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TOWARDS CALIBRATION TRANSFER FOR QUANTITATIVE ANALYSIS OF NUCLEAR MATERIALS BY LIBS

A unified approach for the characterization of
the ablation plasma in various matrices

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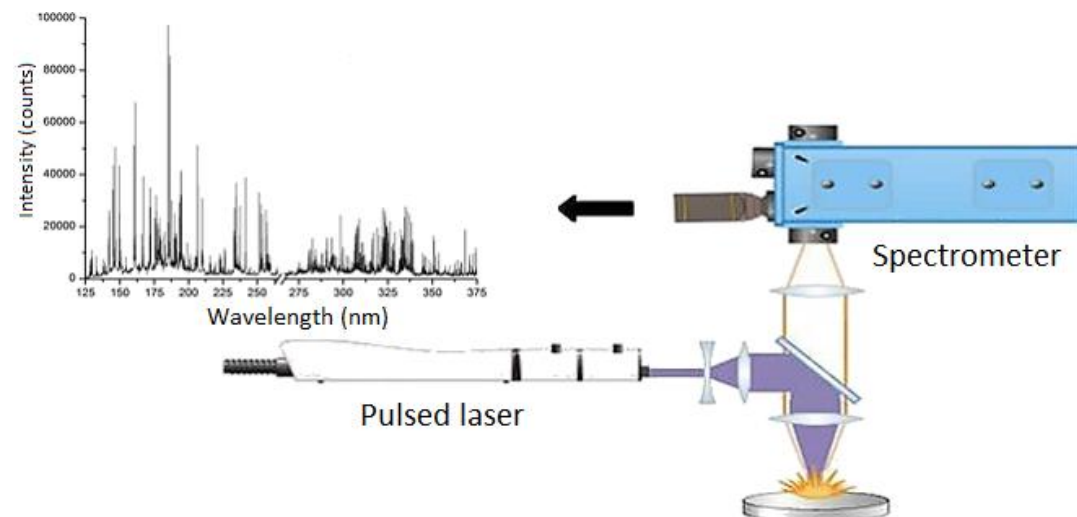
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Some elements of context :

CEA Valduc :

- Chemical analysis: quantification of metal impurities for quality control of nuclear metal materials from production lines...
- Today's methods: **offline** analysis;
 - Sometimes long delays between sampling and results;
 - Time consuming.

→ A first step of **online** quality pre-control may simplify the processes.



Perks of LIBS for this purpose

- Almost no sample preparation;
- Can be done remotely;
- Fast.
 - Optimization of production time;
 - Less irradiation risks;
 - Reduction of wastes.

Impossibility to achieve an analytical development directly with nuclear materials:

- Lack of calibrated samples;
- Complexity of U and Pu spectroscopy;
- Security and wastes constraints.



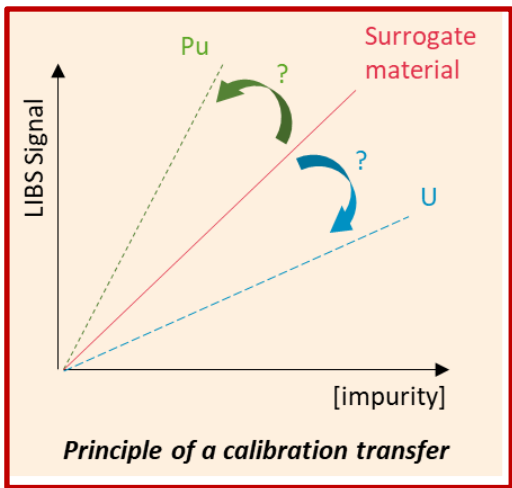
Need for a general method developed from surrogate materials.

Three steps:

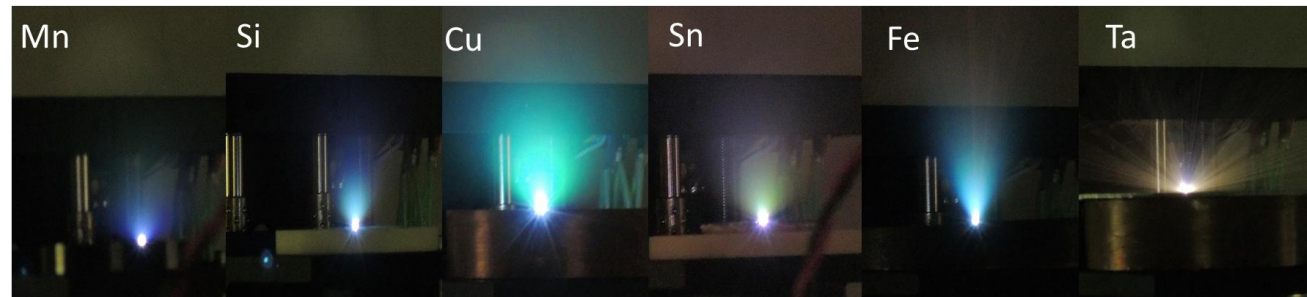
- Identification of surrogate materials;
- Analytical development on these surrogate materials;
- Calibration transfer to nuclear materials



