Towards calibration transfer for quantitative analysis of nuclear materials by LIBS

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DE LA RECHERCHE À L'INDUSTRIE

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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JUNE 27 PAU, FRANCE

14TH EUROPEAN WORKSHOP ON LASER ABLATION

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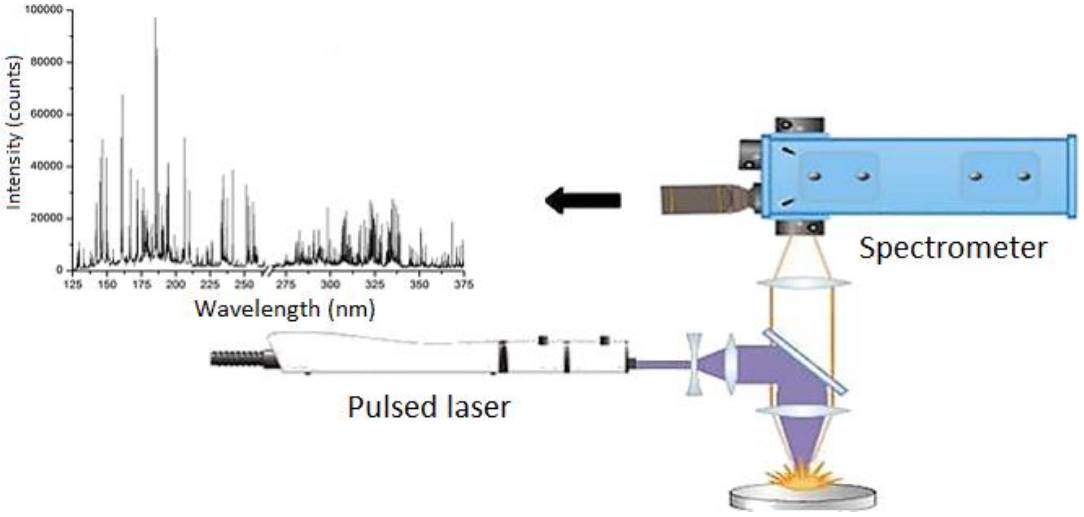
A NEED FOR ONLINE ANALYSIS

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.

CALIBRATION TRANSFER

Impossibility to achieve an analytical development directly with nuclear materials:

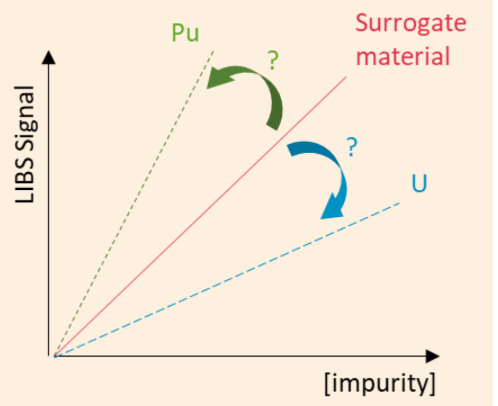
- Lack of calibrated samples;
- Complexity of U and Pu spectroscopy;
- Security and wastes constraints.

→ **Need for a general method developed from surrogate materials.**

Three steps:

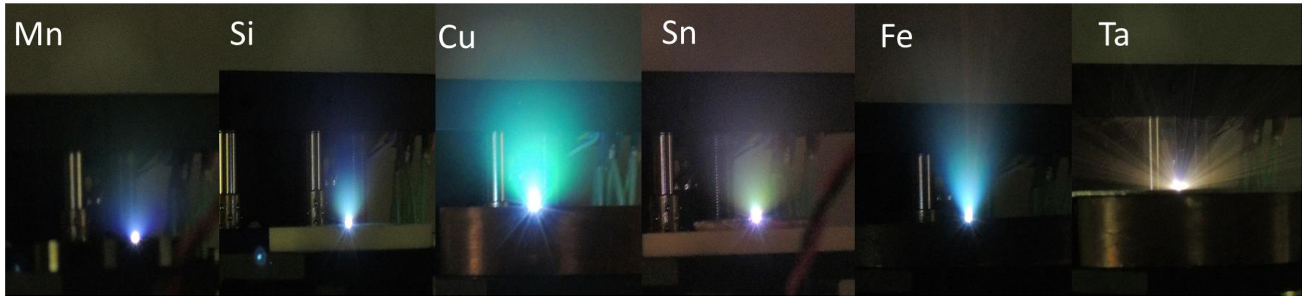
- Identification of surrogate materials;
- Analytical development on these surrogate materials;
- Calibration transfer to nuclear materials

Previous PhD Thesis: Jessica Picard (2012-2015)



