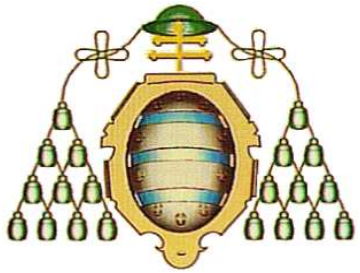
rf Pulsed Glow Discharge - Time of Flight Mass Spectrometry:

Investigation of the Ion Source Design

Rosario Pereiro, Cristina Gonzalez, Marcos Bouza, Lara Lobo, Beatriz

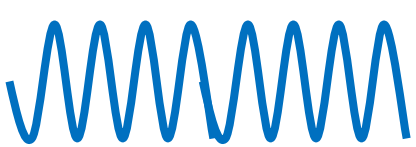
Fernandez, Jorge Pisonero, Nerea Bordel, Alfredo Sanz-Medel



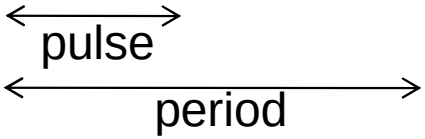
University of Oviedo

Pulsed GD *vs* non-pulsed mode.

Non-pulsed RF GD



Pulsed RF GD



$$\text{Duty cycle} = \frac{\text{pulse}}{\text{period}}$$

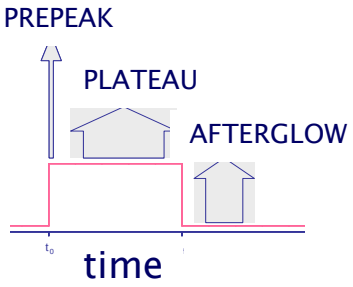
- **Higher instantaneous applied power**:

  - Increased atomization/ionization/excitation.

- **Lower mean applied power**:

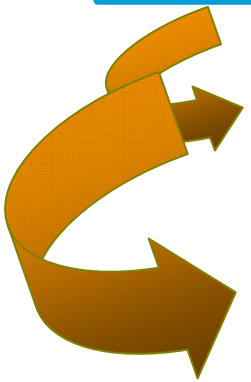
  - Less thermal effects→ Polymer analysis, glasses…

- **Different temporal regions are created** during the cycle:



PULSED GLOW DISCHARGE

TIME OF FLIGHT MASS SPECTROMETER (ToFMS)



Time-gated detection mass analyser.

Quasi-simultaneous spectral generation from fast transient signals.

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

Spectrochimica Acta Part B 66 (2011) 399–412

Review

Present and future of glow discharge — Time of flight mass spectrometry in analytical chemistry

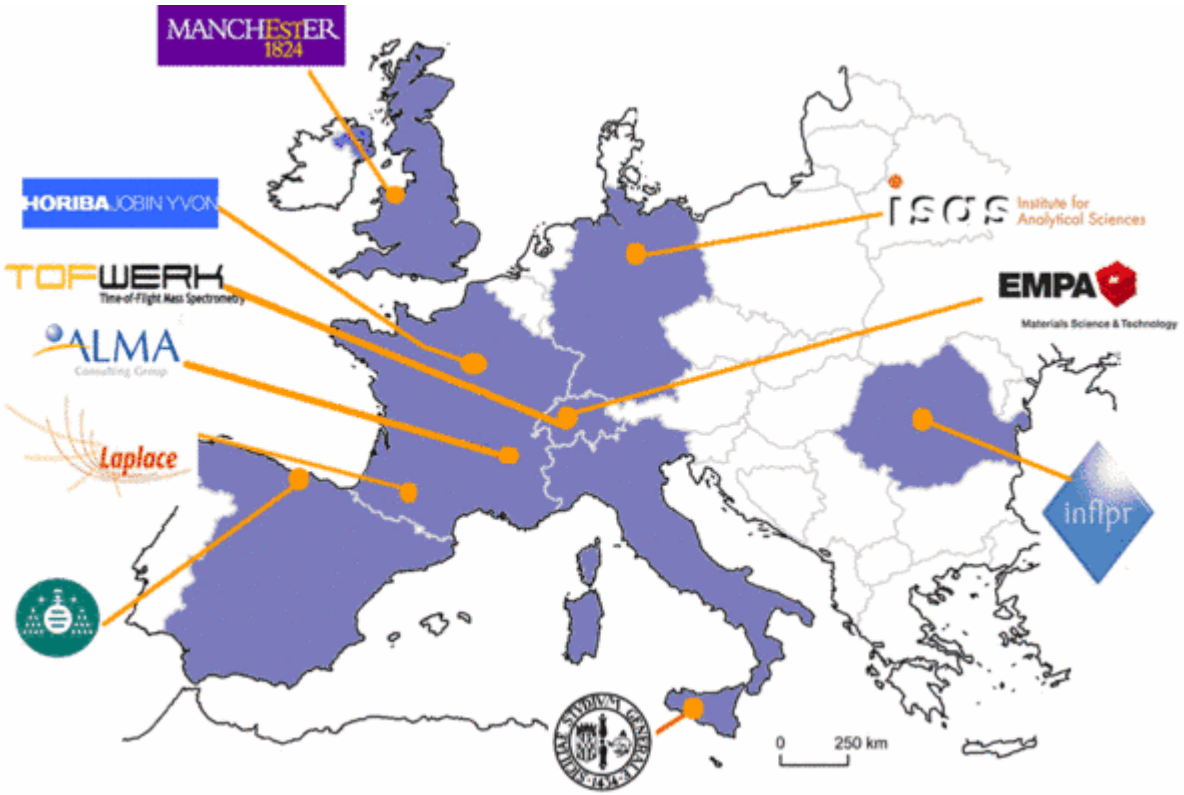
Rosario Pereiro [a,*], Auristela Solà-Vázquez [a], Lara Lobo [a], Jorge Pisonero [b], Nerea Bordel [b], José Manuel Costa [a], Alfredo Sanz-Medel [a,*]

Experimental Set-Up: RF GD-ToFMS Prototype

(Jobin Yvon Emission-Horiba Group & TOFWERK)

European Project: New Elemental and Molecular Depth Profiling Analysis of Advanced Materials by Modulated RF GD-ToFMS.

emdpa
GD - TOF - MS

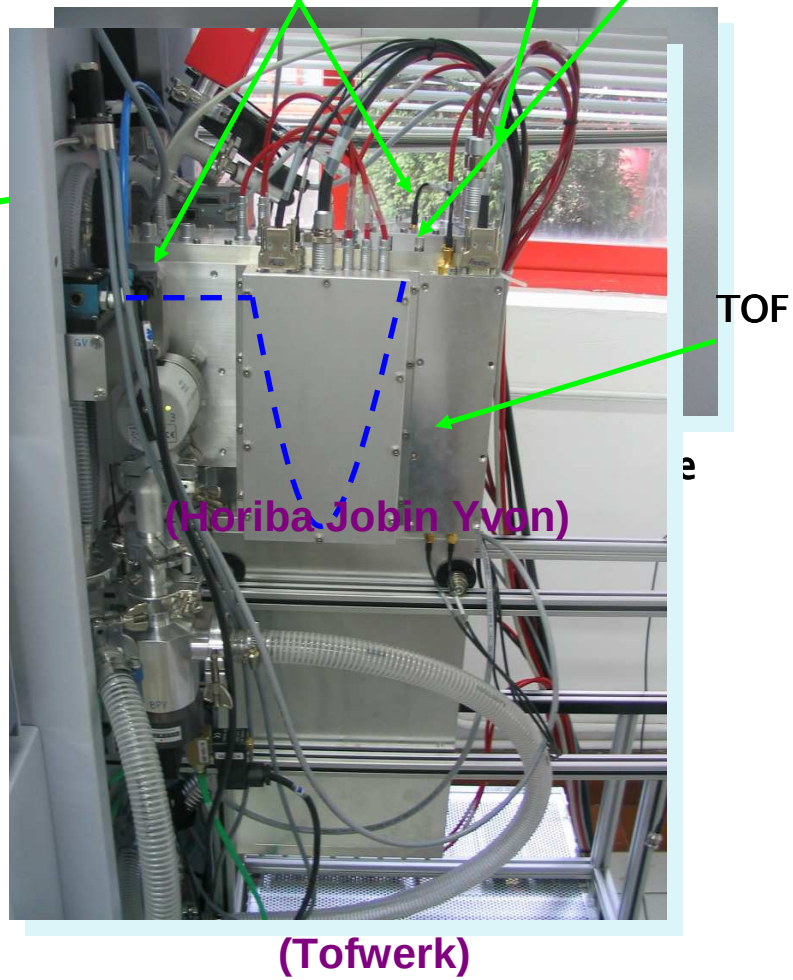


6th Framework programme, Priority 3: *"Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes and devices*"

Experimental Set-Up: GD-ToFMS Prototype

(Jobin Yvon Emission-Horiba Group & TOFWERK)