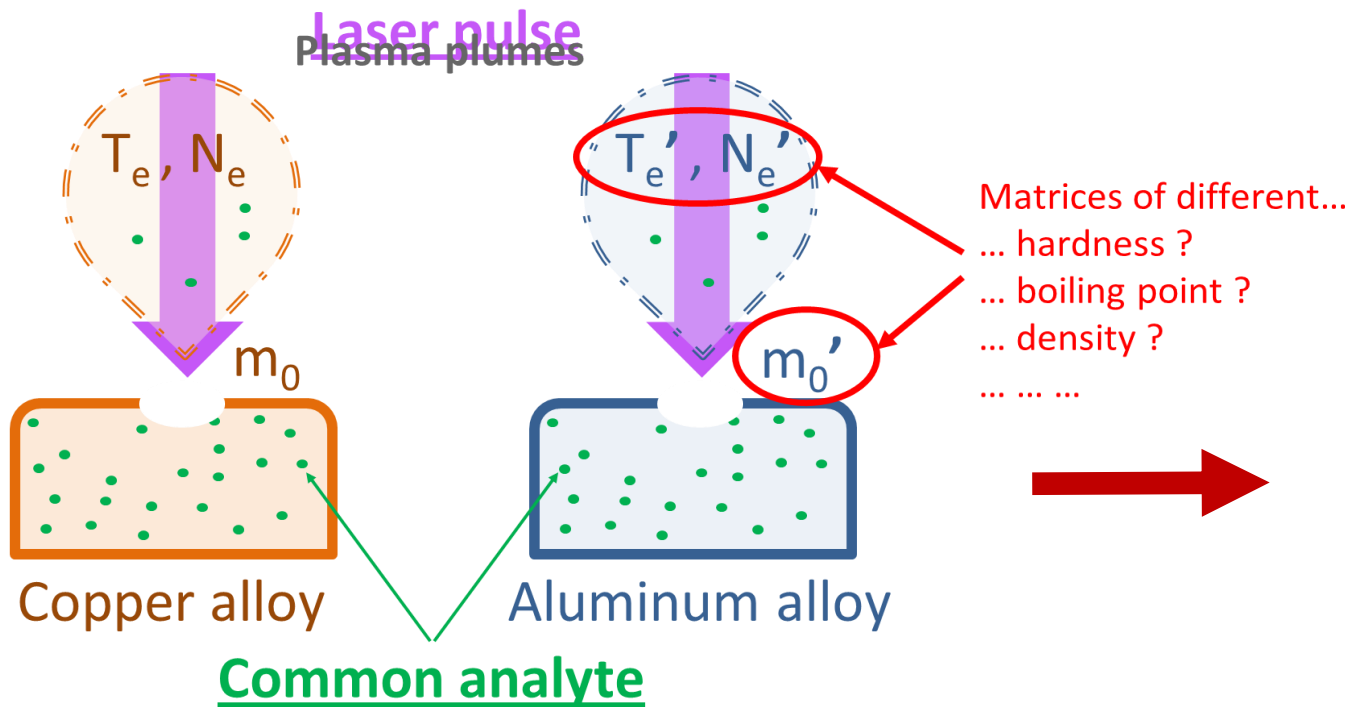
**Previous PhD Thesis:
Jessica Picard
(2012-2015)**



But how can we achieve this calibration transfer ?



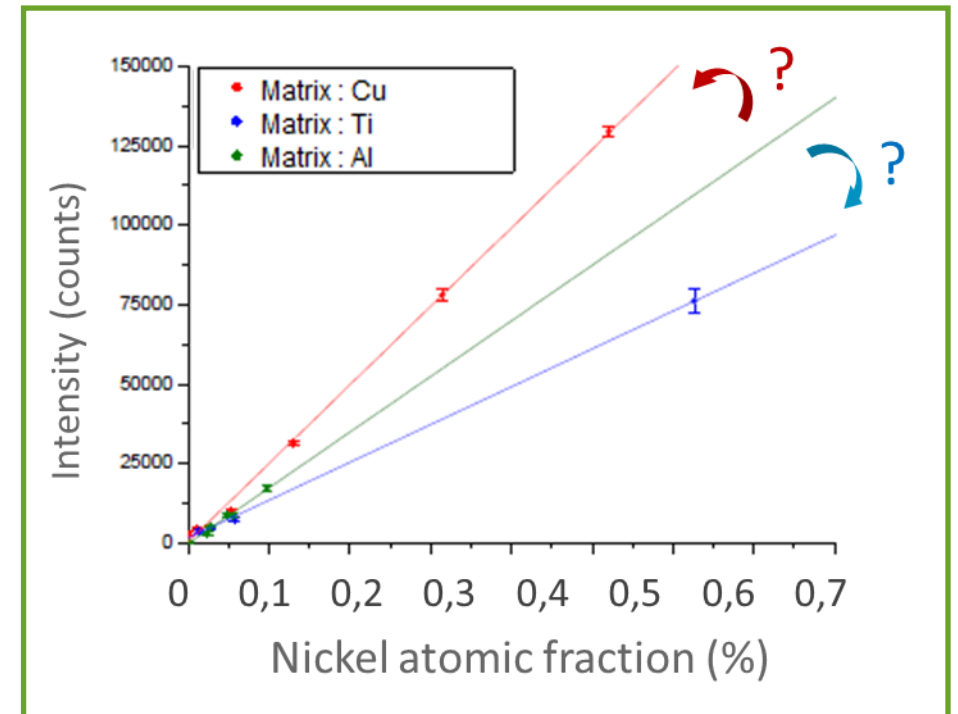
The matrix effects in a nutshell



Number of analyte atoms in gas phase in the plasma: includes m_0 and N_e

$$I_{ij} = F(\lambda) \times \frac{hc}{\lambda} \times N_0 \times \frac{g_i A_{ij}}{Z(T_e)} e^{\left(-\frac{E_i}{k(T_e)}\right)}$$

Temperature of the ablation plasma



→ Need to evaluate ablated mass, plasma temperature and electronic density in various matrices to correct the calibration curves.

- Ablated mass m_0



Previous works : normalization did not fully correct the matrix effects.

- Electron temperature T_e



Today's focus

- Electron density N_e



Future works

Measure them in different matrices in order to:

→ Use them to normalize the calibrations and correct the matrix effects between various metal matrices.

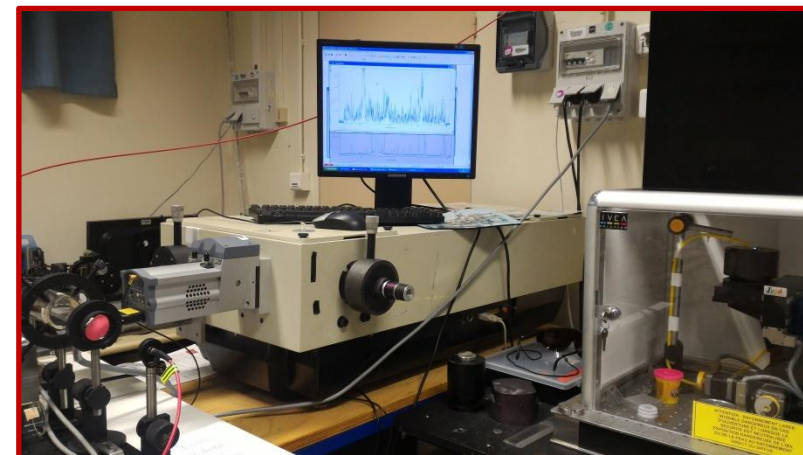
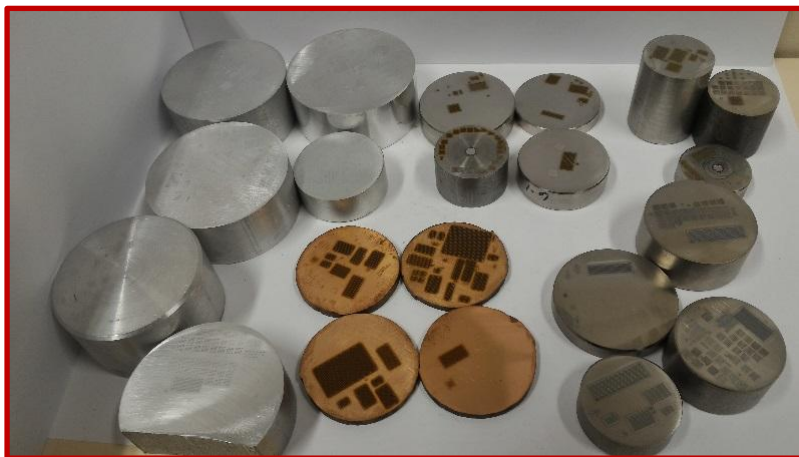
→ Find relationships between them and the physical properties of the matrices in order to acquire a better understanding of the matrix effects.

