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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

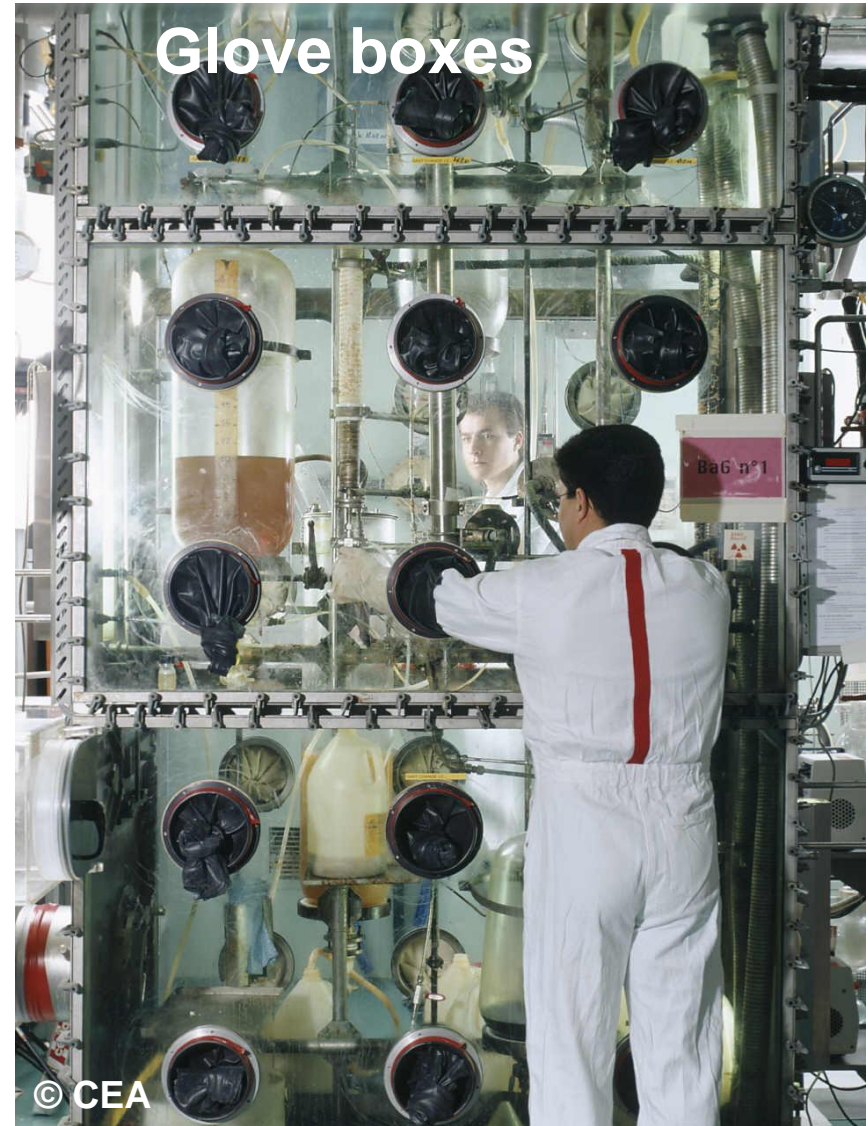
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LIBS 2016, Sept. 12 – 16, 2015, Chamonix-Mont-Blanc







## Decommissioning site



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## CONSTRAINTS

Samples containment

Nuclear materials

In situ analysis

Radioactivity

Complex matrices

No standards

Maintenance is difficult

High robustness required

Resistance to radiation

ANALYSIS

INSTRUMENTATION

## Motivation for chemometrics

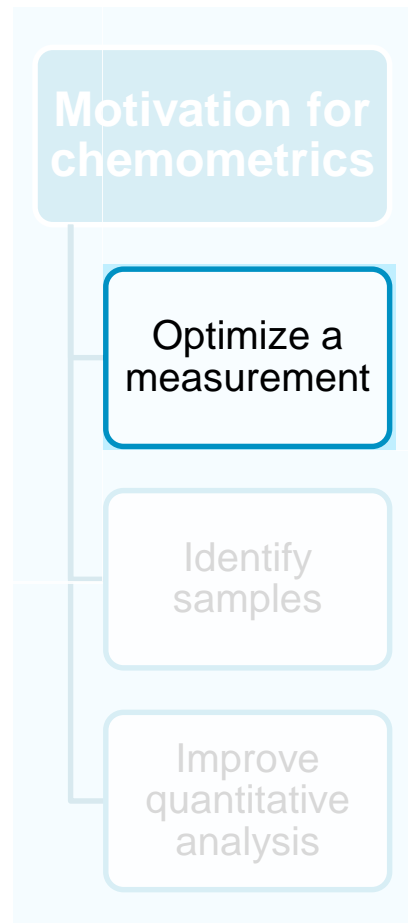
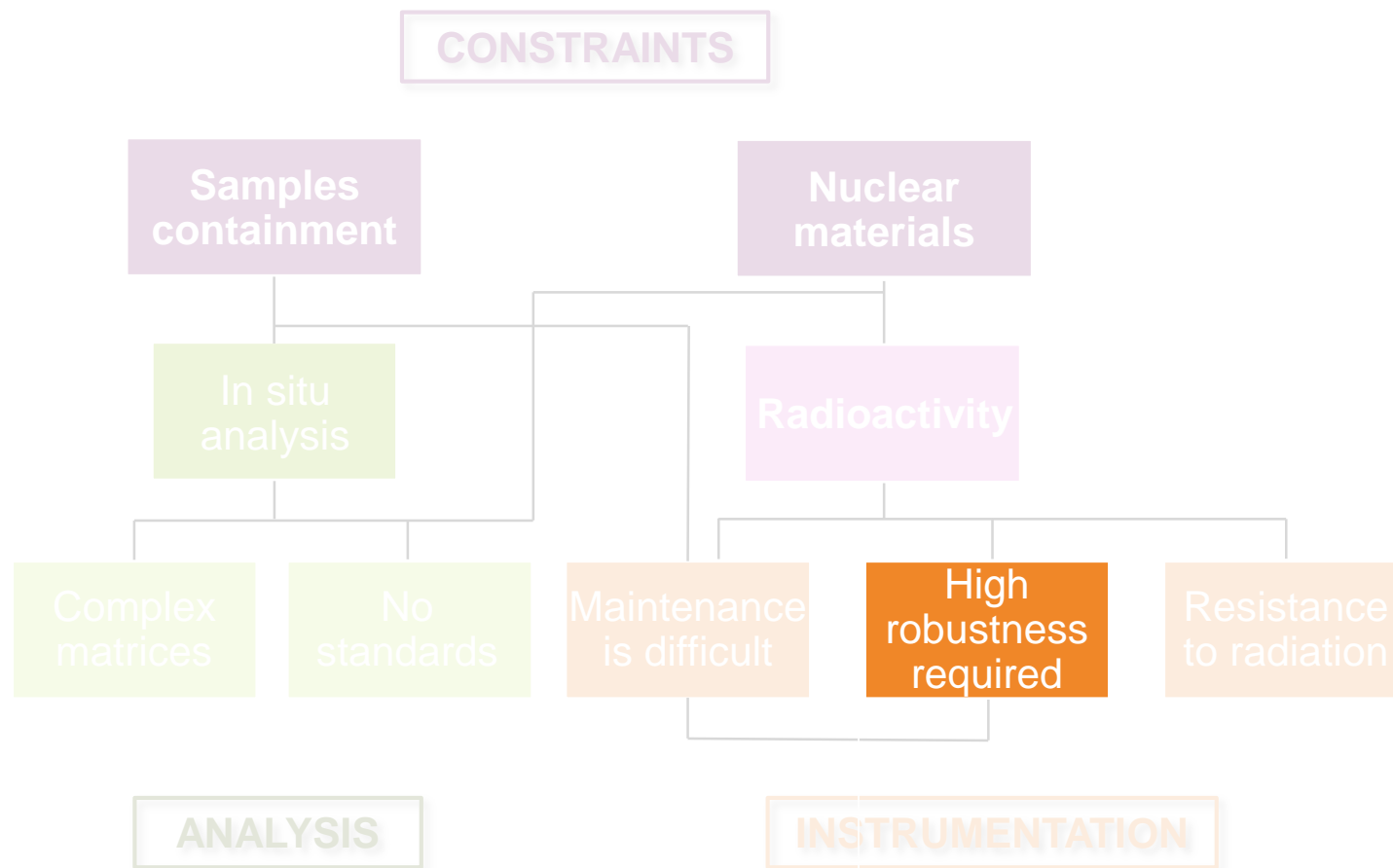
Optimize a measurement

