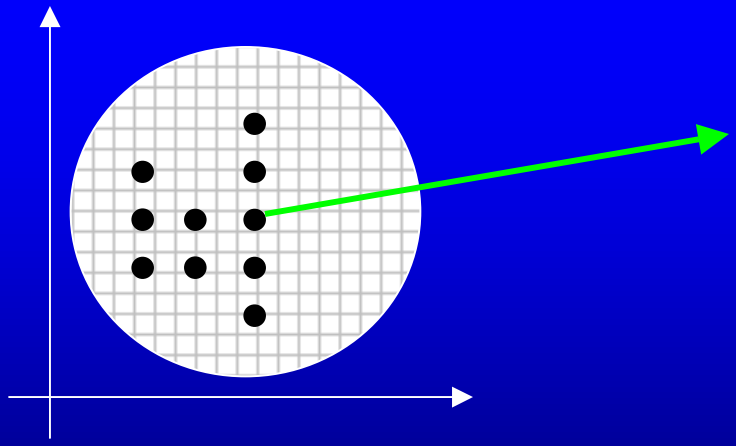
REPRODUCIBILITY

SAMPLE	Film STATUS after electrolysis	APPARENT ISOTOPIC SHIFT	
		Electrolysed	***Reference***
Ni 1bis	Ok	YES	NO
Ni 3bis	Ok	YES	NO
Ni P2	Ok	YES	NO
Ni P3	Ok	NO	NO
Ni 4	Ok	YES	NO

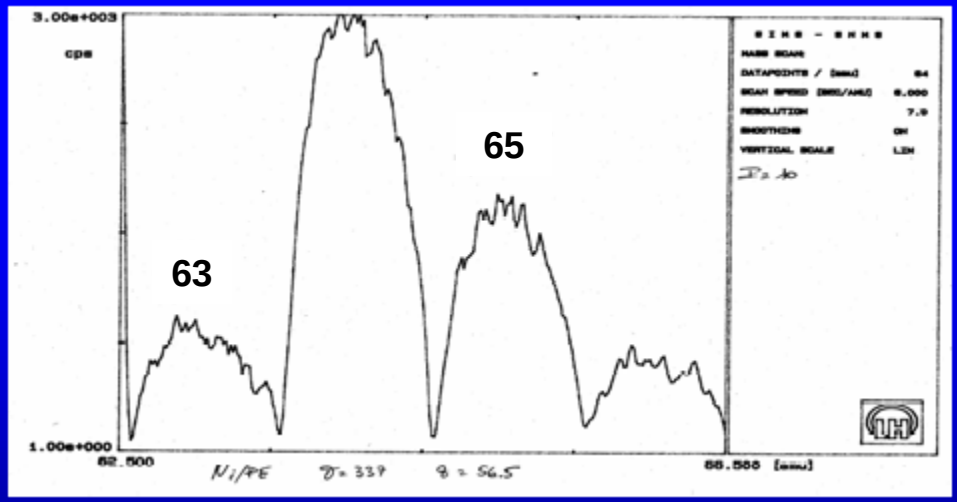
These new results add to the previous ones already shown (ICCF10):
3/5 experiments giving evidence of apparent isotopic shift

SIMS scanning of the sample surface

- The SIMS analysis has been carried out on different points of the sample surface.
- The effect is more relevant in the middle of the sample
- SIMS spot dimension ≅ **2mm**



Ni1bis scanned surface map



SIMS spectrum of Ni1bis electrolysed, in the middle of the sample

Questions

Mass interferences on 65 m/e signal?

Our SIMS resolution is about 100 ($m/\delta m$), not enough to resolve different peaks with the same nominal mass

1. Double ionised atoms
2. Organic contaminants (giving 65 mass fragments)
3. $Ni^{58}Li^{7}$ due to Li_2SO_4 electrolyte
4. $Ni^{64}H$ compound

Mass interferences on 65 m/e signal?

Double ionised atoms?

No signal is observed from 130 atomic mass (Te^{130}, Ba^{130}), which could give a 65 m/e signal when double ionised.