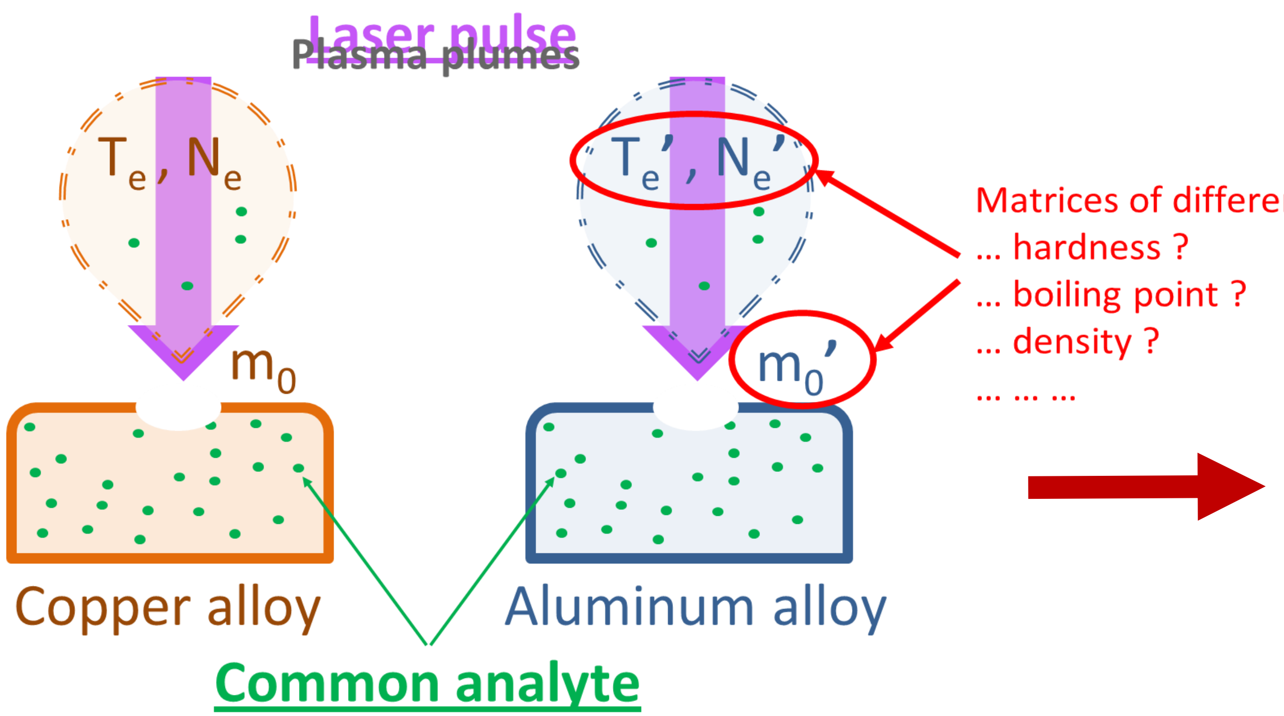
Principle of a calibration transfer

But how can we achieve this calibration transfer ?



MATRIX EFFECTS

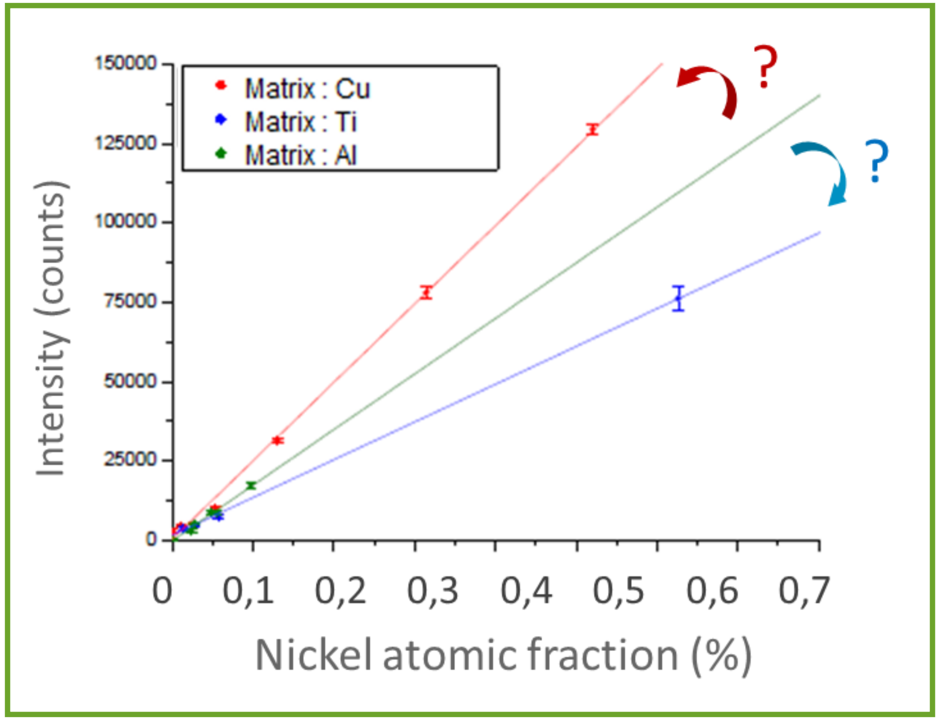
The matrix effects in a nutshell



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.

THREE PARAMETERS

- **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.

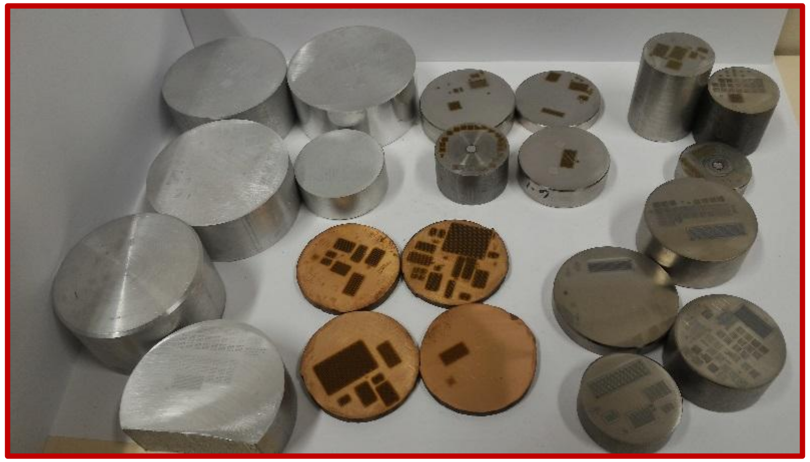
→ Find relationships between them and the physical properties of the matrices in order to acquire a better understanding of the matrix effects.

