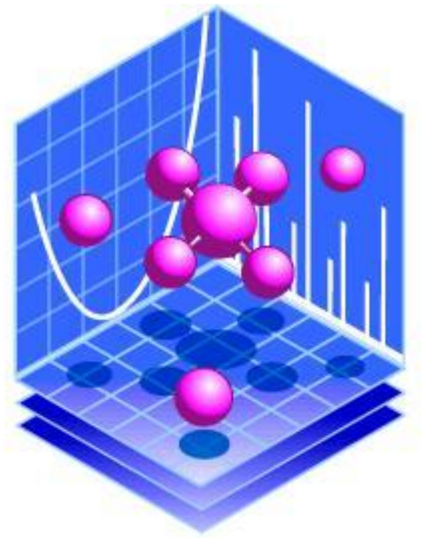
HORIBA
Scientific

JOBIN YVON
Technology



Plasma Profiling Mass Spectrometry (PPMS) zur Analyse von Element- und Isotopenverteilungen in Oberflächen und Schichten

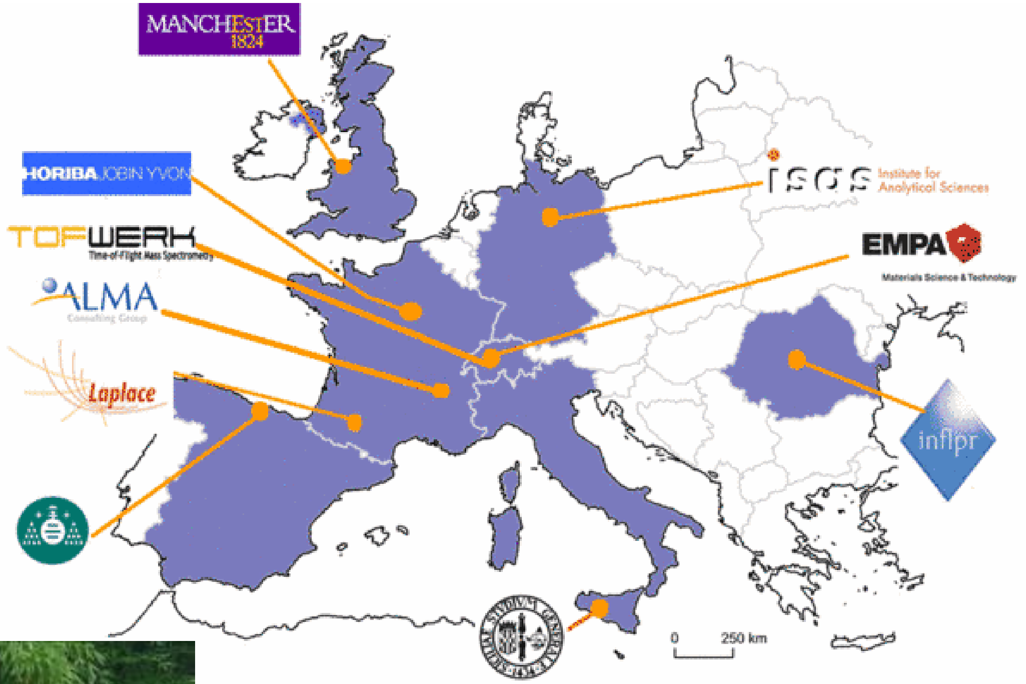
Rainer Nehm, HORIBA Jobin Yvon GmbH, 82008 Unterhaching

Anwendertreffen Analytische Glimmentladungsspektrometrie
23. und 24. November 2013, Duisburg

A European development

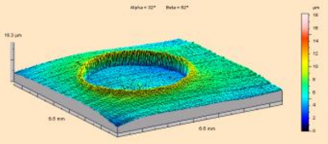
emdpa

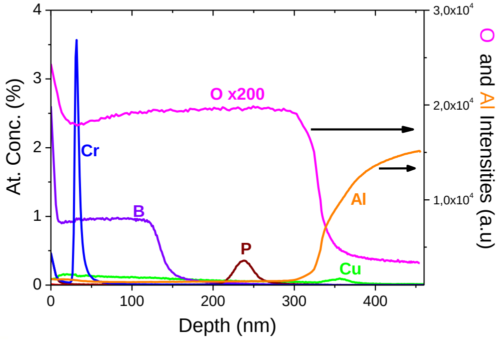
www.emdpa.eu

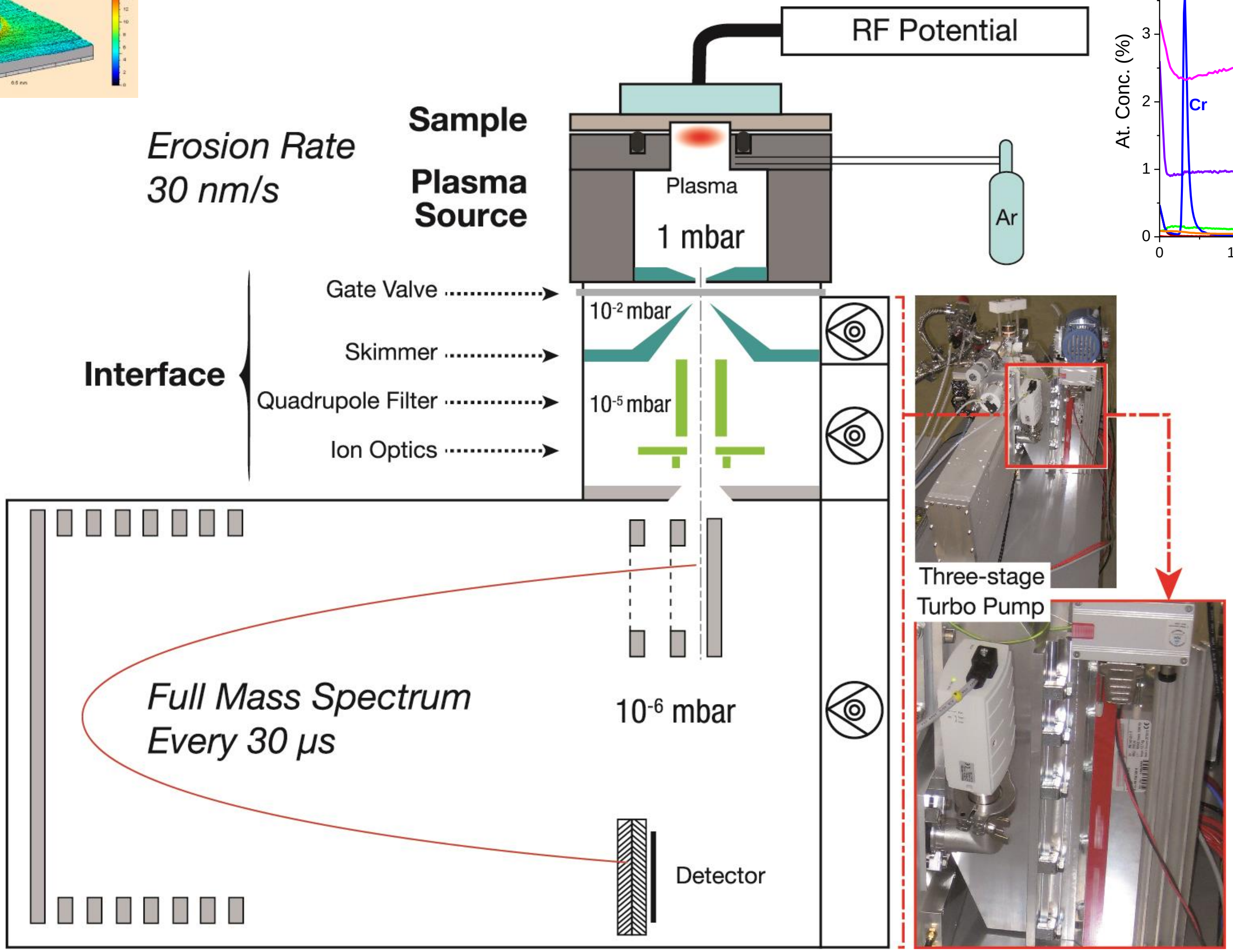


New Elemental and Molecular Depth Profiling Analysis of Materials by Pulsed Radio Frequency Glow Discharge Time of Flight Mass Spectrometry (EMDPA). Start: 2006

PPMS Technique





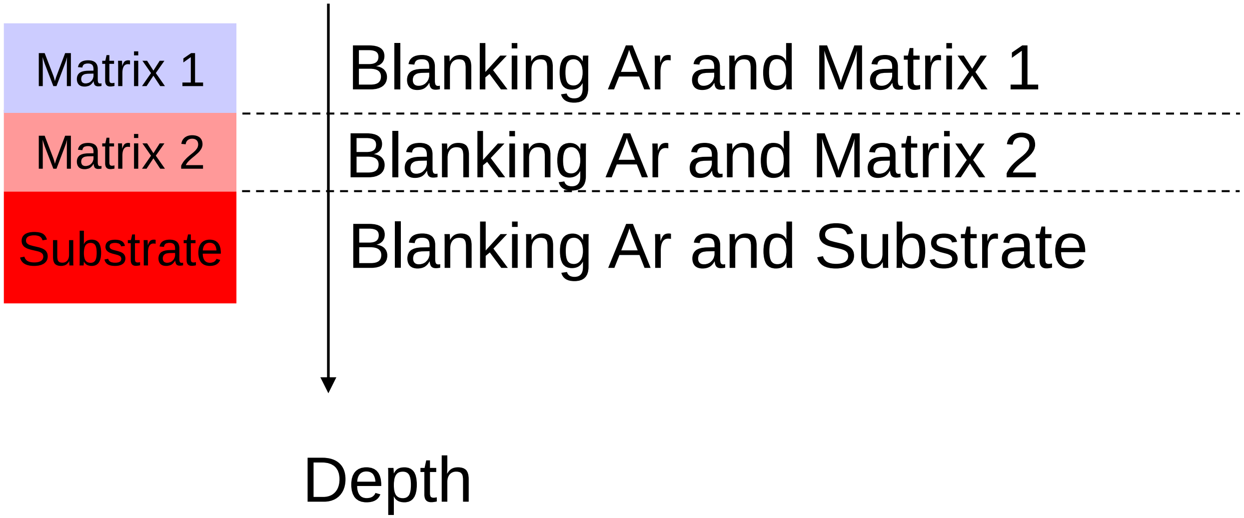


Erosion Rate 30 nm/s

Full Mass Spectrum Every 30 µs

Quadrupol Interface for Blanking (patented)

Blanking of 4 masses simultaneously: Ar related ions (Ar+, Ar dimer) and matrix ions; tuneable for different masses



