

Issues and advances of calibration transfer in LIBS

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ISSUES AND ADVANCES OF CALIBRATION TRANSFER IN LIBS

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CALIBRATION TRANSFER?

LIBS is an **onsite / online / in situ** analytical technique

"exotic" applications

lack of reference materials

analytical development in conditions different from the real ones

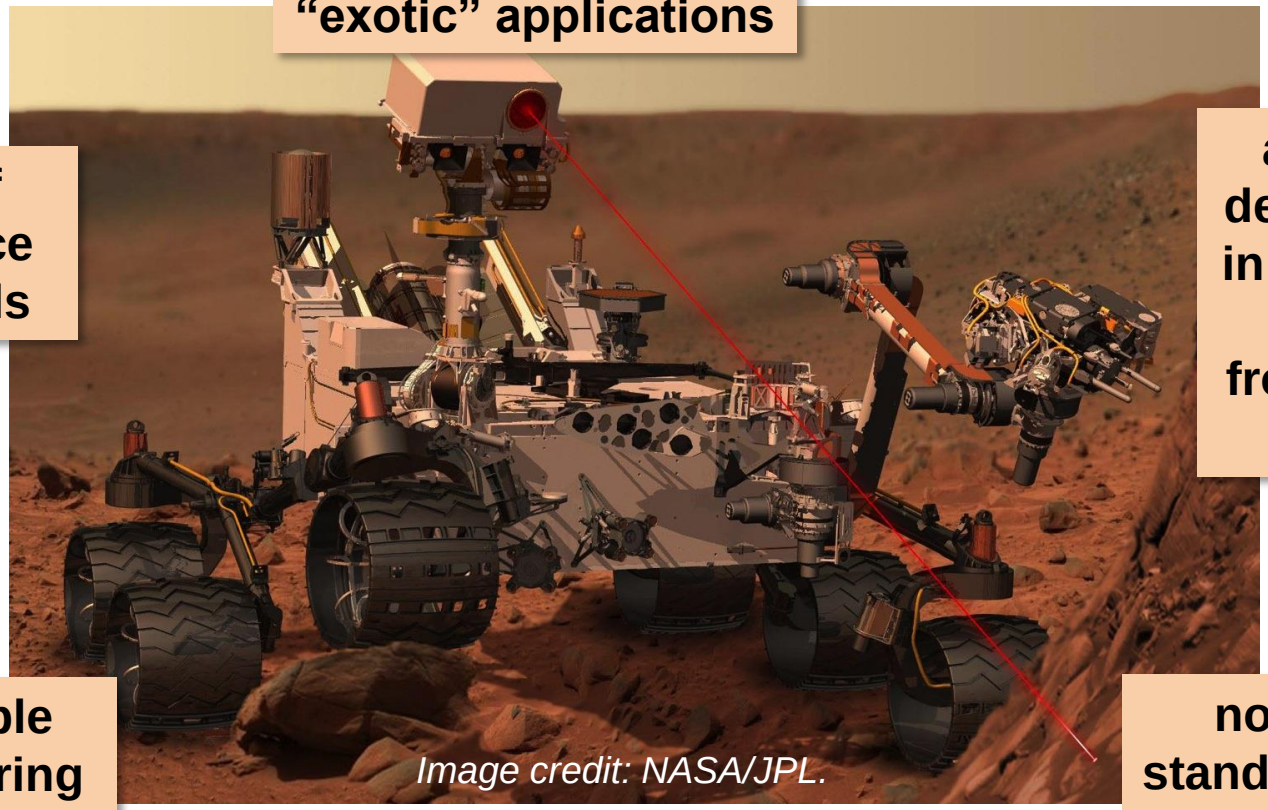


Image credit: NASA/JPL.