Aim: quantify impurities in all kinds of metal matrices using corrected calibrations



- Laser : Nd:YAG 266nm, 4ns and 9mJ pulses, 50 μ m spots
- Spectrometer : Horiba THR 1000 monochromator
- ICCD Andor iStar
- Certified metal standard samples

MobiLIBS system (IVEA Solution)



Important hypothesis : Local Thermodynamic Equilibrium (LTE)

→ Legitimizes the use of spectroscopic methods.

T_e : Boltzmann-plot

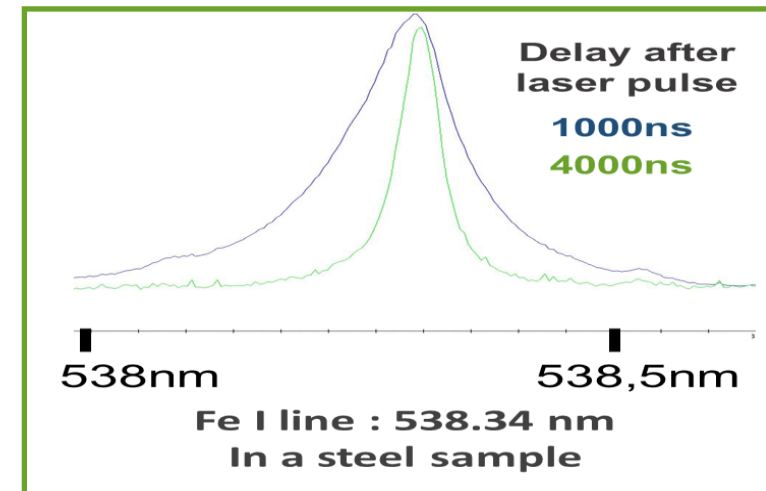
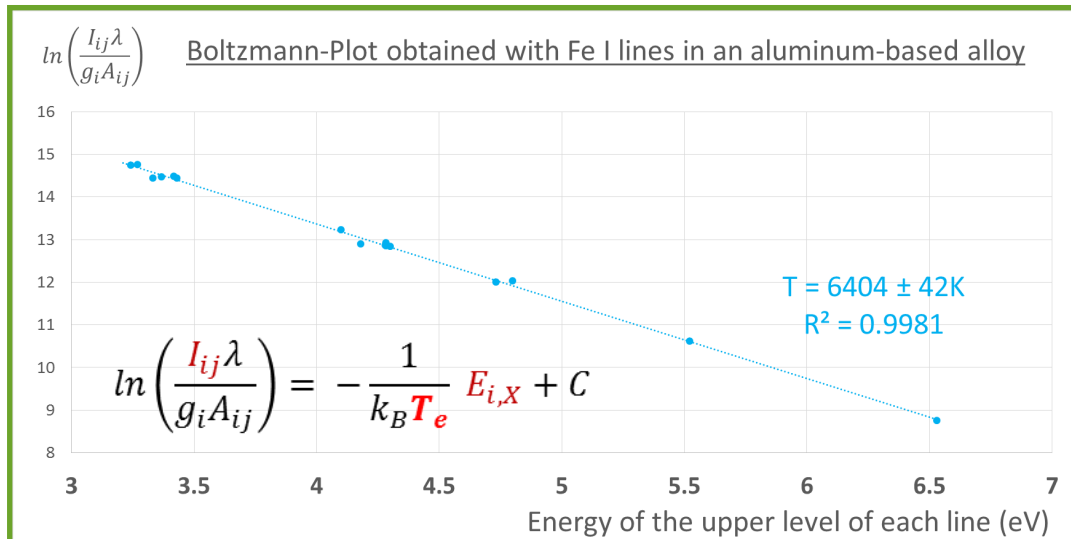
The intensity ratio between two lines of different energy levels is related to plasma temperature.

The hotter the plasma,
the more intense the lines of high energy.

N_e : Stark broadening

The width of a line is related, among other things, to plasma electronic density.

The denser the plasma,
the wider the emission lines



A UNIFIED METHOD FOR TEMPERATURE MEASUREMENTS IN VARIOUS MATRICES

Only small variations
of T_e expected from
one matrix to another.



**Need to find a unified
method to minimize
uncertainties.**



Cannot use matrix lines.
Need to use impurities
common to all matrices.

