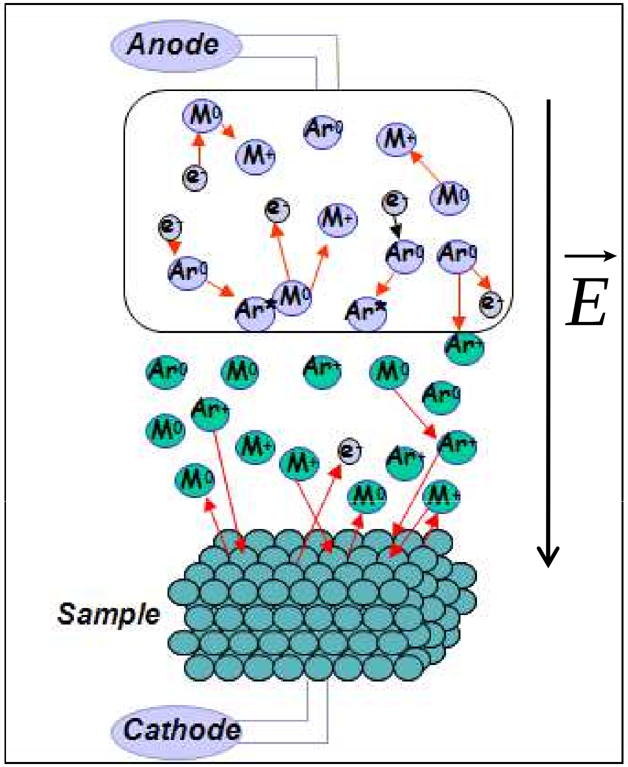
University of Oviedo

Laser and Plasma Spectroscopy
Research Group
www.unioviedo.es/gelp

Magnetically Boosted Glow Discharge Optical Emission Spectroscopy for Analytical Applications: Pros and Cons

J. Pisonero, N. Bordel

Introduction



Rf-GD-OES is an analytical technique widely used for material characterization in different techological fields

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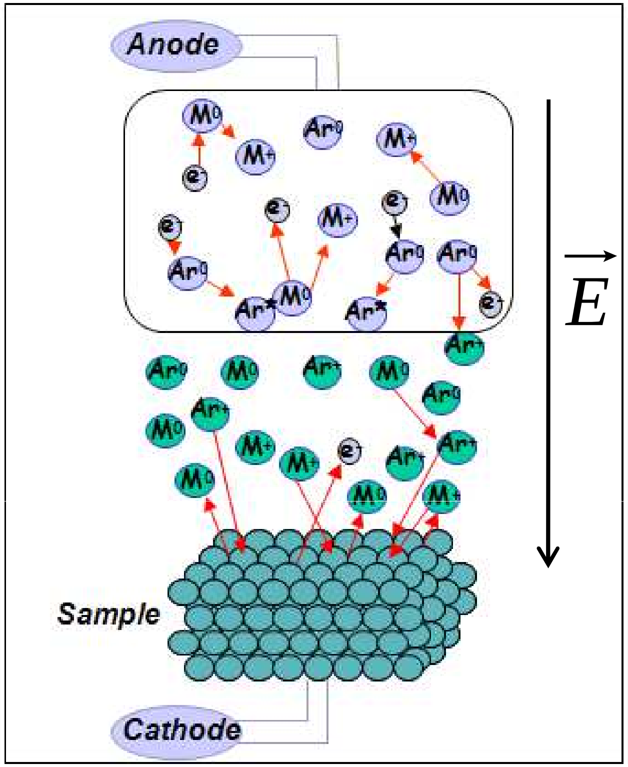

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- ✓ **Fast and sensitive multielemental analysis for solid materials**
- ✓ **Low matrix effects** (separated atomization and excitation/ionization processes)
- ✓ **High depth resolution** (~nm)

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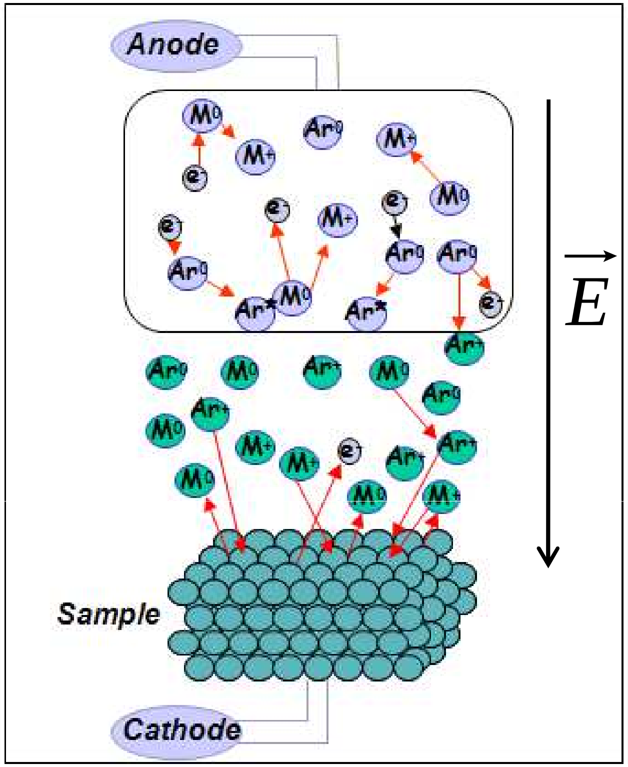

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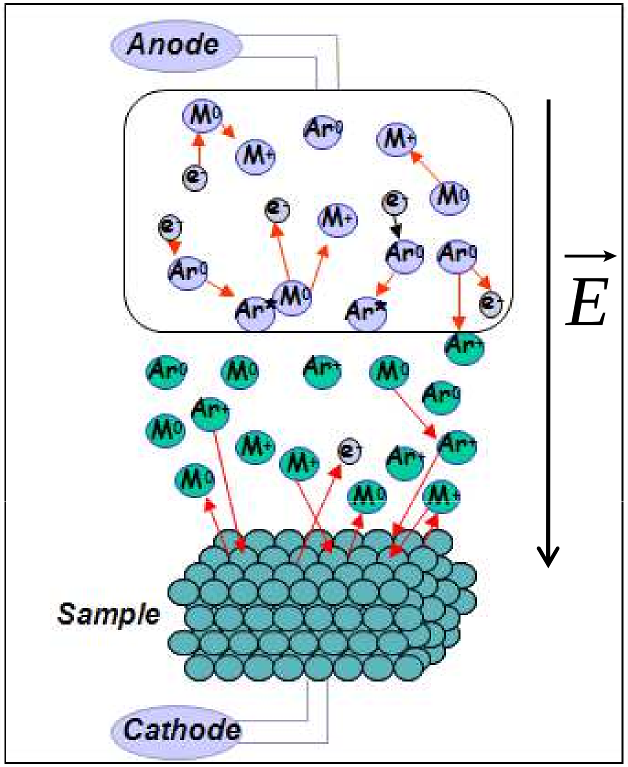

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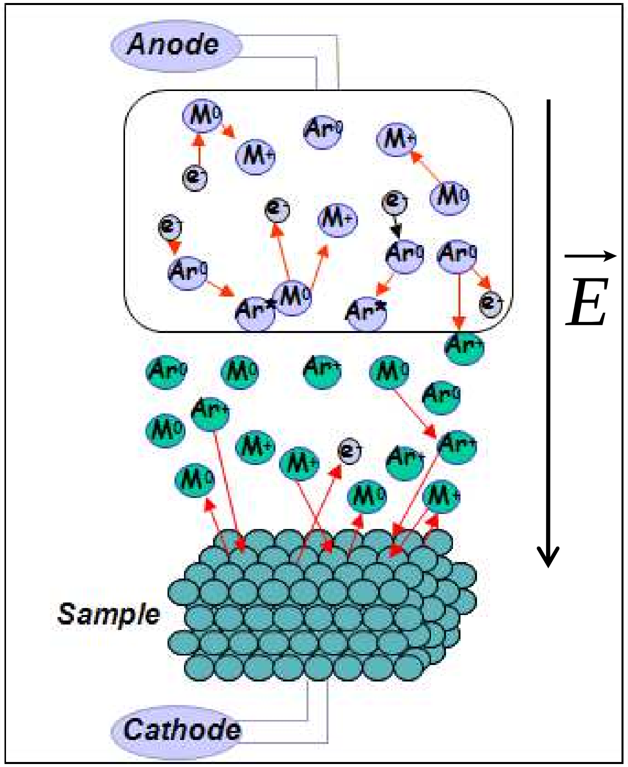

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- Microwaves
- Pulsed voltages
- Gas mixtures
- GD source designs

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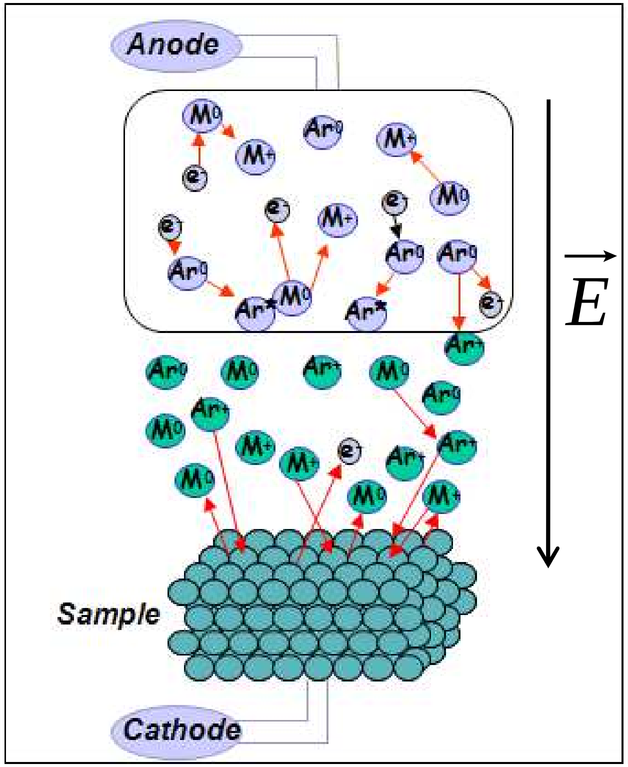

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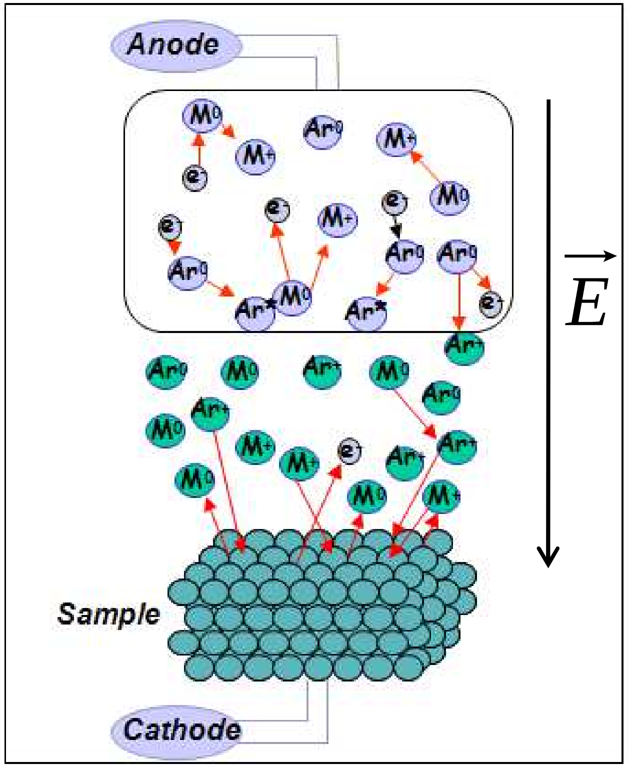
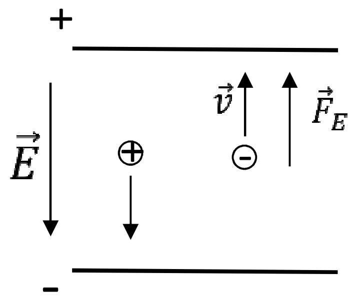
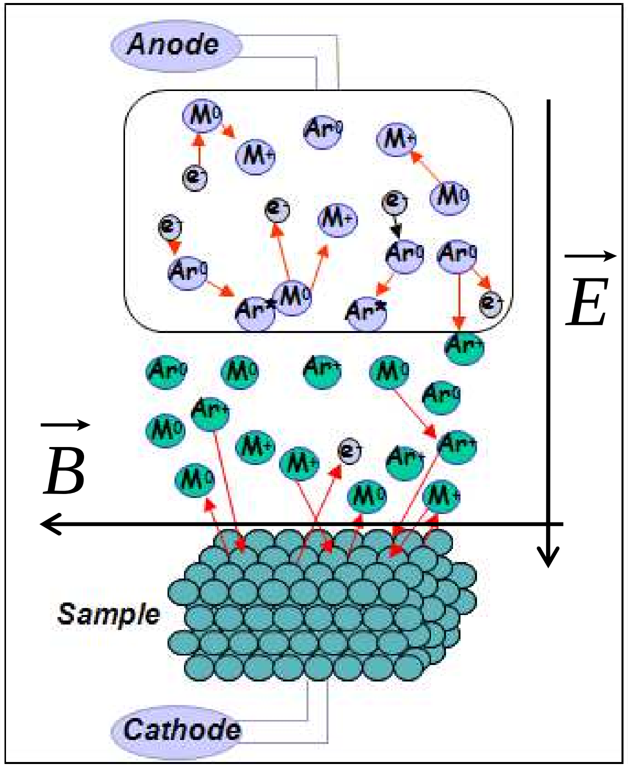
How the magnetic field is affecting the GD and how we can get benefits from it?



