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► **To cite this version:**

M. El Rakwe, D. Rutledge, R. Saad, D. Lhermite, J.-B. Sirven, et al.. Interpreting the temporal emission of LIBS plasmas using advanced chemometric methods. EMSLIBS 2015 - 8th Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy, Sep 2015, Linz, Austria. cea-02491620

HAL Id: cea-02491620

<https://cea.hal.science/cea-02491620>

Submitted on 8 Apr 2020

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Interpreting the temporal emission of LIBS plasmas using advanced chemometric methods

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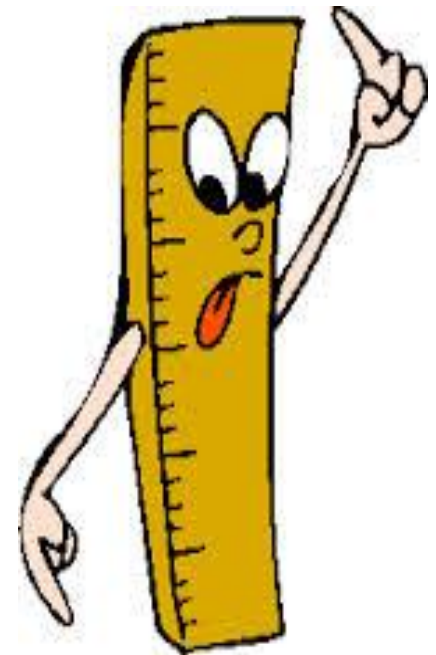
- Context**
- Experimental**
- Results of multivariate analysis of time resolved LIBS spectra**
- Conclusion**

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

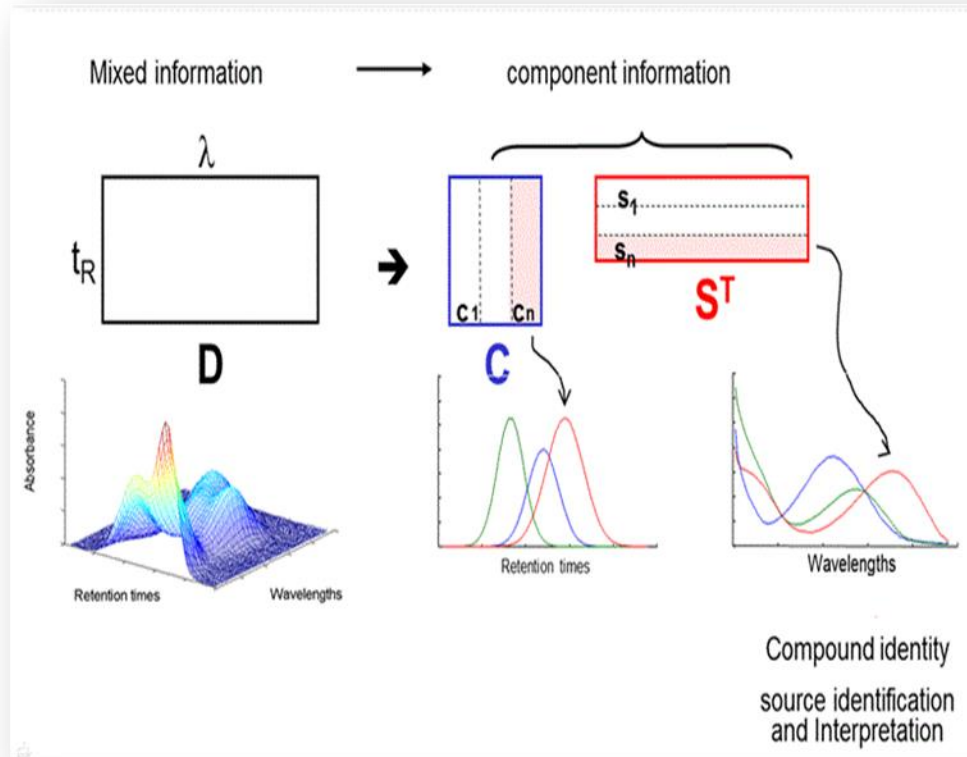
SPECTRAL DIMENSION

**EXPLORE SIMULTANEOUSLY THESE TWO
FACTORS USING CHEMOMETRIC METHODS**



TEMPORAL DIMENSION

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.

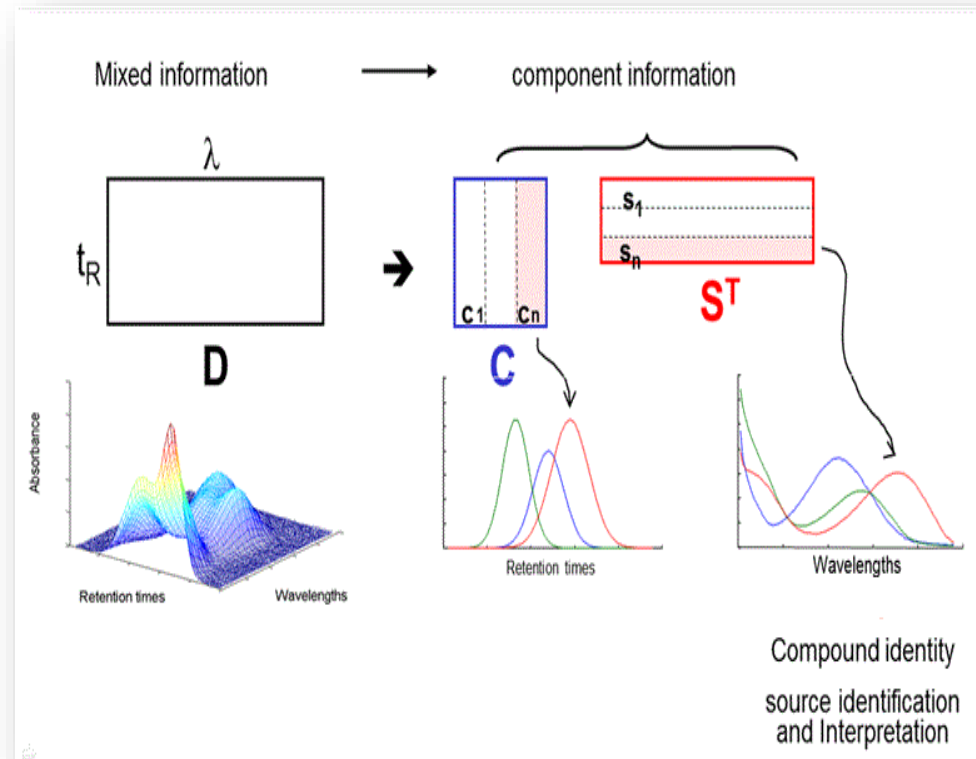
The **scores** is the sample-specific information; namely the amount of the component vector in each sample.