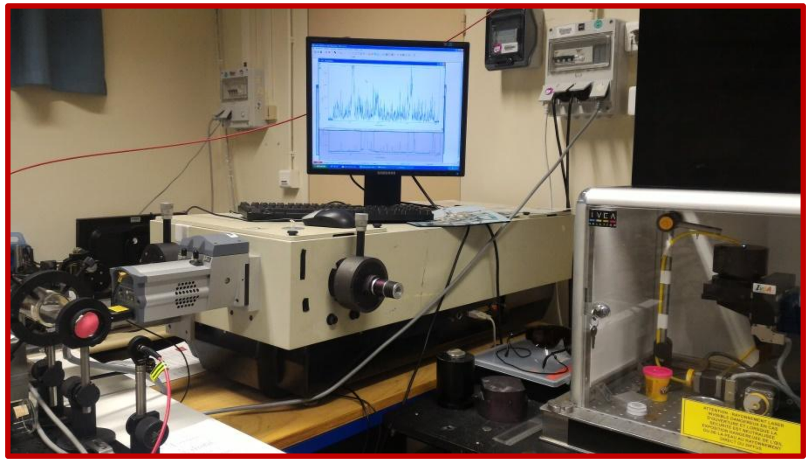
Aim: quantify impurities in all kinds of metal matrices using corrected calibrations

EXPERIMENTAL SETUP

MobiLIBS system (IVEA Solution)

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





MEASUREMENT METHODS

Important hypothesis : Local Thermodynamic Equilibrium (LTE)

➔ Legitimates 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,

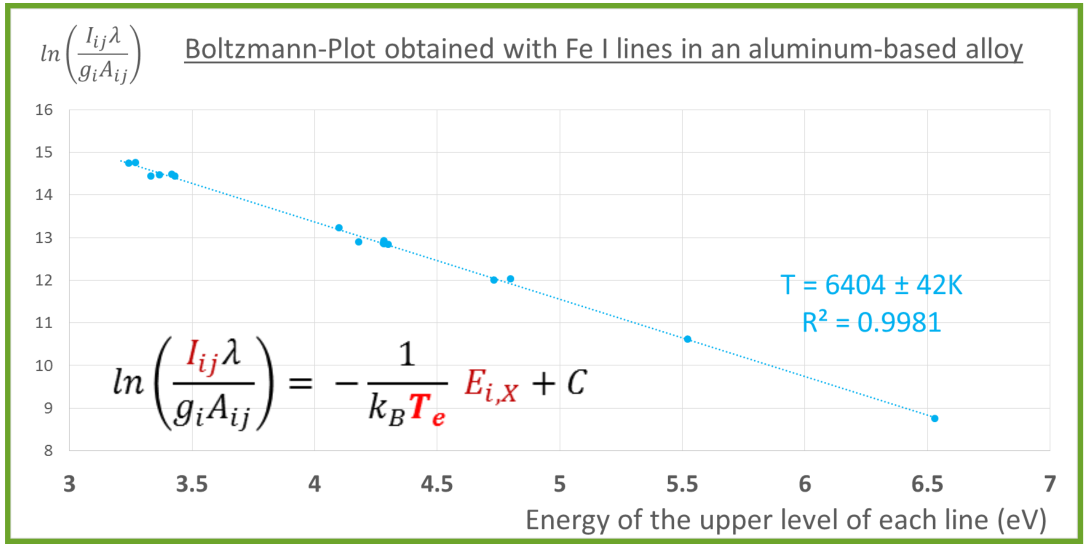
the more intense the lines of high energy.

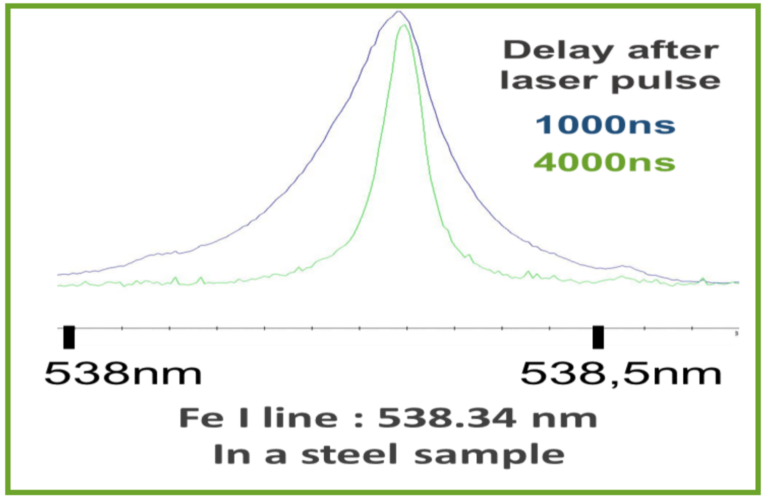
N_e : Stark broadening

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.