Identify samples

Improve quantitative analysis

1/3

# EXPERIMENTAL DESIGNS TO IMPROVE THE ROBUSTNESS OF THE ANALYSIS

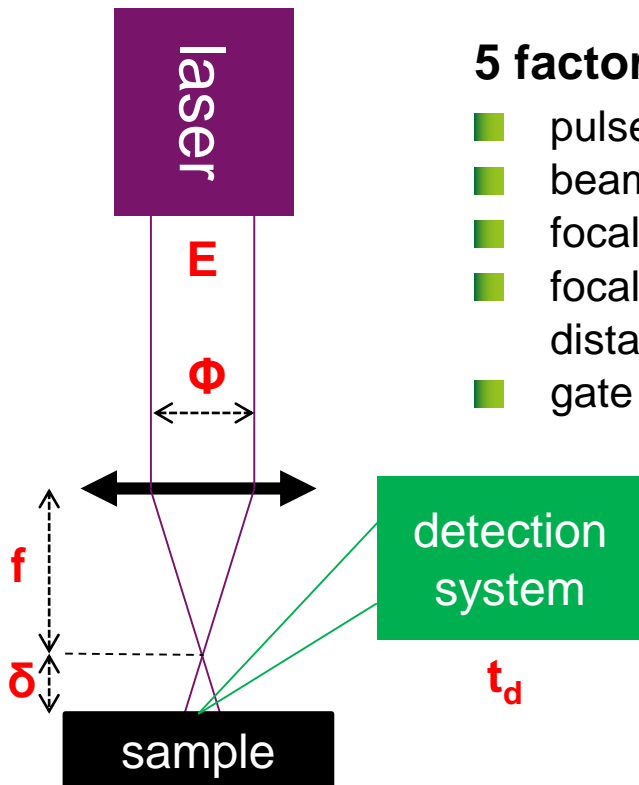




**Objective:** To optimize experimental parameters in order to obtain the best analytical performances, with a **user point of view** and a **minimum of experimental trials**

## → Design Of Experiment

*Maria El Rakwe PhD thesis*



### 5 factors:

- pulse energy ( $E$ )
- beam diameter ( $\Phi$ )
- focal length ( $f$ )
- focal plane – sample distance ( $\delta$ )
- 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**

## Experiment:

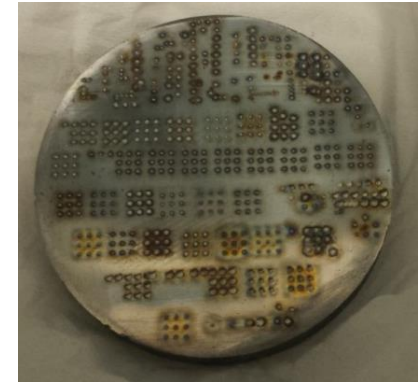
266 nm Nd:YAG laser

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

ICCD

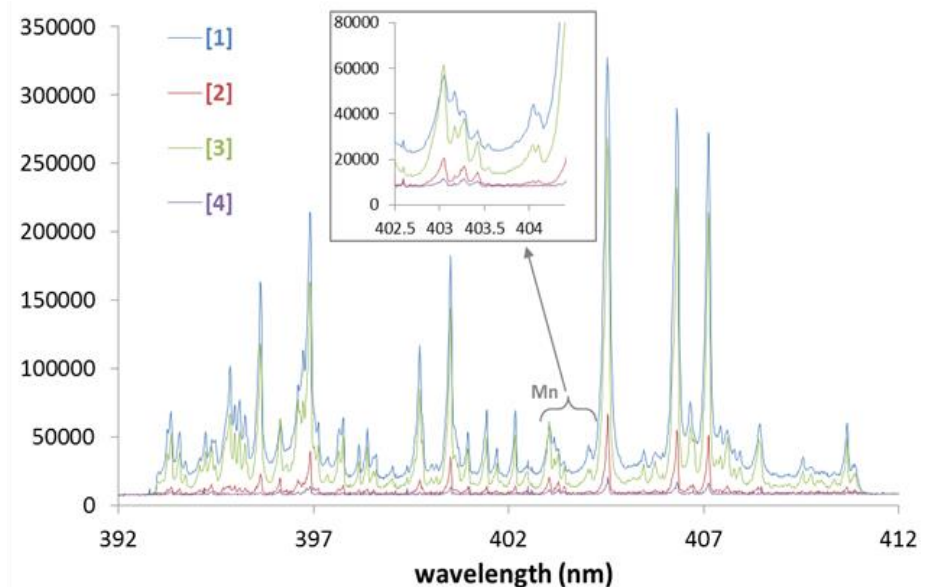
## Sample:

SS59 standard: Fe 99.6 % ; Mn 0.12 %

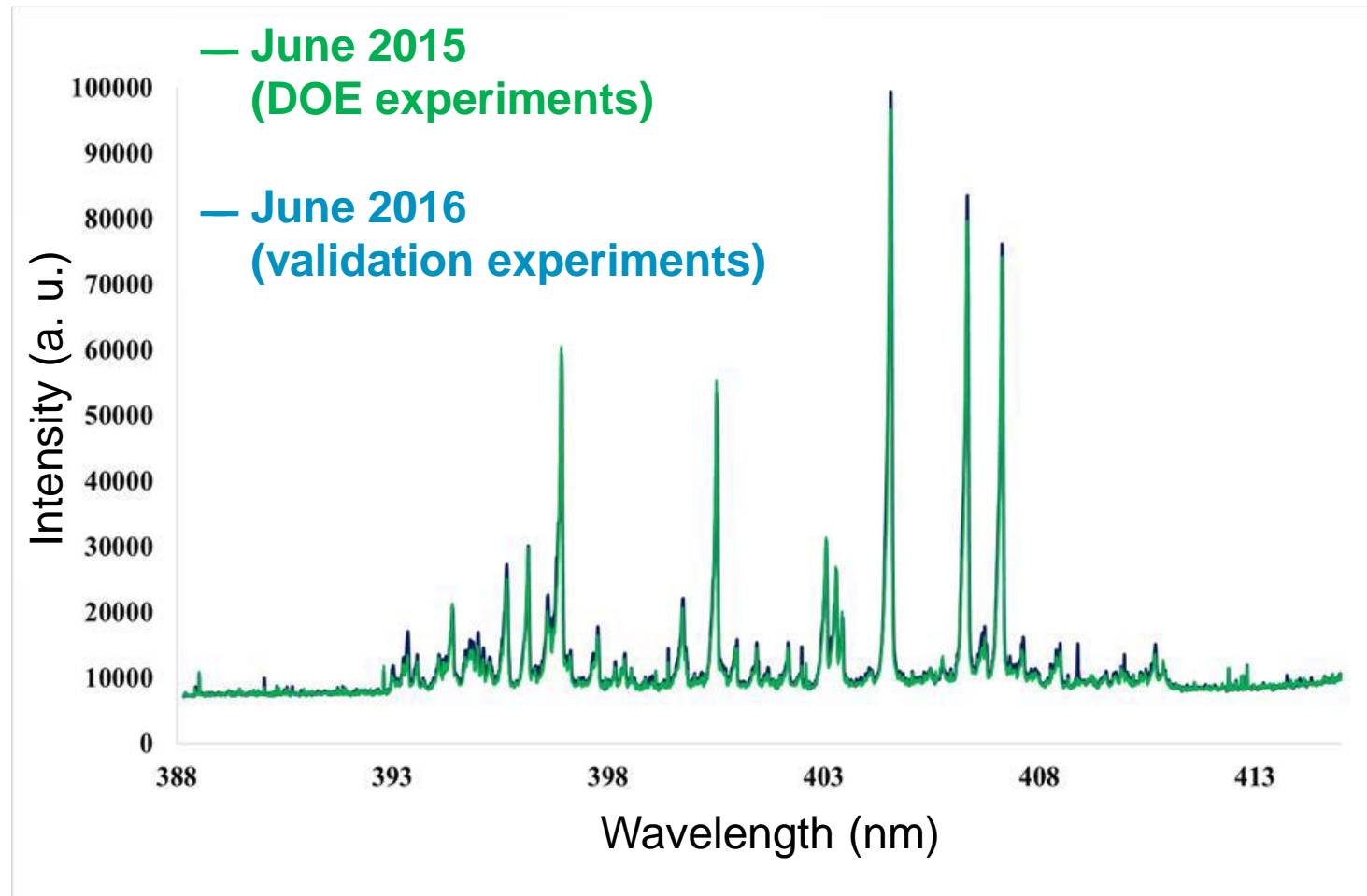


## Central composite DOE (32 experiments)

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



## Experimental reproducibility



## 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 <sup>3</sup> )	(1.45 ± 0.16) 10 <sup>5</sup>	1.27 10 <sup>5</sup>	- 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



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# MATERIALS IDENTIFICATION BY ONSITE LIBS SYSTEMS

## CONSTRAINTS

Samples containment

Nuclear materials

In situ analysis

Radioactivity

Complex matrices

No standards

Maintenance is difficult

High robustness required

Resistance to radiation

## ANALYSIS

## INSTRUMENTATION

Motivation for chemometrics

Optimize a measurement

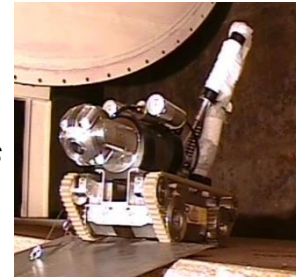
Identify samples

Improve quantitative analysis

## 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*

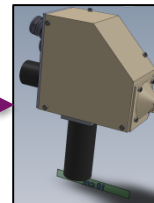
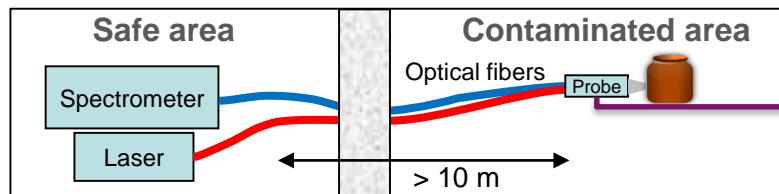


## 2 technologies:

- Portable

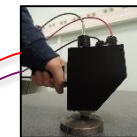
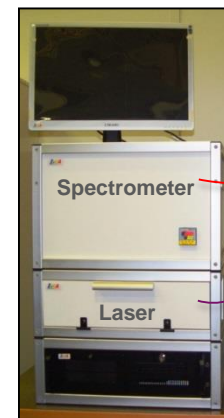