Time-resolved spectra were treated with 3 chemometric methods:

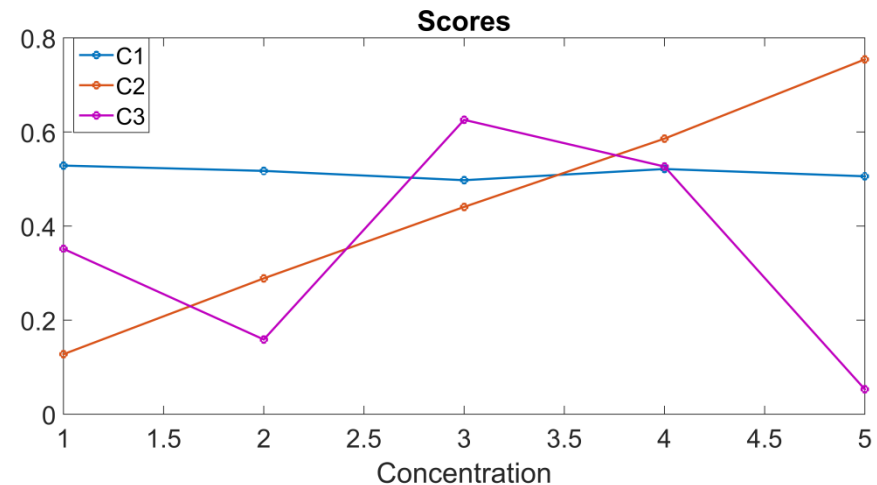
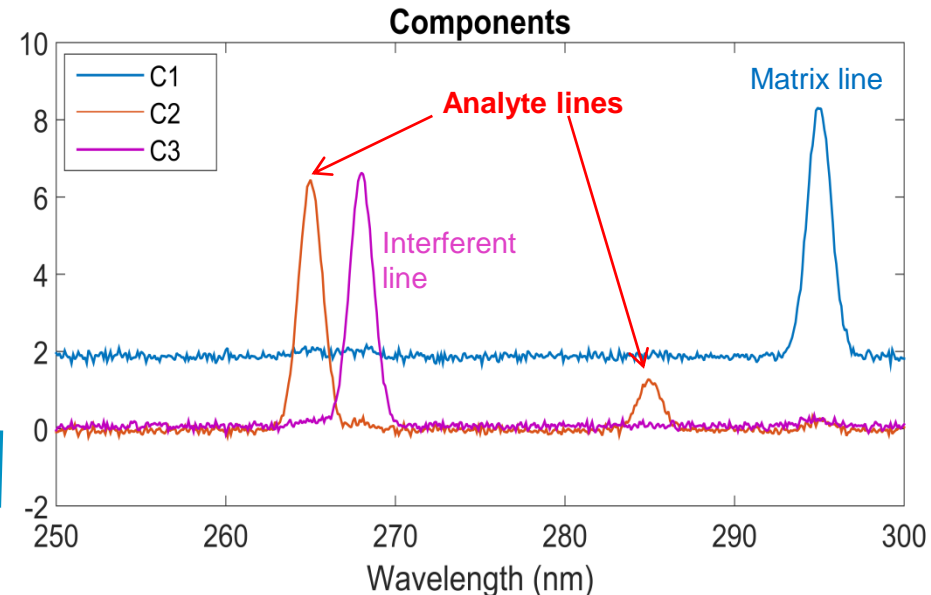
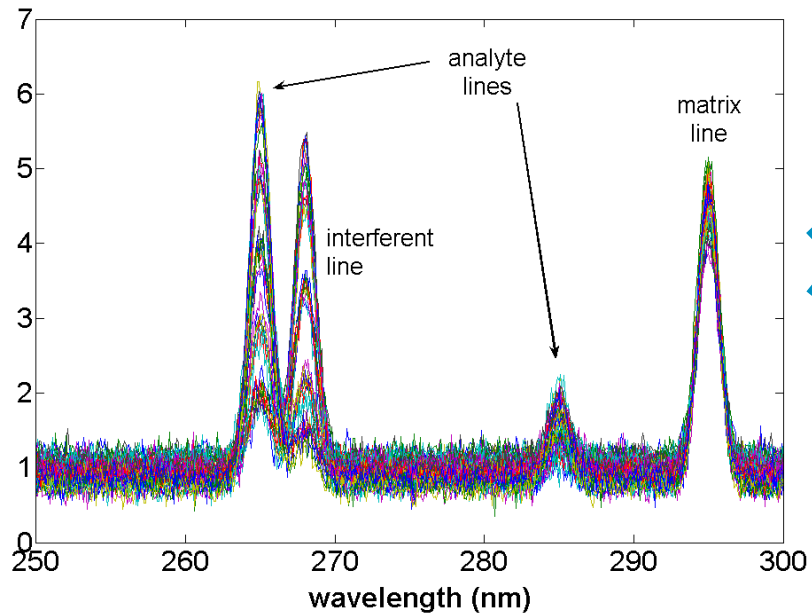
Principal component analysis (**PCA**) → maximise variance criterion

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

Multivariate Curve Resolution-Alternating Least Squares (**MCR-ALS**) → maximize the data variance under a set of constraints.



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



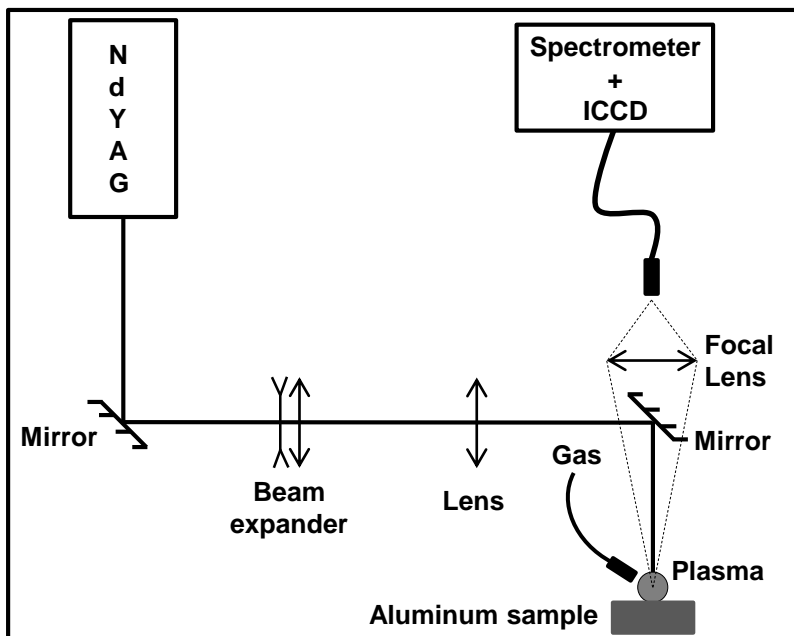
The scores are the amount of the component vector in each sample.

