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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

Normalization Approaches

Ablated mass

Plasma temperature



Surface densities

Calibration-free

Emission lines of elements present in the matrix

Multivariate calibration of spectra obtained by Laser Induced Breakdown Spectroscopy of plutonium oxide surrogate residues

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) was used to determine elemental concentration of plutonium oxide surrogate (cerium oxide) residue for monitoring the fabrication of plutonium oxide surrogate. Quantitative analysis by LIBS is affected by the severe limitation of variation in the induced plasma due to change in the matrix. Multivariate calibration was applied to LIBS data to predict the concentration of Ce, Co, Fe, Mn, and Ni. A total of 18 different samples were prepared to compare calibration from univariate data analysis and from multivariate data analysis. Multivariate calibration was obtained using Principal Component Regression (PCR) and Partial Least Squares (PLS). Univariate calibration was obtained from background corrected emission lines. Calibration results show improvement in the coefficient of determination from 0.70 to 0.92 for the Co compared to univariate calibration. The root mean square error also reduced from 7.46 to 2.83%. A similar trend was obtained for Ce, Fe, Mn, and Ni. These results clearly demonstrate the feasibility of using LIBS for other processes monitoring in a hazardous waste management environment.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has shown its potential as a valuable technique for elemental analysis in a wide range of solid, liquid and gaseous samples [1–5]. Intensity of LIBS signal depends on various factors [2,6,7]. Matrix effect is an important parameter that affects the spectral emission intensity. The physical properties of the sample as well as its chemical composition can affect the elemental emission characteristics. The chemical matrix effect occurs when a change in the concentration of one element affects the spectral emission from another element. Atomic emission depends upon the relative abundance of neutral and ionized species in the induced plasma, collisional interactions in the plasma, self-absorption, and laser-signal coupling [1,2]. Changes in the concentration of minor elements can even influence the spectral emission from the major constituents [8,9]. This poses a serious complication for calibration and hence for applications of LIBS as a quantitative analytical tool.

LIBS spectra have been analyzed with various analytical approaches to extract quantitative information. Traditionally, spectral peak intensity or peak area is analyzed from the LIBS data. A calibration curve is constructed from standard samples that have similar physical and chemical properties as the unknown sample and is used to estimate concentration of various analytes [10]. However this approach is more useful if the analysis is always present in similar matrix.

Calibration-free LIBS is another technique employed for LIBS data analysis. It consists of developing a plasma physics model to quantify element concentration. The plasma temperature is determined from spectral information and is used to derive the local thermal equilibrium (LTE) state. Integral and emission intensity of spectral lines can be calculated assuming a Boltzmann distribution at LTE [11].

LIBS data is also analyzed with statistical approach to overcome matrix effect. An artificial neural network (ANN) is popular among researchers for LIBS data analysis. ANN develops a mathematical model on the basis of information extracted from input examples. It can be considered as an archetype that functions similar to the human neural network [12]. A complete spectrum or spectral peak intensity can be used as ANN input [13]. In our work, we have used another promising statistical data analysis technique, Multivariate Data Analysis (MVA), for quantitative analysis of LIBS spectra. In recent years, MVA has been used to quantify LIBS spectra in forestry [14], biological [15], geological [16], and remote analysis [17] applications among others.

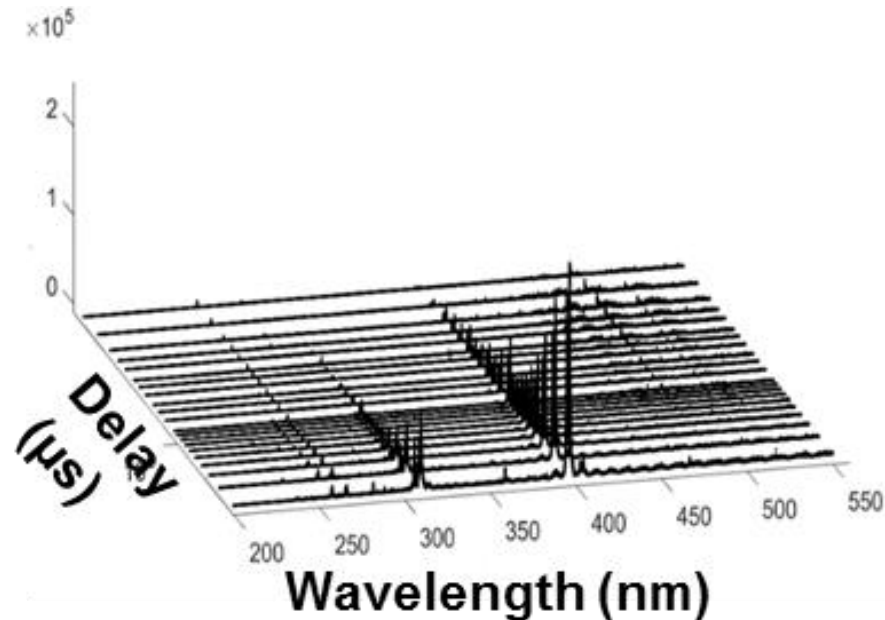
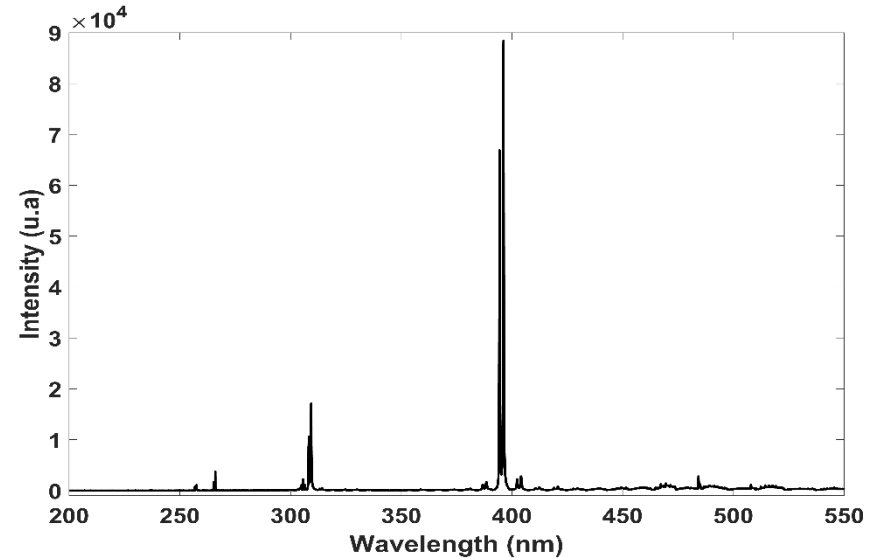
Since plutonium (Pu) is a radioactive element, it can cause severe consequences for human health and the environment. The DOE plans to conduct plutonium disposition project (PDP) at the Savannah River Site (SRS) [18]. An important part of the project is to prepare plutonium lanthanide borosilicate (PuLBs) glass to immobilize the Pu in a high level waste glass for safe storage in a disposal energy facility. Determination of the elemental and isotopic composition of the plutonium feed before mixing with glass is of material importance and for accountability and to avoid criticality [19]. The Savannah River National Laboratory (SRNL) has proposed to use LIBS along with Material Control

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Multivariate
Calibration

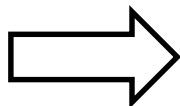
Conventional calibration
methods



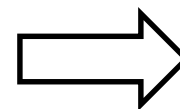
Improvement of quantitative analysis of solids by LIBS using both the spectral and temporal dimensions of the signal.

