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OVERCOMING MATRIX EFFECTS IN LASER-INDUCED BREAKDOWN SPECTROSCOPY USING MULTIVARIATE ANALYSIS OF TIME-RESOLVED SPECTRA

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LIBS2016, 12-16 September, Chamonix/France

CONTEXT

Normalization Approaches

Ablated mass

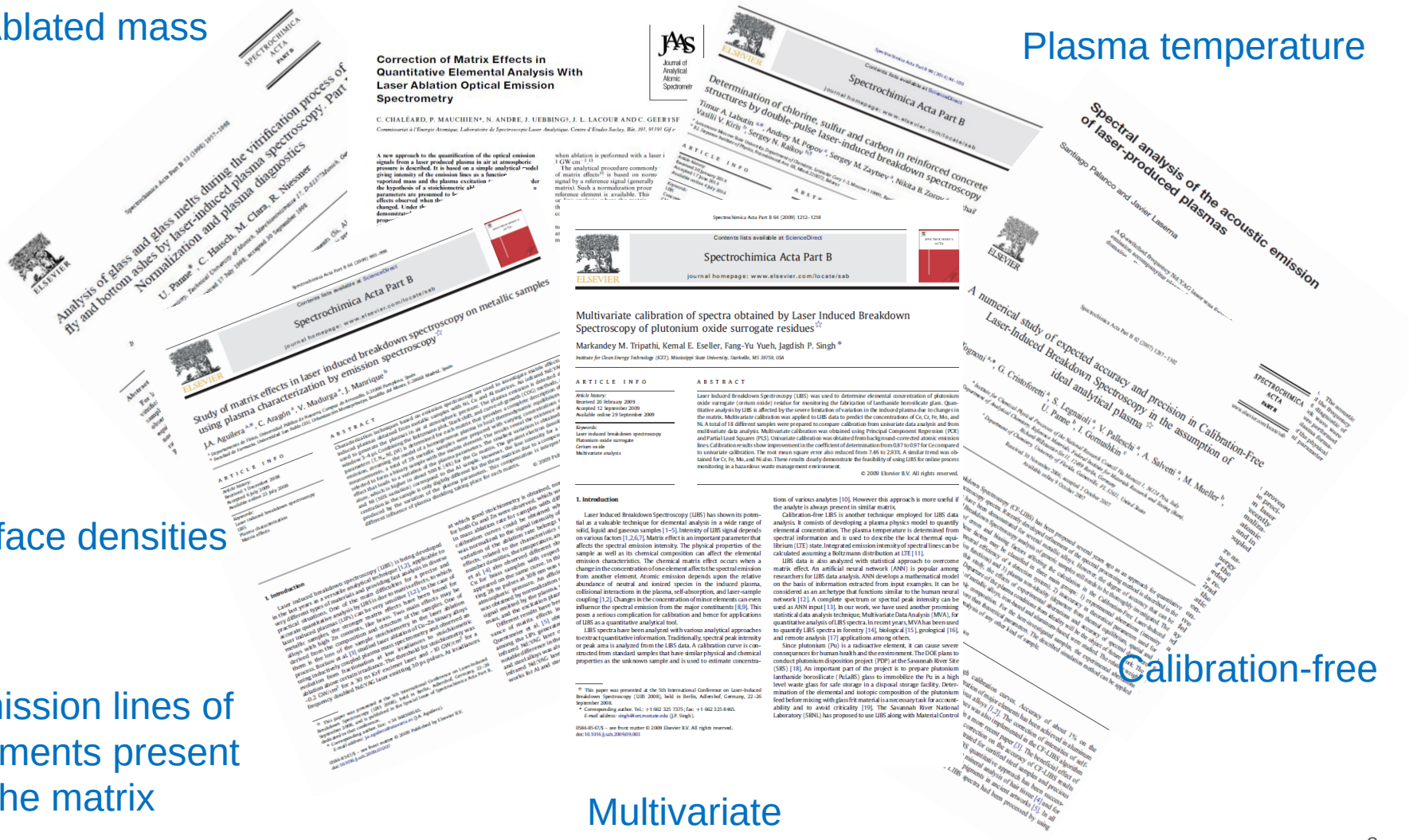
Plasma temperature

Surface densities

Calibration-free

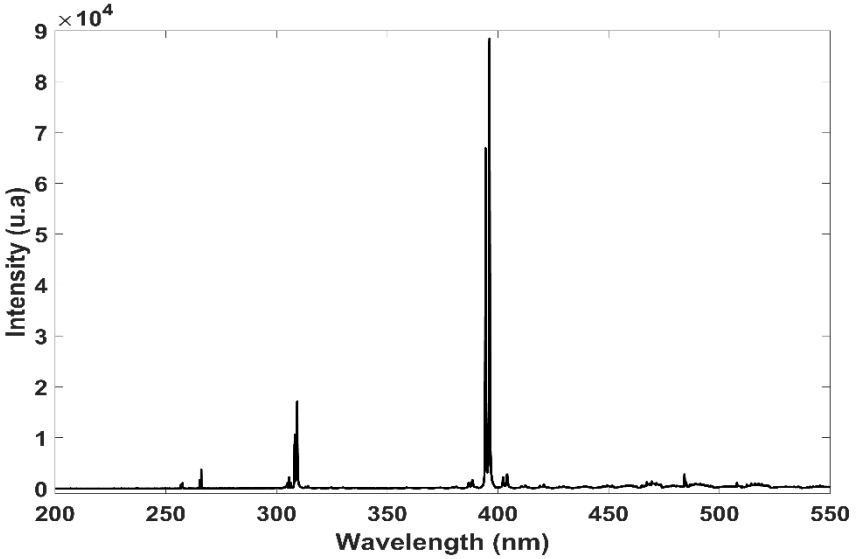
Emission lines of elements present in the matrix

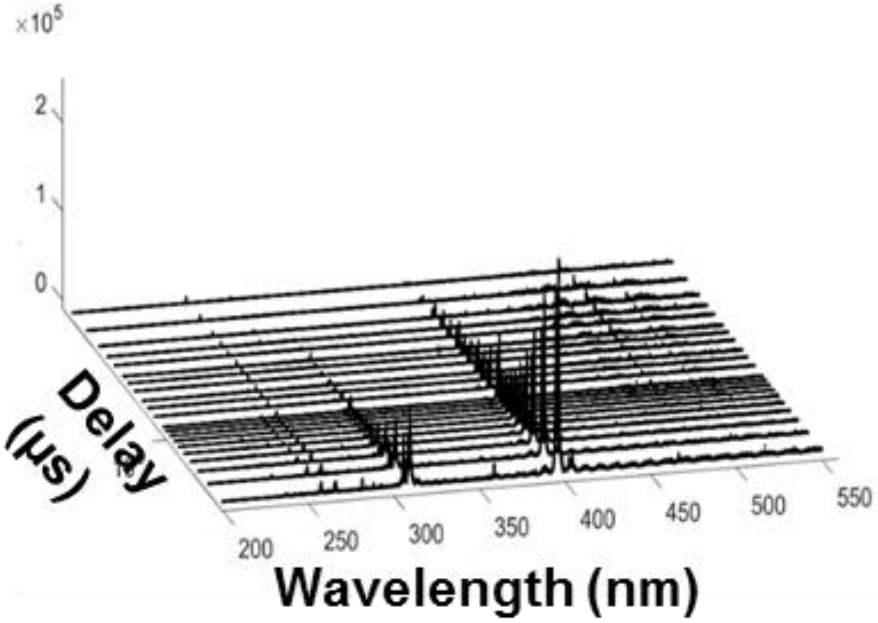
Multivariate Calibration



METHODS

Conventional calibration methods





Improvement of quantitative analysis of solids by LIBS using both the spectral and temporal dimensions of the signal.

