Qualitative and quantitative analysis of materials by LIBS in nuclear environment how multivariate methods can help.

J-B. Sirven, M. El Rakwe, N. Coulon, D. L'Hermite, E. Vors

FROM RESEARCH TO INDUSTRY

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MATERIALS BY LIBS IN NUCLEAR ENVIRONMENT: HOW MULTIVARIATE METHODS CAN HELP

J.-B. Sirven, M. El Rakwe, N. Coulon, D. L'Hermite, E. Vors

CEA, Nuclear Energy Division, Department of Physical Chemistry
F-91191 Gif sur Yvette, France

jean-baptiste.sirven@cea.fr

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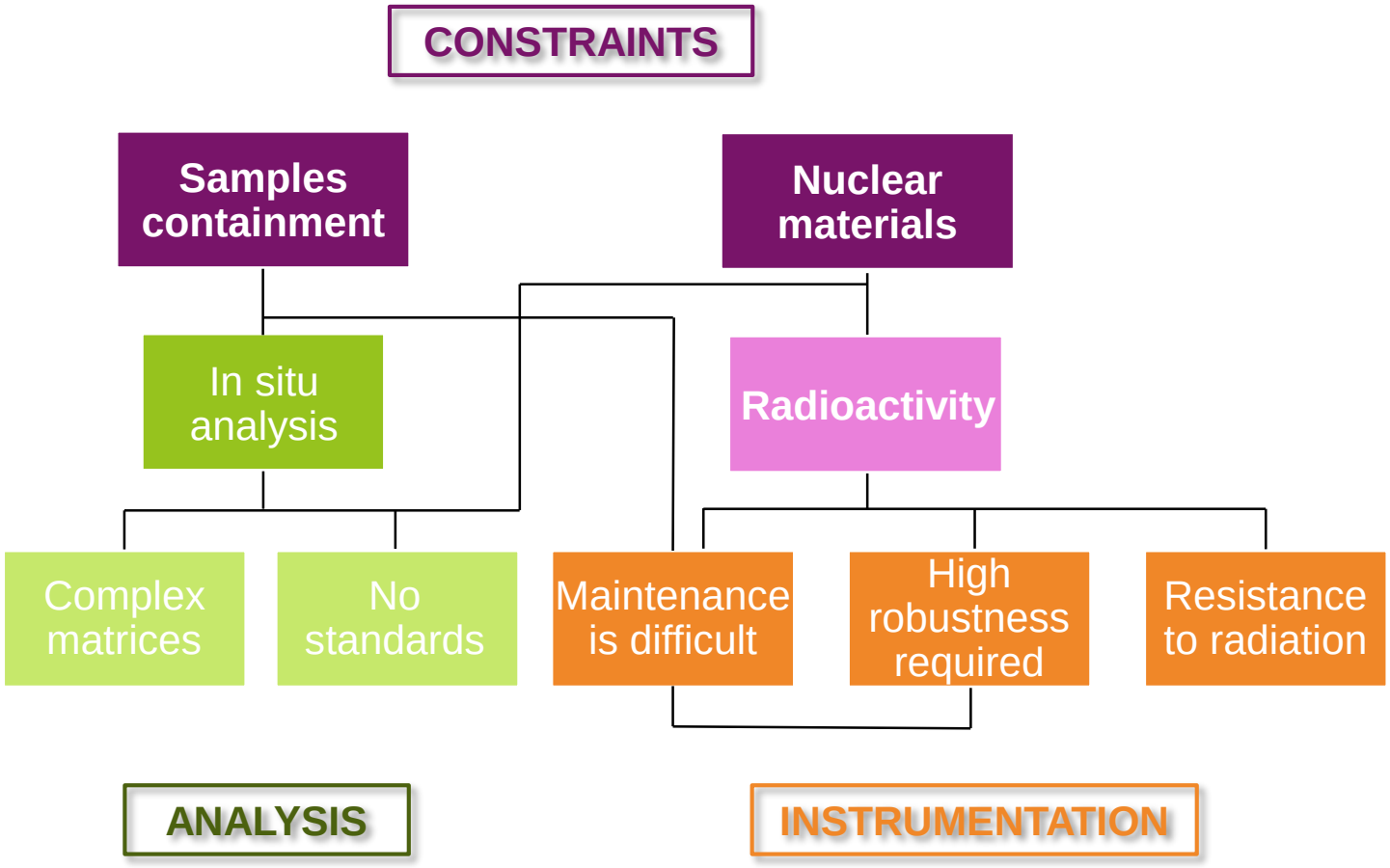
NUCLEAR ENVIRONMENT

NUCLEAR ENVIRONMENT

NUCLEAR ENVIRONMENT

NUCLEAR ENVIRONMENT

ELEMENTAL ANALYSIS IN NUCLEAR ENVIRONMMENT



Motivation for chemometrics

- Optimize a measurement
- Identify samples
- Improve quantitative analysis

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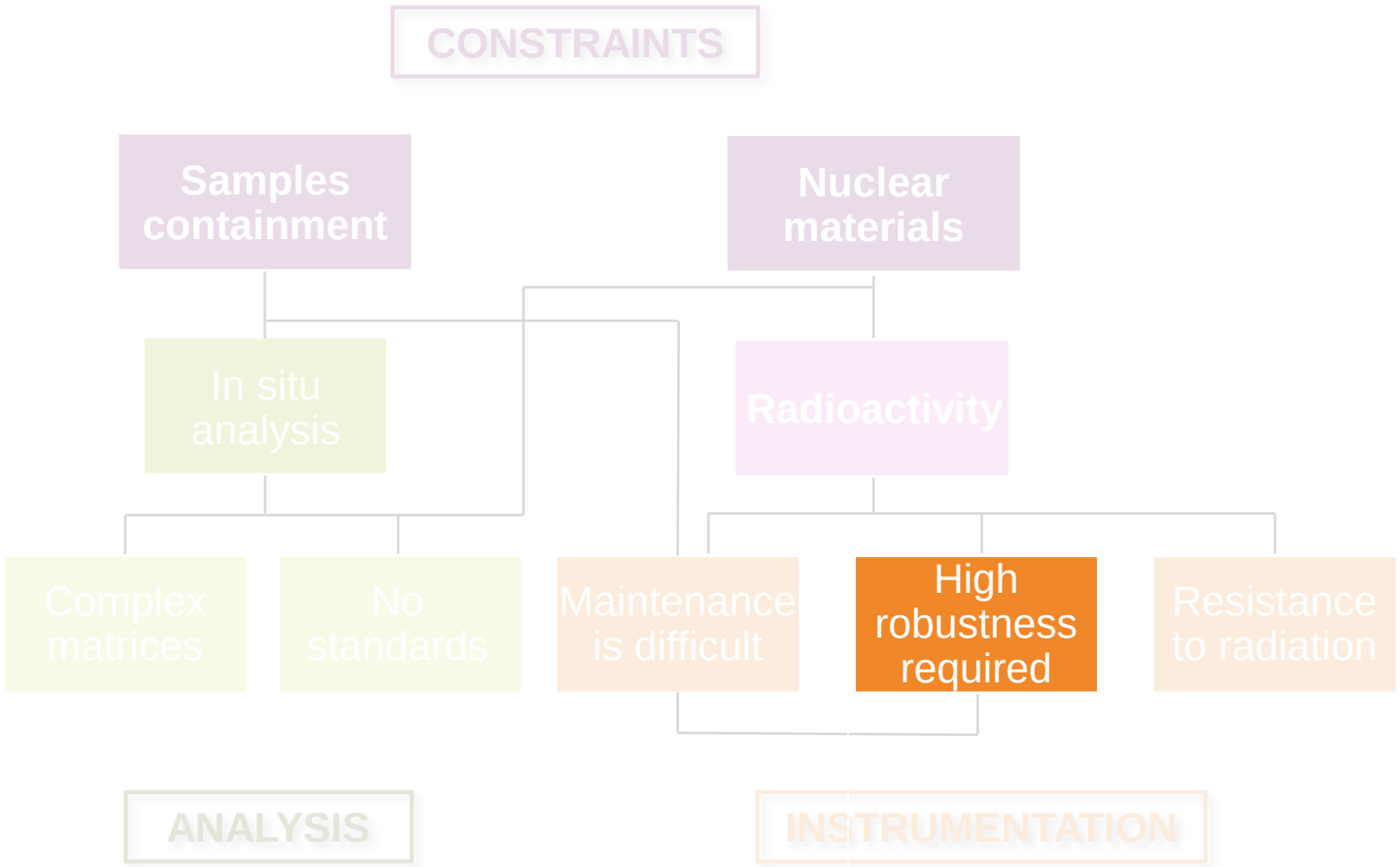
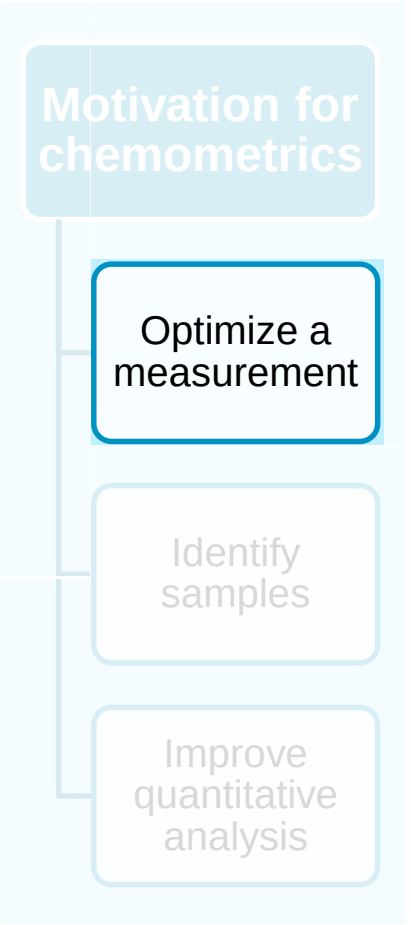
EXPERIMENTAL DESIGNS TO IMPROVE THE ROBUSTNESS OF THE ANALYSIS