variable measuring conditions

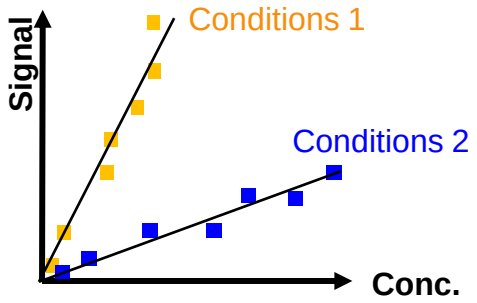
no standard protocol

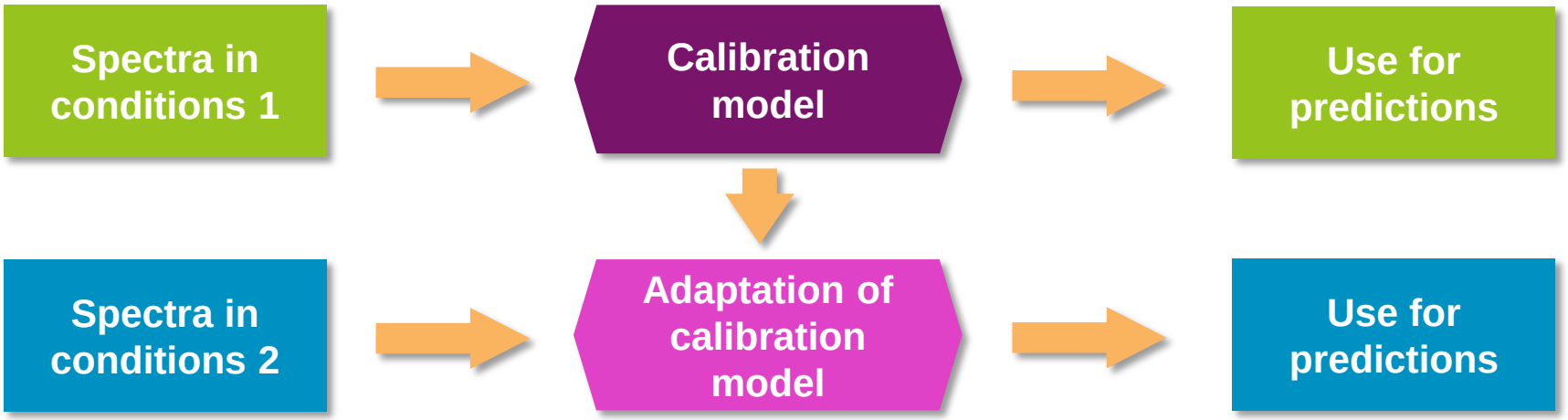
→ Are we able to switch from a calibration model to another one **obtained in different conditions?**

CALIBRATION TRANSFER IN LIBS

Transfer of a calibration model **in different conditions**

- A different spectral line
- A different element
- A different matrix
- Different measuring conditions
- A different instrument (like in NIRS)



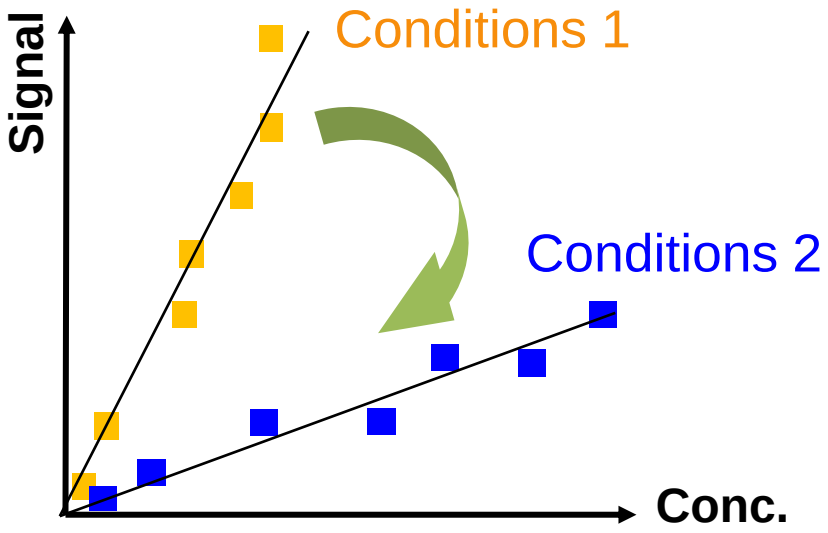


To date, only 2 papers explicitly dealing with calibration transfer in LIBS:

- Lopez-Moreno et al., J. Anal. At. Spectrom. 20 (2005) 1275–12794
- Boucher et al., SciX 2015, abstract #287

CALIBRATION TRANSFER IN LIBS

When making calibrations **lines**, this is equivalent to making a **slope correction**