METHODS

Improvement of quantitative analysis of solids by LIBS using both the spectral and temporal dimensions of the signal.

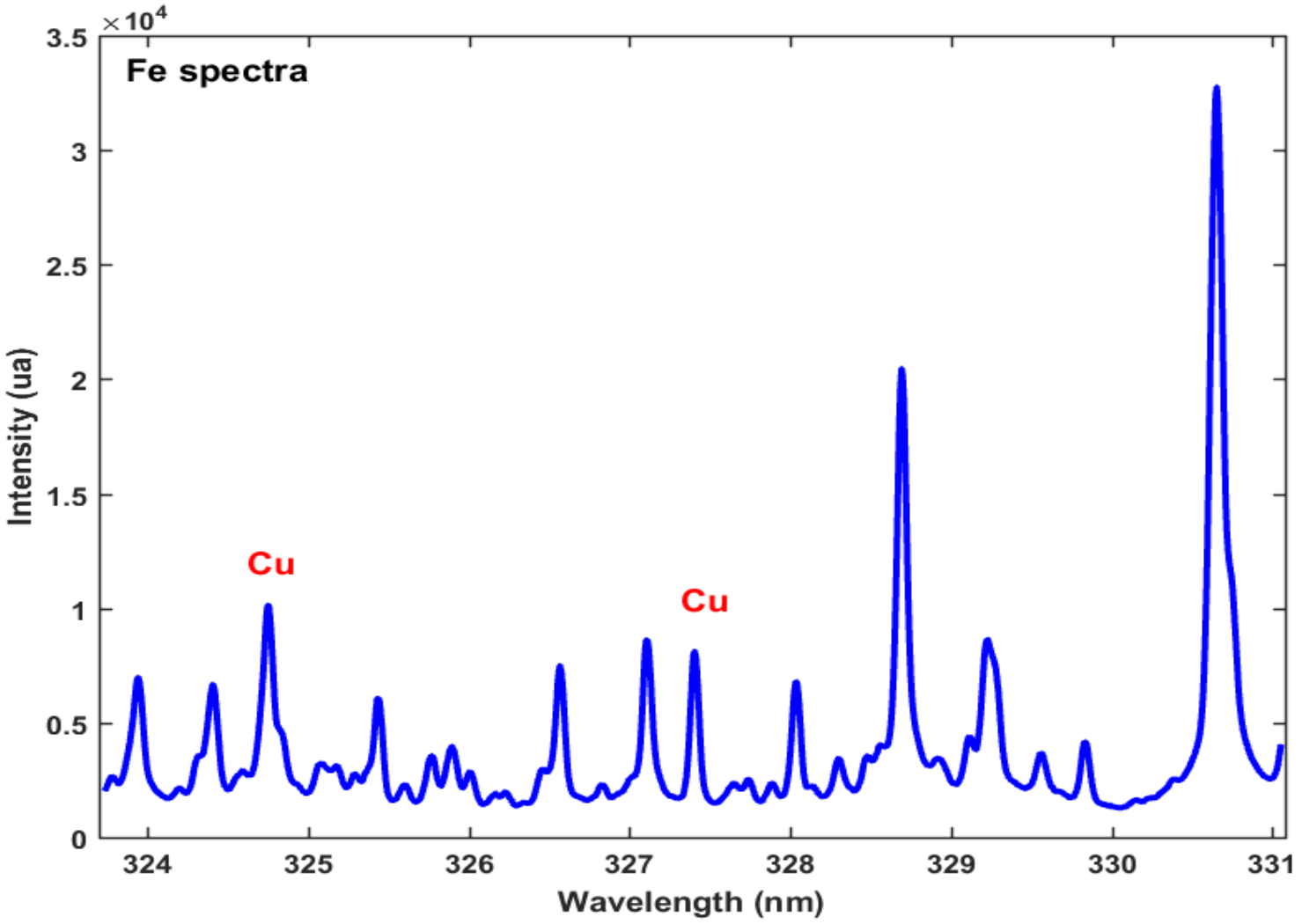
Improvement of quantitative analysis

15 samples of 3 matrices (Fe, Ni, Ti)

Acquisition at different delay

CONVENTIONAL APPROACH

Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



CONVENTIONAL APPROACH

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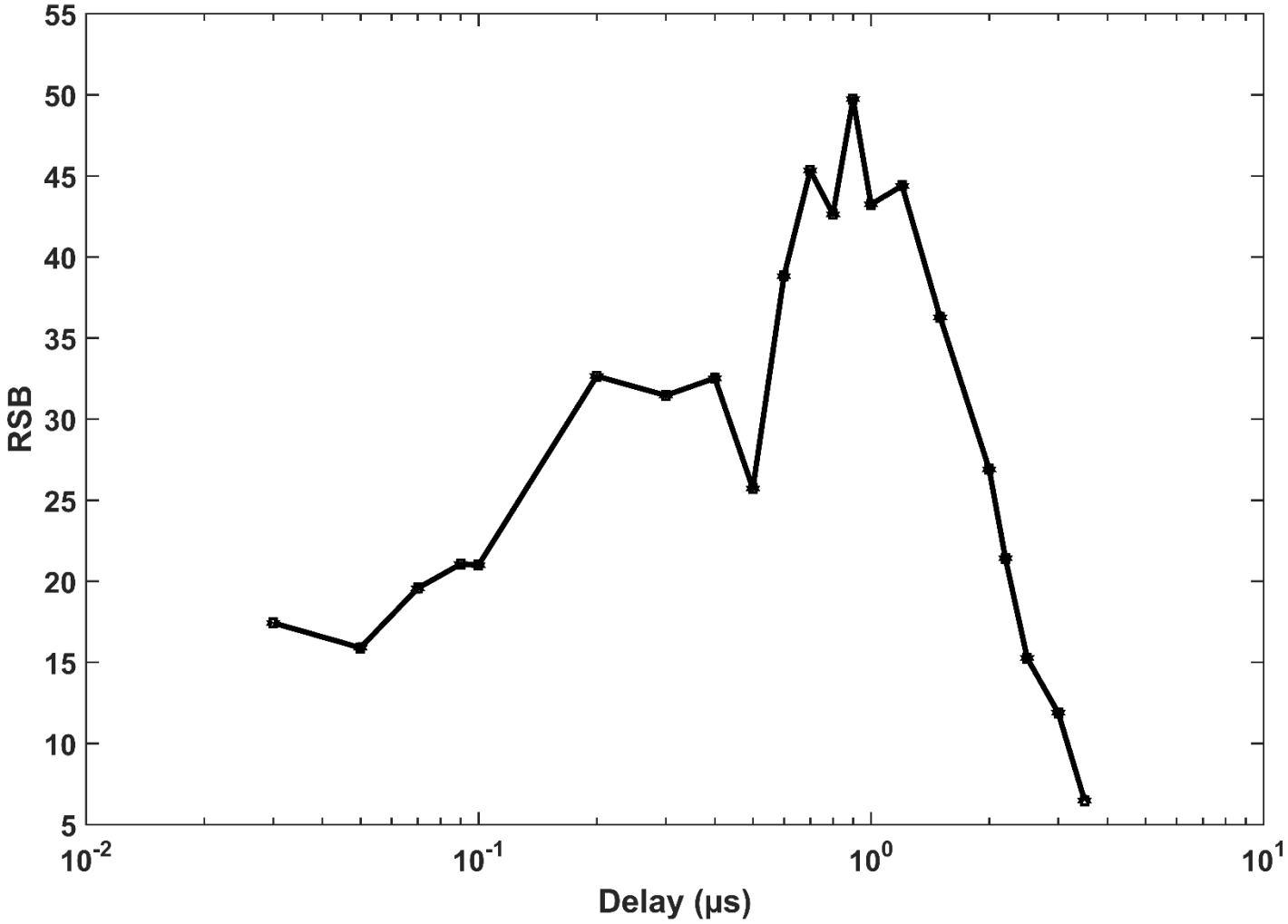