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

**Improvement of
quantitative
analysis**

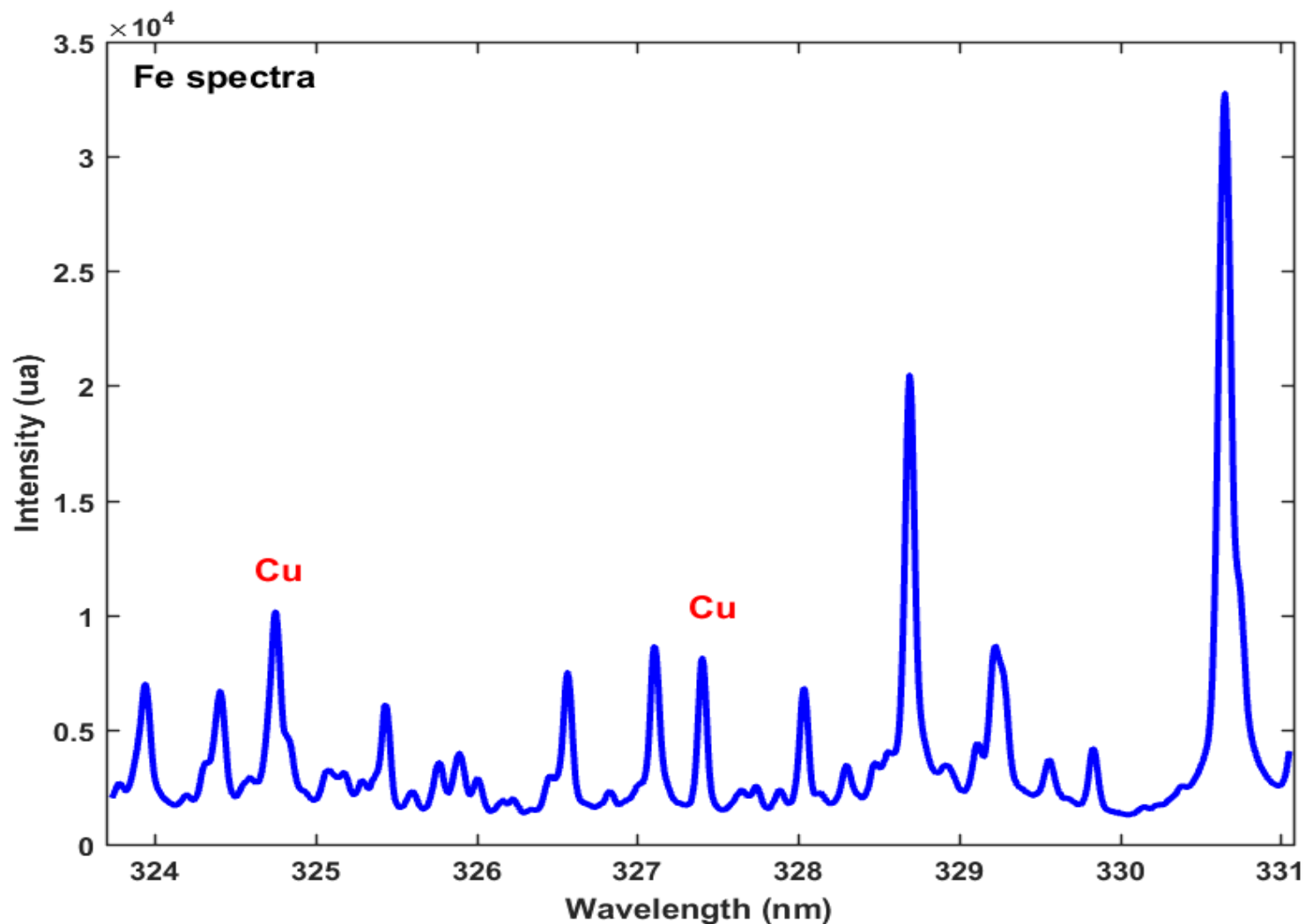


15 samples of 3 matrices
(Fe, Ni, Ti)