Matrix 1

Matrix 2

Substrate

Blanking Ar and Matrix 1

Blanking Ar and Matrix 2

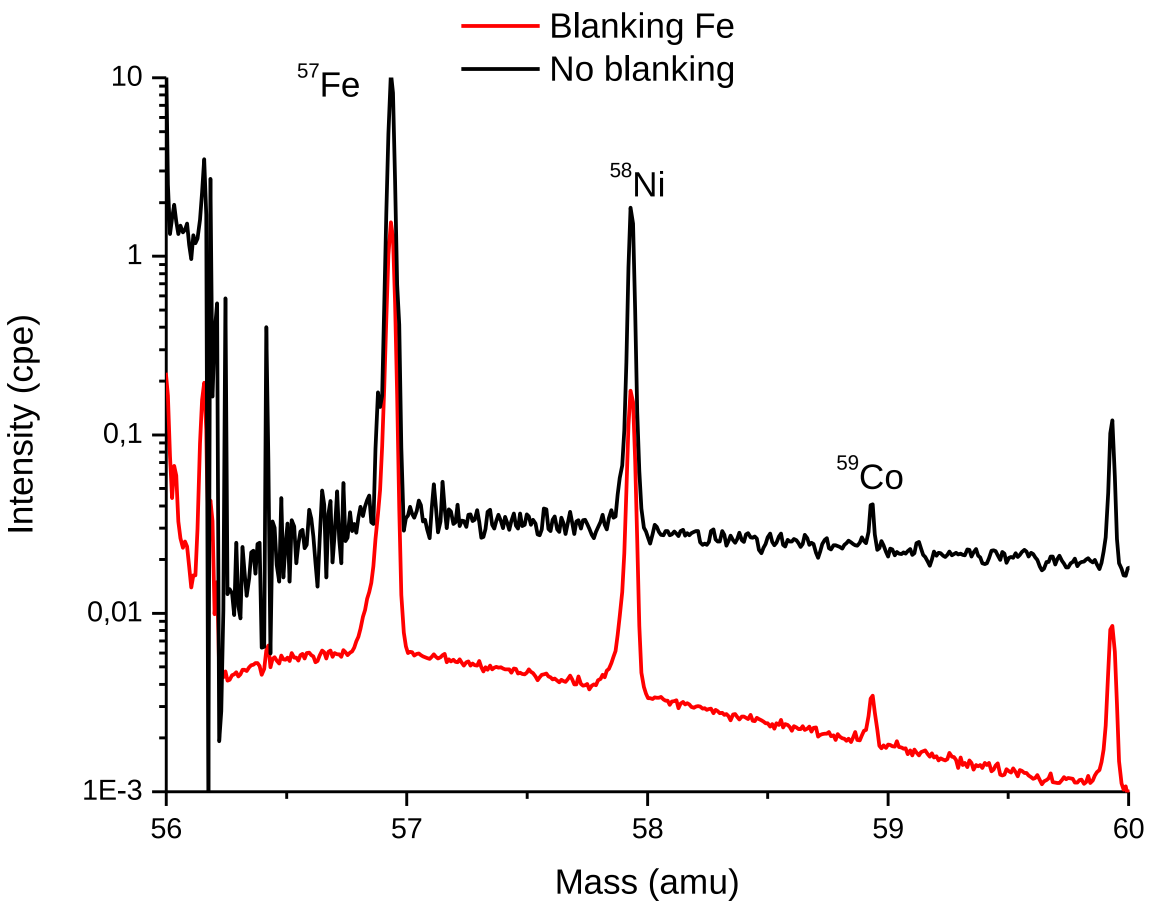
Blanking Ar and Substrate

Depth

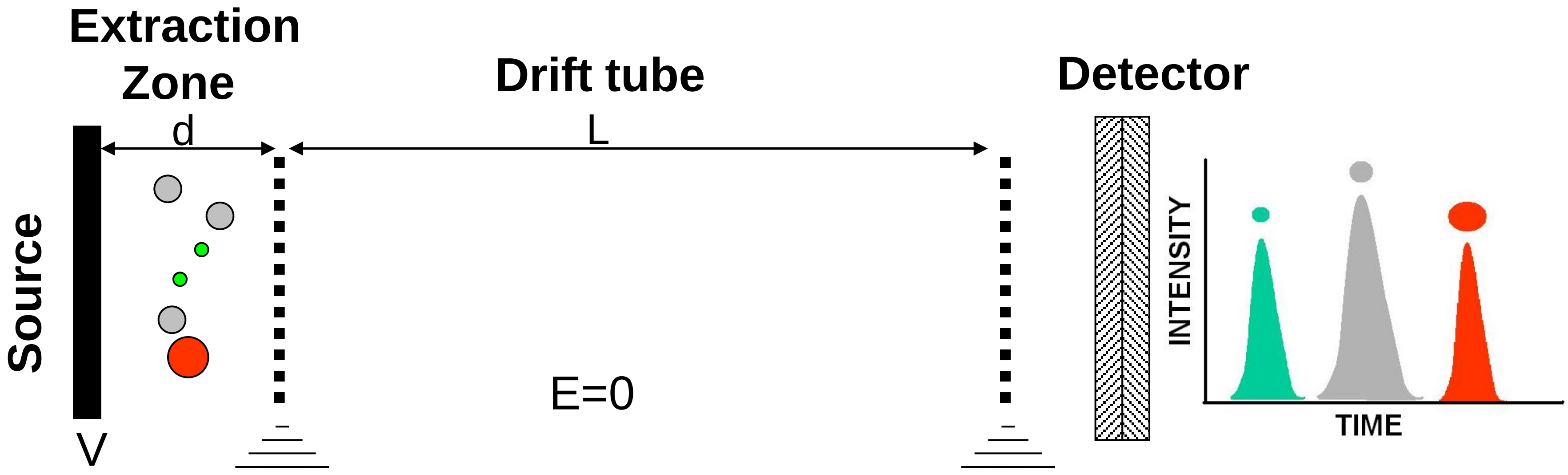
Advantages Blanking:

- Improved signal to noise on neighbouring ions
- Enhanced dynamic range
- Longer detector life time

Blanking


Blanking Fe
No blanking
^{57}Fe
^{58}Ni
^{59}Co
Intensity (cpe)
10
1
0,1
0,01
1E-3
56
57
58
59
60
Mass (amu)

TOF - Time of Flight mass spectrometer



$$\frac{mv^2}{2} = zeV$$

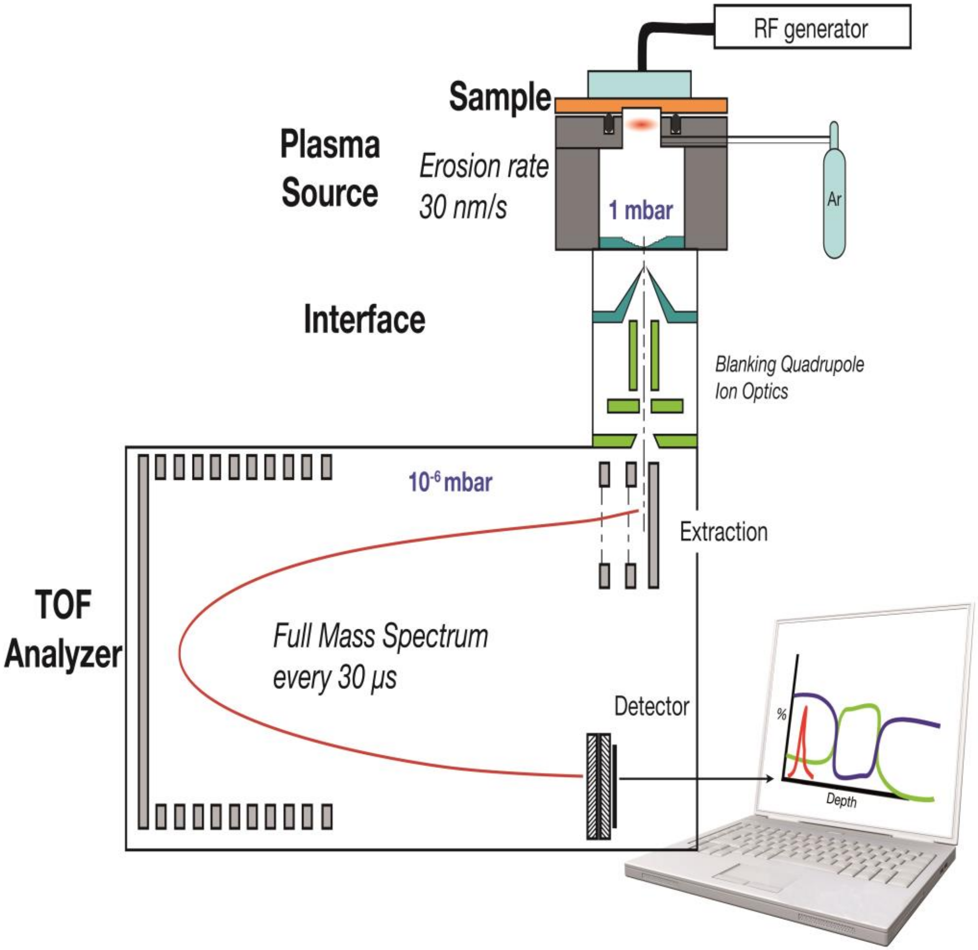
$$\boxed{TOF = a + b\sqrt{m/z}}$$

All ions need to start at the **same time**. **Source** of ions needs to be **pulsed** or the **extraction** of ions needs to be **pulsed**

Specifications of the TOF MS

- Flight Tube : 0.7 m (V mode)
- Flight time : 5 - 100 µs
- Peak width : few ns
- Acquisition speed adjustable

Typical 33 kHz allows measurement of a mass range covering all elements of periodic table