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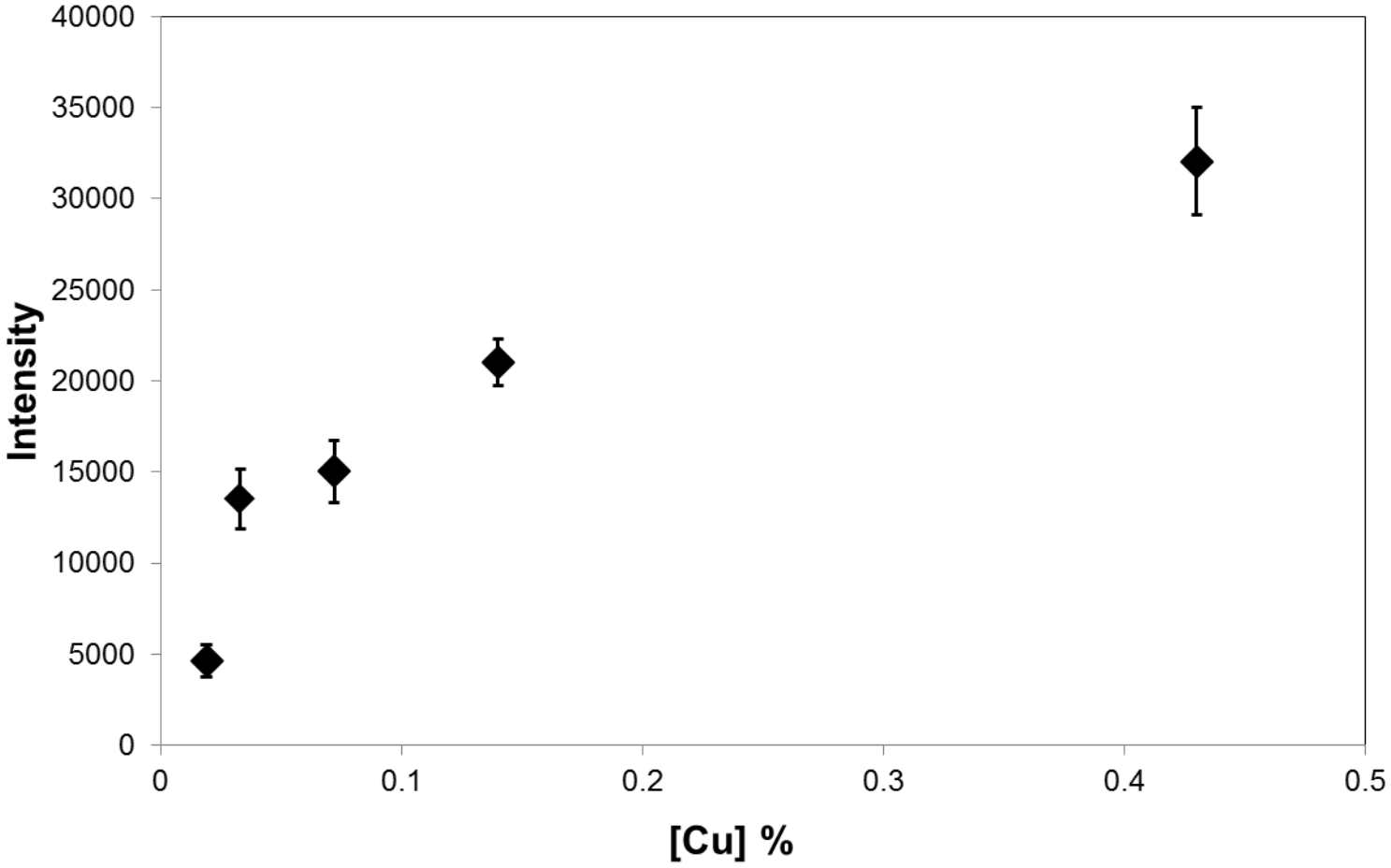
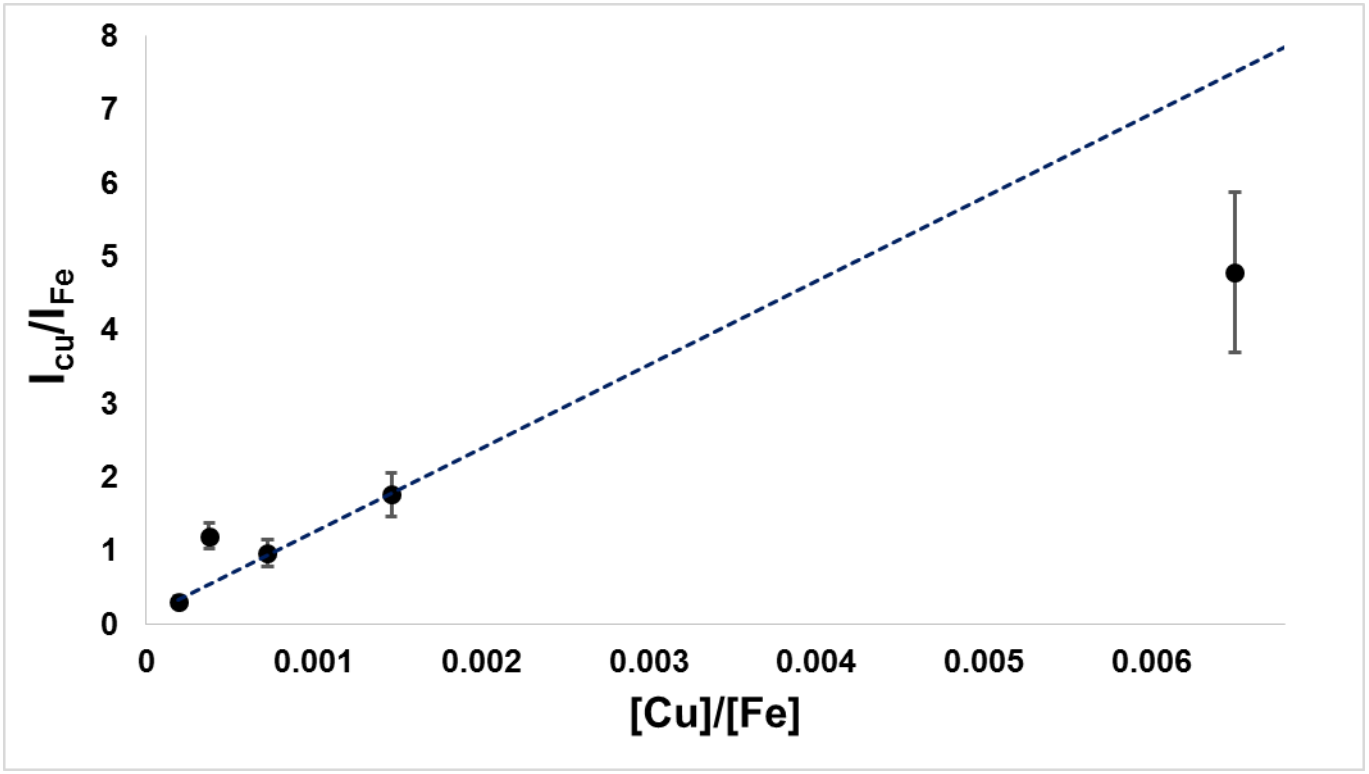


