

# *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**

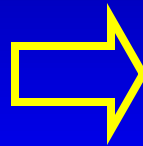
# Experiments on thin films at ENEA

- **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

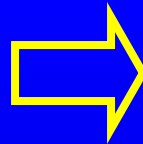
- Polyethylene substrate
- Class 1000 lab
- Chemical cleaning



*Reduction of  
contaminants*

## Ion Beam Etching

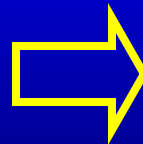
- Strong adhesion to plastic substrate
- Surface roughness



*Good film surface  
status after  
electrolysis*

## Ni Film sputtering

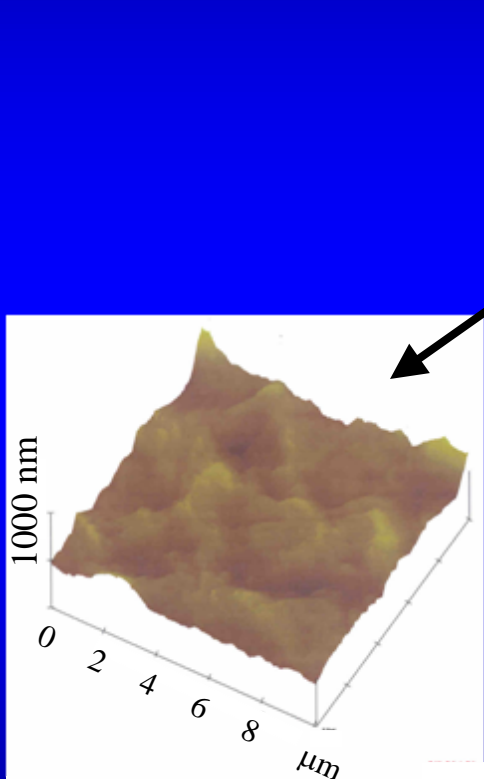
- 6 samples per runs
- 99.98% purity Ni target
- thickness 450 Å



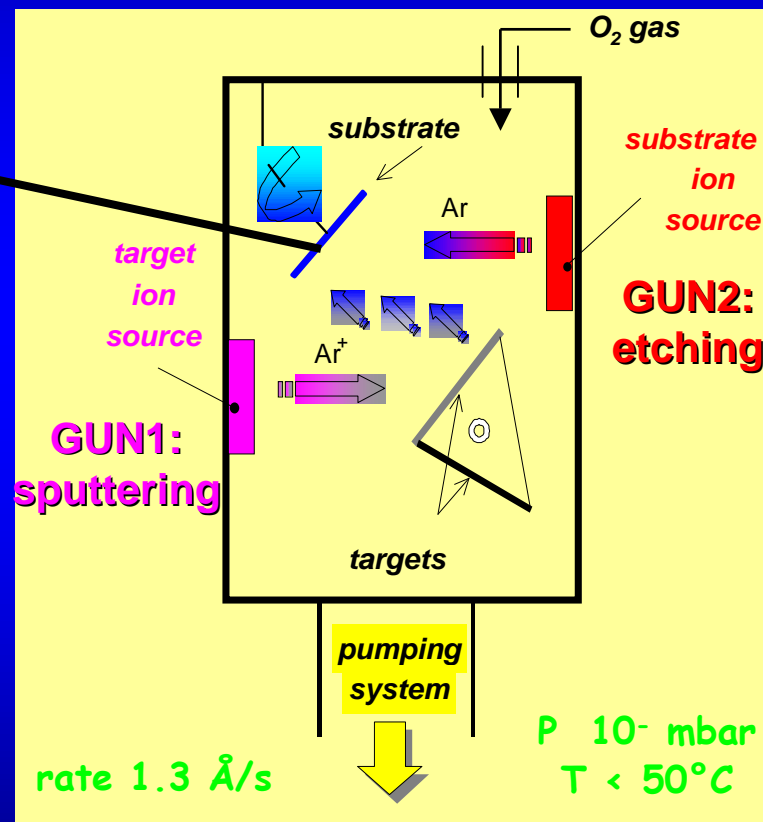
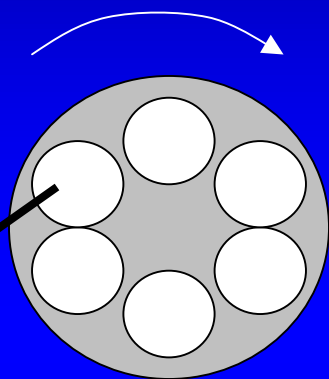
*Identical reference  
and active films*