- Principle and methodology



- Application to physical interpretation of LIBS data and to analytical optimization of the measurement

EXPERIMENTAL



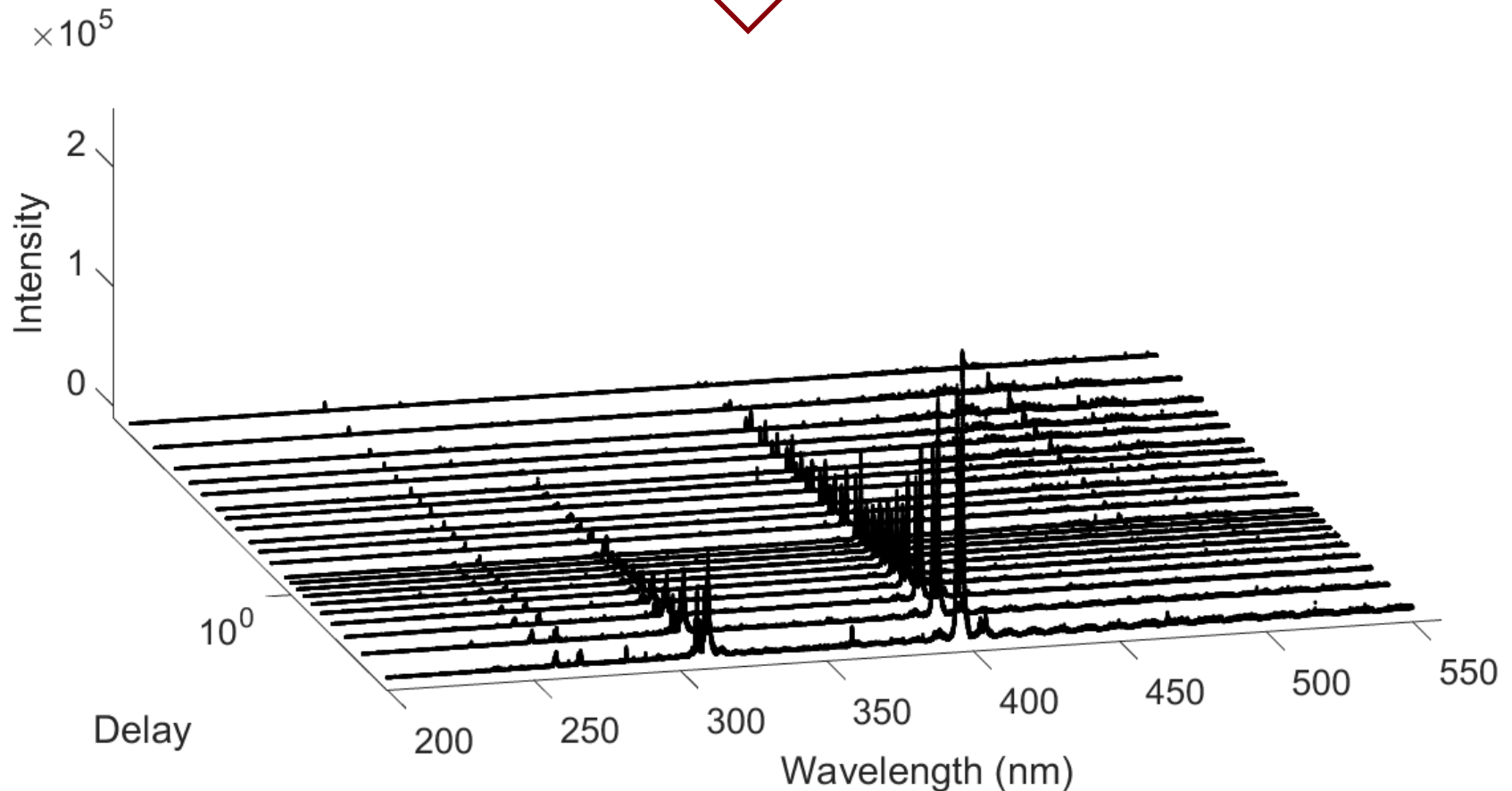
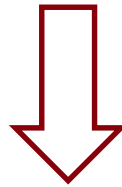
- Laser Nd:YAG @ 266 nm
- Pulse duration: 5 ns
- Frequency: 20 Hz
- Energy: 3 mJ
- Beam diameter: 50 μm
- Irradiance: 30 GW/cm^2
- Focal length: 25 cm
- Pressure: Atm pressure.
- Ambient gas: Air, N_2 , Ne, Ar/Ne

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

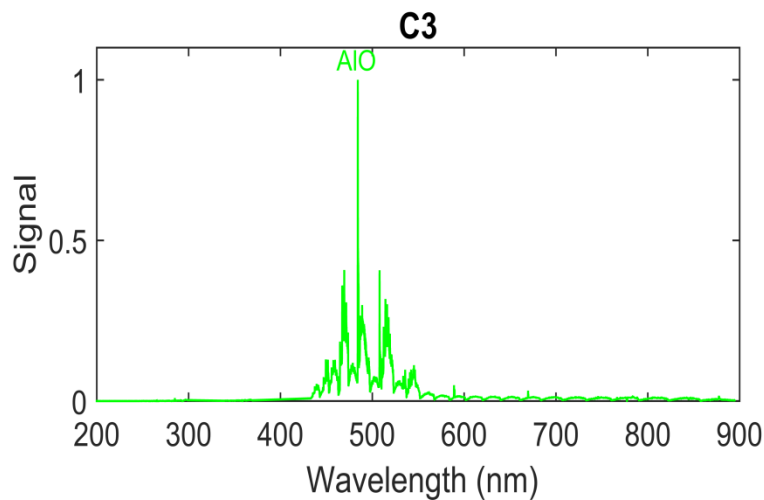
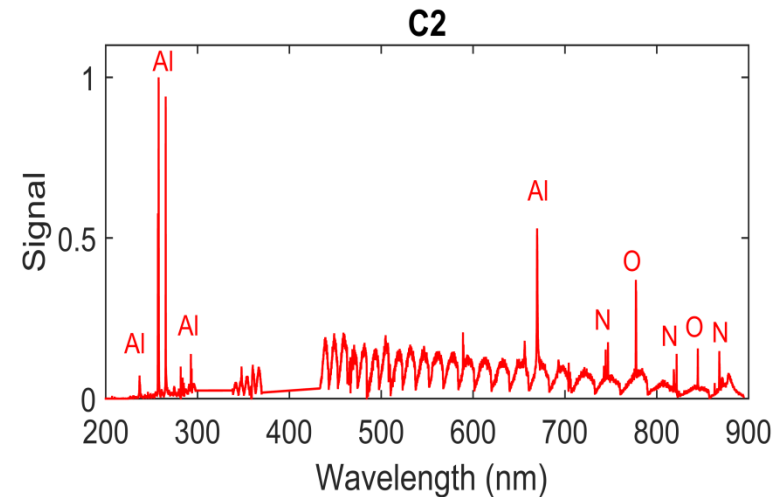
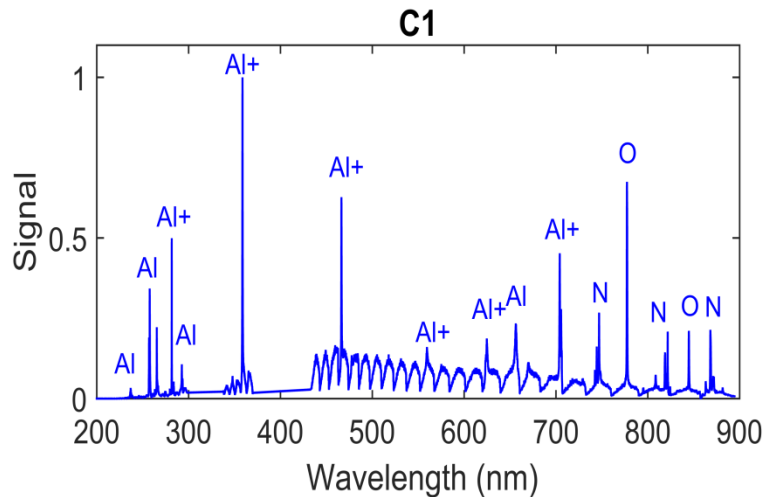
Aluminium Sample (TechLab « 198f »)	
Element	Proportion
Al	99.99%
Cu	0.005%
Si	0.002%
Fe	0.001%

