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

M. El Rakwe¹, D.N. Rutledge², G. Moutiers¹, J.-B. Sirven¹

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Normalization Approaches

Ablated mass

Analysis of glass and melt glass melts during the vitrification process of fly and bottom ashes by laser-induced plasma spectroscopy. Part I: Normalization and plasma diagnostics
U. Panne^{a,*}, C. Baereb, M. Clara, R. Niesner
^a Leibniz-Institut für Umweltklimatologie und Luftreinhaltung, Leipzig, Germany

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

C. CHALÉARD, P. MAUCHEN^a, N. ANDRE, J. UEBBING, J. L. LACOUR AND C. GEERTS
^a 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 presumed to be effects observed when the element is analyzed under different conditions.

When ablation is performed with a laser 1.0 W cm⁻². 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



Determination of chlorine, sulfur and carbon in reinforced concrete structures by double-pulse laser-induced breakdown spectroscopy
Tiharu A. Labatin^{a,*}, Yanhui V. Kilo^a, Sergey A. Rakov^a, Sergey M. Popov^a, Sergey M. Zaytsev^a, Nikita B. Zorov^a
^a Department of Applied Chemistry, Faculty of Chemistry, Saratov State University, 410026 Saratov, Russia

Plasma temperature

Spectral analysis of the acoustic emission of laser-produced plasmas
Santiago Palanco and Javier Luemstra
^a Universidad Politécnica de Valencia, Valencia, Spain

A numerical study of expected accuracy and precision in Calibration-Free Laser-Induced Breakdown Spectroscopy in the assumption of ideal analytical plasma
U. Panne^a, S. Legnietti^b, V. Palleschi^b, A. Salvetti^b, M. Mueller^b
^a Leibniz-Institut für Umweltklimatologie und Luftreinhaltung, Leipzig, Germany; ^b Dipartimento di Chimica, Università degli Studi di Padova, Padova, Italy

Surface densities

Emission lines of elements present in the matrix

Multivariate Calibration

Calibration-free

Study of matrix effects in laser induced breakdown spectroscopy on metallic samples using plasma characterization by emission spectroscopy
JA. Aguilera^{a,*}, C. Aragón^a, V. Madurga^a, J. Manrique^a
^a Departamento de Física, Universidad Pablo de Olavide, Sevilla, Spain

Multivariate calibration of spectra obtained by Laser Induced Breakdown Spectroscopy of plutonium oxide surrogate residues
Markandey M. Tripathi, Kemal E. Eseller, Fang-Yu Vueh, Jagdish P. Singh
^a Institute for Clean Energy Technology (ICET), Mississippi State University, Starkville, MS 39762 USA