- Fibered



Size 10cmx10cm  
Weight < 1Kg

**N. Coulon et al., Poster 149**

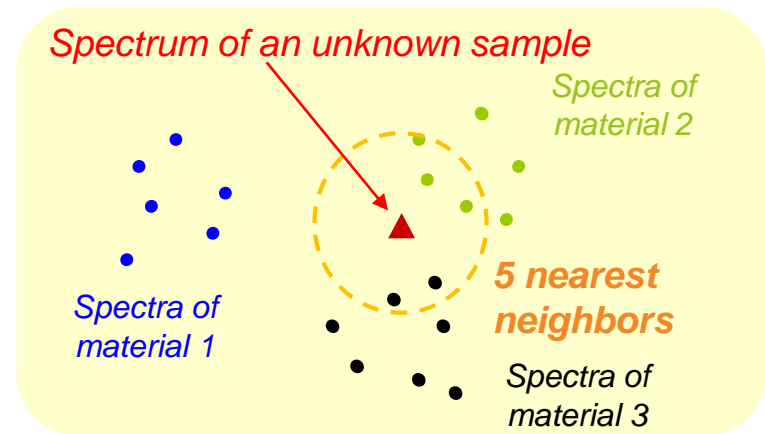
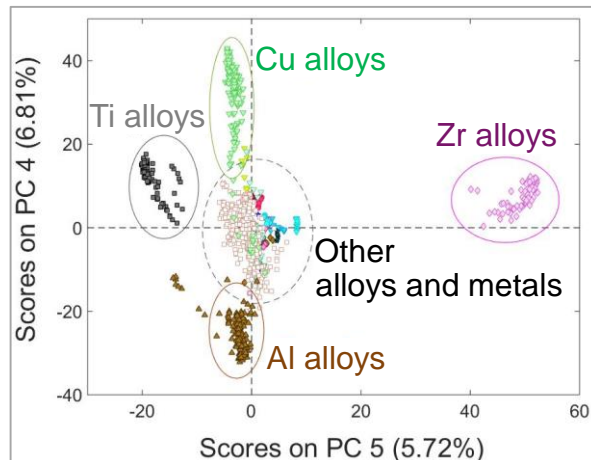
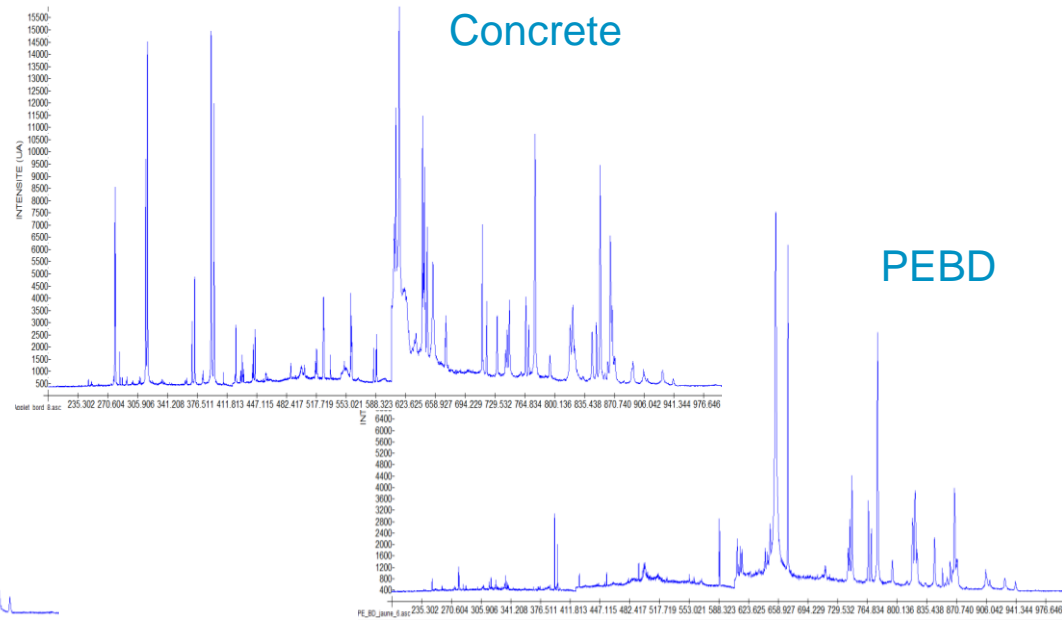
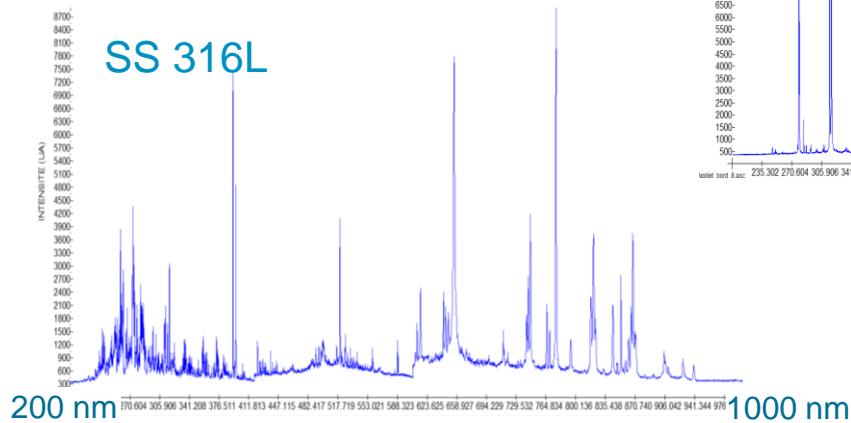


Probe

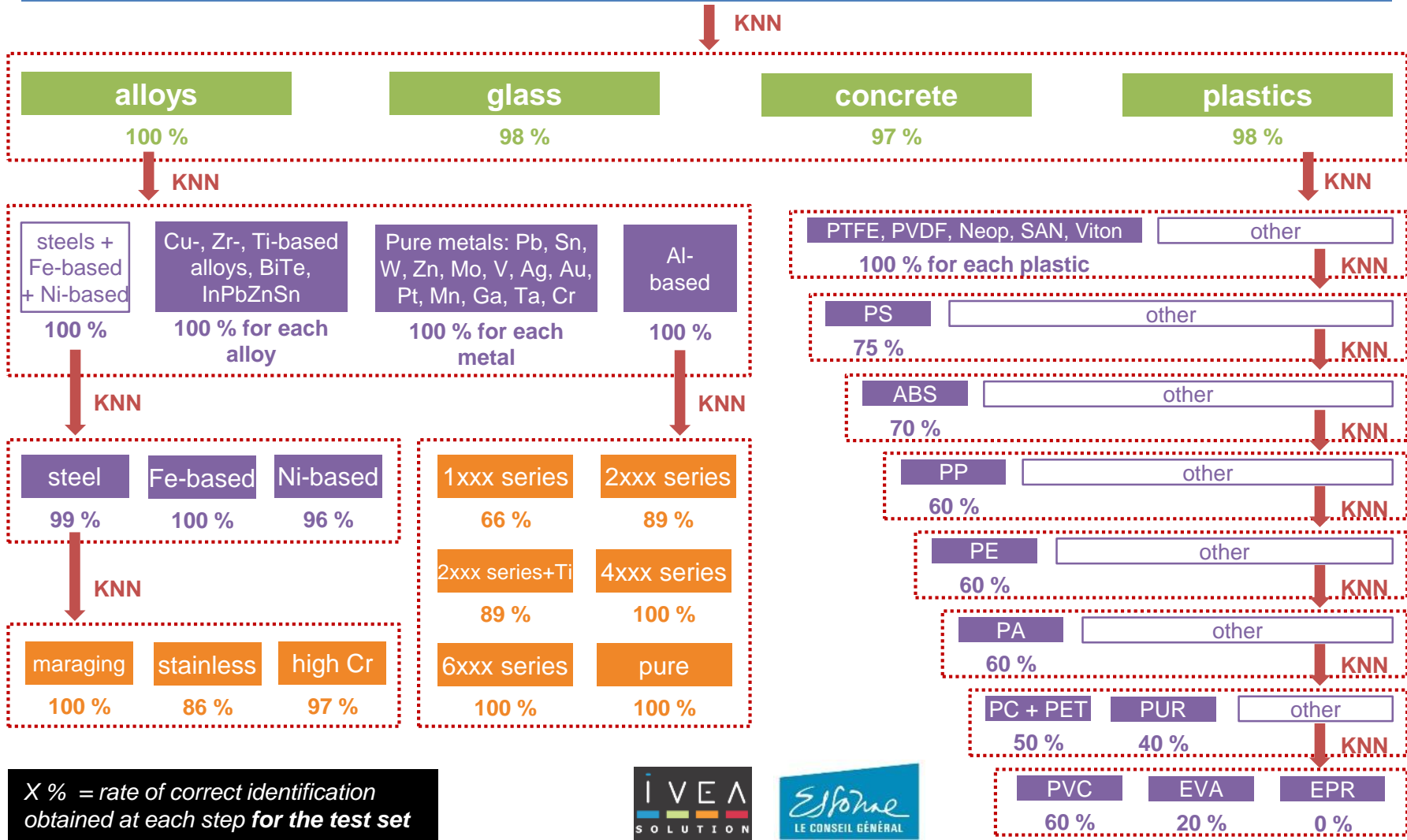
**Sampling characteristics :**  
Depth ~ 1  $\mu\text{m}$  / laser shot  
Analyzed Area ~ (200  $\mu\text{m}$ )<sup>2</sup>  
Ablated mass ~1 ng / laser shot

