Interpreting the temporal emission of LIBS plasmas using advanced chemometric methods

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SUMMARY

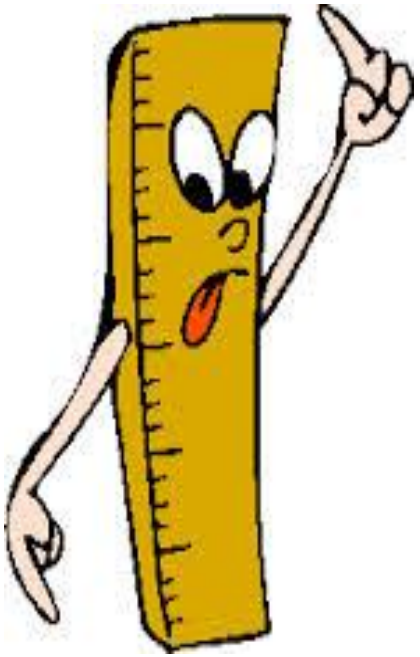
- Context
- Experimental
- Results of multivariate analysis of time resolved LIBS spectra
- Conclusion

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.**

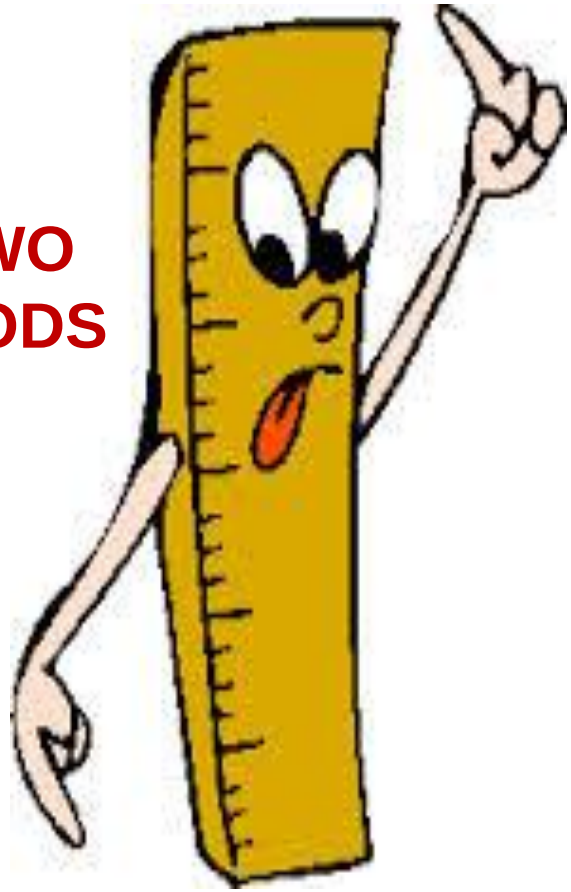


Kinetics studies: spectral lines are selected according to certain criteria

GOAL

SPECTRAL DIMENSION

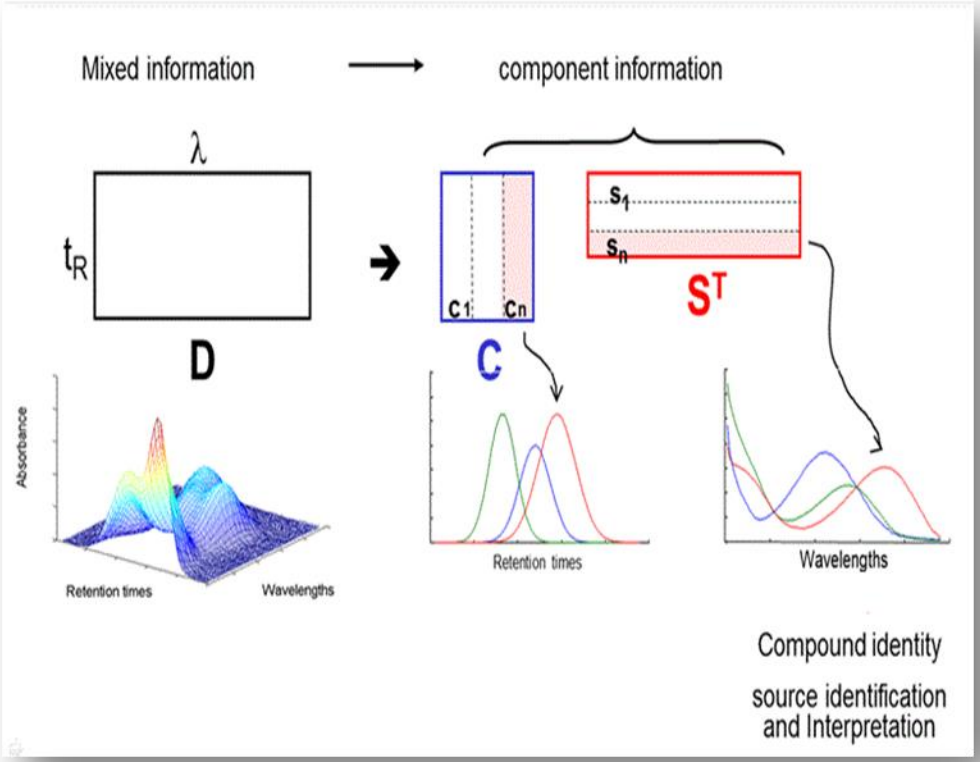
EXPLORE SIMULTANEOUSLY THESE TWO FACTORS USING CHEMOMETRIC METHODS



TEMPORAL DIMENSION

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.

CONTEXT

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.