# Films Deposition Details

*Rotating Sample Holder  
(6 identical locations)*



*Film Surface morphology  
(by Atomic Force Microscopy)*



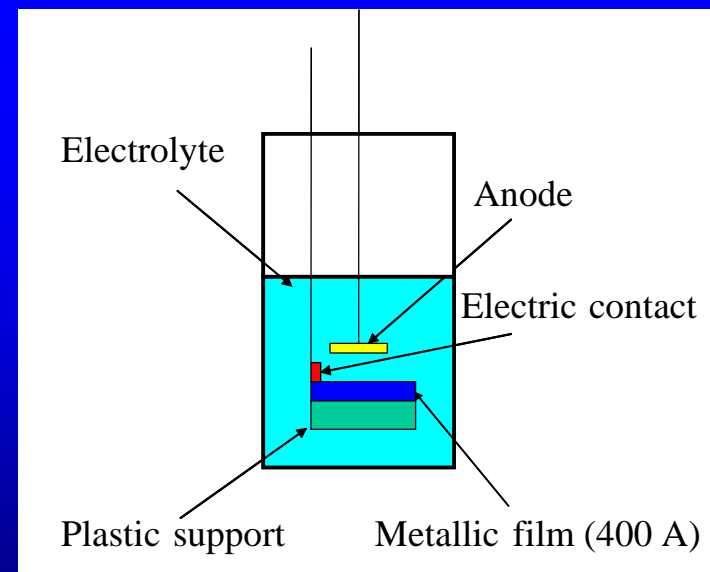
*Dual Ion beam Sputtering plant*

# HYDROGEN LOADING

- Pure Polyethylene (Kartell)
- Pure Pt (99.98) wire
- Light water (18M $\Omega$ ) LiSO<sub>4</sub> 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<sup>+</sup>], spot  $\varnothing \approx 2\text{mm}$ ,  $I \approx 0.5\text{-}2 \mu\text{A}$ ,  $E=1\text{-}5 \text{ KeV}$ ,  $45^\circ$

- **Emergent particles:** Positive and negative ions

- **Mass range:**  $m/e \geq 1$  [0-511 a.m.u.]

- **Resolution:** 0.5 a.m.u.

- **Sensitivity:**  $10^{12} \text{ at/cm}^2$  (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
<b>Ag107</b>	<0,019	<0,034
<b>Ag109</b>	0.025	0.06
<b>Shift Ag%</b>	29.37	47.39

