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# Overcoming matrix effects in laser-induced breakdown spectroscopy using multivariate analysis of time-resolved spectra

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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

DE LA RECHERCHE À L'INDUSTRIE

cea den



## Normalization Approaches

### Ablated mass



### Correction of Matrix Effects in Quantitative Elemental Analysis With Laser Ablation Optical Emission Spectrometry

C. CHALÉARD, P. MAUCHEN\*, N. ANDRE, J. UEBBING, J. L. LACOUR AND C. GEERTS

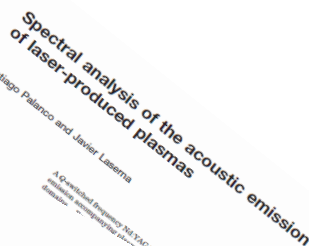
Commissariat à l'Énergie Atomique, Laboratoire de Spectroscopie Laser Analytique, Centre d'Études Saclay, Boite 391, 91191 Gif sur Yvette

A new approach to the quantification of the optical emission spectra from a laser-produced plasma in air at atmospheric pressure is described. It is based on a simple analytical model giving intensity of the emission lines as a function of the ablated mass and the plasma excitation. The hypothesis of a stoichiometric ablation parameters are assumed to be effects observed when the element is changed. Under this assumption, the

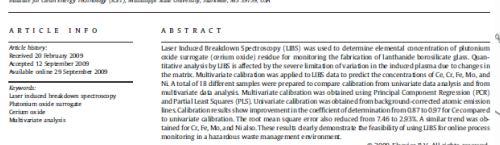
when ablation is performed with a laser 1.0 W cm<sup>-2</sup>. The analytical procedure generally of matrix effects\* is based on a simple signal by a reference signal (generally matrix). Such a normalization procedure reference element is available. This



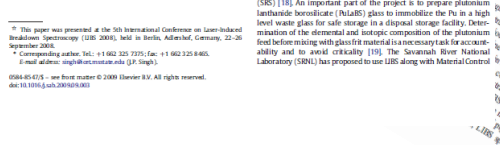
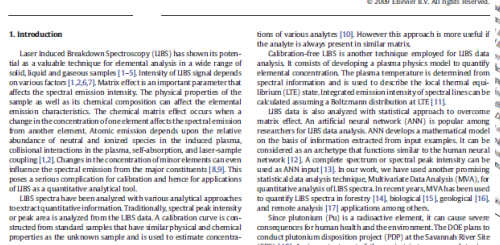
### Plasma temperature



### Surface densities



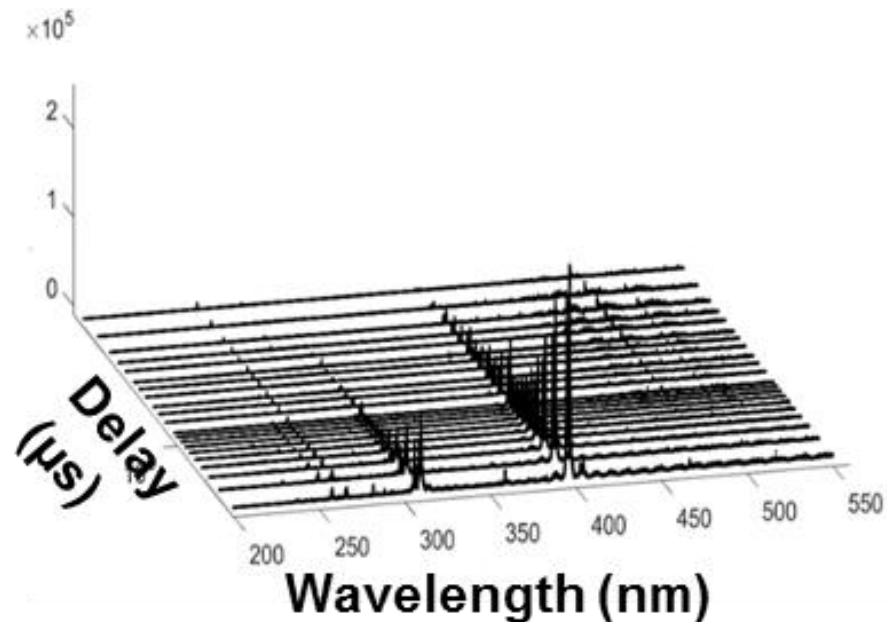
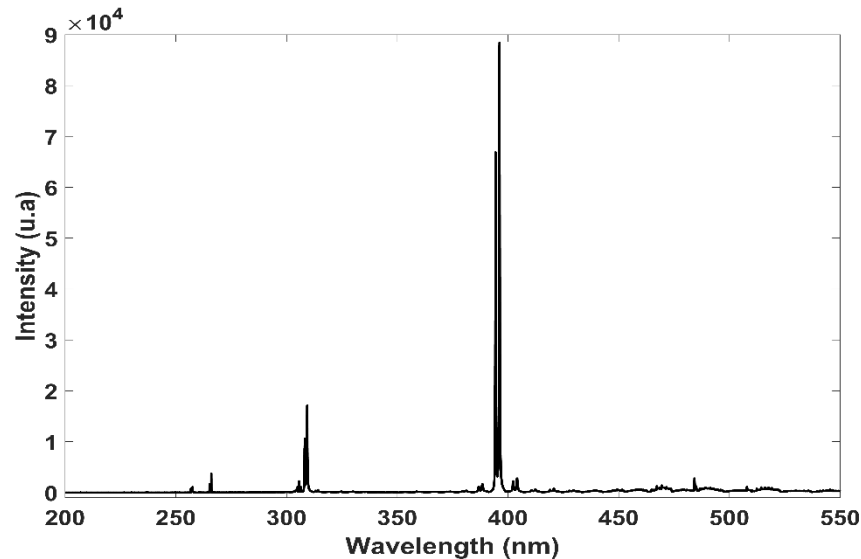
### Emission lines of elements present in the matrix



### Multivariate Calibration

### Calibration-free

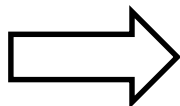
Conventional calibration  
methods



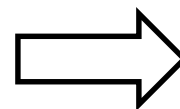
*Improvement of quantitative analysis of solids by LIBS using both the spectral and temporal dimensions of the signal.*

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**Improvement of  
quantitative  
analysis**