## Examples of data treatment

*Single-shot, low resolution spectra (portable system)*



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



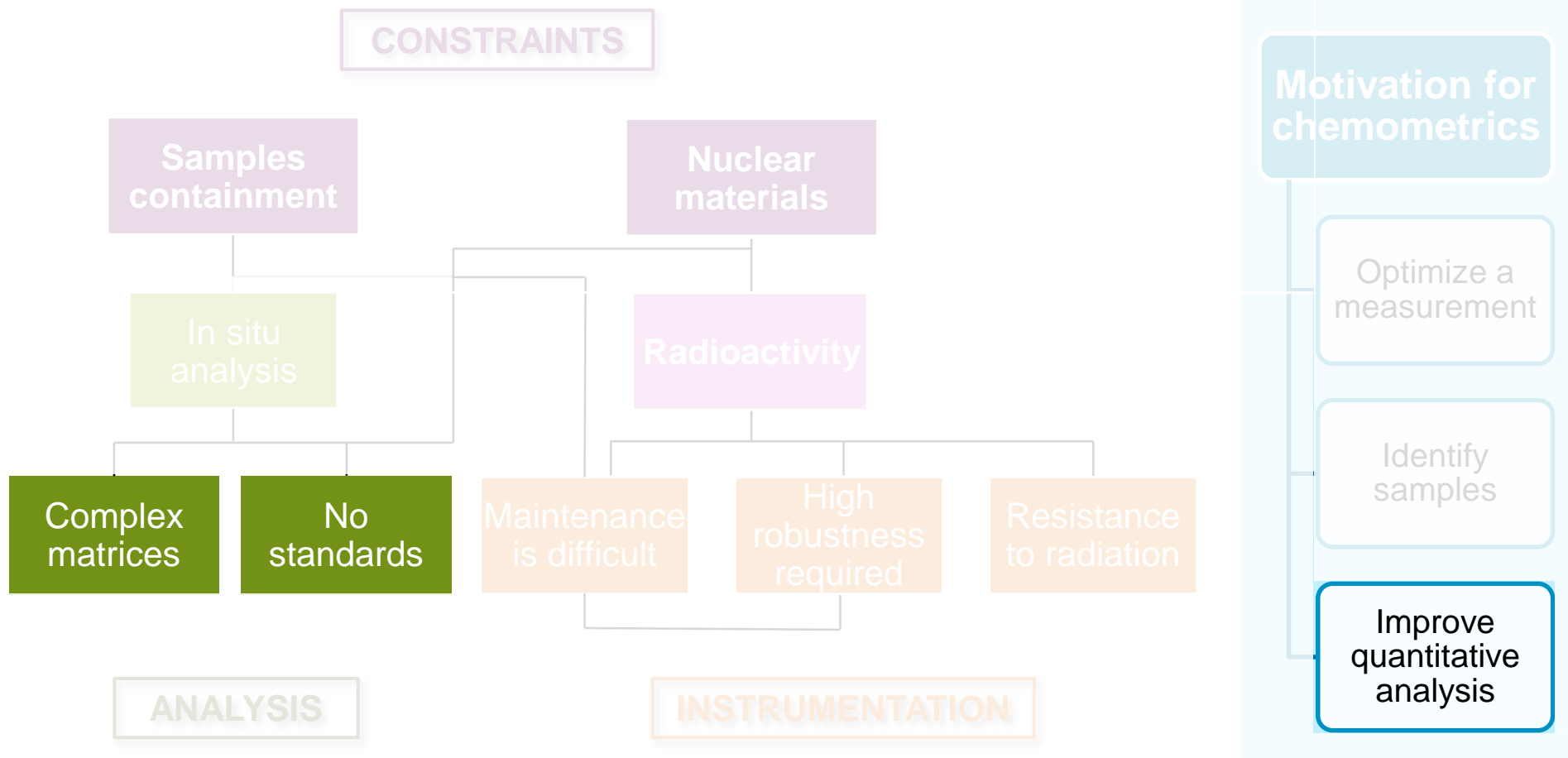
X % = rate of correct identification obtained at each step for the test set





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

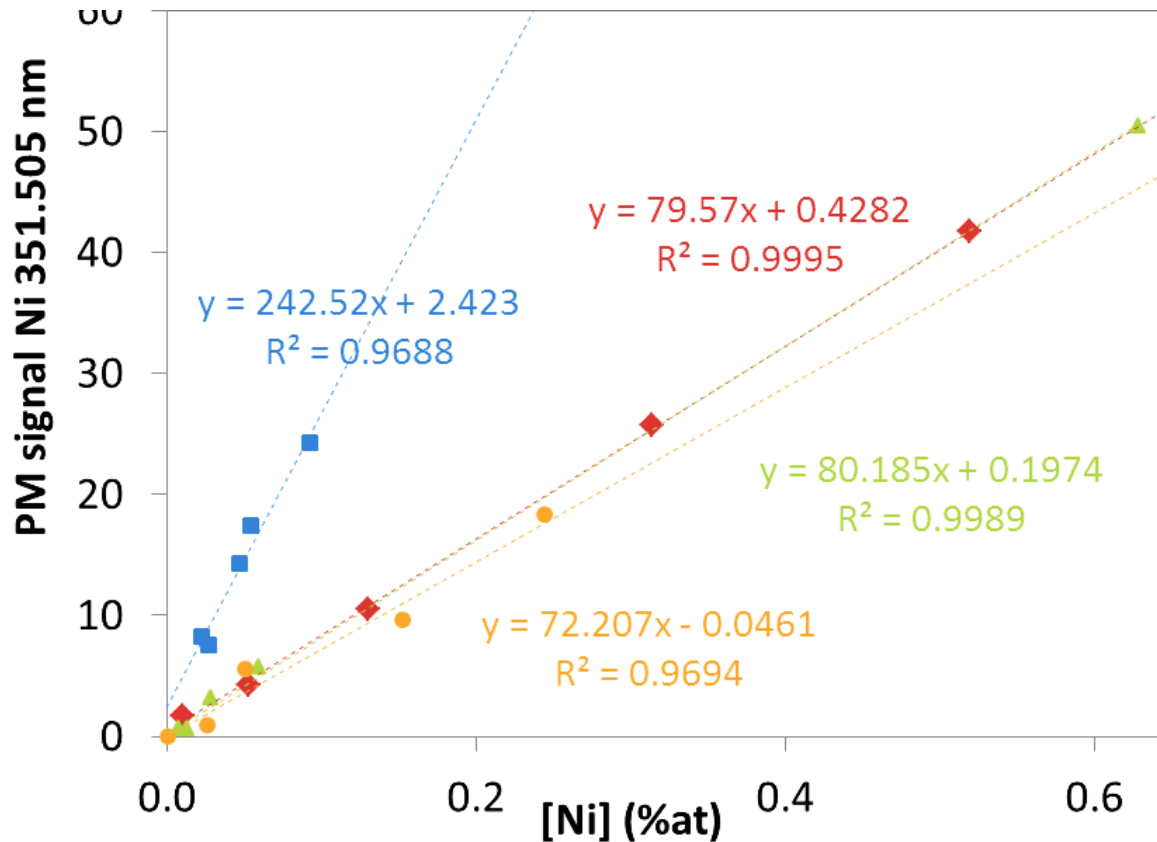


Calibration of [Ni] in...