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

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

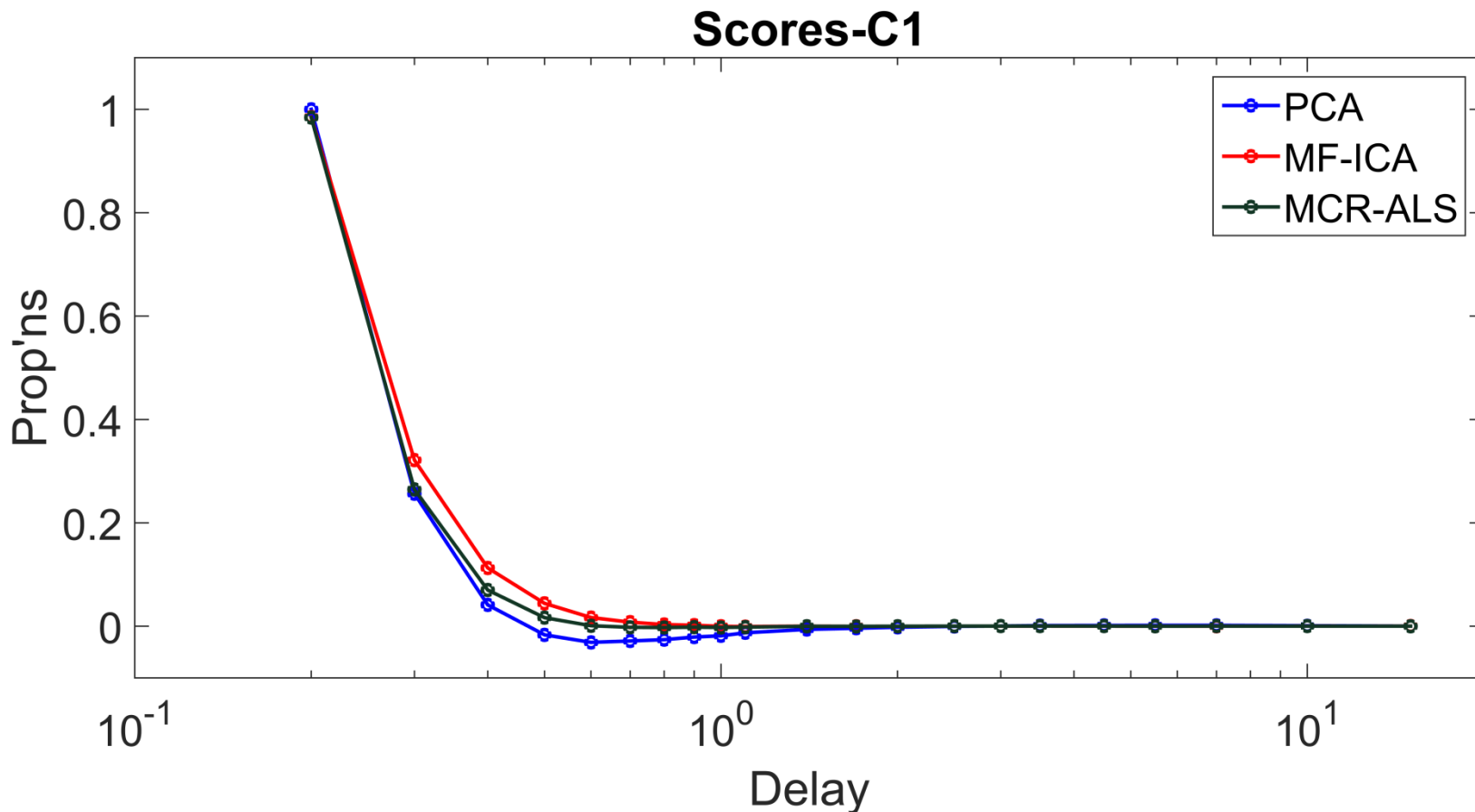


COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



- First component → Ionic lines
- Second component → Neutral lines
- Third component → Molecular bands

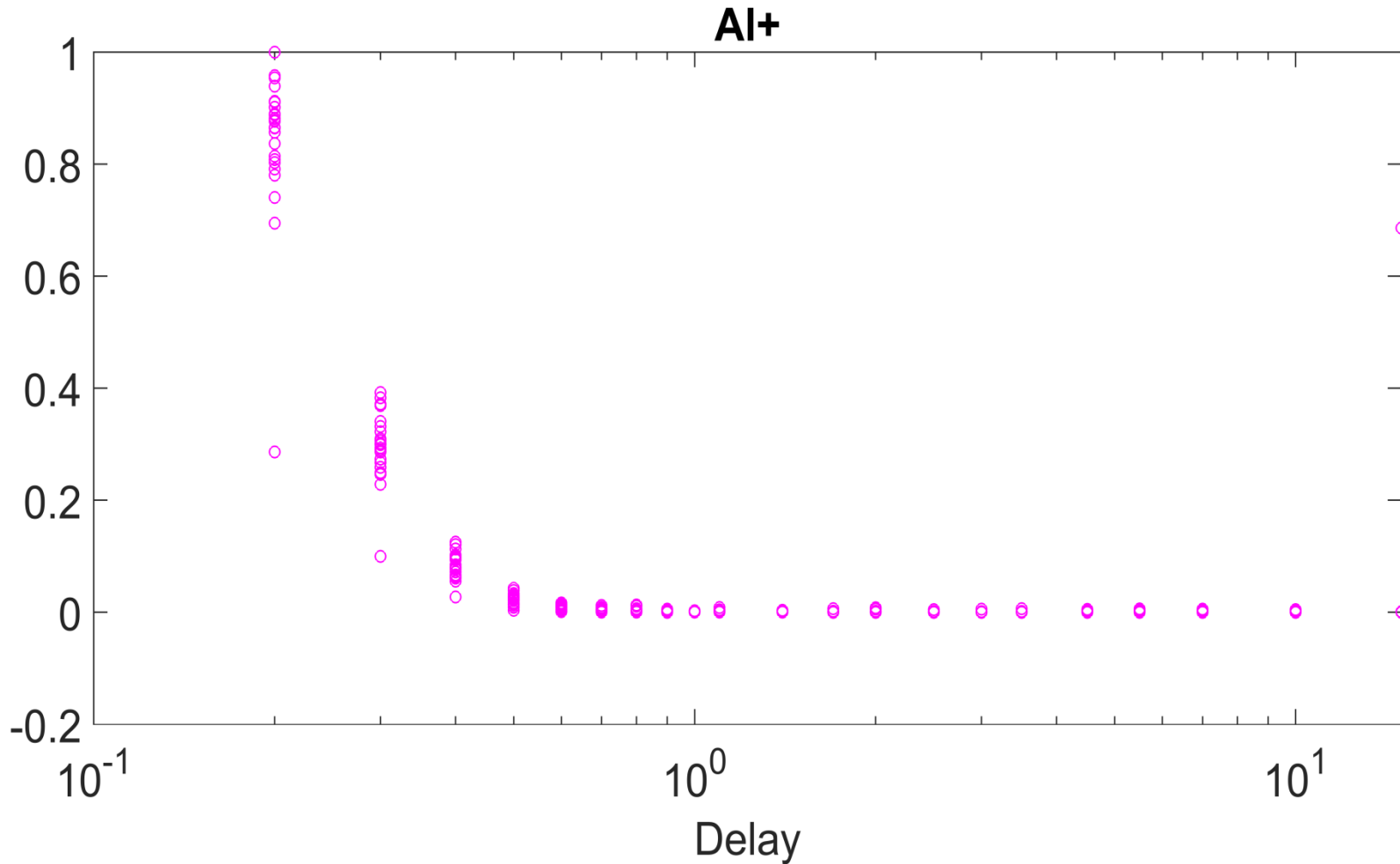
COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