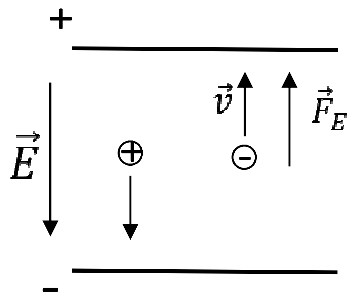


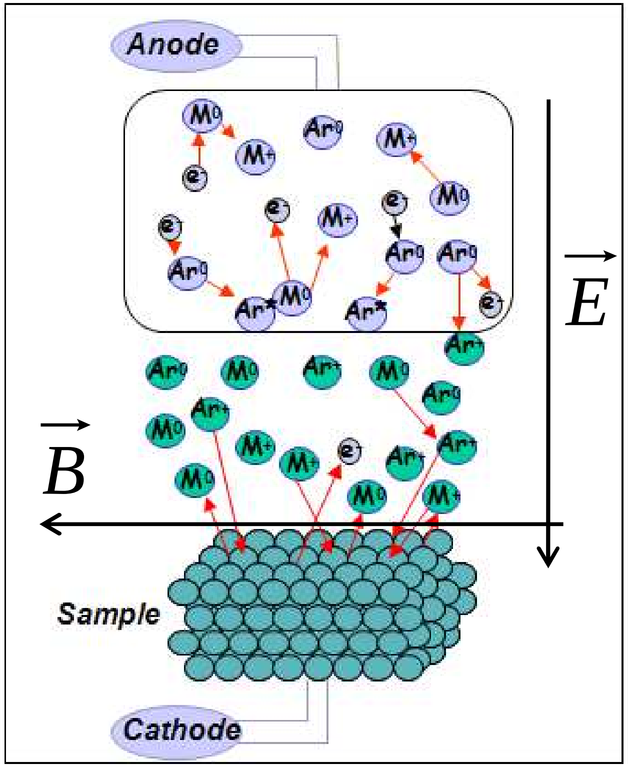


How the magnetic field is affecting the GD and how we can get benefits from it?

Due to the magnetic and electric field combination (defined by the Lorentz Force) the plasma electron paths are modified.

$$\vec{F} = q \cdot \left(\vec{E} + \vec{v} \times \vec{B}\right)$$





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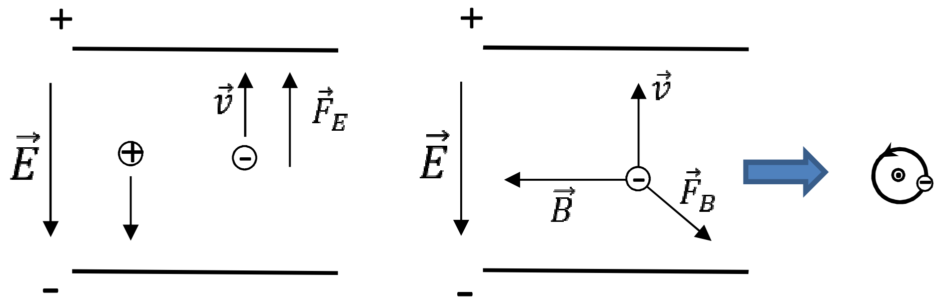

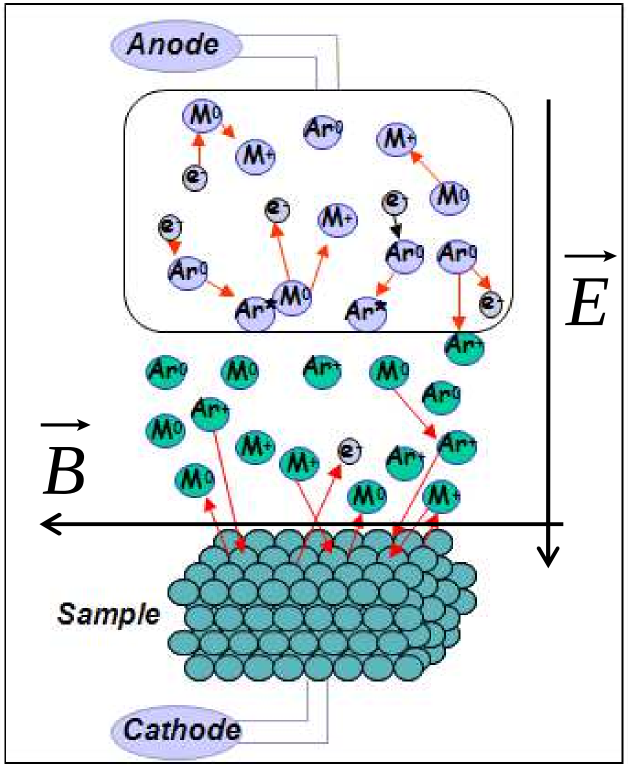

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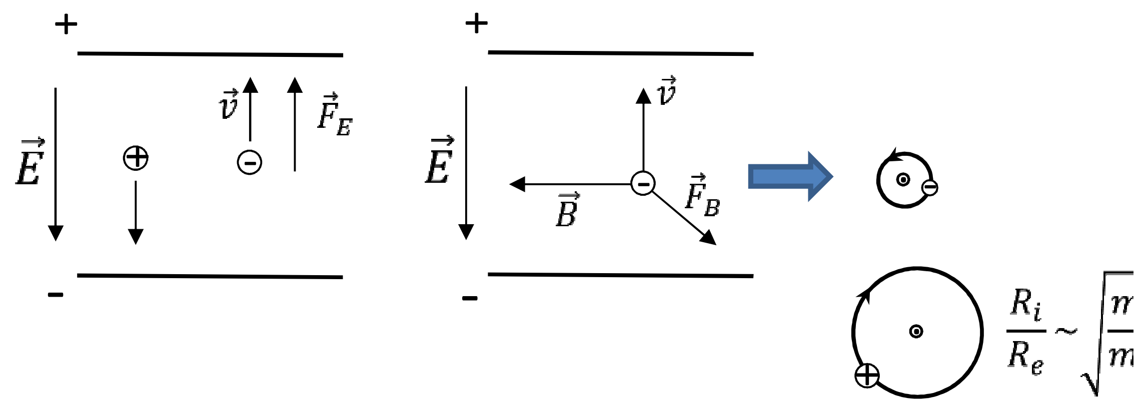

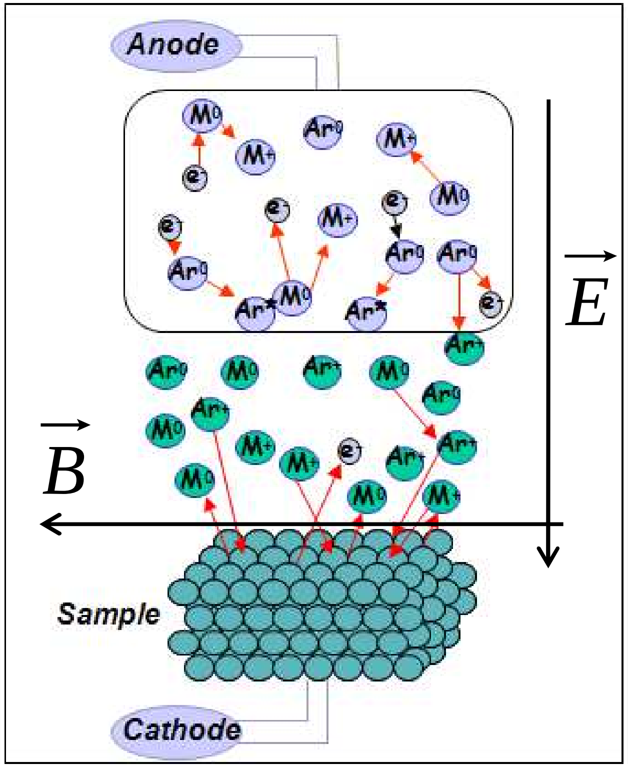

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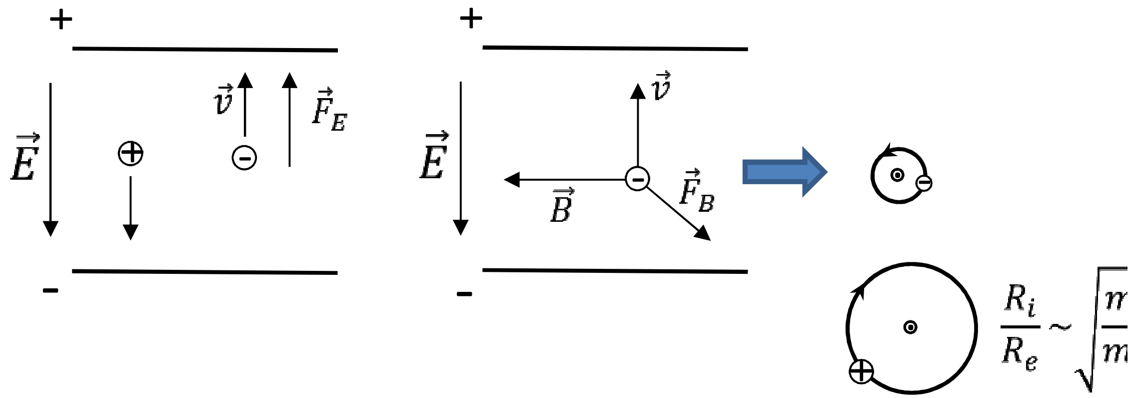

- Electrons are more effectively confined than ions by the magnetic field – R_e is aprox. 300 lower than R_i
- Ions are not affected by the presence of the magnetic field - R_i is higher that the size of the plasma
- The higher the magnetic field the lower the radius

How the magnetic field is affecting the GD and how we can get benefits from it?

The electron residence time on the GD plasma is enlarged and collision probability is increased.

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Excitation/ionization efficiencies, plasma distribution, transport processes….may be affected.

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Effect of the magnetic field on
- **Emission intensities**
- **Depth resolution**
- **Sputtering rates**

GD TYPE	*MAGNETIC FIELD*	*EMISSION LINES*	*ENHANCEMENT FACTOR*	*REFERENCE*
Hollow cathode	50 mT on magnet surface (plasma site)	Mg I – 285.2 nm	up to 3	Raghani *et al.* *Appl. Spectrosc.*, 1996, **50**, 417
Hollow cathode	100 mT on cathode axis (plasma site)	Cu I – 324.7 nm	up to 4	Simonneau *et al.* *Appl. Spectrosc.*, 1989, **43**, 141
Planar cathode	60 mT on cathode surface (sample backside)	Cu I – 406.2 nm Al I – 396.2 nm	up to 7 up to 7	Mc.Caig *et al.* *Appl. Spectrosc.*, 1990, **44**, 1176
Planar cathode	30 mT on cathode surface (plasma site)	Cu I – 324.7 nm Al I – 396.2 nm Ni I – 341.5 nm	up to 1.3 up to 1.5 up to 1.8	Chen *et al.* *SAB* 1997, **52**, 1161
Grimm	10 mT on cathode surface (sample backside)	Al I – 396.2 nm	up to 1.5	Alberts *et al.* *JAAS*, 2010, **25**, 1247
Grimm	32 mT on cathode surface (sample backside)	Cu I – 282.4 nm	up to 2	Heintz *et al.* *Appl. Spectrosc.*, 1995, **49**, 241

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Planar cathode	60 mT on cat… (sample b…		up to 7 up to 7	Mc.Caig *et al.* *Appl. Spectrosc.*, 1990, **44**, 1176
Planar cathode	30 mT on cat… (plasm…		up to 1.3 up to 1.5 up to 1.8	Chen *et al.* *SAB* 1997, **52**, 1161
Grimm	10 mT on cathode surface (sample backside)	Al I – 396.2 nm	up to 1.5	Alberts *et al.* *JAAS*, 2010, **25**, 1247
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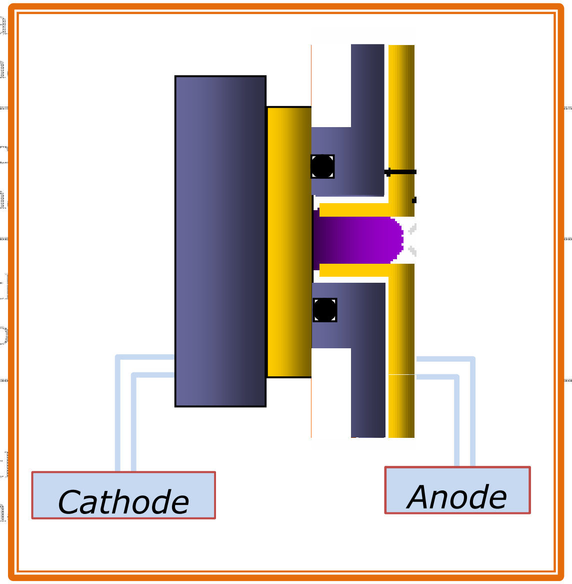
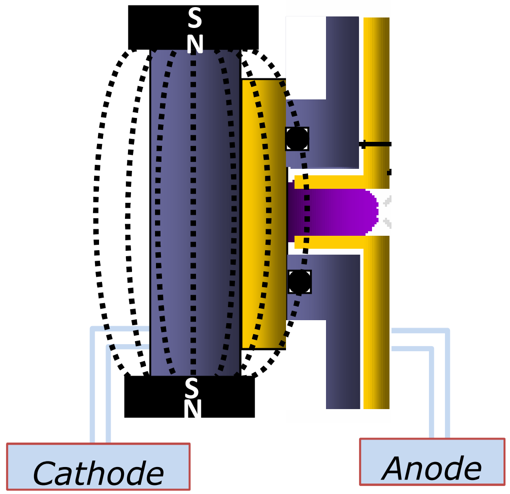
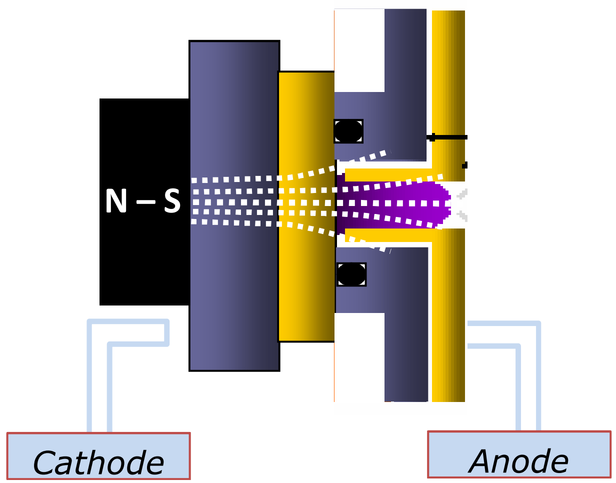