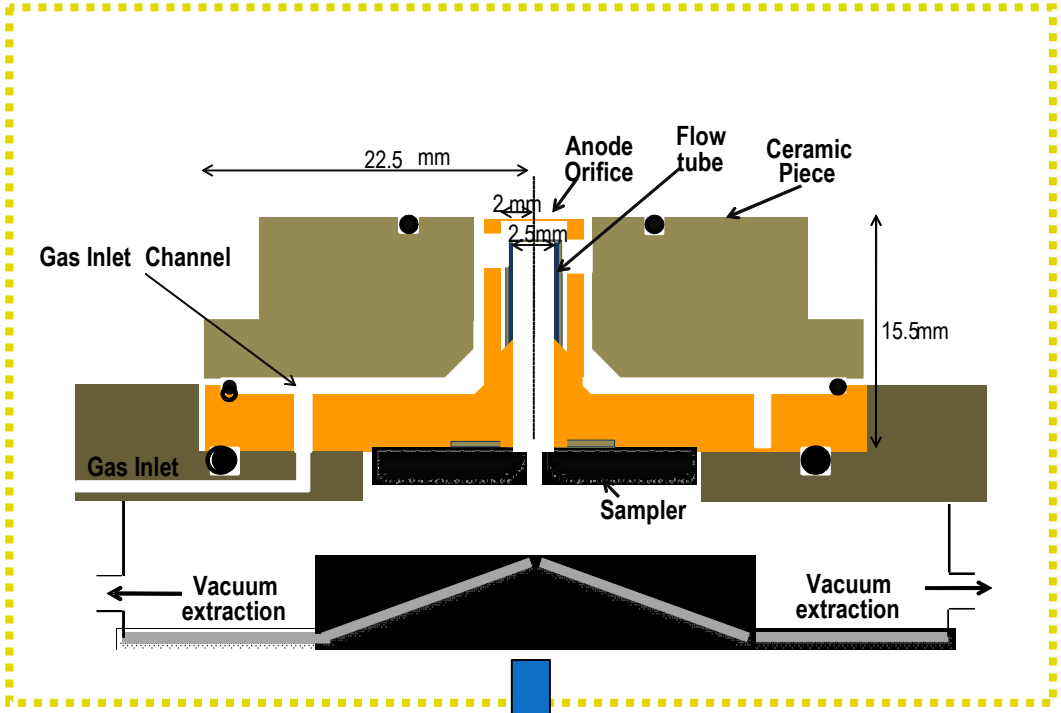
pulsed RF-GD-ToFMS



(Tofwerk)

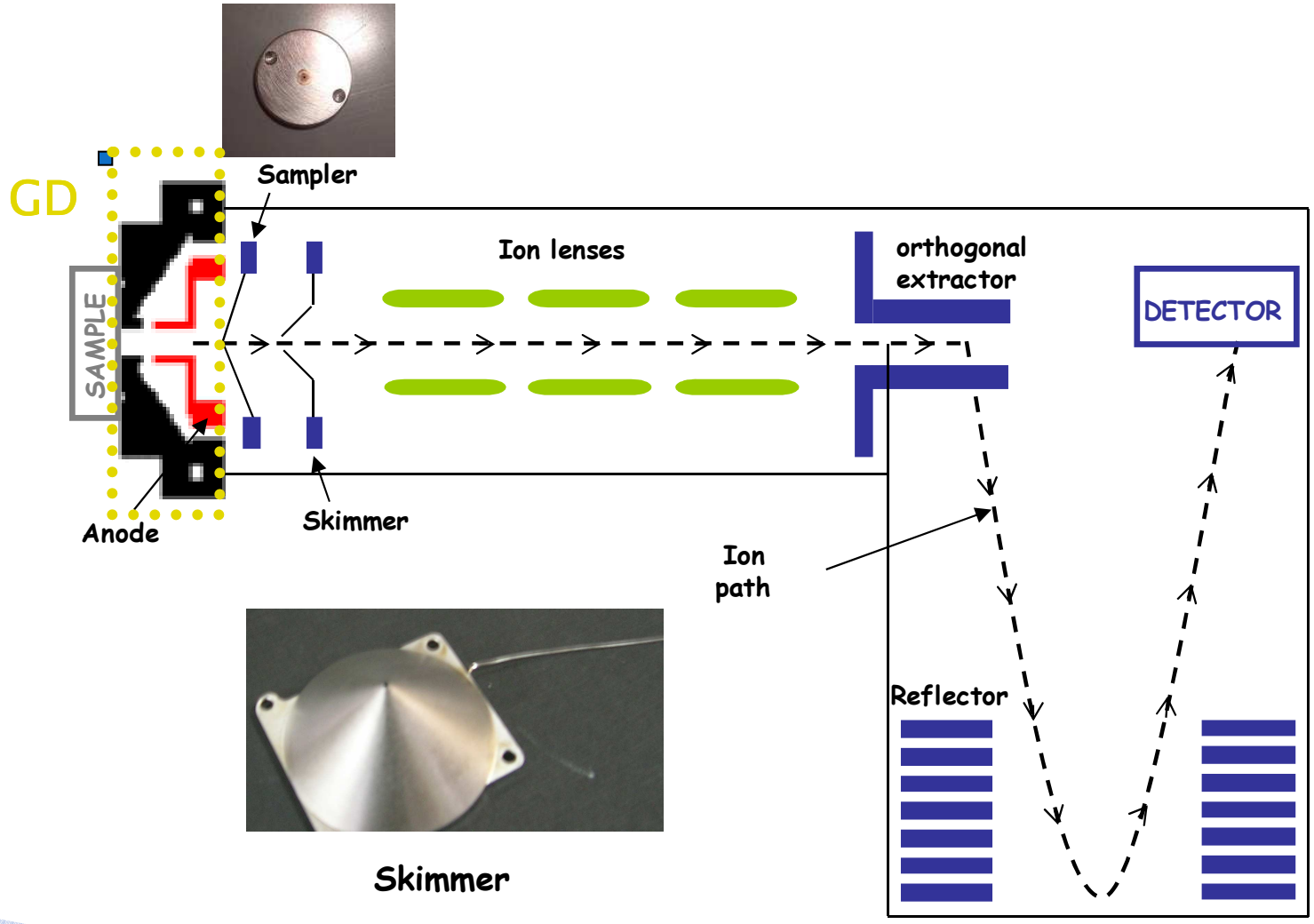
GD chamber: “GD.1”

Flow tube



MS

Instrumental set-up.



Skimmer

Objectives

1. **UNIOVI GD** design.

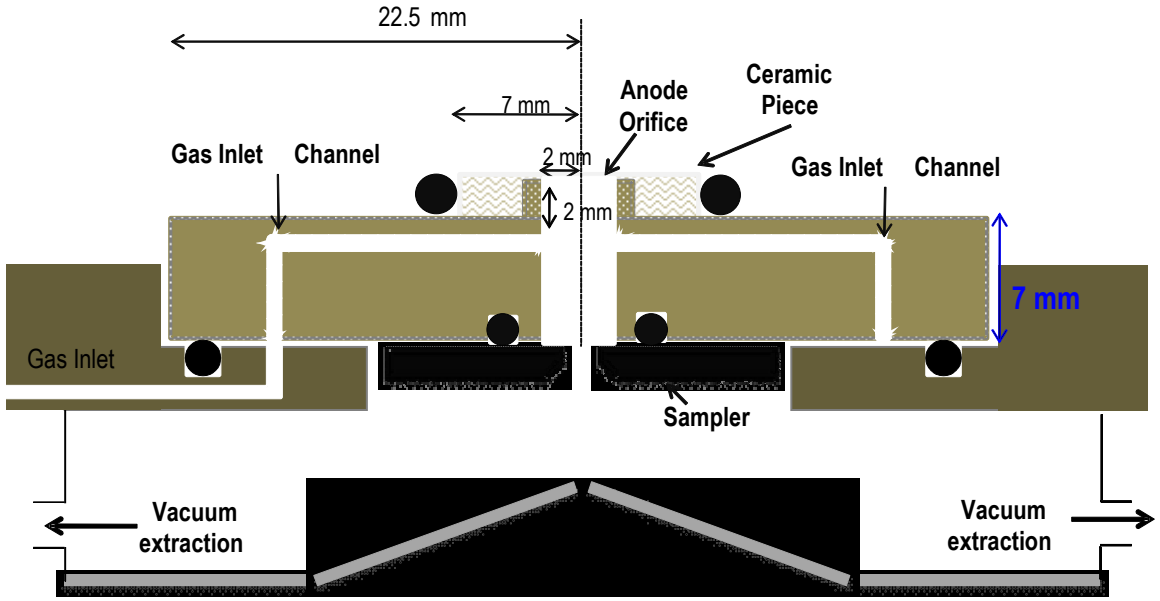
2. Behavior of the pulse profiles in the **UNIOVI's** chamber.

3. Optimization of the experimental conditions for the analysis of glass using the **UNIOVI GD** and **GD.1** chamber (**RF-PGD-ToFMS**) and comparison of the analytical performance.