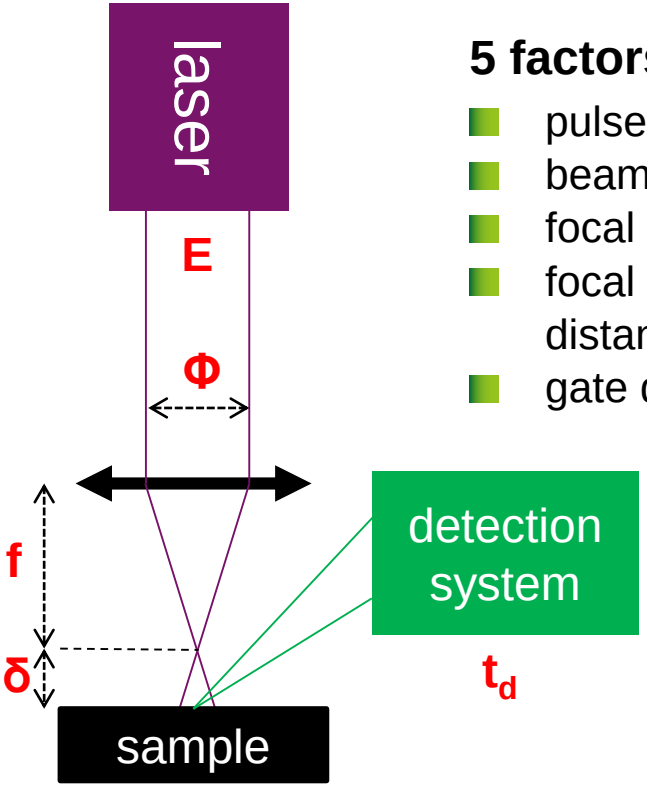


OPTIMIZATION OF INSTRUMENTAL PARAMETERS USING A DESIGN OF EXPERIMENTS

Objective: To optimize experimental parameters in ordre to obtain the best analytical performances, with a **user point of view** and a **minimum of experimental trials**

→ **Design Of Experiment**

Maria El Rakwe PhD thesis



5 factors:

- pulse energy (**E**)
- beam diameter (**Φ**)
- focal length (**f**)
- focal plane – sample distance (**δ**)
- gate delay (t_d)

4 responses:

- Ablated volume
- Line ratio (plasma temperature indicator)
- Signal intensity
- Signal repeatability

Physical responses

Analytical responses

Taking into account that

- The relation between factors and responses is **non-linear**
- Factors are strongly **coupled**

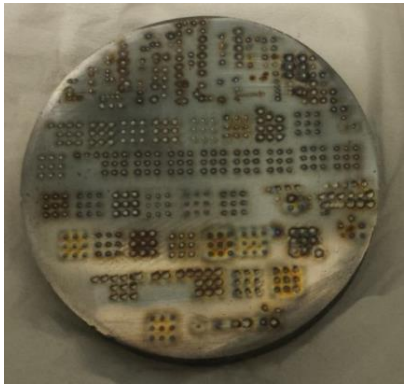
OPTIMIZATION OF INSTRUMENTAL PARAMETERS USING A DESIGN OF EXPERIMENTS

Experiment:

266 nm Nd:YAG laser

Czerny-Turner monochromator, 300 mm, 2400 g/mm grating

ICCD

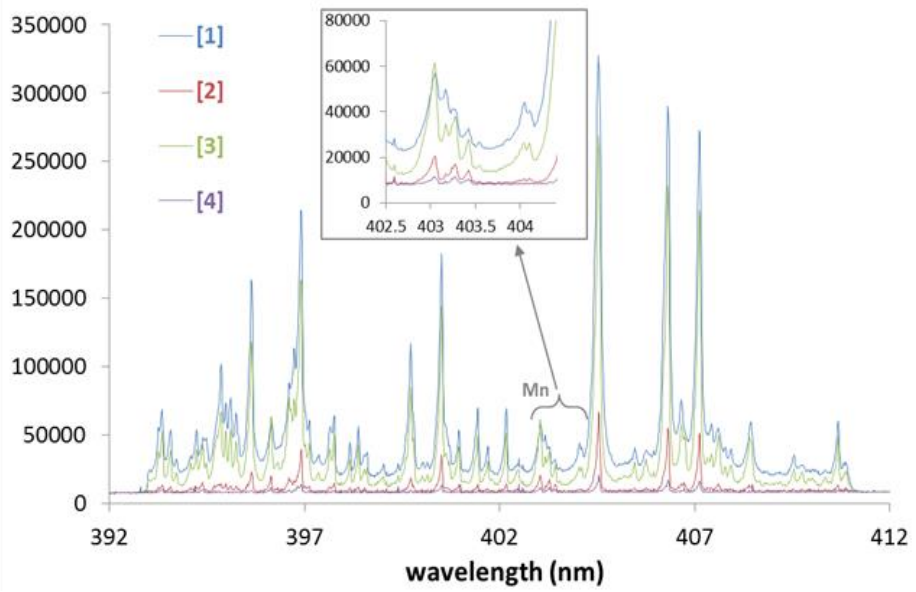


Sample:

SS59 standard: Fe 99.6 % ; **Mn 0.12 %**

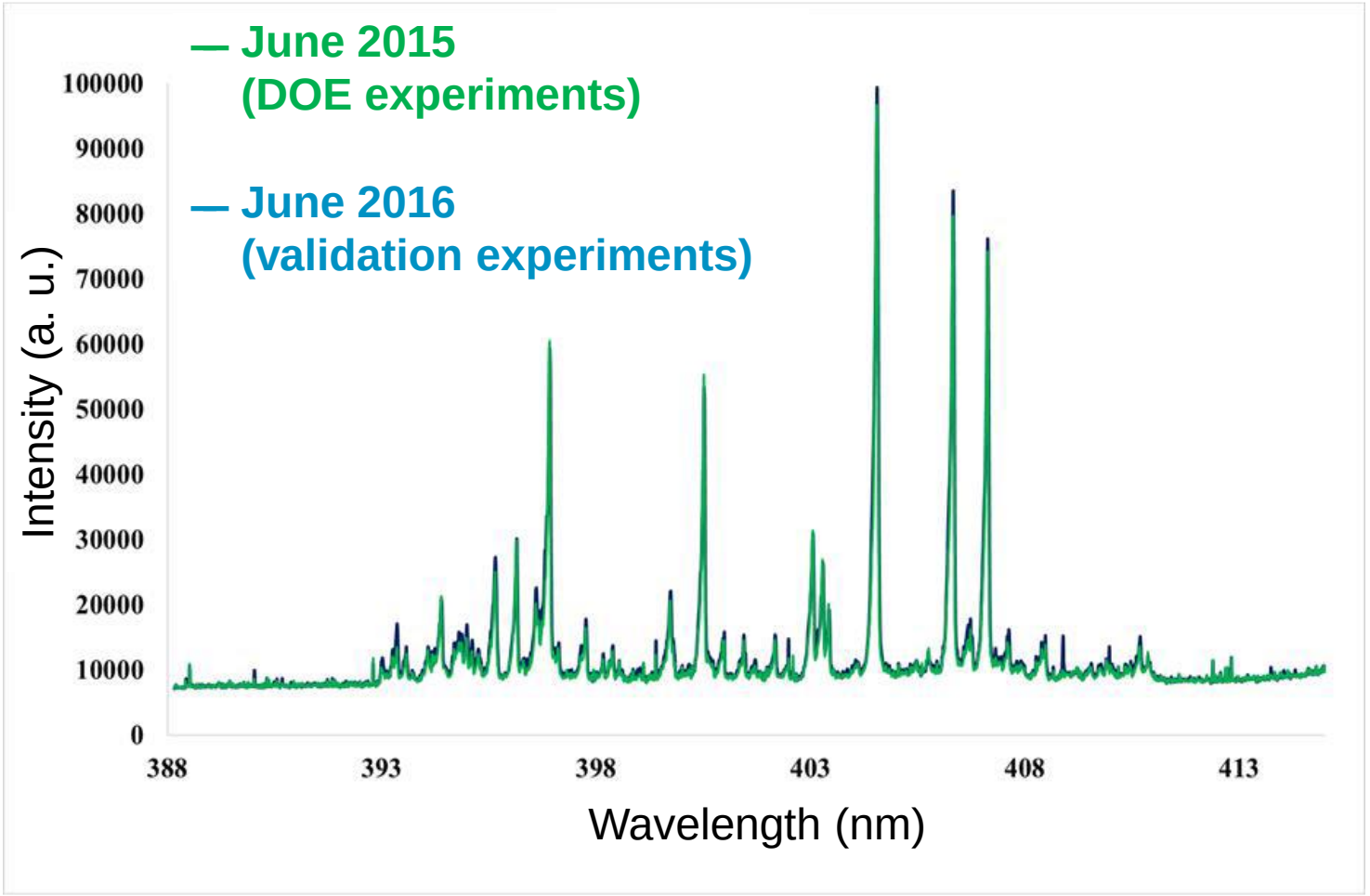
Central composite DOE (32 experiments)

1. Modeling of relation between factors and responses
2. Simultaneous optimization of analytical responses
3. Check of experimental reproducibility
4. Experimental validation of the predictive ability of the model



OPTIMIZATION OF INSTRUMENTAL PARAMETERS USING A DESIGN OF EXPERIMENTS

Experimental reproducibility



OPTIMIZATION OF INSTRUMENTAL PARAMETERS USING A DESIGN OF EXPERIMENTS

Model validation

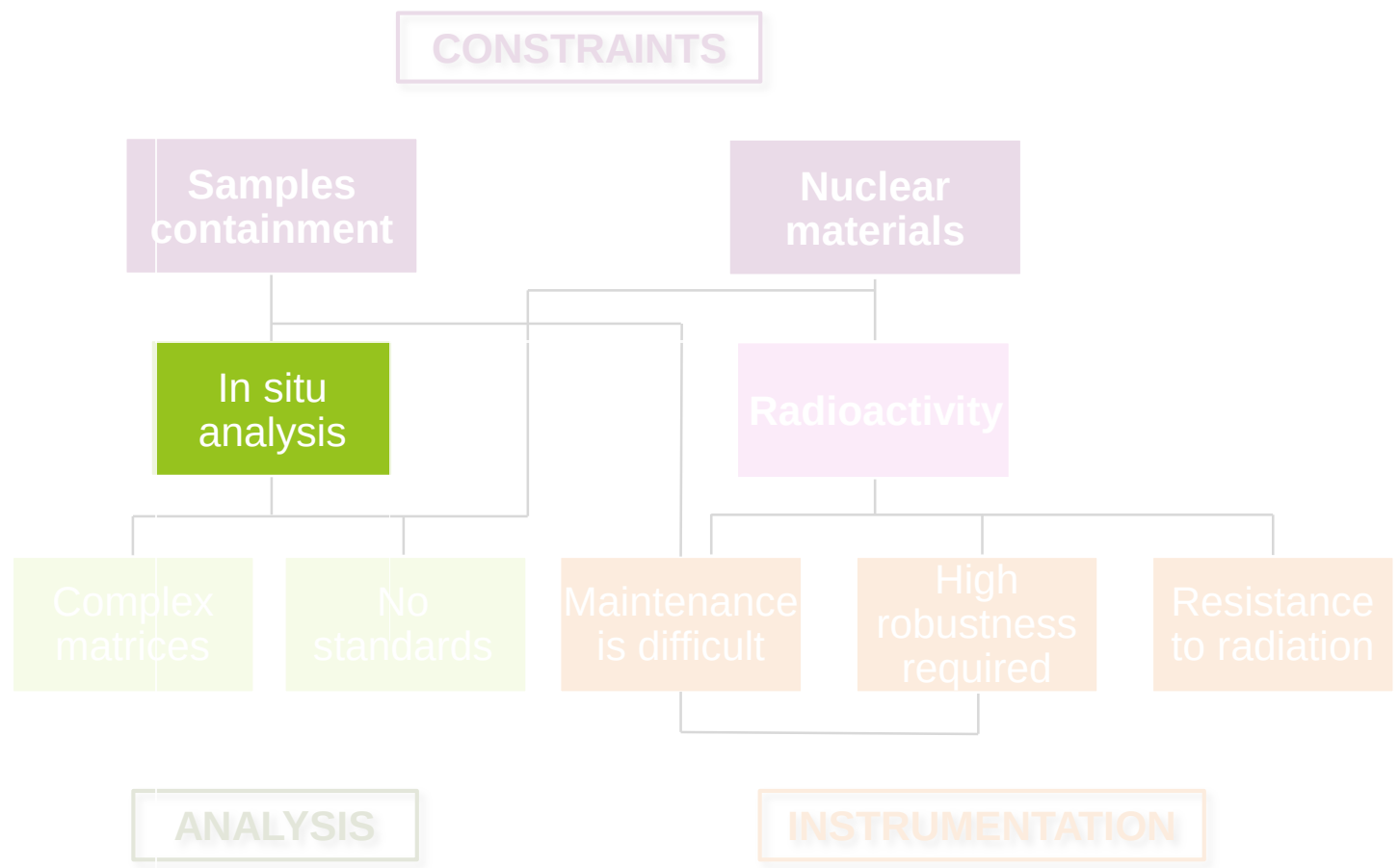
Responses	Predicted values	Experimental values	Relative deviation
Mn signal intensity	7260 ± 1740	7530	**- 3.7%**
Mn signal RSD	1 % (< 6 %)	3.5 %	**+ 250%**
Ablated volume (μm^3)	(1.45 ± 0.16) 10^5	1.27 10^5	**- 12%**
Line ratio (plasma temperature indicator)	1.7 ± 1.7	2.9	**+ 68%**

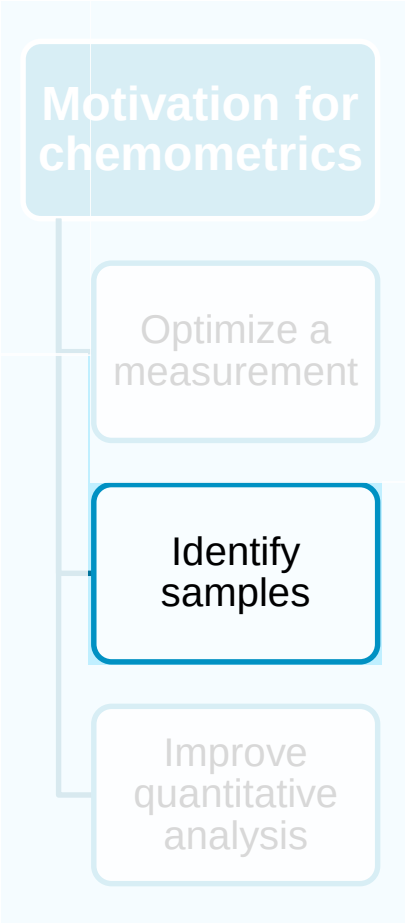
The model is satisfactorily predictive → it can be used:

- To determine the effect of the chosen experimental parameters on different responses (e.g. SBR, LOD…)
- To estimate the **instrumental robustness** in a given configuration

2/3

MATERIALS IDENTIFICATION BY ONSITE LIBS SYSTEMS



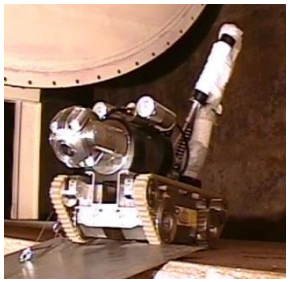


ONSITE IDENTIFICATION OF MATERIALS

Motivation:

- Inventory before nuclear decommissioning
- Control of contamination
- Identification of wastes prior to treatment / sorting

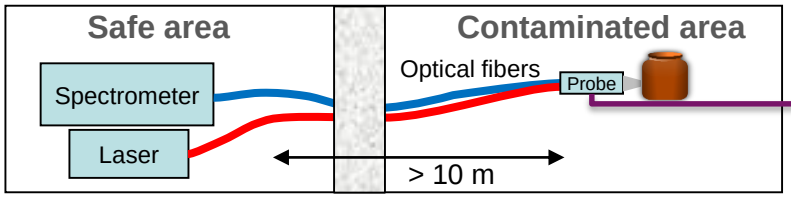
RICA robot developed at CEA for in situ measurements in nuclear environment

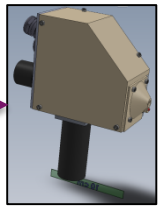


2 technologies:

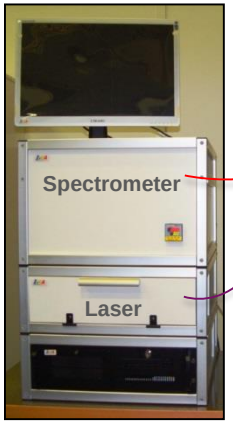
- Portable

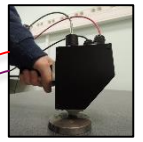
- Fibered





Size 10cmx10cm
Weight < 1Kg





Probe

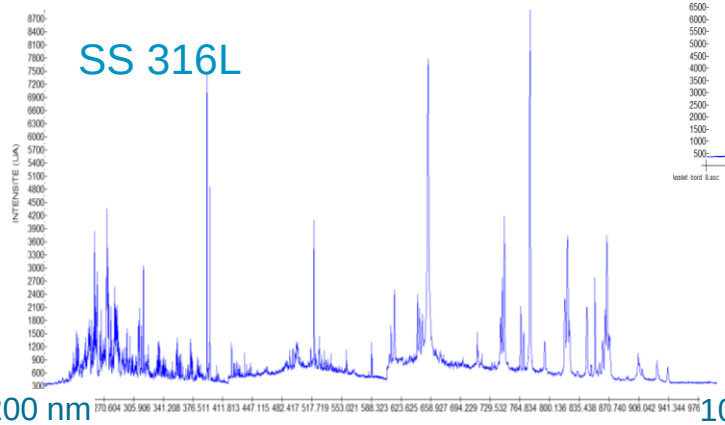
Sampling characteristics :
Depth ~ 1 µm / laser shot
Analyzed Area ~ (200 µm)²
Ablated mass ~1 ng / laser shot

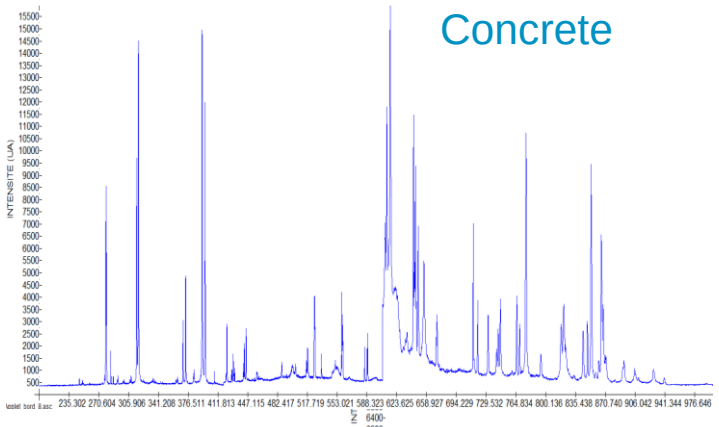
N. Coulon et al., Poster 149

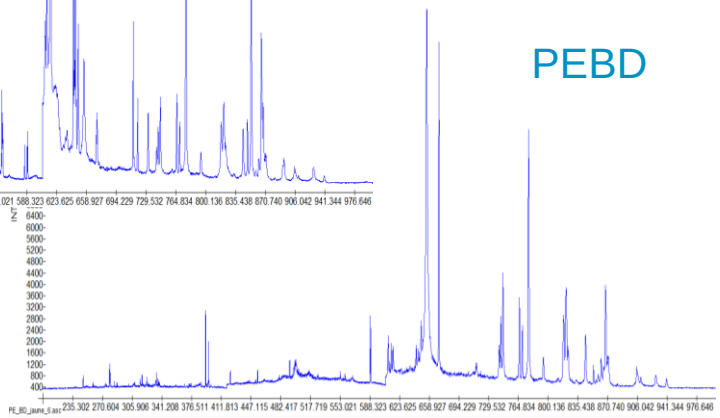
ONSITE IDENTIFICATION OF MATERIALS

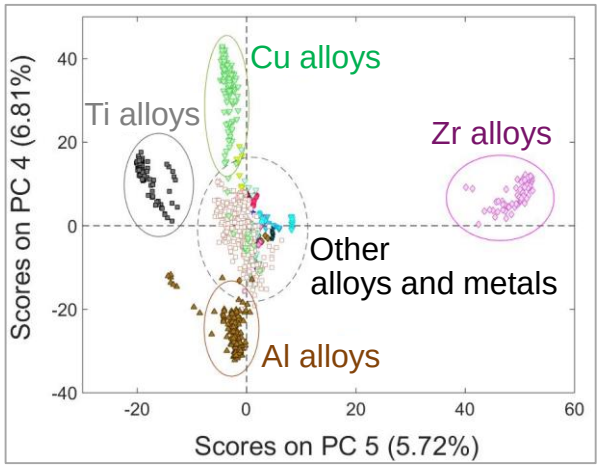
Examples of data treatment

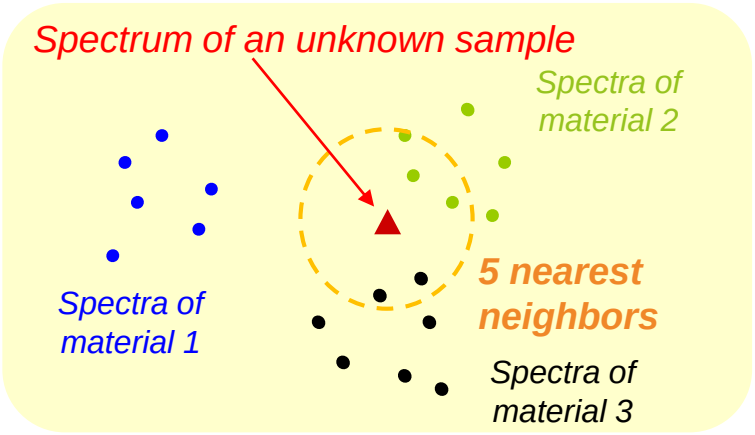
Single-shot, low resolution spectra (portable system)











ONSITE IDENTIFICATION OF MATERIALS

50 spectra of concrete + 430 spectra of glass + 1260 spectra of alloys + 660 spectra of plastics