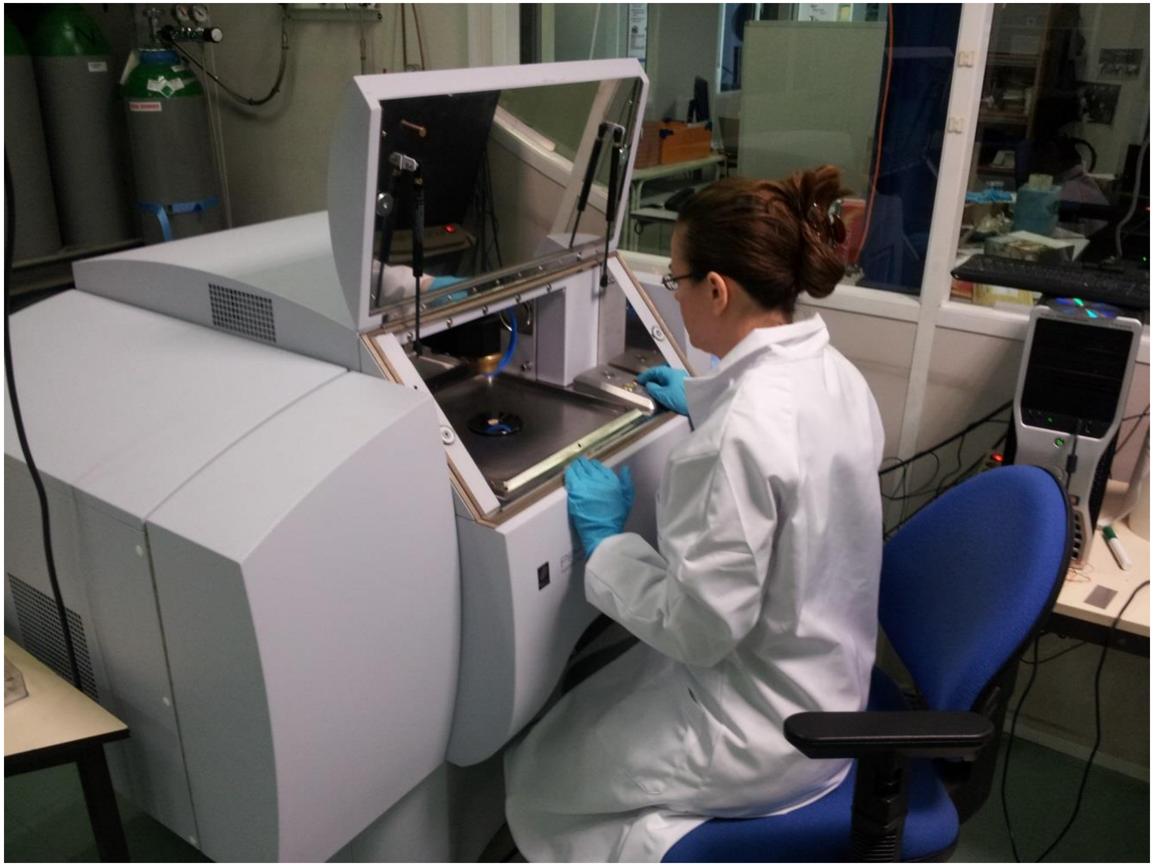
HORIBA Scientific

PPMS

Compact Instrument

Mass resolution: 3000 at m/z 208
HR mode 5000
Dynamic Range: 10^8 in several s
Mass Accuracy: 40 ppm

Comfortable Sitting Position
Panel Display for Status Check



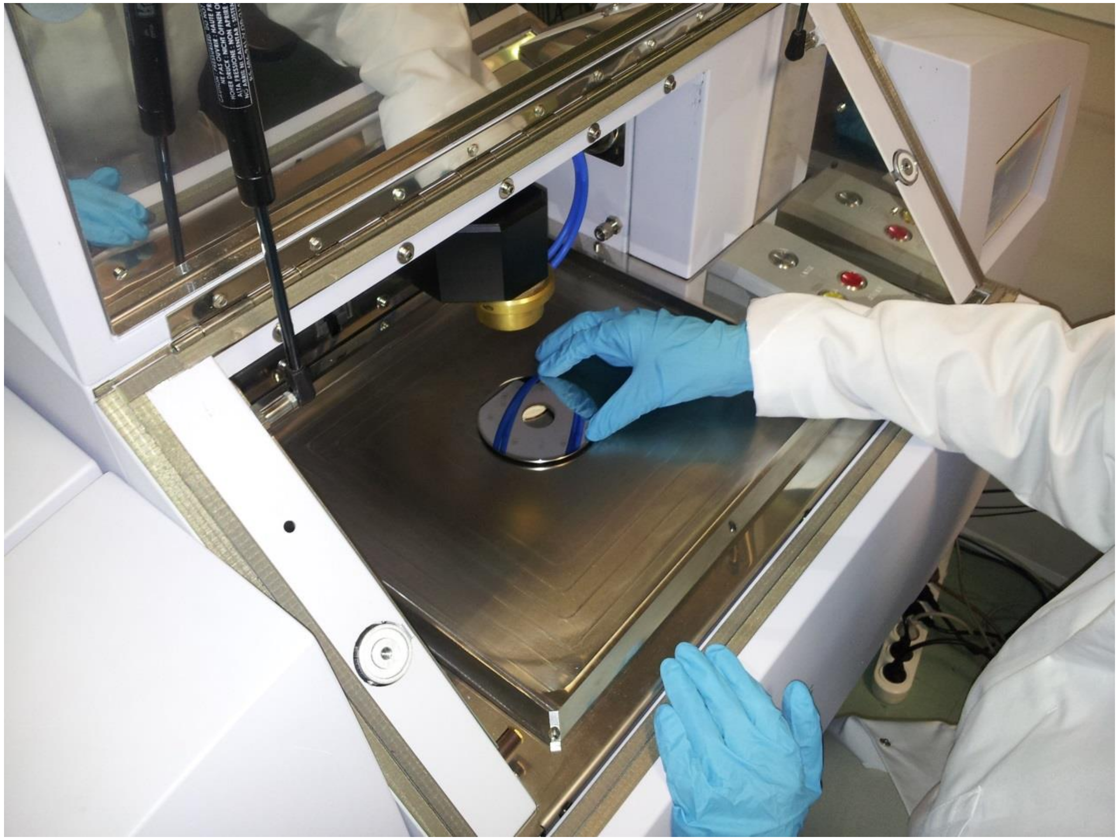
PP-TOFMS

Sample Stage

Horizontal and Easy Sample Mounting

Laser positioning

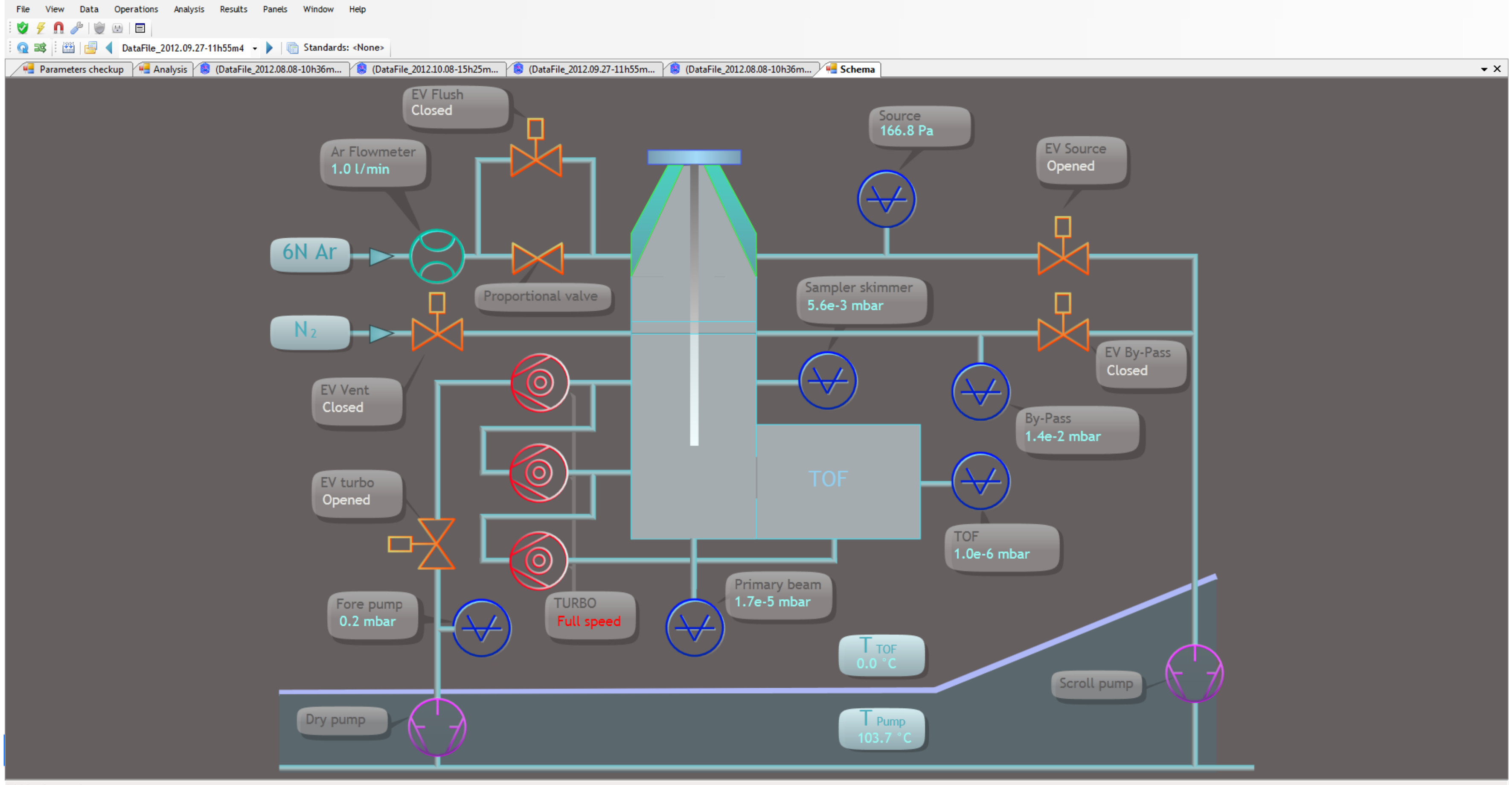
Accepting wide range of sample size From 1 cm to 40 cm



PPMS Software

Global Real-Time Schematics Diagram of the full instrument

At any time, expert user may check status of all pressure gauges, valves and pump status…