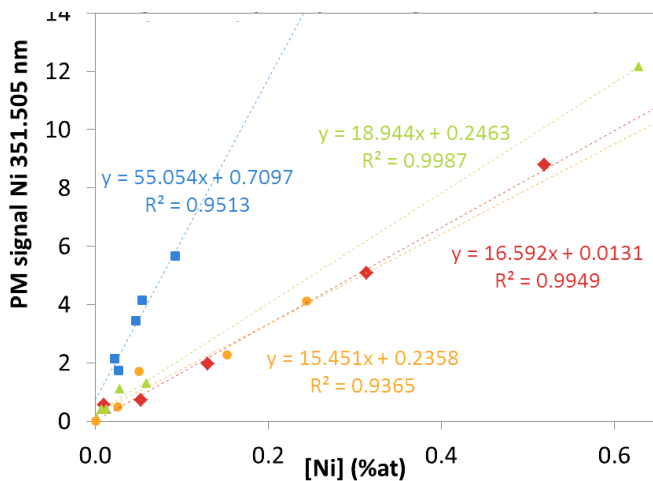
- ◆ Cu matrix
- ▲ Ti matrix
- Al matrix
- Zr matrix

Gate delay = 1.5 μs

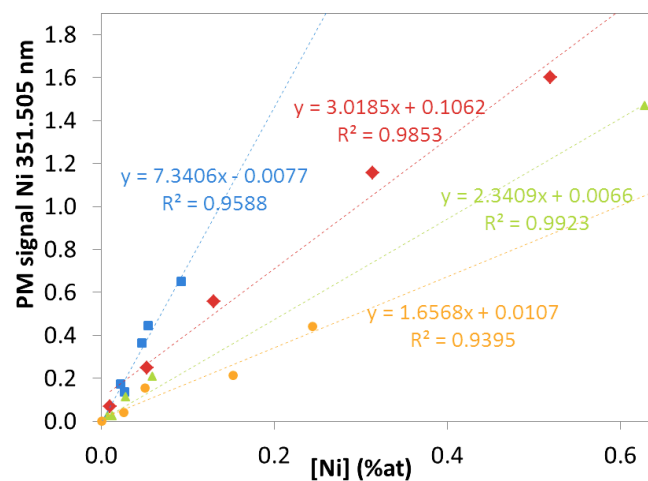
Gate width = 3 μs



Gate delay 1.5  $\mu$ s



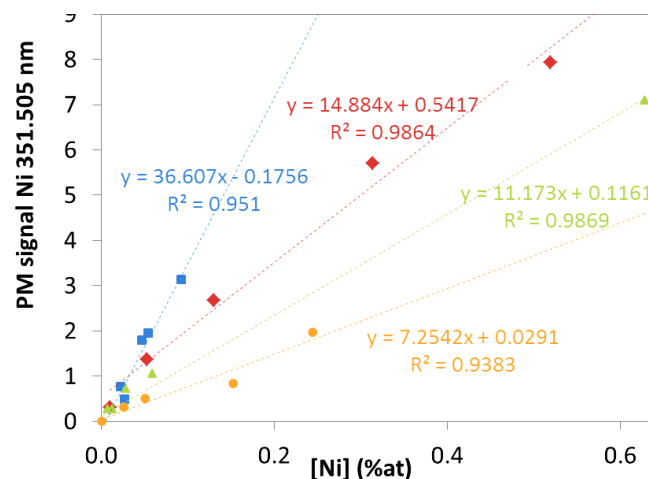
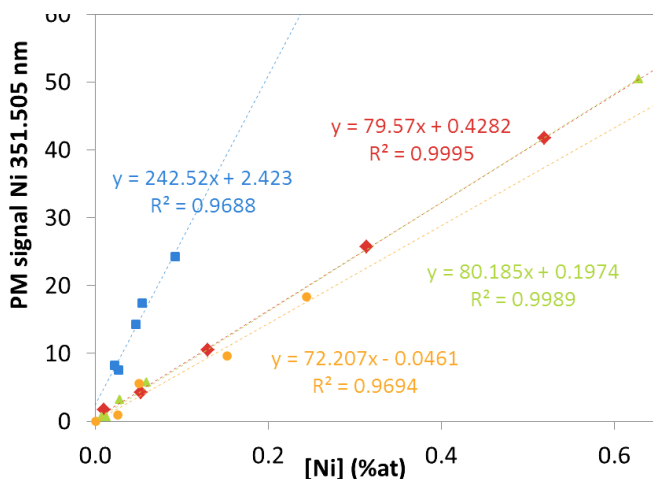
Gate delay 9.5  $\mu$ s



Ni in...

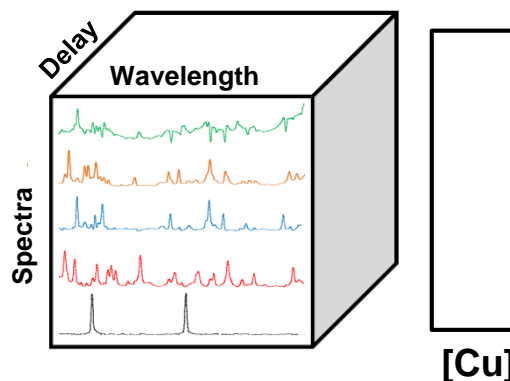
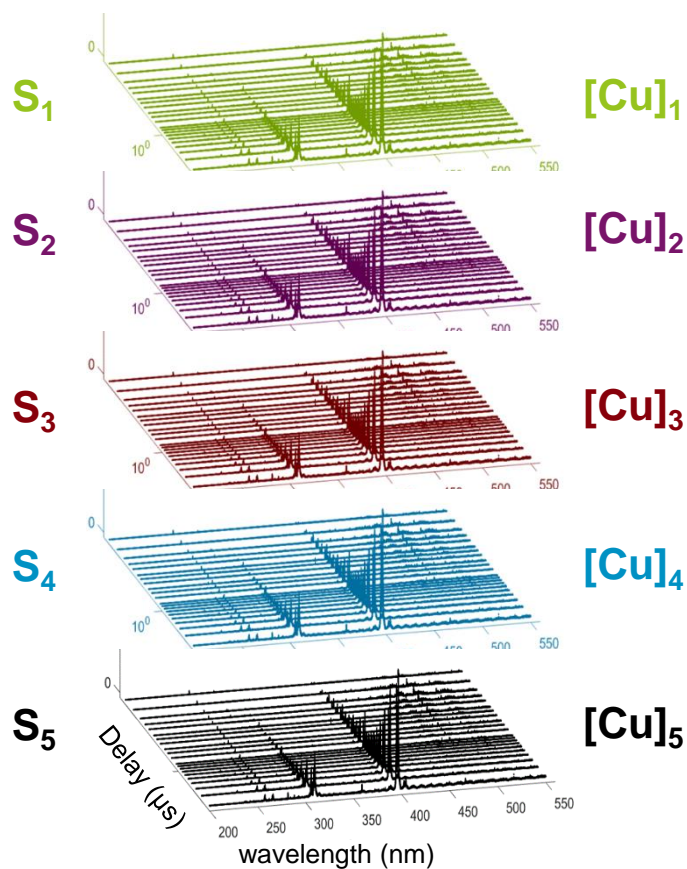
- ◆ Cu matrix
- ▲ Ti matrix
- Al matrix
- Zr matrix

Gate width 3  $\mu$ s

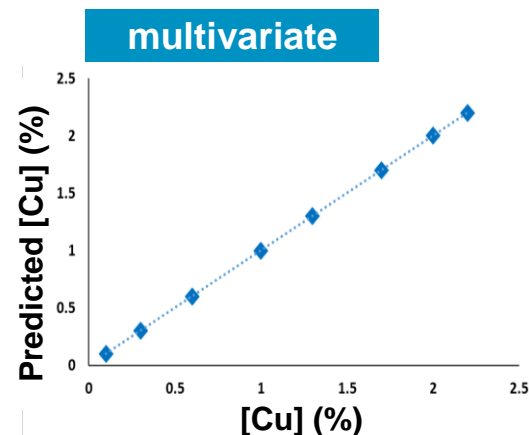
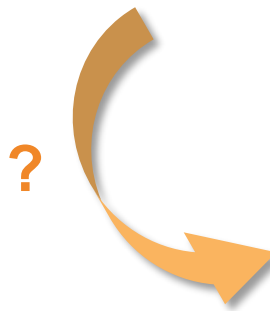


What if we take into account the temporal dimension of the LIBS signal?