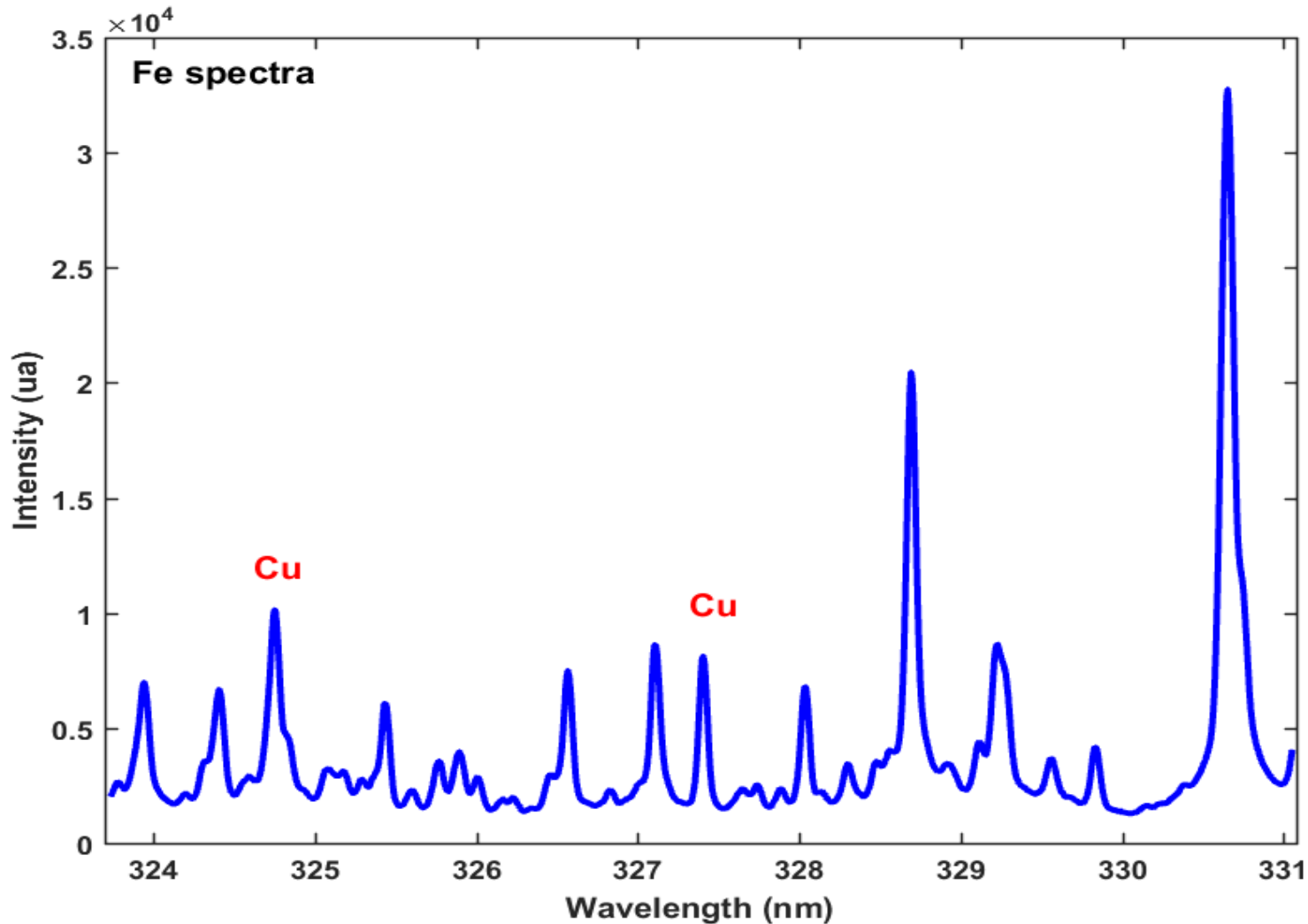


15 samples of 3 matrices  
(Fe, Ni, Ti)