CONVENTIONAL APPROACH

Cu spectral intensity values at 327.4 nm are normalized by Fe spectral intensity values



LDD=1300ppm
R^2 = 0.973

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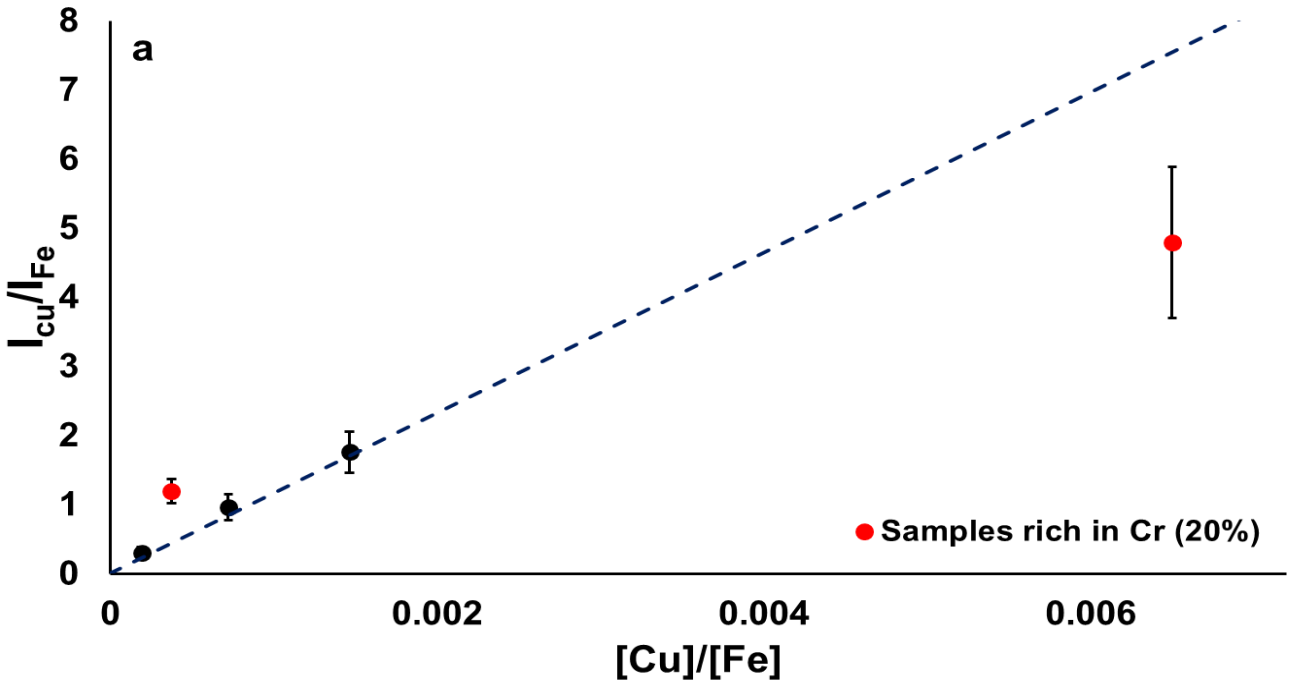


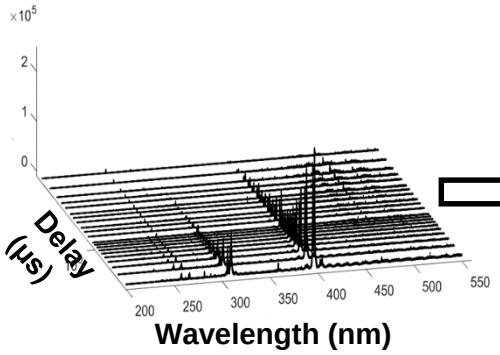
LDD=1300ppm
R^2 = 0.973

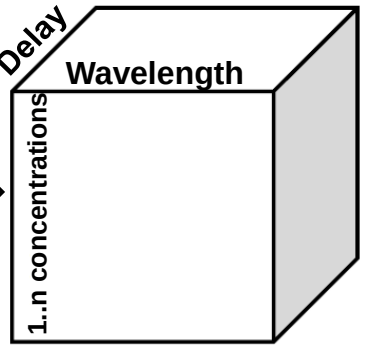
Improved calibration curve is observed by standardizing but analytical performance still insufficient.