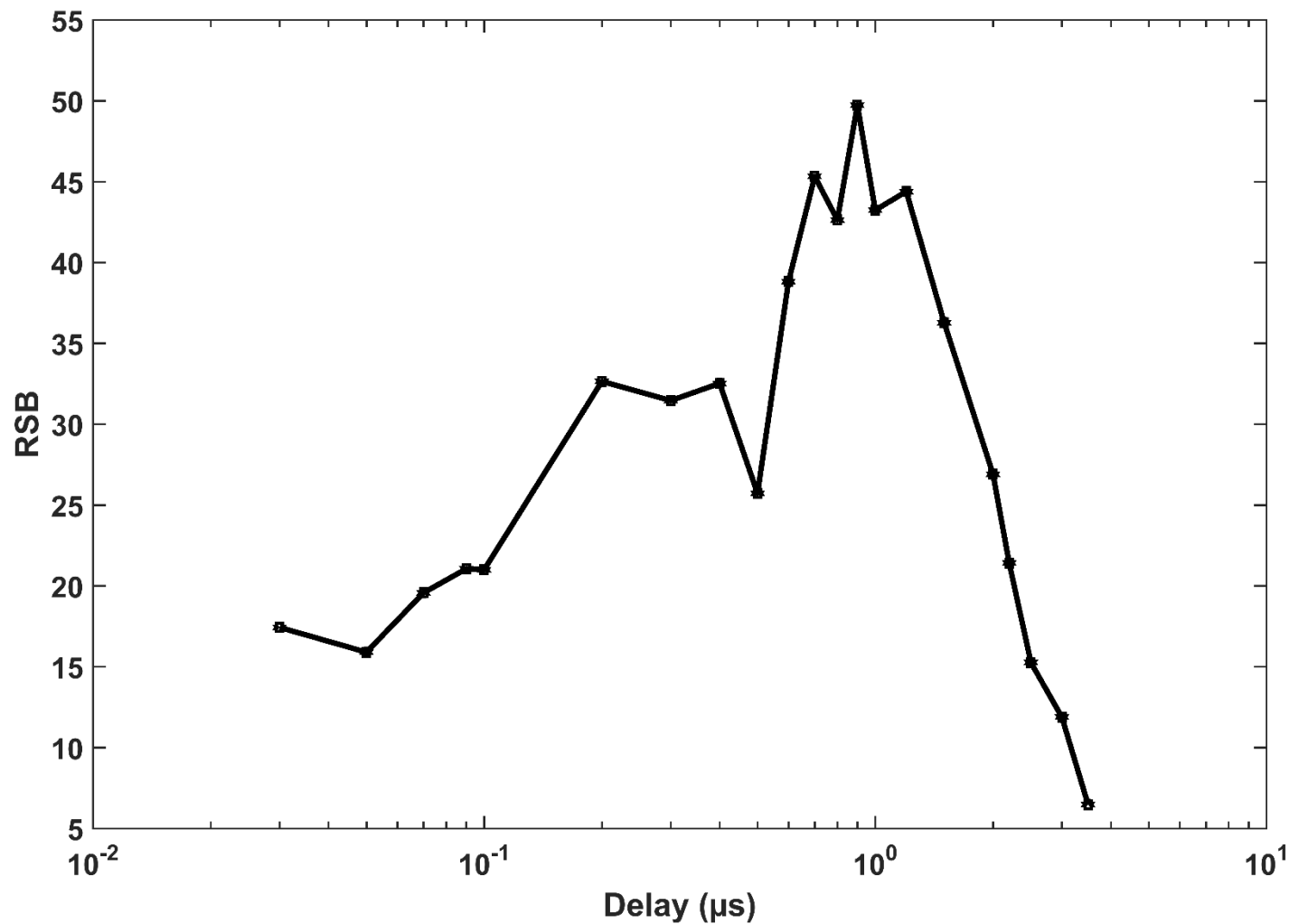


Acquisition at different delay

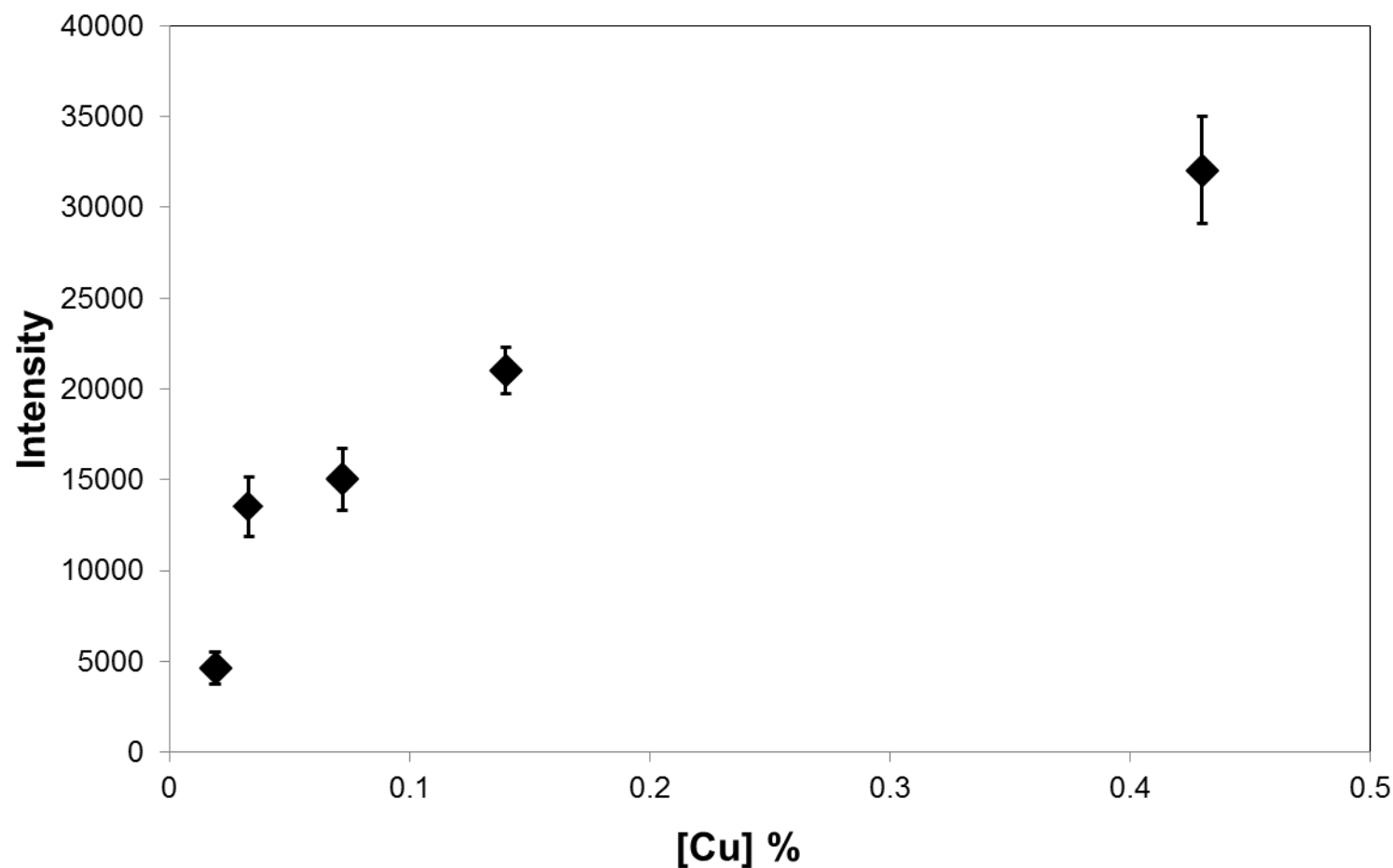
Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



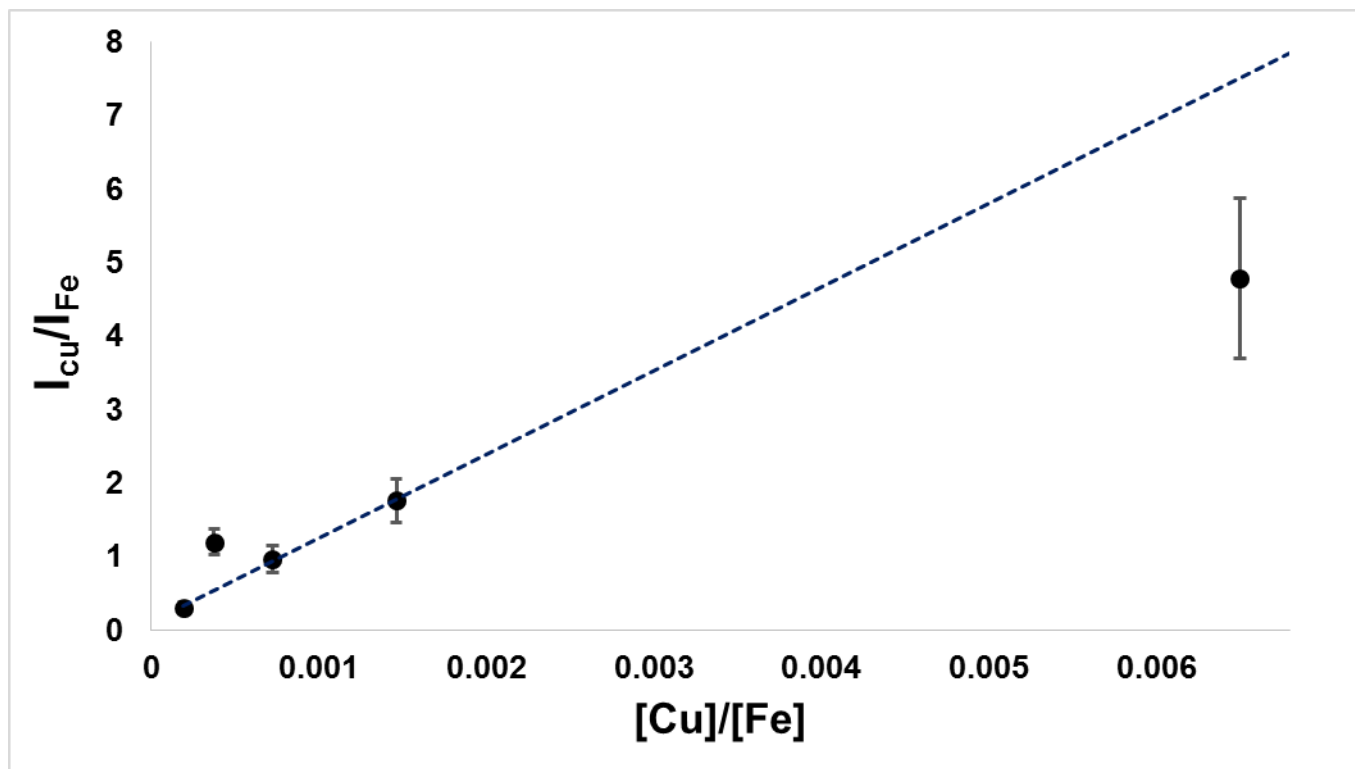
Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