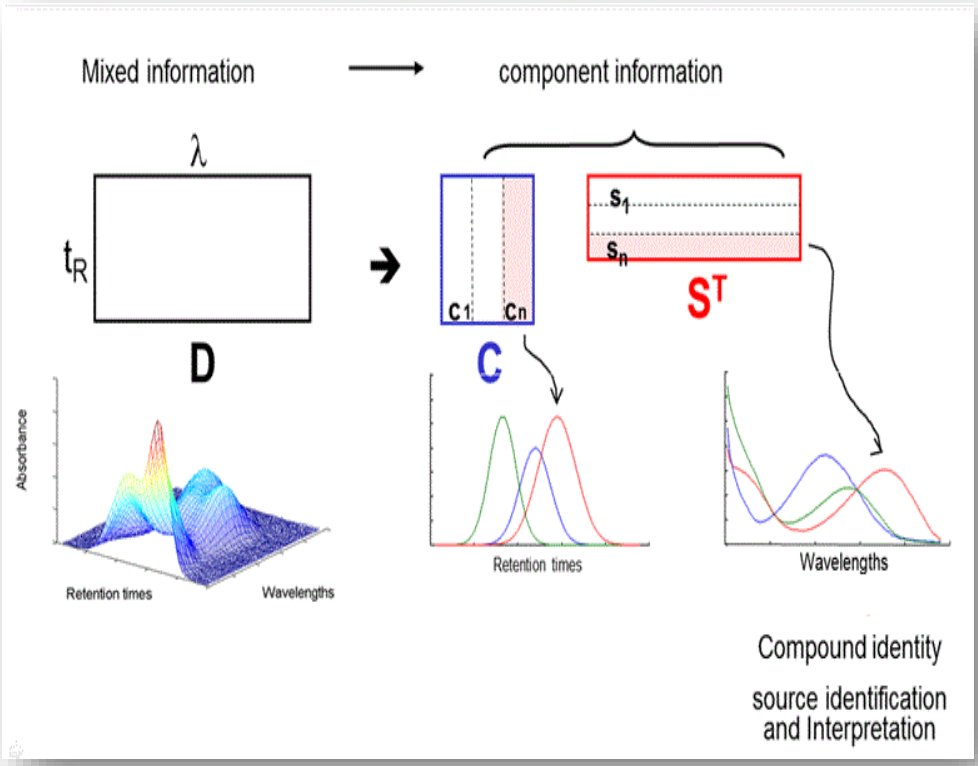
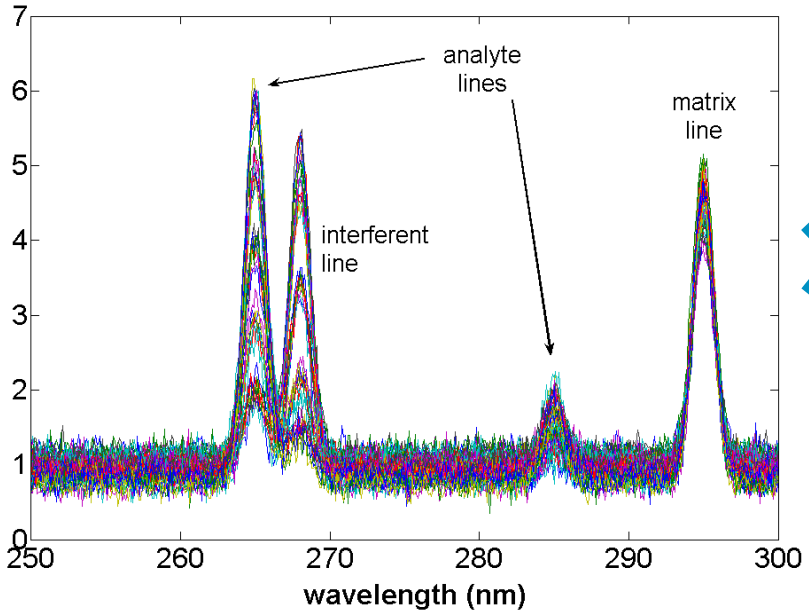
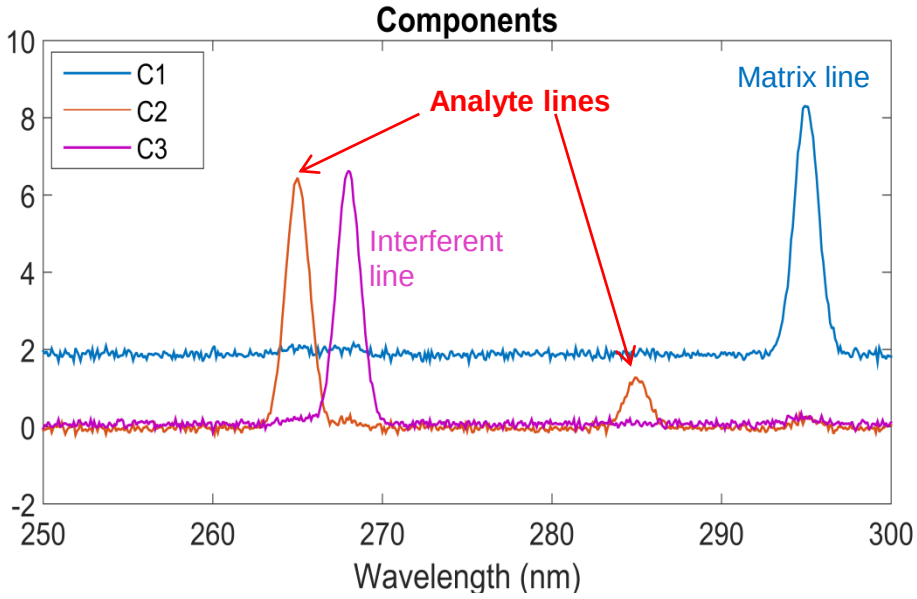
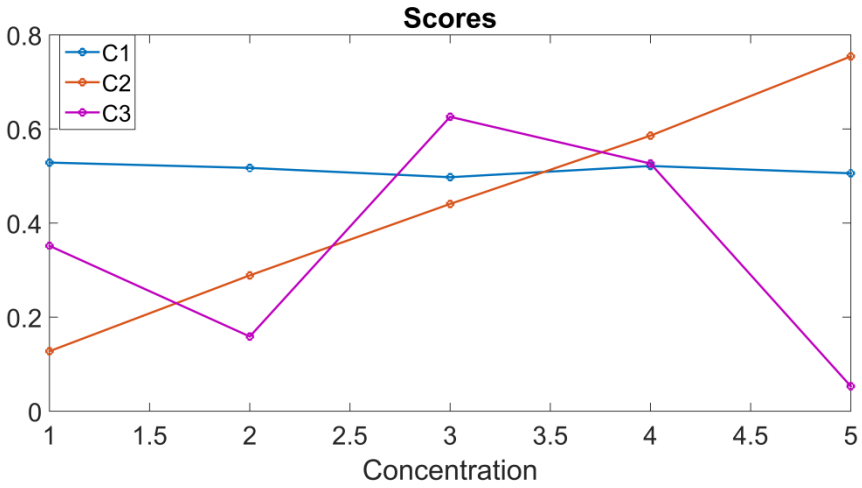


ILLUSTRATION ON SIMULATED DATA

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







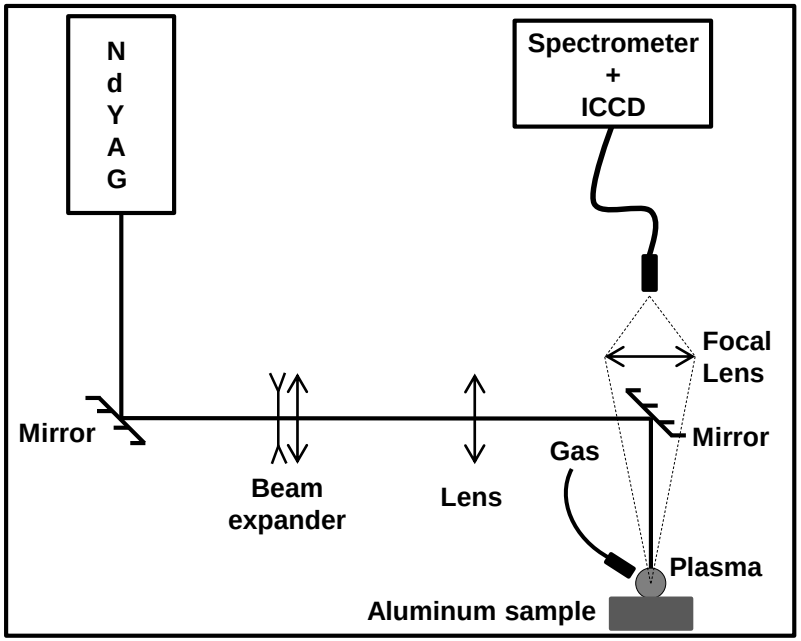
The scores are the amount of the component vector in each sample.

MULTIVARIATE ANALYSIS OF TIME RESOLVED LIBS SPECTRA

- Principle and methodology

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

EXPERIMENTAL



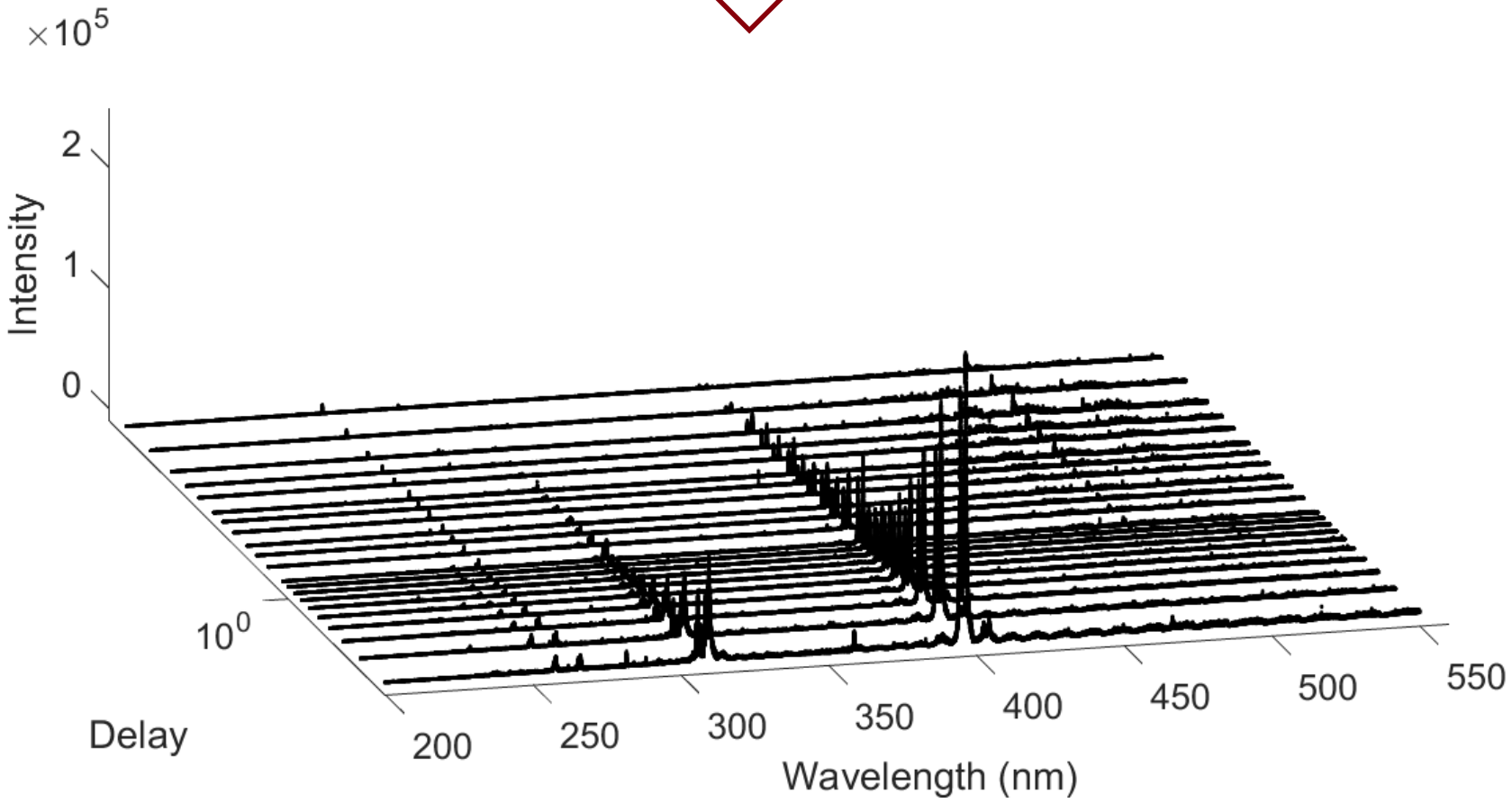
- Laser Nd:YAG @ 266 nm
- Pulse duration: 5 ns
- Frequency: 20 Hz
- Energy: 3 mJ
- Beam diameter: 50 µm
- Irradiance: 30 GW/cm^2
- Focal length: 25 cm
- Pressure Atm pressure.
- Ambient gas: Air, N_2, Ne, Ar/Ne