Glasses are fragile materials when exposed to thermal stress. They are used as substrate for many types of layered materials (functional glass coatings)

- Crater shapes on samples.
- Lowest spectral interferences.
- Highest analytical sensitivity

UNIOVI GD chamber



- **Shorter distance sample-sampler than “GD.1”**
- **No flow tube**

SIMPLER DESIGN

Objectives

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HOMOGENEOUS GLASS SAMPLES

1.8 mm thick glass from *Saint-Gobain Glass Company.*

Concentrations (% w/w) of a 6 mm thick glass (Breitländer)

	B_2O_3	Na_2O	Al_2O_3	SiO_2	MnO	CoO	NiO	CuO	ZnO
	4.0%	15.3%	8.5%	48.9%	6.5%	0.8%	1.85%	0.82%	0.95%
	As_2O_3	SrO	Ag_2O	In_2O_3	Sn_2O	Sb_2O_3	BaO	PbO	Bi_2O_3
	0.44%	0.31%	0.13%	0.1%	0.6%	0.43%	4.6%	0.45%	0.1%

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	0.44%	0.31%	0.13%	0.1%	0.6%	0.43%	4.6%	0.45%	0.1%

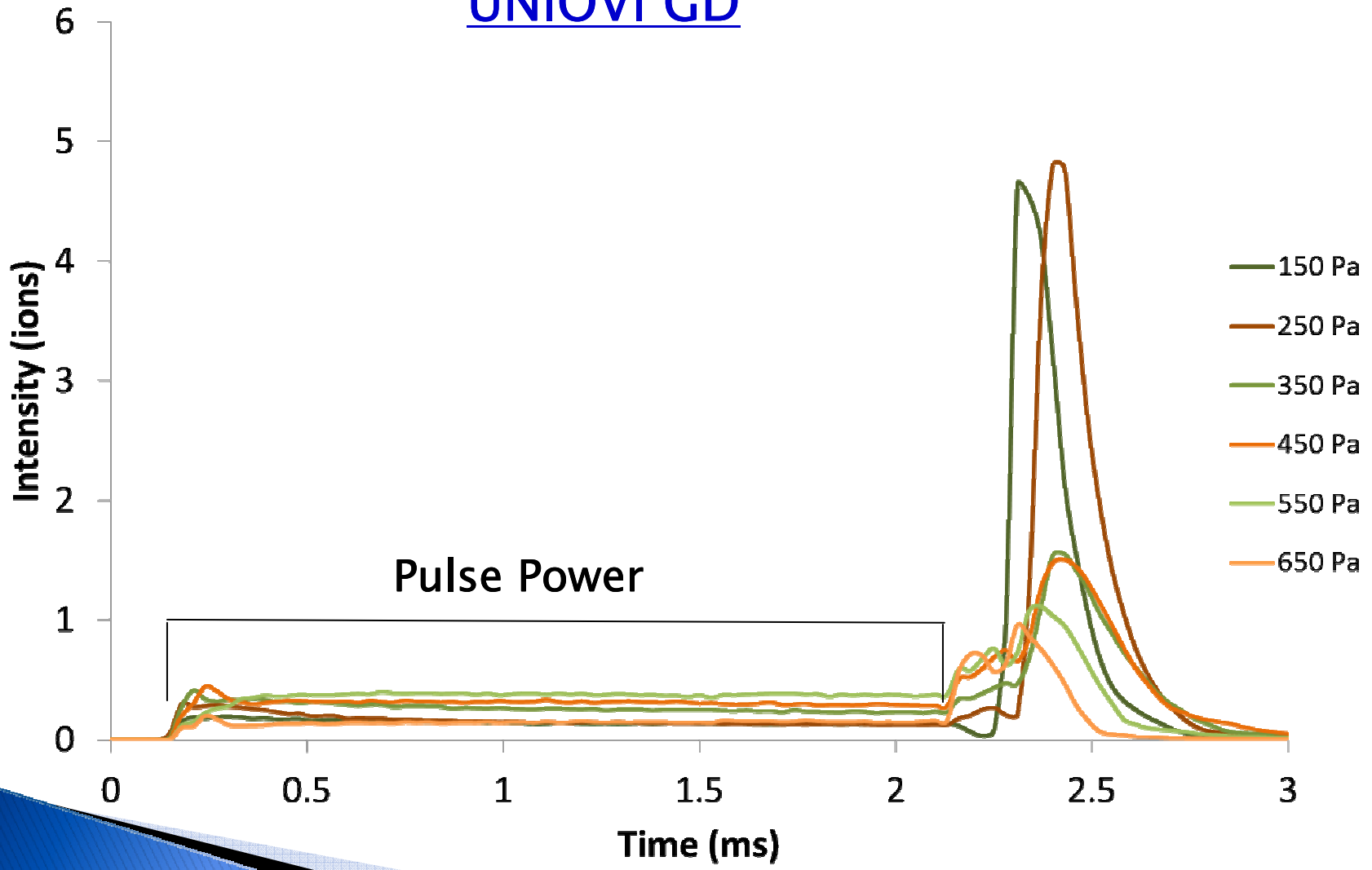
Pulsed RF GD Operation Conditions:

Pulse period: 4 ms Duty cycle: 50%

Applied GD power: *applied power during the power-on region*.

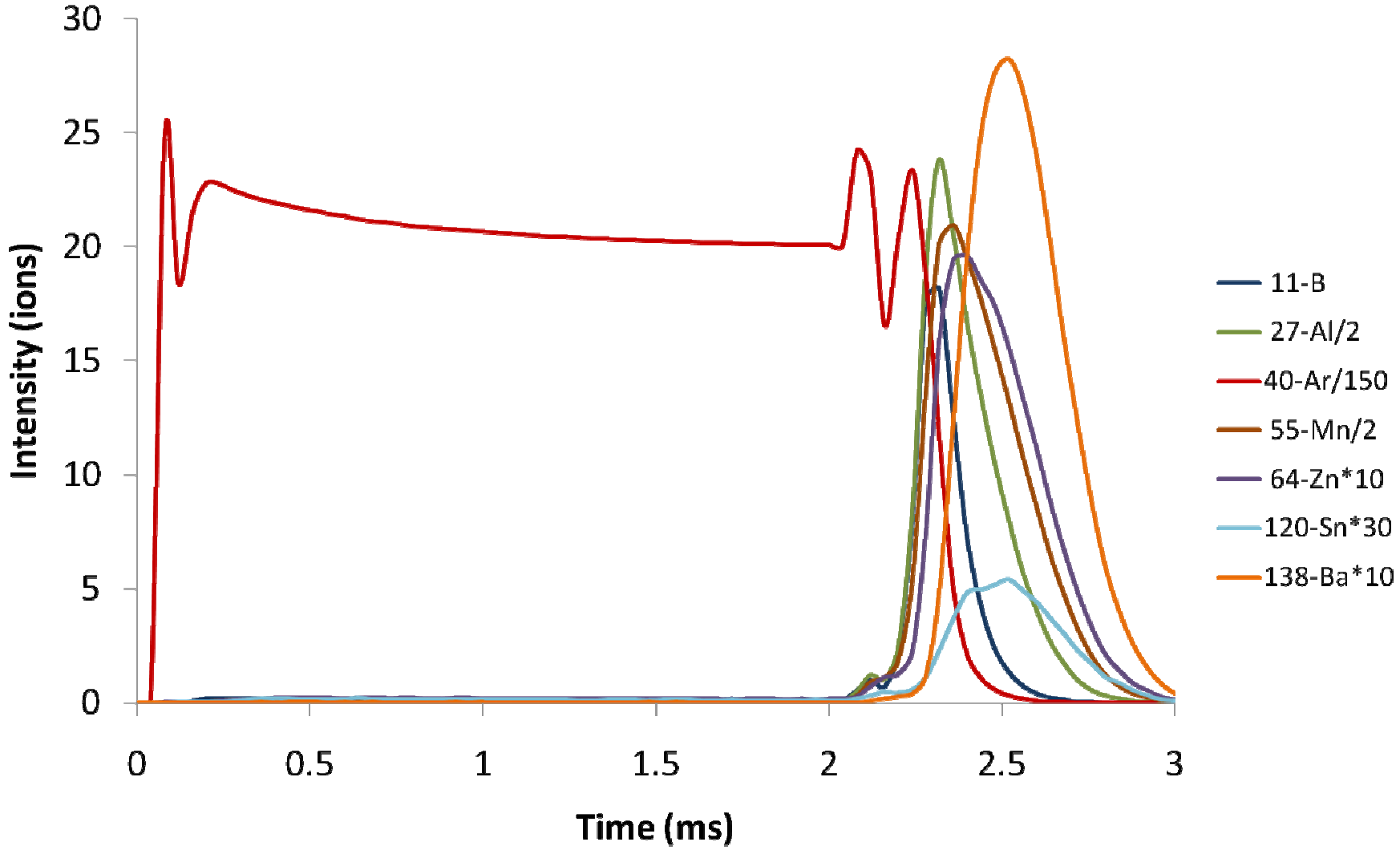
$^{27}Al^{+}$ pulse profiles variation with the pressure