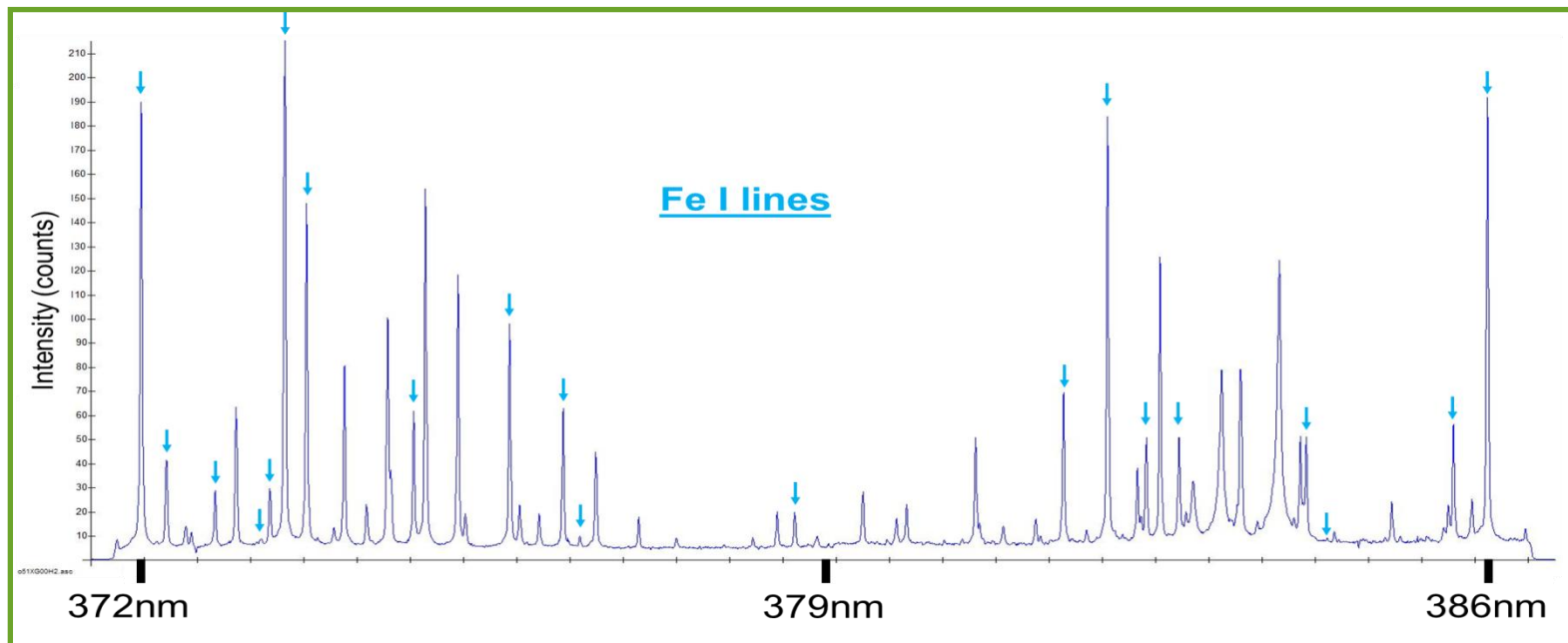


What lines can we use ?

Need of many lines of
different energies for
accurate measurements.



**Iron strong lines:
370-386nm**



Spectrum of an aluminum alloy
with 3500 ppm of iron.
Accumulation of 400 laser shots.

A UNIFIED METHOD FOR TEMPERATURE MEASUREMENTS IN VARIOUS MATRICES

Purpose: a common indicator for all matrices.

Problem: too many degrees of freedom: time dependency, geometry...

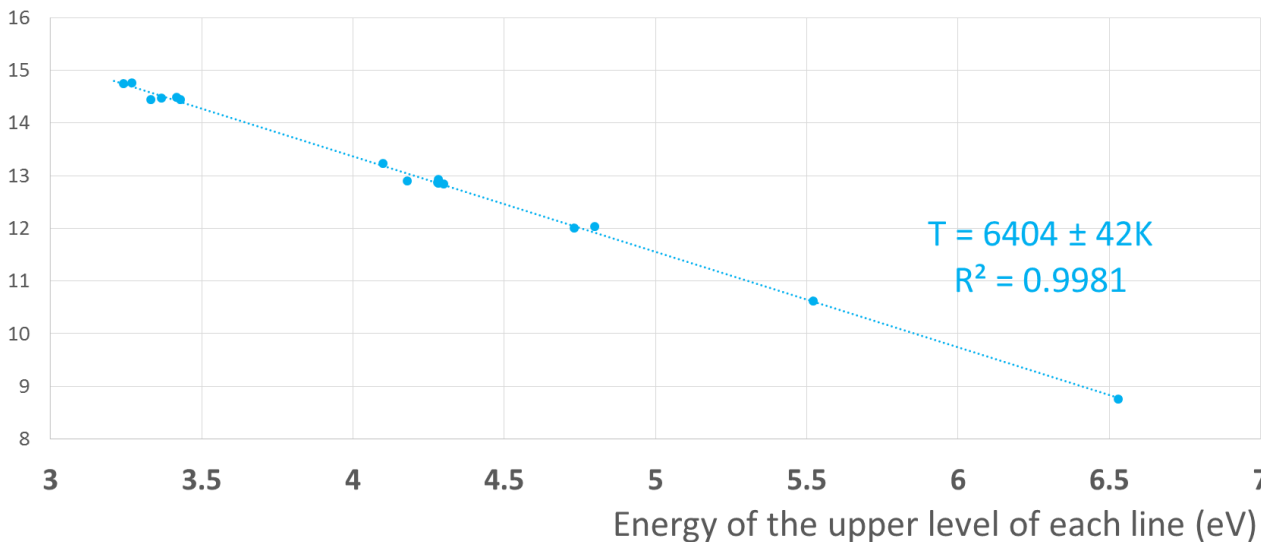
Time and space integrated indicators.

From 1 to 10 μ s after the laser pulse

Light collected from the whole plasma

What can we measure ?

$\ln\left(\frac{I_{ij}\lambda}{g_i A_{ij}}\right)$ Boltzmann-Plot obtained with Fe I lines in an aluminum-based alloy



But thermodynamic equilibrium at these scales doesn't make a lot of sense.

Nonetheless...