EV Flush
Closed

Source
166.8 Pa

Ar Flowmeter
1.0 l/min

EV Source
Opened

Sampler skimmer
5.6e-3 mbar

EV By-Pass
Closed

EV Vent
Closed

By-Pass
1.4e-2 mbar

EV turbo
Opened

TOF
1.0e-6 mbar

Fore pump
0.2 mbar

TURBO
Full speed

Primary beam
1.7e-5 mbar

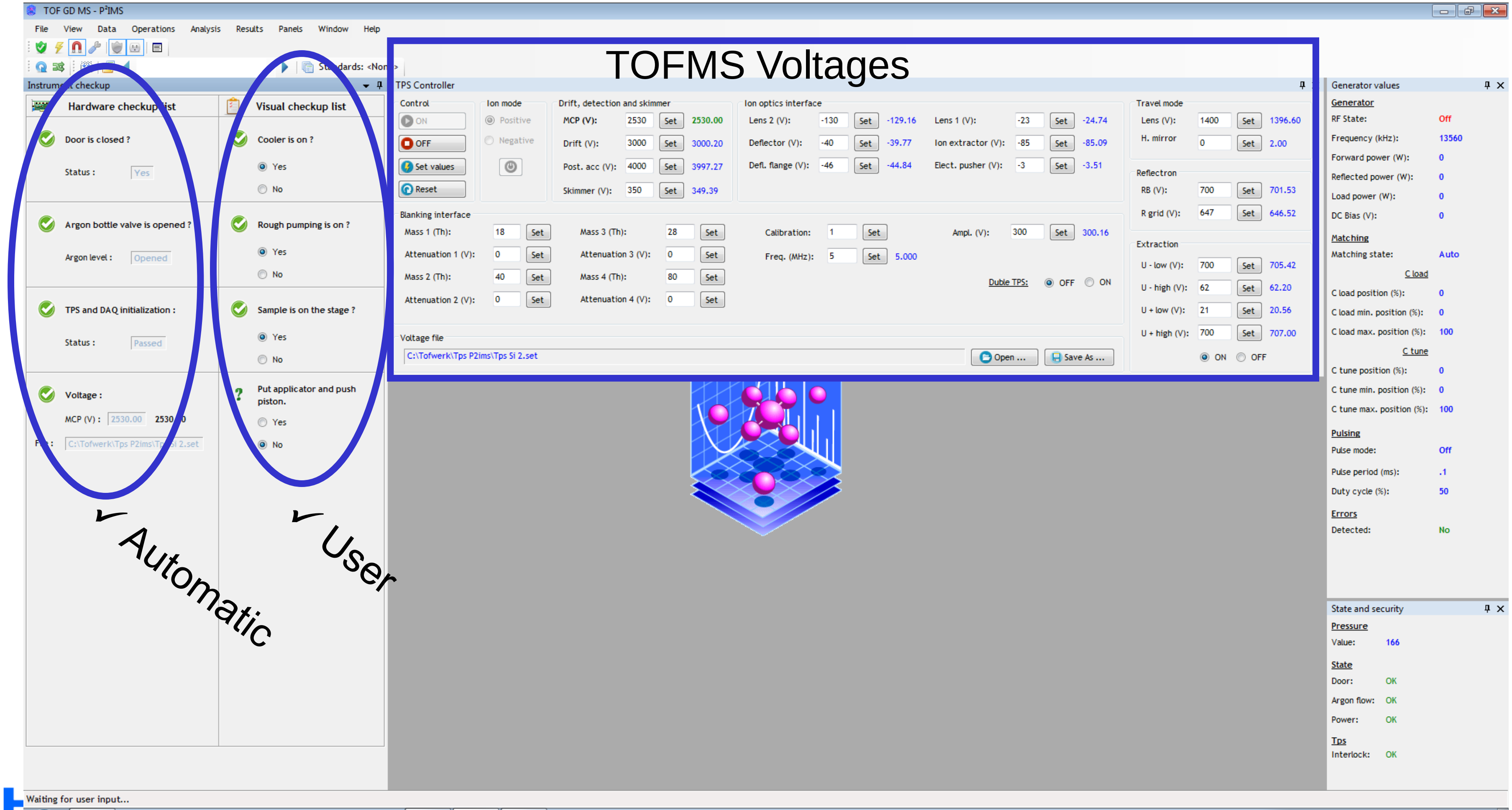
T TOF
0.0 °C

T Pump
103.7 °C

Waiting for user input...

PPMS Software

First screen: Start of the instrument



TOFMS Voltages

✓ Automatic

✓ User

Hardware checkup list

✓ Door is closed ?
Status : Yes

✓ Argon bottle valve is opened ?
Argon level : Opened

✓ TPS and DAQ initialization :
Status : Passed

✓ Voltage :
MCP (V) : 2530.00 2530.00
File : C:\Tofwerk\Tps P2ims\Tps Si 2.set

Visual checkup list

✓ Cooler is on ?
● Yes
○ No

✓ Rough pumping is on ?
● Yes
○ No

✓ Sample is on the stage ?
● Yes
○ No

? Put applicator and push piston.
○ Yes
● No

TPS Controller

Ion mode
○ Positive
○ Negative

Drift, detection and skimmer

MCP (V):	2530	Set	2530.00
Drift (V):	3000	Set	3000.20
Post. acc (V):	4000	Set	3997.27
Skimmer (V):	350	Set	349.39

Ion optics interface

Lens 2 (V):	-130	Set	-129.16
Deflector (V):	-40	Set	-39.77
Defl. flange (V):	-46	Set	-44.84
Lens 1 (V):	-23	Set	-24.74
Ion extractor (V):	-85	Set	-85.09
Elect. pusher (V):	-3	Set	-3.51

Travel mode

Lens (V):	1400	Set	1396.60
H. mirror	0	Set	2.00

Reflectron

RB (V):	700	Set	701.53
R grid (V):	647	Set	646.52

Blanking interface

Mass 1 (Th):	18	Set
Attenuation 1 (V):	0	Set
Mass 2 (Th):	40	Set
Attenuation 2 (V):	0	Set
Mass 3 (Th):	28	Set
Attenuation 3 (V):	0	Set
Mass 4 (Th):	80	Set
Attenuation 4 (V):	0	Set

Calibration:	1	Set	
Freq. (MHz):	5	Set	5.000
Ampl. (V):	300	Set	300.16

Duble TPS: ● OFF ○ ON

Extraction

U - low (V):	700	Set	705.42
U - high (V):	62	Set	62.20
U + low (V):	21	Set	20.56
U + high (V):	700	Set	707.00

● ON ○ OFF

Voltage file
C:\Tofwerk\Tps P2ims\Tps Si 2.set

Generator values

Generator
RF State: Off
Frequency (kHz): 13560
Forward power (W): 0
Reflected power (W): 0
Load power (W): 0
DC Bias (V): 0

Matching
Matching state: Auto

C load
C load position (%): 0
C load min. position (%): 0
C load max. position (%): 100

C tune
C tune position (%): 0
C tune min. position (%): 0
C tune max. position (%): 100

Pulsing
Pulse mode: Off
Pulse period (ms): .1
Duty cycle (%): 50

Errors
Detected: No

State and security

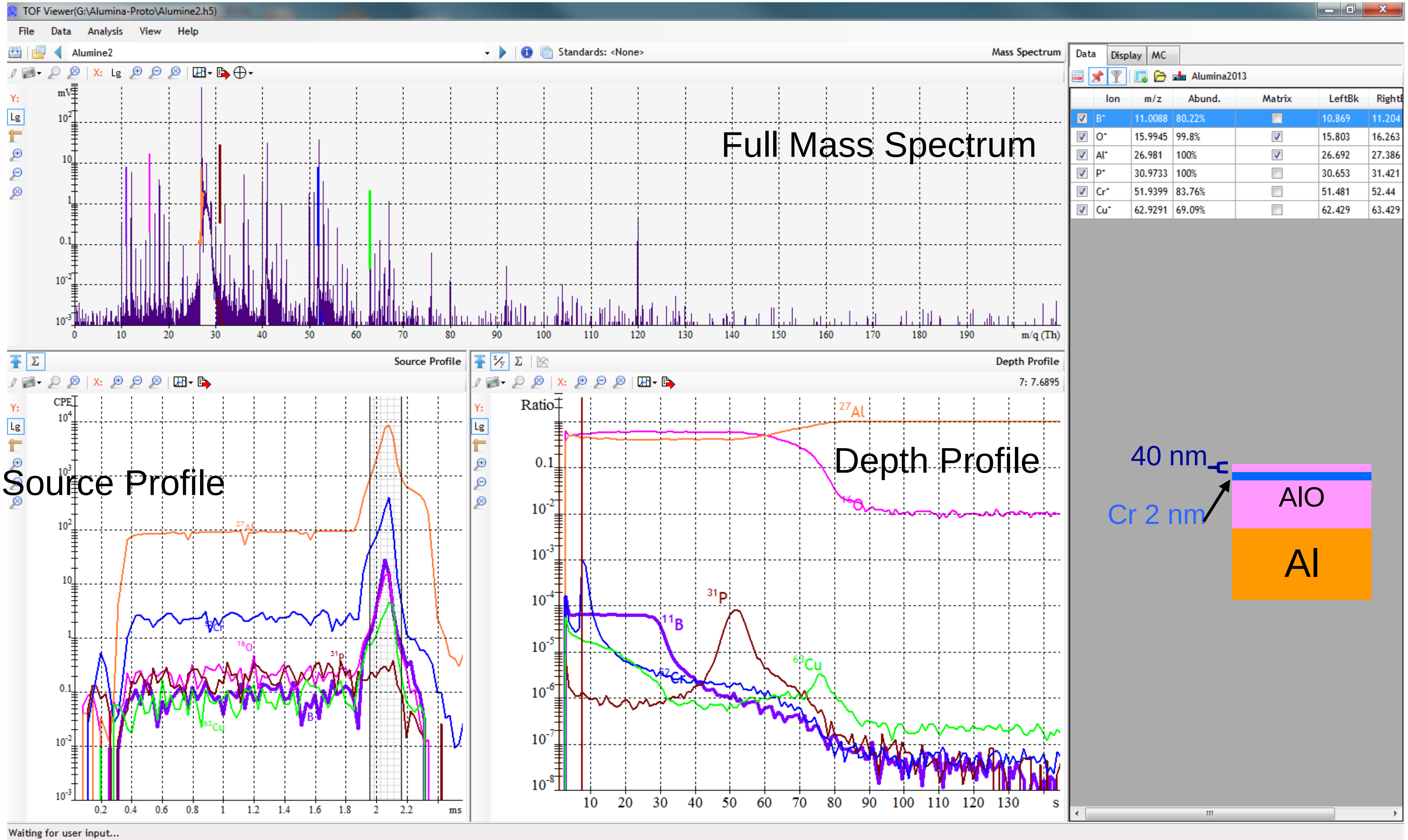
Pressure
Value: 166

State
Door: OK
Argon flow: OK
Power: OK

Tps
Interlock: OK

Waiting for user input...