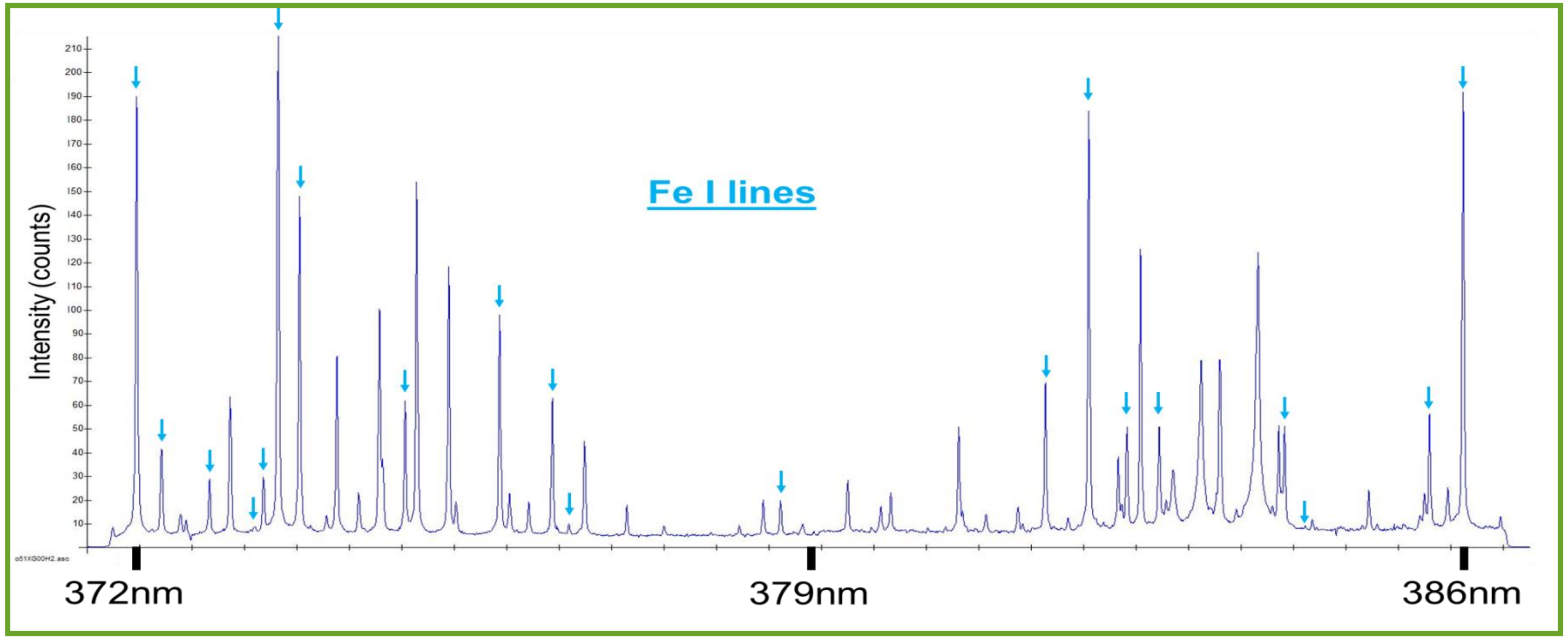
→ **Need to find a unified method to minimize uncertainties.**

→ 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…

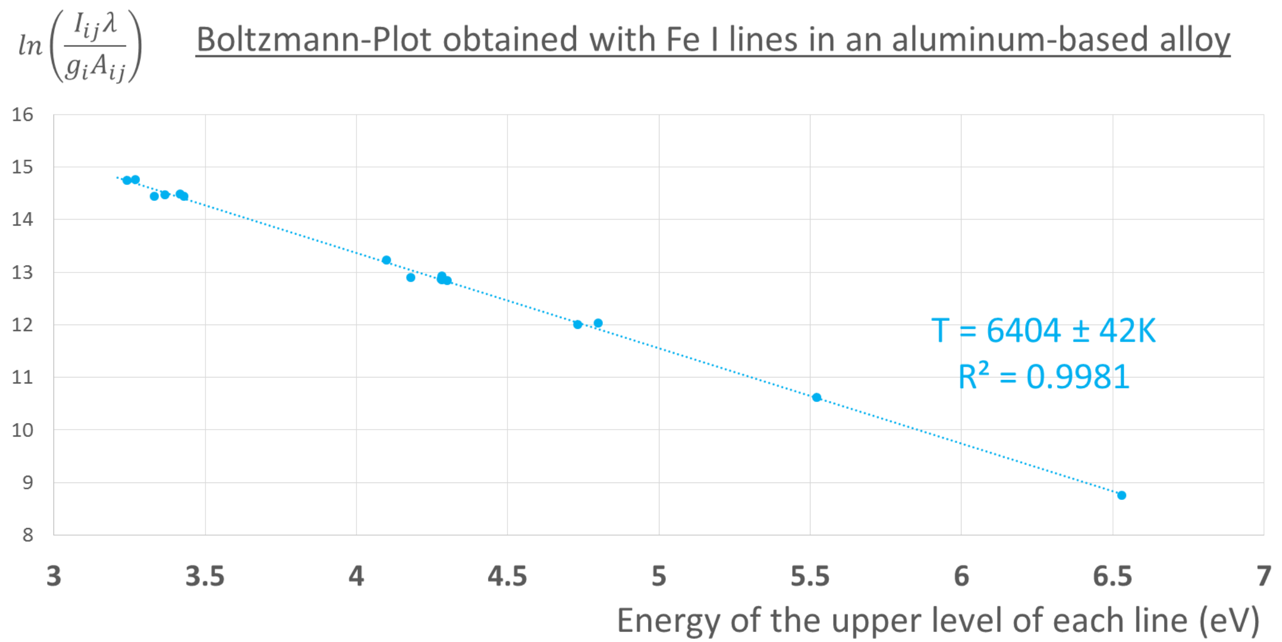
→ Time and space integrated indicators.