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

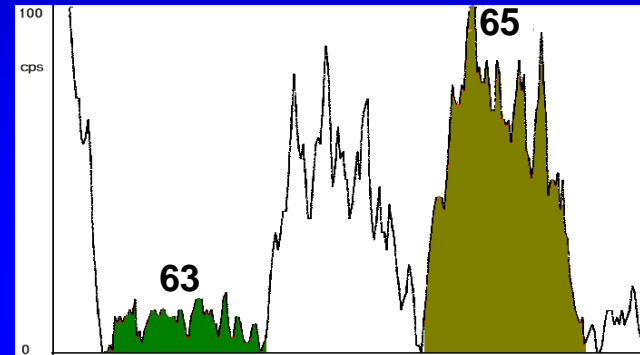
# Preliminary Results

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

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

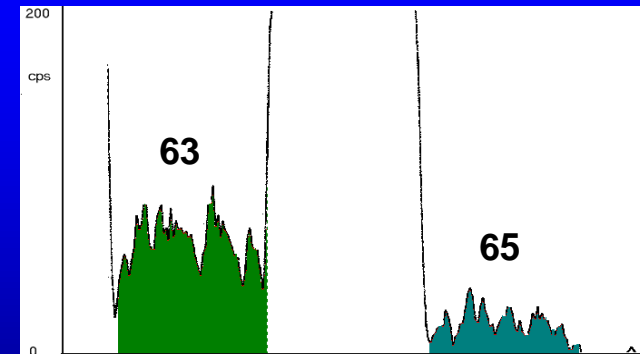


SIMS spectrum of electrolysed film

## Reference film:

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

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



SIMS spectrum of reference film

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

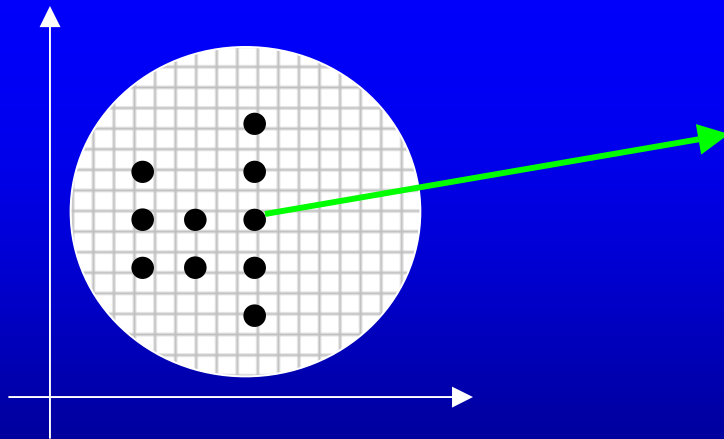
# REPRODUCIBILITY

SAMPLE	Film STATUS after electrolysis	APPARENT ISOTOPIC SHIFT	
		<i>Electrolysed</i>	<i>Reference</i>
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

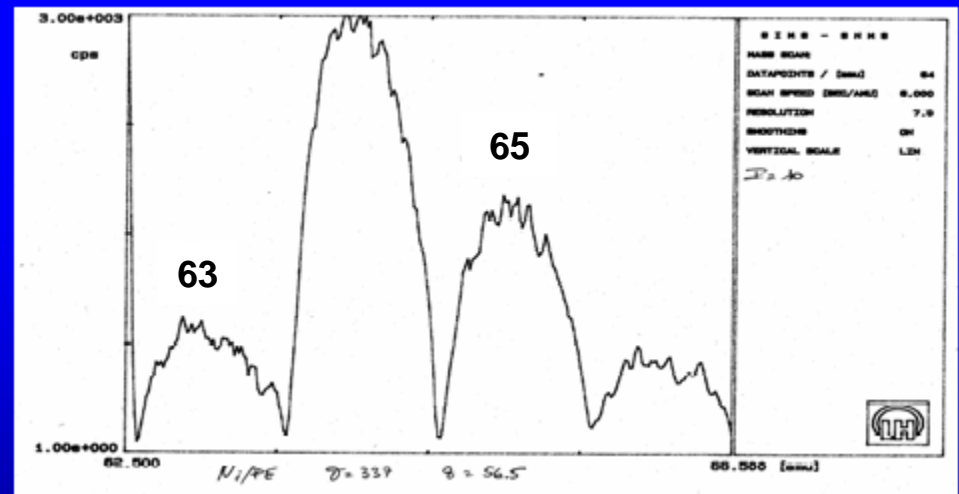
These new results add to the previous ones already shown (ICCF10):  
3/5 experiments giving evidence of apparent isotopic shift

# 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  $\cong 2\text{mm}$



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.  $\text{Ni}^{58}\text{Li}^7$  due to  $\text{Li}_2\text{SO}_4$  electrolyte
4.  $\text{Ni}^{64}\text{H}$  compound

***Mass interferences on 65 m/e signal?***  
**Double ionised atoms?**

No signal is observed from 130 atomic mass ( $\text{Te}^{130}$ ,  $\text{Ba}^{130}$ ), 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 <sub>2</sub>	CH <sub>3</sub>
C <sub>2</sub> H <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>		
C <sub>3</sub> H <sub>3</sub>	C <sub>3</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>	
C <sub>4</sub> H <sub>3</sub>	C <sub>4</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>7</sub>	C <sub>4</sub> H <sub>9</sub>
C <sub>5</sub> H <sub>3</sub>	C <sub>5</sub> H <sub>5</sub>	C <sub>5</sub> H <sub>7</sub>	C <sub>5</sub> H <sub>9</sub>