UNIOVI GD



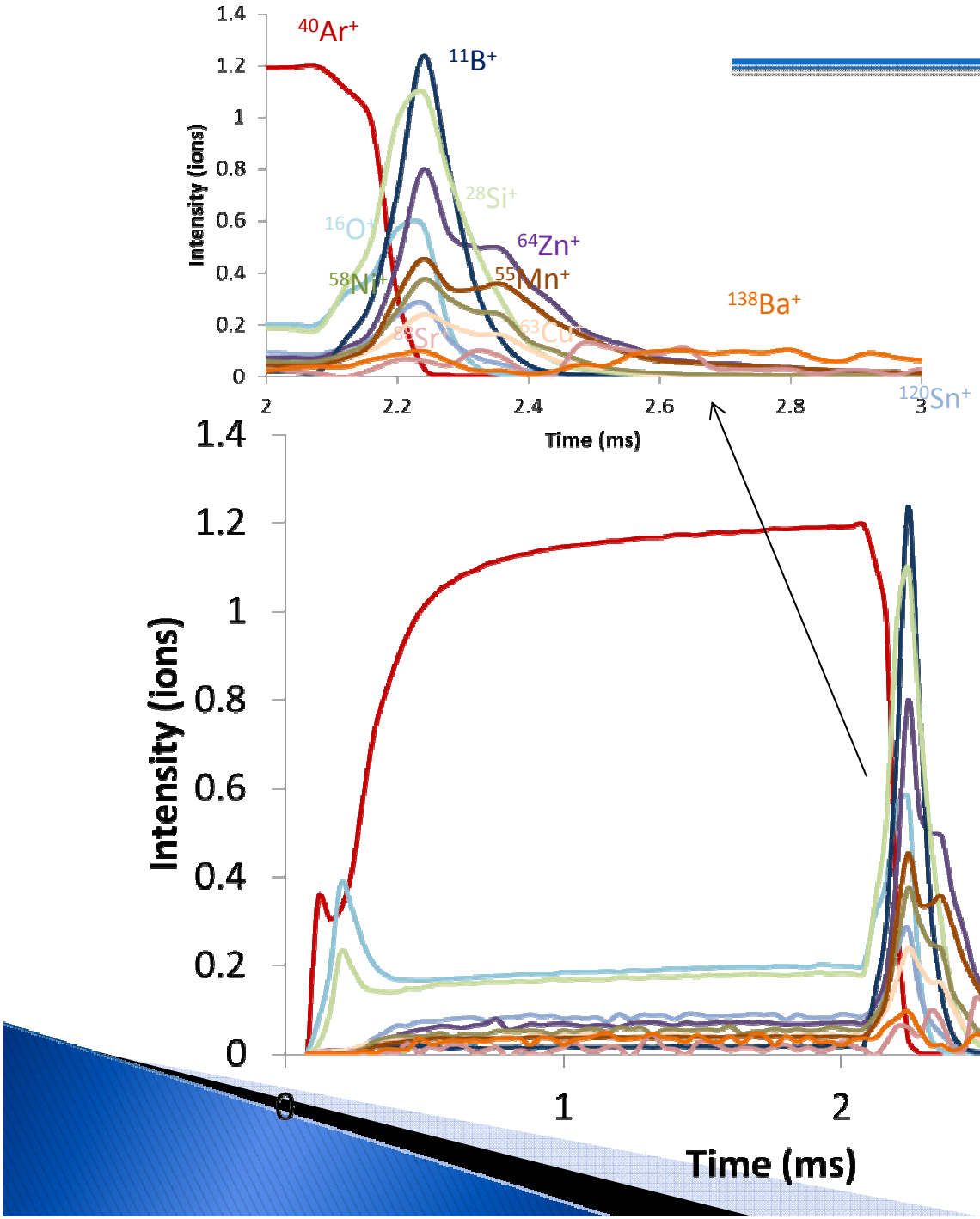
Saint Gobain sample

UNIOVI GD chamber: 250 Pa, 80 W

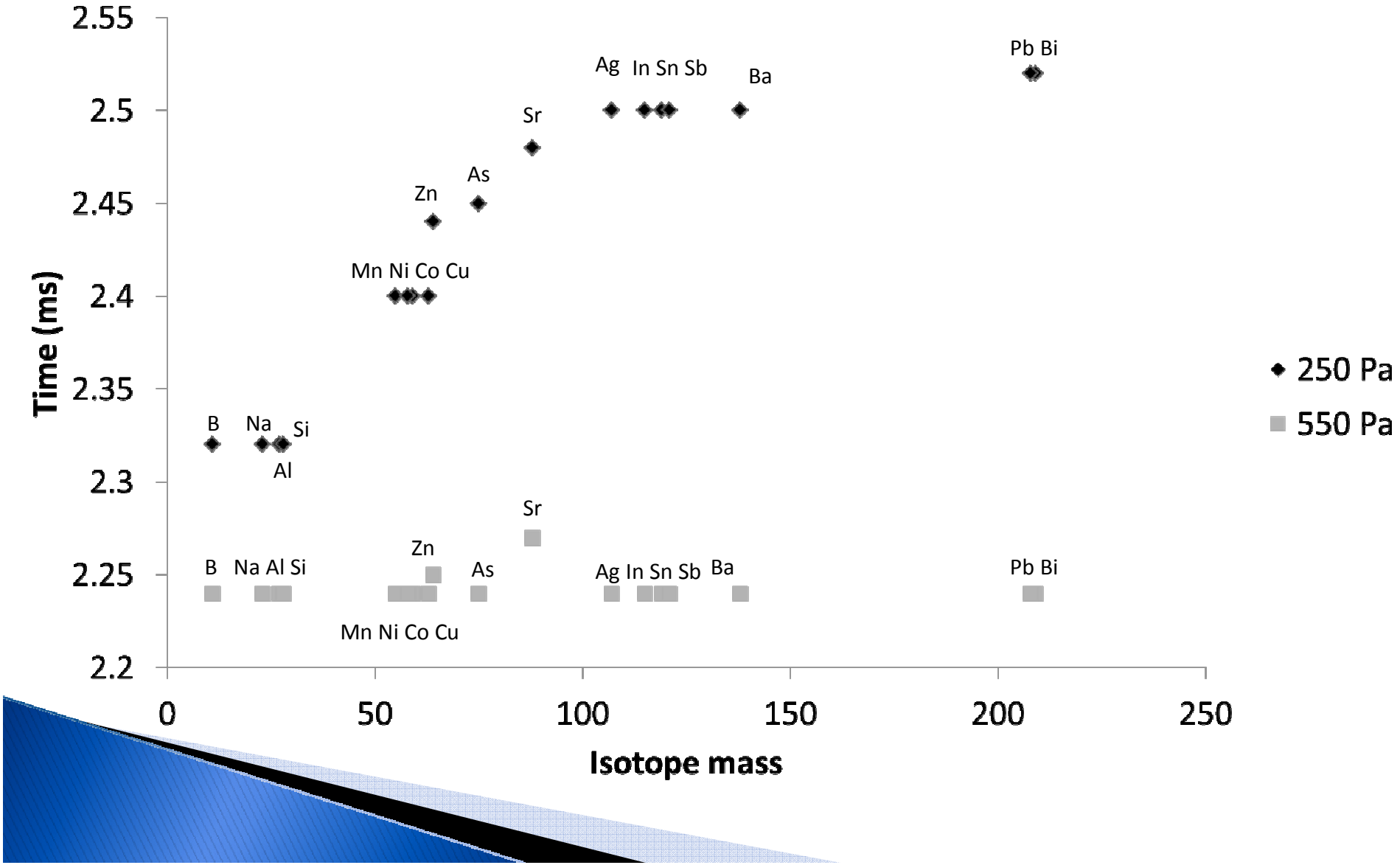


Multicomponent glass sample