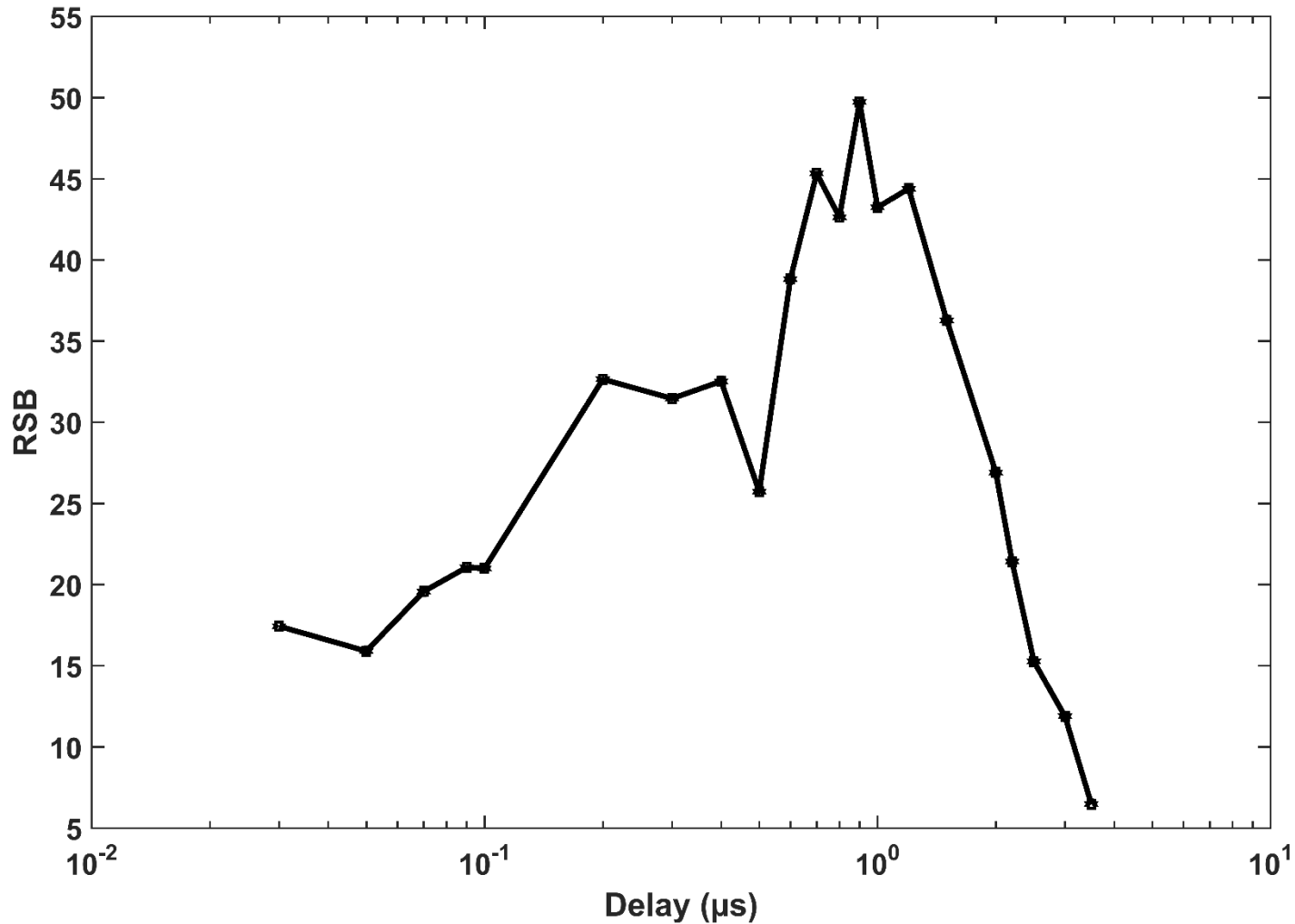


Acquisition at different delay

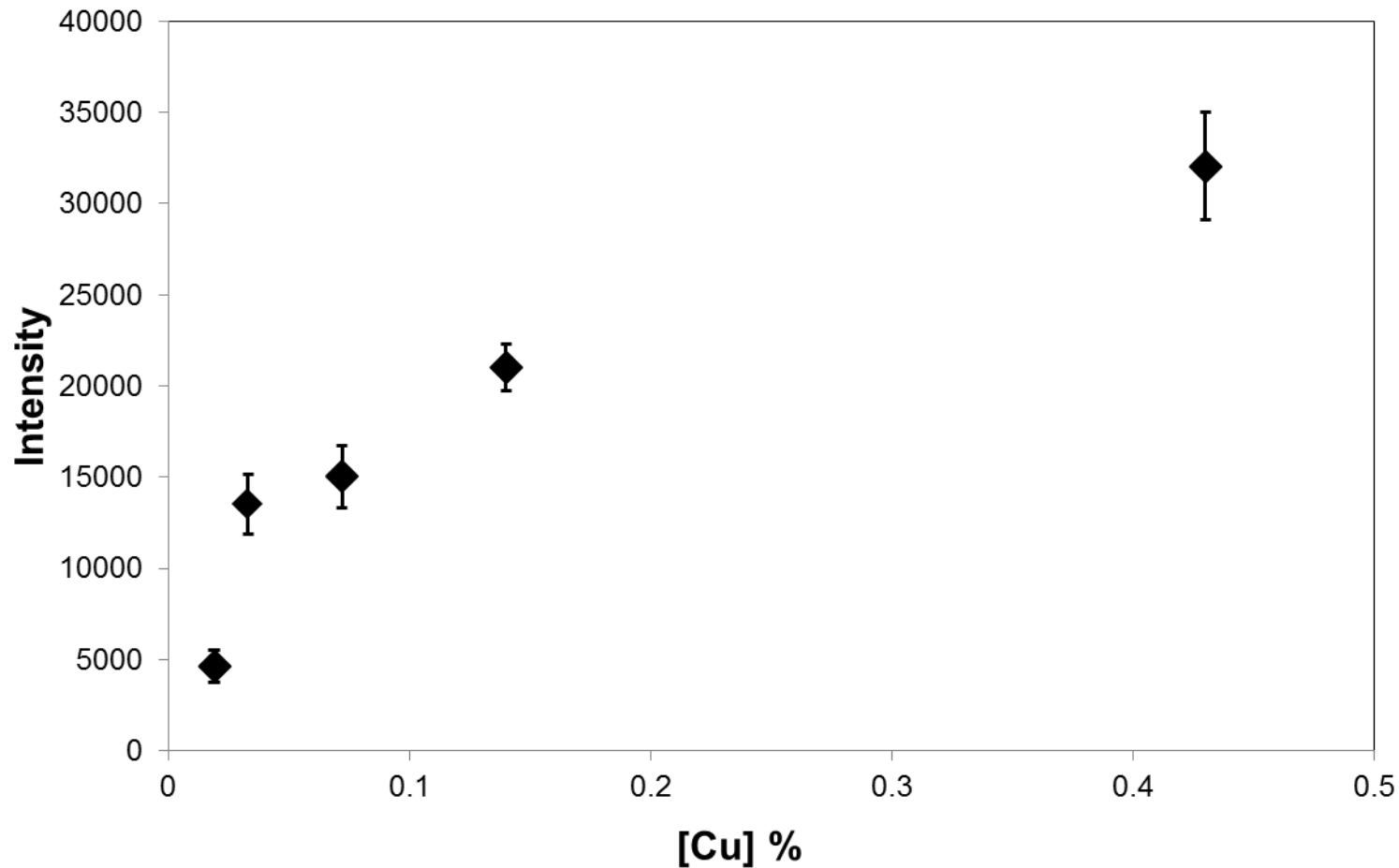
## Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