Configurations



Magnetic field parallel to the sample surface



Magnetic field perpendicular to the sample surface

Type of magnet	Magnetic field	Properties	T. Curie (ºC)
Ferrite	low	Brittle, cheap	300
AlNiCo	medium	Brittle, expensive	540
Nd-Fe-B	high	Tough, medium price	140
Sm-Co	high	Tough, expensive	300

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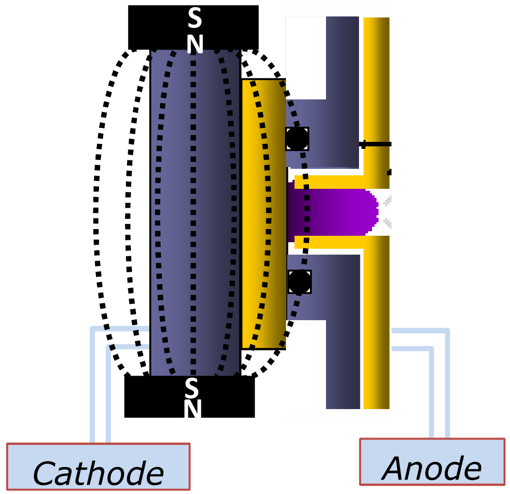

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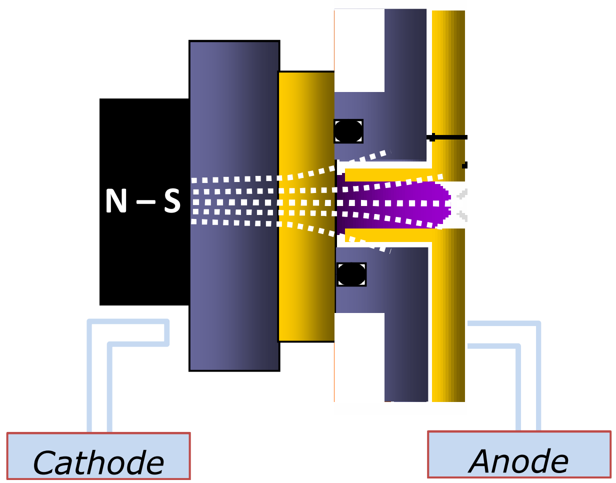

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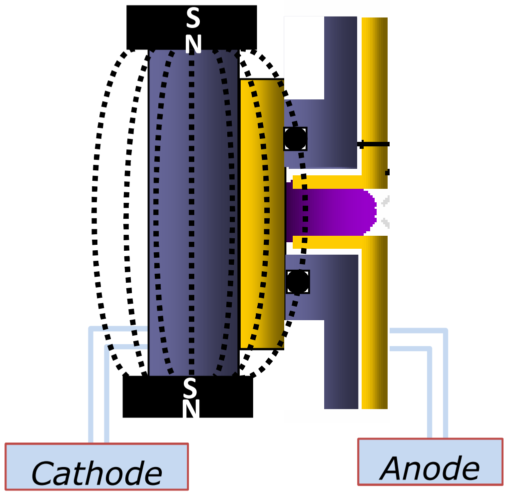
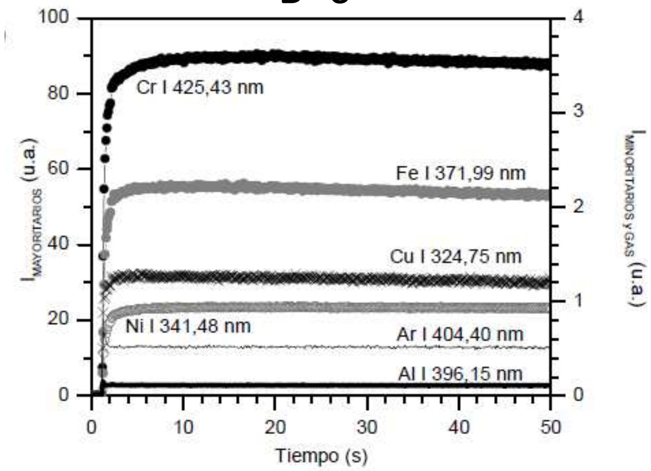


Magnetic field parallel to the sample surface

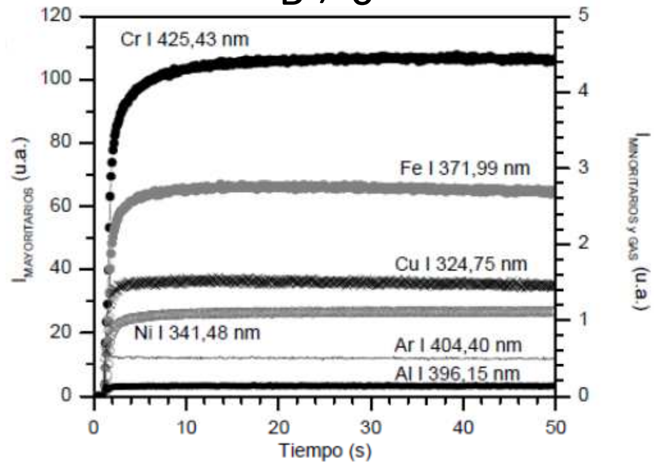
Type of magnets	Nº of magnets	Magnetic field (mT)
Ferrite	2x1	20
	2x2	30
	2x3	38
Nd-Fe-B	2x1	40

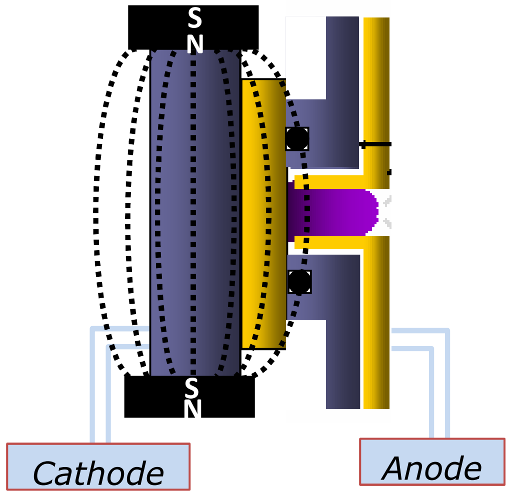
Sample BSH8: Ni (41.8%), Fe(14.6%), Cr (29.4%)

B=0



B ≠ 0





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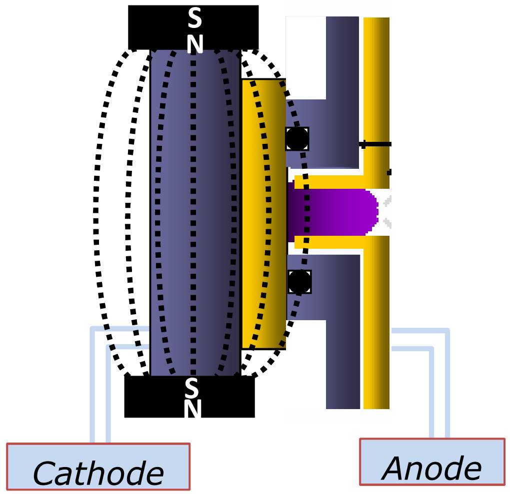
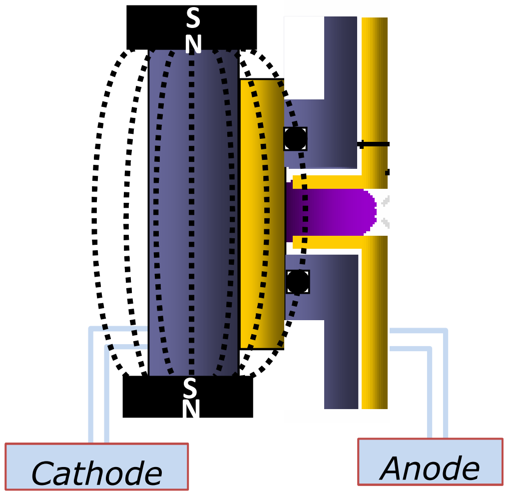
20 mT on sample surface

The magnetic field depends on the sample thickness



Magnetic field parallel to the sample surface

Similar configuration but the magnetic field is independent of the sample thickness



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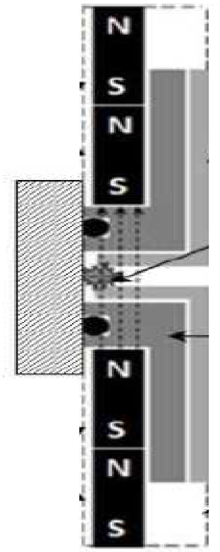

Permanent magnets produce low magnetic fields in the plasma regions

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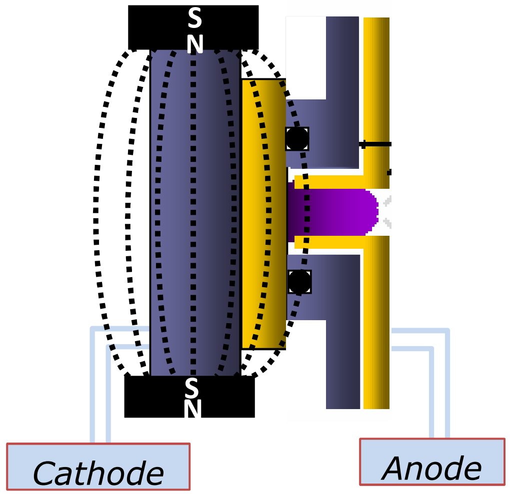
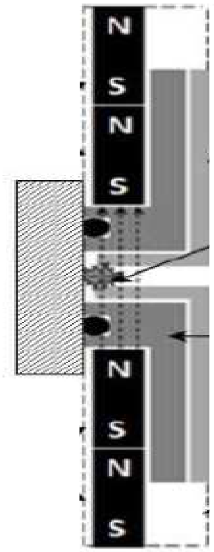