⇩

Spectro-temporal approach using chemometrics

MULTIVARIATE APPROACH

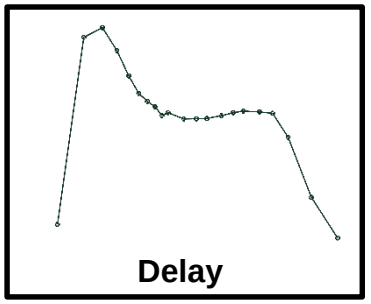


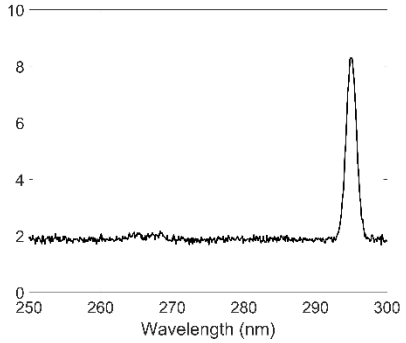


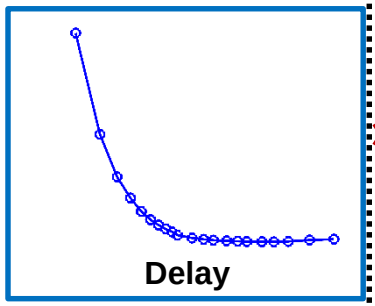
ICA

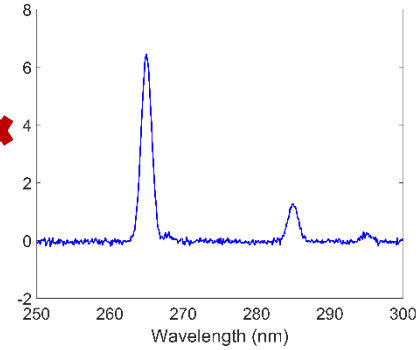
Proportions

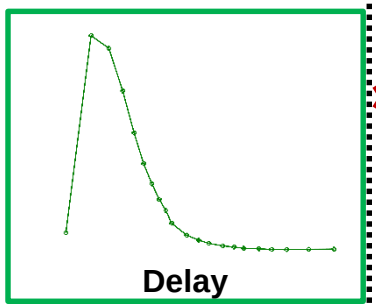
Components

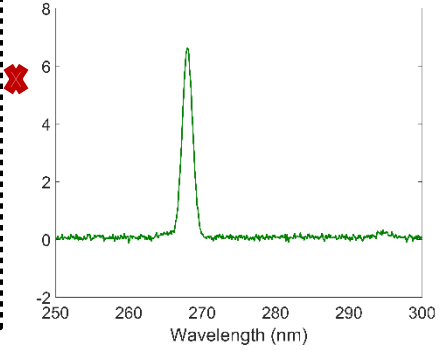




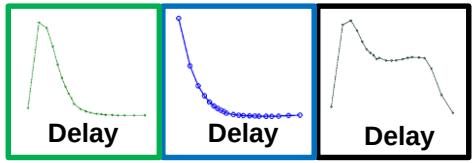




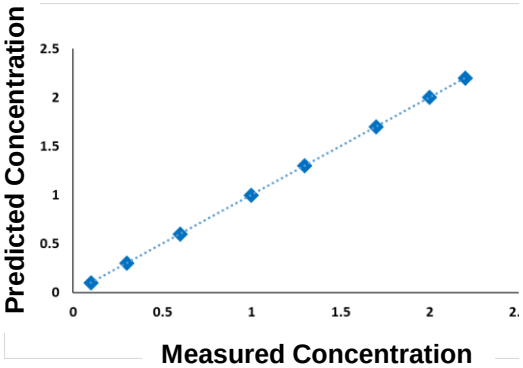


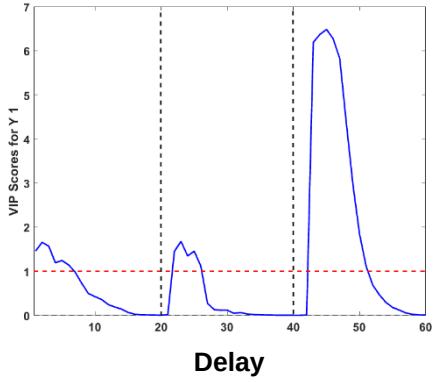


[Cu]

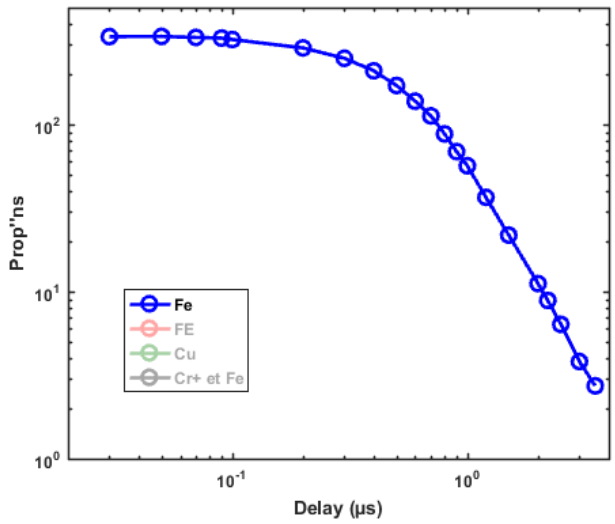


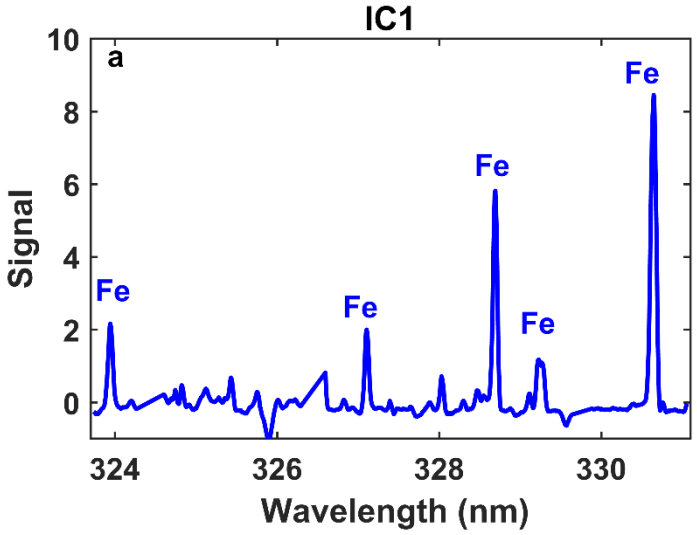
PLS

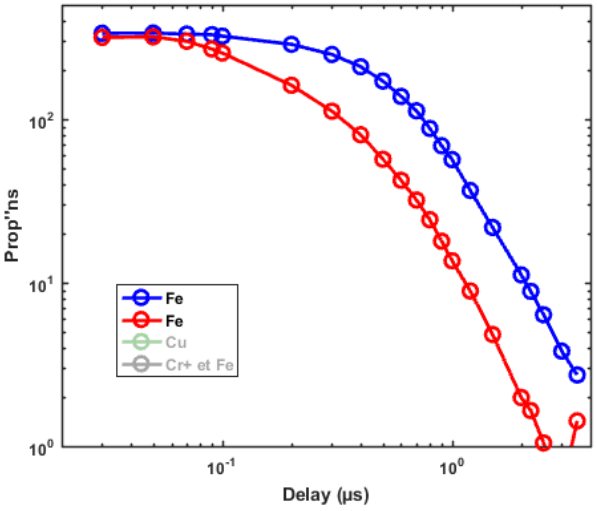


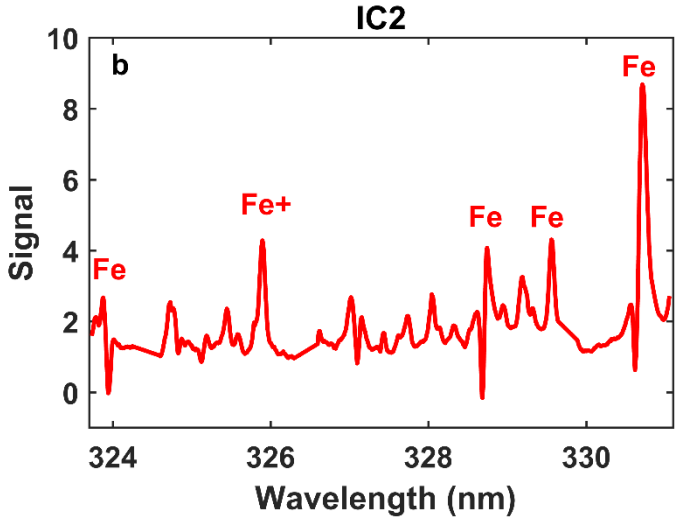


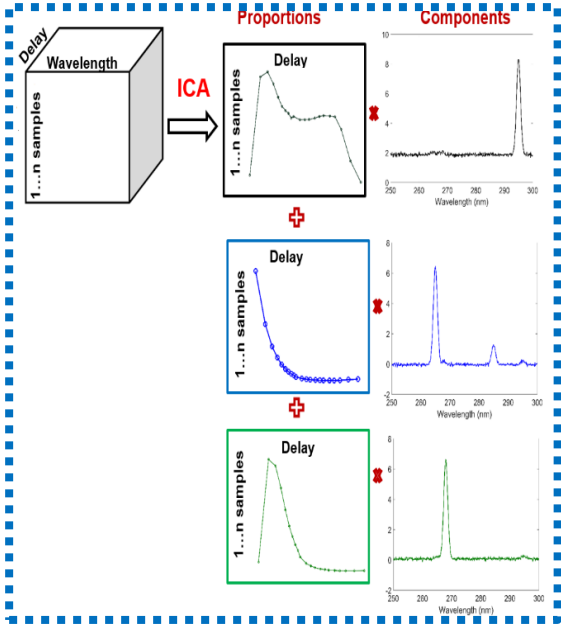
MULTIVARIATE APPROACH











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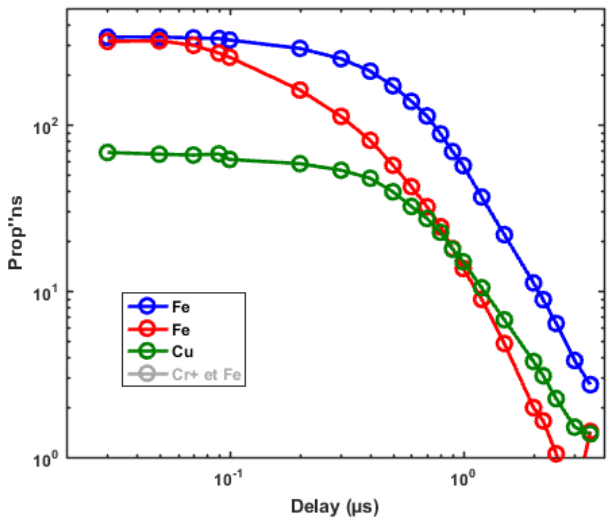