KNN

alloys	glass	concrete	plastics
100 %	98 %	97 %	98 %

KNN

steels + Fe-based + Ni-based	Cu-, Zr-, Ti-based alloys, BiTe, InPbZnSn	Pure metals: Pb, Sn, W, Zn, Mo, V, Ag, Au, Pt, Mn, Ga, Ta, Cr	Al-based
100 %	100 % for each alloy	100 % for each metal	100 %

KNN

steel	Fe-based	Ni-based
99 %	100 %	96 %

KNN

maraging	stainless	high Cr
100 %	86 %	97 %

KNN

1xxx series	2xxx series
66 %	89 %

2xxx series+Ti	4xxx series
89 %	100 %

6xxx series	pure
100 %	100 %

KNN

PTFE, PVDF, Neop, SAN, Viton	other
100 % for each plastic	KNN

PS	other
75 %	KNN

ABS	other
70 %	KNN

PP	other
60 %	KNN

PE	other
60 %	KNN

PA	other
60 %	KNN

PC + PET	PUR	other
50 %	40 %	KNN

PVC	EVA	EPR
60 %	20 %	0 %

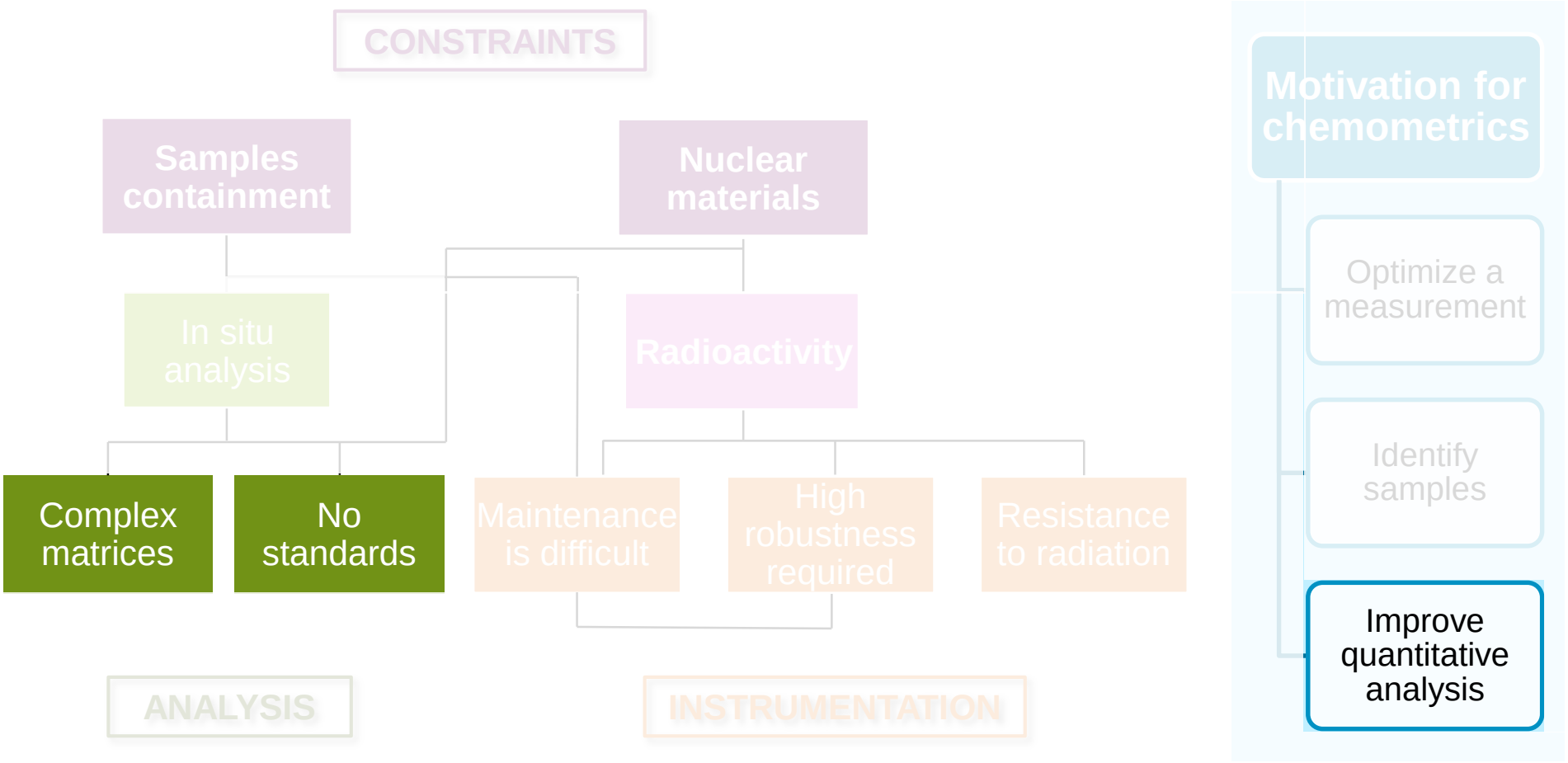
X % = rate of correct identification obtained at each step ***for the test set***