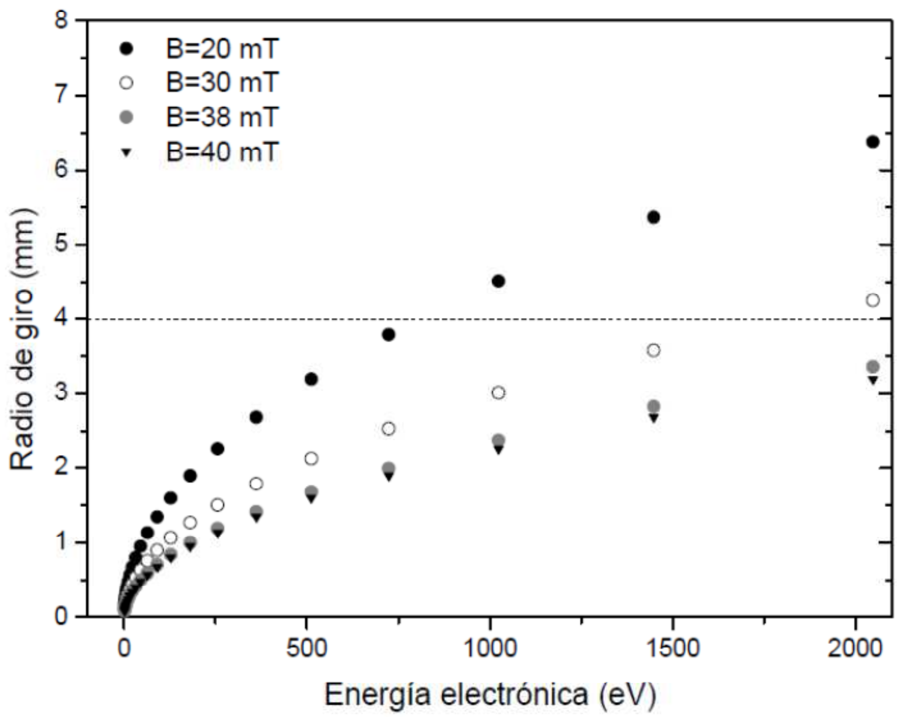


Magnetic field parallel to the sample surface

$$R = \frac{\sqrt{2 \cdot E \cdot m}}{q \cdot B}$$

E: electron energy
m: electron mass
q: charge
B: magnetic field

Radius of the electron trajectories



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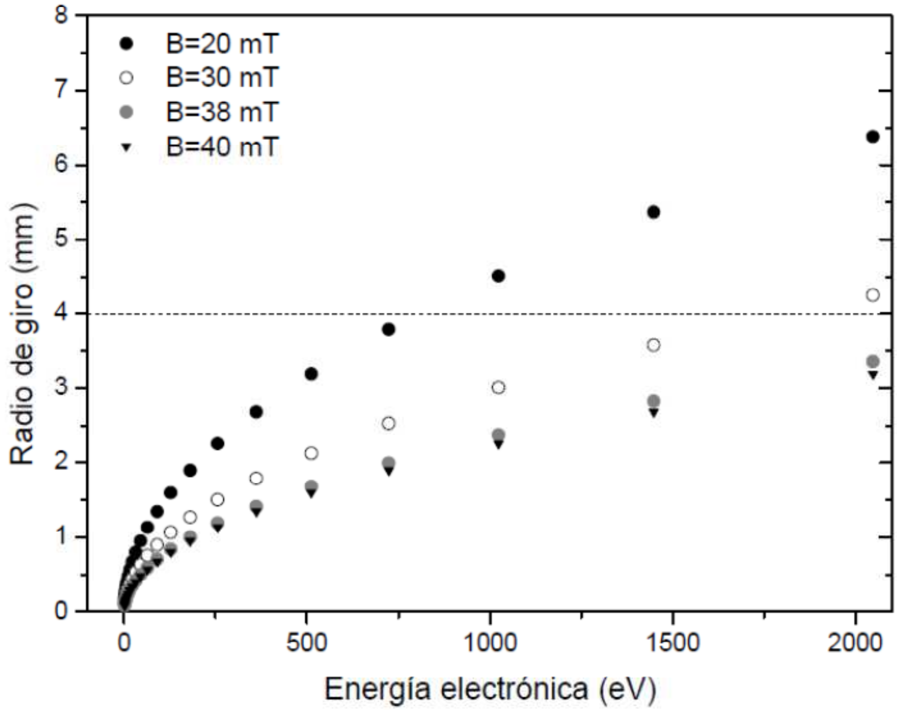
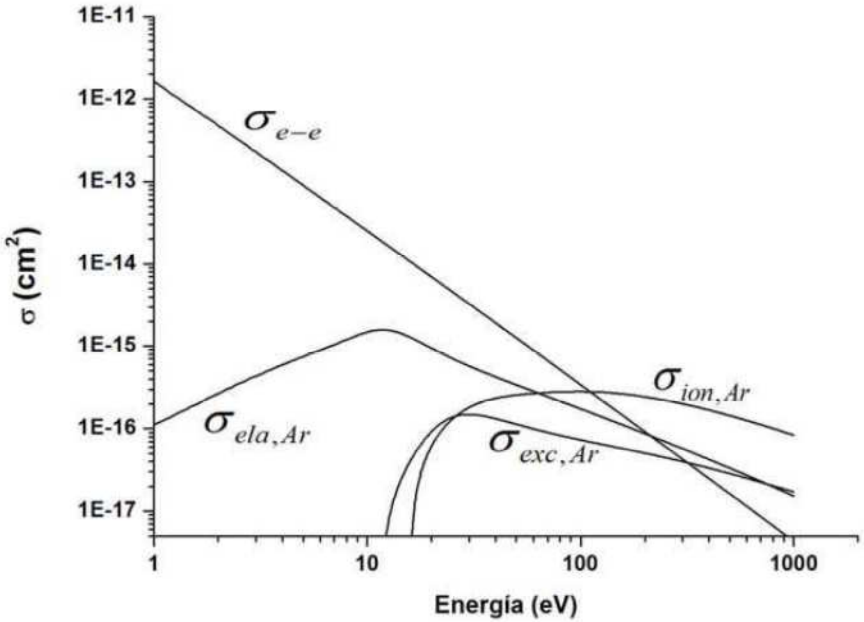
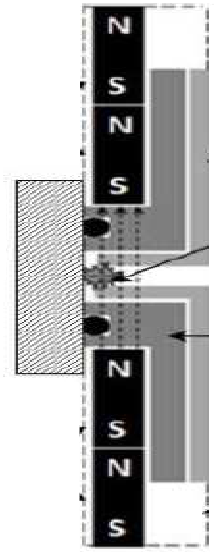


Cross sections



Permanent magnets produce low magnetic fields in the plasma regions



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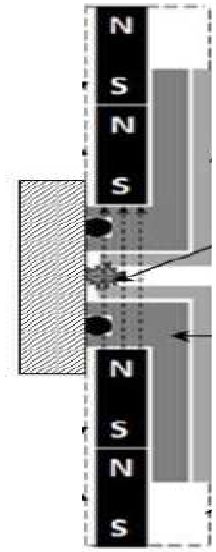
An electromagnet could be used

- Higher magnetic fields can be achieved
- Magnetic field can be regulated by the electrical current in the coil



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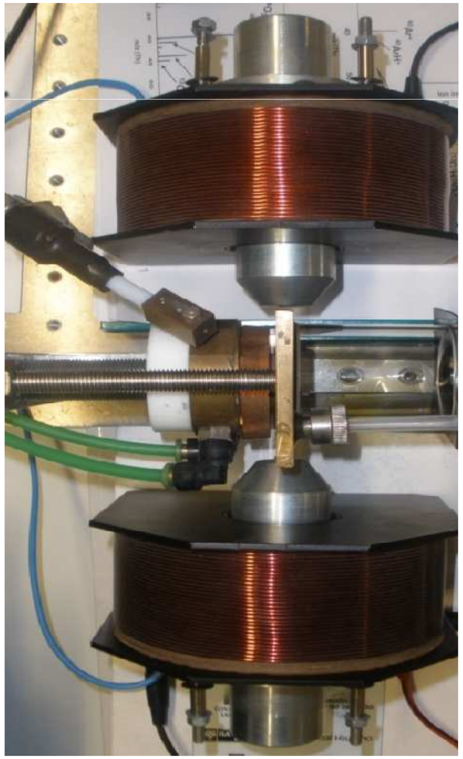

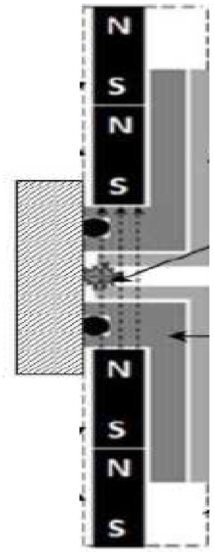

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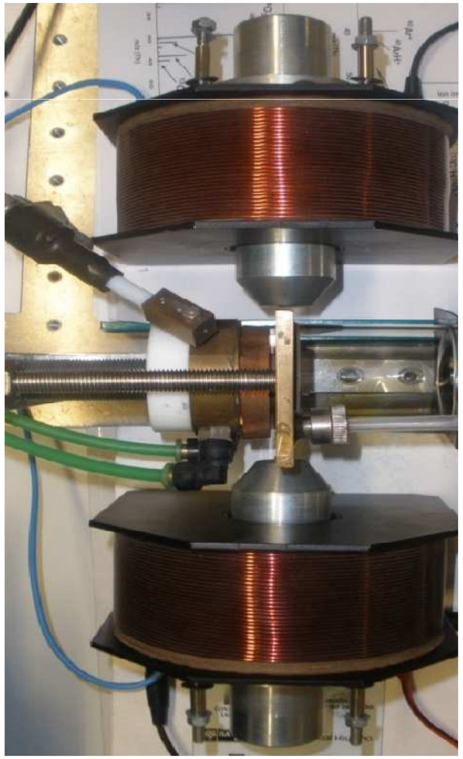
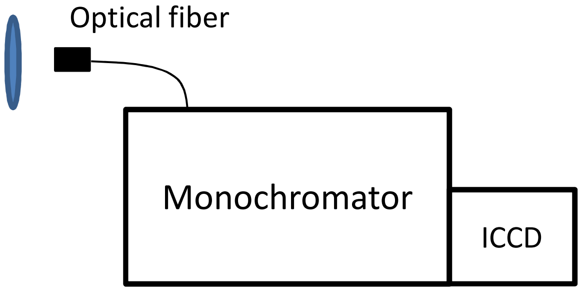
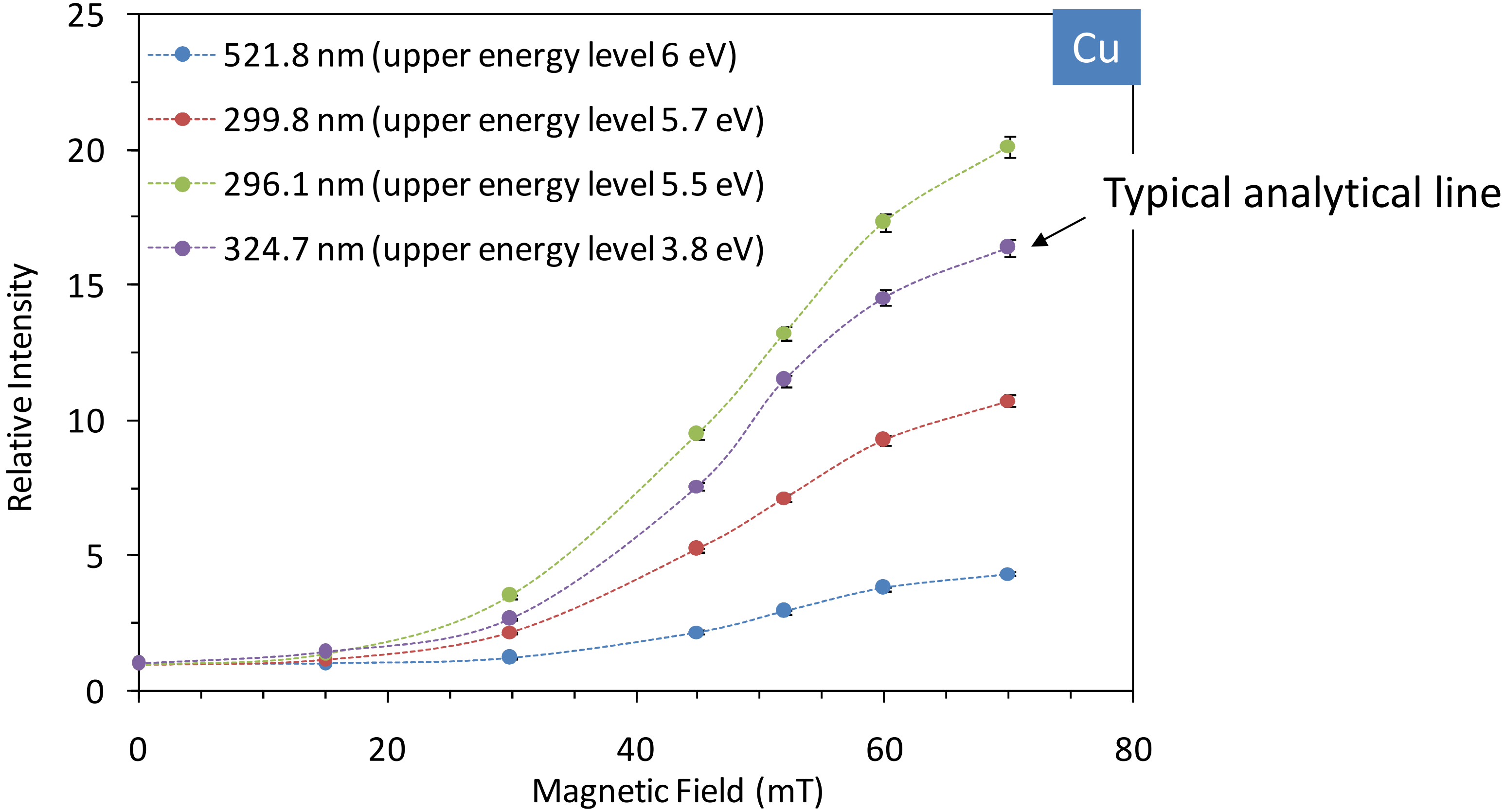