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

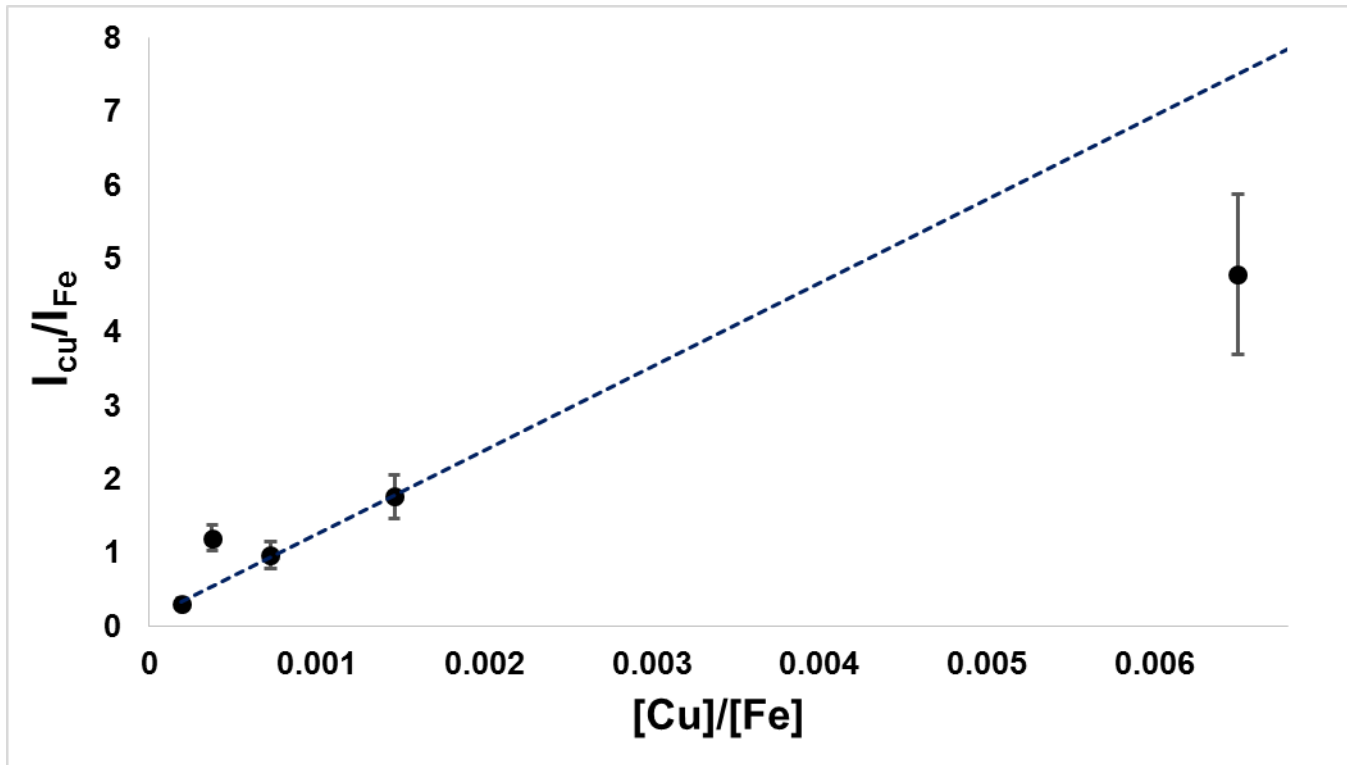


## Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



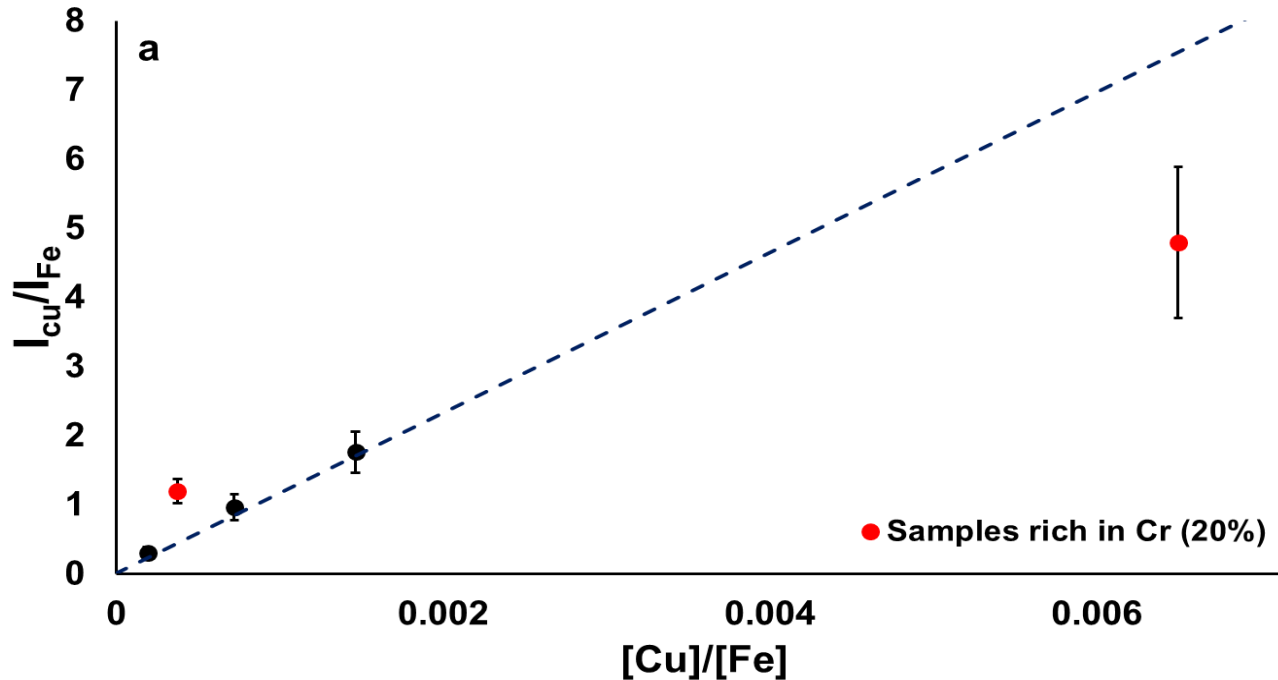


Cu spectral intensity values at 327.4 nm are normalized by Fe spectral intensity values