Mass interferences on 65 m/e signal?
Organic contaminants ?

- 65 mass $C_5H_5^+$ ion is very reactive, but it could be produced during the SIMS analysis by fragmentation of higher mass organic molecules (hydrocarbons).

- Typical spectra of hydrocarbon contaminants show groups of odd mass peaks with 12 a.m.u. periodicity (due to 1 C atom increment in the chain fragment)

12	13	14	15
27	29		
39	41	43	
51	53	55	57
63	65	67	69

C	CH	CH_2	CH_3
C_2H_3	C_2H_5		
C_3H_3	C_3H_5	C_3H_7	
C_4H_3	C_4H_5	C_4H_7	C_4H_9
C_5H_3	C_5H_5	C_5H_7	C_5H_9

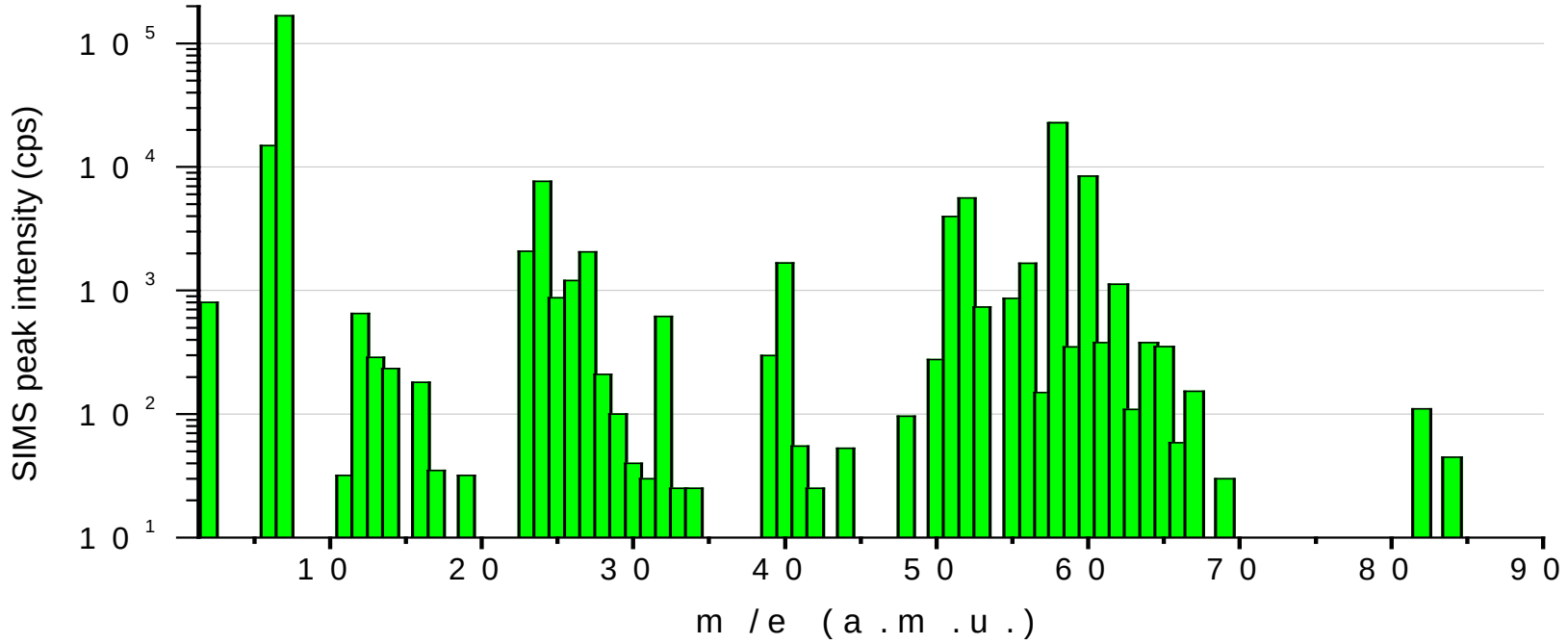
References:

SIMS technical report by RIBER Instrumentation Ultra-vide, France

Integrated Spectral Data Base System for Organic Compounds by National Institute of Advanced Industrial Science & Technology, SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/

Organic Compound Database by Harold M. Bell at Virginia Tech., http://www.colby.edu/chemistry/cmp/cmp.html

SIMS spectrum of electrolysed samples



Fragmentation pattern of organic contaminants is not observed

- 15, 43, 69 masses are not detected
- 51, 53, 55, 57 masses are masked by isotopes of clearly identified elements, present also in the reference sample (V^{51}, Cr^{53} 53, Mn^{55}, Fe^{57})

Organic contaminants (continue)?

From the polymeric substrate?

- SIMS depth profile shows that the 65 signal is not correlated with the increase of the ^{12}C when the interface between the film and the substrate is reached.

Mass peak ratio	On the surface	Close to the substrate
Ni58/C12	35 ± 2	8.1 ± 0.5
Ni58/mass65	65 ± 6	49 ± 16

From the electrolyte?

- Gas cromatography analysis of the electrolyte shows that organic contaminants are less than 1ppb.

From the surface?

- The blank sample has beem immersed for 2 days in iso-octane to remove organic contaminants eventually adsorbed on the surface.

  Gas cromatography analysis of the liquid did not reveal any organic contaminant down to 1ppb.

Mass interferences on 65 m/e signal?

$Ni^{58}Li^{7}$ due to Li_2SO_4 electrolyte?

- Despite of NiLi is not a stable compound however Li is detected on the film surface after electrolysis by SIMS.
- $Ni^{60}Li^{7}$ and $Ni^{58}Li^{7}OH$, $Ni^{60}Li^{7}OH$ mass peaks should be observed together the $Ni^{58}Li^{7}$ signal.

In our SIMS spectrum 65, 67 and 82, 84 mass peaks are present, which can be associated to the $Ni^{58}Li^{7}$, $Ni^{60}Li^{7}$ and $Ni^{58}Li^{7}OH$, $Ni^{60}Li^{7OH}$ compounds.

The ratio between these peaks intensity turns out to be equal to the natural isotopic ratio of Ni^{58} and Ni^{60}

$Ni^{58}Li^{7}$/ $Ni^{60}Li^{7}$	2.0±0.5
$Ni^{58}Li^{7}OH$/ $Ni^{60}Li^{7OH}$	2.5±0.5
Ni^{58}/Ni^{60}	2.71±0.01
Ni^{58}/Ni^{60} nat.	2.60

$Ni^{58}Li^{7}$ due to Li_2SO_4 electrolyte? (continue)

but

The isotopic ratio of the compound related to the Li^7, Li^6 isotopes ($Ni^{58}Li^7/Ni^{58}Li^6$) does not match the natural value, but it cannot be determined with enough accuracy due to the Ni^{64} contribution to the 64 mass peak.

Some samples have been electrolysed but have not shown the 65-mass extra signal

Contribution to the 65 mass peak from $Ni^{58}Li^7$ ion cannot be excluded.

Mass interferences on 65 m/e signal?

$Ni^{64}H$ compound?

$Ni^{64}H$ (65mass) detection is unlikely because the isotopic ratio $Ni^{62}H$ (63 mass) / $Ni^{64}H$ (65 mass) of Ni isotopes does not match the natural value (3.9): the observed results goes into the opposite direction!

CONCLUSIONS

- *Previous NAA results revealed isotopic shift for Ag contaminant in Ni electrolysed films.*
- *Preliminary results gave evidence of an apparent isotopic shift on the Cu masses (65 too high) in Ni hydrogenated films*

but

- All possible interpretations of the experimental data must be considered in order to get certain results
- The system complexity and the very small size of the foreseen effects requires suitable and very high performance experimental apparatus
- Cross matched analysis are necessary to get completely convincing conclusions