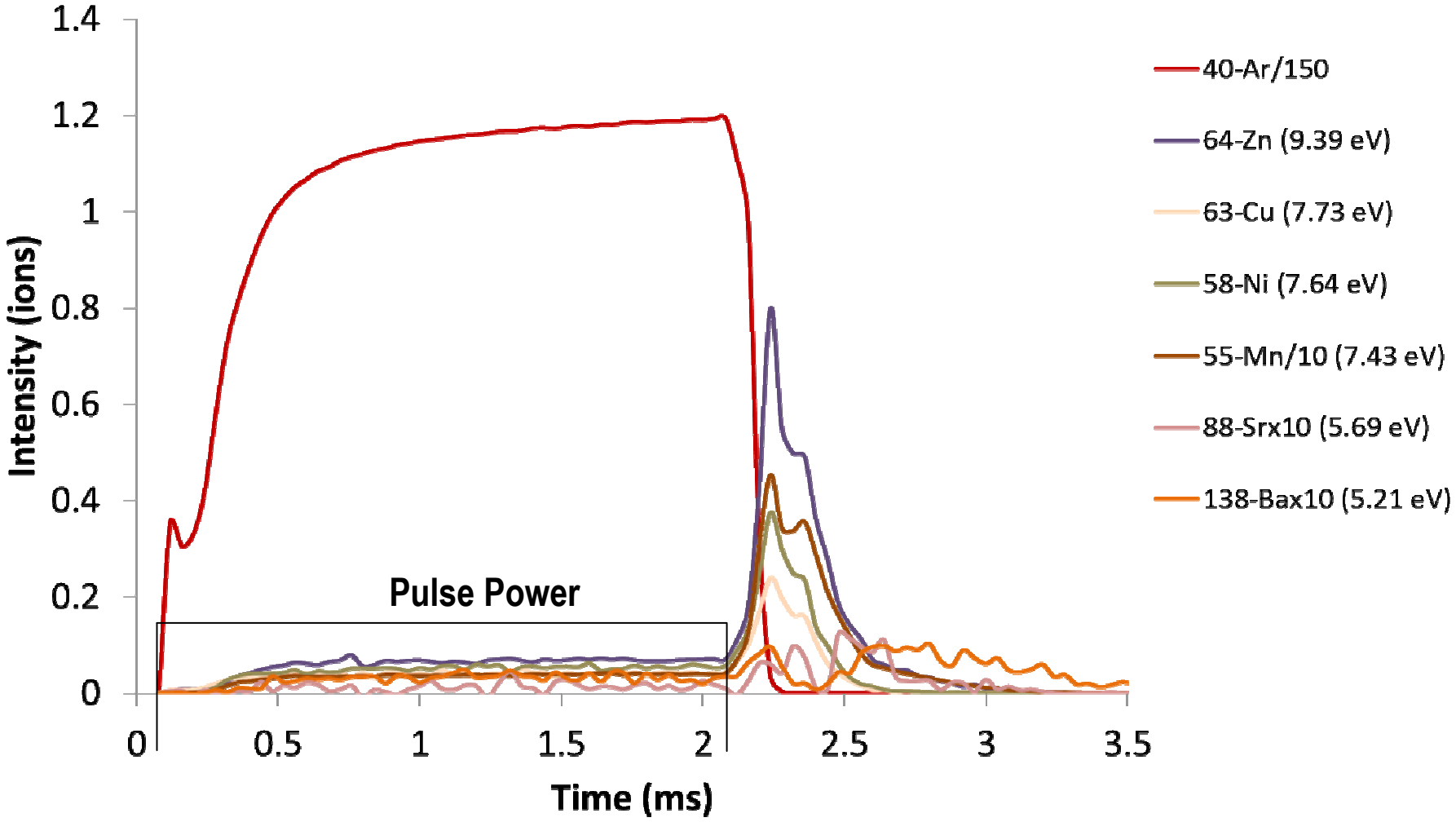
UNIOVI GD: 550 Pa, 80 W



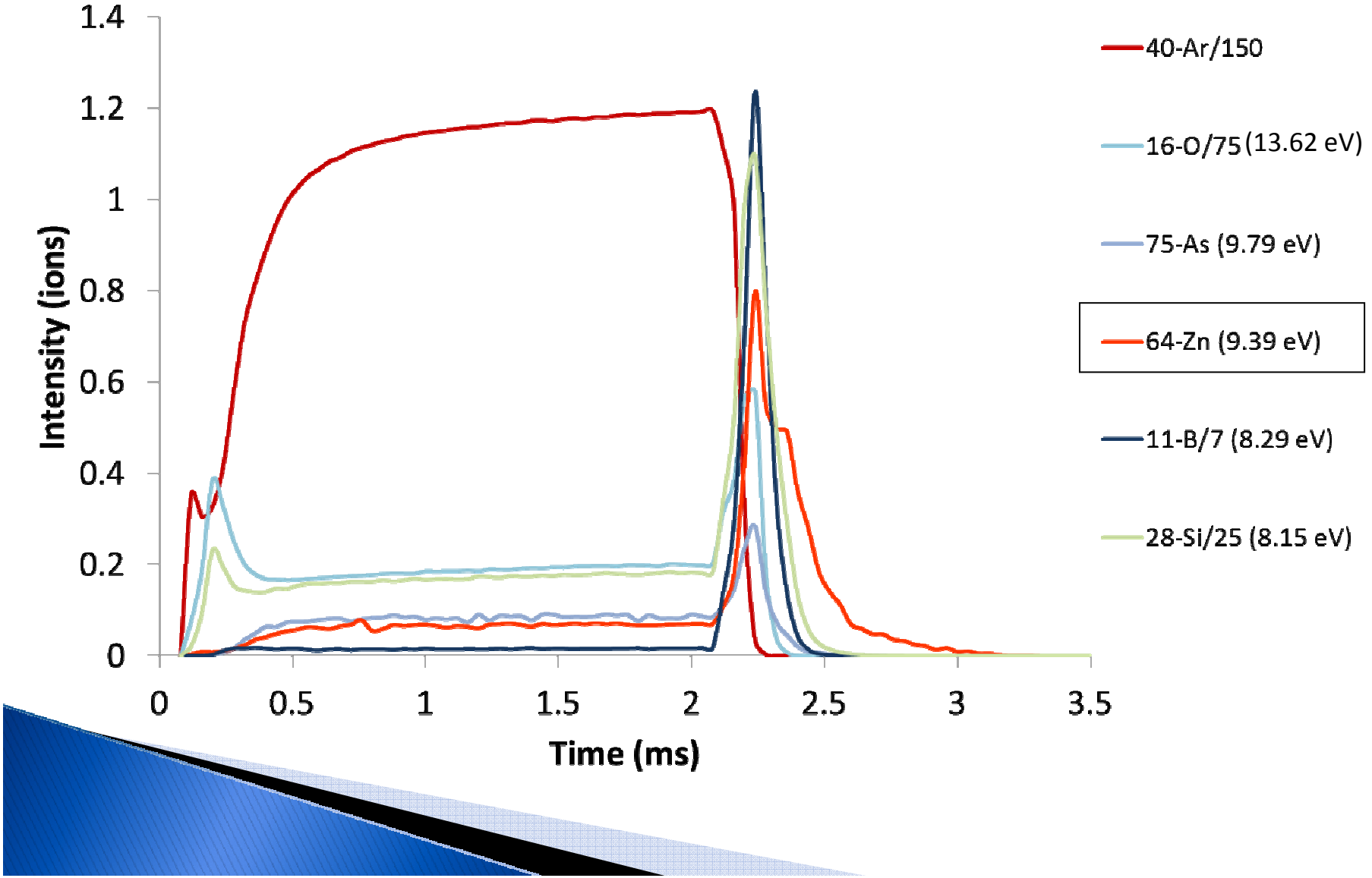
Time appearing the afterpeak maxima with UNIOVI GD: 250 Pa and 550 Pa