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

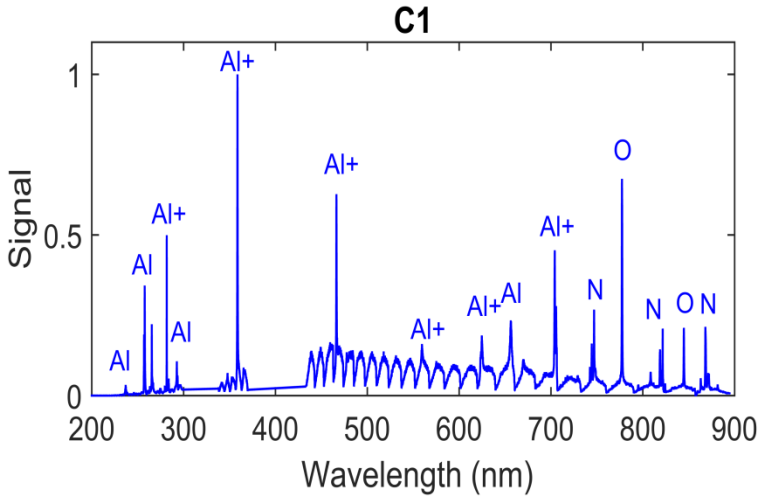
Aluminium Sample (TechLab « 198f »)	
Element	**Proportion**
Al	**99.99%**
Cu	**0.005%**
Si	**0.002%**
Fe	**0.001%**

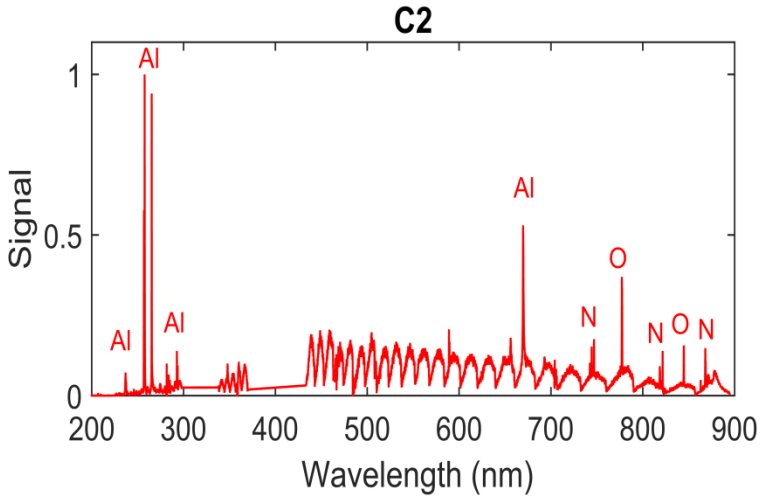
COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

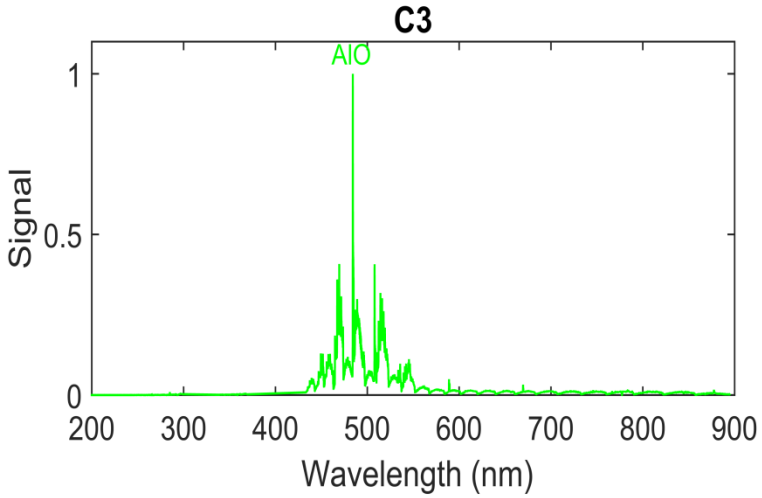
To validate the potential of the three chemometric methods selected for the physical interpretation of the temporal evolution of the spectra.