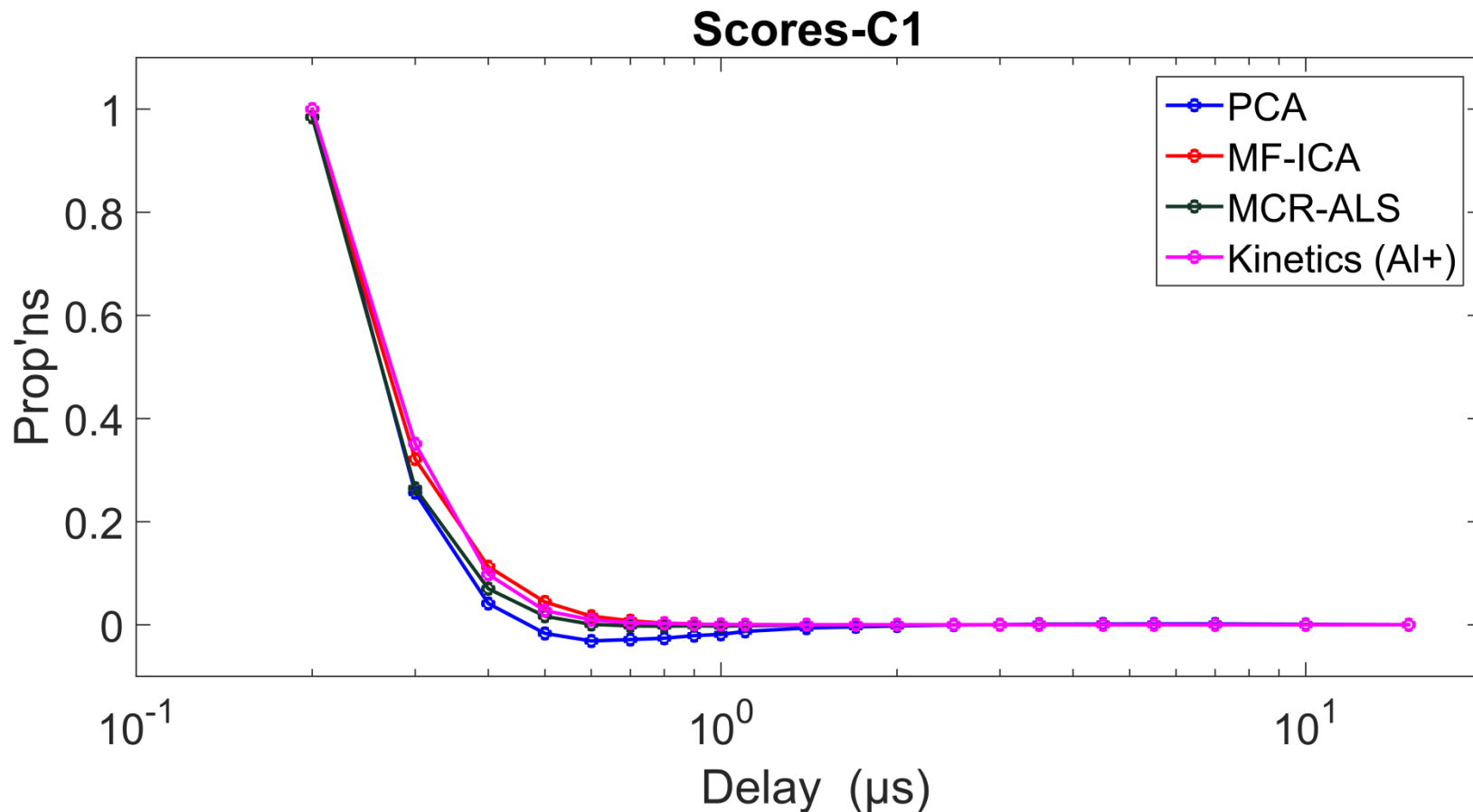
The ion population decreases with time; this is due to the recombination with the electrons to form neutral atoms.

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

Reference method (*Kinetics*)