### References:

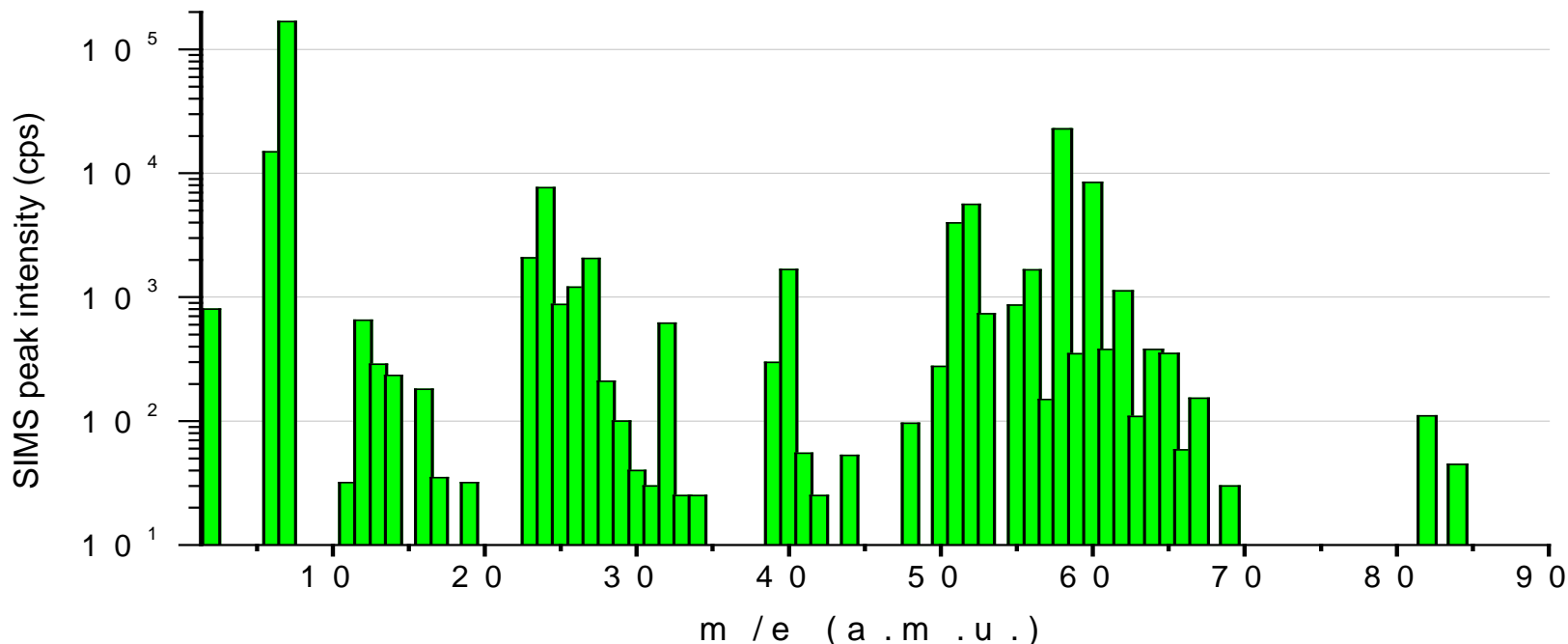
*SIMS technical report by RIBER Instrumentation Ultra-vide, France*

*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 ( $V^{51}$ ,  $Cr^{53}$ ,  $Mn^{55}$ ,  $Fe^{57}$ )

# Organic contaminants (continue)?

## *From the polymeric substrate?*

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

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

## *From the electrolyte?*

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

## *From the surface?*

- The blank sample has been immersed for 2 days in iso-octane to remove organic contaminants eventually adsorbed on the surface. Gas chromatography analysis of the liquid did not reveal any organic contaminant down to 1ppb.