COMPARISON BETWEEN 3 CHEMOMETRIC METHODS





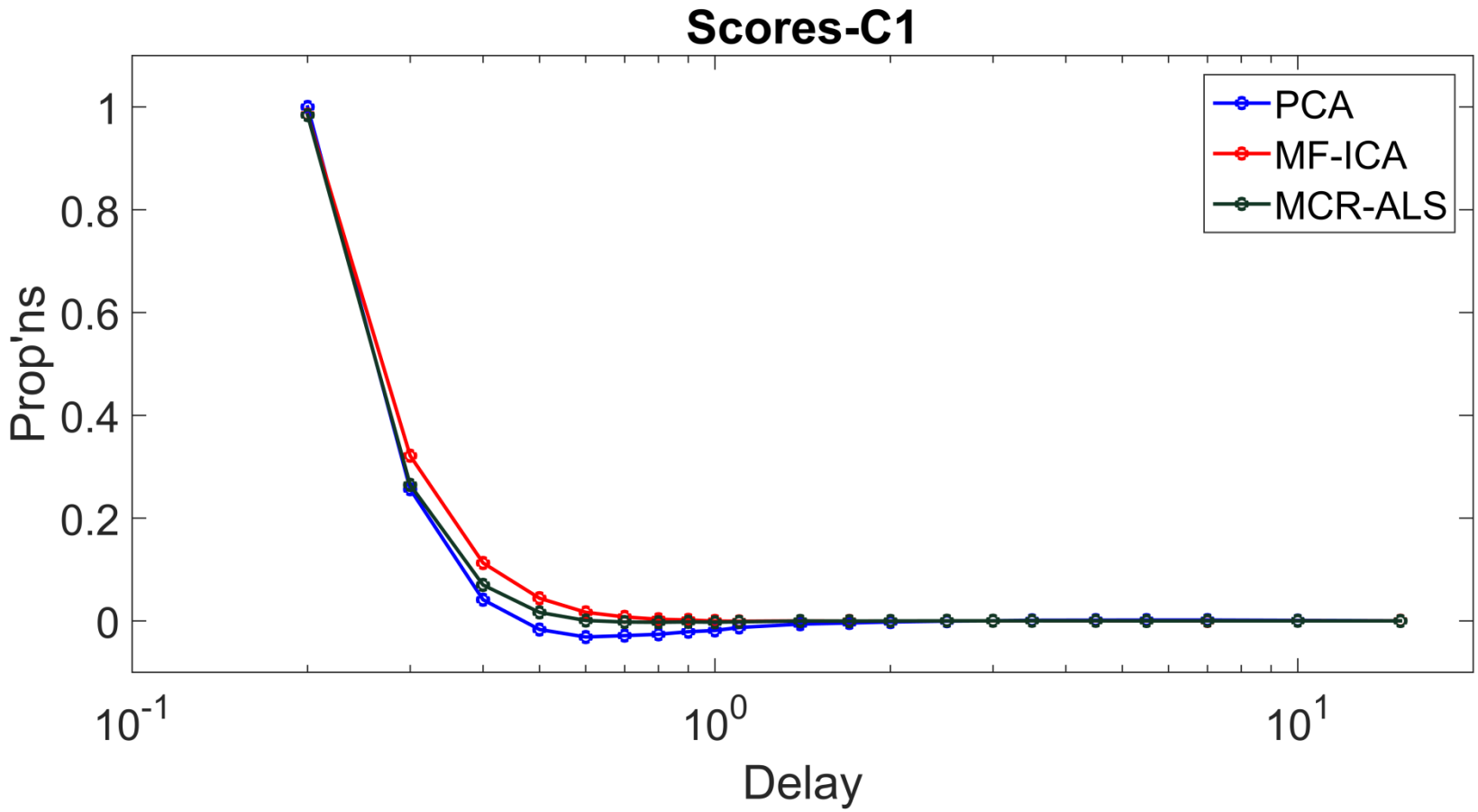


First component → Ionic lines

Second component → Neutral lines

Third component → Molecular bands

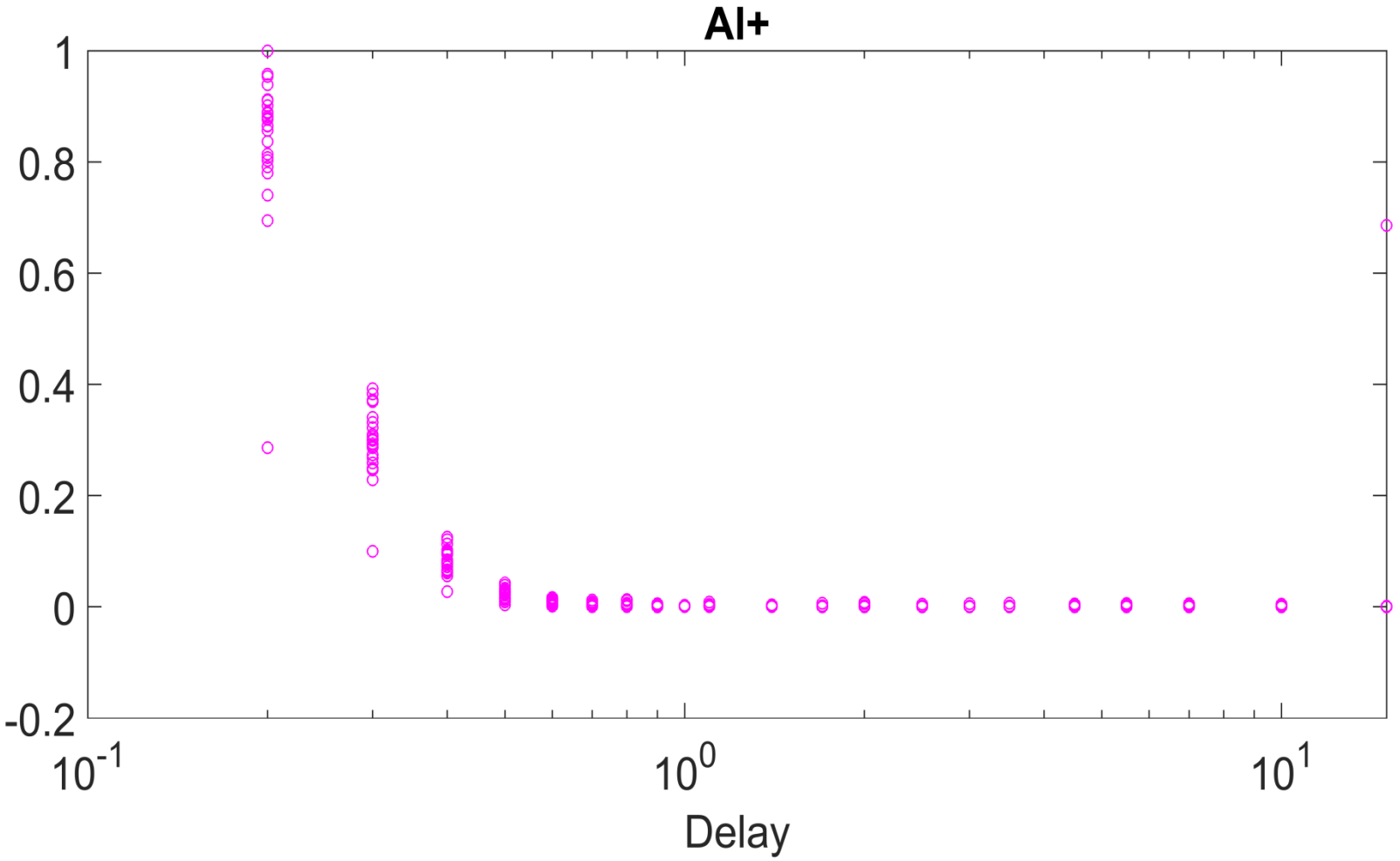
COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



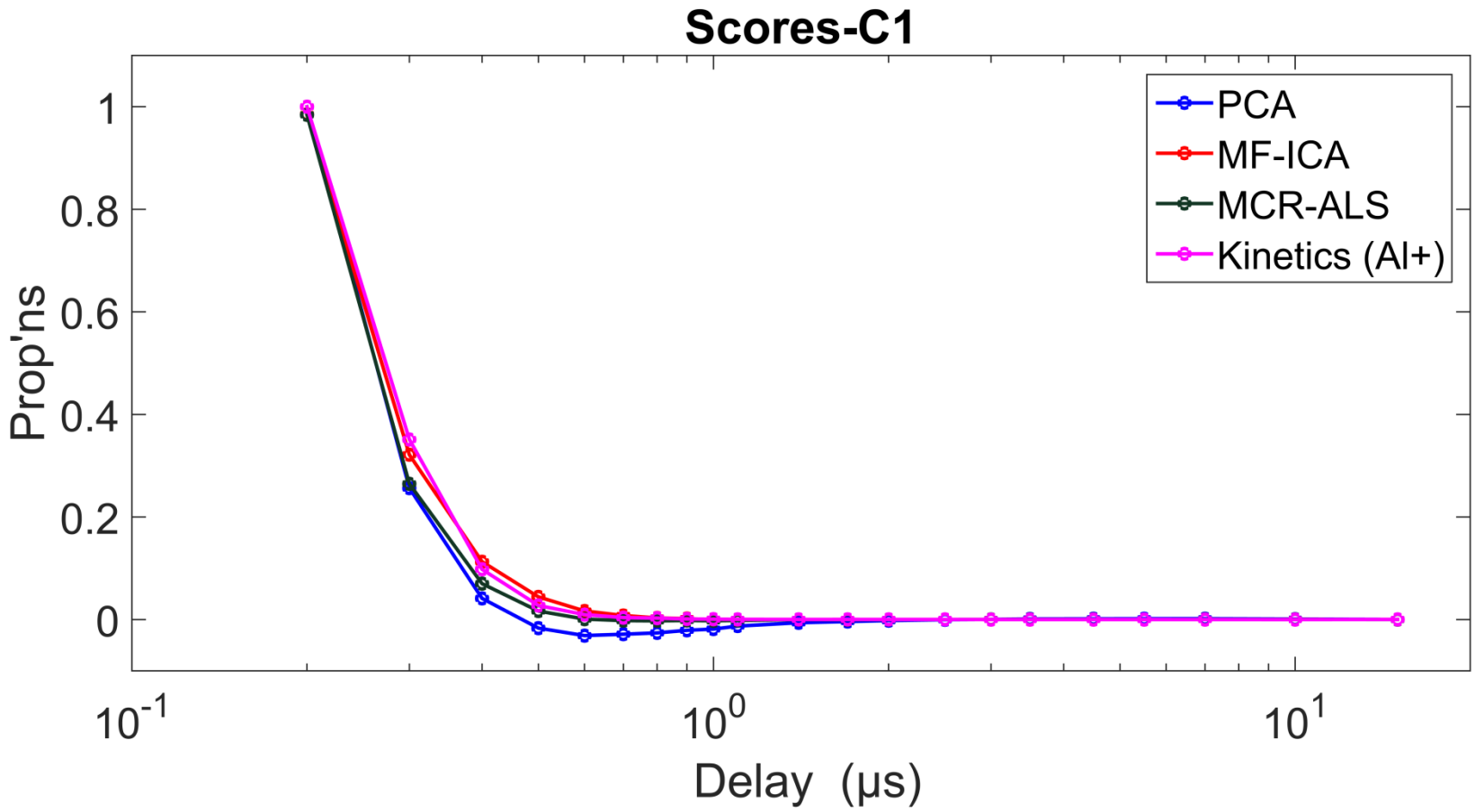
The ion population decreases with time; this is due to the recombination with the electrons to form neutral atoms.