From 1 to 10 μs after the laser pulse

Light collected from the whole plasma

What can we measure ?

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.

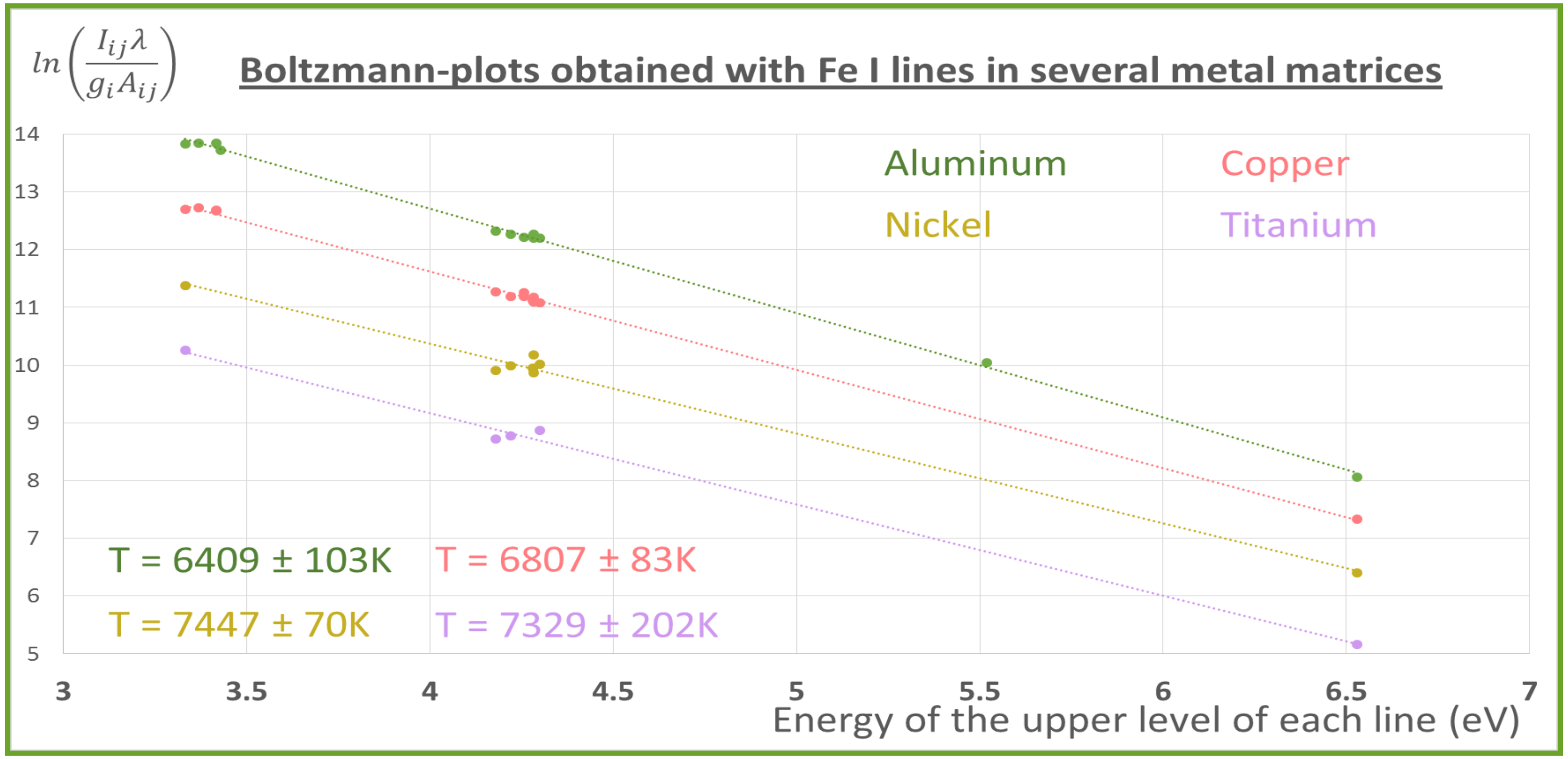
Possibility to measure an indicator for T_e, which we can use to compare matrices