➔ **What does the slopes ratio mean?**

➔ **Can we predict it?**

➔ **Are there cases where slopes are equal?**

THE LIBS SIGNAL

The well-known **Boltzmann equation**:

analyte concentration

ablated mass (depends on the matrix)

spectroscopic data (depend on the analyte and on the spectral line)

$$I_{ij} = F_{exp} \times C m_0 \times \frac{hc}{\lambda} \times \frac{g_i A_{ij}}{Z(T_{exc})} e^{\left(-E_i / kT_{exc}\right)} = a \times C$$

experimental factor (depends on the geometry and efficiency of the plasma emission collection setup, on the matrix, and on time)

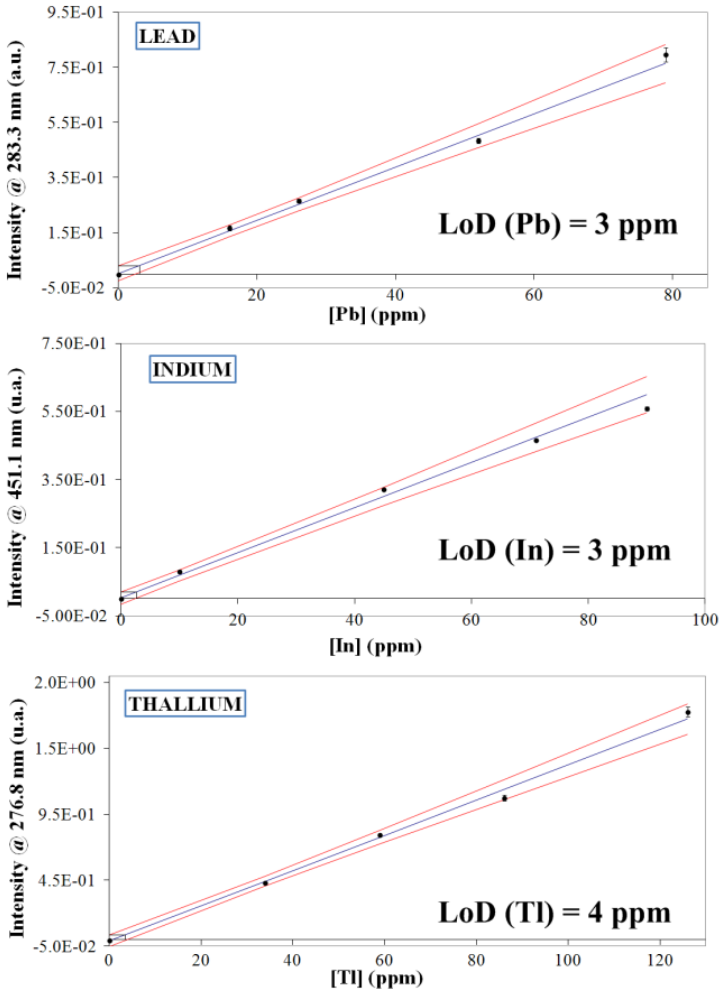
electron temperature (depends on the matrix and on time)

(for given experimental and measuring conditions)