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

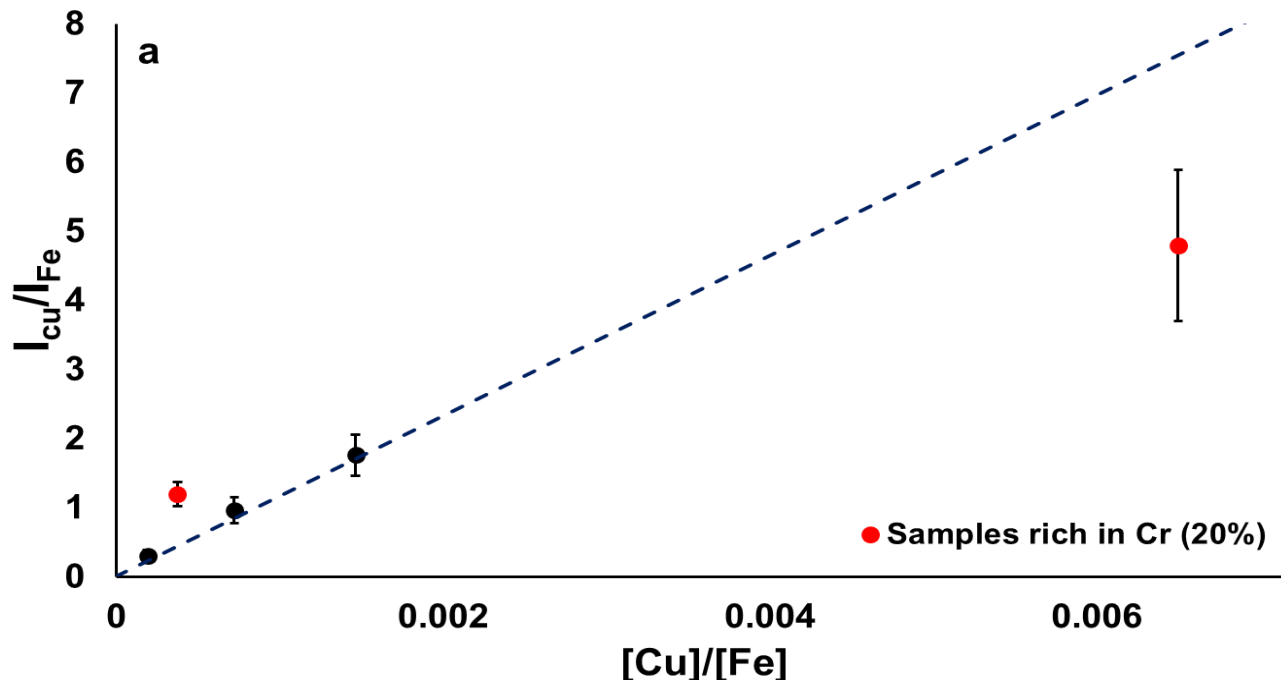


Cu spectral intensity values at 327.4 nm are normalized by Fe spectral intensity values