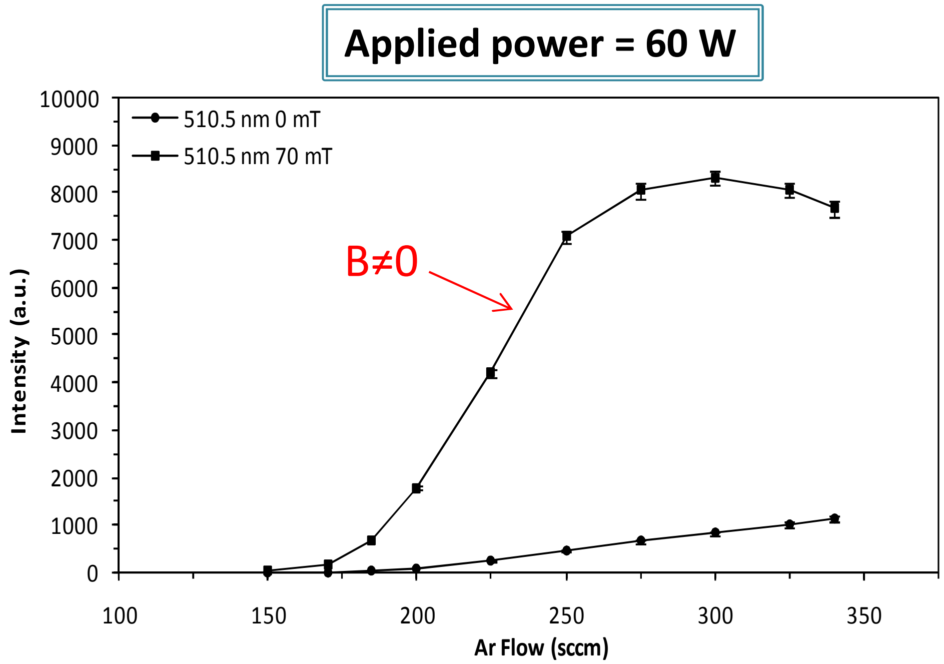


Discharge Conditions: 450 Pa & 50W

Relative Intensity
$I_r = I_{B\neq 0}/I_{B=0}$



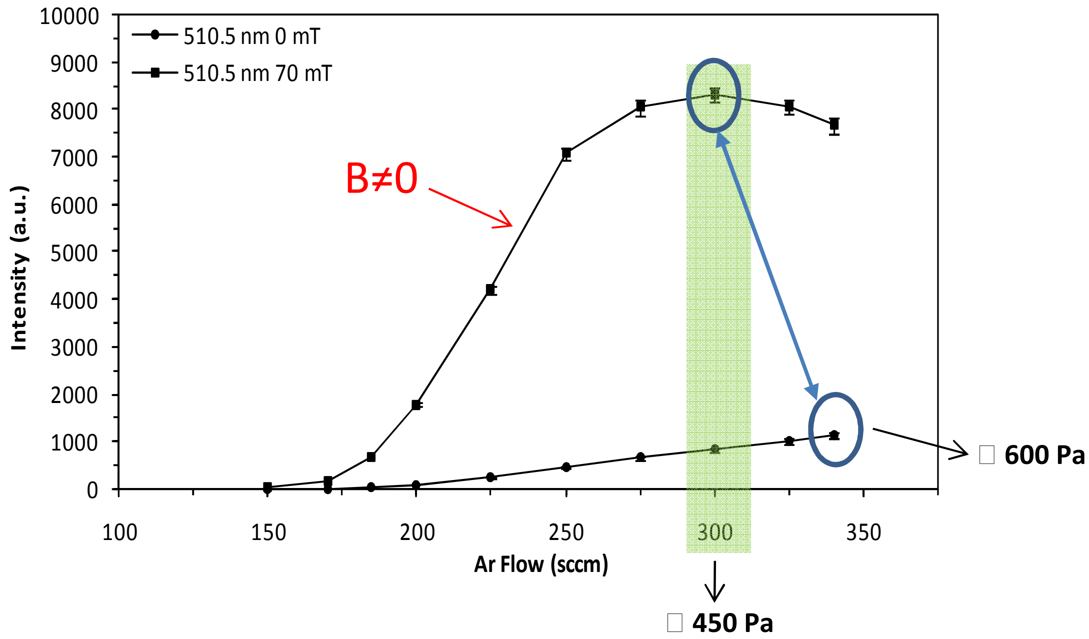
Effect of the pressure and applied power



Cu – 510.5 nm

Effect of the pressure and applied power

Applied power = 60 W



Cu – 510.5 nm

Higher pressures ⇒ Increase number of collisions

⇓

Magnetic field produces lower effect

Effect of the pressure and applied power

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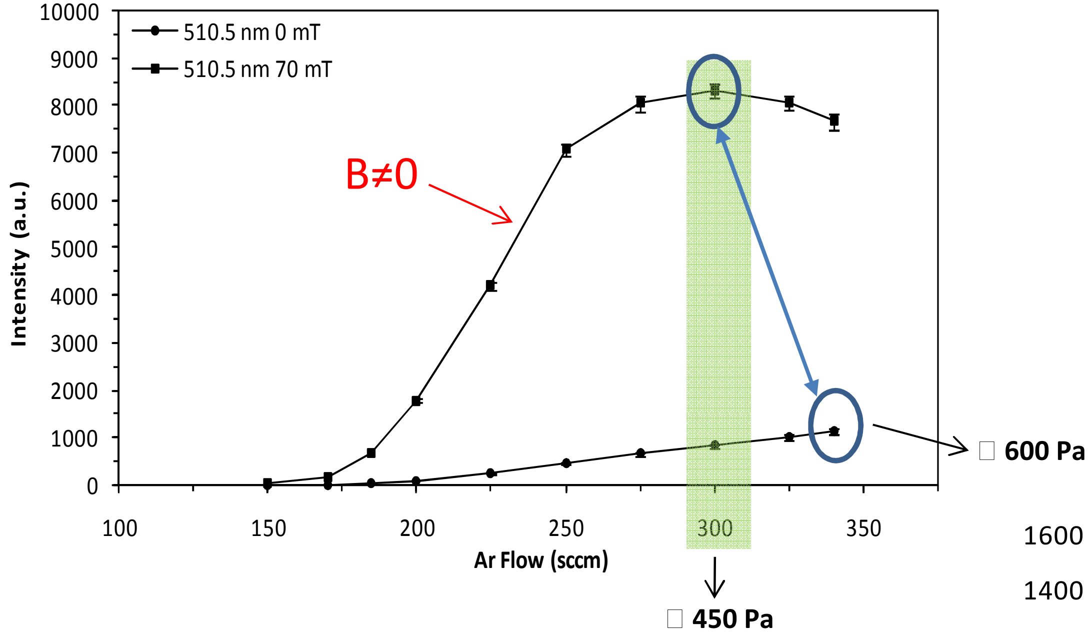
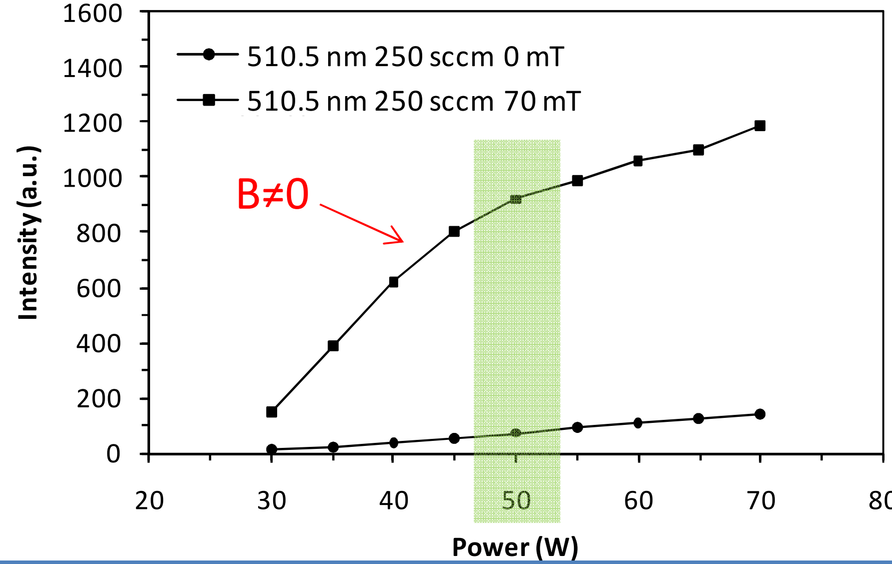


Cu – 510.5 nm

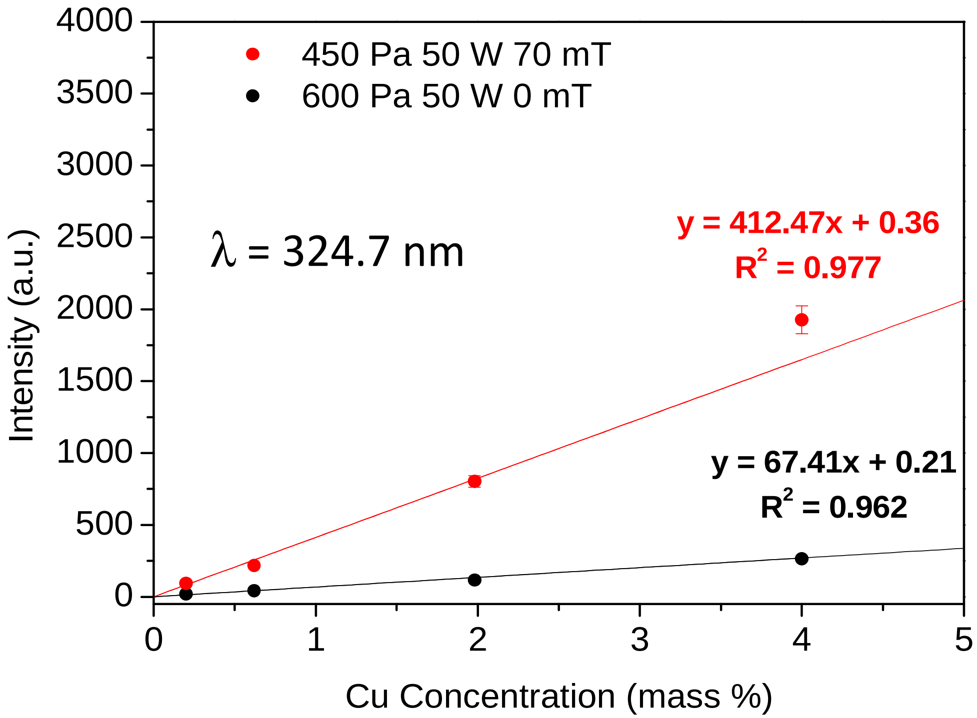
Pressure = 400 Pa



Calibration and limit of detection

aluminum matrix *set of samples with* ***variable copper content***

Reference Material	Cu (mass %)	Al (mass%)
VAW E-2/8	0.20	96.21
VAW 3015-4	0.62	83.80
VAW3035-3	1.98	84.90
VAW E-3/8	4.00	84.28



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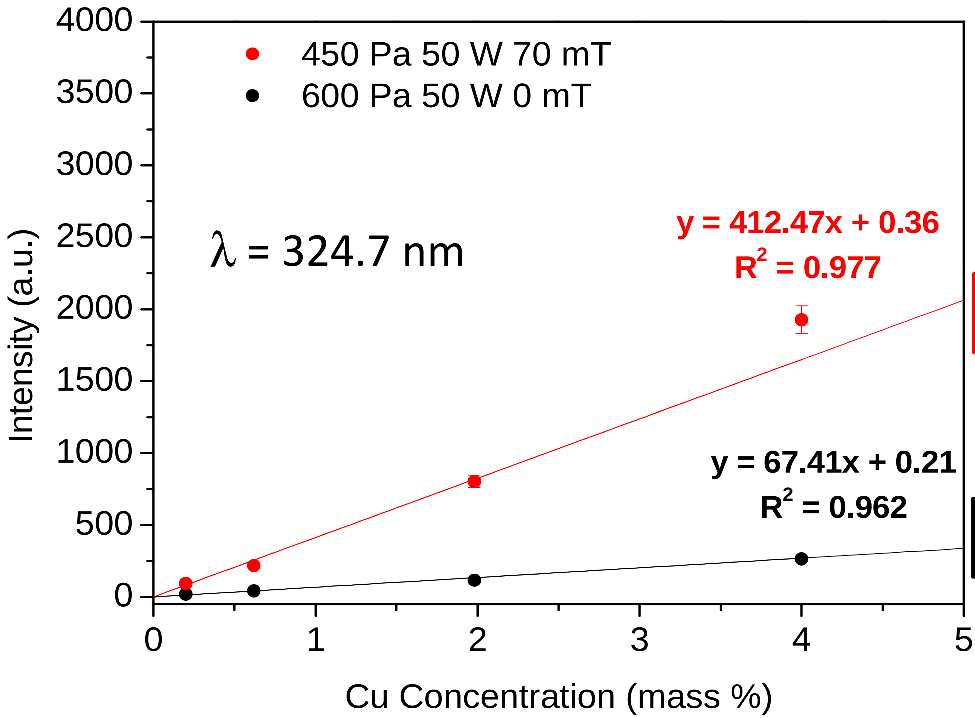


Limit of Detection = $3\sigma_b/m$

σ_b : background noise

m : calibration curve slope

LOD = 0.003 %

LOD = 0.02 %

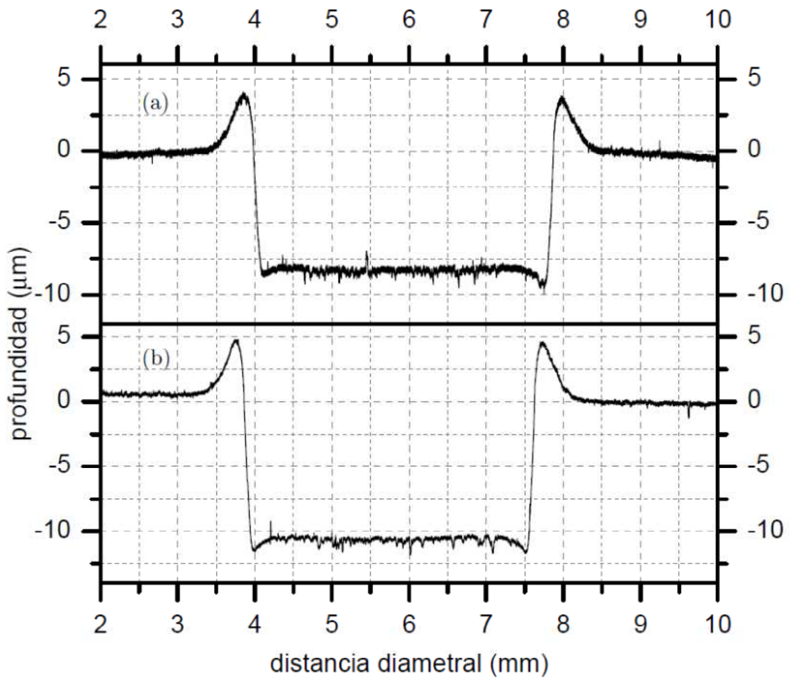
The magnetic field application improves the LOD in one order of magnitude

