

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

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## Ceaden





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

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## Ceaden NUCLEAR ENVIRONMENT





FROM RESEARCH TO INDUSTRY

## Ceaden NUCLEAR ENVIRONMENT





FROM RESEARCH TO INDUSTRY

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## Ceaden NUCLEAR ENVIRONMENT











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## EXPERIMENTAL DESIGNS TO IMPROVE THE ROBUSTNESS OF THE ANALYSIS



#### is non-linear δ td Factors are strongly **coupled** sample

**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

**OPTIMIZATION OF INSTRUMENTAL** 

Ceaden PARAMETERS USING A DESIGN OF

detection

gate delay (t<sub>d</sub>)

Φ

**EXPERIMENTS** 



Taking into account that system The relation between factors and responses

Signal repeatability

responses

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#### **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 INSTRUMENTALCeaderPARAMETERS USING A DESIGN OFEXPERIMENTS

## **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



## MATERIALS IDENTIFICATION BY ONSITE LIBS SYSTEMS



## Inventory before nuclear decommissioning Control of contamination Control of contamination

Identification of wastes prior to treatment / sorting

### 2 technologies:

Portable

Fibered

**Motivation:** 





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











## Ceaden ONSITE IDENTIFICATION OF MATERIALS

15500-15000-14500-14000-13500-13500-12500-12500-12500-11500-

11000



#### **Examples of data treatment**

Single-shot, low resolution spectra (portable system)







## ONSITE IDENTIFICATION OF MATERIALS







ANALYSIS

INSTRUMENTATION

FROM RESEARCH TO INDUSTRY

## Ceaden calibration by LIBS



### Calibration of [Ni] in...



#### • Zr matrix

Cu matrix

- Gate delay =  $1.5 \ \mu s$
- Gate width =  $3 \mu s$



## Ceaden EFFECT OF TIME RESOLUTION ON CALIBRATION LINES





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## Ceaden 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?



## Ceaden A PRACTICAL EXAMPLE





## CALIBRATION LINE VS PLS VS ICA-PLS





	Calibration	Trueness	Precision	LOD (ppm)	
	Cu line intensity			900	
	Cu line / background			400	
	PLS			350	
Sirven et al	ICA-PLS			180	can help   PAGE

## Ceaden MULTI-MATERIALS QUANTITATIVE ANALYSIS





### Measured Concentration (ppm at)

## Ceaden 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!

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## eaden Abstract



Elemental analysis in the nuclear field is essential in a number of situations, from the frontend 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.