# Mass interferences on 65 m/e signal?

## Ni<sup>58</sup>Li<sup>7</sup> due to Li<sub>2</sub>SO<sub>4</sub> electrolyte?

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

In our SIMS spectrum 65, 67 and 82, 84 mass peaks are present, which can be associated to the Ni<sup>58</sup>Li<sup>7</sup> , Ni<sup>60</sup>Li<sup>7</sup> and Ni<sup>58</sup>Li<sup>7</sup>OH , Ni<sup>60</sup>Li<sup>7</sup>OH compounds.

The ratio between these peaks intensity turns out to be equal to the natural isotopic ratio of Ni<sup>58</sup> and Ni<sup>60</sup>

Ni <sup>58</sup> Li <sup>7</sup> / Ni <sup>60</sup> Li <sup>7</sup>	2.0±0.5
Ni <sup>58</sup> Li <sup>7</sup> OH/ Ni <sup>60</sup> Li <sup>7</sup> OH	2.5±0.5
Ni <sup>58</sup> /Ni <sup>60</sup>	2.71±0.01
Ni <sup>58</sup> /Ni <sup>60</sup> nat.	2.60

## Ni<sup>58</sup>Li<sup>7</sup> due to Li<sub>2</sub>SO<sub>4</sub> electrolyte? (continue)

**but**

The isotopic ratio of the compound related to the Li<sup>7</sup>, Li<sup>6</sup> isotopes (Ni<sup>58</sup>Li<sup>7</sup>/Ni<sup>58</sup>Li<sup>6</sup>) does not match the natural value, but it cannot be determined with enough accuracy due to the Ni<sup>64</sup> 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<sup>58</sup>Li<sup>7</sup> ion cannot be excluded.***

# ***Mass interferences on 65 m/e signal?***

## **Ni<sup>64</sup>H compound?**

Ni<sup>64</sup>H (65mass) detection is unlikely because the isotopic ratio Ni<sup>62</sup>H (63 mass) / Ni<sup>64</sup>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:*

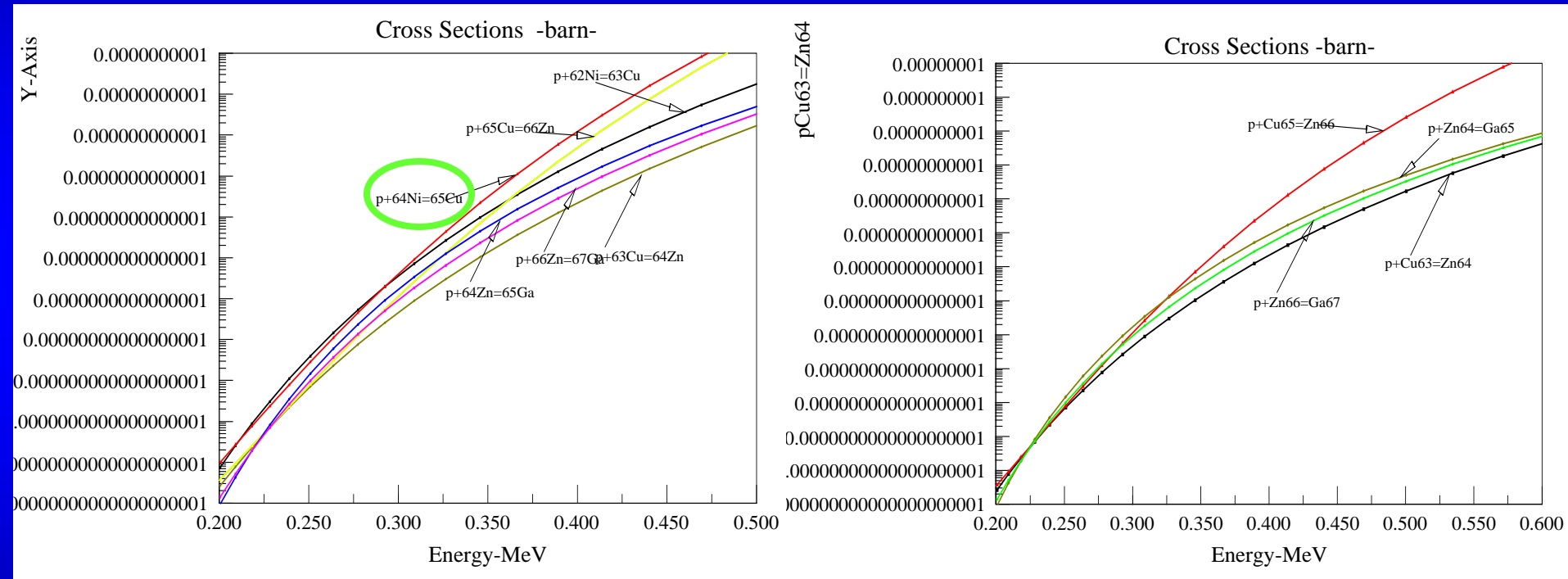
- Ultra-high resolution SIMS apparatus ( $\delta m \leq 0.02$ ,  $m / \delta m > 3000$ )
- Test experiments by changing the electrolyte (for ex. NaOH)
- Cross matched analysis by other methods (for ex. Nuclear Activation Analysis)