LDD=1300ppm  
 $R^2 = 0.973$

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

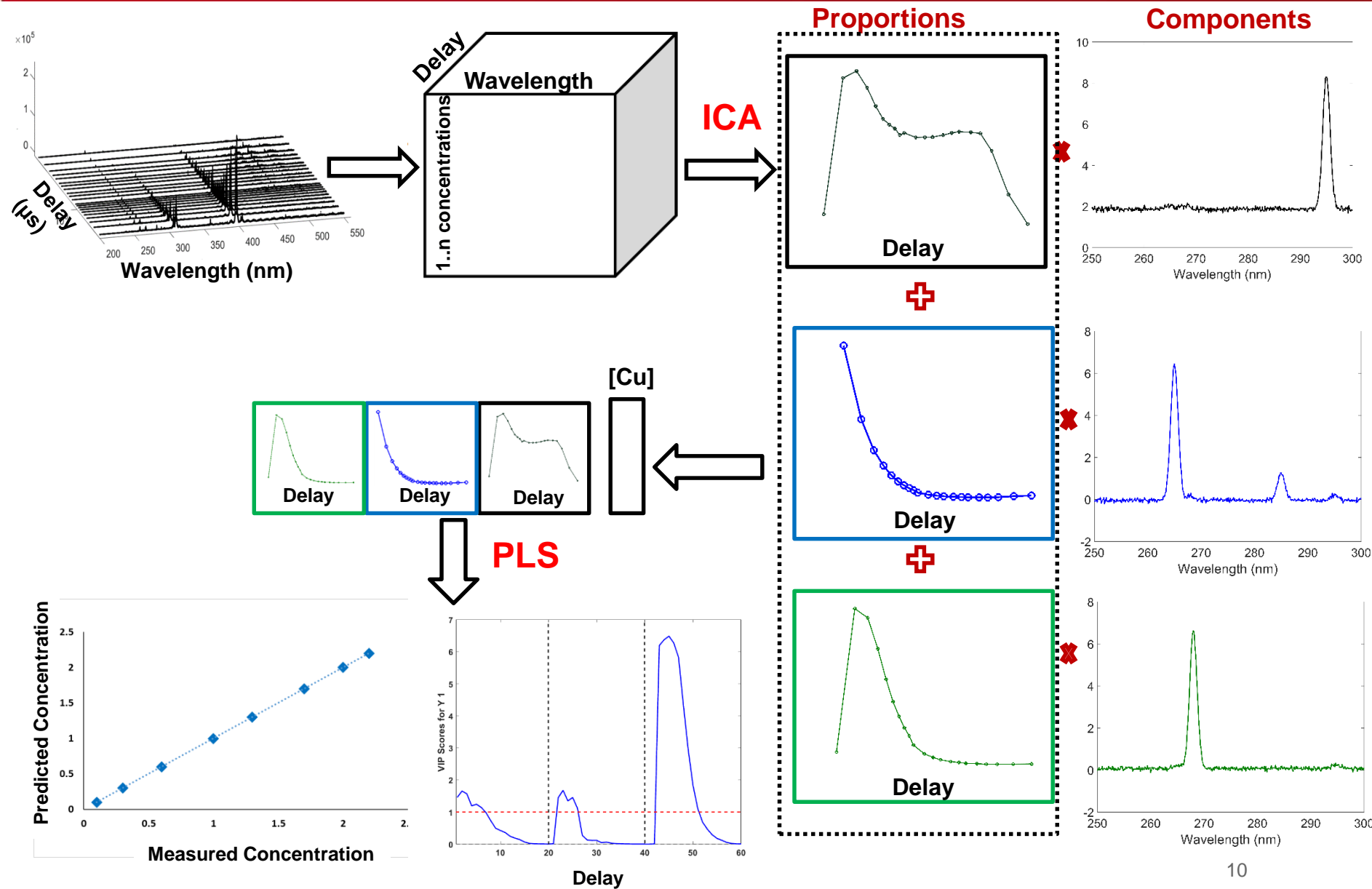


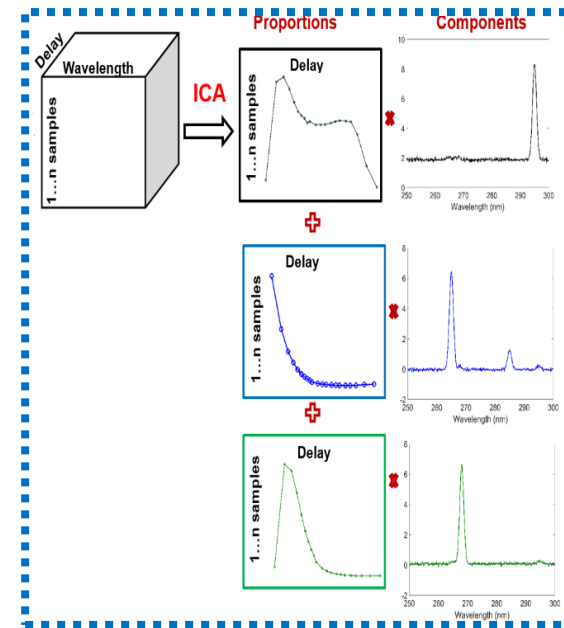
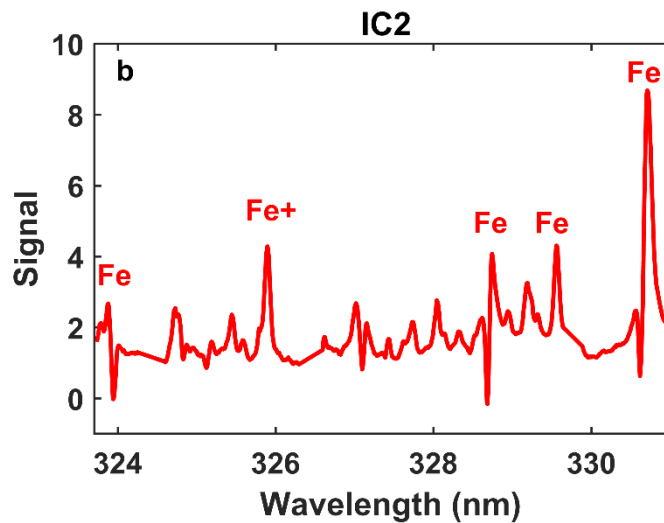
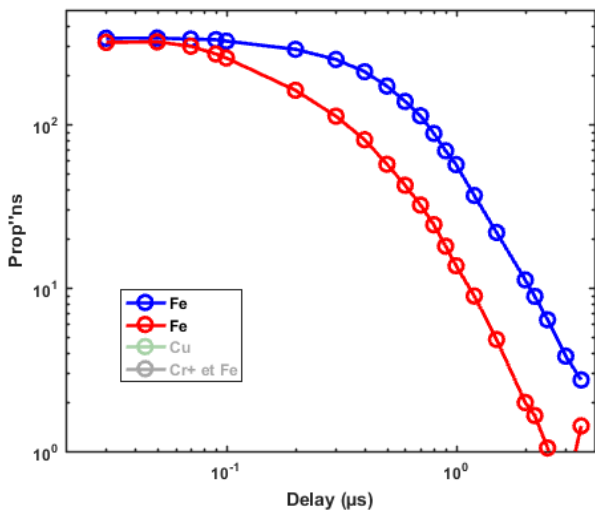
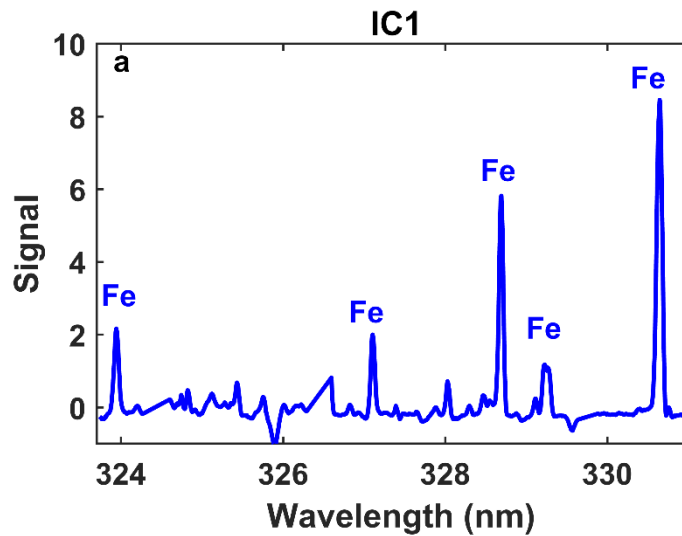
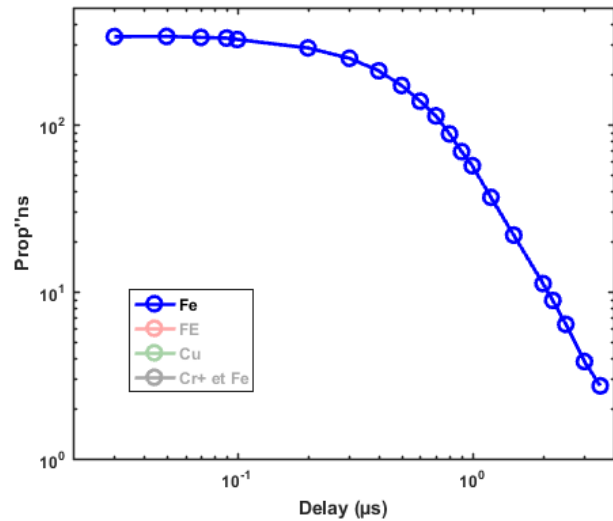
LDD=1300ppm  