IVEA SOLUTION

Essonne LE CONSEIL GÉNÉRAL

3/3

QUANTITATION APPROACHES BASED ON THE EXPLOITATION OF THE SPECTRAL AND TEMPORAL DIMENSIONS OF THE LIBS SIGNAL



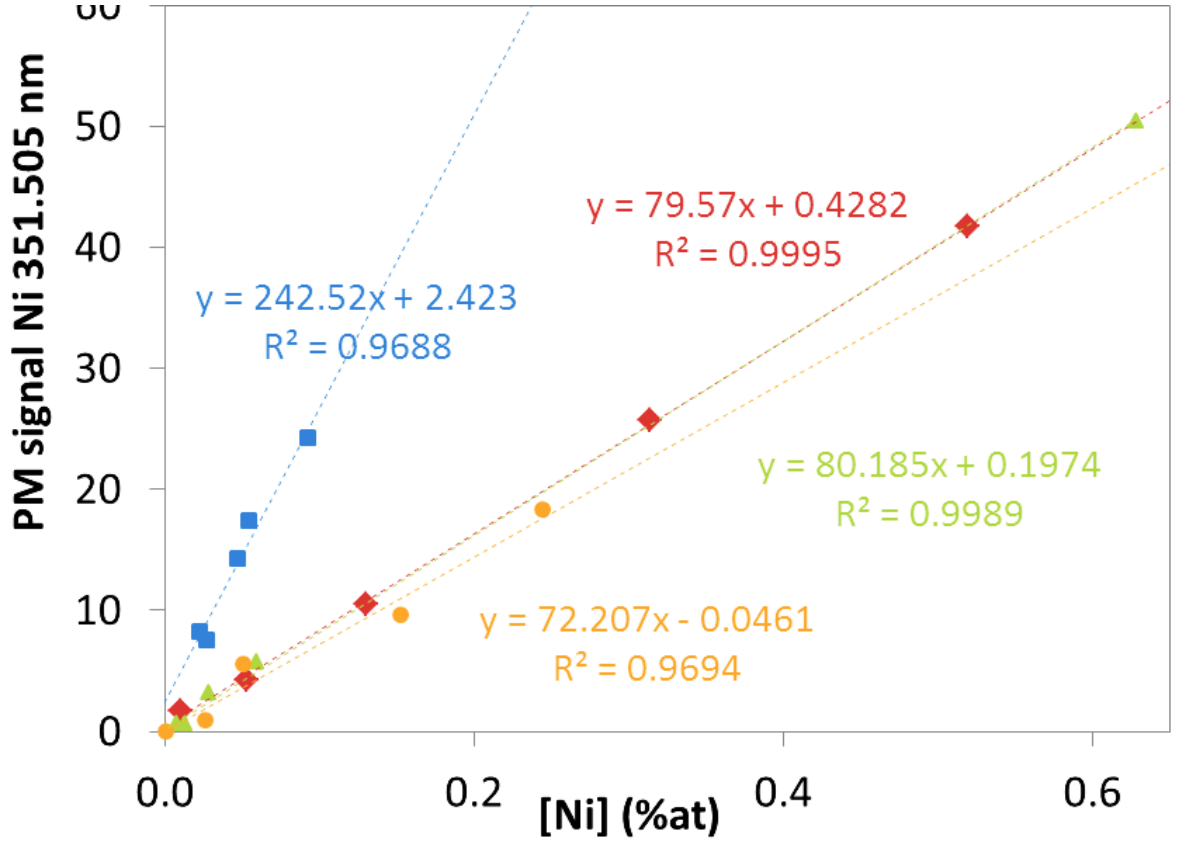
CALIBRATION BY LIBS

Calibration of [Ni] in…

- Cu matrix
- Ti matrix
- Al matrix
- Zr matrix

Gate delay = 1.5 µs

Gate width = 3 µs



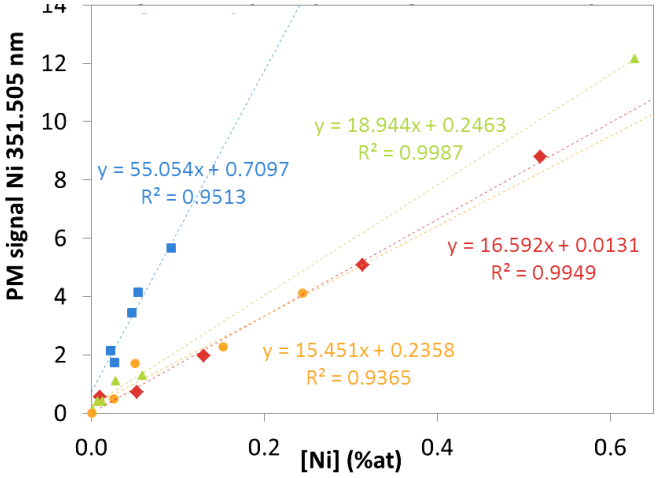
EFFECT OF TIME RESOLUTION ON CALIBRATION LINES

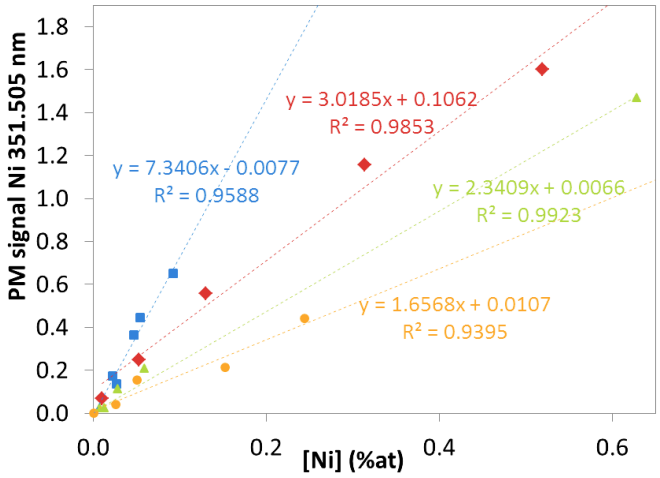
Gate delay 1.5 µs

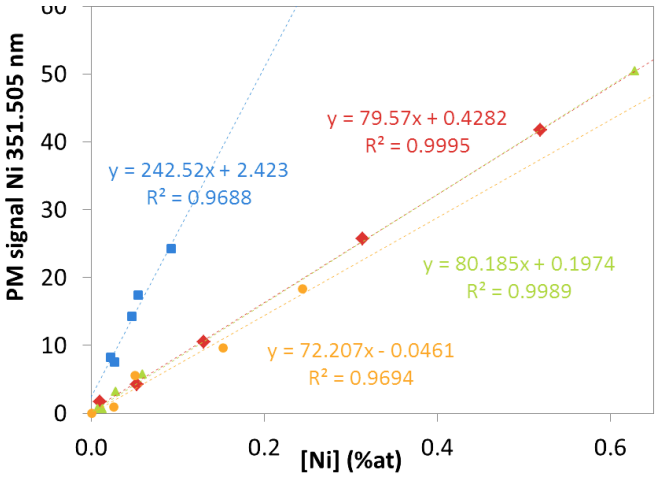
Gate delay 9.5 µs

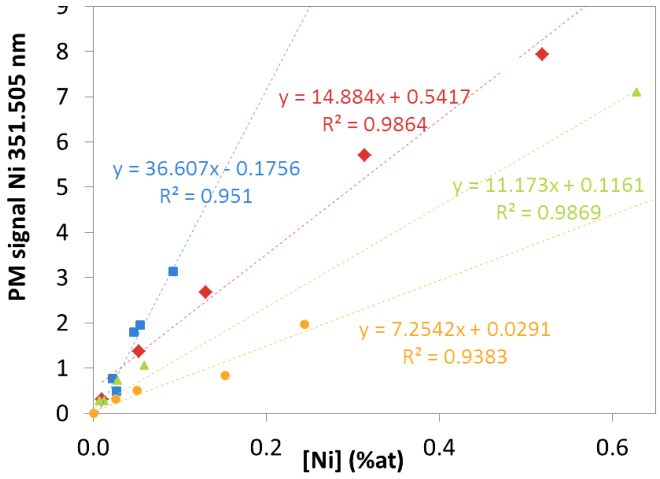
Gate width 0.5 µs

Gate width 3 µs









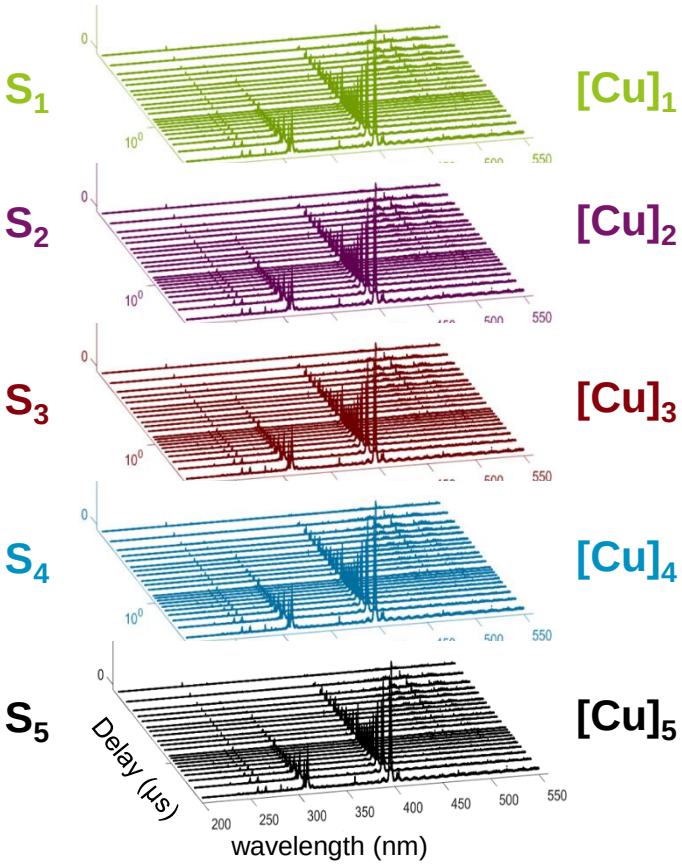
Ni in…

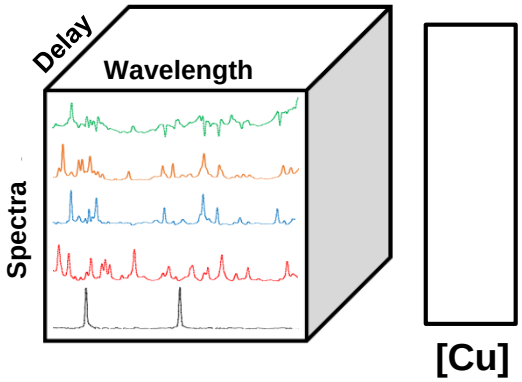
- Cu matrix
- Ti matrix
- Al matrix
- Zr matrix

CALIBRATION USING TIME-RESOLVED SPECTRA

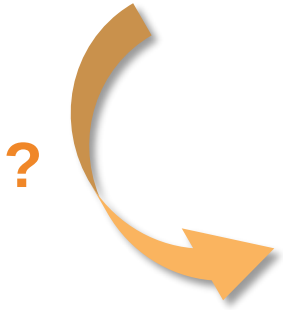
What if we take into account the temporal dimension of the LIBS signal?