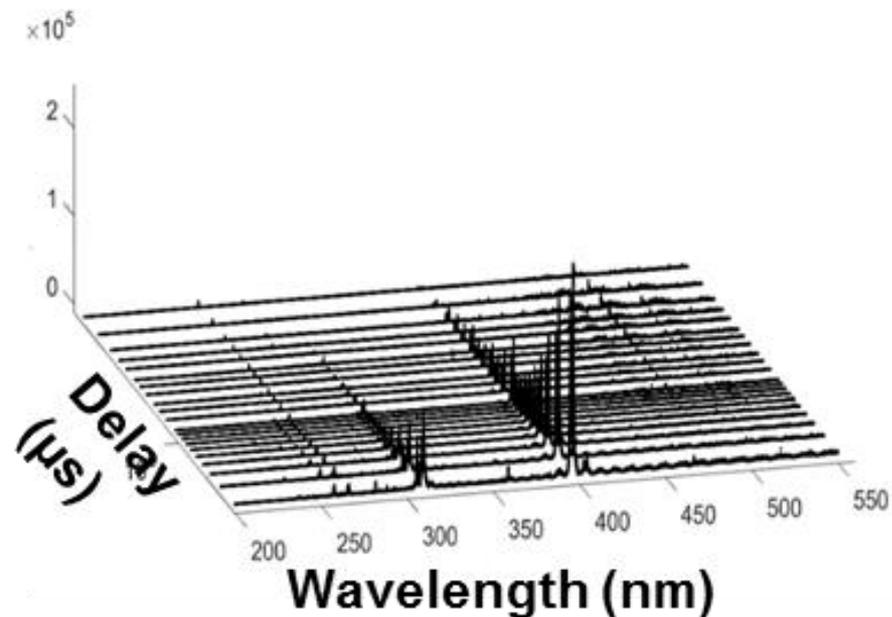
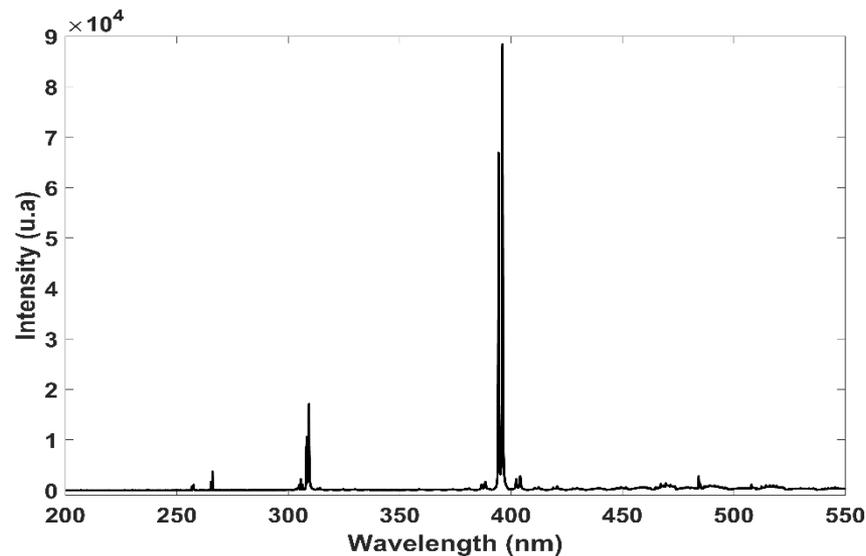
Laser Induced Breakdown Spectroscopy (LIBS) was used to determine elemental concentration of plutonium oxide surrogate (cerium oxide) residue for monitoring the fabrication of lanthanide boronate glass. Quantitative analysis by LIBS is affected by the severe limitation of variation in the induced plasma 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 atomic emission lines. Calibration results show improvement in the coefficient of determination from 0.81 to 0.93. Coefficient of correlation to univariate calibration. The root mean square error also reduced from 7.46 to 2.93%. A similar trend was obtained for Co, Fe, Mn, and Ni. These results clearly demonstrate the feasibility of using LIBS for other processes monitoring in a hazardous waste management environment.

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 [1,2,6,7]. 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-sample coupling [1,2]. Changes in the concentration of matrix 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 it is used to estimate concentration of various analytes [10]. However this approach is more useful if the analyte 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 describe the local thermal equilibrium (LTE) state. Integrated 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 boronate (PuLBs) glass to immobilize the Pu in a high level waste glass for safe storage in a deep geological facility. Determination of the elemental and isotopic composition of the plutonium feed before mixing with glass frit materials is necessary and for accountability and to avoid critically [19]. The Savannah River National Laboratory (SRNL) has proposed to use LIBS along with Maternal Control

Calibration-free LIBS (CF-LIBS) has been proposed several years ago as an approach for quantitative analysis of samples. It consists of developing a plasma physics model to quantify element concentration. The plasma temperature is determined from spectral information and is used to describe the local thermal equilibrium (LTE) state. Integrated emission intensity of spectral lines can be calculated assuming a Boltzmann distribution at LTE [11].
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doi:10.1016/j.saa.2008.10.003

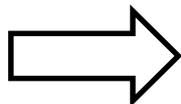
Conventional calibration
methods



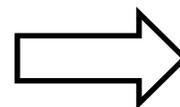
Improvement of quantitative analysis of solids by LIBS using both the spectral and temporal dimensions of the signal.