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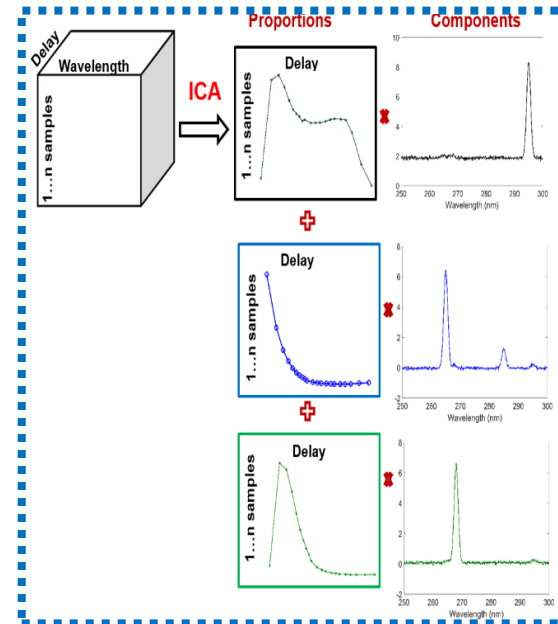
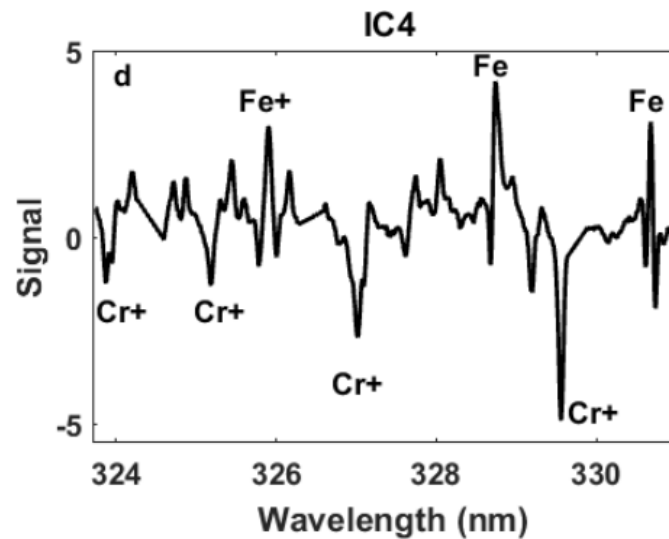
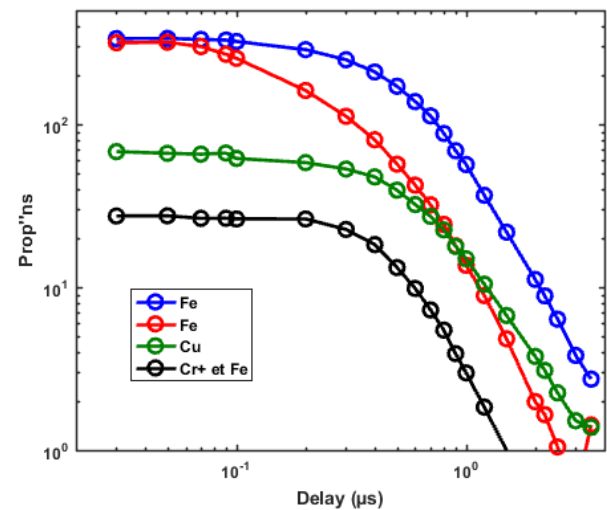
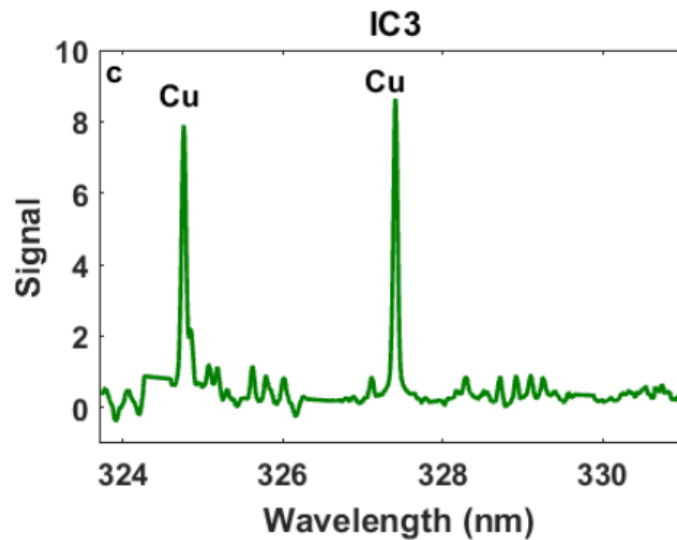
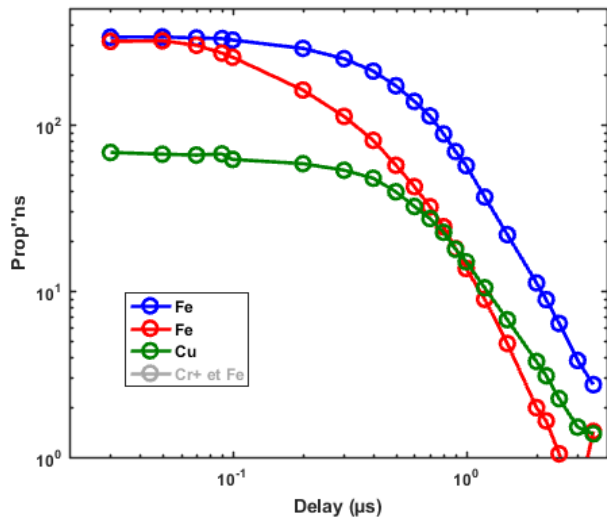
Improved calibration curve is observed by standardizing but analytical performance still insufficient.