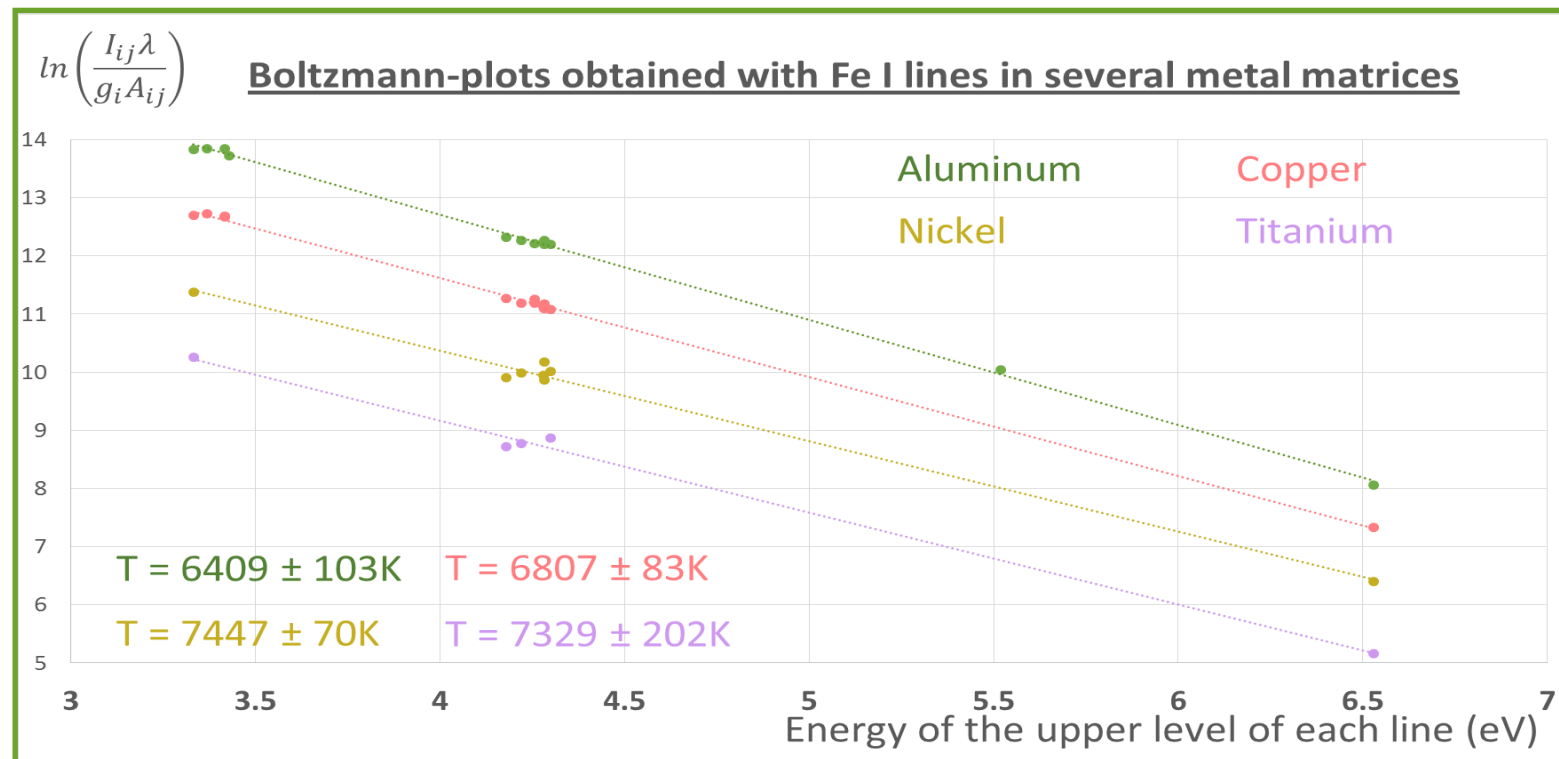
- Boltzmann-plots are very linear.
- McWhirter criterion seems verified.

Possibility to measure an indicator for T_e , which we can use to compare matrices

Lots of spectral interferences with elements of the matrices especially Ti and Ni

→ Trade-off between the number of measured lines and the precision of their measurement in every matrix.

Either we keep the best lines for each matrix...

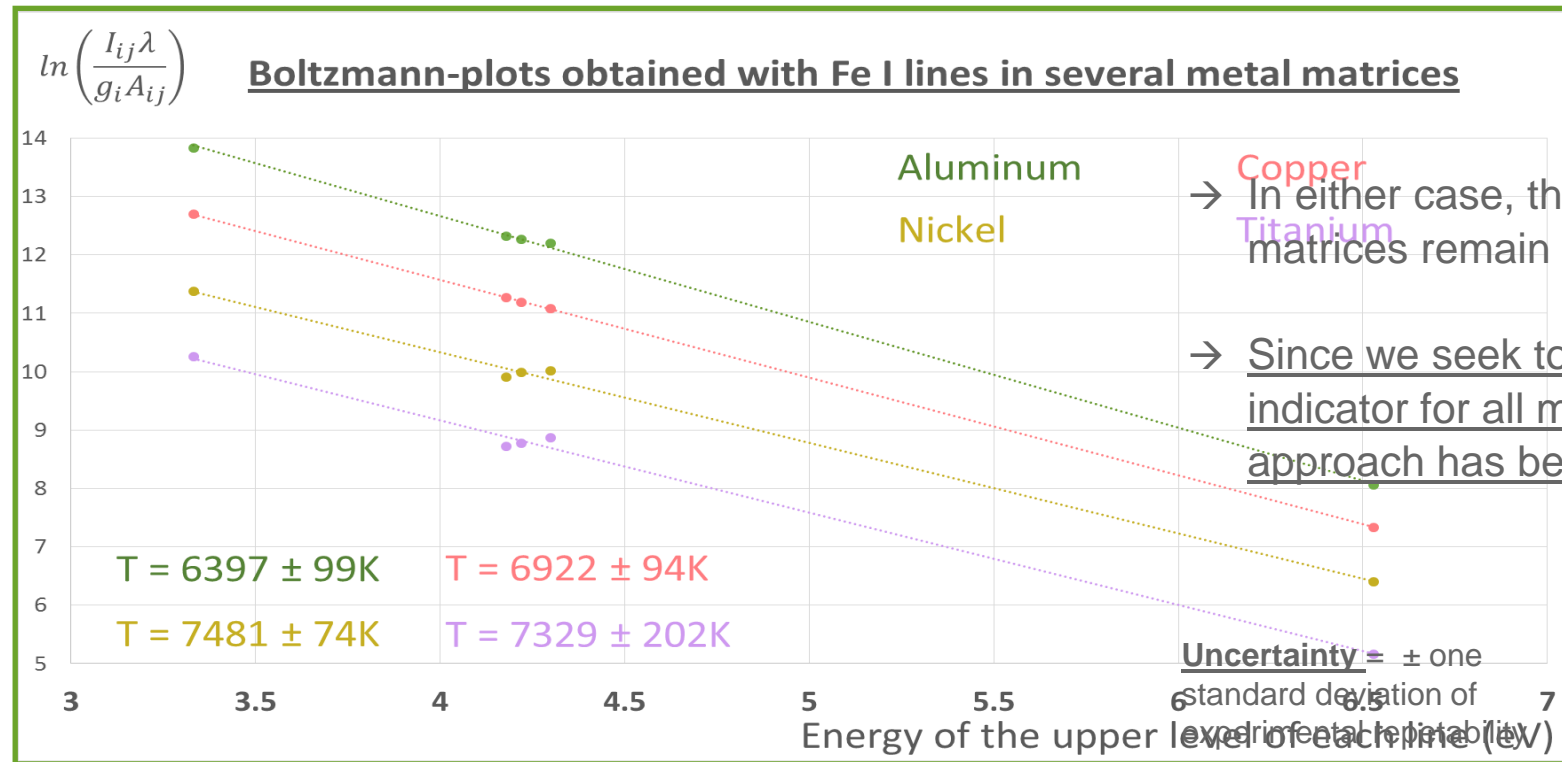


Uncertainty = \pm one standard deviation of experimental repeatability

Lots of spectral interferences with elements of the matrices especially Ti and Ni

→ Trade-off between the number of measured lines and the precision of their measurement in every matrix.