Pulsed Mode + TOFMS

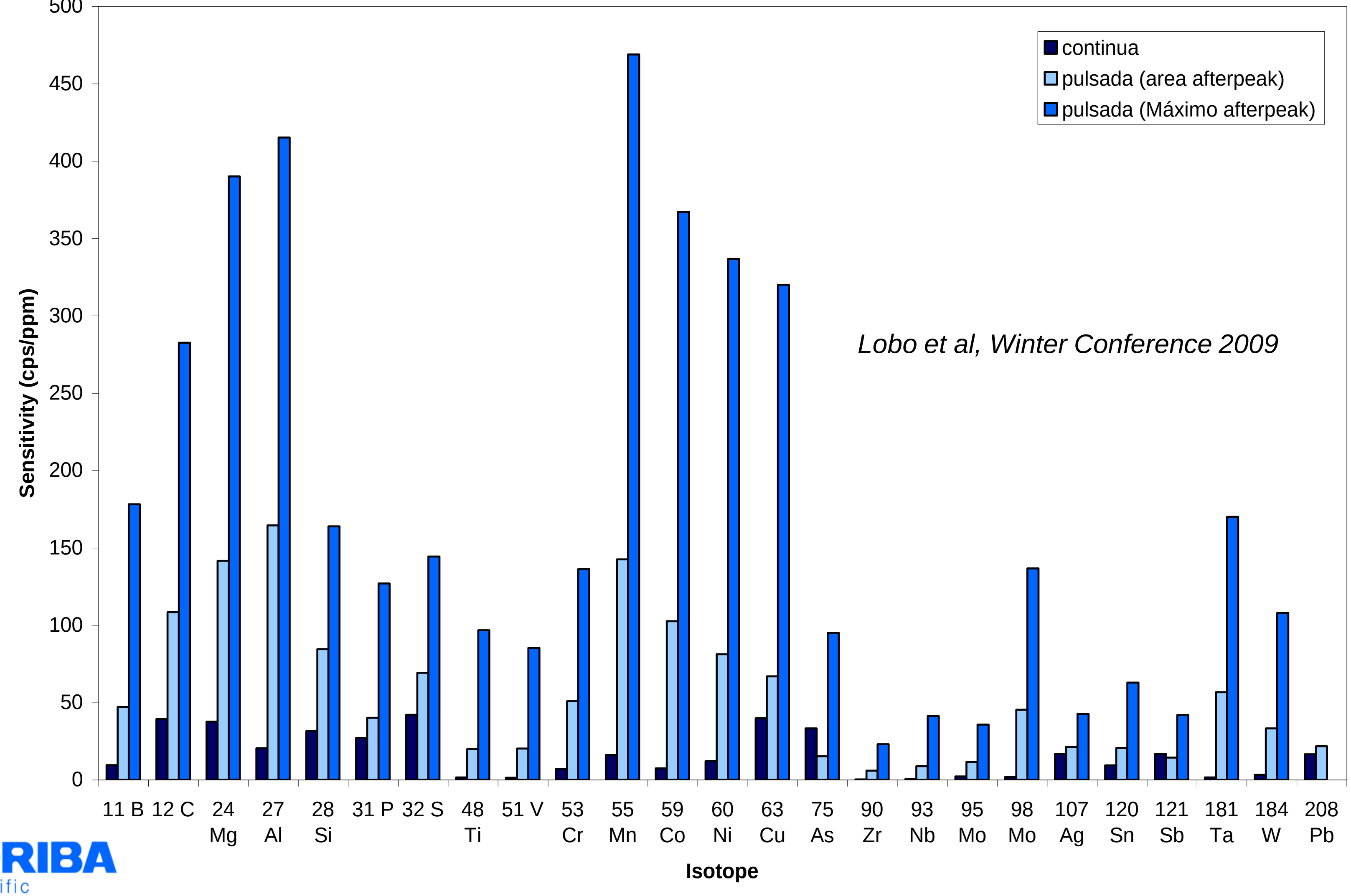


	Ion	m/z	Abund.	Matrix	LeftBk	Right
☑	B^+	11.0088	80.22%	☐	10.869	11.204
☑	O^+	15.9945	99.8%	☑	15.803	16.263
☑	Al^+	26.981	100%	☑	26.692	27.386
☑	P^+	30.9733	100%	☐	30.653	31.421
☑	Cr^+	51.9399	83.76%	☐	51.481	52.44
☑	Cu^+	62.9291	69.09%	☐	62.429	63.429

Waiting for user input...

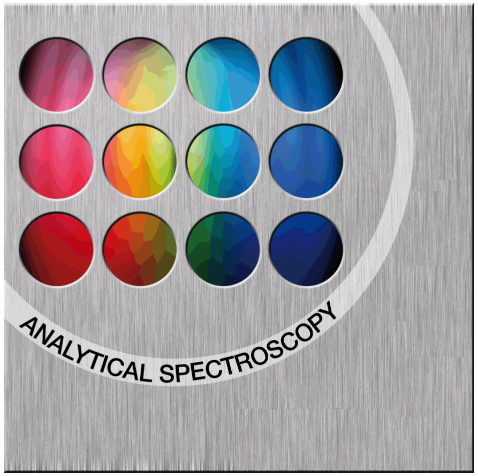
Measurement in pulsed mode

Signal enhancement in afterglow –up to 1e3



Lobo et al, Winter Conference 2009

Surface analysis with Plasma Profiling Mass Spectrometry – Examples for elemental and isotopic information

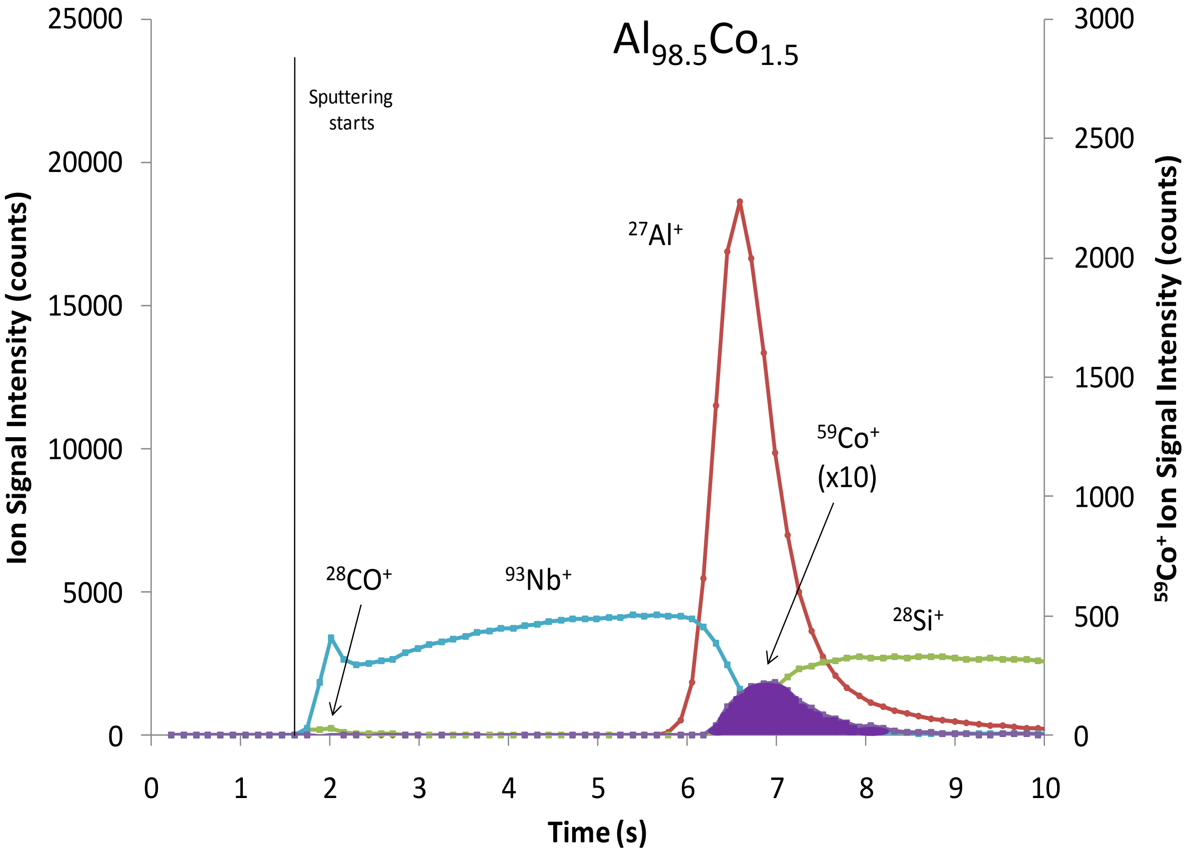


Analysis of ultra-thin layers - minor elements

Nb/Al$_{(100-x)}$Co$_x$/Si

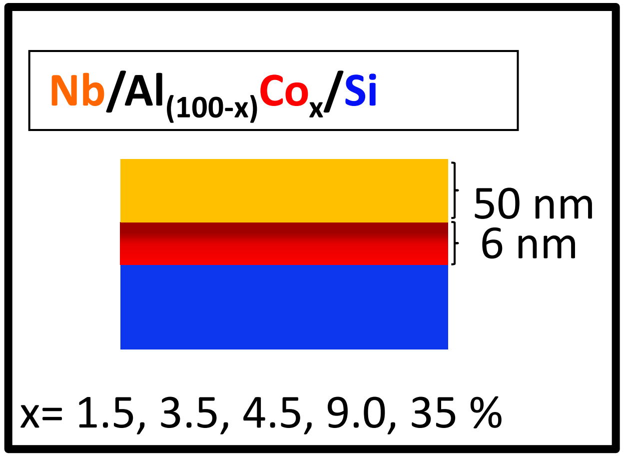
x= 1.5, 3.5, 4.5, 9.0, 35 %

Constant thickness of internal layer, but variation of the Al-Co stoichiometry



Pisonero et al, Winter Plasma Conference 2011

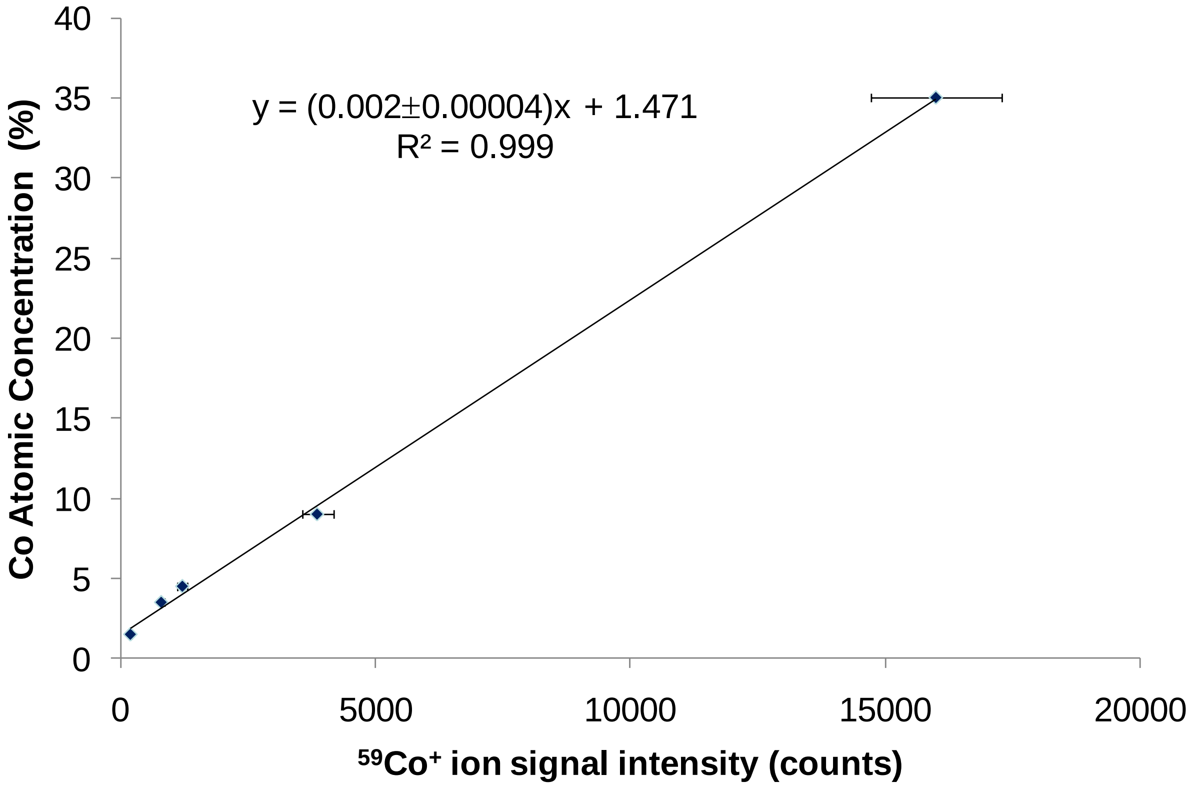
Analysis of ultra-thin layers - minor elements