MEASURING T_E IN VARIOUS 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…



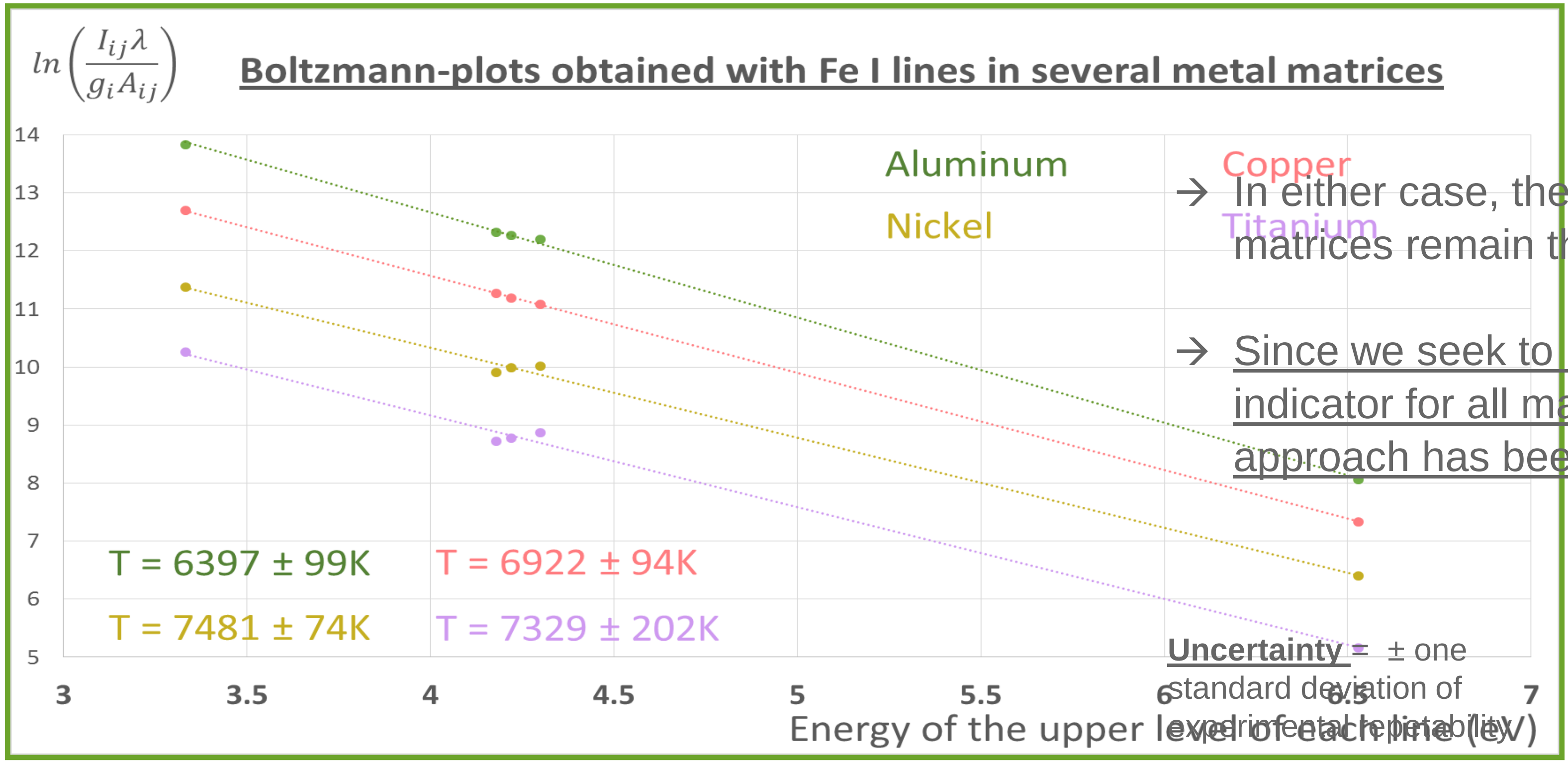
Uncertainty = ± one standard deviation of experimental repetability

MEASURING T_E IN VARIOUS 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.

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.

Uncertainty = ± one standard deviation of experimental repeatability

MEASURING T_E IN VARIOUS MATRICES

The experimental procedure in a nutshell

Accumulation of laser shots…

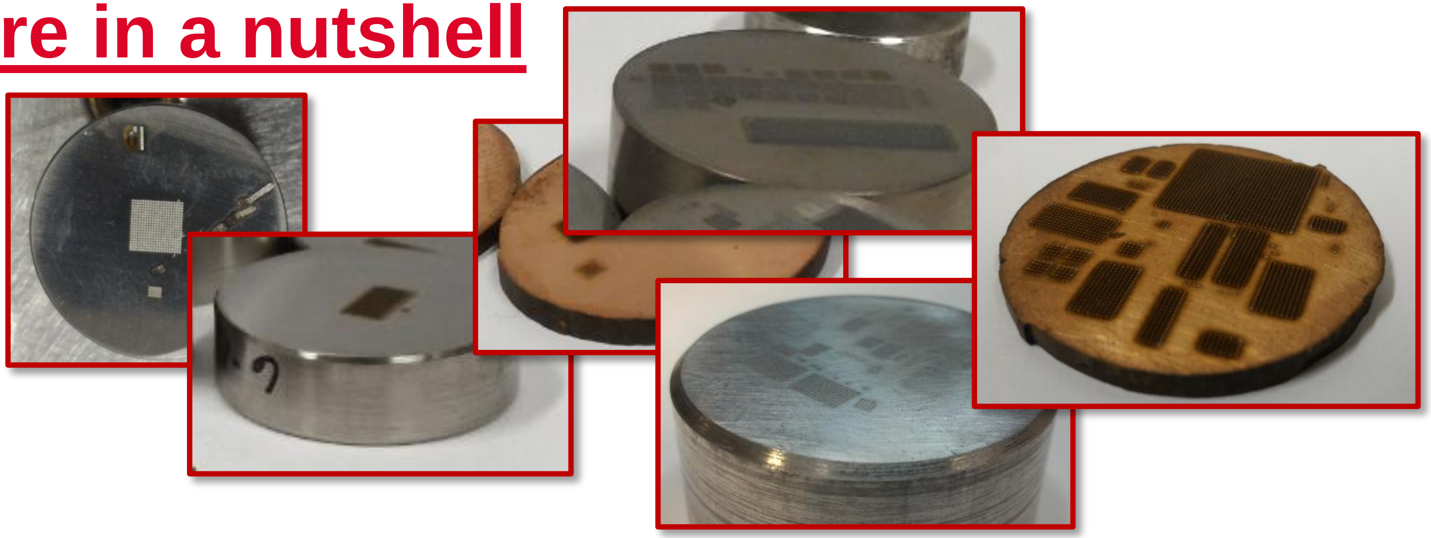
On several samples…

Of several matrices...