UNIOVI GD chamber: 550 Pa, 80 W



UNIOVI GD chamber: 550 Pa / 80 W



Objectives

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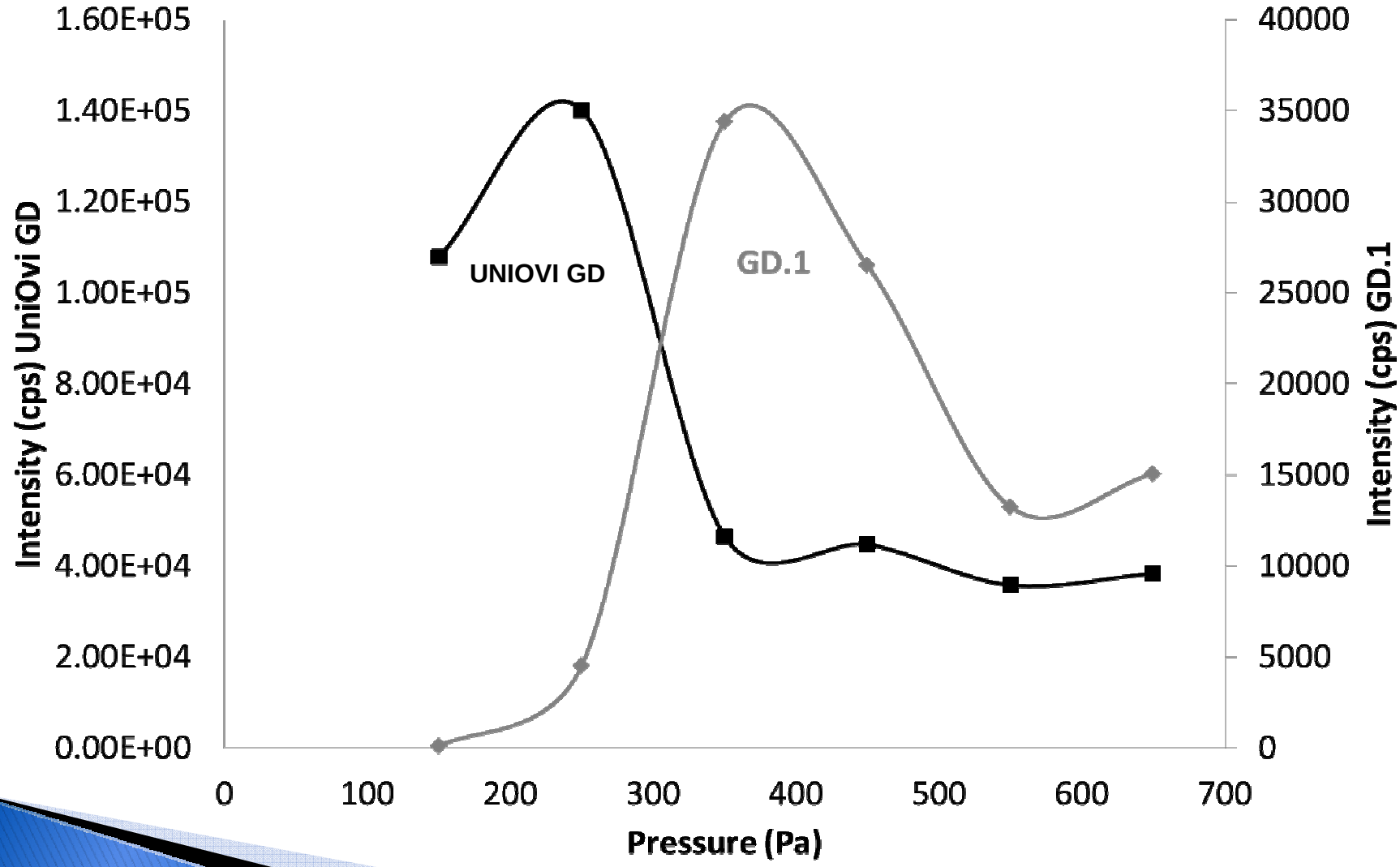
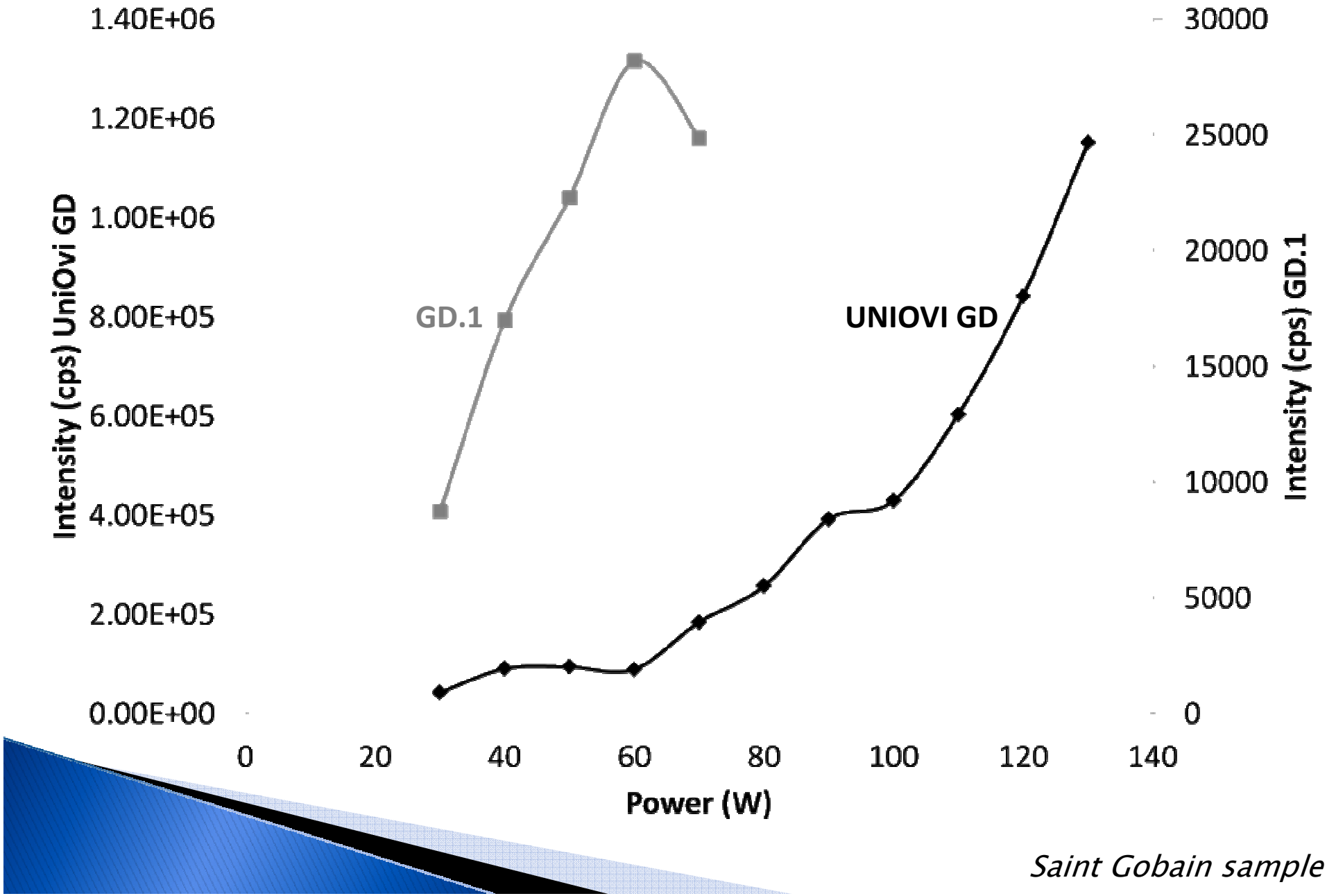
Optimization of GD PRESSURE: $^{27}Al^{+}$



Saint Gobain sample

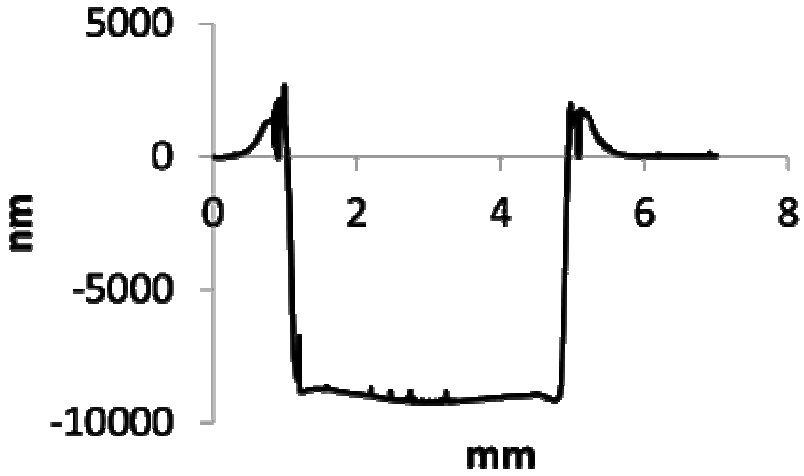
Optimization of GD POWER: $^{27}Al^{+}$



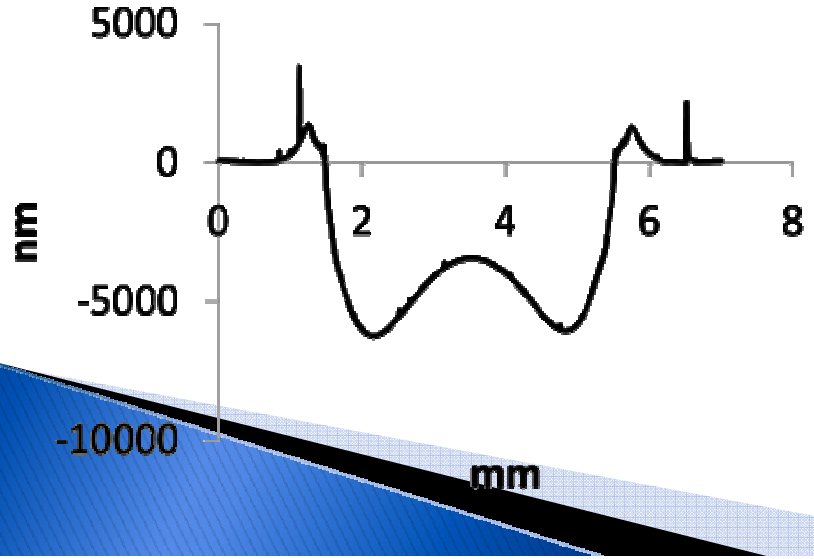
Saint Gobain sample

Crater shapes (glass from Saint Gobain)