Or we keep only the lines that are ok for every matrix...



→ In either case, the variations between matrices remain the same.

→ Since we seek to measure a common indicator for all matrices, this second approach has been preferred.

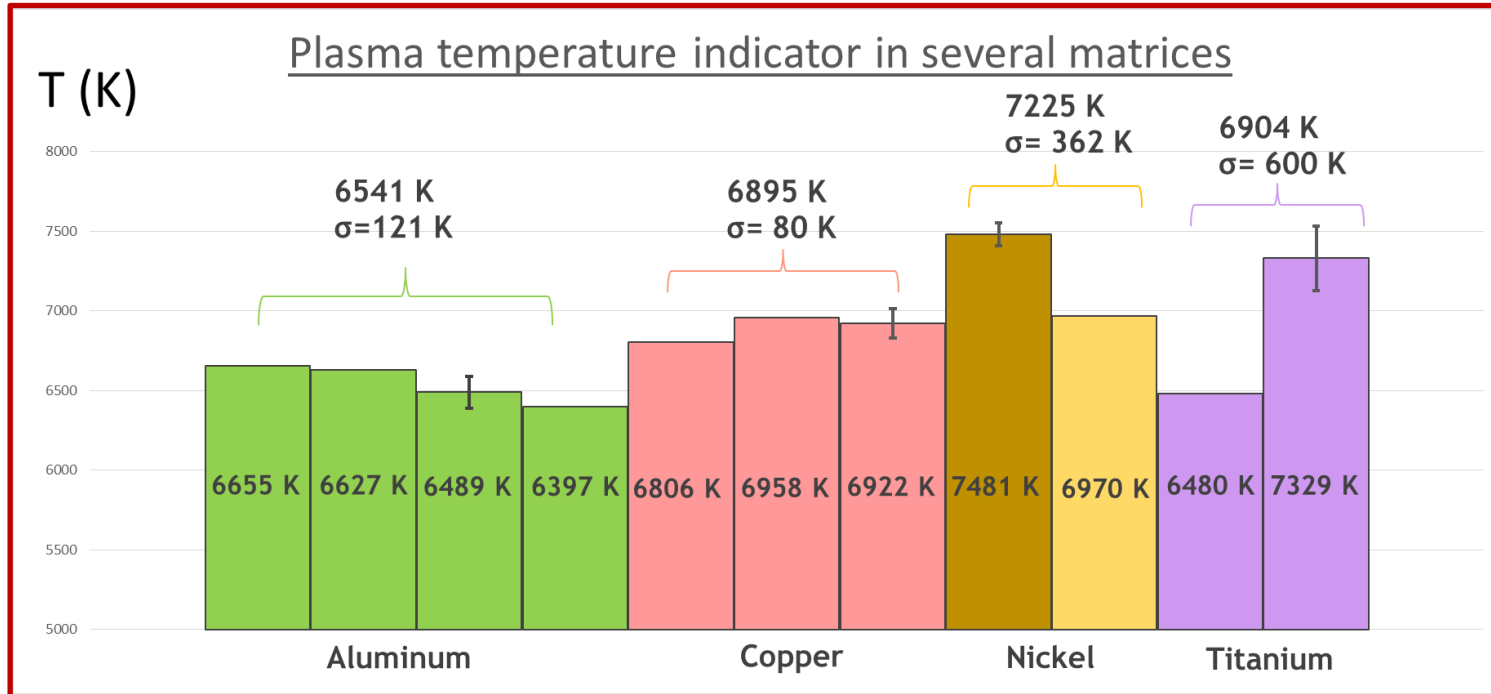
The experimental procedure in a nutshell

Accumulation of laser shots...
On several samples...
Of several matrices...
Aaaaaaaannnnndddd...
Even more laser shots



...





4 matrices
11 samples

Error bars = ± one standard deviation of experimental repeatability

σ = standard deviation for different samples of a same matrix

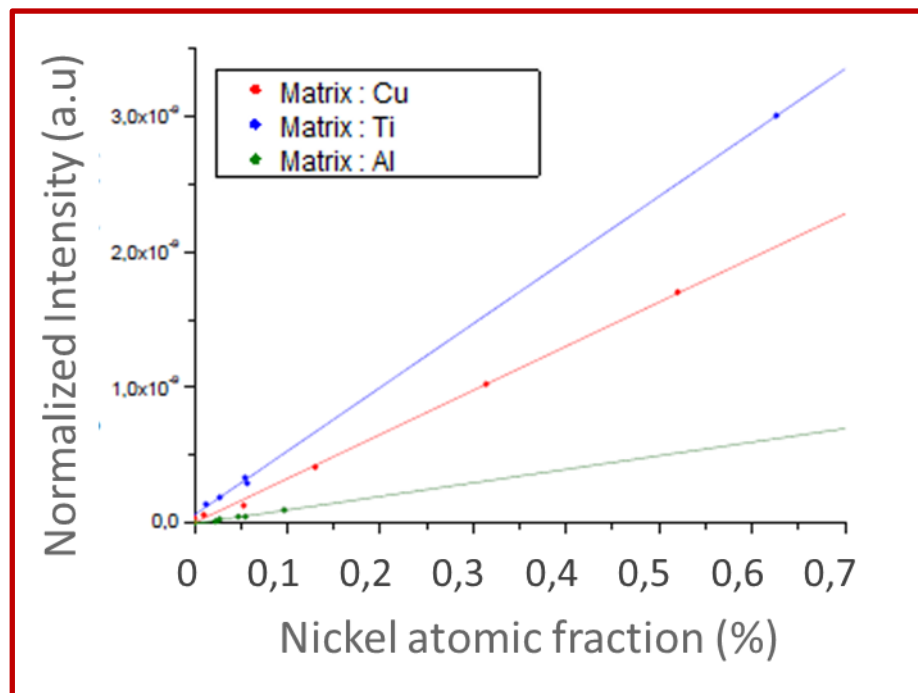


Not really significant for Ni or Ti, though T_e in Ni seems higher

Small but significant variations between Al and Cu

Temperature variations in a same matrix: different compositions, self-absorption...