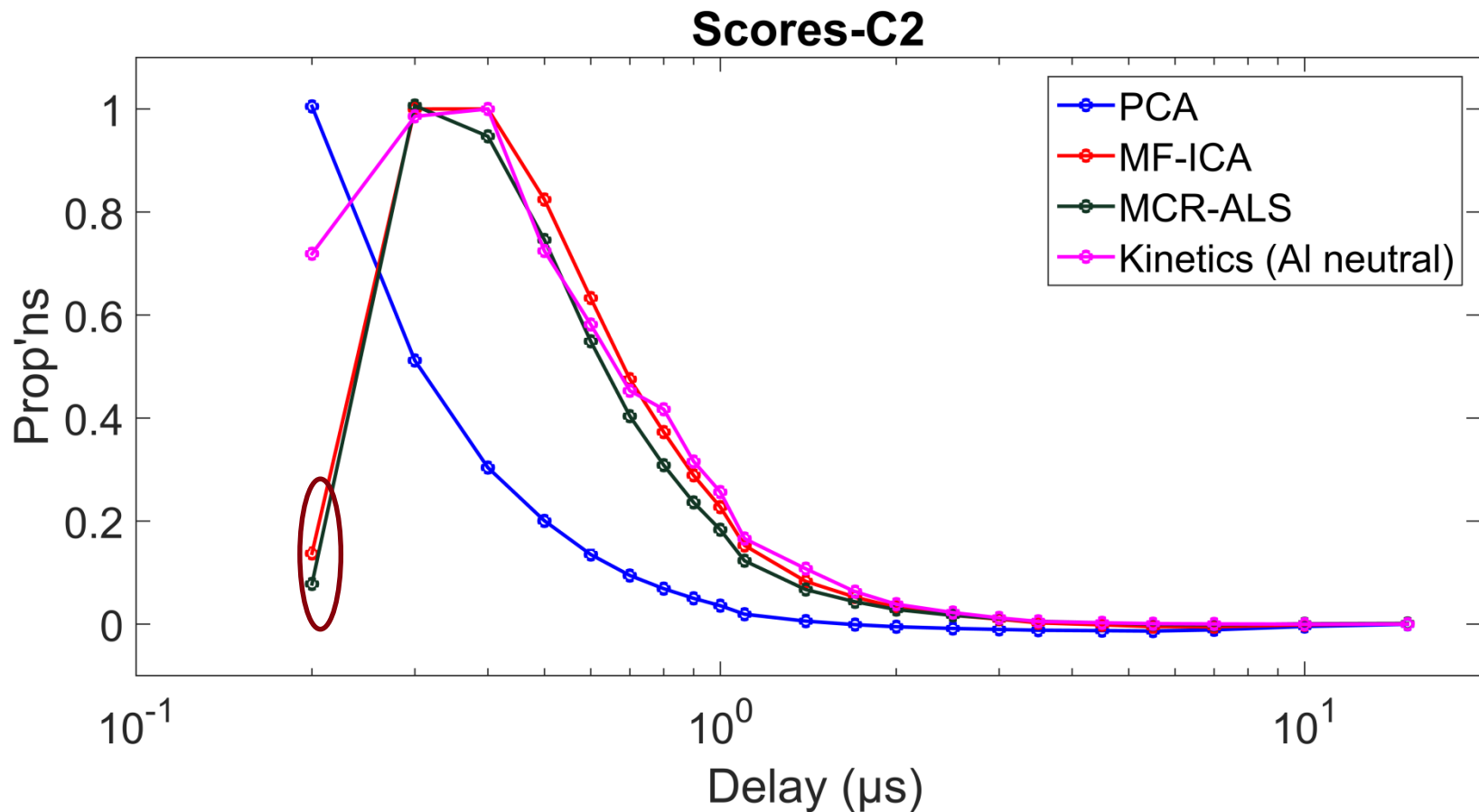


COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



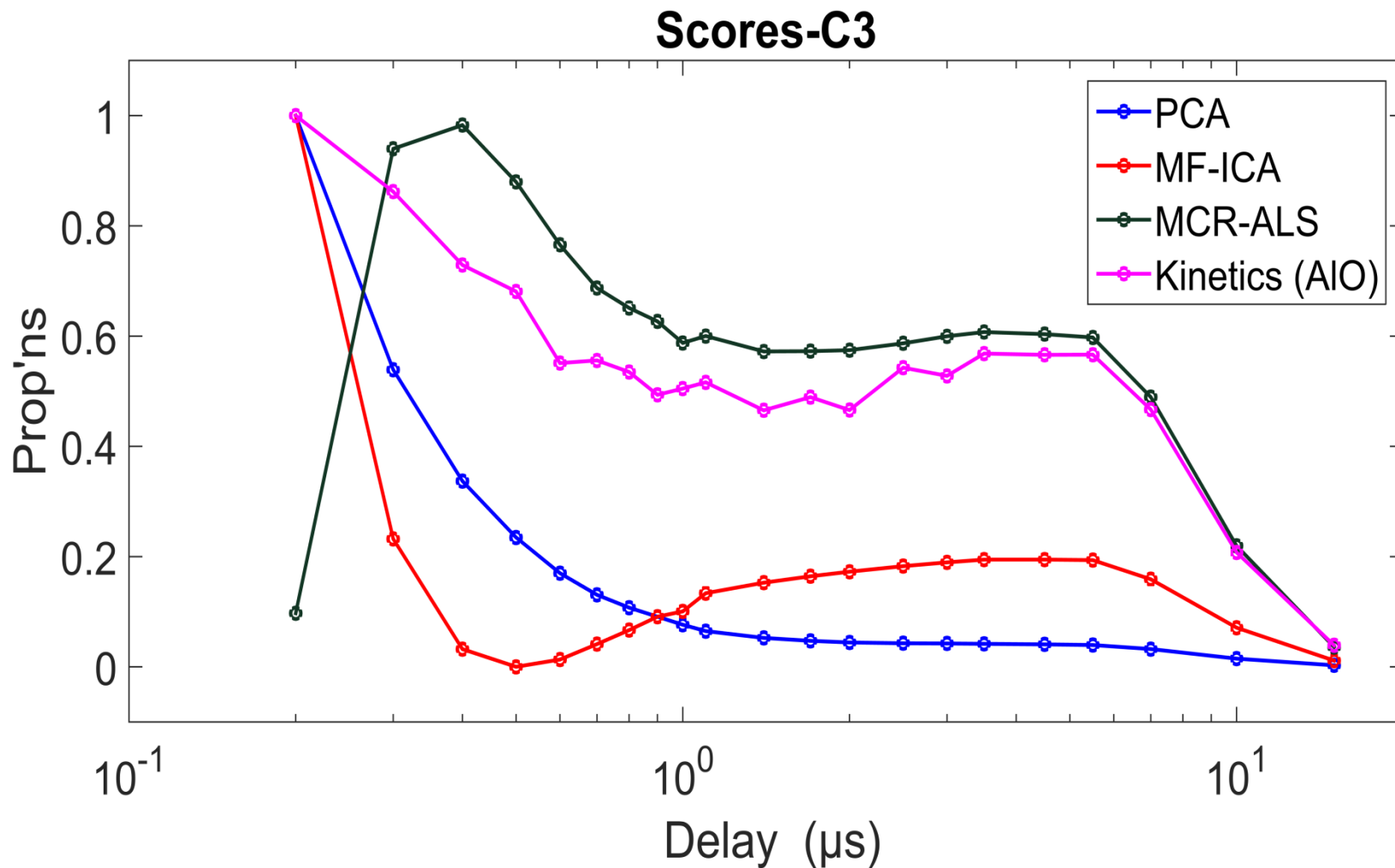
The scores of the three methods follow a similar trend to that of the intensities of Al ionic line