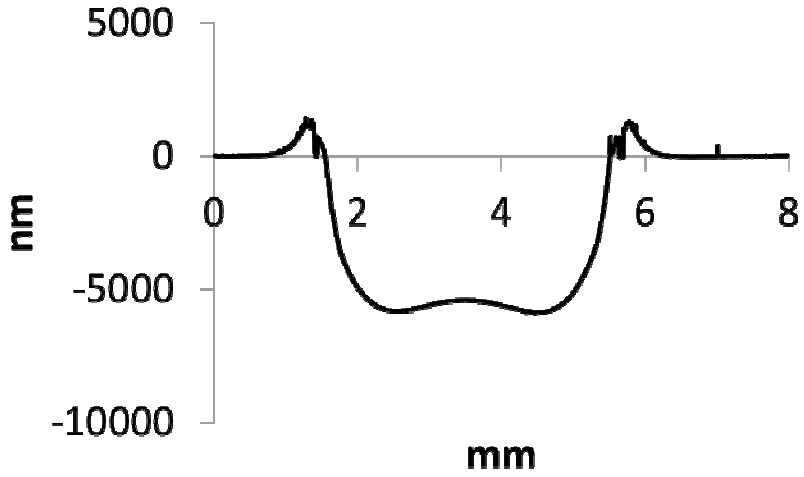
UNIOVI GD: 250 Pa and 80 W



GD.1: 350 Pa and 60 W



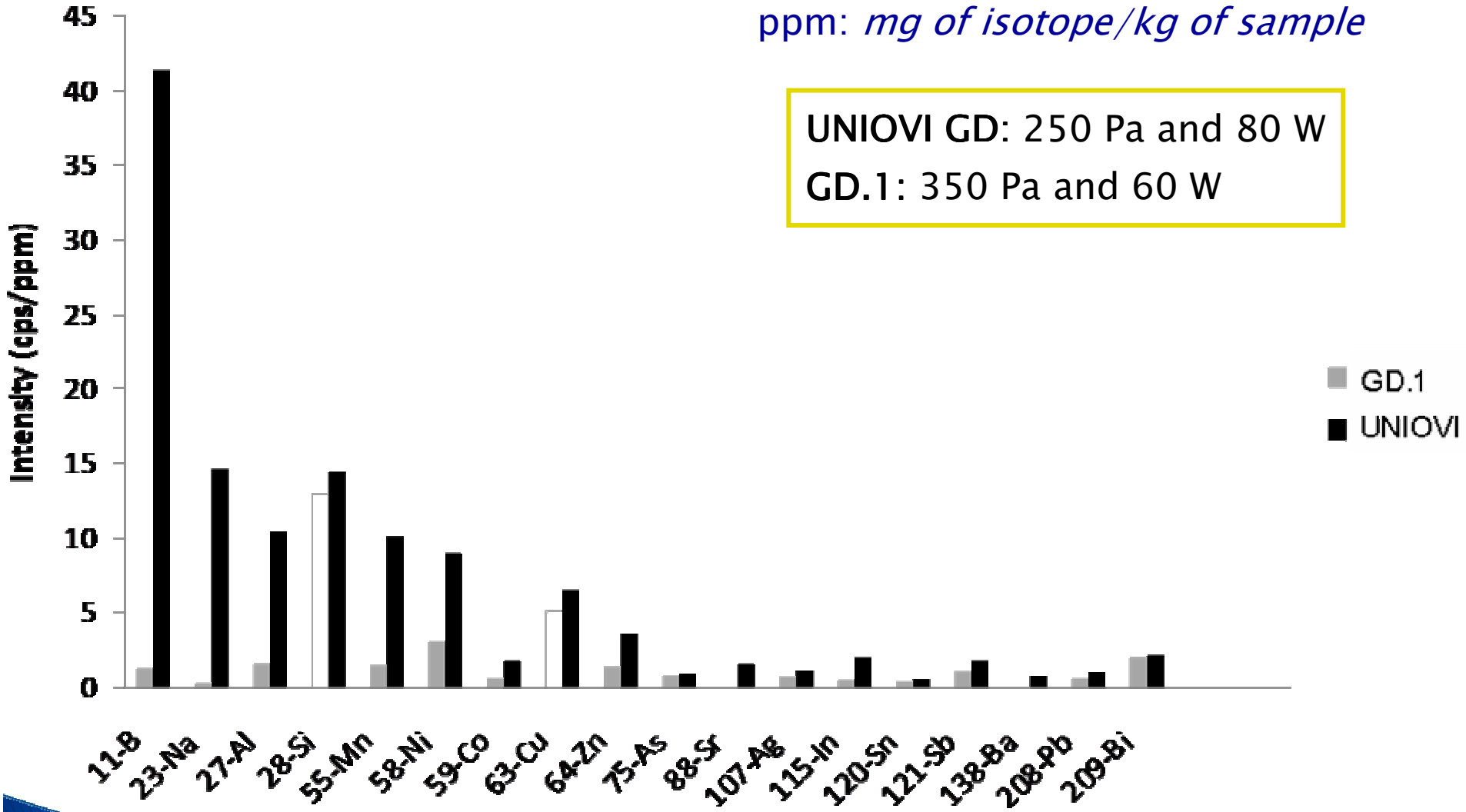
GD.1: 200 Pa and 50 W



Comparison of the sensitivity (RF-PGD-ToFMS)