LDD=1300ppm
 $R^2 = 0.973$

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

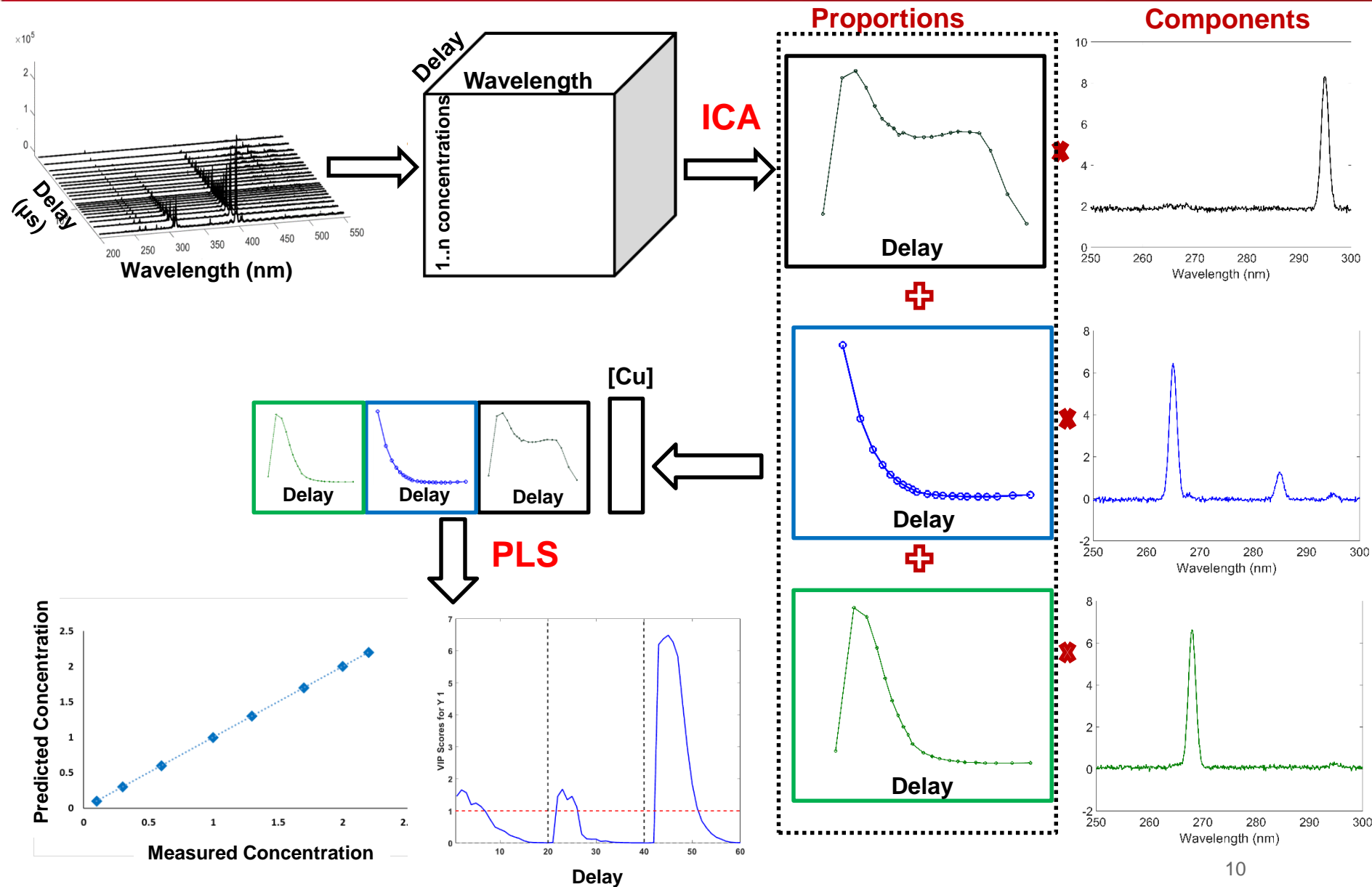


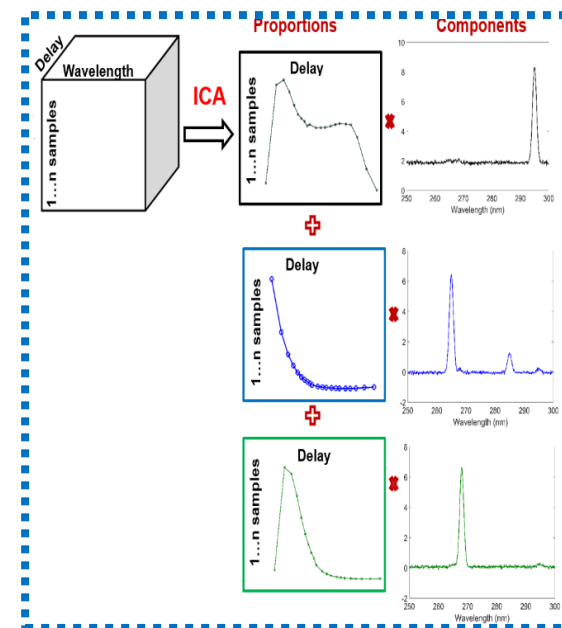
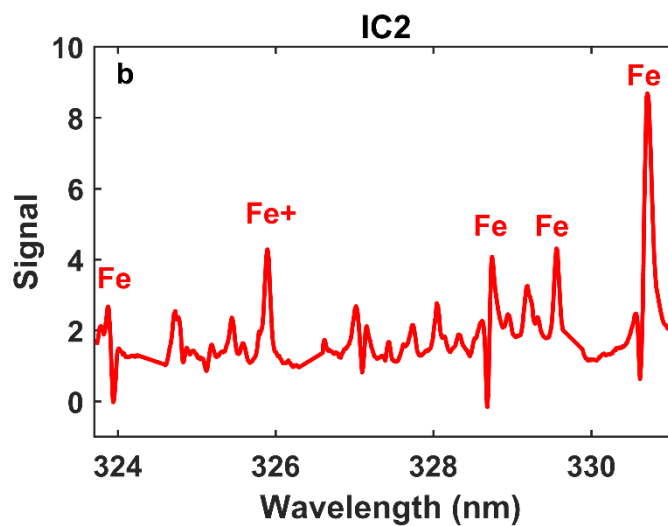
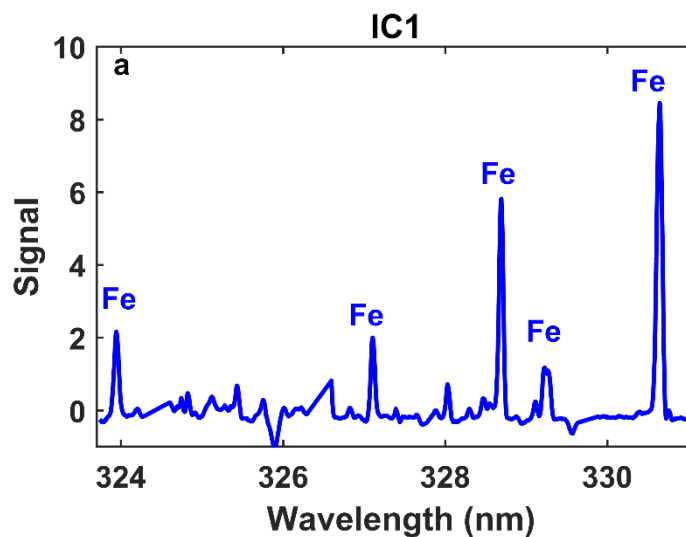
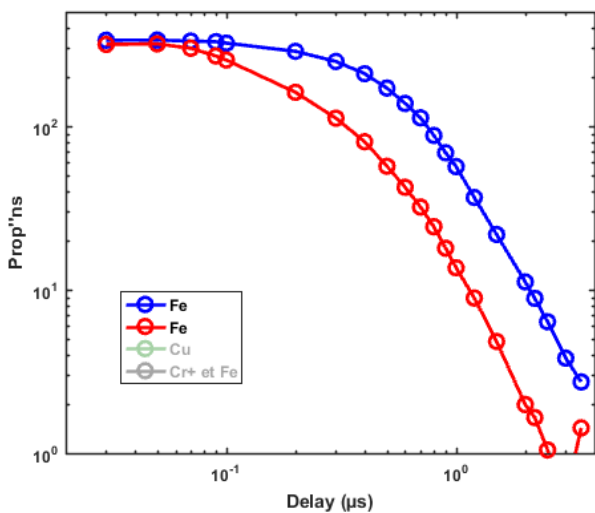
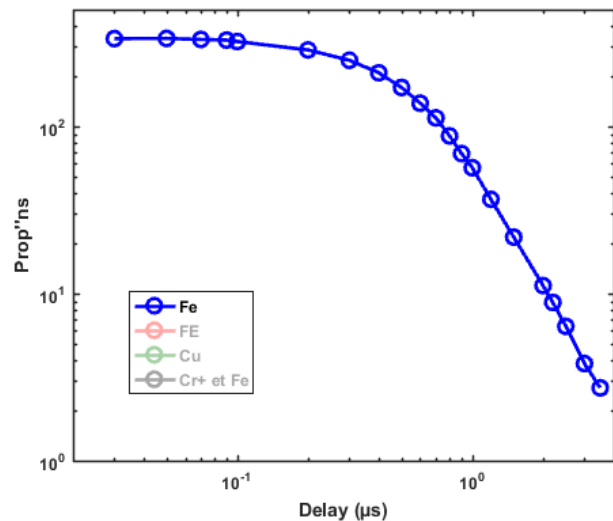
LDD=1300ppm
 $R^2 = 0.973$