Towards a deeper understanding

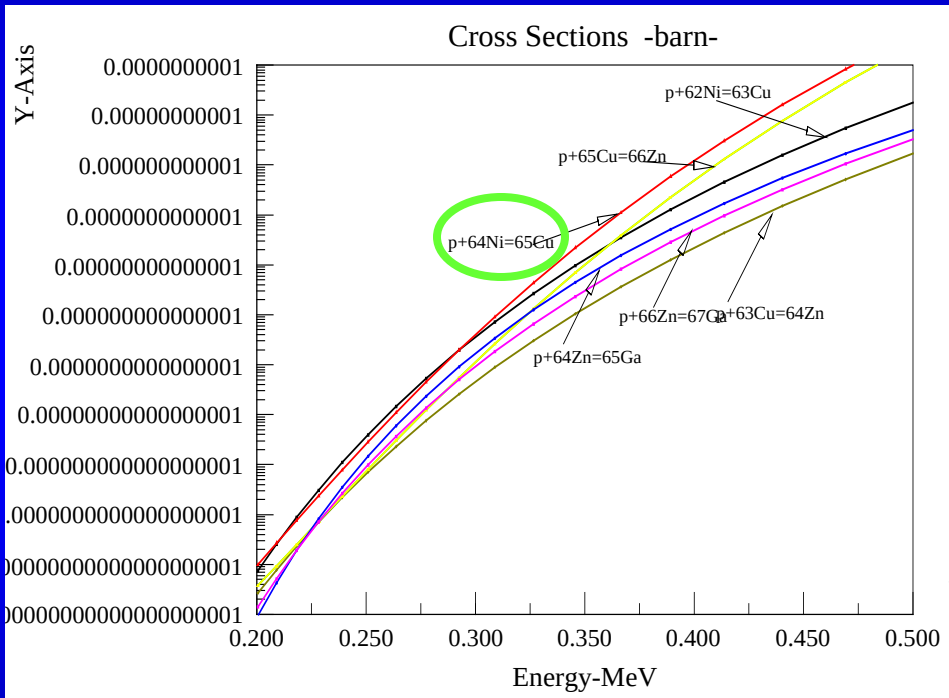
In the present experiment, something more for the next:

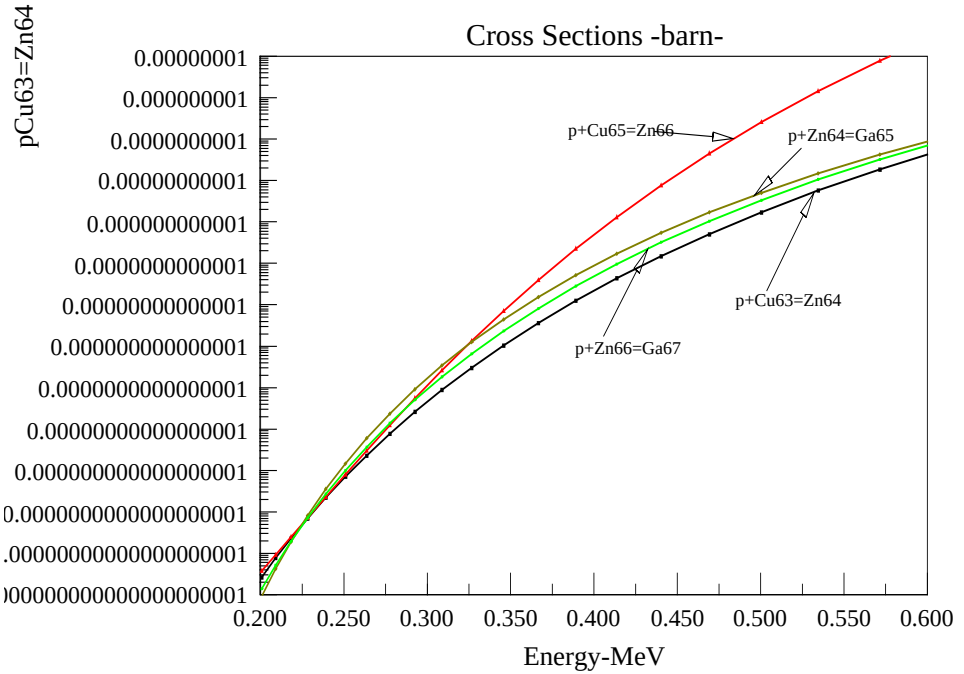
- Ultra-high resolution SIMS apparatus ($\delta m \leq 0.02$, $m/\delta m > 3000$)
- Test experiments by changing the electrolyte (for ex. NaOH)
- Cross matched analysis by other methods (for ex. Nuclear Activation Analysis)

Aknowledgements

The authors thank Dr. K. Grabowski and Dr. M. Melich for the important help received on this matter.