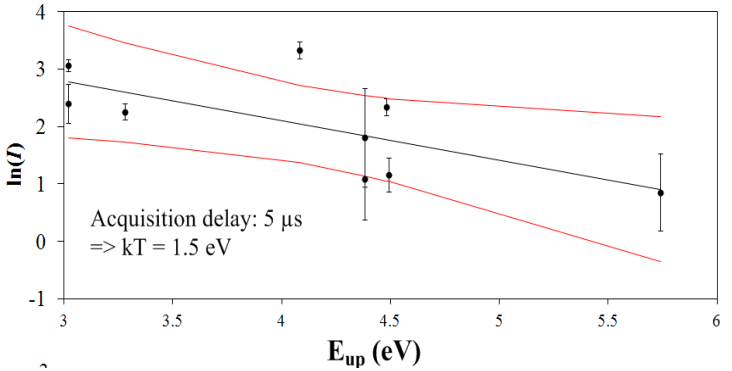
TRANSFER FROM ONE ELEMENT TO ANOTHER

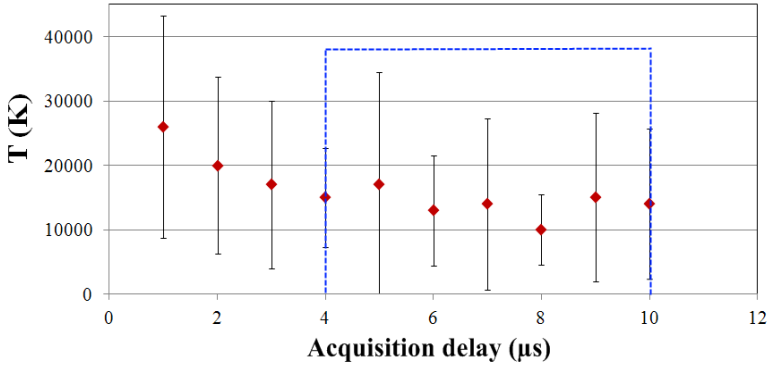
Calibration of metal impurities concentration (Pb, In, Tl) in liquid sodium

Gate delay 4 µs, gate width 6 µs, 4000 laser shots



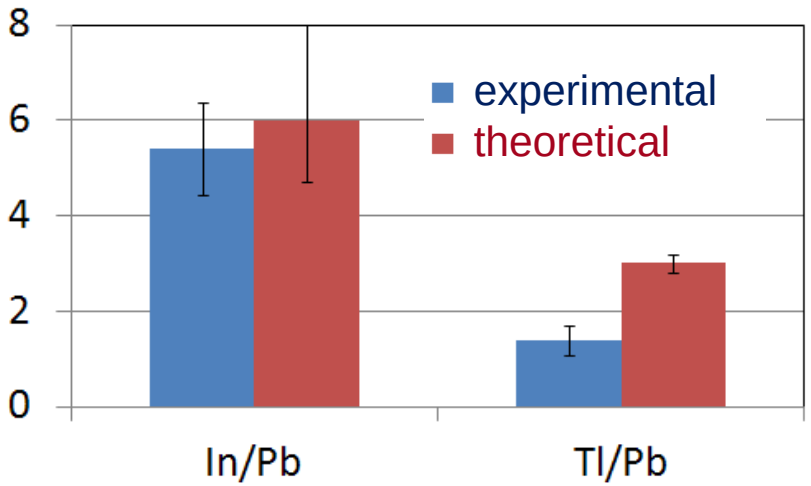
Determination of $T_e(t)$ by a **multi-elemental Boltzmann plot** based on trace element lines:





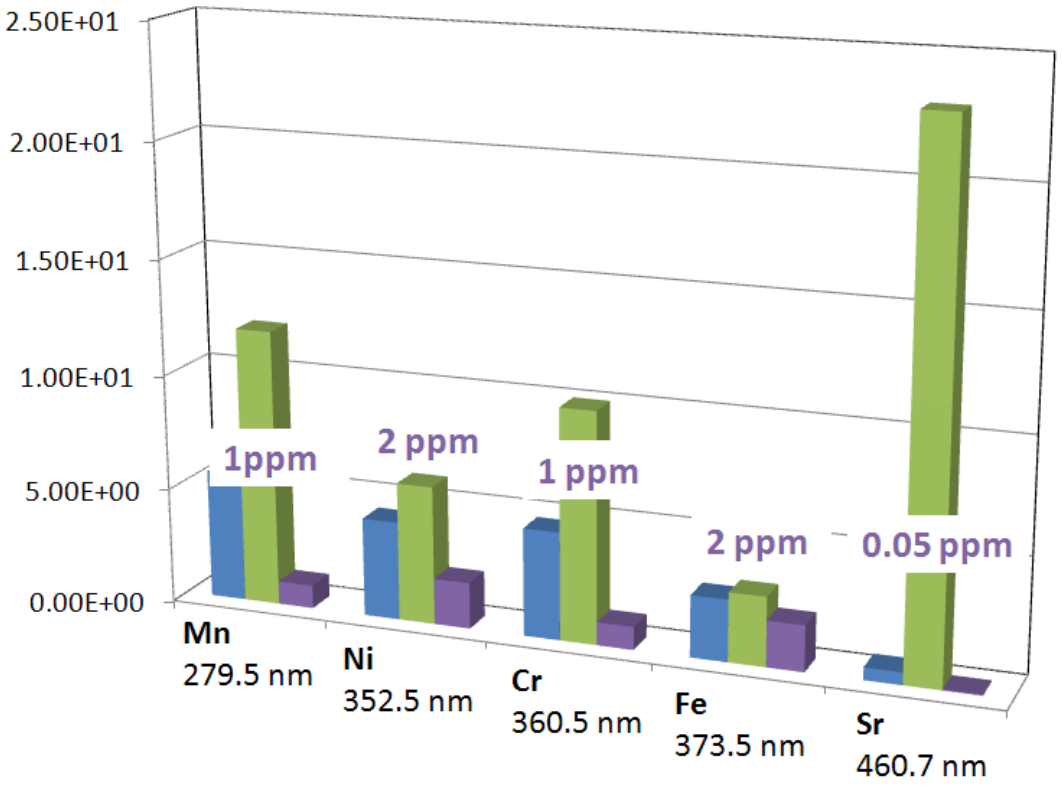
TRANSFER FROM ONE ELEMENT TO ANOTHER

Calibration lines slopes ratio:



The error bars take into account the uncertainty on T_e

Application to the **extrapolation of detection limits** of elements of interest in a given matrix:



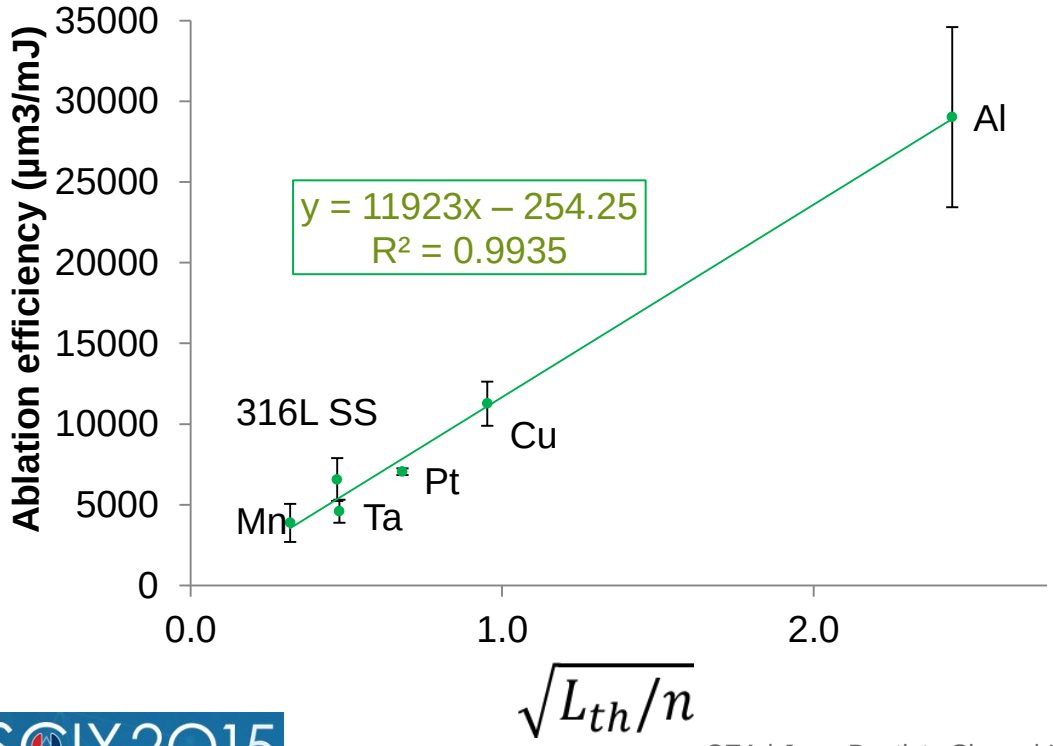
- Background noise (measured experimentally on a blank) (x 10^{-6})
- Slopes ratio (wrt Pb)
- Predicted detection limit (ppm)

CAN WE PREDICT THE ABLATED MASS?