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

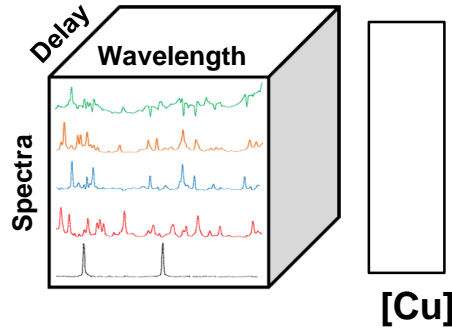


*Maria El Rakwe PhD thesis*

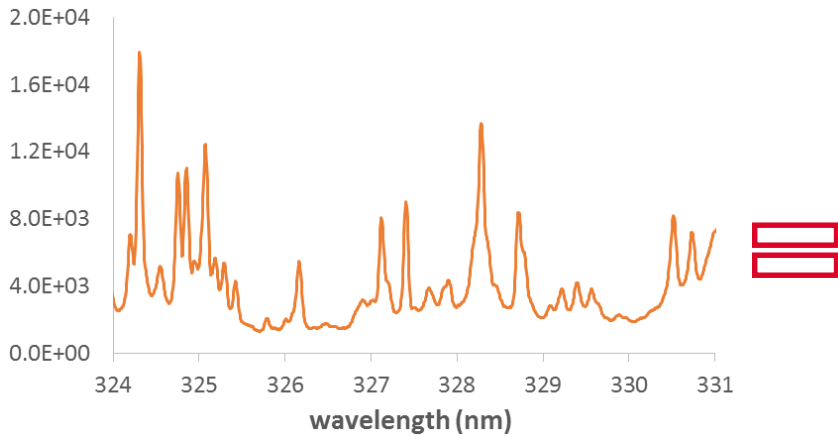




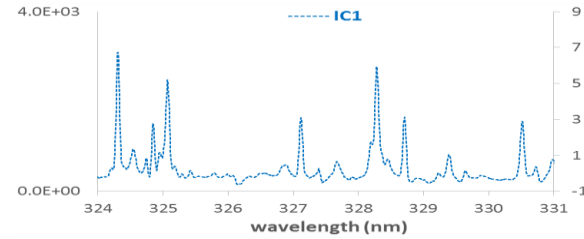
Dataset = calibration of [Cu] in Ni



For each given delay and [Cu] concentration:

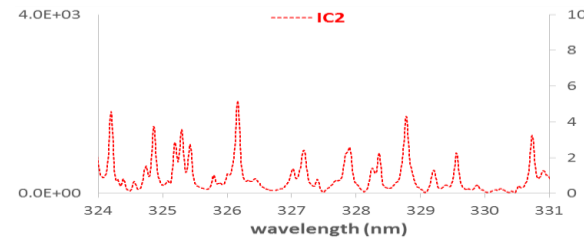


$a_1 \times$



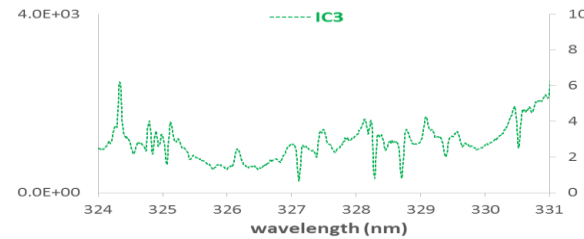
Mostly Ni (+ Cr)

$a_2 \times$



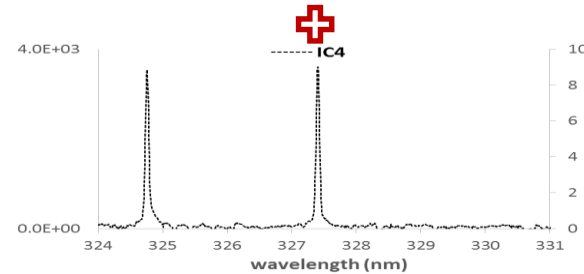
Mostly Ti (+ Cr)

$a_3 \times$

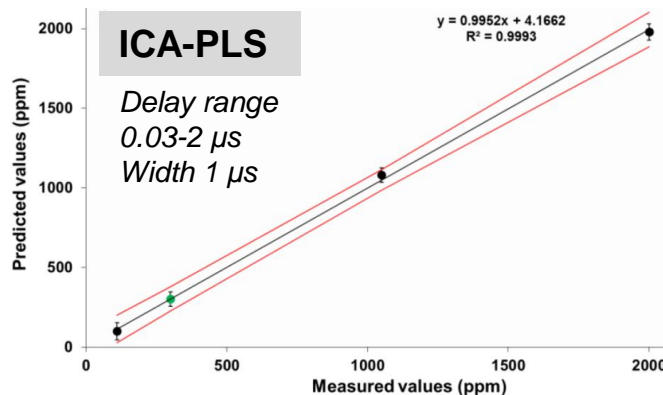
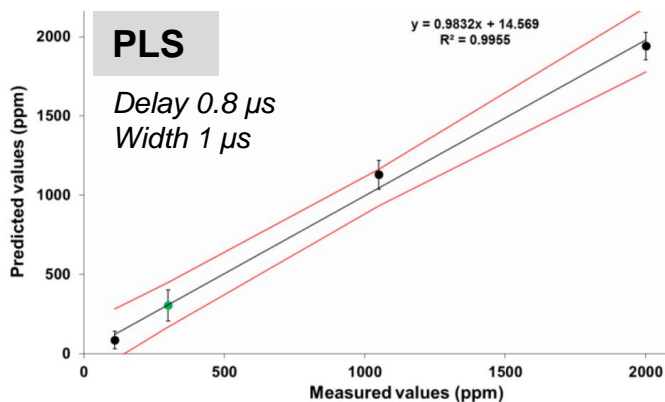
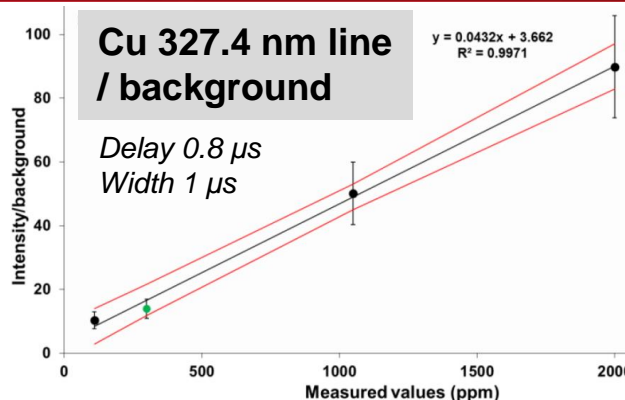
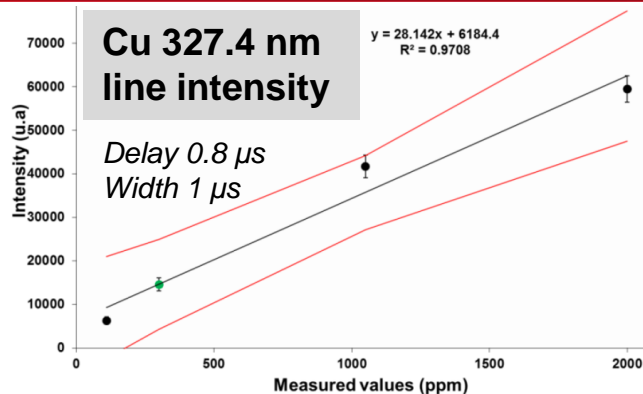


