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Interpreting the temporal emission of LIBS plasmas using advanced chemometric methods

<u>M. El Rakwe¹</u>, D.N. Rutledge², R. Saad¹, D. L'Hermite¹, G. Moutiers¹, J.-B. Sirven¹

1 CEA, DEN, DANS, DPC, SEARS, LANIE, F-91191 Gif-sur-Yvette, France.

2 AgroParisTech, UMR 1145 IngénierieProcédés Aliments, 16 rue Claude Bernard, 75005 Paris, France.

maria.elrakwe@cea.fr





Results of multivariate analysis of time resolved LIBS spectra

Conclusion



CONTEXT

LIBS measurements consist of spectrally- and time-resolved analysis of atomic and ionic lines emitted by the plasma.

Spectroscopic measurements: gate delay and width are fixed

- Complex spectra (elements such as Fe, Ni, Cr, Ti, Zr, U, Pu ...).
- Unknown materials.
- Self -Absorption.



Kinetics studies: spectral lines are selected according to certain criteria





SPECTRAL DIMENSION

EXPLORE SIMULTANEOUSLY THESE TWO FACTORS USING CHEMOMETRIC METHODS

TEMPORAL DIMENSION

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CONTEXT

Chemometrics is the combination of mathematical, statistical, and other logic-based methods to efficiently manage and interpret data.



The **components** matrix is the source signal matrix.

The **scores** is the sample-specific information; namely the amount of the component vector in each sample.

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CONTEXT

Time-resolved spectra were treated with 3 chemometric methods:

Principal component analysis (PCA) -> maximise variance criterion

Mean Field-Independent Components Analysis(MF-ICA) \longrightarrow the most independent and least Gaussian possible sources. Non-negativity can be applied on both signal and scores.



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Data: simulation of 50 spectra with 2 analyte lines and a matrix line. The analyte concentration is variable (10 samples per concentration).





The scores are the amount of the component vector in each sample.

Ceaden MULTIVARIATE ANALYSIS OF TIME RESOLVED LIBS SPECTRA

Principle and methodology



 Application to physical interpretation of LIBS data and to analytical optimization of the measurement DE LA RECHERCHE À L'INDUSTRIE

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EXPERIMENTAL



Data: pure AI sample spectra, gate delay 0.2 to 15 µs, 50 acc. laser shots

•	Laser Nd:YAG @	266 nm
•	Pulse duration:	5 ns
•	Frequency:	20 Hz
•	Energy:	3 mJ
•	Beam diameter:	50 µm
•	Irradiance:	30 GW/cm ²
•	Focal length:	25 cm
•	Pressure	Atm pressure.
•	Ambient gas:	Air, N ₂ Ne, Ar/Ne

Aluminium Sample (TechLab « 198f »)		
Element	Proportion	
AI	99.99%	
Cu	0.005%	
Si	0.002%	
Fe	0.001%	

To validate the potential of the three chemometric methods selected for the physical interpretation of the temporal evolution of the spectra.



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The ion population decreases with time; this is due to the recombination with the electrons to form neutral atoms.

Reference method (Kinetics)



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The scores of the three methods follow a similar trend to that of the intensities of Al ionic line

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At shortest time, the reference measurement is dominated by the continuum. While the scores obtained by the two methods give a result with more physical meaning.

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COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

ICA and MCR look for components with physical sense (pure species) while the PCA looks for a component that has a mathematical sense. Furthermore, by applying the constraint of non-negativity MCR-ALS and MF-ICA give a more physical sense to our results.

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

Species populations are not independent. The MCR-ALS technique gives the clearest, directly interpretable results, which is validated by comparison to the univariate measure.

Ceaden MULTIVARIATE ANALYSIS OF TIME RESOLVED LIBS SPECTRA

- Application to physical interpretation of LIBS data and to analytical optimization of the measurement
- Retrieving physical information on the plasma.

• Optimizing the detection of an analyte.



Retrieving physical information on the plasma from the analysis of time-resolved spectra by MCR-ALS

Dataset: time-resolved spectra of pure AI in air and in neon



Al-Ne 1 0.8 1 0.8 0.6 0.4 0.2 0.1 0.2 0.1 10^{-1} 10^{0} 10^{0} 10^{1} Al⁺ emission lasts longer in Ne than in air \rightarrow higher Al⁺/Al in Ne

→ From the Saha-Boltzmann law, the electron density is probably lower in Ne than in air

Consistent with the ionization potential of Ne > ionization potential of O and N

MCR-ALS analysis can be physically interpreted to extract information on plasma features (electron temperature and density), and on kinetics of ionic recombination and molecules formation

Optimizing the detection of an analyte

Dataset: time-resolved spectra of an Al alloy with 10 % Si



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Si lines are detected in components 1 and 2, with a S/B ratio higher in C2 C2 scores are maximum between 0.3 and 0.5 μ s \rightarrow best temporal parameters for Si analysis Identical results are obtained with a 10 times less concentrated alloy (1 % Si)

MCR-ALS can be used to optimize the detection gating for quantitative analysis

Optimizing the detection of an analyte in a complex matrix

Dataset: time-resolved spectra of a Ti alloy (88.2 % Ti, 4.1 % V)



Application of the same approach to the case of complex spectra Detection of V in a Ti matrix Optimum signal between 0.8 and 1.5 µs

Multivariate methods are particularly interesting to develop for complex spectra, for which a parametric optimization approach is not always suitable Ceaden

CONCLUSION

In LIBS, chemometrics have been extensively applied for ~ 20 years, to perform samples identification (PCA, SIMCA, PLS-DA, ANN...) or quantitative measurements (PCR, PLS, ANN...). Innovative approach of chemometric methods for physical understanding. These methods can be used to describe time-resolved spectra and to understand the physical mechanisms. They can be used for analytical optimization.



Thank you for your attention!

maria.elrakwe@cea.fr

Commissariat à l'énergie atomique et aux énergies alternatives Centre de Saclay | 91191 Gif-sur-Yvette Cedex

Etablissement public à caractère industriel et commercial | R.C.S Paris B 775 685 019

Direction de l'énergie nucléaire Direction déléguée aux activités nucléaires de Saclay Département de physico-chimie 9 Service d'études analytiques et de réactivité des surfaces Laboratoire de développement analytique nucléaire, isotopique et élémentaire