COMPARISON BETWEEN 3 CHEMOMETRIC METHODS

Reference method (*Kinetics*)

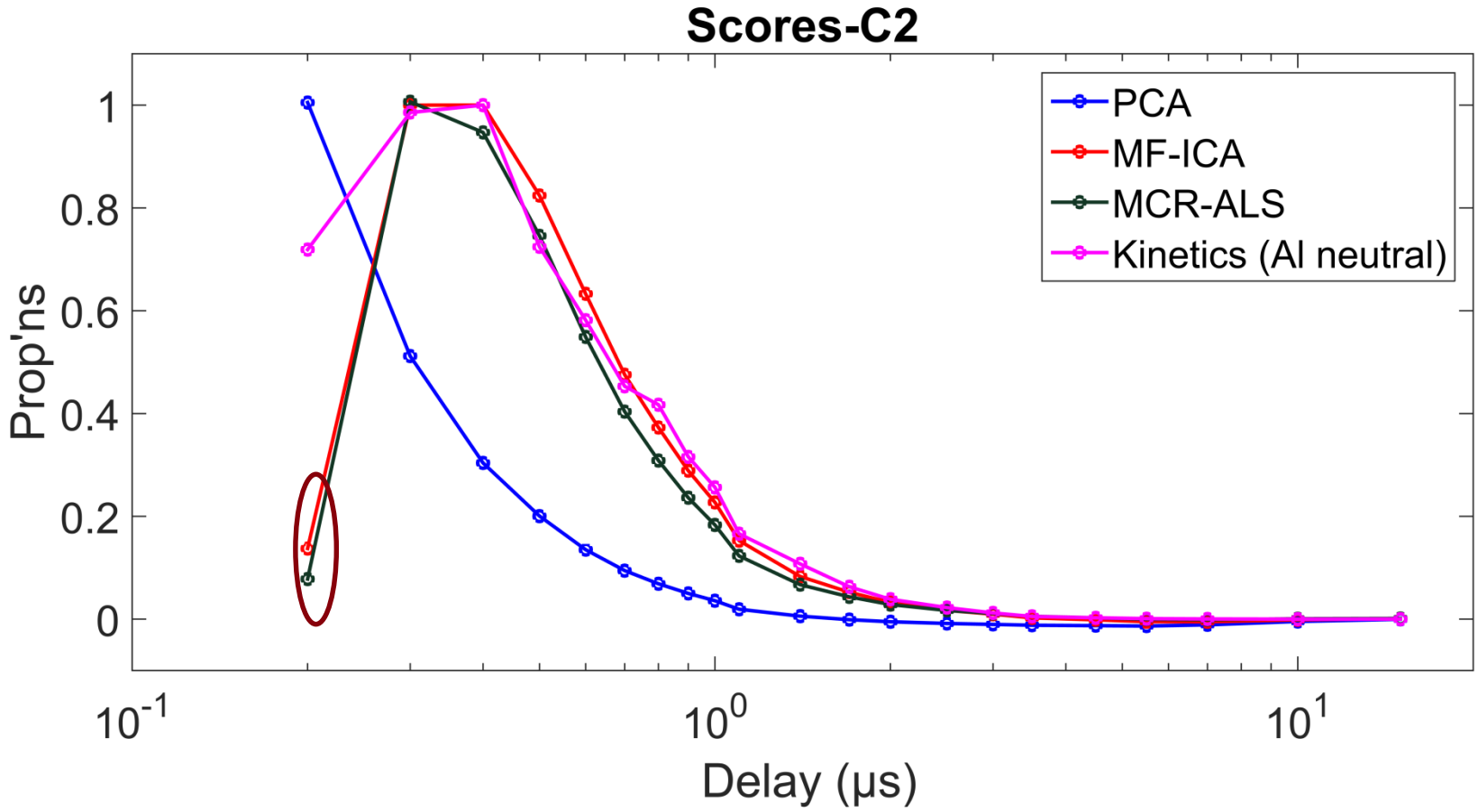


COMPARISON BETWEEN 3 CHEMOMETRIC METHODS



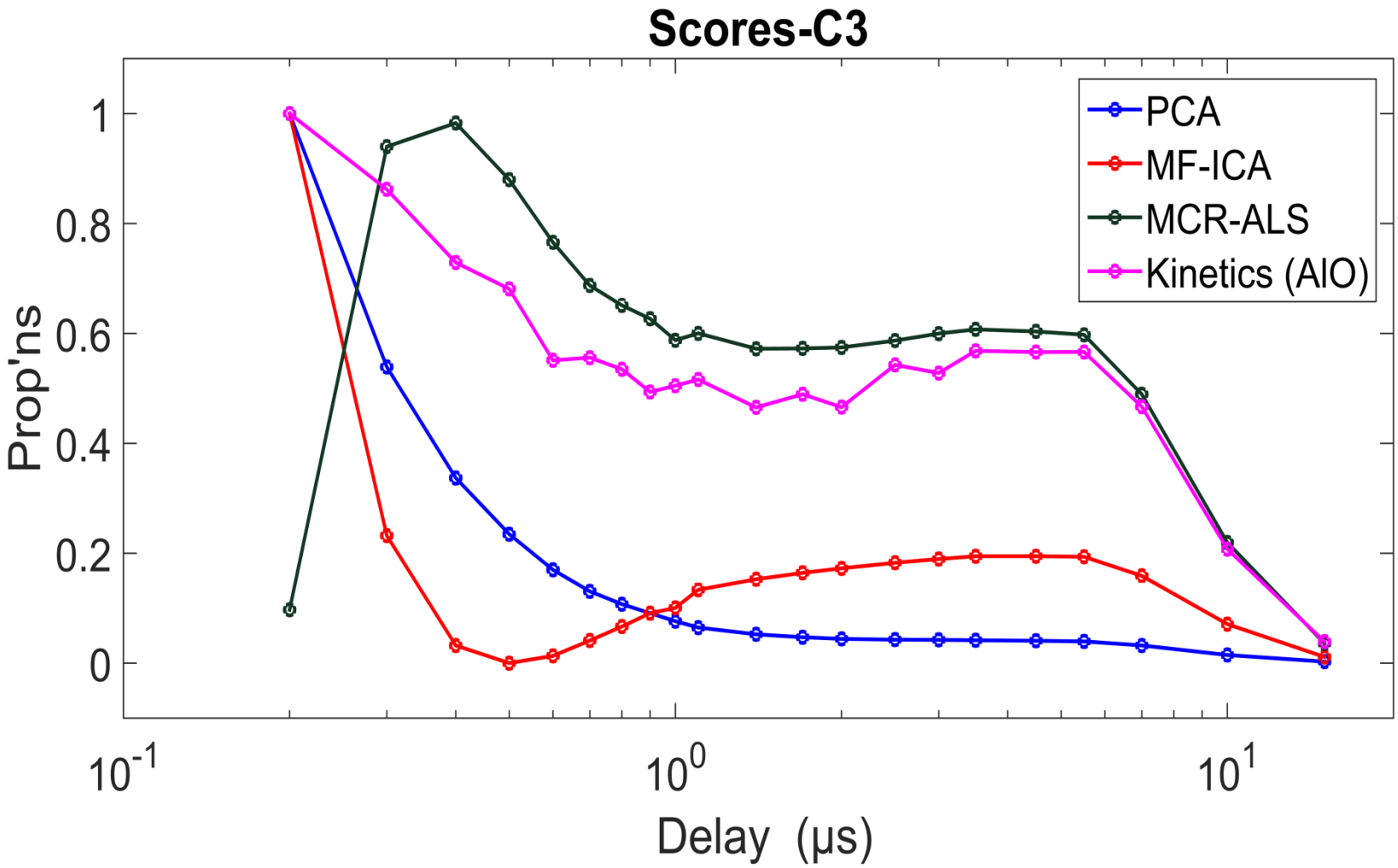
The scores of the three methods follow a similar trend to that of the intensities of Al ionic line