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

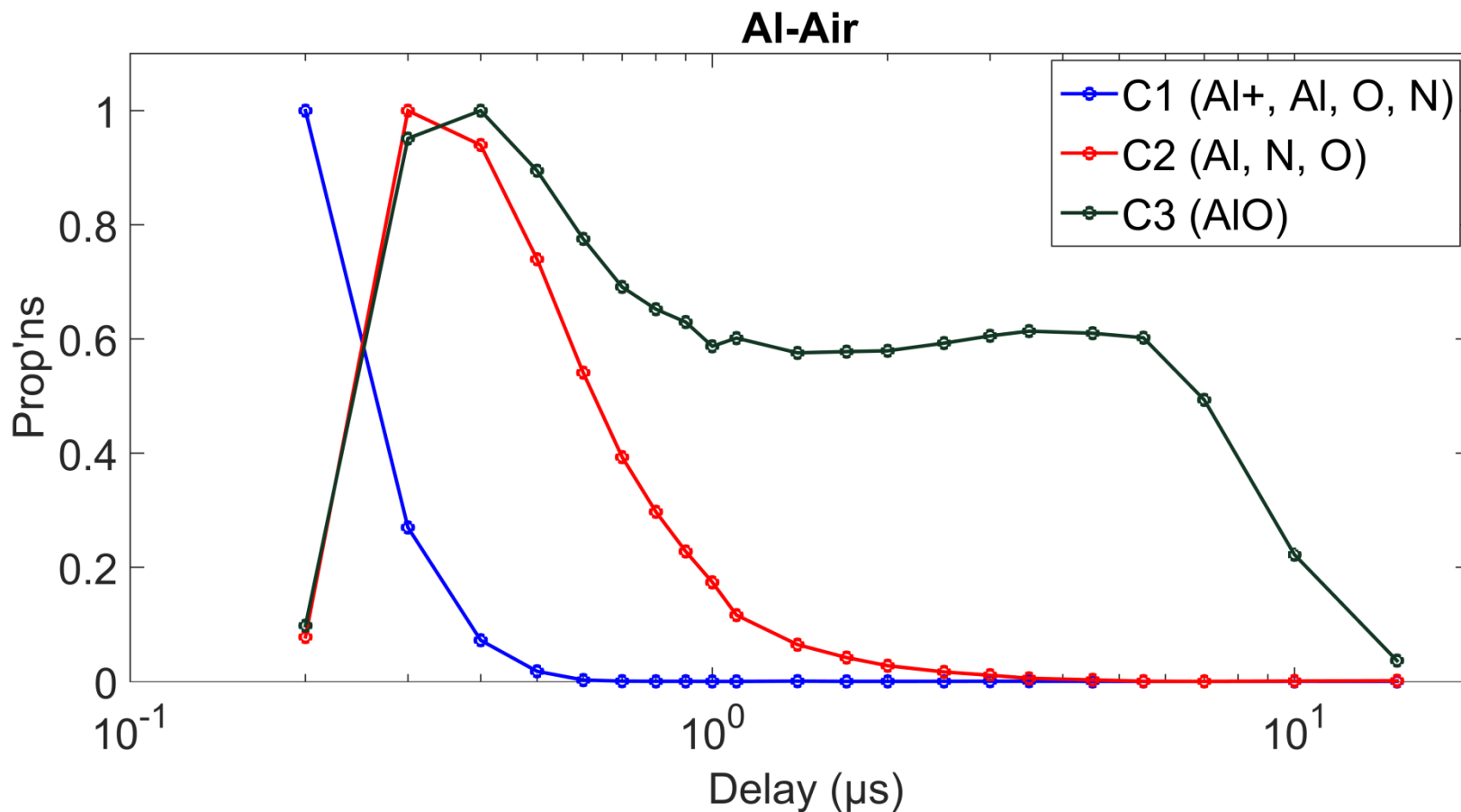


At shortest time, the reference measurement is dominated by the continuum. While the scores obtained by the two methods give a result with more physical meaning.

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



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.

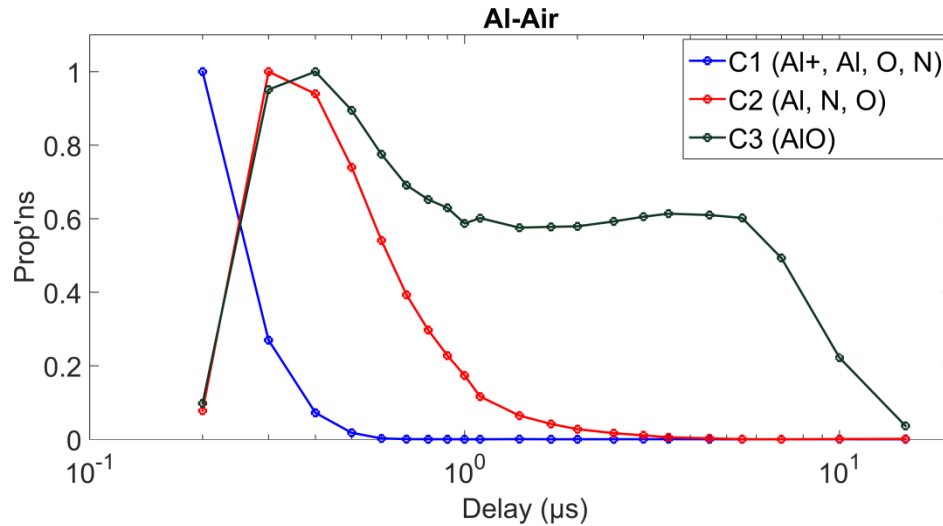


□ Application to physical interpretation of LIBS data and to analytical optimization of the measurement

- Retrieving physical information on the plasma.
- Optimizing the detection of an analyte.



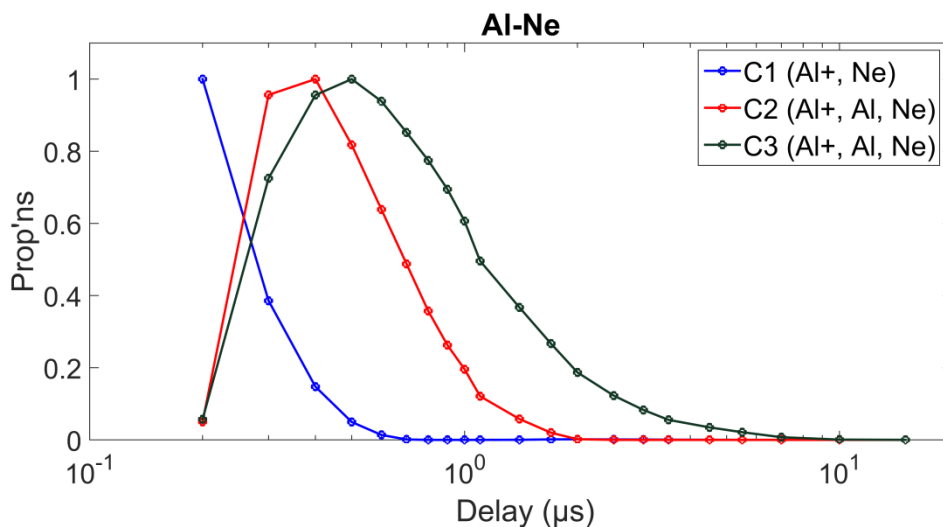
Dataset: time-resolved spectra of pure Al in air and in neon