Continuum + most intense reversed Ni lines

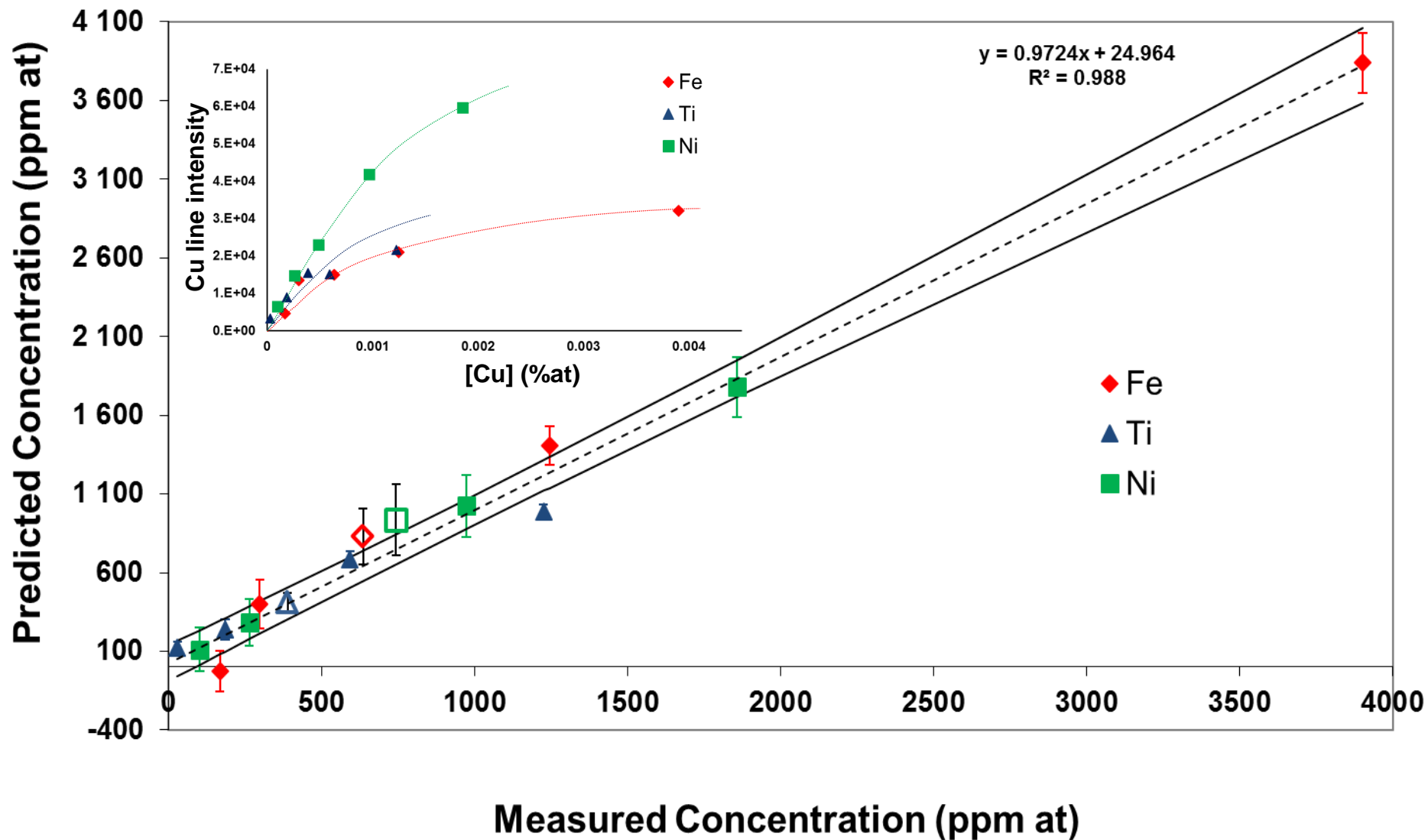
$a_4 \times$



Cu



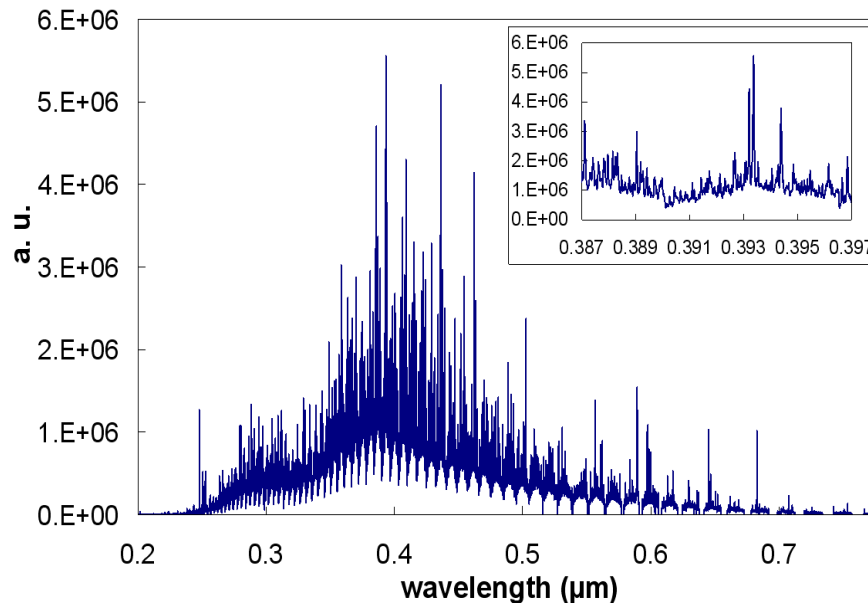
Calibration	Trueness	Precision	LOD (ppm)
Cu line intensity			900
Cu line / background			400
PLS			350
ICA-PLS			180



## Elemental analysis in nuclear environment:

- Strong instrumental constraints
- Complex spectra
- Few (sometimes no) standards available
- Approaches based on Boltzmann modeling (CF-LIBS,  $C\sigma$ , 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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Thomas Vercouter

# Thank you for your attention!

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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.