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



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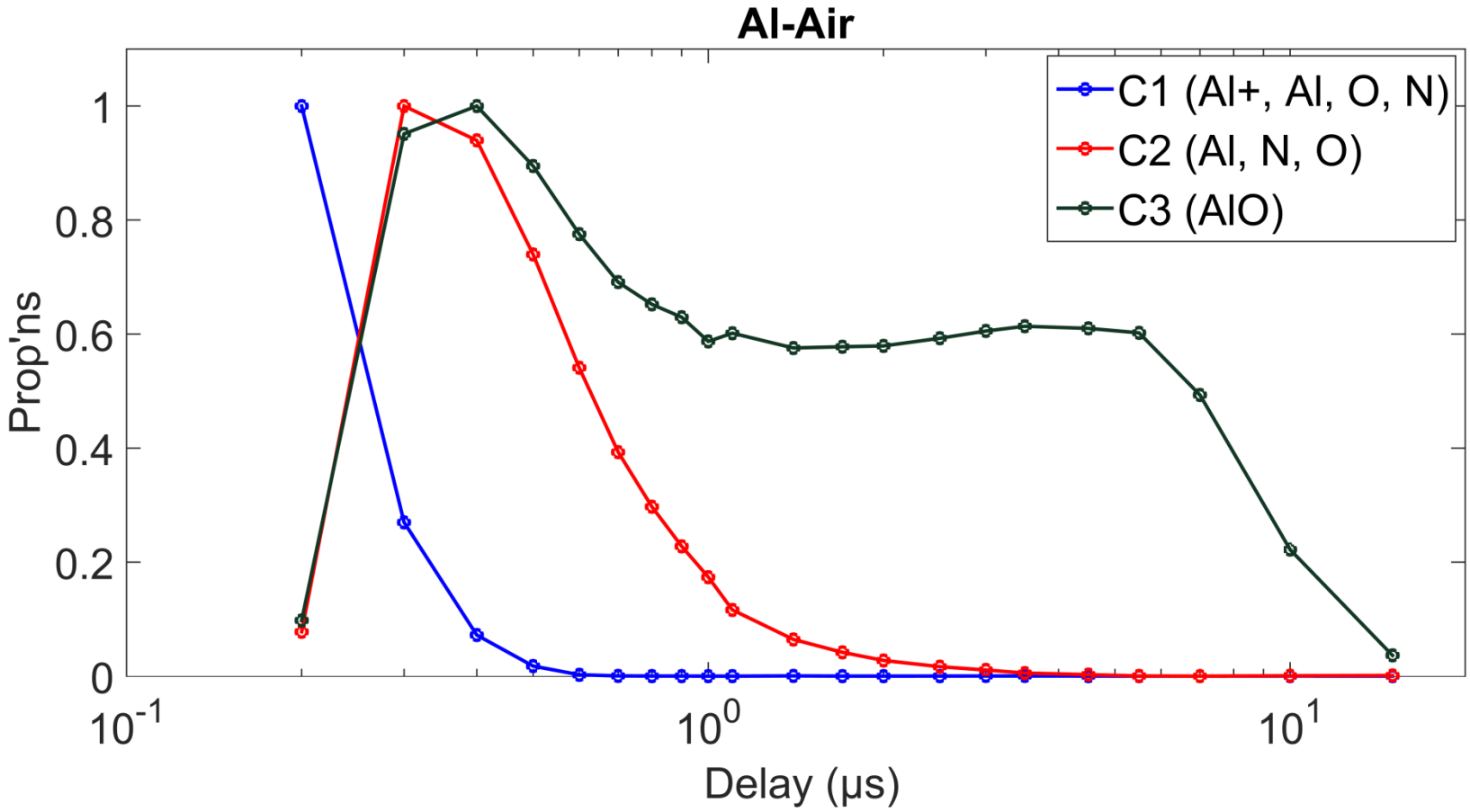

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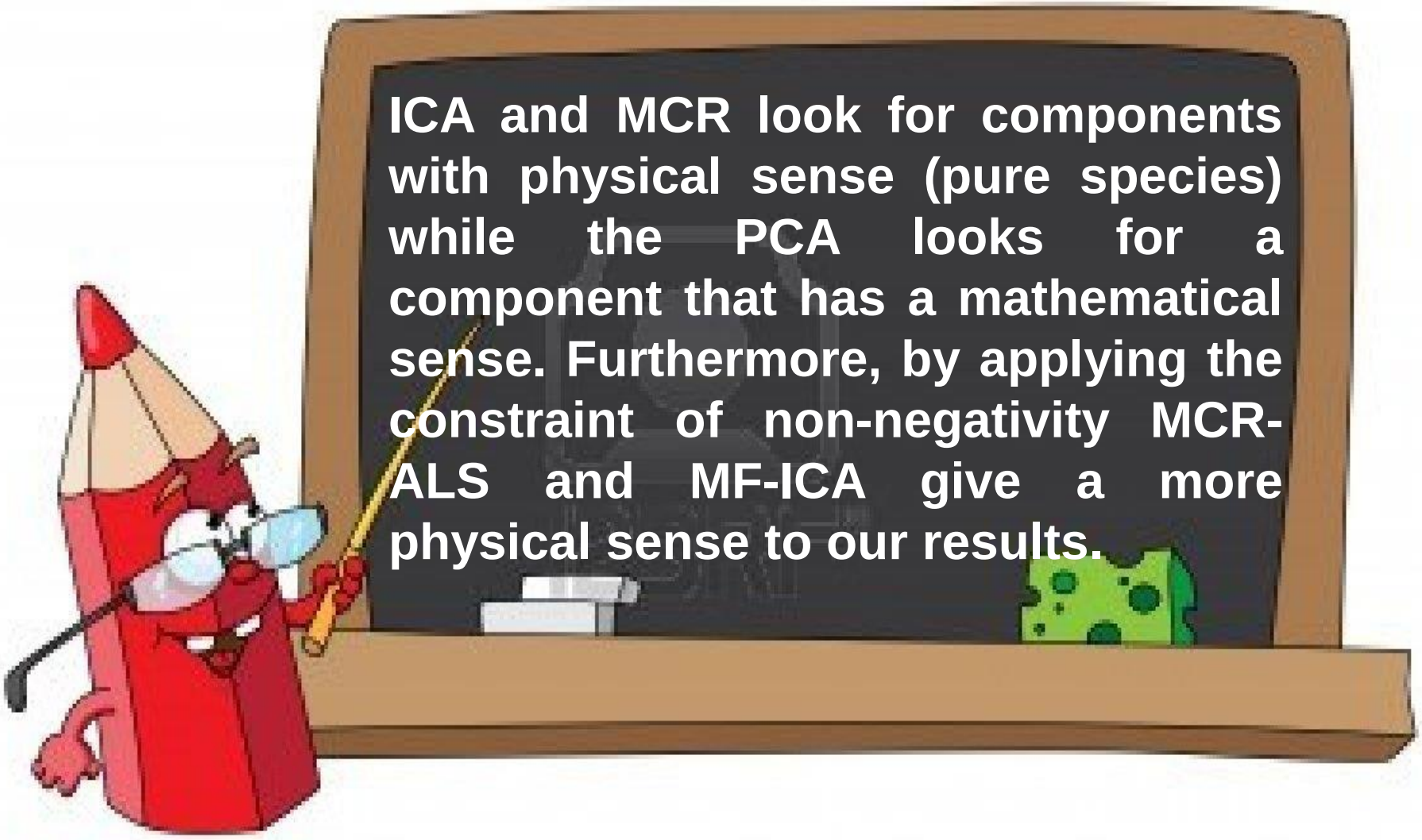