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

**Improvement of
quantitative
analysis**

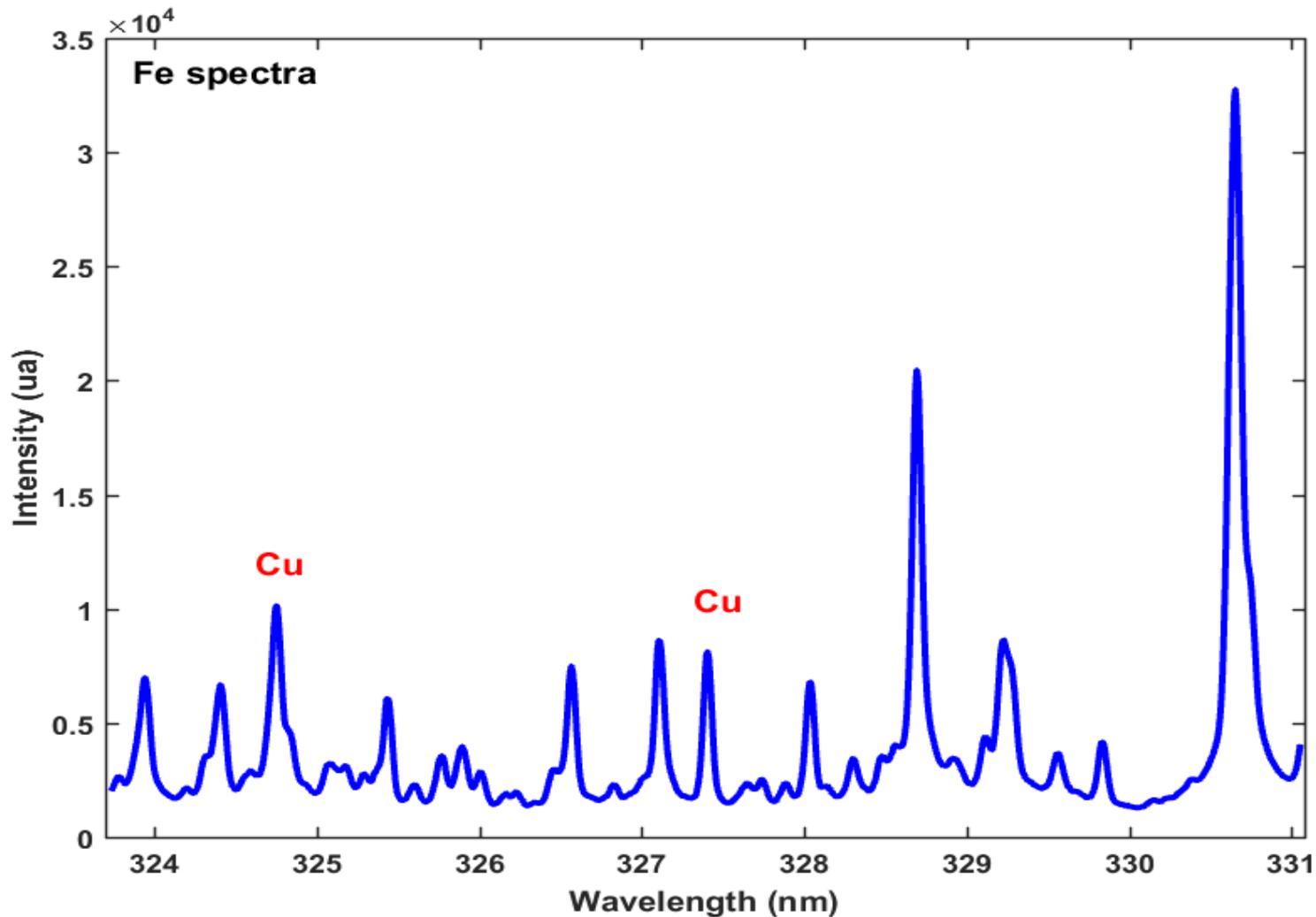


15 samples of 3 matrices
(Fe, Ni, Ti)