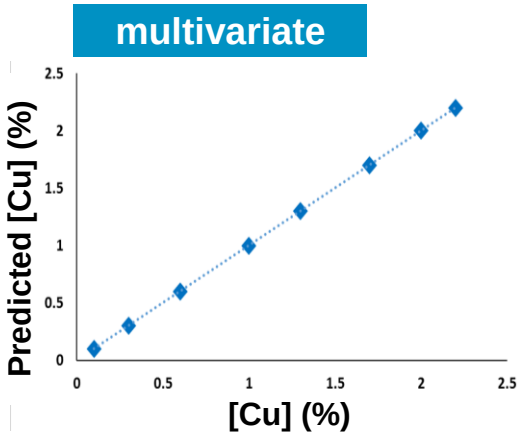
1. Does it improve analytical performances?
2. Can we take advantage of it to correct matrix effects?





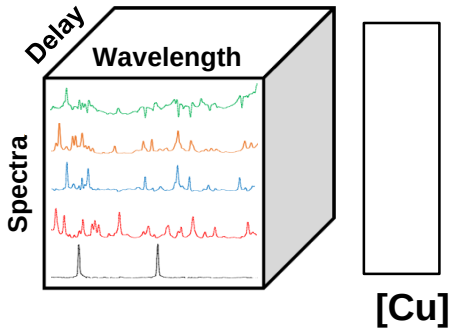
Maria El Rakwe PhD thesis



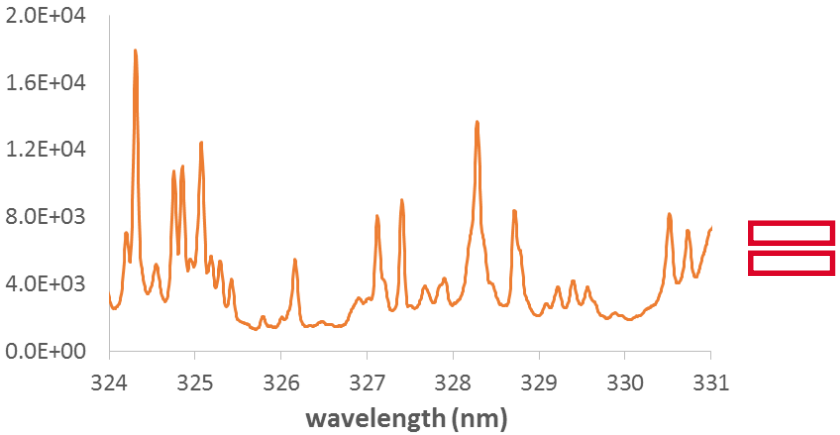


A PRACTICAL EXAMPLE

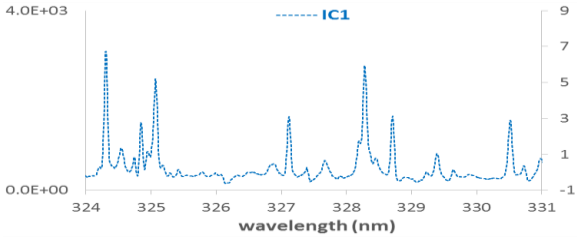
Dataset = calibration of [Cu] in Ni



For each given delay and [Cu] concentration:

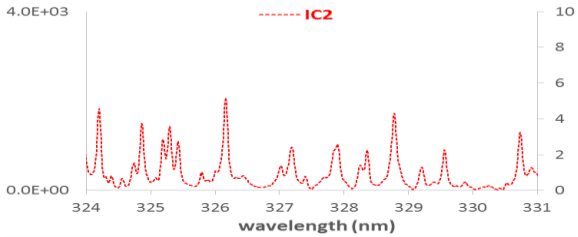


a_1 ×



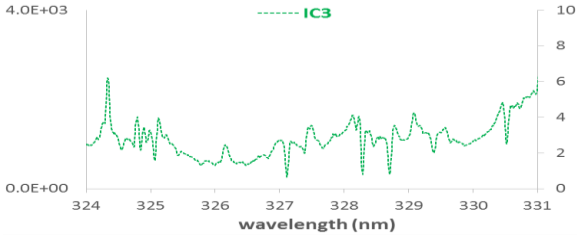
Mostly Ni (+ Cr)

a_2 ×



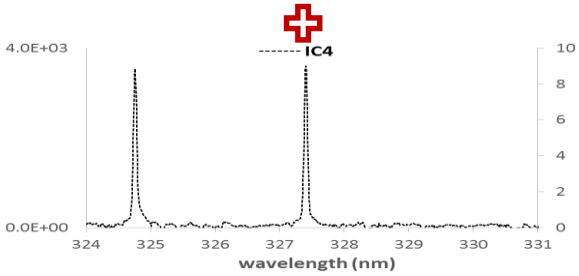
Mostly Ti (+ Cr)

a_3 ×



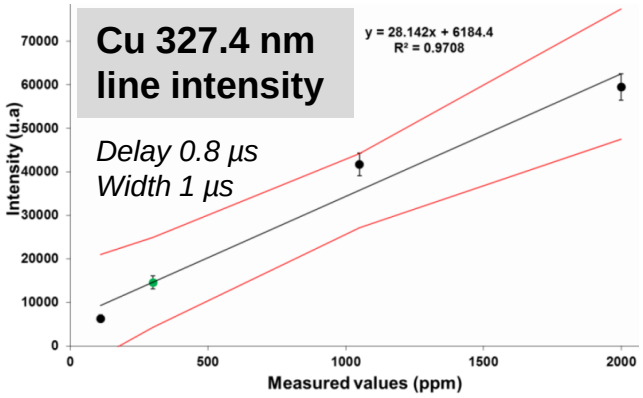
Continuum + most intense reversed Ni lines