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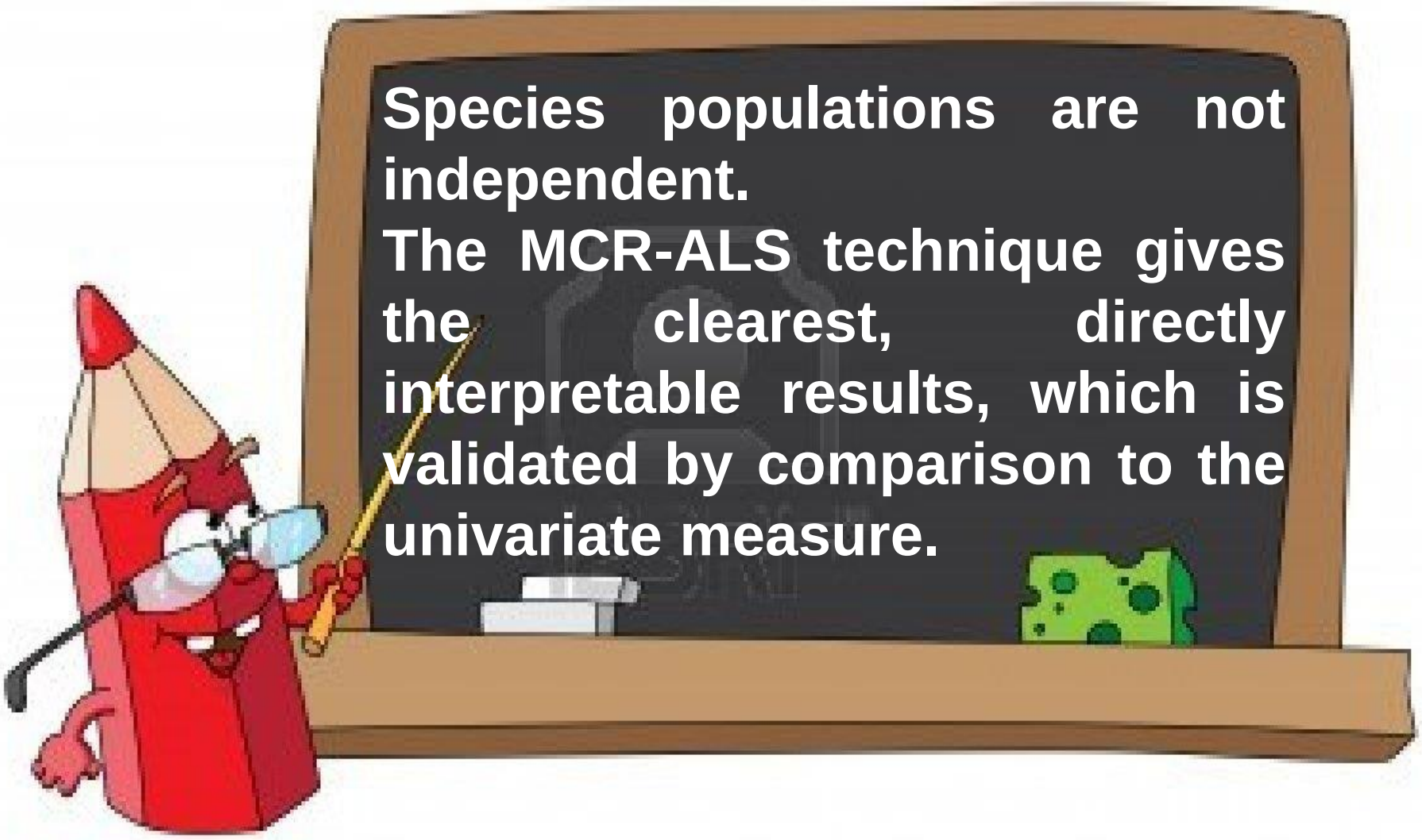


MULTIVARIATE ANALYSIS OF TIME RESOLVED LIBS SPECTRA

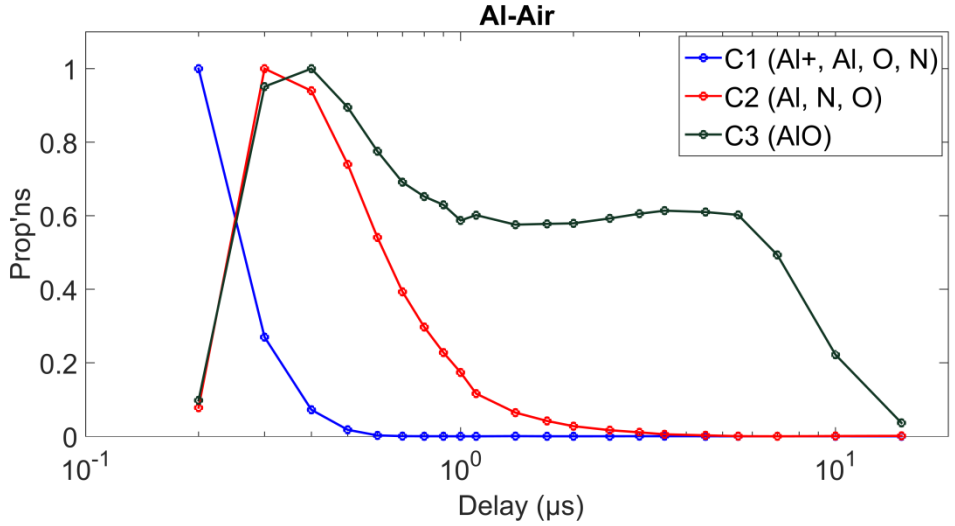
- **Application to physical interpretation of LIBS data and to analytical optimization of the measurement**

- 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

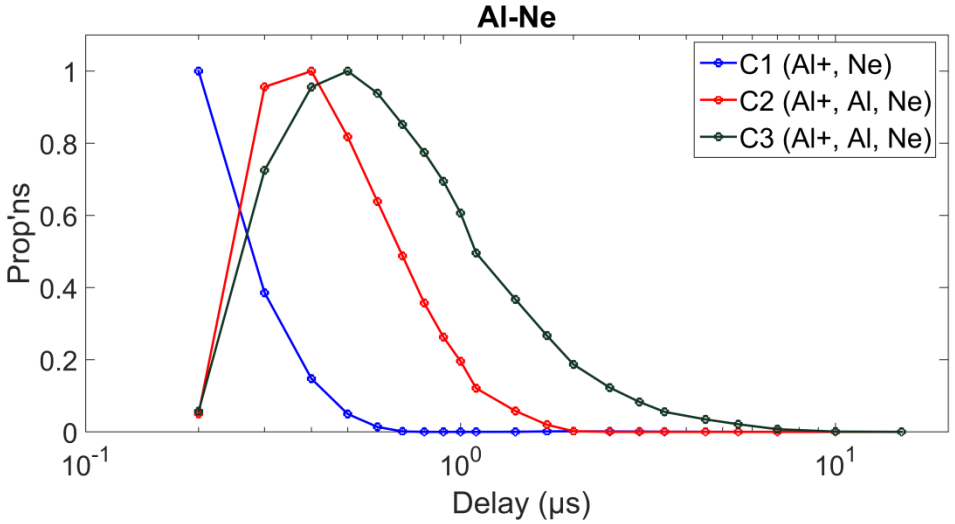
Dataset: time-resolved spectra of pure Al in air and in neon



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

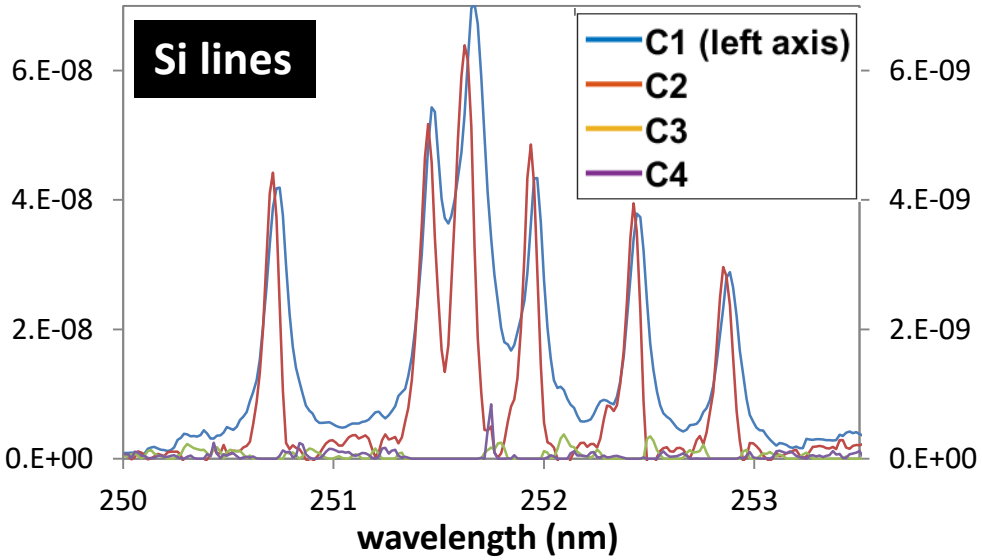
Consistent with the ionization potential of Ne > ionization potential of O and N