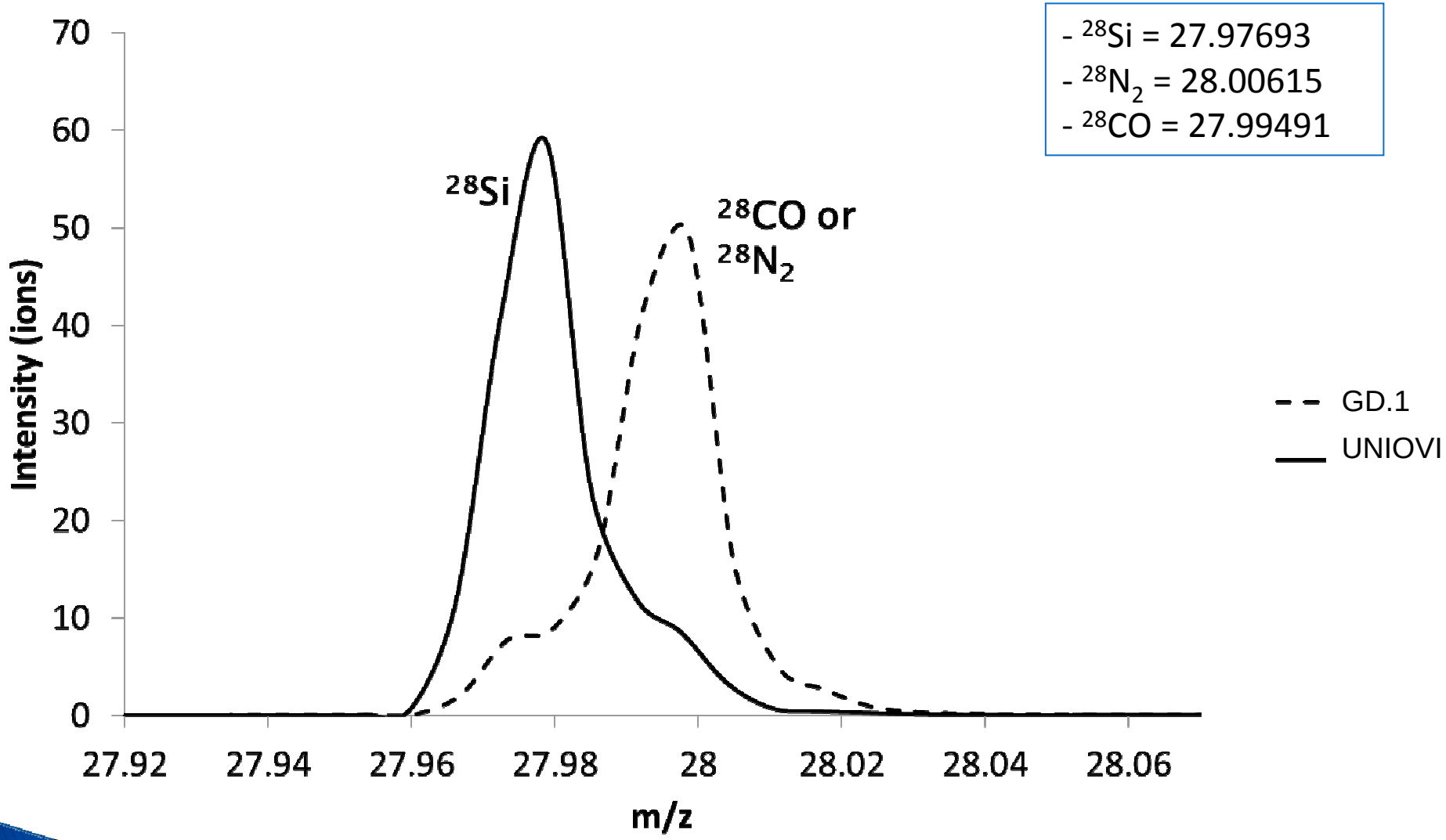
ppm: *mg of isotope/kg of sample*

UNIOVI GD: 250 Pa and 80 W
GD.1: 350 Pa and 60 W



6 mm thick multicomponent glass

- ^{28}Si = 27.97693
- $^{28}N_2$ = 28.00615
- ^{28}CO = 27.99491



Measured at the maximum of the afterglow

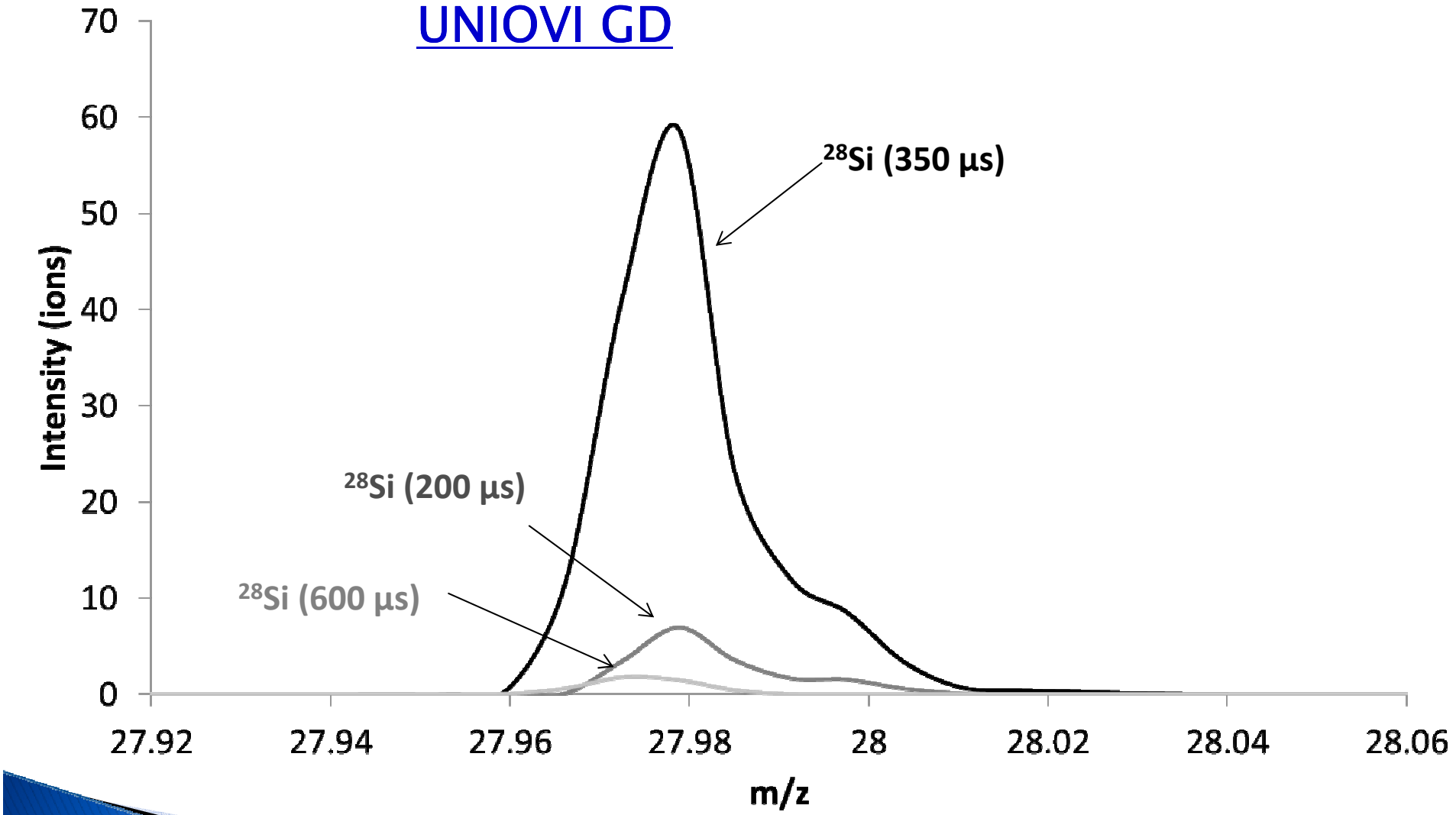
(for optimum conditions in each ion source configuration)

- ^{28}Si = 27.97693
- $^{28}N_2$ = 28.00615
- ^{28}CO = 27.99491

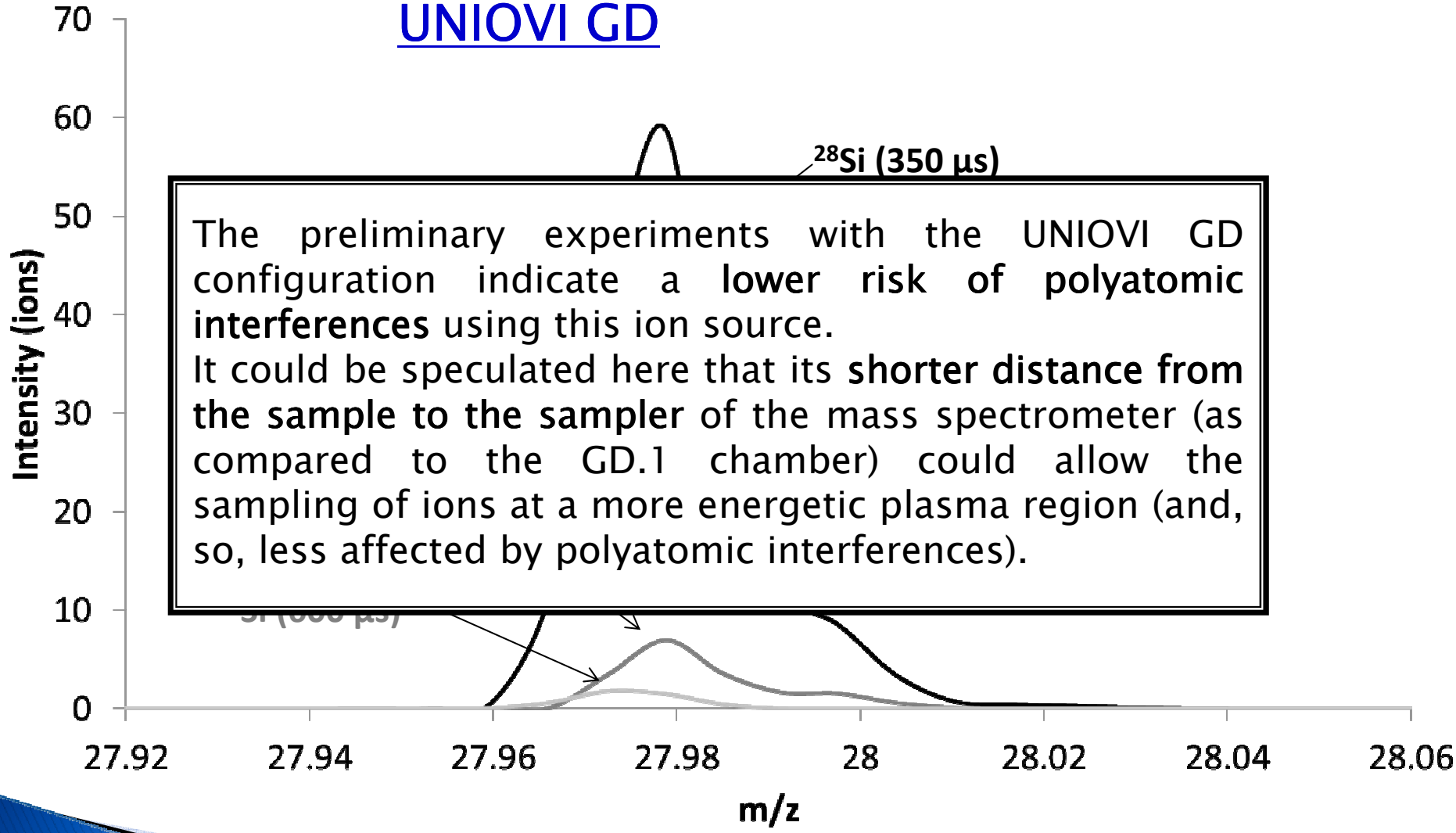
A comparison of non-pulsed radiofrequency and pulsed radiofrequency glow discharge orthogonal time-of flight mass spectrometry for analytical purposes.

L. Lobo, J. Pisonero, N. Bordel, R. Pereiro, A. Tempez, P. Chapon, J. Michler, M. Hohl and A. Sanz-Medel,

J. Anal. At. Spectrom., 2009, 24, 1373–1381


UNIOVI GD
70
60
50
40
30
20
10
0
Intensity (ions)
28Si (350 µs)
28Si (200 µs)
28Si (600 µs)
27.92
27.94
27.96
27.98
28
28.02
28.04
28.06
m/z

UNIOVI GD



The preliminary experiments with the UNIOVI GD configuration indicate a **lower risk of polyatomic interferences** using this ion source.

It could be speculated here that its **shorter distance from the sample to the sampler** of the mass spectrometer (as compared to the GD.1 chamber) could allow the sampling of ions at a more energetic plasma region (and, so, less affected by polyatomic interferences).

Analysis of glass (6 mm thick)

The isotope measured for each analyte is indicated.

	11-B	23-Na	27-Al	28-Si	55-Mn	58-Ni	59-Co	63-Cu	64-Zn
GD.1	17	65	38		90	50	53		49
UNIOVI GD	0.7	4.7	4.4	25	7.3	5.9	10	4.4	2.3
	75-As	88-Sr	107-Ag	115-In	120-Sn	121-Sb	138-Ba	208-Pb	209-Bi
GD.1	48	-	42	6.5	26	8.6	52	77	6.7
UNIOVI GD	6.9	6.2	4.6	3.1	4.7	2.2	23	7.1	2.1

GD.1: 350 Pa, 60 W
UNIOVI GD: 250 Pa, 80 W

Detection limits were calculated as the concentration corresponding to three times the standard deviation of ten independent measurements (the sample was kept fixed to the GD chamber, but the GD was switched off for 2 min before each new measurement) of the spectrum background near the corresponding isotope mass.

CONCLUSIONS

• Experiments on the effect of GD operation conditions have shown that more than one ionization mechanism seems to operate for the observed afterglow shapes. In fact, the influence of factors such as **isotope mass** and the **chemical nature of the elements seem to play a role**.

• The UNIOVI GD chamber provides **improved analytical features** for the analysis of glass materials by RF-PGD-ToFMS as compared to the former GD.1, in terms of:
- Less thermal effects on the glass samples.
- Better crater shapes.
- Lower risk of interferences from polyatomics.
- Better limits of detection.

The improved analytical features obtained with the UNIOVI GD configuration for the analysis of glasses, warrants further investigation to develop depth profiling methods for elemental quantification of multilayered glass samples of present technological interest.

Organizing Committee

- **Financial support from:**
  - Spanish Ministry of Science and Innovation through project MAT2010-20921.
  - Contract with Horiba Jobin Yvon for the loan of the GD-TOFMS instrument.

- **All of you.**