$Nb/Al_{(100-x)}Co_x/Si$

x= 1.5, 3.5, 4.5, 9.0, 35 %

Constant thickness of internal layer, but variation of the Al-Co stoichiometry



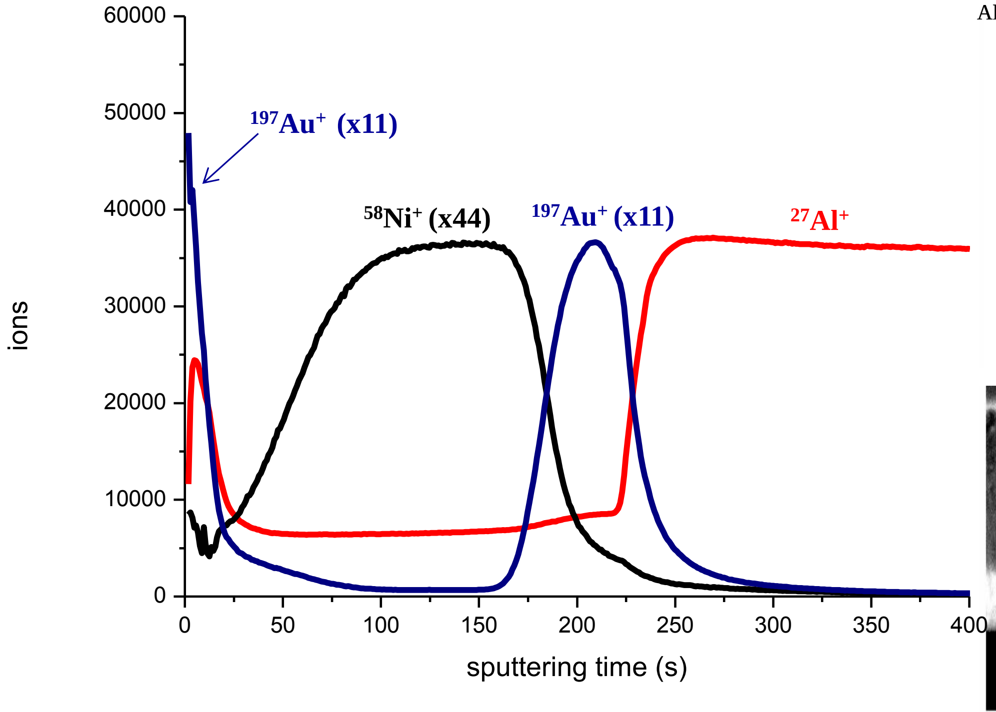
Calibration of Co atomic concentration in 6 nm AlCo layers

Pisonero et al, Winter Plasma Conference 2011

Analysis of Multilayered Metal Nanowires

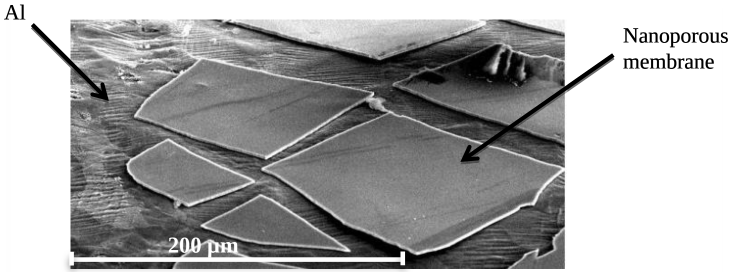
Template filled with trilayer nanowires (3.5 μm nanopore length)

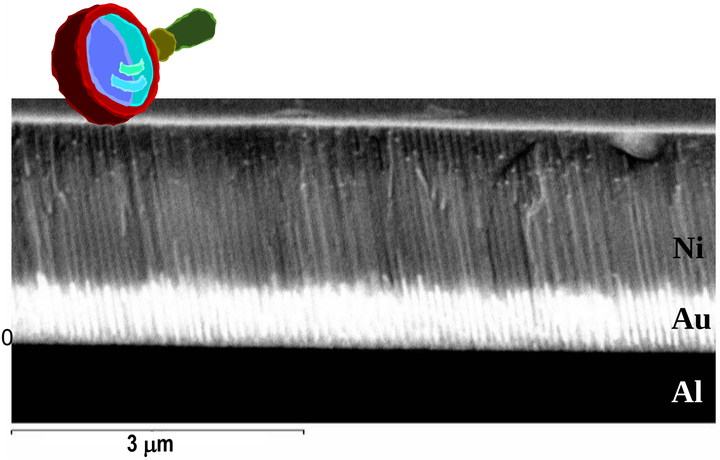
☐ **Pulsed rf-GD-ToFMS qualitative depth profile**



Au(--)/Ni(1.9 μm)/Au(0.9 μm)/Substrate

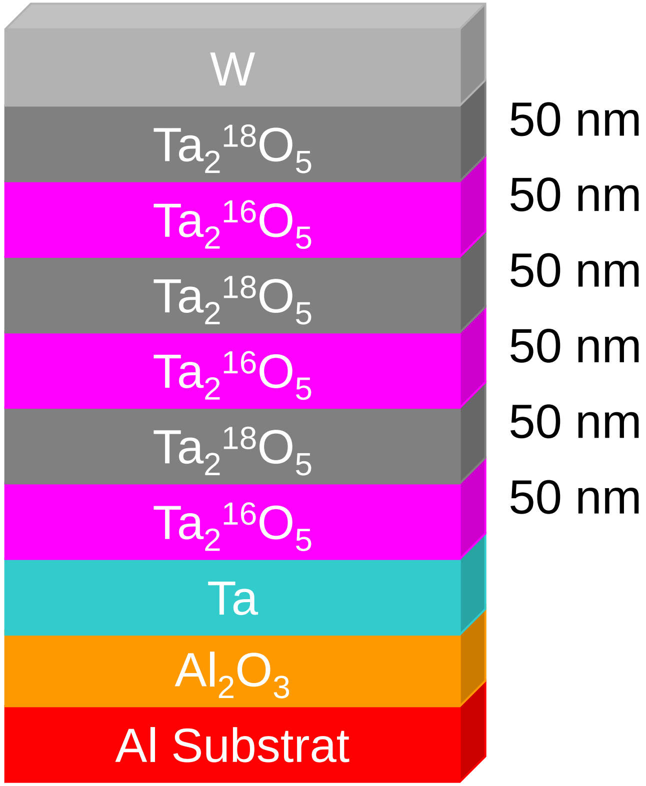
☐ **SEM cross-sectional view**





- **Pulsed rf-GD-ToFMS allows a fast and reliable depth characterization of nanopores quality,** of critical importance to assist the optimization of electrodeposition procedures as well as to evaluate their routine manufacturing quality (e.g. evaluating the possible failure in electrodeposion process)

Isotopic Analysis



6. Steps 4 & 5 repeated, on top W surface with 25 nm thickness

5. $Ta_2{}^{18}O_5$ Anodisation in sodium tungstate prepared with ^{18}O enriched H_2O

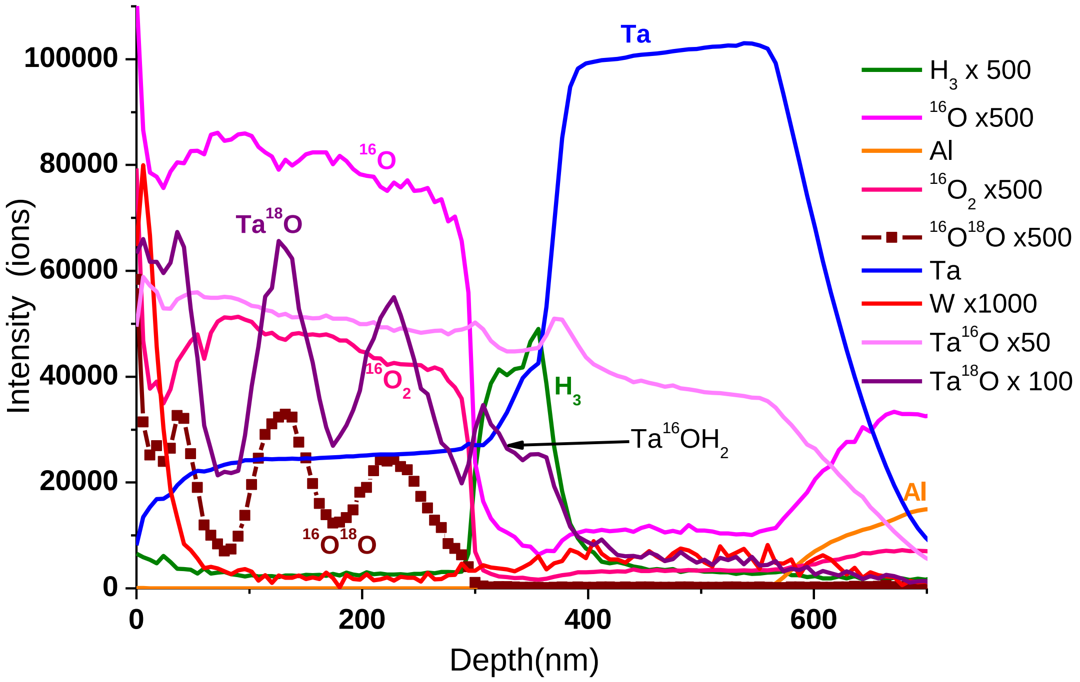
4. $Ta_2{}^{16}O_5$ Anodisation in sodium tungstate (Na_2WO_4)