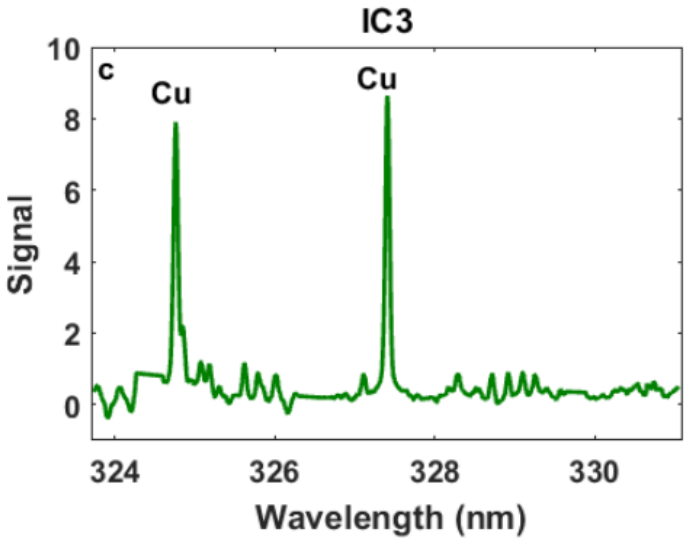

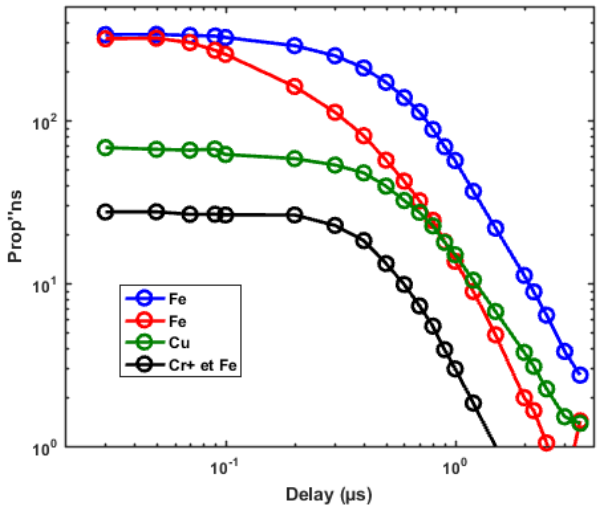

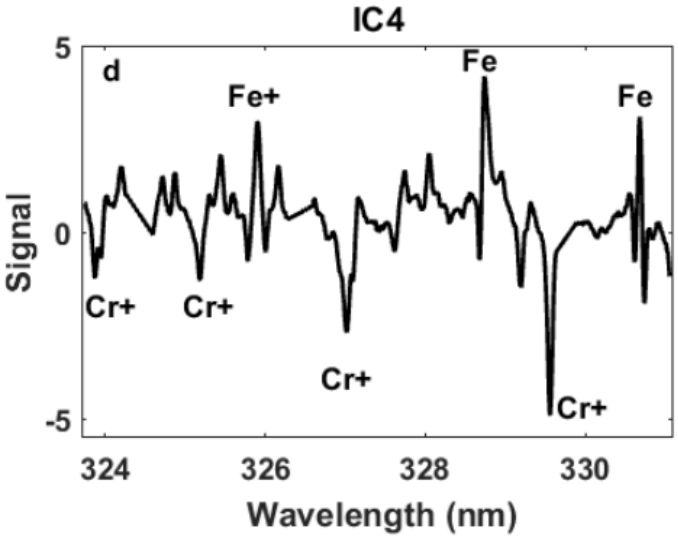

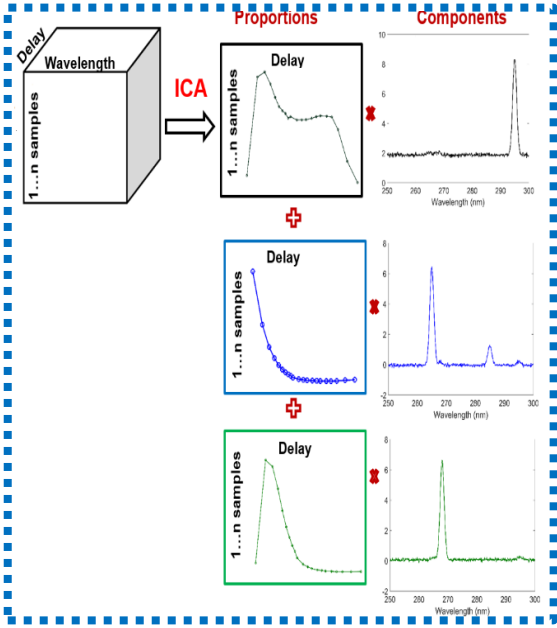

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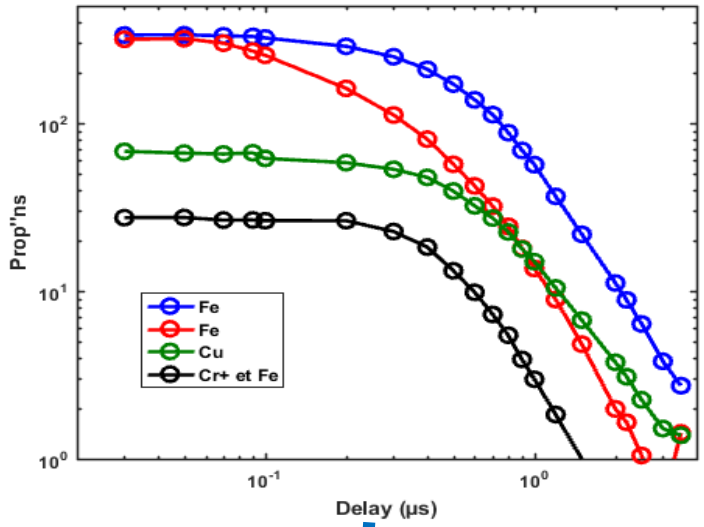
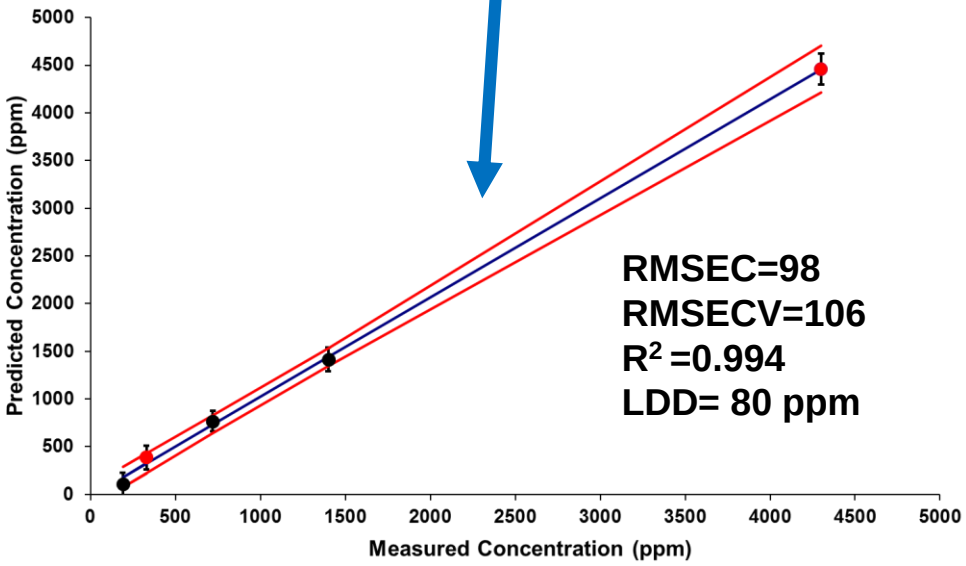
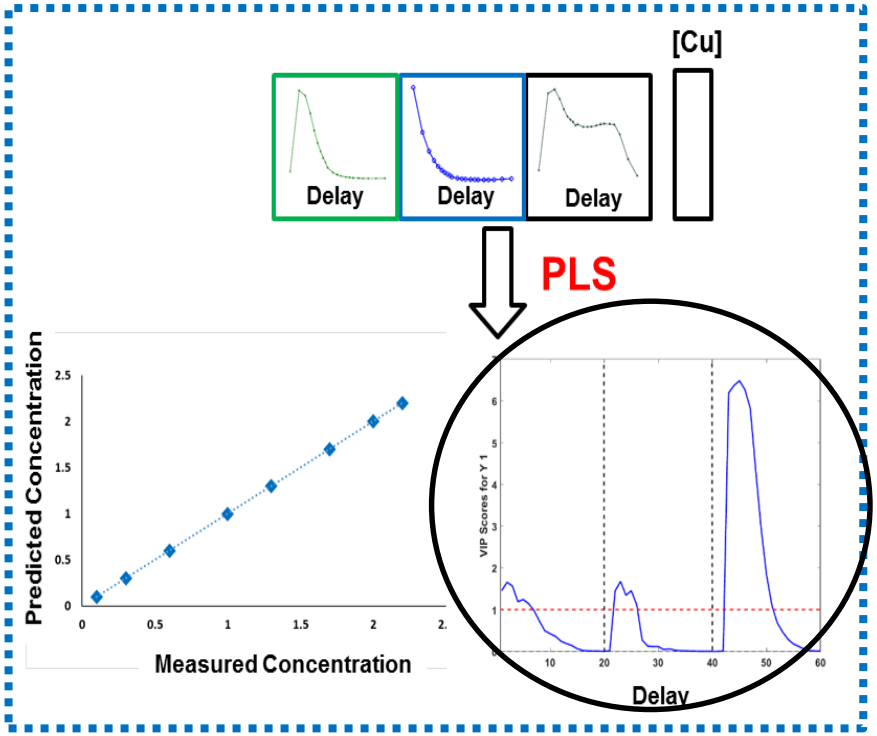