Experiment:

- Samples: several pure metals and one alloy (Mn, 316L Stainless Steel, Ta, Pt, Al, Cu)
- 10 laser shots at 1 bar, 266 nm, irradiance 0-50 GW/cm² (linear regime)
- The ablation efficiency is the slope of the line Volume = f(Pulse energy)

Empirical model between ablation efficiency and physical properties of metals



With :

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

D_{th} : thermal diffusivity

τ : pulse duration

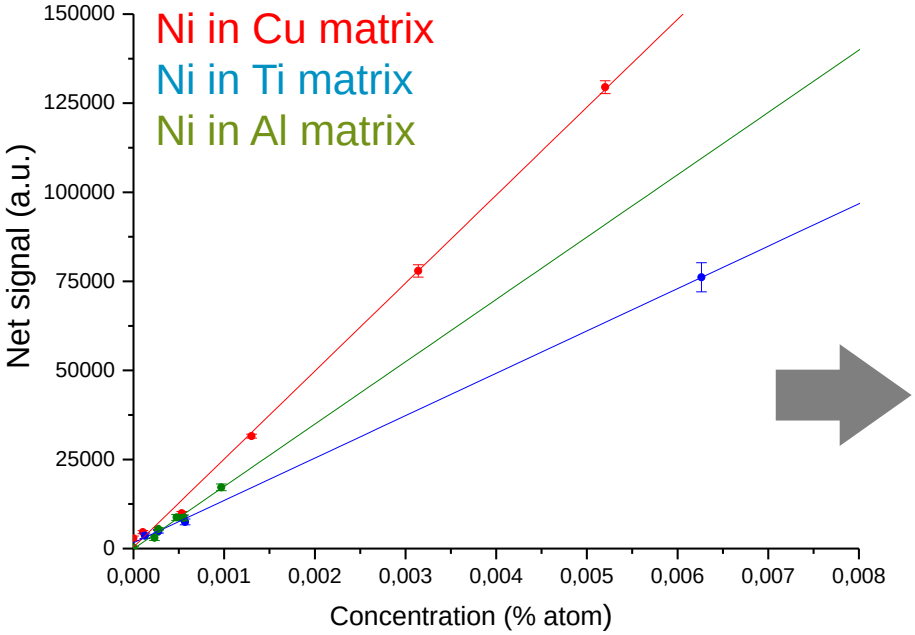
n : real part of the refractive index

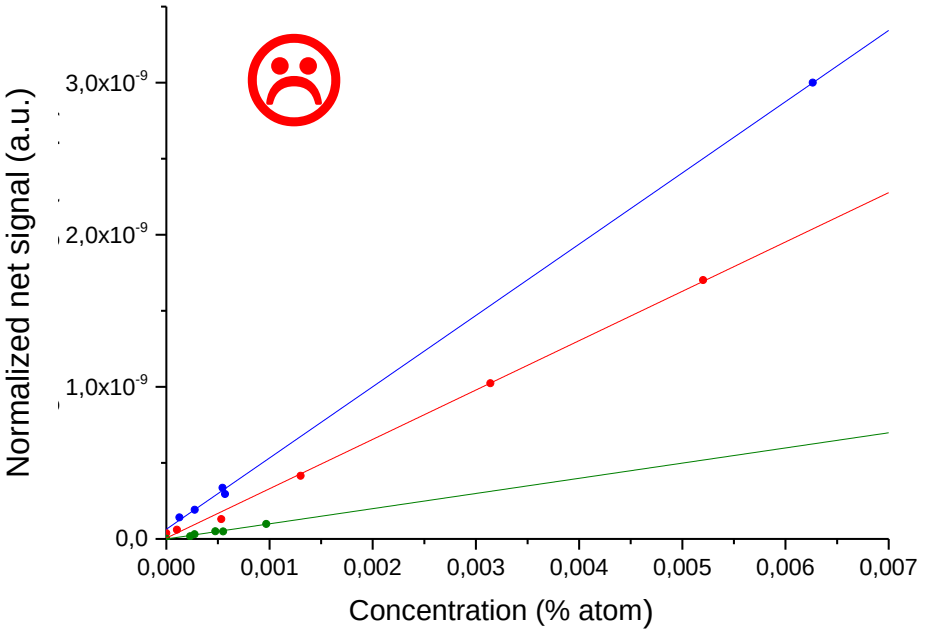
Very nice correlation between ablation efficiency and some physical parameters of metals…

… but not clearly explained…

IS IT SUFFICIENT TO CORRECT MATRIX EFFECTS?

Normalization of calibration lines by the ablation efficiency





The plasma temperature?