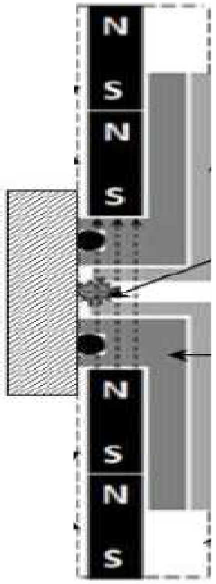
Effect of the magnetic field on

- **Emission intensities**
  - Higher LODs – 1 order of mag.
  - Low pressure and power with high intensity
  - Background and noise is not affected
- **Depth resolution**
- **Sputtering rates**

Depth resolution

Sample BSH8: Ni (41.8%), Fe(14.6%), Cr (29.4%)

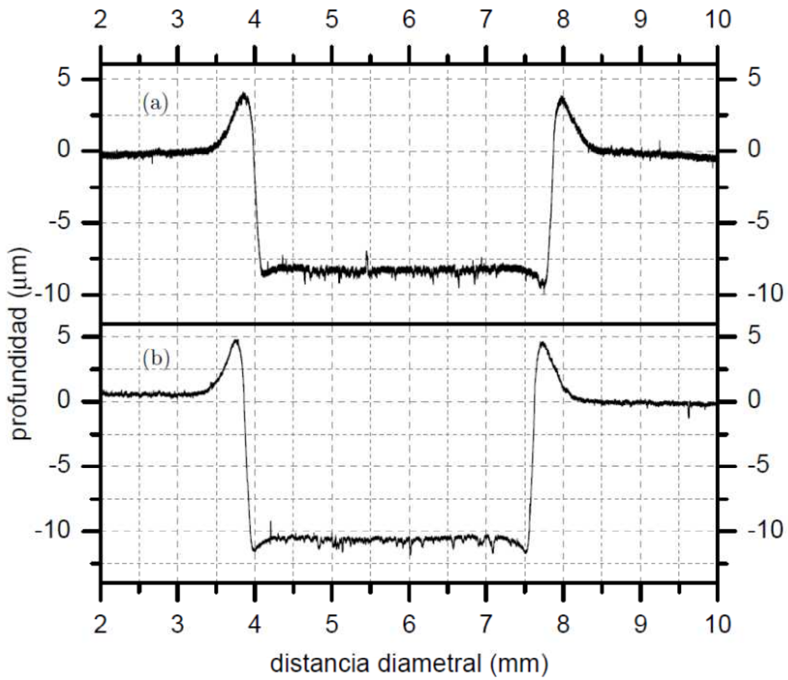


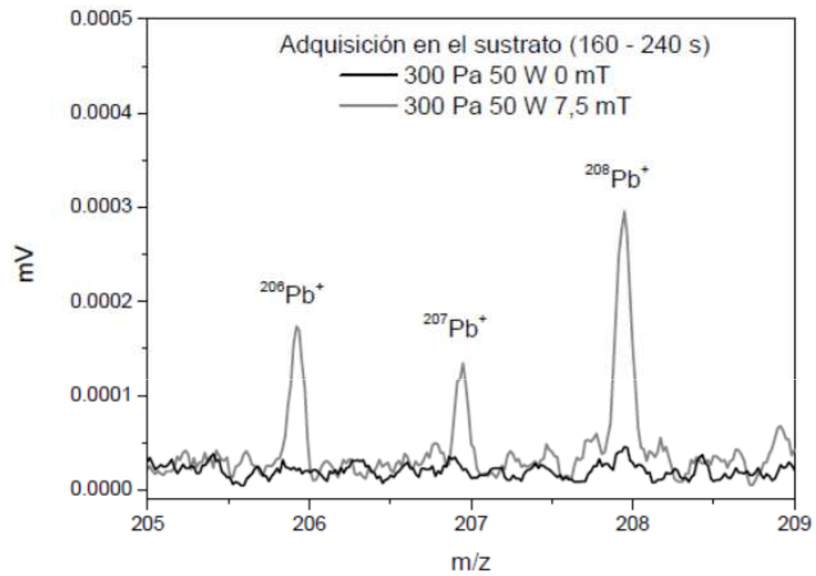


GD Parameters: 300 Pa – 50 W	B= 0 mT	B= 7.5 mT
Sputtering time (s)	224	226
Crater volumen (x10^7 µm^3)	8.1±0.3	10.1±0.4
Sputtering rate (µg/s)	3.3±0.5	3.9±9.6

Depth resolution

Sample BSH8: Ni (41.8%), Fe(14.6%), Cr (29.4%)

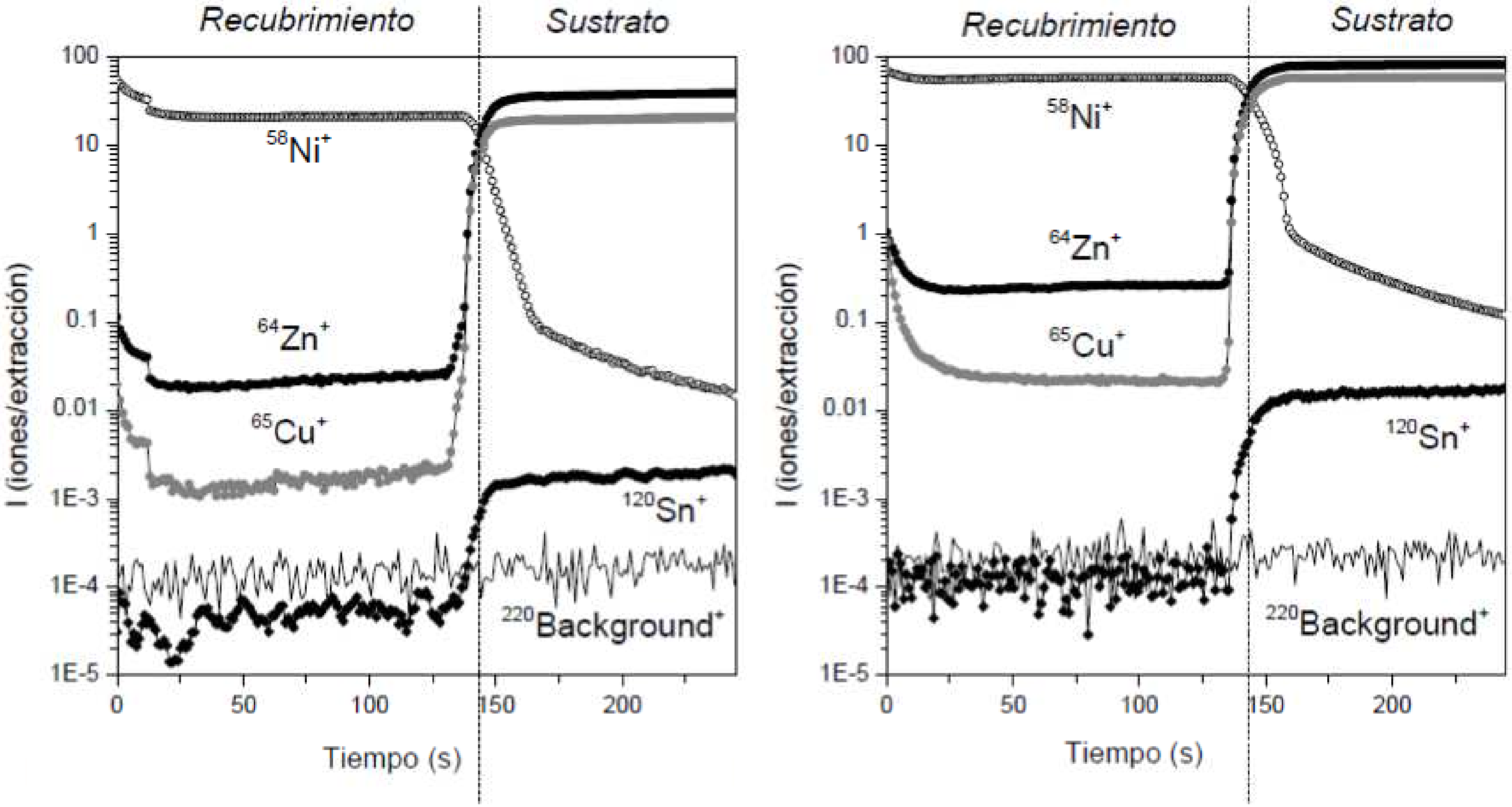




GD Parameters: 300 Pa – 50 W	B= 0 mT	B= 7.5 mT
Sputtering time (s)	224	226
Crater volumen (x10^7 μm^3)	8.1±0.3	10.1±0.4
Sputtering rate (µg/s)	3.3±0.5	3.9±9.6

Depth resolution

Sample: Ni (12.9 μm)/brass



B=0 **B≠0**

Bibliographic data: WO2009130424 (A1) — 2009-10-29

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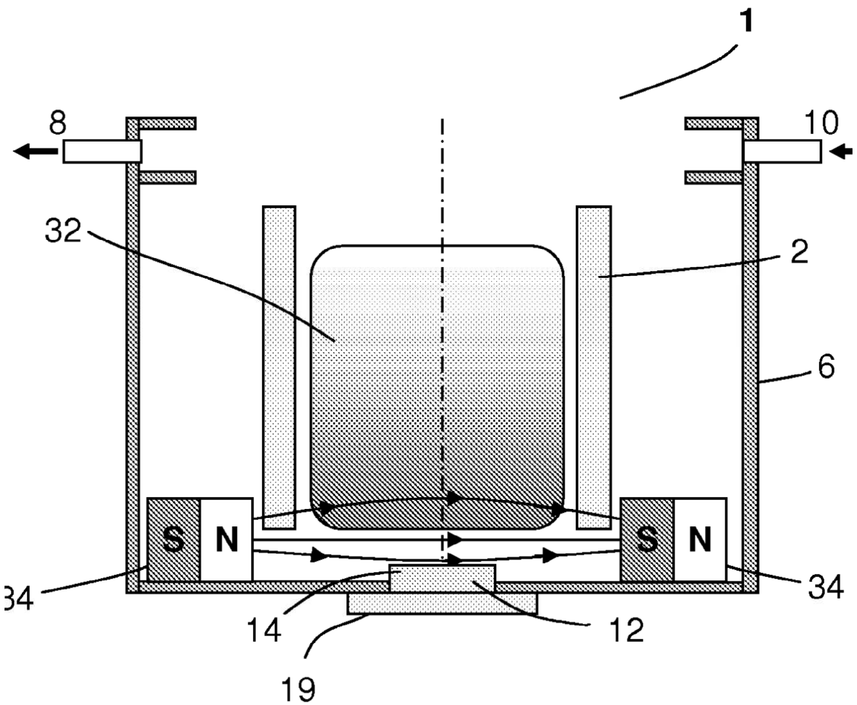
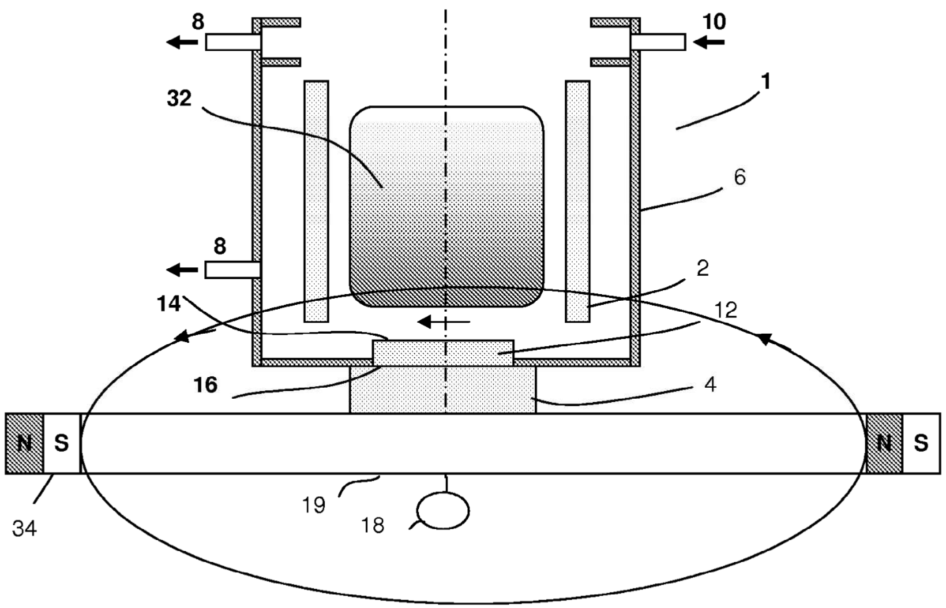
MAGNETRON SOURCE FOR A GLOW DISCHARGE SPECTROMETER

Page bookmark	WO2009130424 (A1) - MAGNETRON SOURCE FOR A GLOW DISCHARGE SPECTROMETER
Inventor(s):	GANCIU-PETCU MIHAI [RO]; DIPLASU CONSTANTIN [RO]; SURMEIAN AGAVNI [RO]; GROZA ANDREEA-LILIANA [RO]; TEMPEZ AGNES [FR]; CHAPON PATRICK [FR]; CASARES MARCO [FR]; ROGERIEUX OLIVIER [FR] +
Applicant(s):	HORIBA JOBIN YVON SAS [FR]; NAT INST OF LASERS PLASMA AND [RO]; GANCIU-PETCU MIHAI [RO]; DIPLASU CONSTANTIN [RO]; SURMEIAN AGAVNI [RO]; GROZA ANDREEA-LILIANA [RO]; TEMPEZ AGNES [FR]; CHAPON PATRICK [FR]; CASARES MARCO [FR]; ROGERIEUX OLIVIER [FR] +





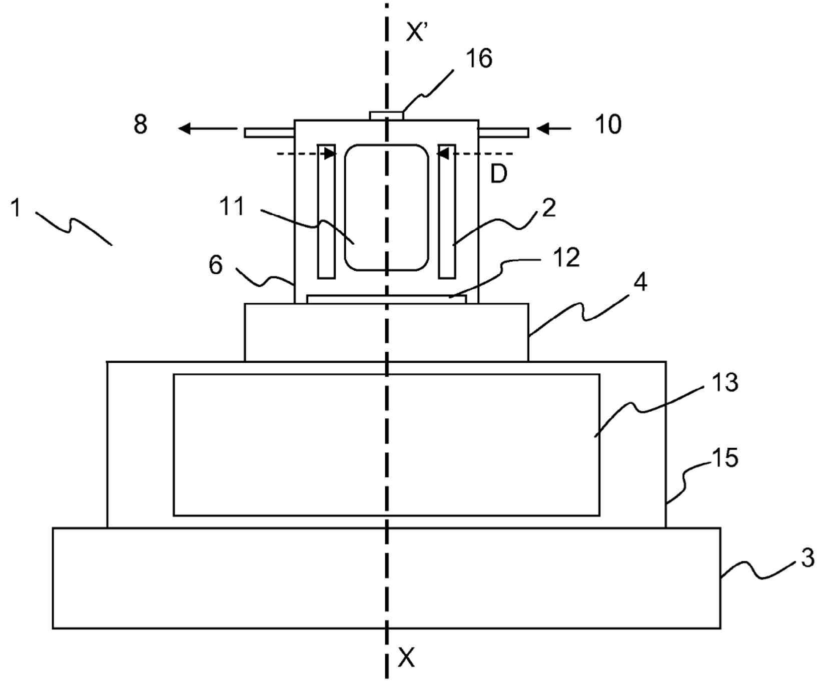
(10) **Patent No.:** **US 8,581,494 B2**
(45) **Date of Patent:** **Nov. 12, 2013**

(12) **United States Patent**
Ganciu-Petcu et al.