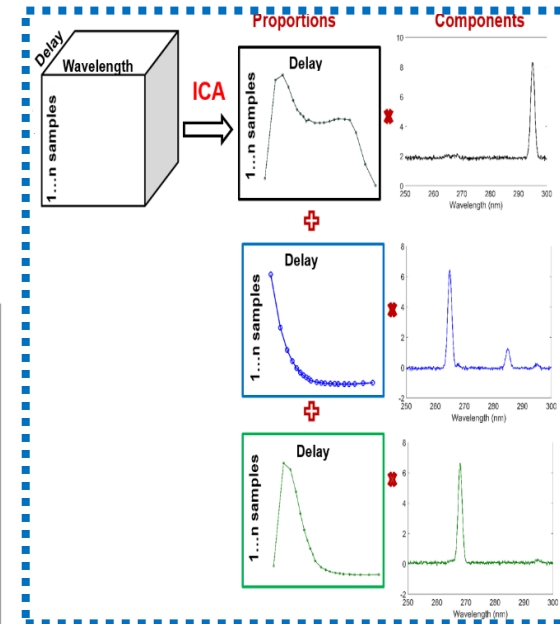
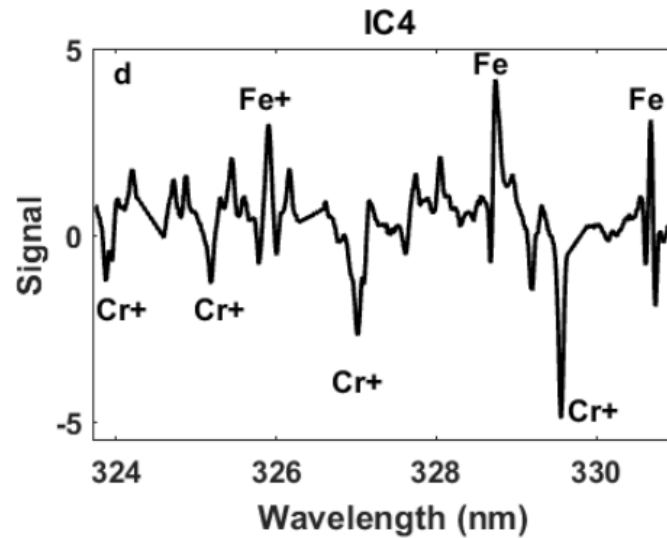
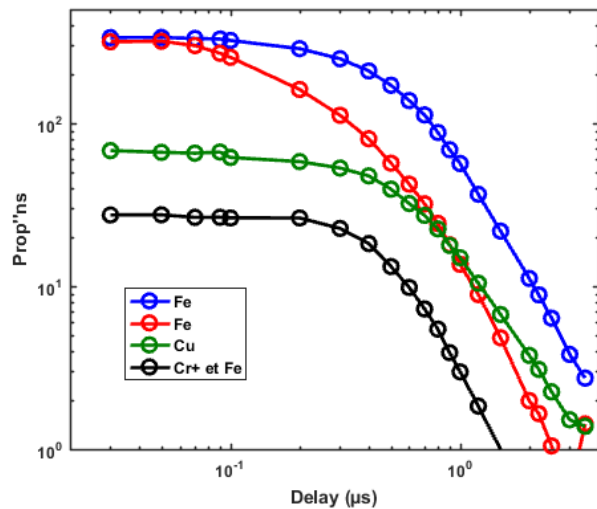
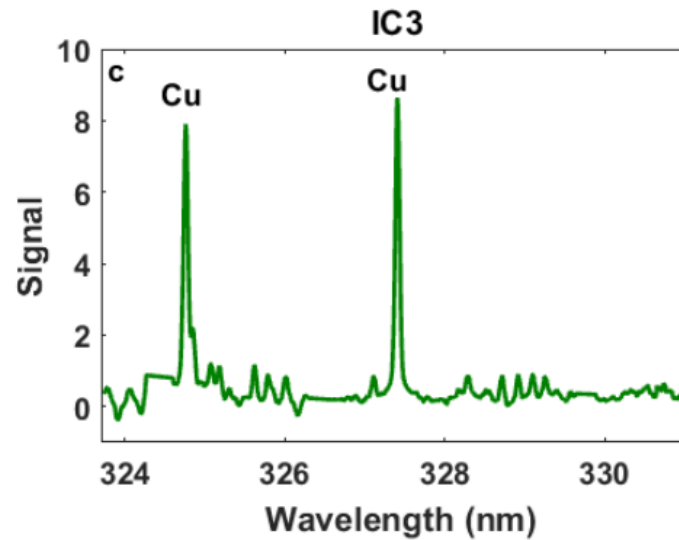
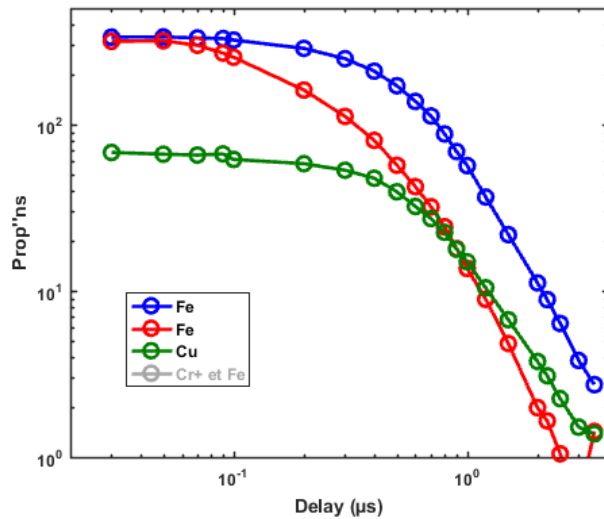
Improved calibration curve is observed by standardizing but analytical performance still insufficient.