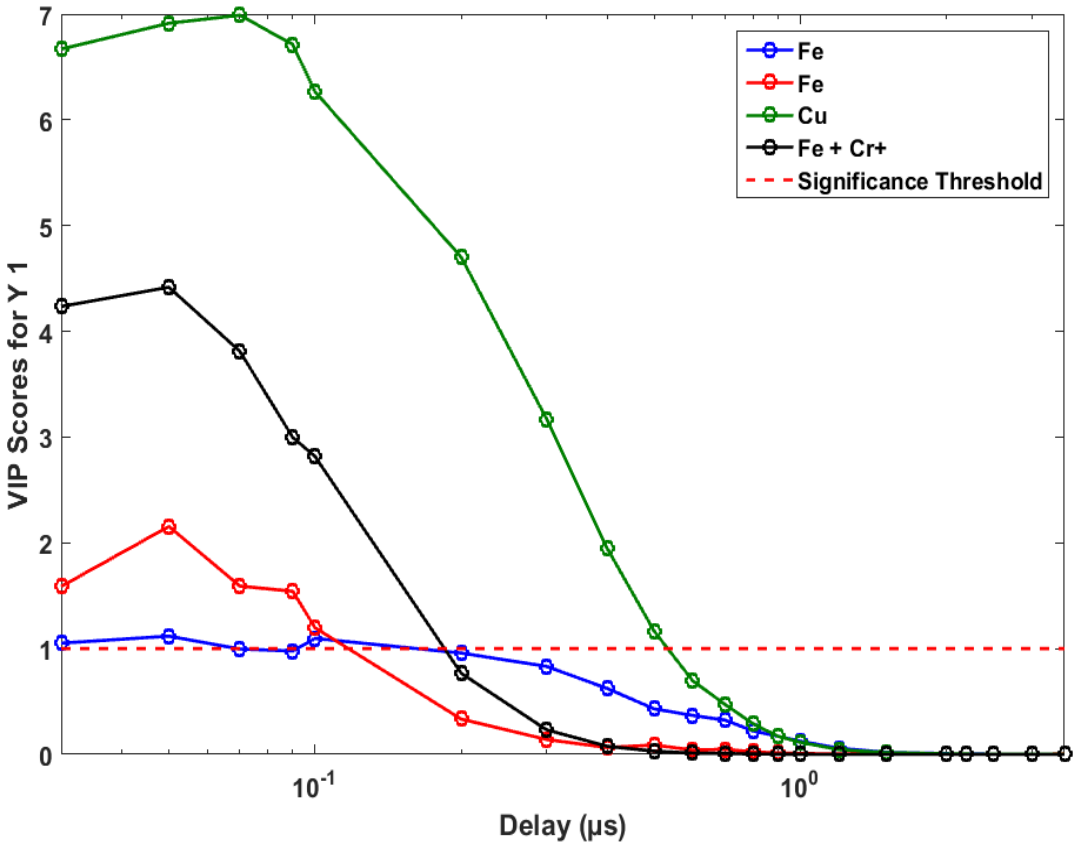


RMSEC=98
RMSECV=106
R^2 =0.994
LDD= 80 ppm



MULTIVARIATE APPROACH

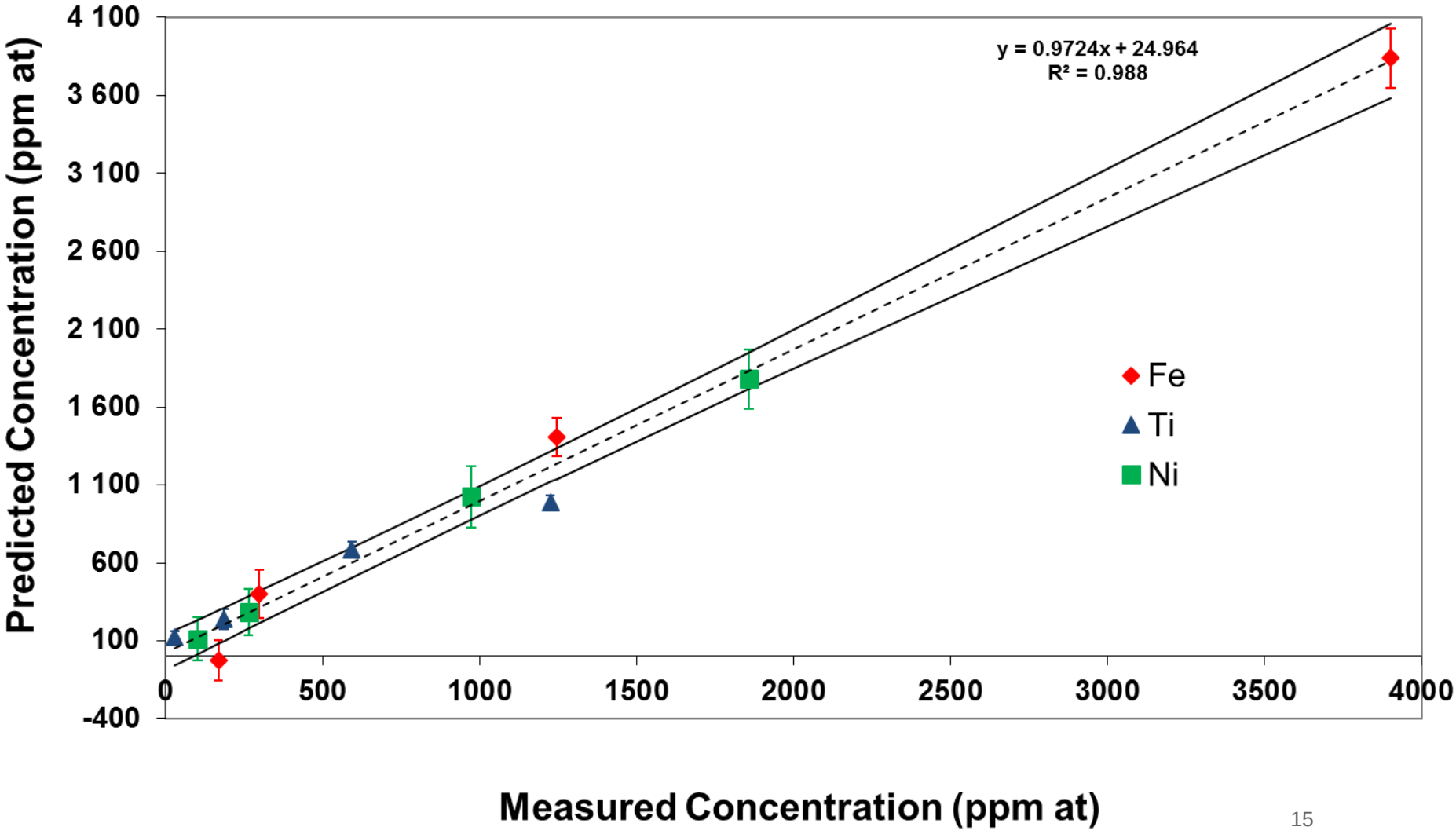
Variable Importance in Projection (VIP) scores estimate the importance of each variable in the projection used in a PLS model and is often used for variable selection. A variable with a VIP Score close to or greater than 1 (one) can be considered important in given model.



The copper concentration is determined from the intensity of that element at short delay and corrected in the first place by the intensity of the interferent (Cr) and secondly by the intensity of the matrix (Fe).

MULTIVARIATE APPROACH

Multi materials