Calculated cross section for different nuclear reaction





By NOT-SMOKER web database by Prof. Thomas Raucher.

TOF-SIMS analysis at ETH

- A couple of reference and active samples have been also analysed by TOF-SIMS at ETH, to check our results.
- Cs^+ primary, negative secondary ions
- Cu63/Cu63 isotopic ratio after calibration of data with a standard:

Electrolysed sample: Cu63/Cu65 = **2.40±0.31**

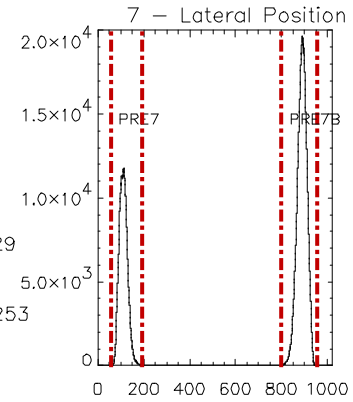
Reference sample: Cu63/Cu65 = **1.79±0.02**

Lateral Position Spectra

FILE cu1011
AAB

cuboid cut
10=3+3/1+2
11=4+4/5+5

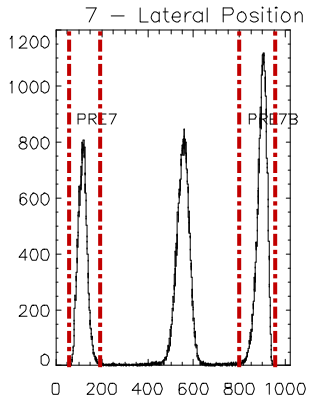
GATE PRE7:Σ=529229
MAX=11766 (#112)
GATE PRE7B:Σ=993253
MAX=19630 (#890)



FILE cu1013s
AAB

cuboid cut
10=3+3/1+2
11=4+4/5+5

GATE PRE7:Σ=37610
MAX=808 (#120)
GATE PRE7B:Σ=54879
MAX=1118 (#906)



Peak in gate PRE7: ^{65}Cu

Peak in gate PRE7B: ^{63}Cu

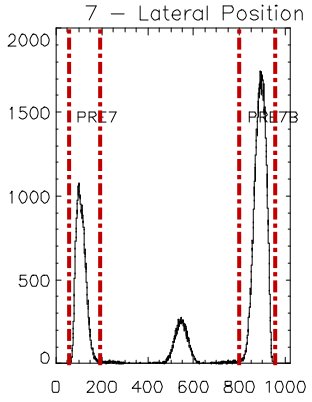
Peak around channel 550: mass 64, ^{64}Ni

Sample 2, Ni 1 bis

FILE cu1020s
AAB

cuboid cut
10=3+3/1+2
11=4+4/5+5

GATE PRE7:Σ=53873
MAX=1079 (#102)
GATE PRE7B:Σ=110002
MAX=1743 (#890)



Mass interferences on 65 m/e signal?

$Ni^{58}Li^{7}$ due to Li_2SO_4 electrolyte?

- Despite of NiLi is not a stable compound however Li is detected on the film surface after electrolysis by SIMS.
- Evidence of $PdNa^+$ compound comes from reference SIMS spectra of standard samples (by RIBER). The $PdNa^+$ mass peaks are coupled with the presence of $PdNaOH^+$ and $PdNaO^+$ mass signals.
- $NiLi^+$ formation is possible because Ni and Li belong to the same groups of Pd and Na respectively on the periodic table of the elements.