→ Intensity ratio for lines of different upper level energy:

Matrix	Cu	Ti	Al
Ni lines ratio $I_{231,6}/I_{230,3}$	1,3	1,4	1,3
Fe lines ratio $I_{239,56}/I_{238,2}$	0,78	0,77	0,79

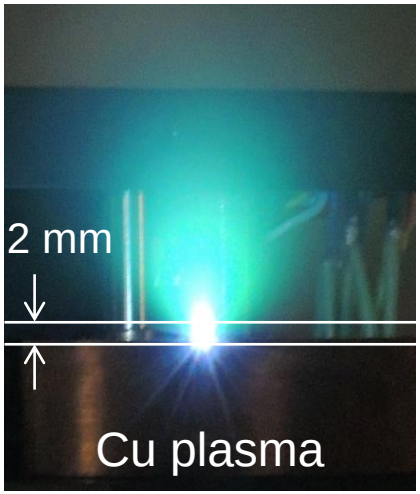
No significant difference

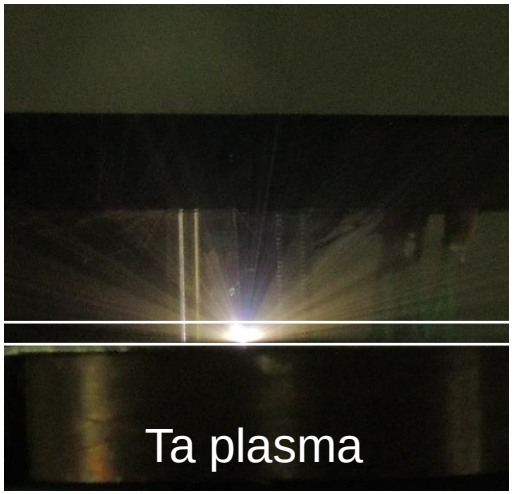
A POSSIBLE EXPLANATION

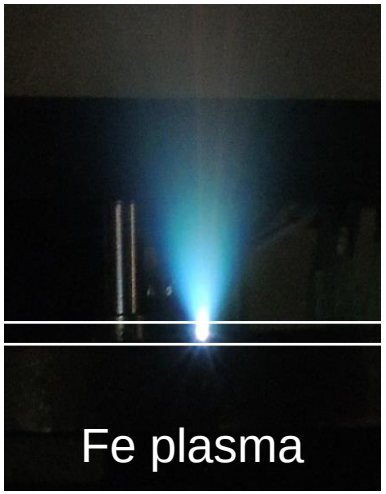
Not that surprising, see e.g. Aguilera et al., Spectrochimica Acta Part B 64 (2009) 993–998:

Matrix	T (K)	N_e (10^{17} cm^{-3})	Nl (10^{20} m^{-2})	βA (a.u.)
Ni	11,500 ± 200	0.58 ± 0.02	1.8 ± 0.2	91 ± 4
Cu	12,100 ± 200	0.55 ± 0.05	1.9 ± 0.1	71 ± 3
Al	11,700 ± 200	0.66 ± 0.05	2.7 ± 0.5	70 ± 4

What about the plasma / spectrometer coupling?