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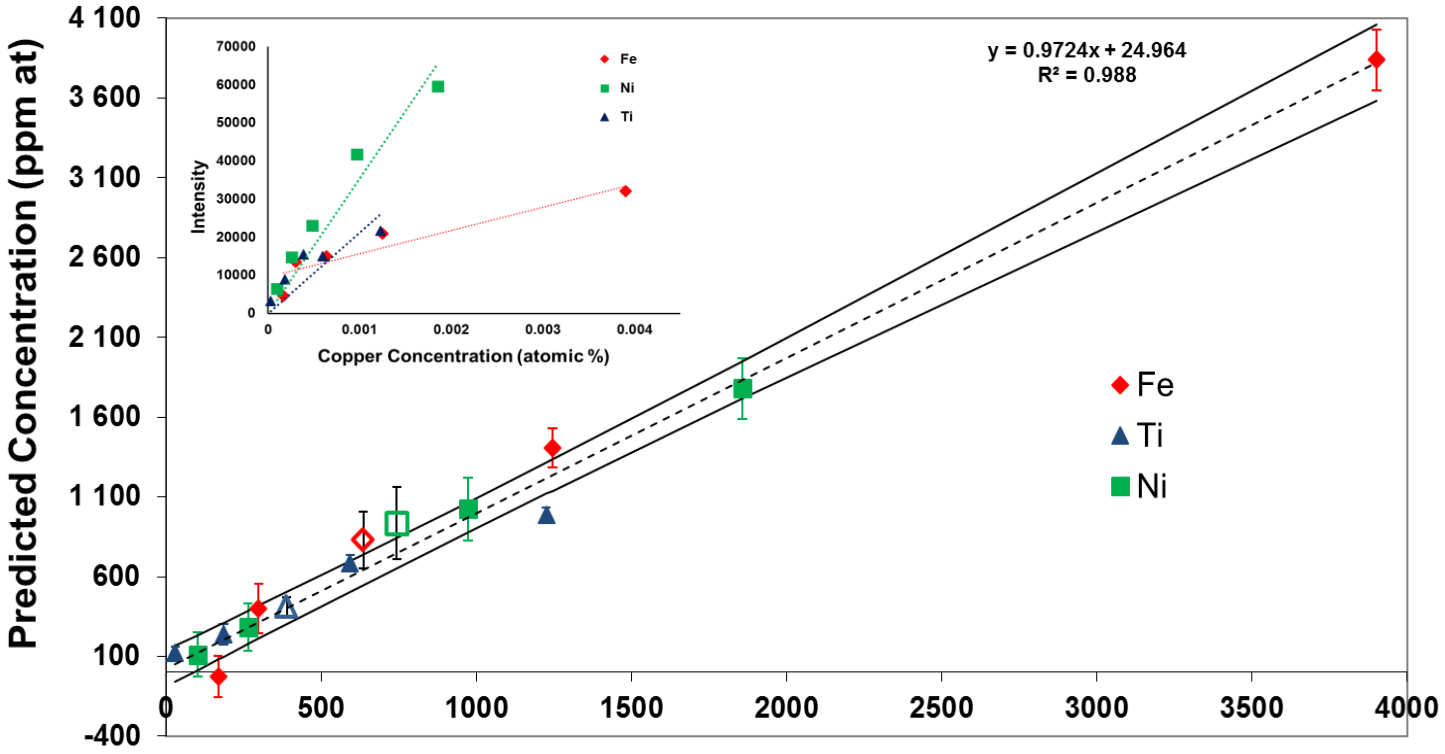

Measured Concentration (ppm at)

Measured Values	Predicted values	Relative Bias
Cu dans Ti (513 ppm)	430 ppm (±15%)	(-16 %)
Cu dans Ni (800 ppm)	700 ppm (±24%)	(-12 %)
Cu dans Fe (720 ppm)	790 ppm (±21%)	(+8%)

CONCLUSION

- Taking into account both dimensions of the analytical signal allows a significantly better correction of matrix effects.
- The interpretation of ICA proportions and components offers an insight into the elemental information, spectral and temporal regions used by the model to determine the analyte concentration.

- External parameter orthogonalisation of PLS.
- Multi-block methods

THANK YOU FOR YOUR ATTENTION