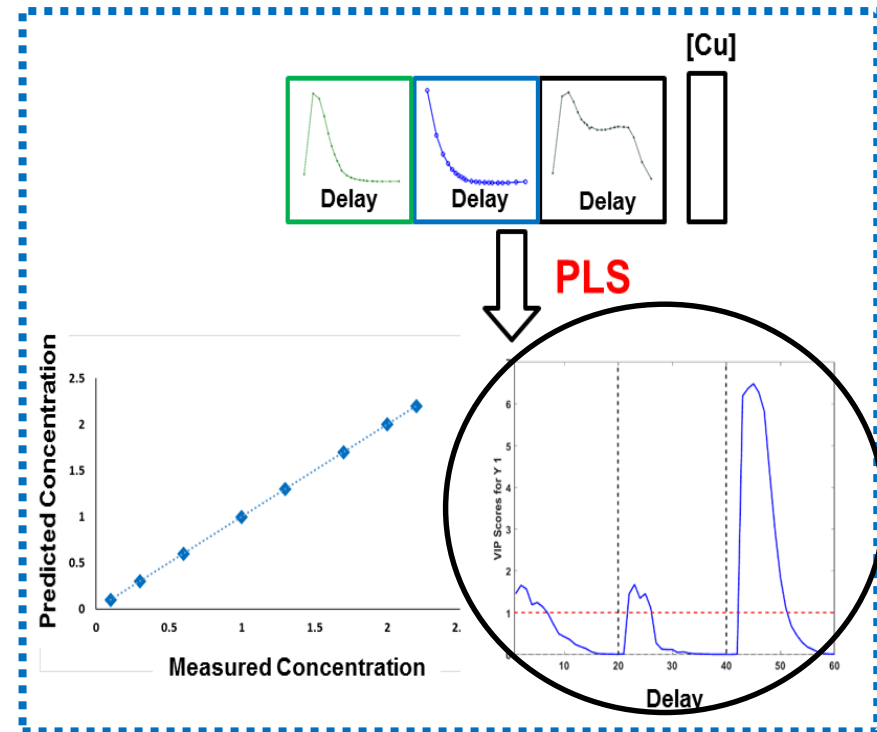
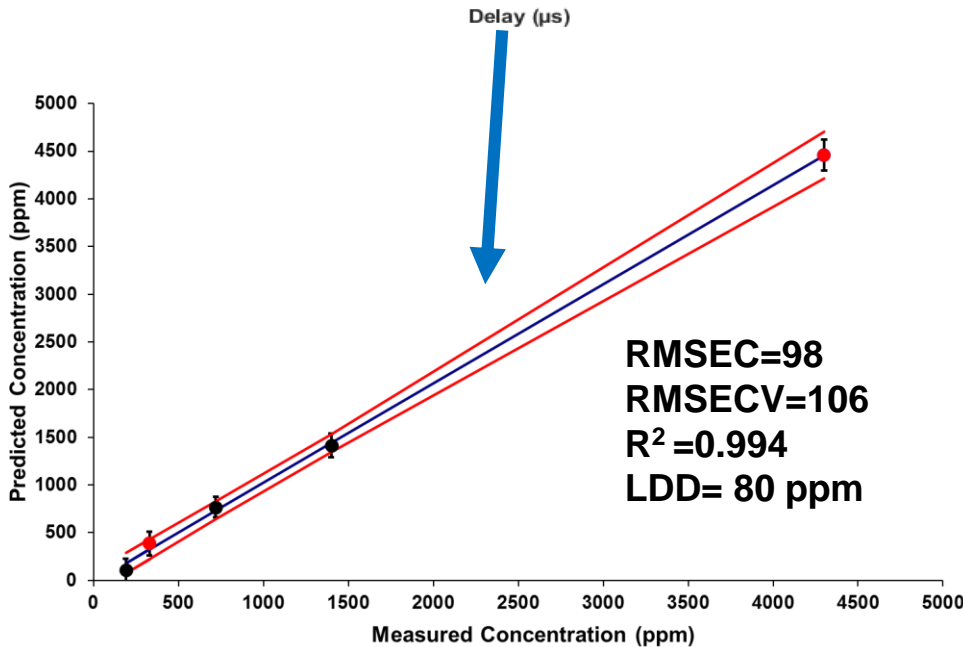
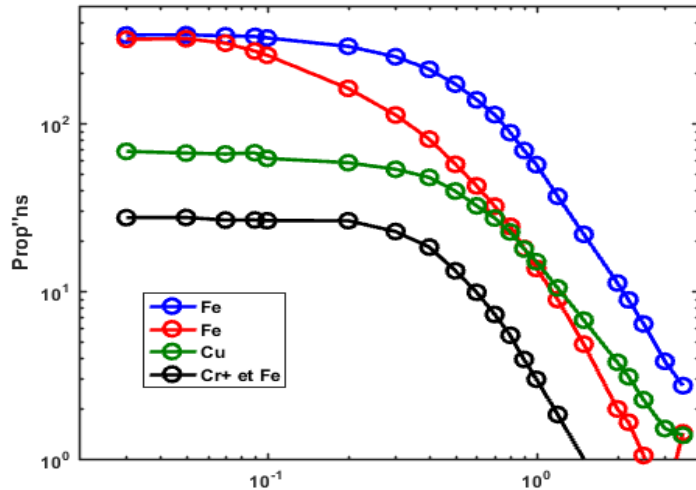