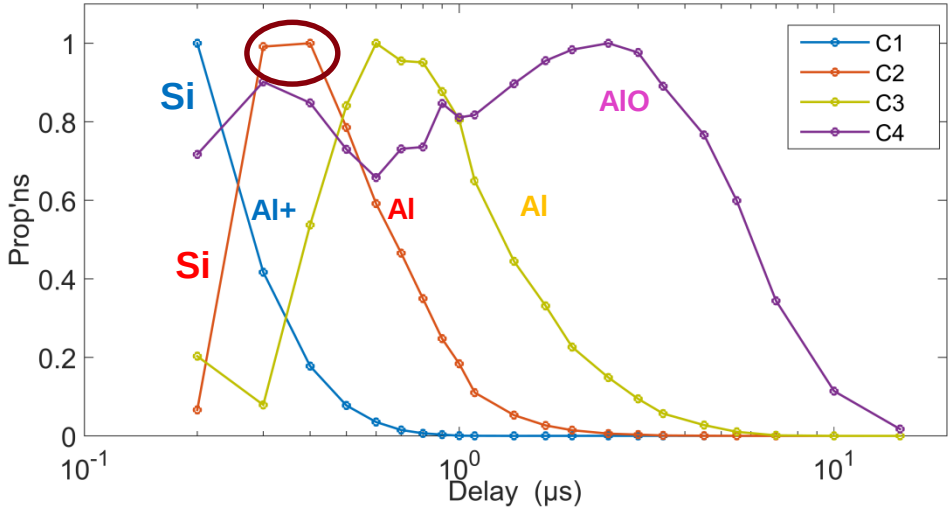


MCR-ALS analysis can be physically interpreted to extract information on plasma features (electron temperature and density), and on kinetics of ionic recombination and molecules formation

Optimizing the detection of an analyte

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

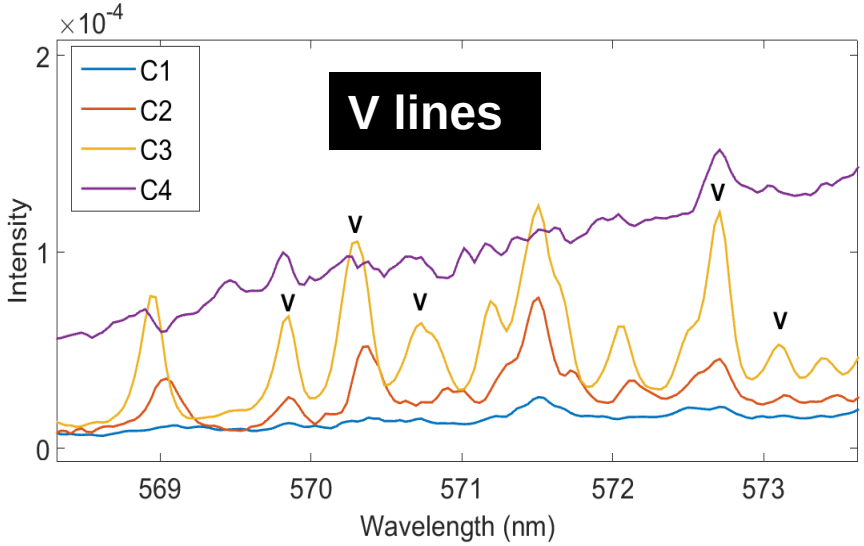
C2 scores are maximum between 0.3 and 0.5 µs → best temporal parameters for Si analysis

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

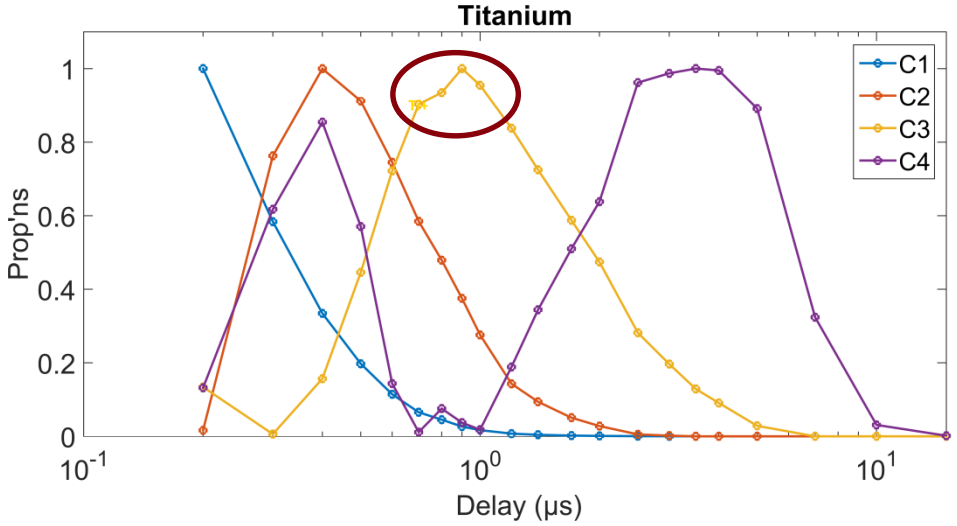
Dataset: time-resolved spectra of a Ti alloy (88.2 % Ti, 4.1 % V)



Application of the same approach to the case of complex spectra

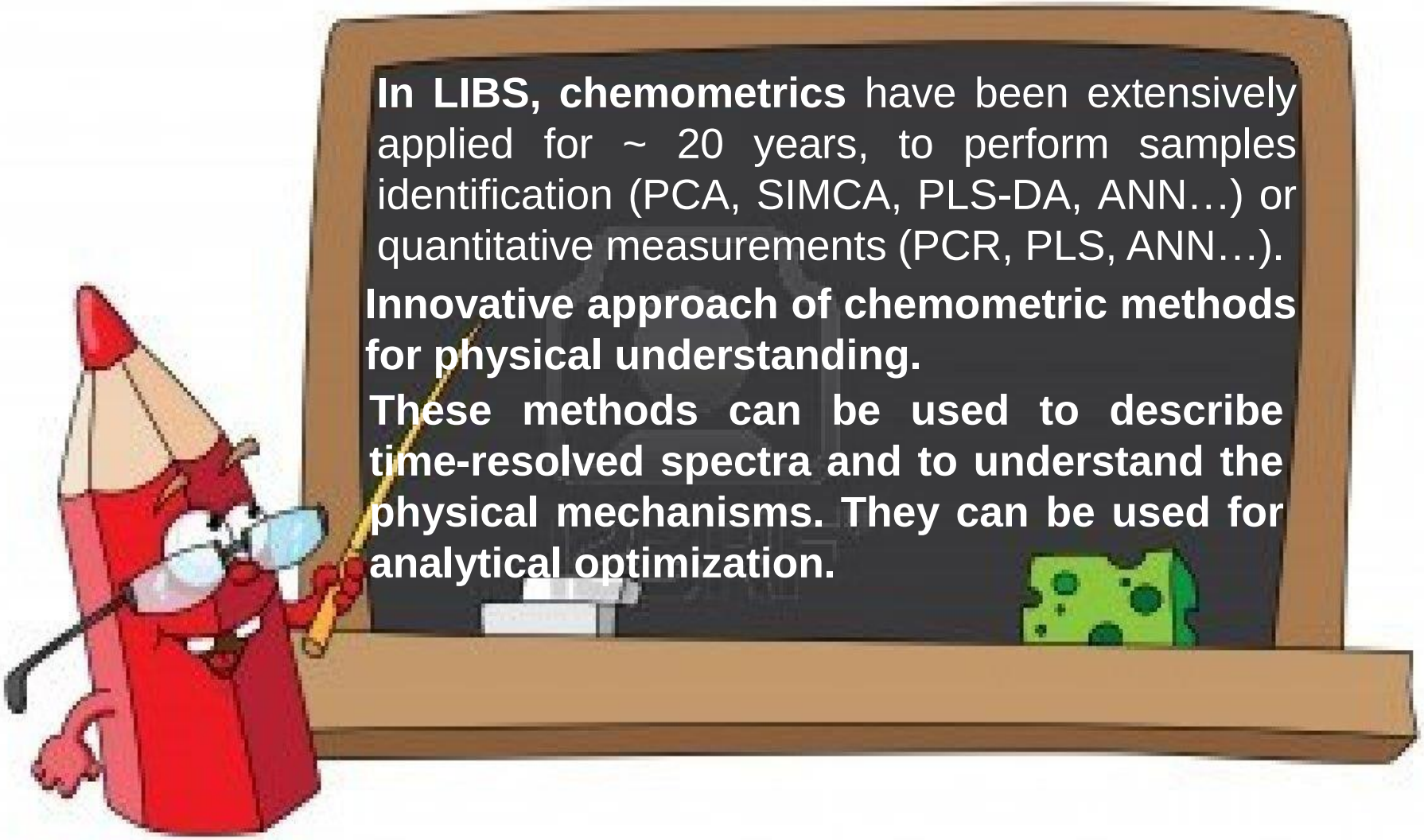
Detection of V in a Ti matrix

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

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!

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