3. Ta Sputtering deposition

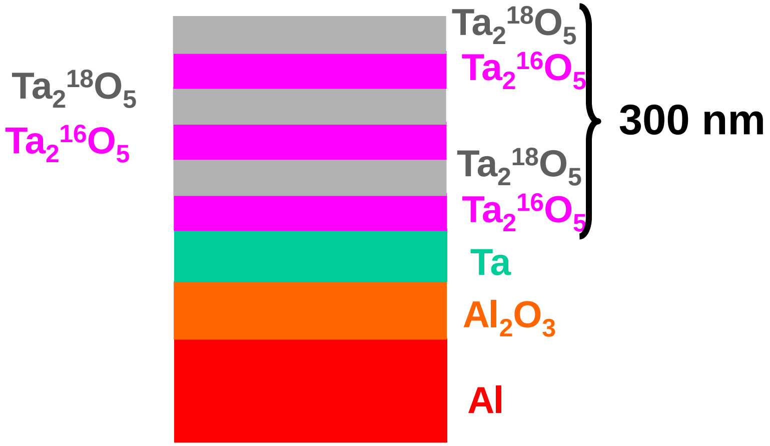
2. Al_2O_3 Anodisation in ammonium pentaborate ($NH_4B_5O_8{\cdot}4H_2O$)

1. Al Substrate: pure foil 0.3 mm thick

Example 5: ^{18}O enriched thin tantalum oxide bilayers



Analysis Conditions
Plasma 600 Pa, 45 W
Puls mode 0.8 ms /4 ms

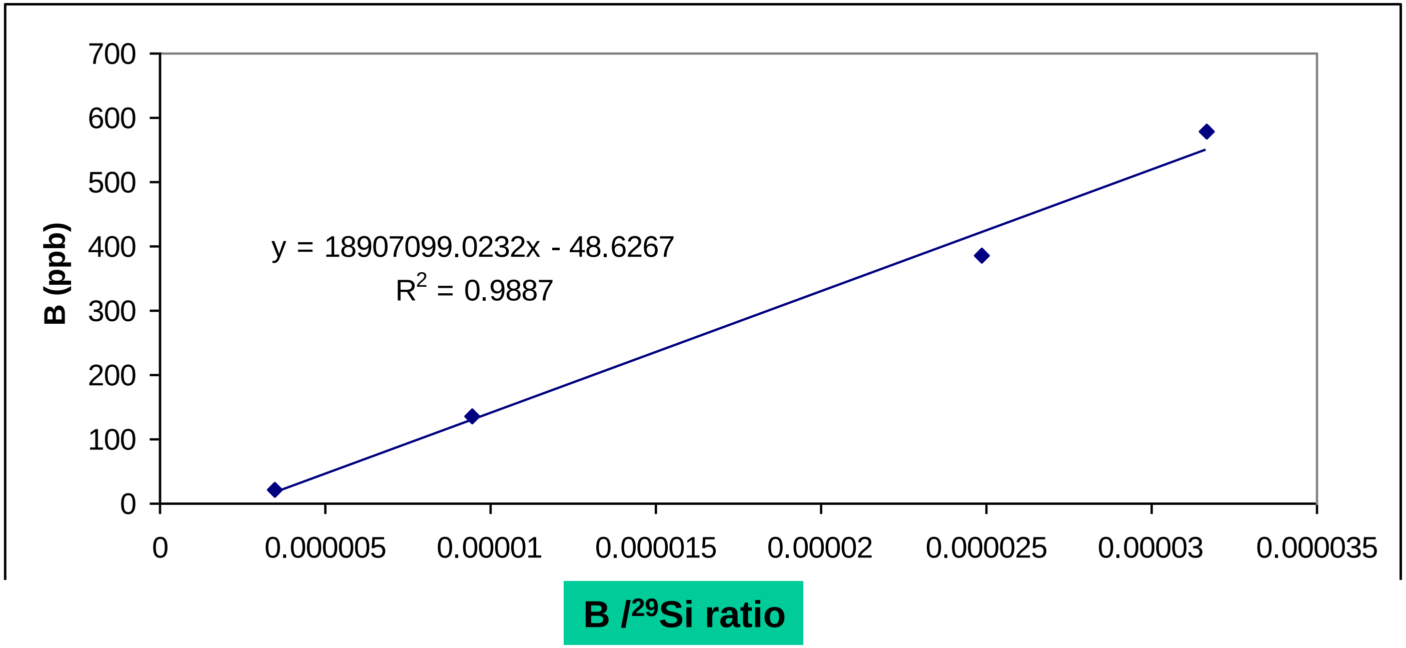


- Detection of marker W on top surface with expected thickness ~ 25 nm
- Resolution of labeled layers ^{18}O (looking at $^{16}O^{18}O$ and $Ta^{18}O$)
- Detection of H at the interface oxide/ metal

A. Tempez *et al*, Surface and Interface Analysis, 41, 966 (2009).

Photovoltaics: Si

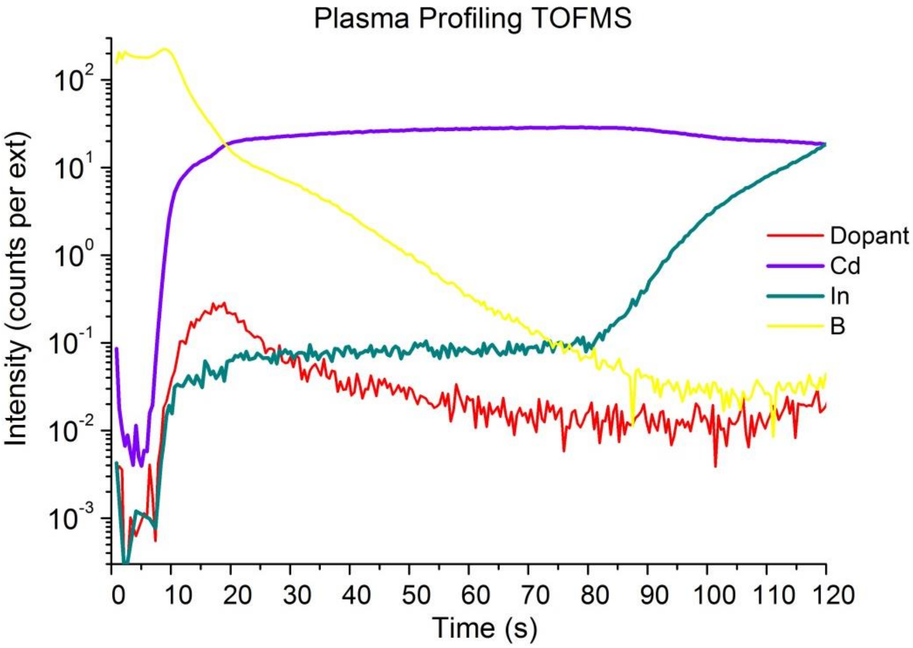
Quantification of B in Solar Grade Silicon: PP-TOFMS