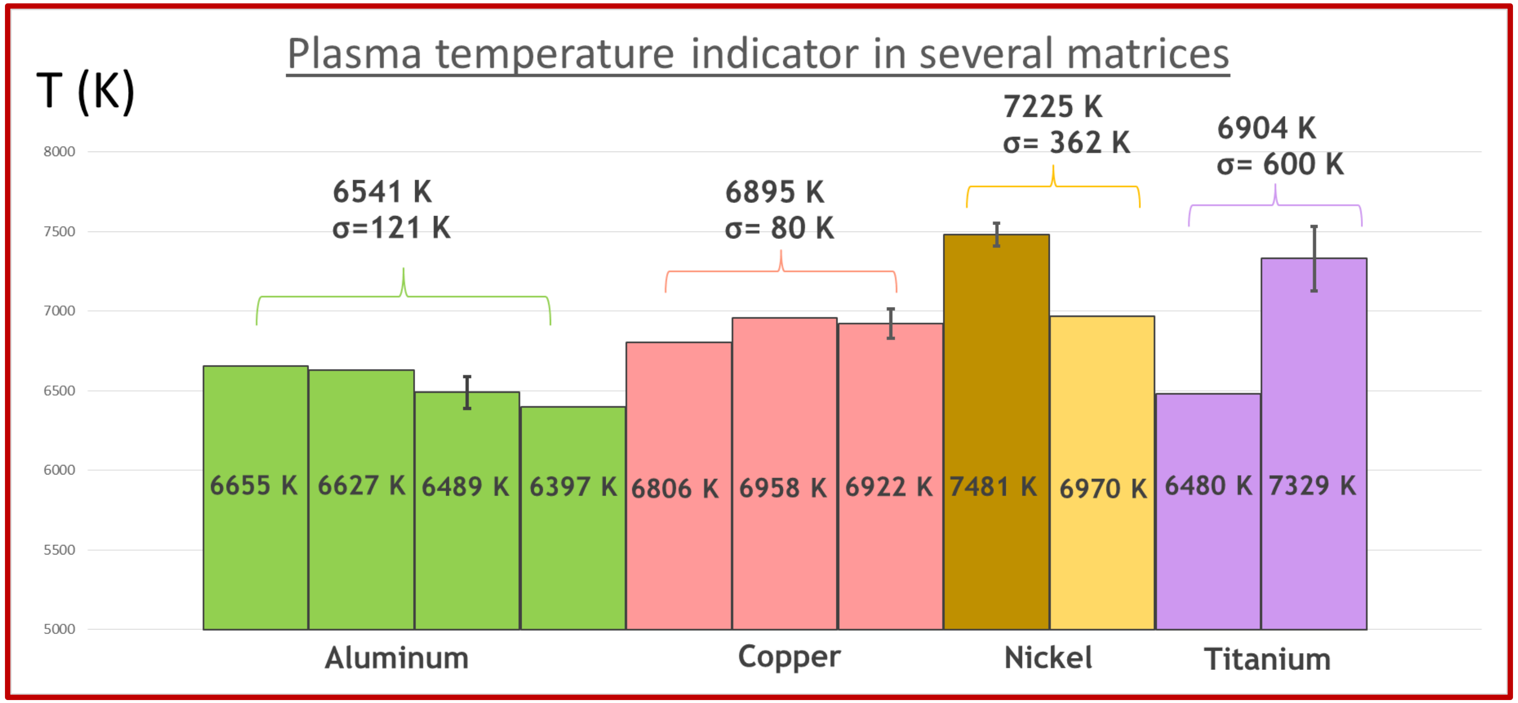
Aaaaaaaannnndddddd…

Even more laser shots

…



RESULTS



4 matrices
11 samples

Error bars = ± one standard deviation of experimental repetability

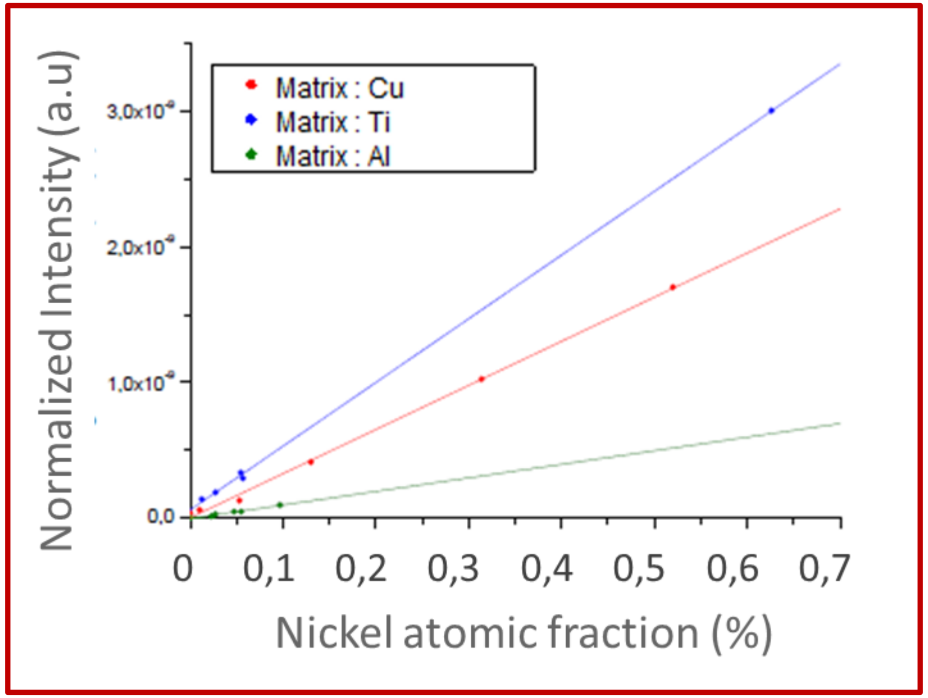
σ = standard deviation for different samples of a same matrix

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

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

Temperature of the ablation plasma

The higher the temperature, the higher the slope.