Calibrations from previous works : normalized with ablated mass



Boltzmann Equation :

Number of analyte atoms in gas phase in the plasma

$$I_{ij} = F(\lambda) \times \frac{hc}{\lambda} \times N_0 \times \frac{g_i A_{ij}}{Z(T_e)} e^{-\frac{E_i}{k T_e}}$$

Temperature of the ablation plasma

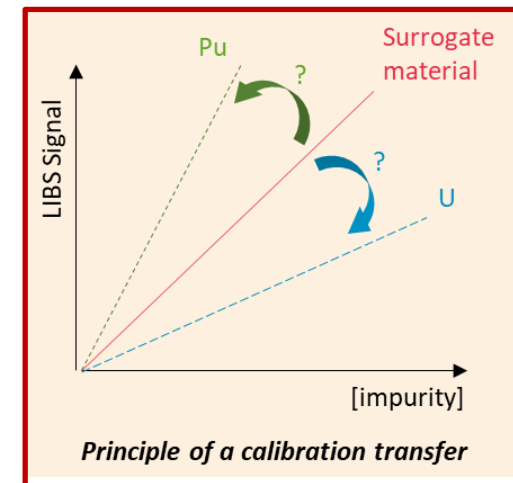
The higher the temperature, the higher the slope.

→ In agreement with our temperature indicator

Need a whole new set of experiments with simultaneous measurements of m_0 , T_e and N_e to make sure of the possible correction of matrix effects.

What we found:

- We can measure an indicator for plasma temperature using integrated spectra. This indicator depends greatly on the matrix but only slightly on the precise composition of the sample.
- This indicator can help us correct the matrix effect.



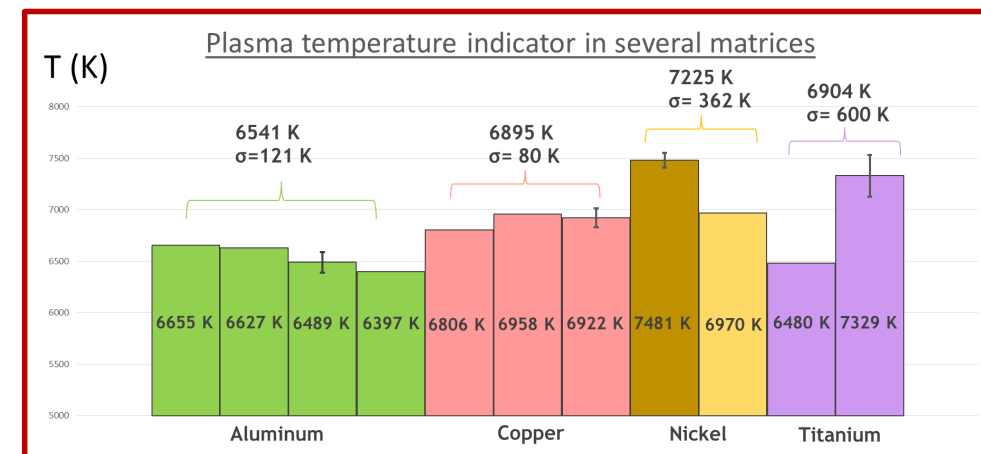
What limits us:

No control over the composition of the samples.

→ Spectral interferences with other impurities, self-absorption...

What we will try:

- Find a way to work with pure metals or more controlled samples.
- Find an indicator for the electron density.



**Thank you for your
attention !**

Any questions ?