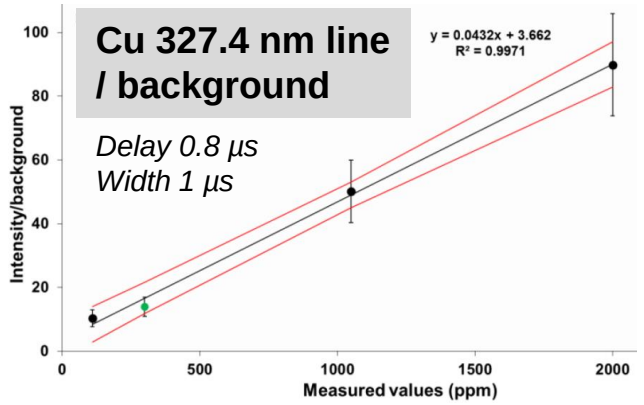
a_4 ×

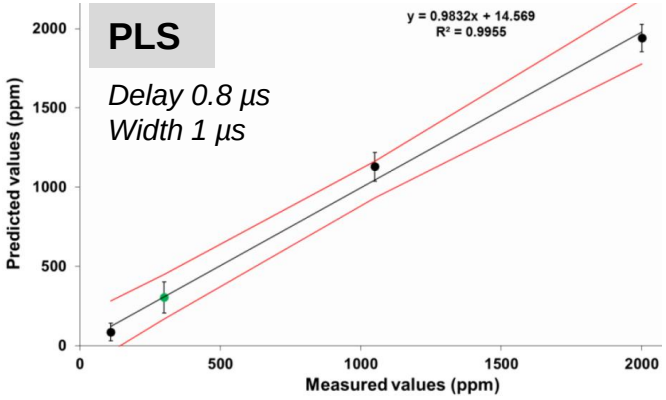


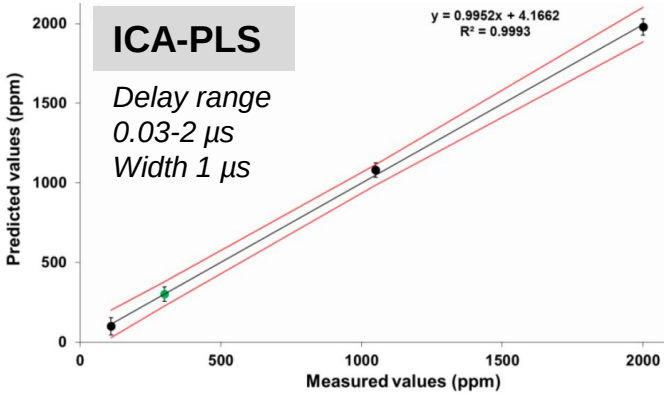
Cu

CALIBRATION LINE VS PLS VS ICA-PLS



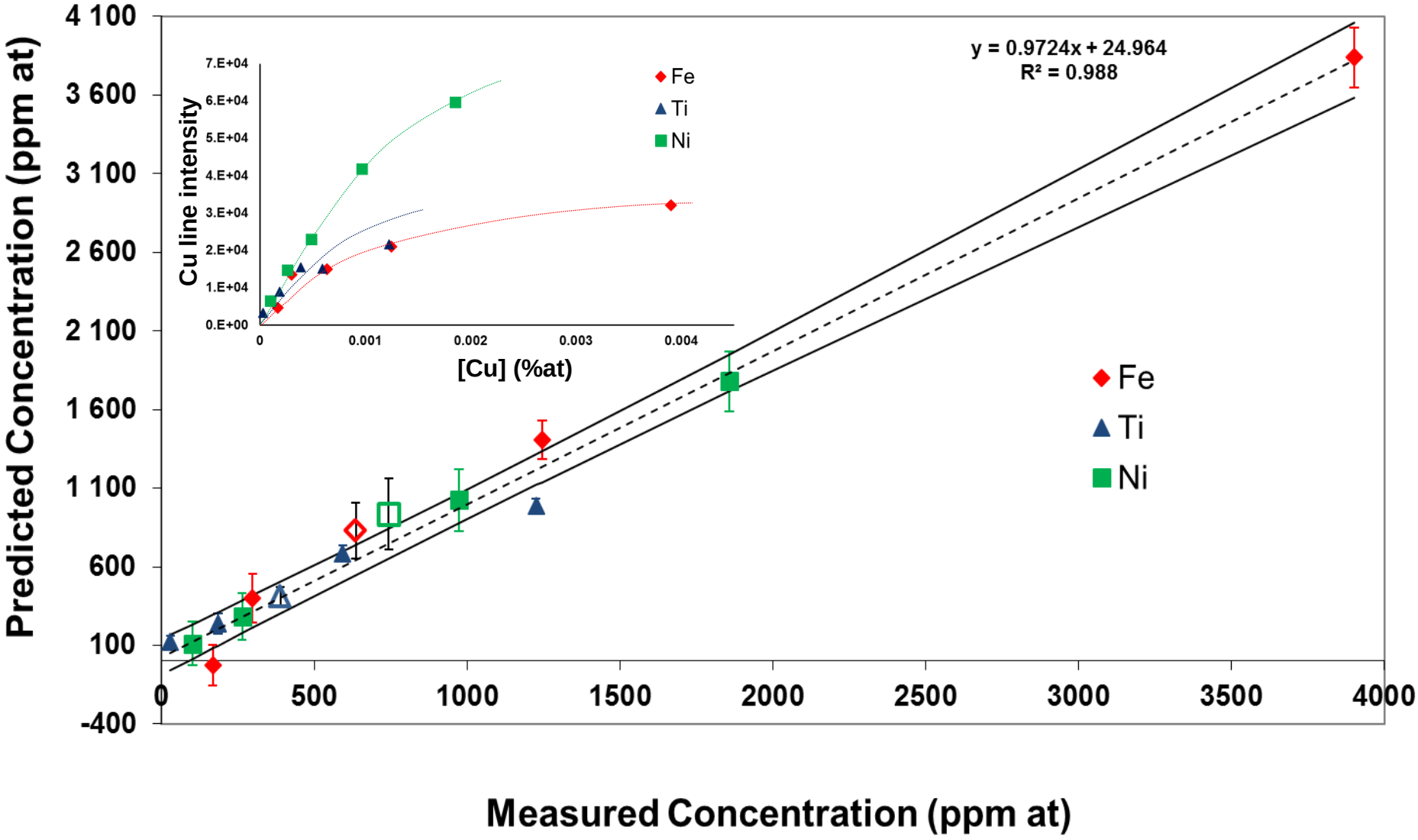






Calibration	Trueness	Precision	LOD (ppm)
Cu line intensity			900
Cu line / background			400
PLS			350
ICA-PLS			180

MULTI-MATERIALS QUANTITATIVE ANALYSIS

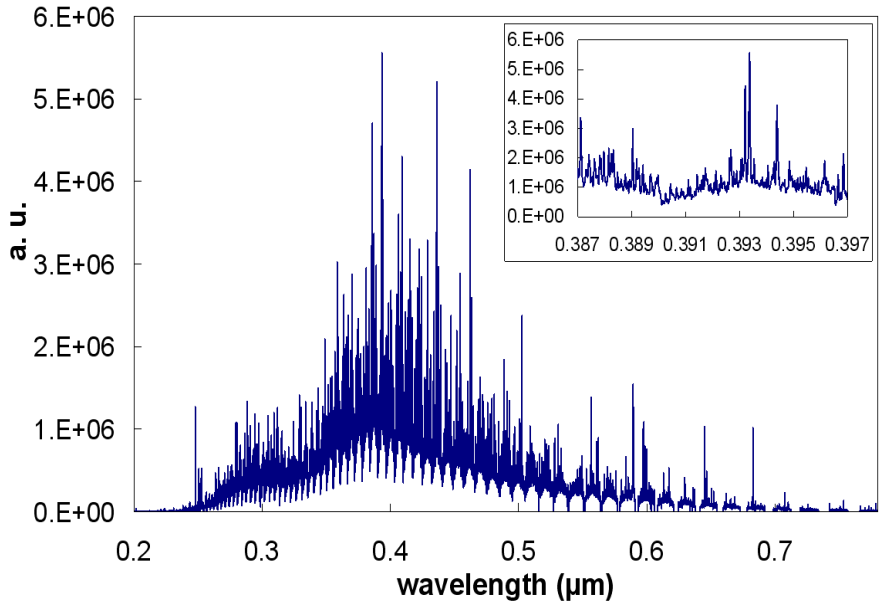


CONCLUSION

Elemental analysis in nuclear environment:

- Strong instrumental constraints
- Complex spectra
- Few (sometimes no) standards available
- Approaches based on Boltzmann modeling (CF-LIBS, Cσ, FP…) difficult to implement

Chemometrics is useful to overcome (to a certain extent) those difficulties (but it is not magic… and requires careful validation…)



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Thank you for your attention!

jean-baptiste.sirven@cea.fr

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 43 71

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ABSTRACT

Elemental analysis in the nuclear field is essential in a number of situations, from the front-end of the fuel cycle to the waste management, either for process control, compliance checking, or waste characterization prior to conditioning. Yet, it is special for two main reasons.

First, due to their radioactivity, the samples are confined inside containments such as controlled areas, glove boxes or hot cells. Those safety and security constraints inherent in nuclear environment strongly restrict the possibility of sampling, transportation and handling of materials. Therefore, onsite or even in situ analytical techniques, such as LIBS, are of high interest, as they enable to limit the workers exposure to radiation and contamination, as well as the production of waste and effluents generated by conventional laboratory analysis. One important consequence is that the instruments must be very robust and require as little maintenance as possible.

Secondly, the matrices can be very complex due to the presence of many interfering elements including actinides and lanthanides. And a large variety of materials need to be characterized (fuel, alloys, glasses, concrete, solutions, etc.), both qualitatively and quantitatively. In this latter case, calibration samples are not always available and alternative approaches must be developed.

As shown by the abundant literature on the subject in other areas of analytical spectroscopy, multivariate methods are very helpful to cope with such issues. We will show how similar strategies can be implemented in LIBS, taking into account the peculiarities of the technique. Different applications of interest in the nuclear field will be reviewed: materials identification by onsite LIBS systems; use of experimental designs to improve the robustness of the analysis; innovative quantitation approaches based on the exploitation of the spectral and temporal dimensions of the LIBS signal; and isotopic analysis by an original method based on the self-absorption of intense emission lines.