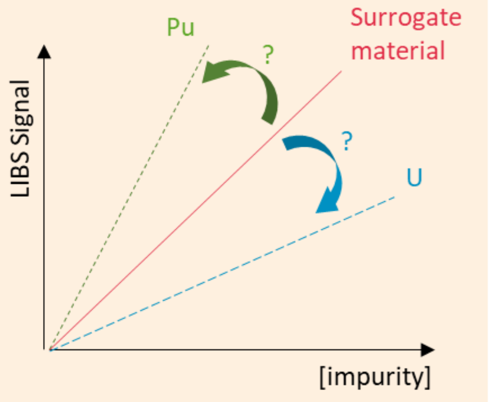
→ In agreement with our temperature indicator

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

CONCLUSION AND FUTURE WORKS

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.

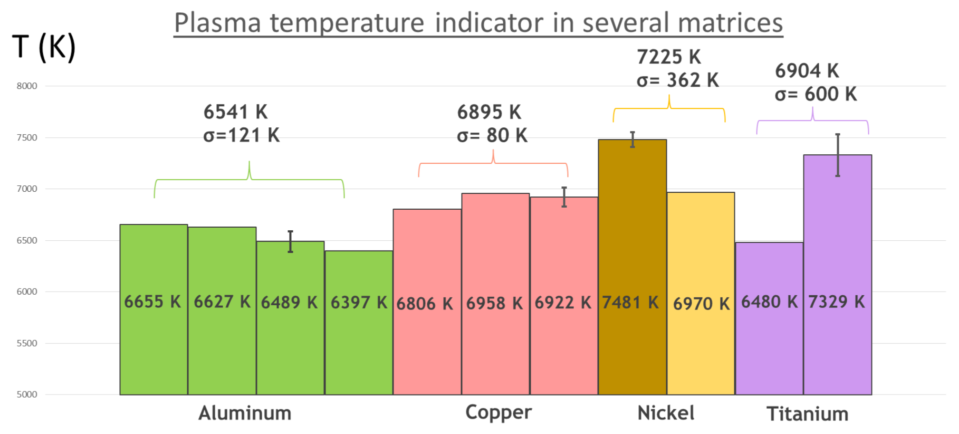


Principle of a calibration transfer

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 ?

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Appendix

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SAMPLES

		Al							Cu					Ni			Steel				Ti			
	Samples	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	BSTSU-1
Element	Molar mass																							
%massique																								
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	0.068
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																							0.079
Te	127.6								0.053	0.036	0.022	0.011	0.0064											
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																		

TEMPERATURE AND ELECTRONIC DENSITY

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

Number of analyte atoms in gas phase in the plasma

Boltzmann equation :

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

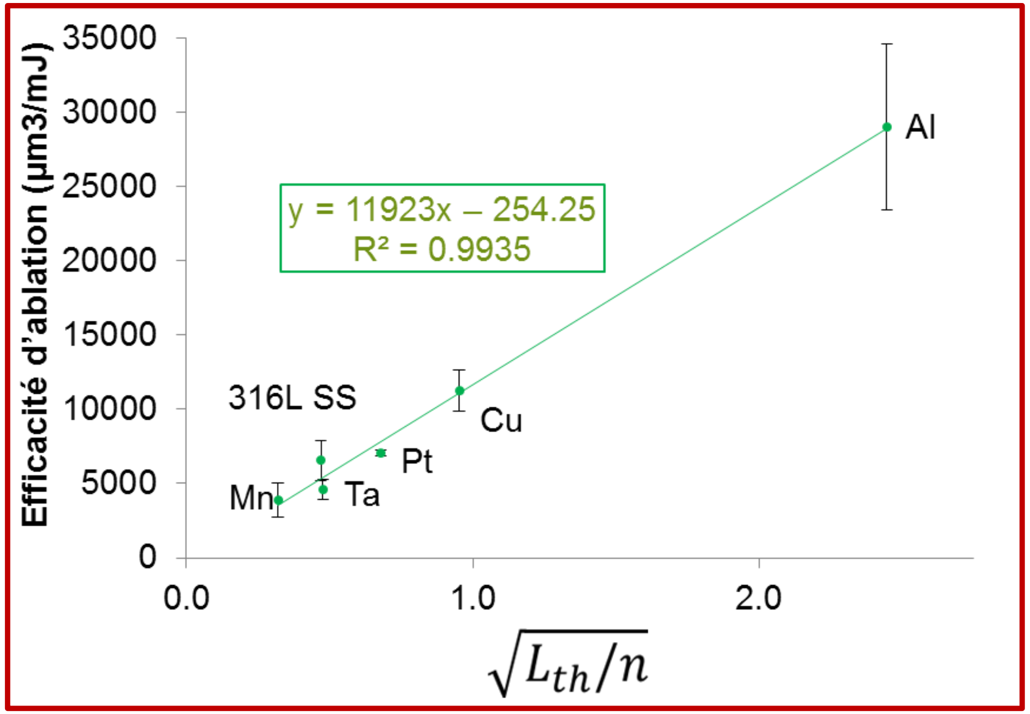
Temperature of the ablation plasma

Saha equation :

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

ABLATED MASS

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



With:

$L_{th} = 2.\sqrt{D_{th}.\tau}$: 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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