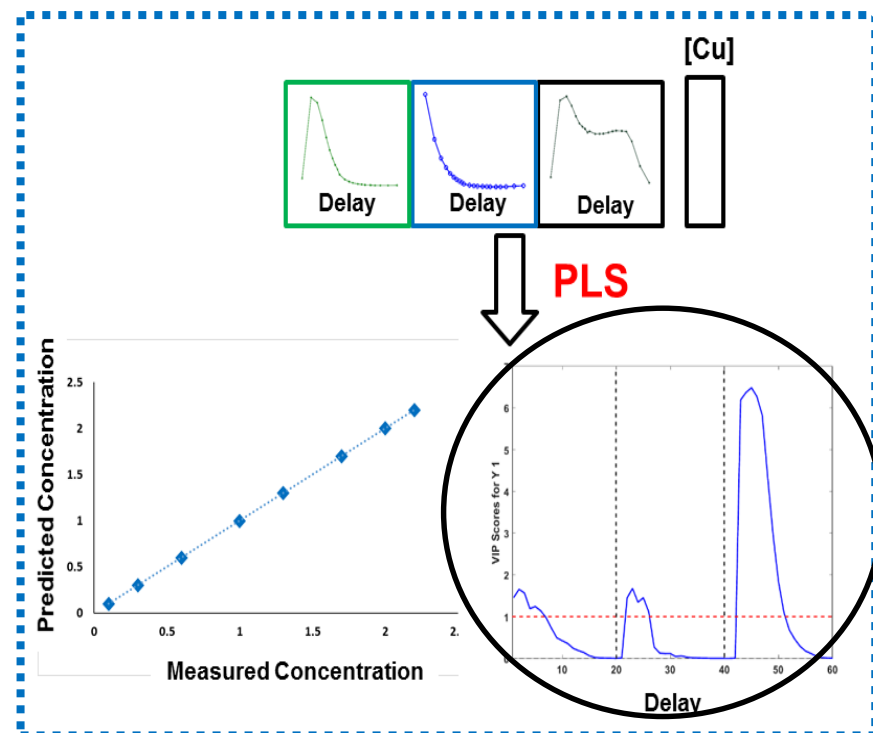
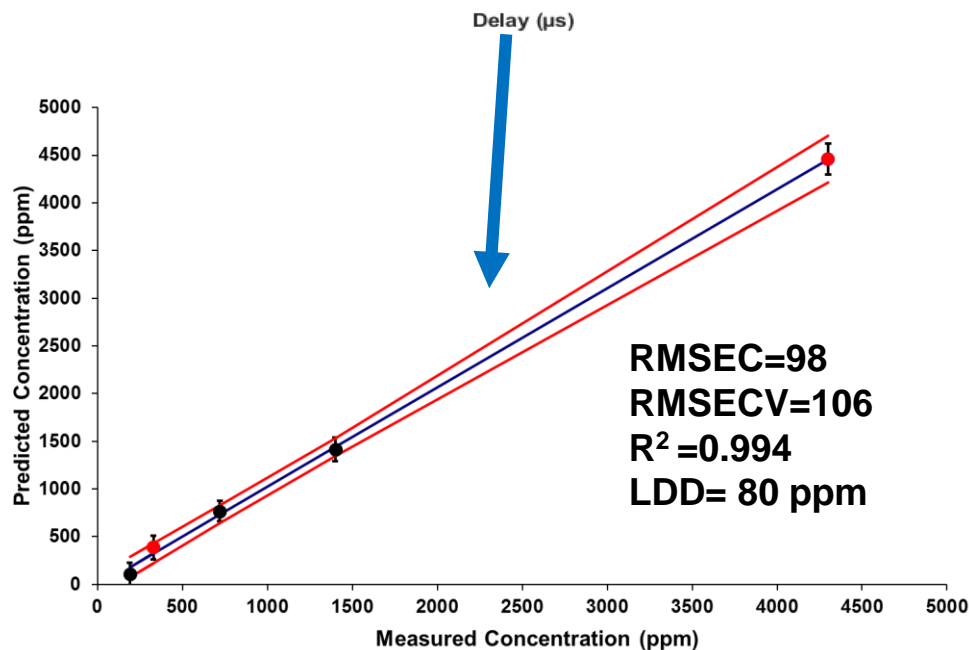
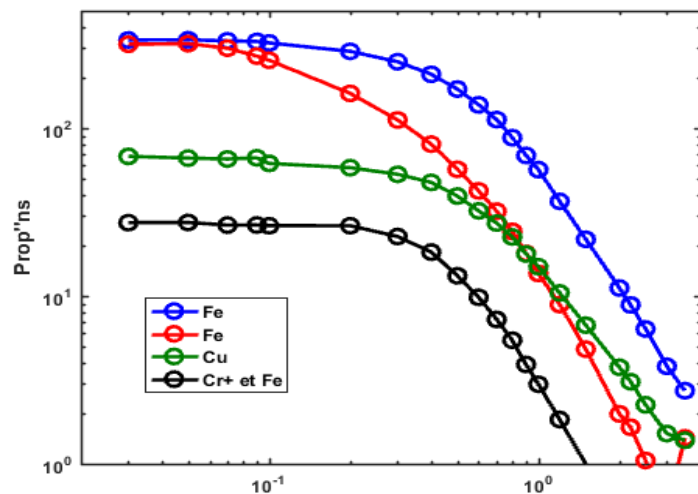