Edouard.rollin@cea.fr



**KEEP
CALM
AND
COLLECT
MORE DATA**

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Appendix

Element	Molar mass	Al							Cu					Ni			Steel				Ti				
		51XG00H2	637C/01	01002	311/01	124/04	35831	63698	CT1	CT2	CT3	CT4	CT5	B7011	B7004	F294	284-2	BSCA316-3	ECRM 289-1	BS85D	BST81	IA271A	BST22	BTSU-1	
Ag	107.87					0.019			0.057	0.042	0.026	0.016	0.0062												
Al	26.982	98.3517	95.2308	81.4136	98.52	99.0654	97.4932	95.08						1.2	1.64	0.05	0.0027	0.004	0.199	0.13	0.0664	5.28	0.004	6.11	
As	74.922	0.005							0.32	0.22	0.11	0.05	0.0056				0.0063	0.006	0.0056	0.006					
B	10.81			0.0002		0.0002			0.024	0.033	0.00093	0.0042	0.011				0.0026	0.0005	0.0044	0.0006	0.0082			0.01	
Be	9.0122					0.0019																			
Bi	208.98	0.011				0.0151			0.018	0.013	0.0067	0.0043	0.0011												
C	12.011													0.095	0.01		0.0201	0.018	0.0489	0.049	0.0161	0.026	0.005	0.062	
Ca	40.078					0.0003												0.003		0.0004					
Cd	112.41	0.0031				0.021																			
Ce	140.12					0.0451																			
Co	58.933					0.0201			0.051	0.033	0.013	0.011	0.0061	17	0.06	0.51	0.0525	0.22	0.065	0.97	0.0395			0.061	
Cr	51.996	0.0174	0.3514	0.062	0.095	0.0509	0.0023	0.03						19.7	19.6	0.04	16.811	17.49	14.63	17.09	0.0294	0.016	1.22	0.07	
Cu	63.546	0.111	0.379	4.33	0.044	0.0533	0.065	0.4	97.766	98.441	98.95037	98.7735	98.4161	0.065	0.14	0.11	0.1831	0.43		0.45	0.0244	0.004	0.04	0.073	
Fe	55.845	0.356	0.377	0.076	0.21	0.145	0.558	0.81	0.17	0.1	0.083	0.045	0.016	0.34	0.97	0.06	67.496	66.1381	55.3209	67.6372	0.1144	0.31	1.19	0.22	
H	1.008																				0.0035	0.013			
Ga	69.723	0.011	0.0495			0.0365																			
Ge	72.63																								
La	138.91					0.0307																			
Mg	24.305	0.093	1.468	1.66	0.34	0.0558	0.208	1.36								0.02							0.003	0.005	
Mn	54.938	0.154	0.304	0.305	0.42	0.054	0.108	0.69						0.16	0.08	0.1	1.745	1.6	1.016	1.69	0.0404	0.002	2.02	0.065	
Mo	95.95													0.2	0.06		2.111	2.04	1.102	0.59	0.0279	0.011	1.15	0.067	
N	14.007																0.0151	0.058		0.016	0.0037	0.012	0.01	0.02	
Nb	92.906																	0.031		0.065	0.0191	0.01	0.01	0.068	
Ni	58.693	0.119	0.1026	0.203	0.05	0.0592	0.0575		0.48	0.29	0.12	0.049	0.0095	58.17	74.64	98.99	10.72	11.26	24.68	10.03	0.009	0.035	0.008	0.073	
O	15.999																0.0099	0.0026		0.0014	0.0669	0.16	0.09	0.191	
P	30.974								0.082	0.059	0.038	0.02	0.0059				0.0258	0.027	0.0114	0.025		0.002		0.009	
Pb	207.2	0.114	0.02	0.0517	0.042	0.0232	0.08		0.013	0.086	0.31	0.88	1.48						0.0008	0.0004					
Pd	106.42																				0.0398			0.15	
Ru	101.07																				0.031			0.07	
S	32.06								0.054	0.036	0.012	0.006	0.0024				0.0237	0.024	0.0027	0.024		0.002	0.002	0.008	
Sb	127.76	0.0265		0.0403		0.0252			0.33	0.24	0.11	0.049	0.01					0.0018	0.0013	0.001					
Se	78.971								0.062	0.041	0.018	0.011	0.0069												
Si	28.085	0.35	1.569	10.94	0.055	0.105	1.1	1.33						1.02	0.17	0.09	0.537	0.49	0.531	0.55	0.0474	0.021	0.02	0.057	
Sn	118.71	0.0065	0.0022	0.0242		0.0208	0.051		0.24	0.14	0.07	0.025	0.007				0.0047	0.01	0.111		0.0155	2.49	0.019	0.076	
Ta	180.95																								
Te	127.6								0.053	0.036	0.022	0.011	0.0064											0.079	
Ti	47.867	0.128	0.0648	0.2301	0.09	0.0505	0.166	0.06						2.05	2.63	0.03	0.191	0.033	2.01	0.48	99.3236	91.511	93.189	88.184	
V	50.942	0.0148	0.0291	0.125	0.059	0.0449											0.0425	0.063	0.26	0.134	0.0186	0.09	0.5	4.12	
W	183.84																	0.05		0.06		0.0372		0.51	0.075
Y	88.906																				0.0017			0.009	
Zn	65.38	0.113	0.0011	0.2999	0.075	0.0515	0.111	0.24	0.28	0.19	0.11	0.045	0.0098								0.0163	0.015	0.01	0.068	
Zr	91.224	0.015	0.0515	0.239		0.0054																			

- Local Thermodynamic Equilibrium (LTE) hypothesis
- Lines of neutral species

Boltzmann equation :

$$I_{ij} = F(\lambda) \times \frac{hc}{\lambda} \times N_0 \times \frac{g_i A_{ij}}{Z(T_e)} e^{\left(-\frac{E_i}{k T_e}\right)}$$

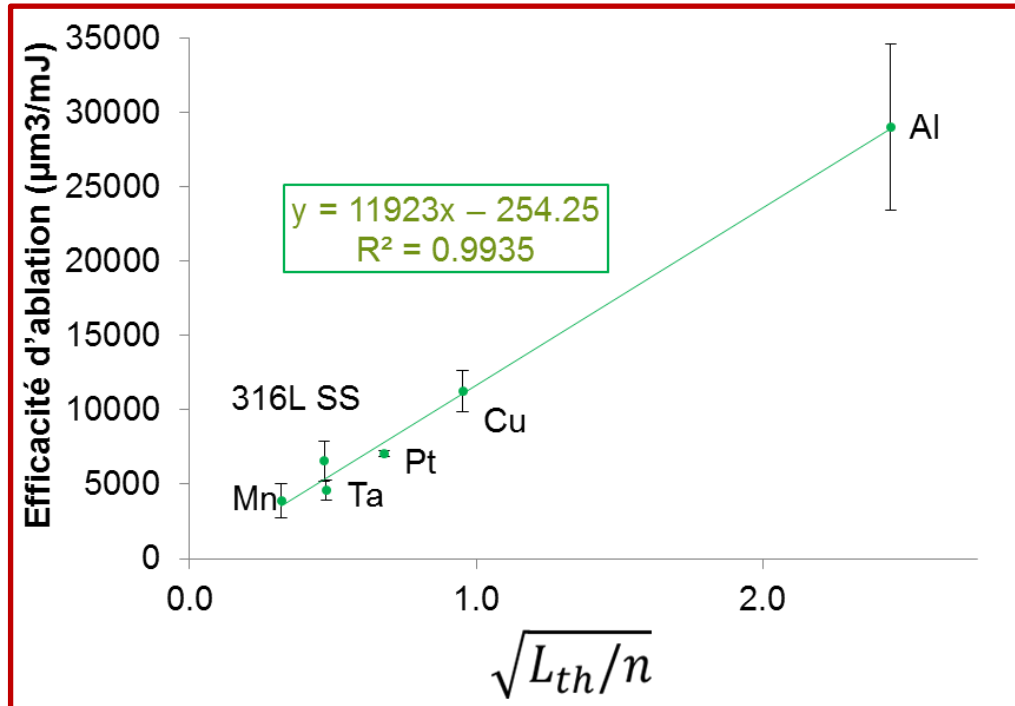
Number of analyte atoms in gas phase in the plasma

Temperature of the ablation plasma

Saha equation :

$$\frac{N_{1,X}}{N_{0,X}} N_e = \frac{2}{\Lambda^3} \frac{Z_{1,X}(T_e)}{Z_{0,X}(T_e)} e^{\frac{-E_X}{k_B T_e}}$$

Correlation between the ablated mass and the physical properties of the matrices



With:

$L_{th} = 2 \cdot \sqrt{D_{th} \cdot \tau}$: Thermal diffusion length

D_{th} : Thermal diffusivity

τ : Pulse duration

n : Real part of the refractive index

J. Picard, "Développement de la LIBS pour l'analyse en ligne de produits uranifères ou plutonifères solides," Dijon, 2015.

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