Spectro-temporal approach using chemometrics

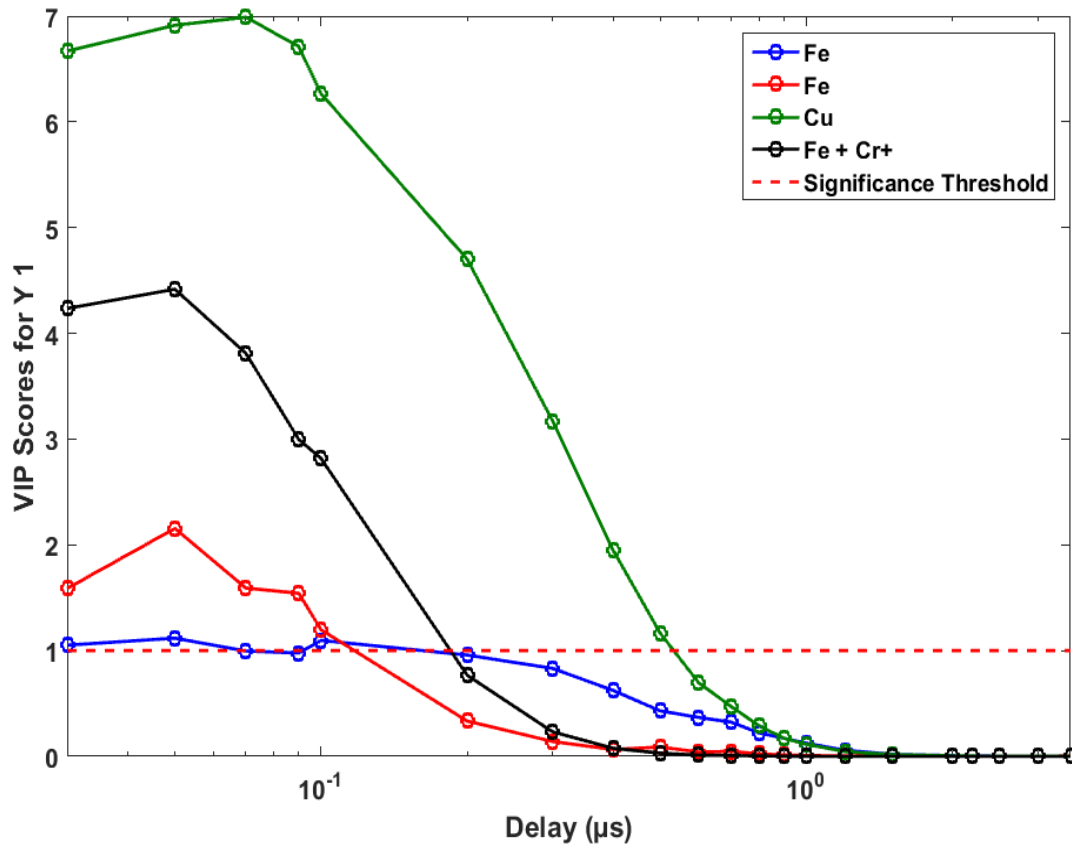






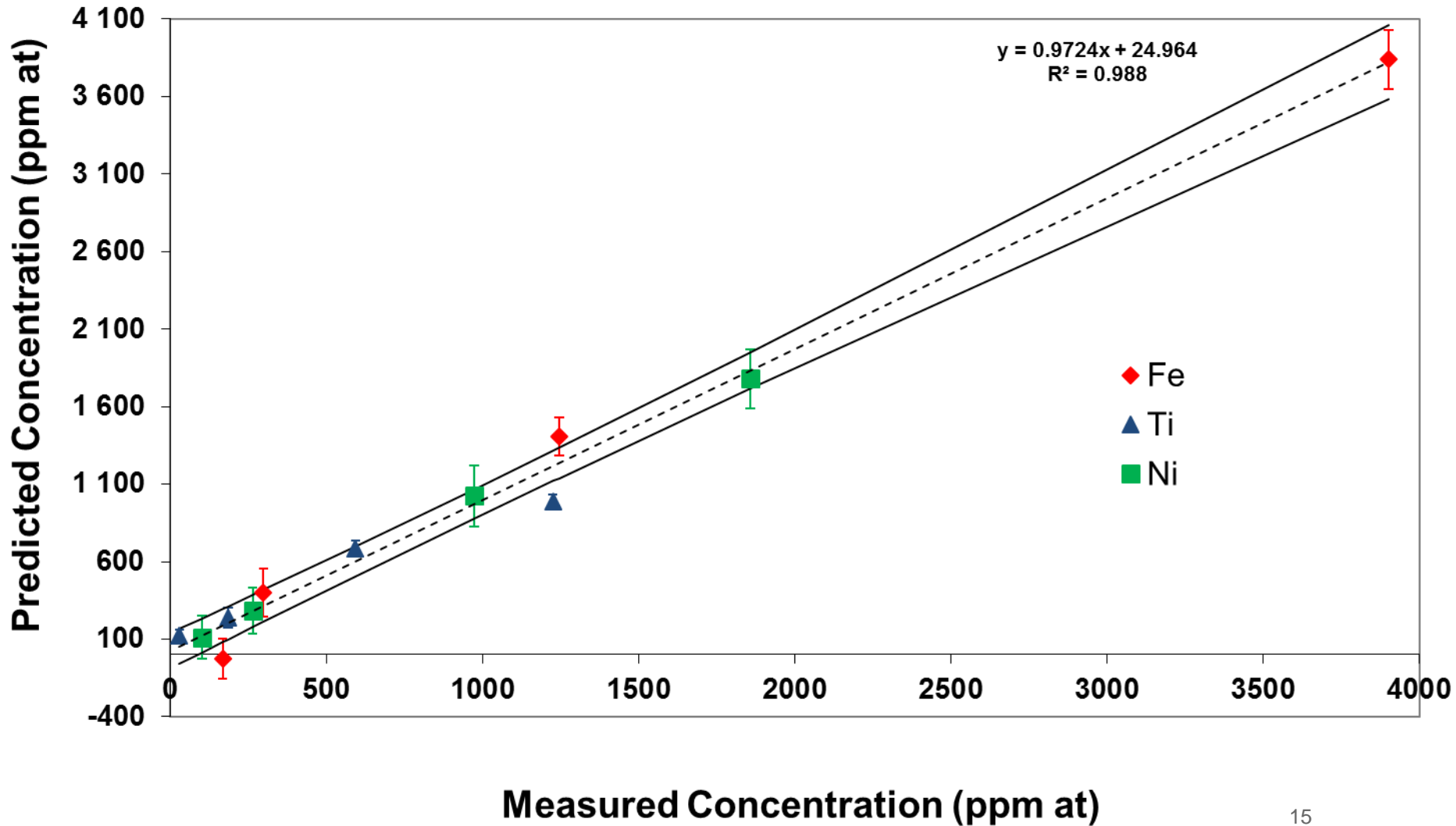


Variable Importance in Projection (VIP) scores estimate the importance of each variable in the projection used in a PLS model and is often used for variable selection. A variable with a VIP Score close to or greater than 1 (one) can be considered important in given model.



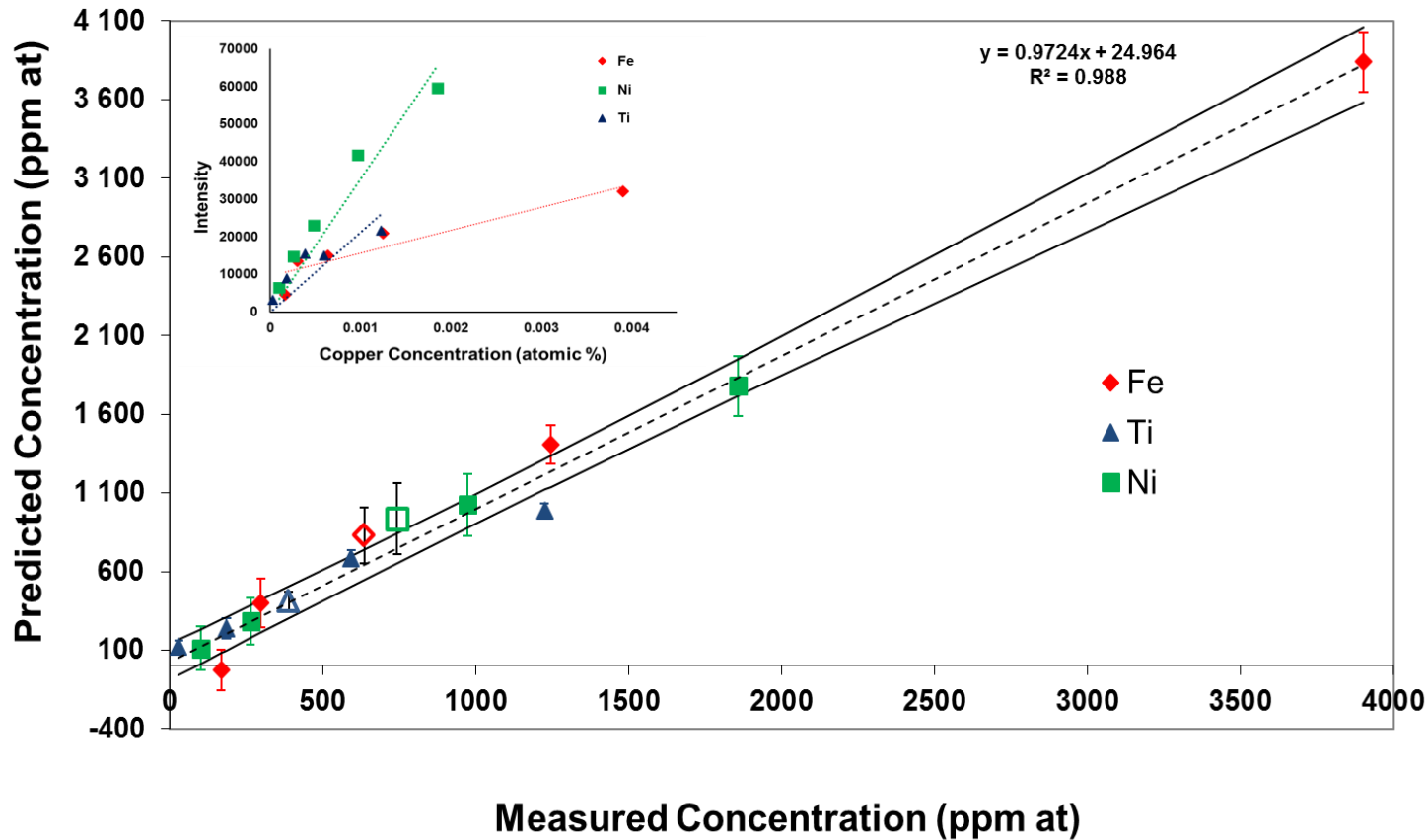
The copper concentration is determined from the intensity of that element at short delay and corrected in the first place by the intensity of the interferent (Cr) and secondly by the intensity of the matrix (Fe).

## Multi materials





## Multi materials



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%)



- ❖ 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

**Questions**



**THANK YOU  
FOR YOUR  
ATTENTION**