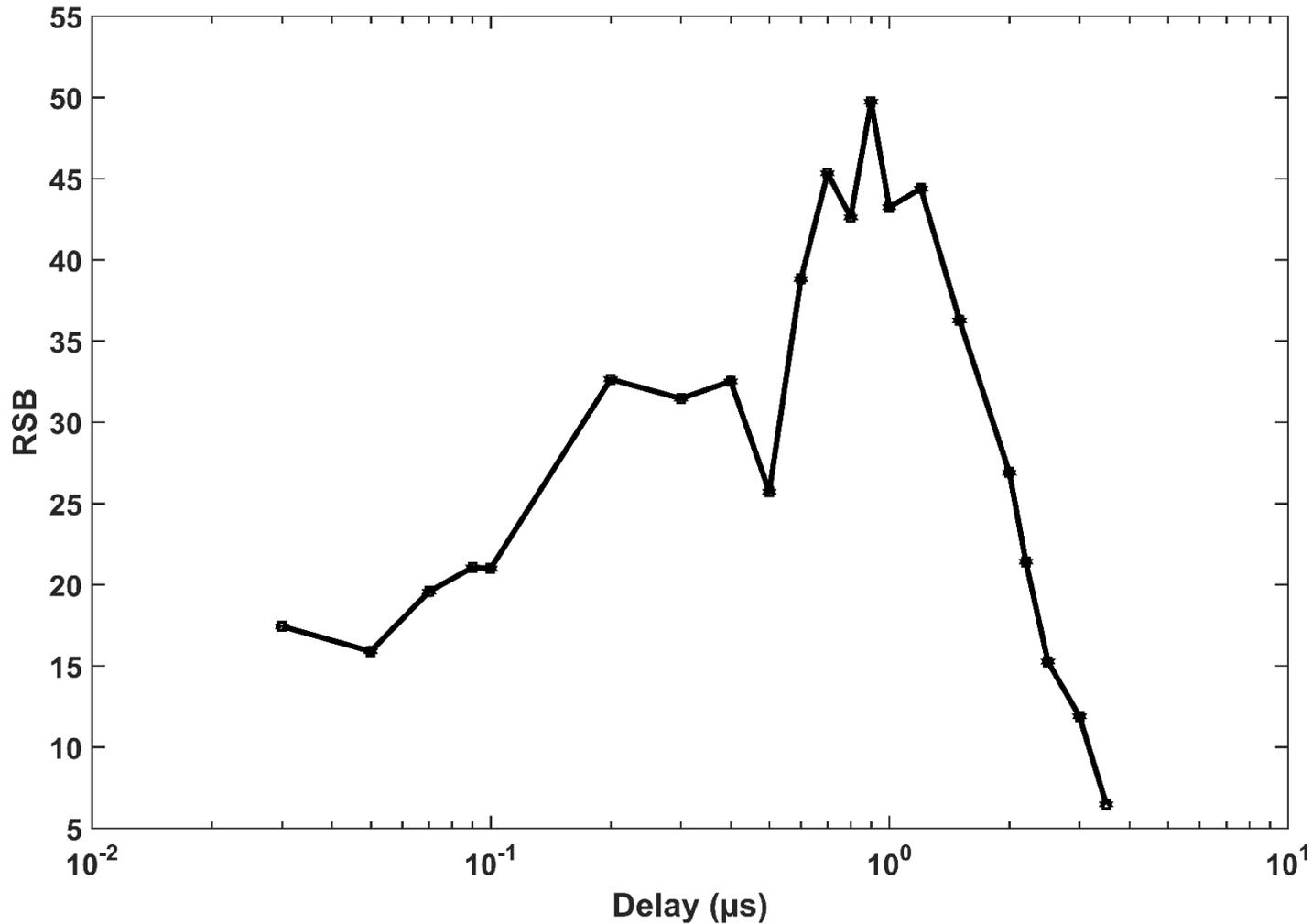


Acquisition at different delay