Al⁺ emission lasts longer in Ne than in air → higher Al⁺/Al in Ne

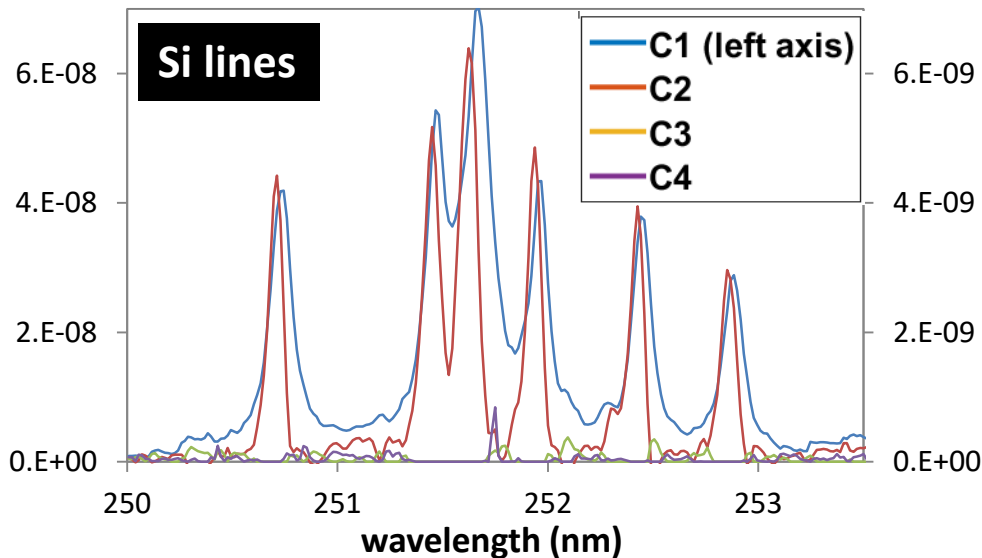
→ From the Saha-Boltzmann law, the electron density is probably lower in Ne than in air

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

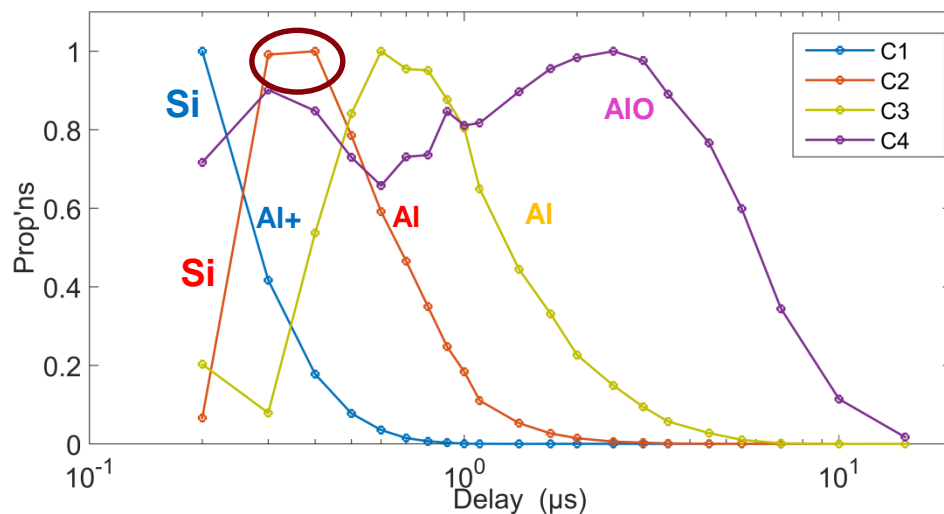
Dataset: time-resolved spectra of an Al alloy with 10 % Si



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 μs \rightarrow best temporal parameters for Si analysis

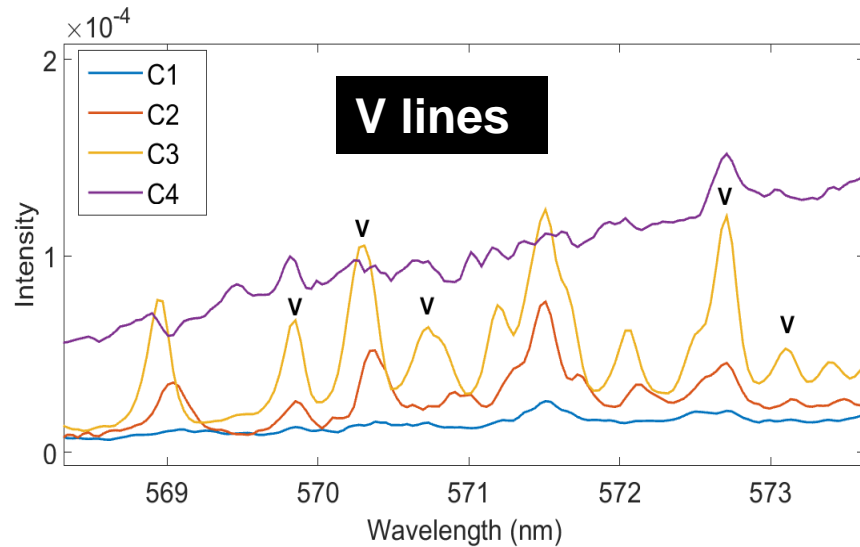
Identical results are obtained with a 10 times less concentrated alloy (1 % Si)



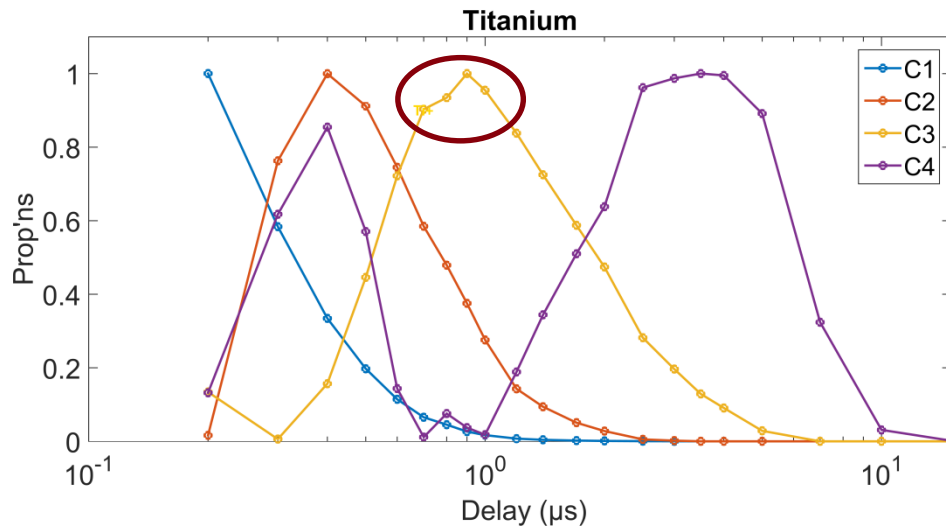
MCR-ALS can be used to optimize the detection gating for quantitative analysis

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 μ s



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

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.





Questions

**Thank you for
your attention!**

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