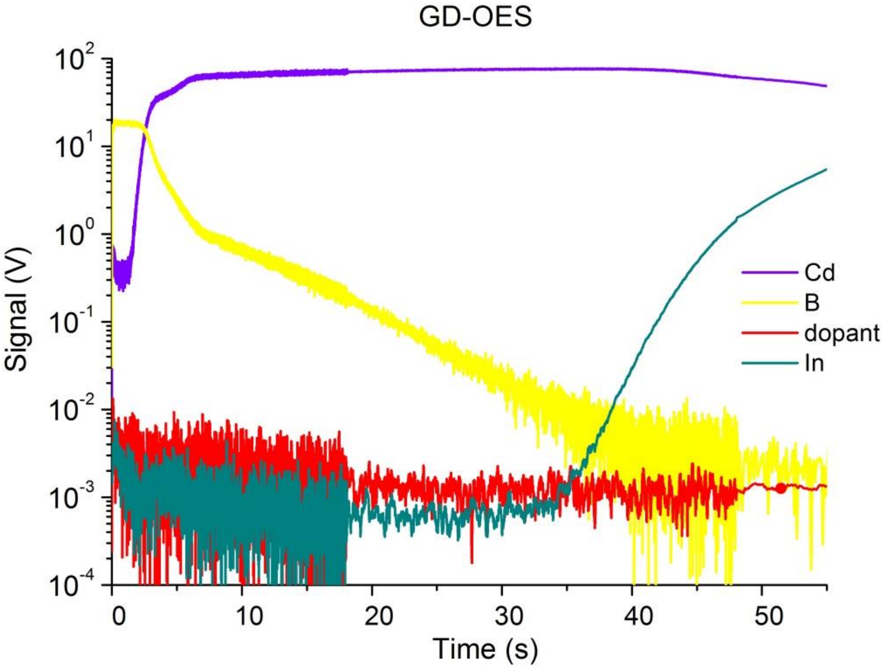


Sample	B (ppb)	Intensity (cps)	B (ppb) Estimated (b)
267 B	**1800**	**220**	1842

Photovoltaics: CdTe

CdTe thin films PV

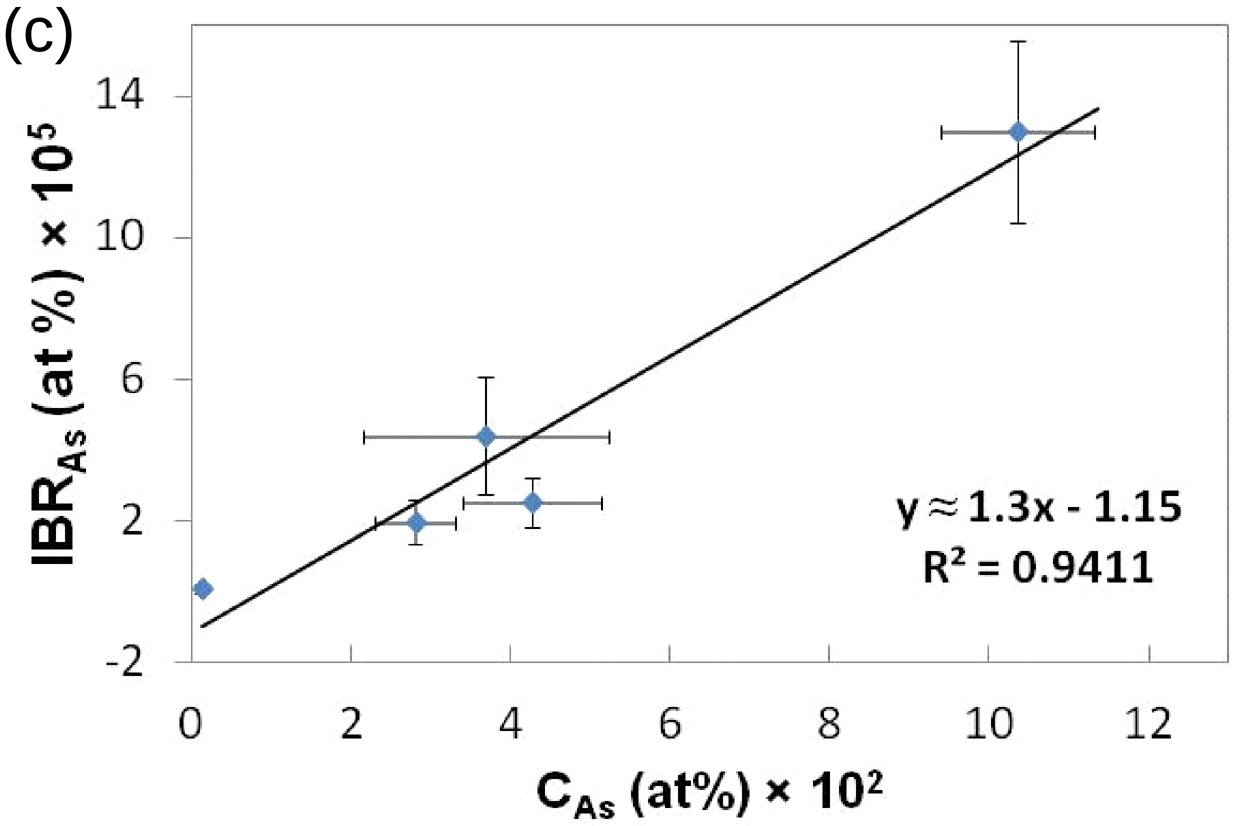




Presented at PVsat13, collaboration with CSER, UK

Photovoltaics: CdTe

CdTe thin films PV- Quantification using SIMS



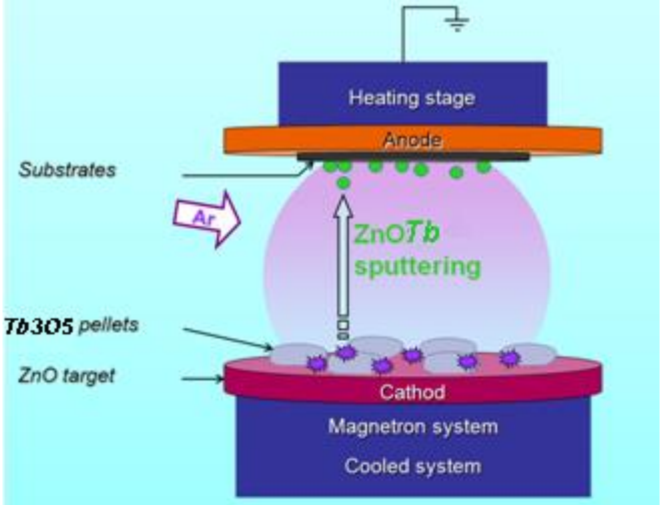
Presented at PVsat13, collaboration with CSER, UK

Photonics: Rare Earth Doped ZnO

Electroluminescent Devices - White LEDs

Optimization of structural and optical properties in terms of electrical properties and PL intensity with sputtering growth parameters.

RF magnetron sputtering



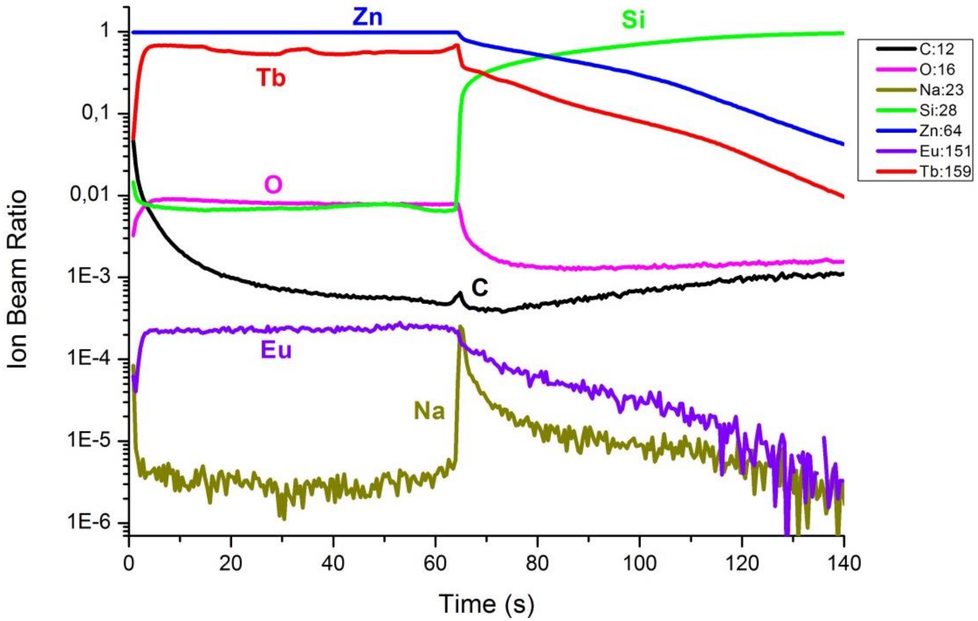
CIMAP (Ions, Materials and Photonics Research Center), University of Caen.

__Growth parameters__

- T_s = RT - 400° C
- P= 15 µbar
- RF power: 75, 100, 125 and 150 W
- d: electrode distance (7 cm)
- Number of pellets:10 (Tb3O5)
- Target surface: 77 cm^2
- Substrates: (100)-oriented p-Si
- Deposition rate: 10 nm/min

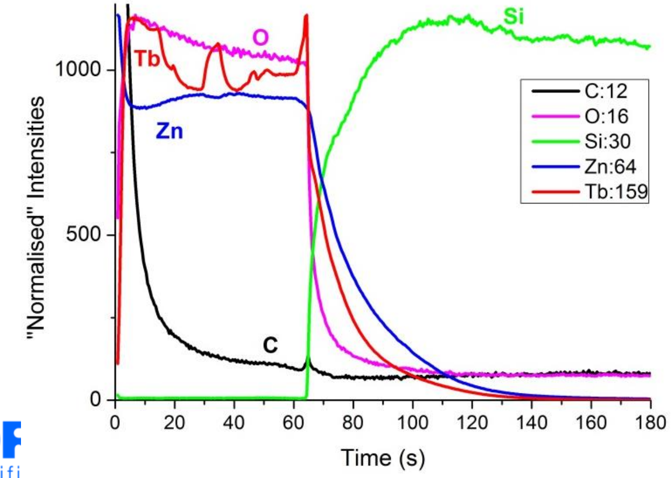
SPIE Photonics West 2013

Photonics: Rare Earth Doped ZnO



Na, C at interfaces
Tb high at % level

High sensitivity
High dynamic range



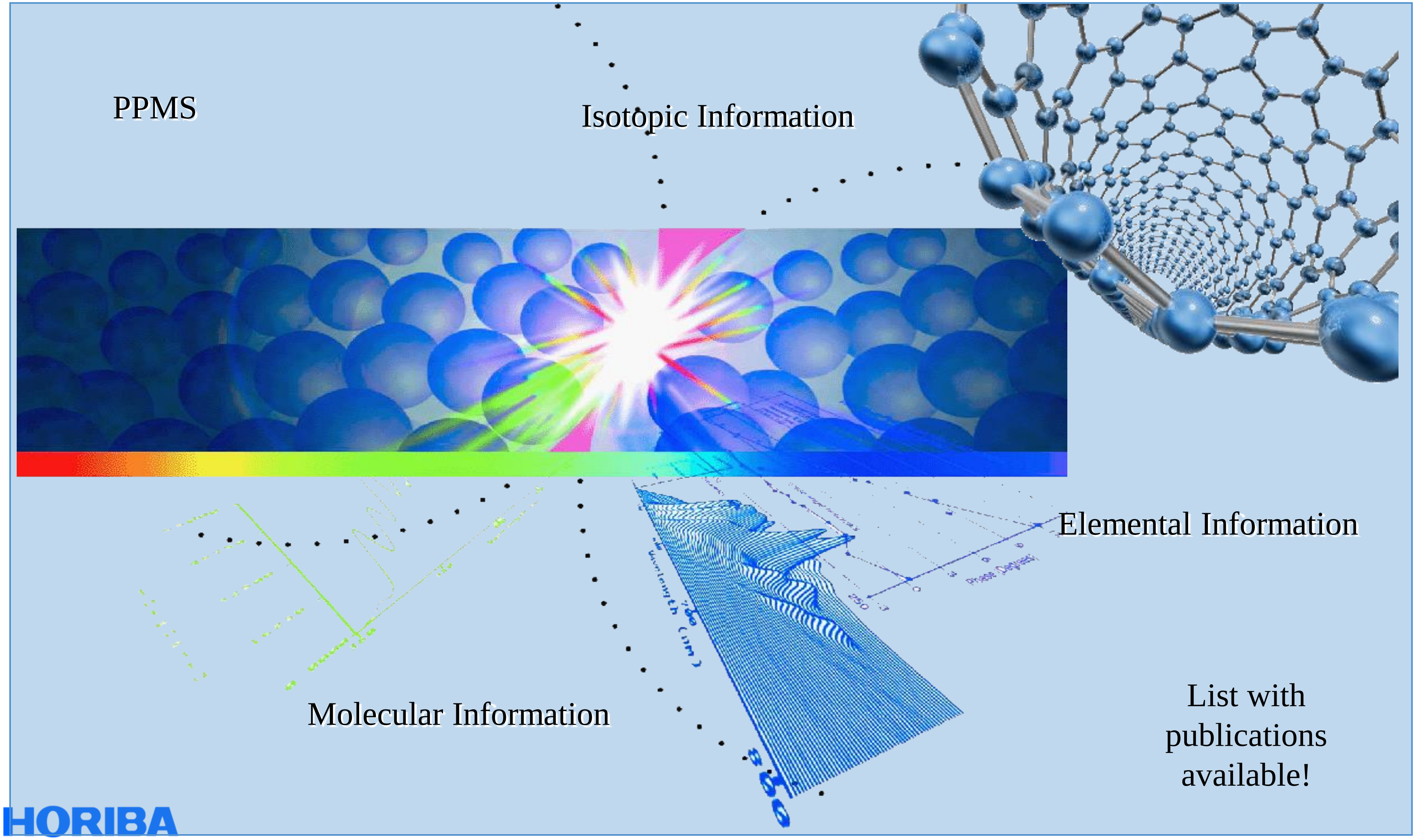
Tb variations from Tb pellets position on target

Conclusion

Plasma Profiling Mass Spectrometry …

- allows the analysis of conductive and non-conductive samples
- easy to use, no sample preparation
- simulteneous analysis, retro perspective analysis always possible
- compared with other surface techniques like SIMS, XPS or Auger spectroscopy very fast technique (analysis time and time ready to analyse)
- higher sensitivity than classical GD-OES
- for layers from a few nm up to several µm
- provides elemental, isotopic (molecular) information

Thank you.



PPMS

Isotopic Information

Elemental Information

Molecular Information

List with
publications
available!