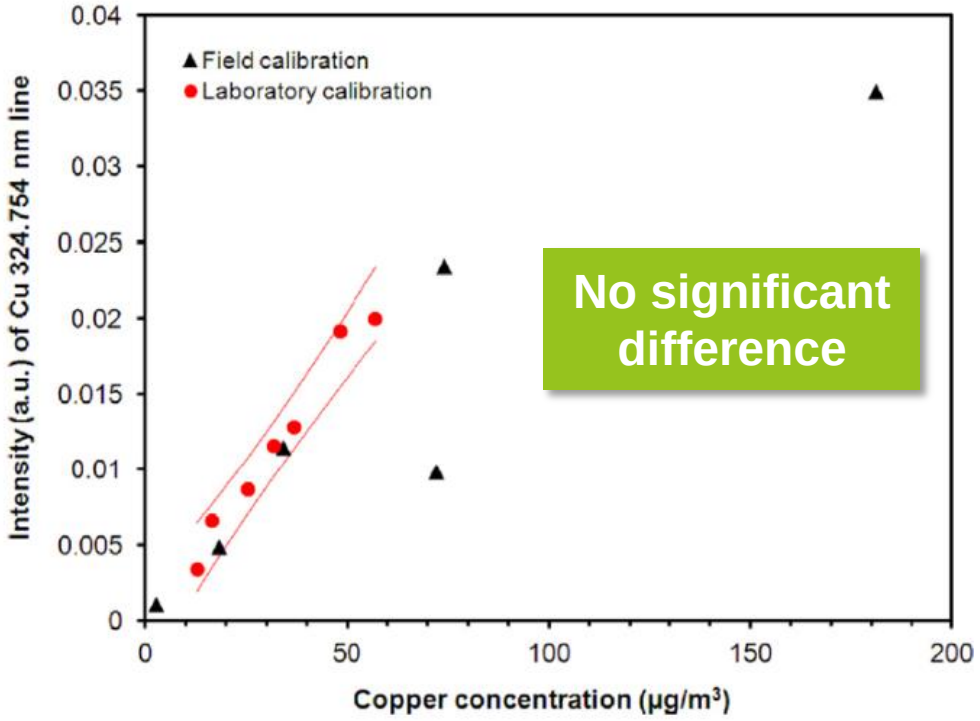


TBC…

CALIBRATION TRANSFER IN PARTICLES ANALYSIS

Red: calibration in laboratory of Cu concentration in an aerosol of $CuSO_4$ micrometric particles

Black: in situ calibration, several months after, with the same instrument, on the exhaust duct of a melting furnace → metal particles of various composition (Cu, Al, Ca, Ti, K…)



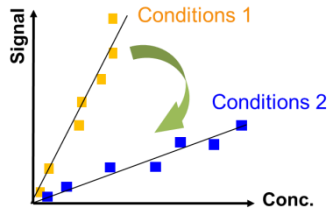
Dutouquet et al., Talanta 127 (2014) 75–81

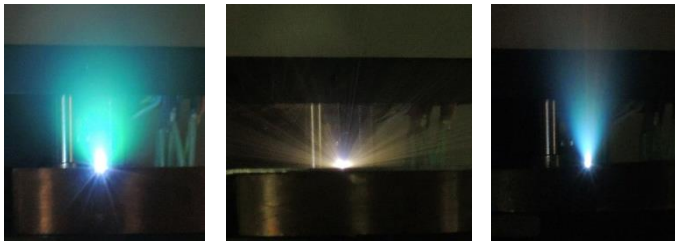
CONCLUSION

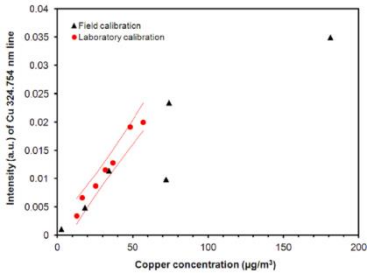
Calibration transfer approaches are particularly relevant for analytical development of an **in situ** measuring system

To a large extent, in LIBS this issue overlaps with that of **matrix effects**

A fundamental approach of the question is necessary, but **more operational multivariate tools** (NIRS inspired) can prove efficient and shall be tested and adapted







Special thanks to:

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Thank you for your attention!

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ABSTRACT

As a fast, direct and remote technique, laser-induced breakdown spectroscopy is particularly relevant for online or in situ analysis, or to measure samples with limited access, like in the nuclear sector or in planetary exploration. In these cases, quantitative analysis can be difficult for different reasons. First, environmental conditions are not completely controlled and instrumental drifts may occur. Secondly, matrix-matched calibration samples are not always available. Thirdly, the samples matrix is known to a certain extent, with a possible high variability that can induce unexpected spectral interferences. In addition, due to practical or cost constraints, feasibility studies are frequently performed on matrices and/or analytes and/or experimental conditions other than that of interest, and the question of analytical performances that would be obtained in the real situation is raised.

Calibration transfer could be helpful to cope with those issues. In the field of NIR spectroscopy, where it is widely studied, this concept generally relates to the use of a multivariate calibration model obtained with an instrument to predict samples measured with another instrument. In LIBS, this definition is somewhat restrictive and can be broadened in different ways. Thus, we could consider transferring a calibration from one matrix to another, which is equivalent to compensating for matrix effects. But it can also be related to the calibration transfer for a given matrix from one element to another, or for a given element, from one line to another. Furthermore, a change in experimental conditions can also be dealt with by calibration transfer approaches.

In this talk we will review the interest of calibration transfer in LIBS as well as the existing works on the subject. Recent results obtained in our laboratory will be presented to illustrate the different definitions of calibration transfer given above. Issues and perspectives of such approaches will be discussed.