Spectro-temporal approach using chemometrics

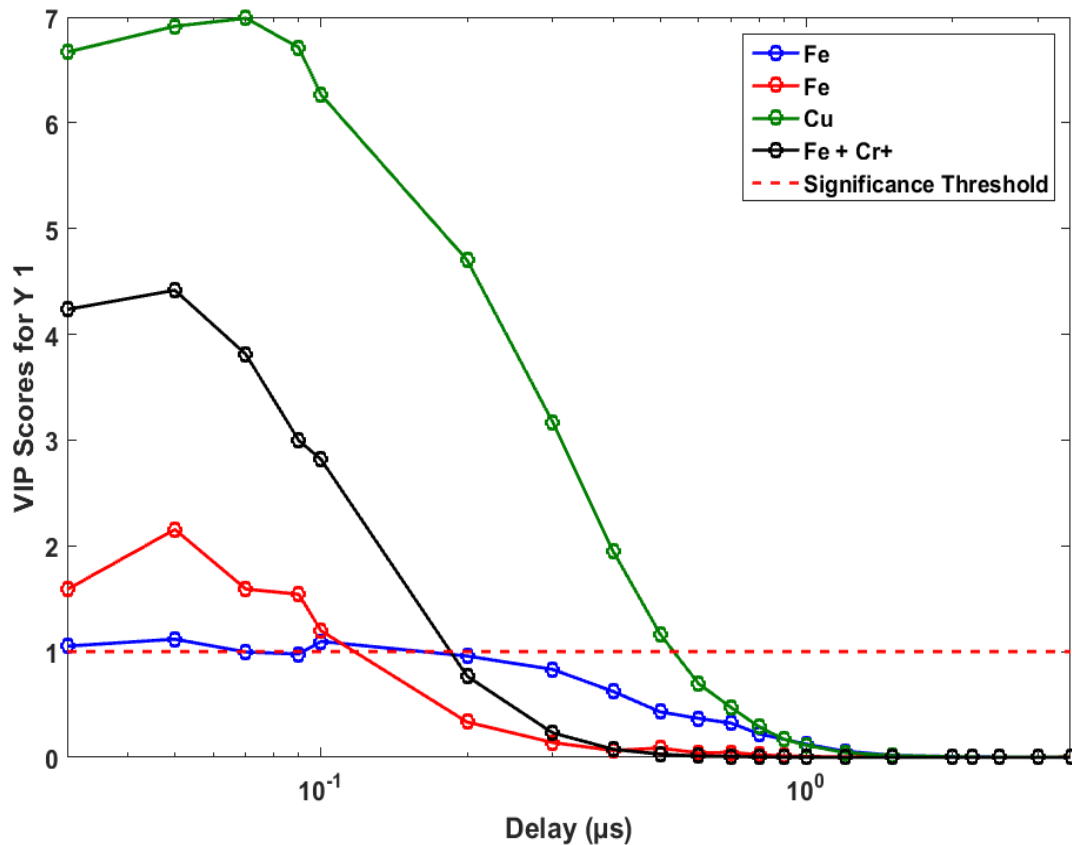






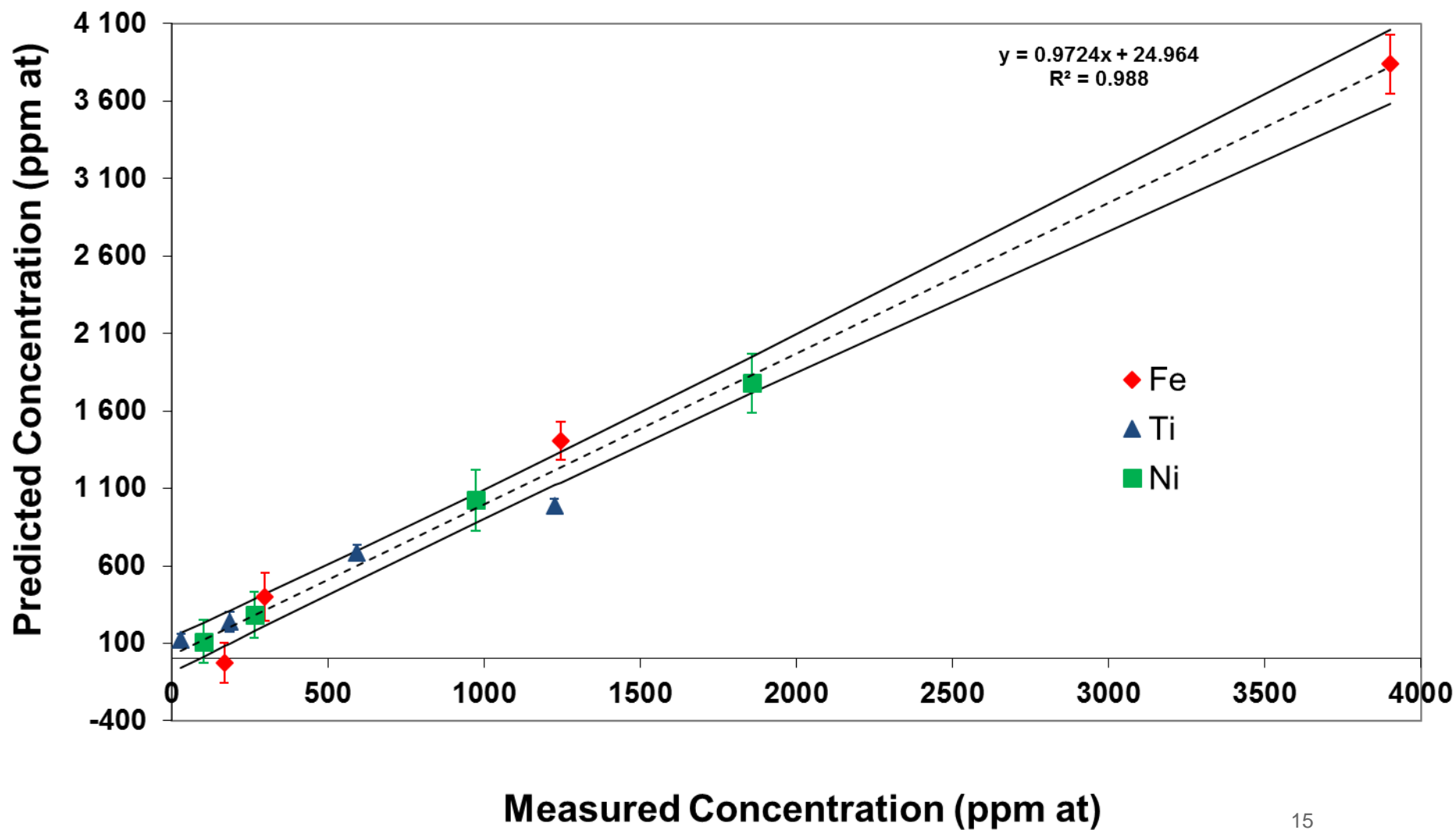


Variable Importance in Projection (VIP) scores estimate the importance of each variable in the projection used in a PLS model and is often used for variable selection. A variable with a VIP Score close to or greater than 1 (one) can be considered important in given model.

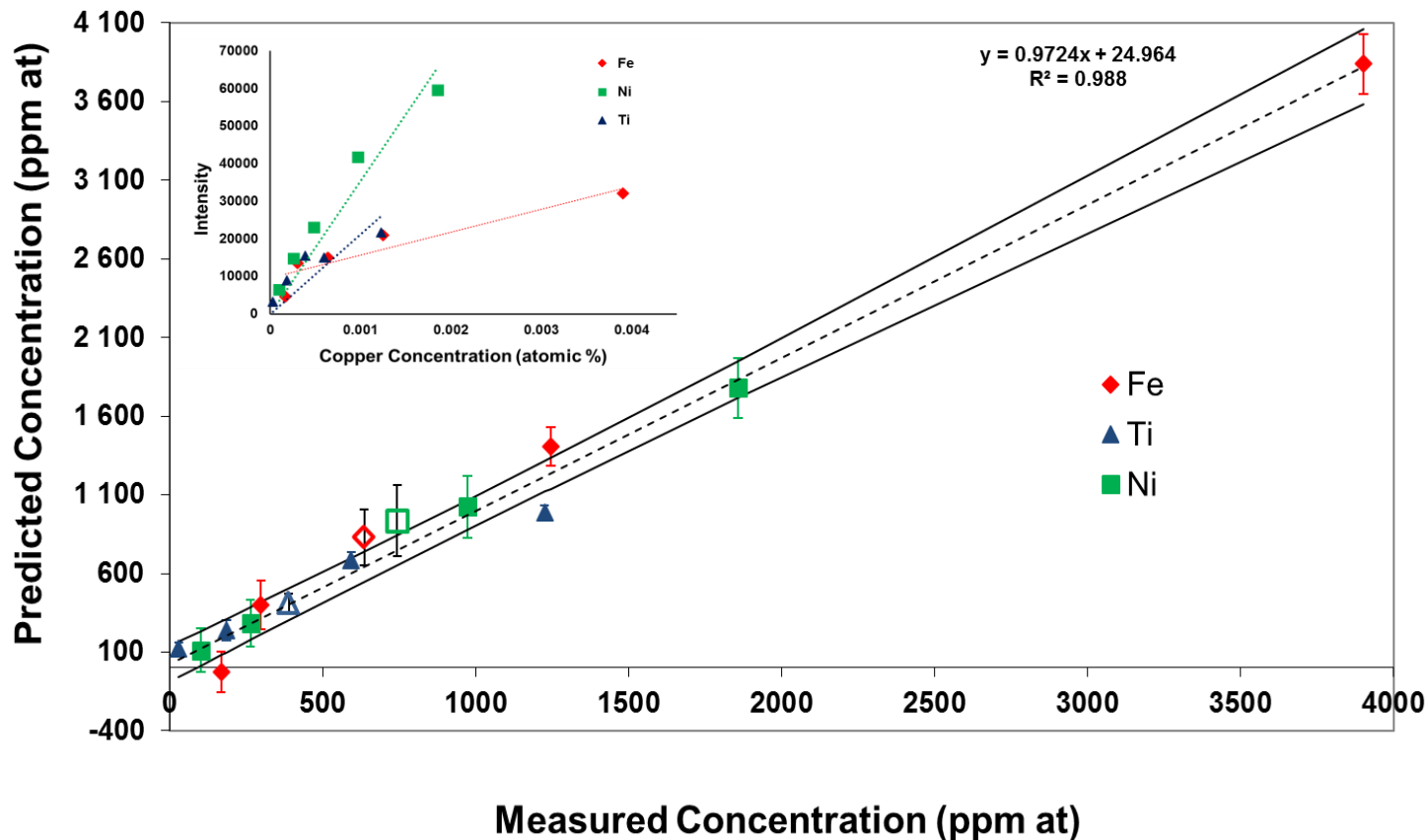


The copper concentration is determined from the intensity of that element at short delay and corrected in the first place by the intensity of the interferent (Cr) and secondly by the intensity of the matrix (Fe).

Multi materials



Multi materials



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