# 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<sup>+</sup> primary, negative secondary ions
- Cu<sup>63</sup>/Cu<sup>65</sup> isotopic ratio after calibration of data with a standard:

***Electrolysed*** sample: Cu<sup>63</sup>/Cu<sup>65</sup> = **2.40±0.31**

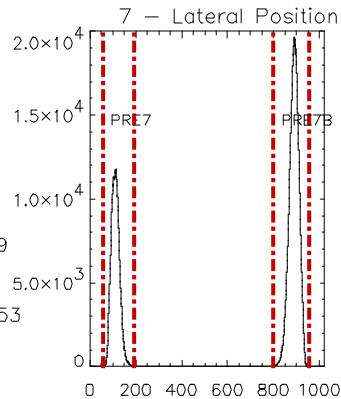
***Reference*** sample: Cu<sup>63</sup>/Cu<sup>65</sup> = **1.79±0.02**

# Lateral Position Spectra

FILE cu1011  
AAB

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

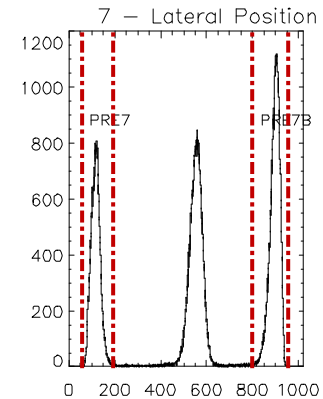
GATE PRE7: $\Sigma=529229$   
MAX=11766 (#112)  
GATE PRE7B: $\Sigma=993253$   
MAX=19630 (#890)



FILE cu1013s  
AAB

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

GATE PRE7: $\Sigma=37610$   
MAX=808 (#120)  
GATE PRE7B: $\Sigma=54879$   
MAX=1118 (#906)



Peak in gate PRE7:  $^{65}\text{Cu}$

Peak in gate PRE7B:  $^{63}\text{Cu}$

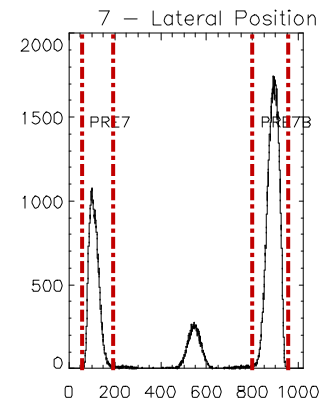
Peak around channel 550: mass 64,  $^{64}\text{Ni}$

## Sample 2, Ni 1 bis

FILE cu1020s  
AAB

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

GATE PRE7: $\Sigma=53873$   
MAX=1079 (#102)  
GATE PRE7B: $\Sigma=110002$   
MAX=1743 (#890)



# Mass interferences on 65 m/e signal?

## Ni<sup>58</sup>Li<sup>7</sup> due to Li<sub>2</sub>SO<sub>4</sub> electrolyte?

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