(54) **DISCHARGE LAMP FOR GDS WITH AN AXIAL MAGNETIC FIELD**

(75) Inventors: **Mihai Ganciu-Petcu**, Bucarest (RO); **Virgil Mircea Udrea**, Bucarest (RO); **Agnes Tempez**, Massy (FR); **Patrick Chapon**, Villebon sur Yvette (FR)

(73) Assignee: **Horiba Jobin Yvon SAS**, Longjumeau (FR)



(10) **Patent No.:** **US 8,581,494 B2**
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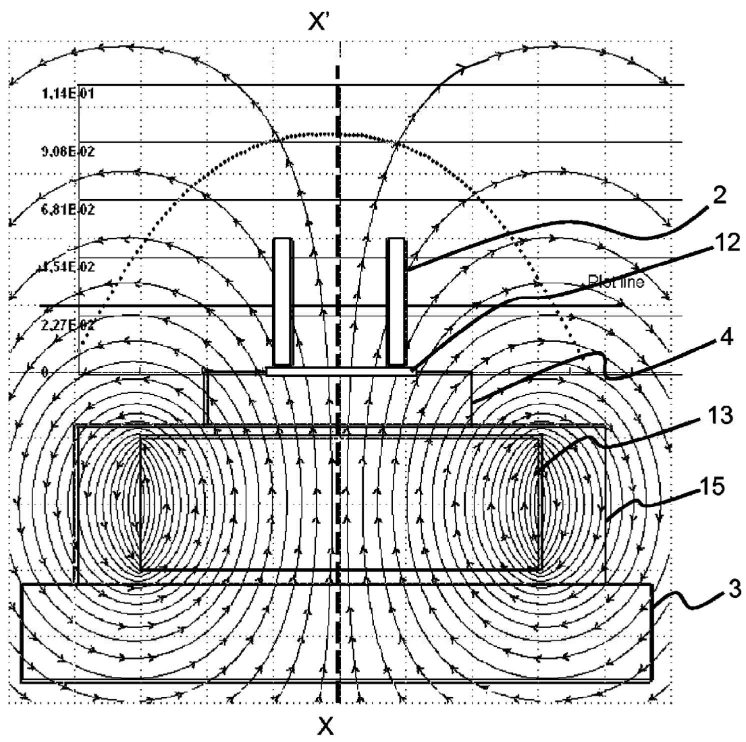
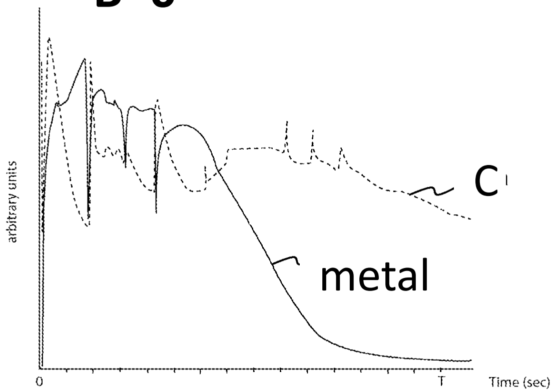


(10) **Patent No.:** **US 8,581,494 B2**
(45) **Date of Patent:** **Nov. 12, 2013**

(54) **DISCHARGE LAMP FOR GDS WITH AN AXIAL MAGNETIC FIELD**

Sample: metal/polymer film

B=0



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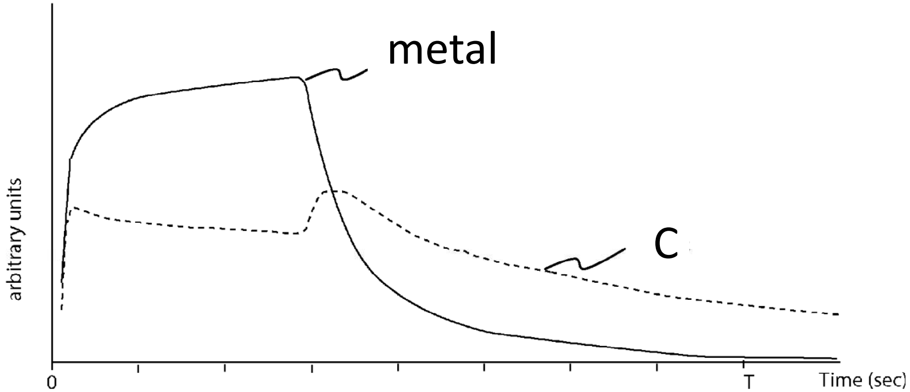

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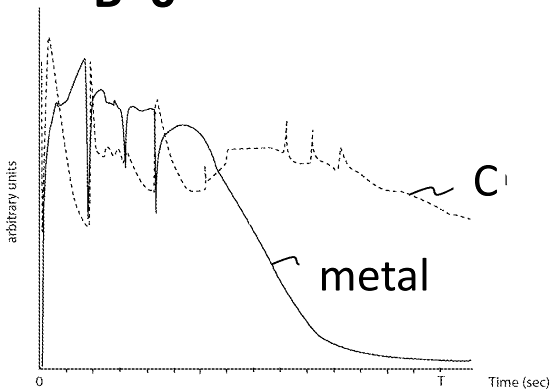
(45) **Date of Patent:** **Nov. 12, 2013**

(54) **DISCHARGE LAMP FOR GDS WITH AN AXIAL MAGNETIC FIELD**

Sample: metal/polymer film

B=0



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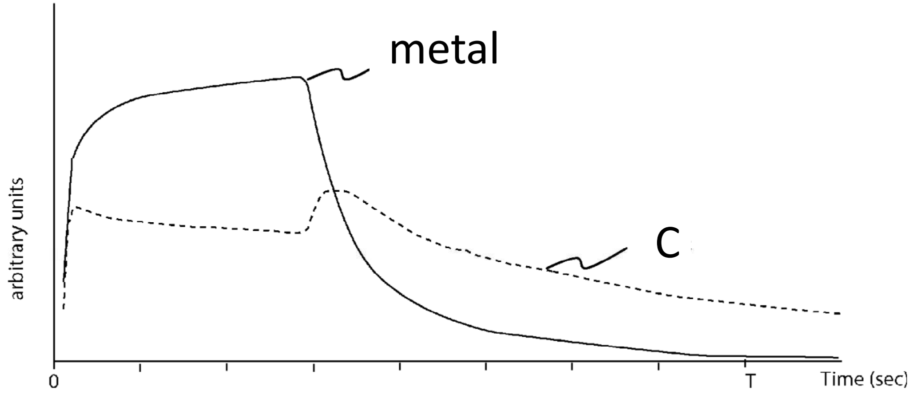
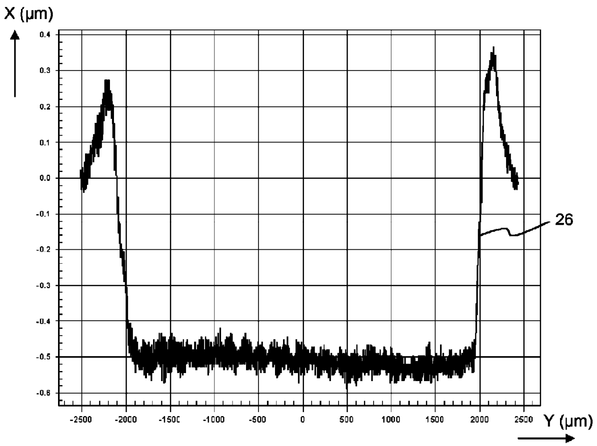




Sample: thick glass

Conclusions

- ❑ The application of a magnetic field can increase the plasma emission. The magnetic field should be higher than a threshold to obtain noticeable enhancements

- ❑ Depending on the magnet configuration, the resulting magnetic field can be parallel or perpendicular to the sample surface.

- ❑ Depending on the magnets placement the value of the magnetic field on the plasma site can depend on the sample thickness

- ❑ Limits of detection an order of magnitude lower than those obtained without magnetic field can be achieved. Elements not detected in absence of magnetic field can be observed by applying an appropriate magnetic field

- ❑ It is posible to use lower pressures and powers which results extremely convenient for the analysis of polymers and organic samples.

Acknowledgments

- Financial support from the Ministry of Economy and Competitiveness and the Principality of Asturias through the research projects CTQ2013-49032-C2-2-R and GRUPIN14-040

- Horiba

Thank you for your attention!

University of Oviedo

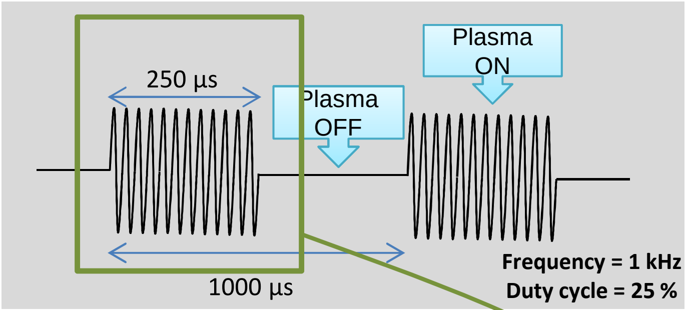
Laser and Plasma Spectroscopy Research Group

www.unioviedo.es/gelp

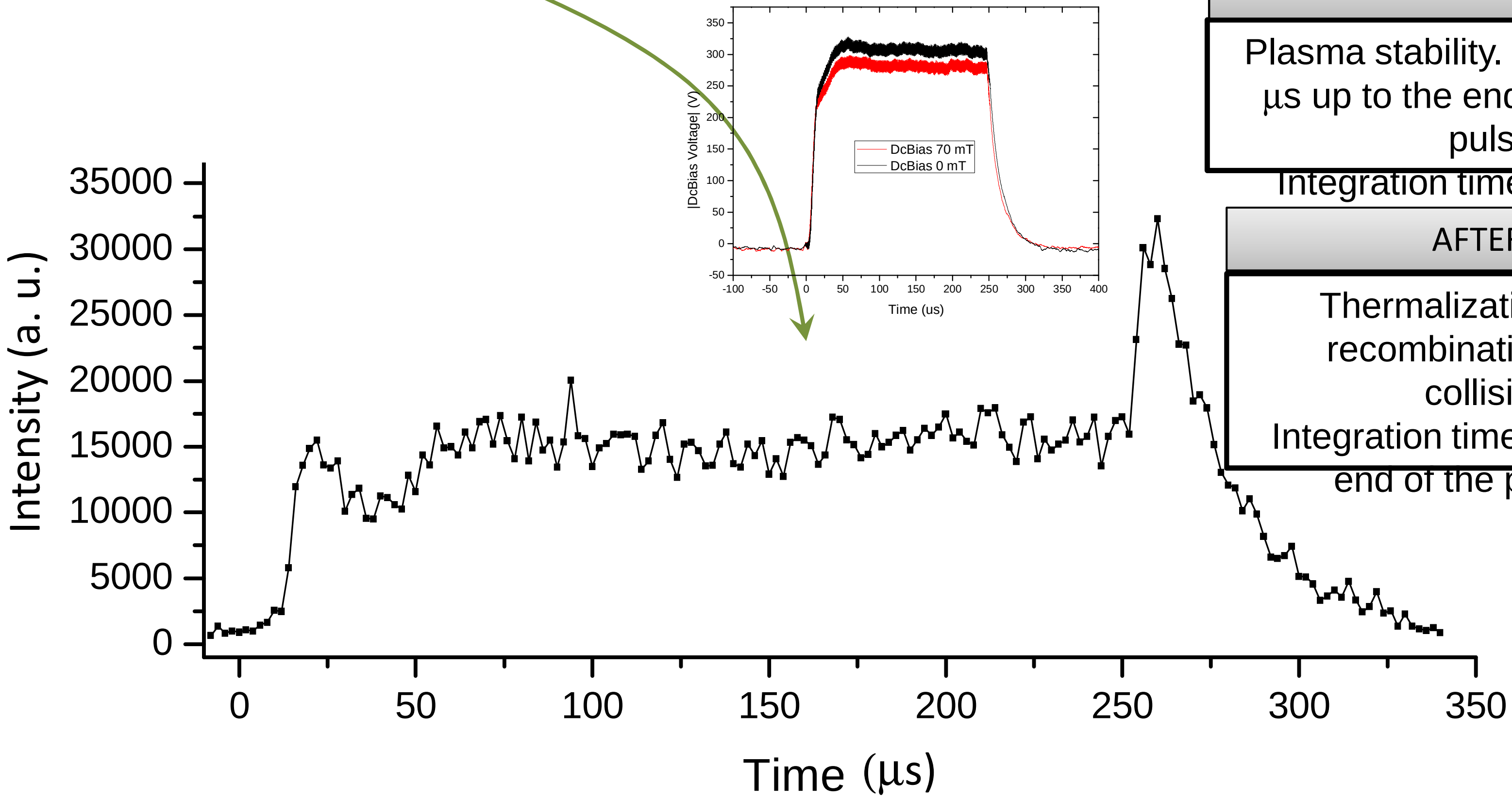
Magnetically Boosted Glow Discharge Optical Emission Spectroscopy for Analytical Applications: Pros and Cons

J. Pisonero, N. Bordel

Results: pulsed rf-GD-OES



Pulse width: 250 µs
Frequency: 1 kHz
Duty cycle: 25%



Cu I PREPEAK

Since the start of the power pulse up to the dc-bias voltage reaches its stable level.
Integration time 0-50 µs

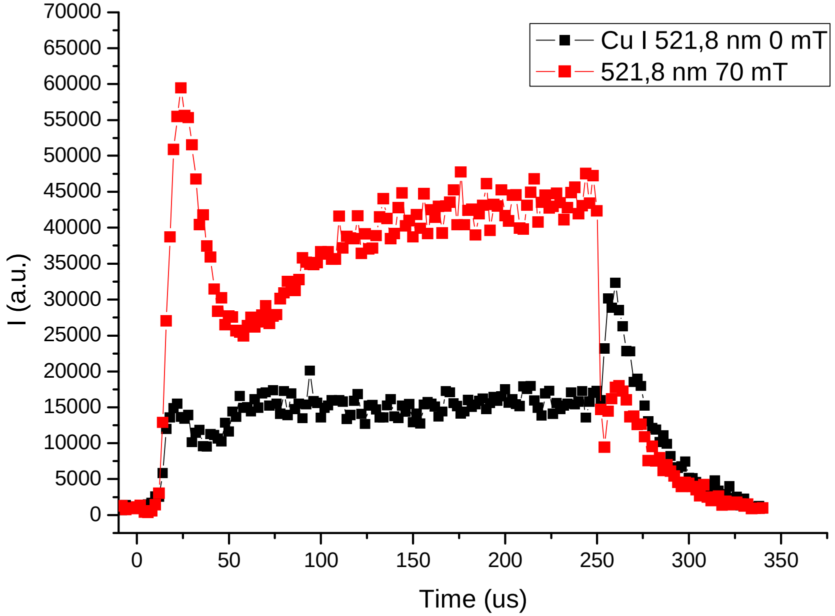
PLATEAU

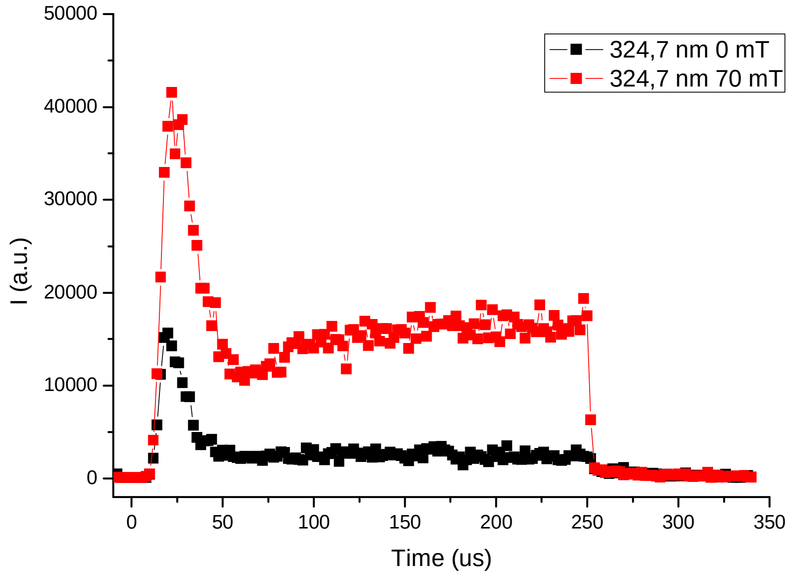
Plasma stability. It lasts from 50 µs up to the end of the power pulse.
Integration time 100-200 µs

AFTERPEAK

Thermalization of e-, Ar+ recombination, Penning collisions…
Integration time 50 µs after the end of the power pulse

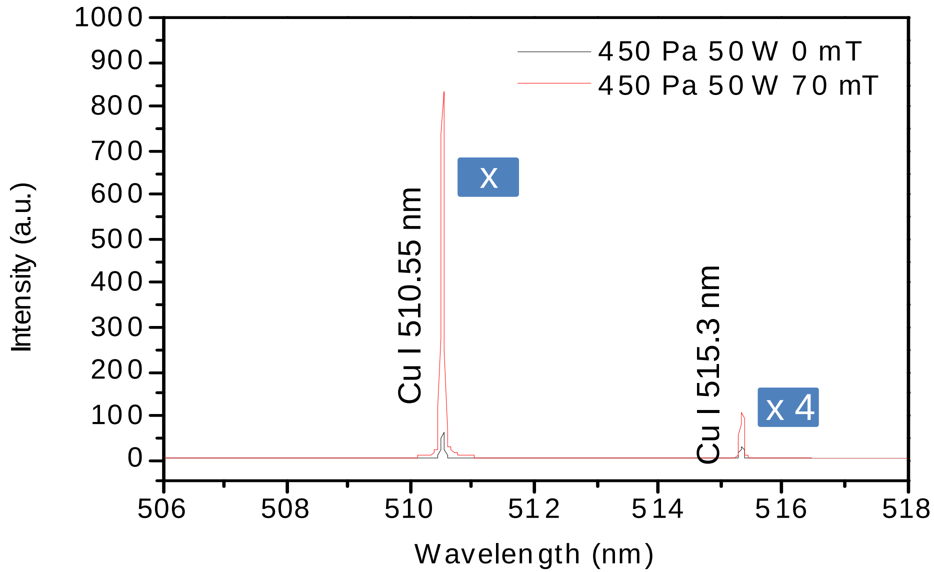
Flow rate: 300 sccm
Applied power: 80 W



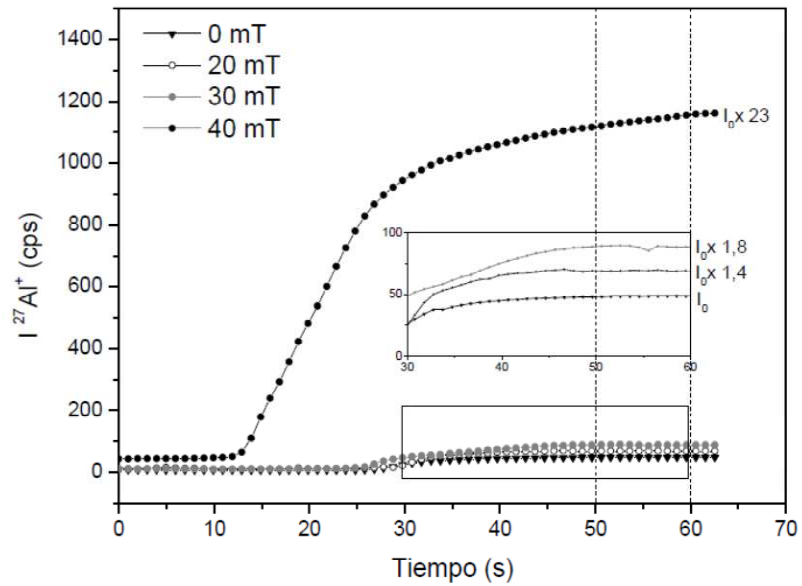


The magnetic field affects the emission when electrons are present in the plasma

Results: non pulsed rf-GD-OES



✓ **Background level is not affected by the magnetic field**



a 2.17: señal iónica del aluminio (m/z = 27) adquirido en el equipo rf-GD-TOFMS a unas
ndiciones de 400 Pa de presión y 40 W de potencia, en presencia de diferentes campos
ticos. Para facilitar la interpretación del gráfico se incluye una vista ampliada de la región
lrada. Se indica la zona en la que se han calculado los factores de incremento respecto a la
intensidad registrada en ausencia de campo así como dichos factores.

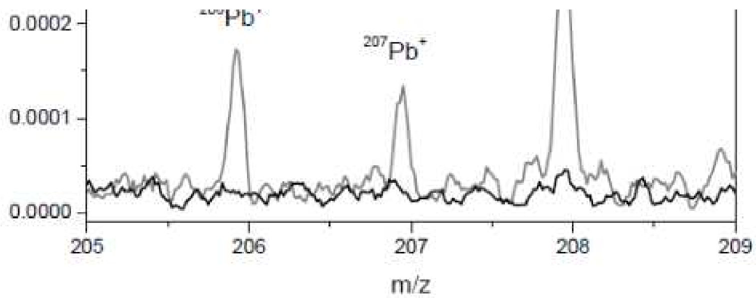
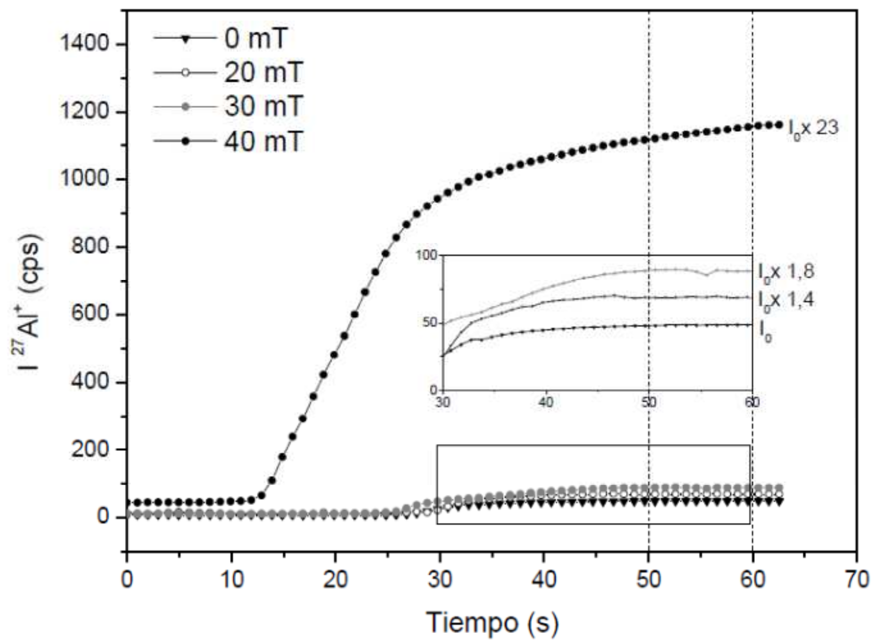


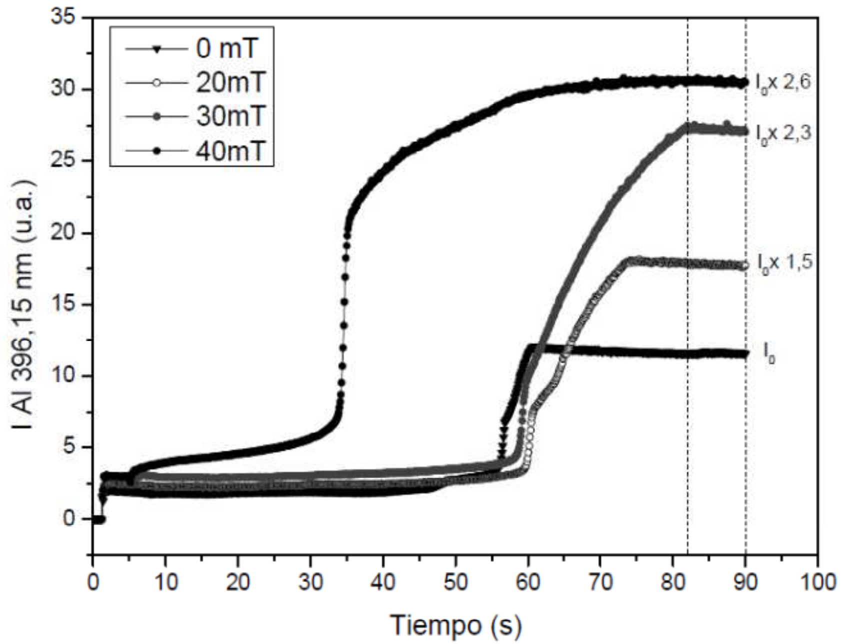
Figura 2.20: espectros de masas con y sin campo en la región del plomo; espectro adquirido en

Alumina layer on Aluminum

RF-GD-TOFMS



RF-GD-OES



The sputtering rate seems to be higher at the higher magnetic field employed
The depth resolution seems worse when the magnetic field is applied but the experimental parameters selected are the optimum for the analysis without magnetic field