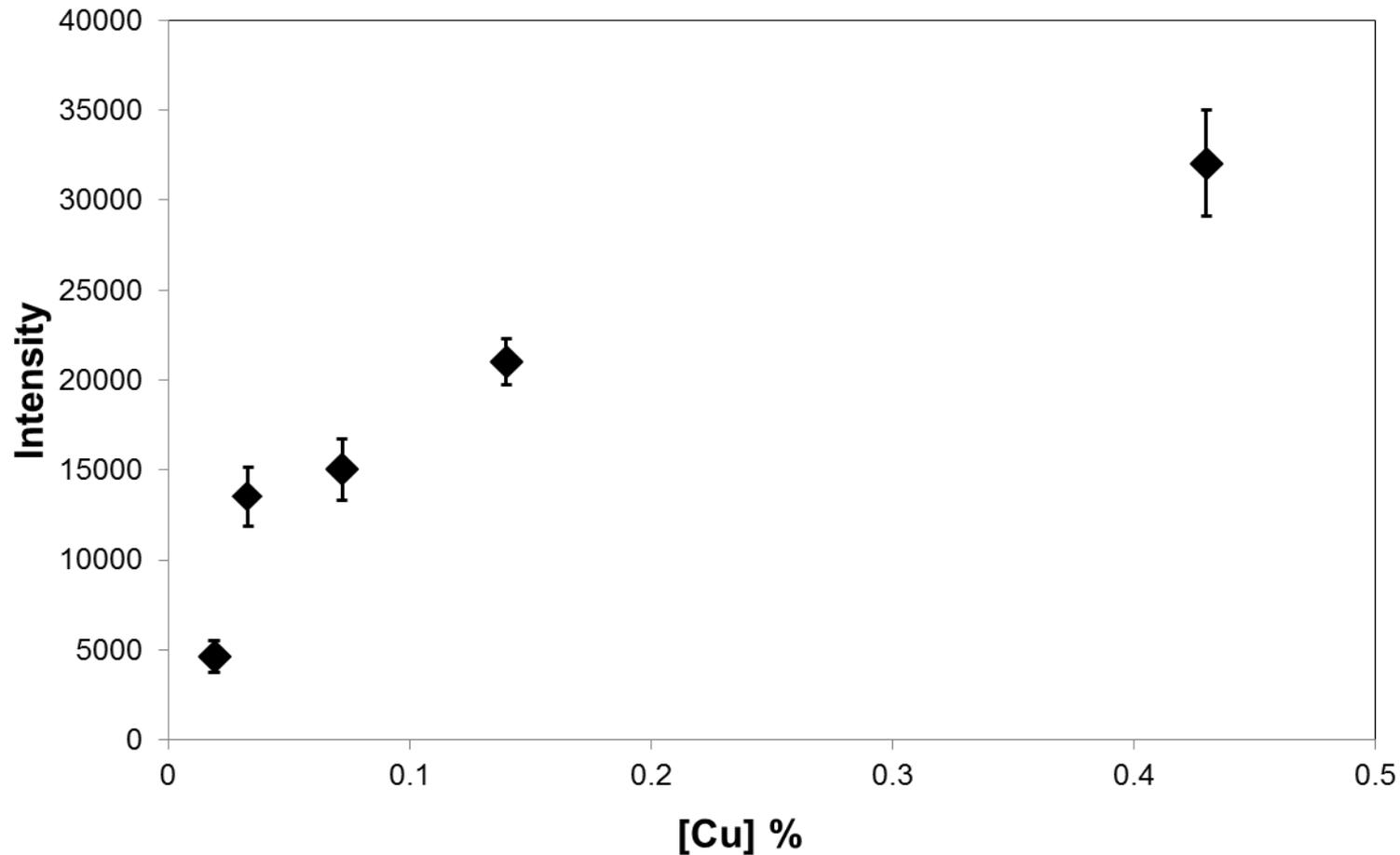
Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



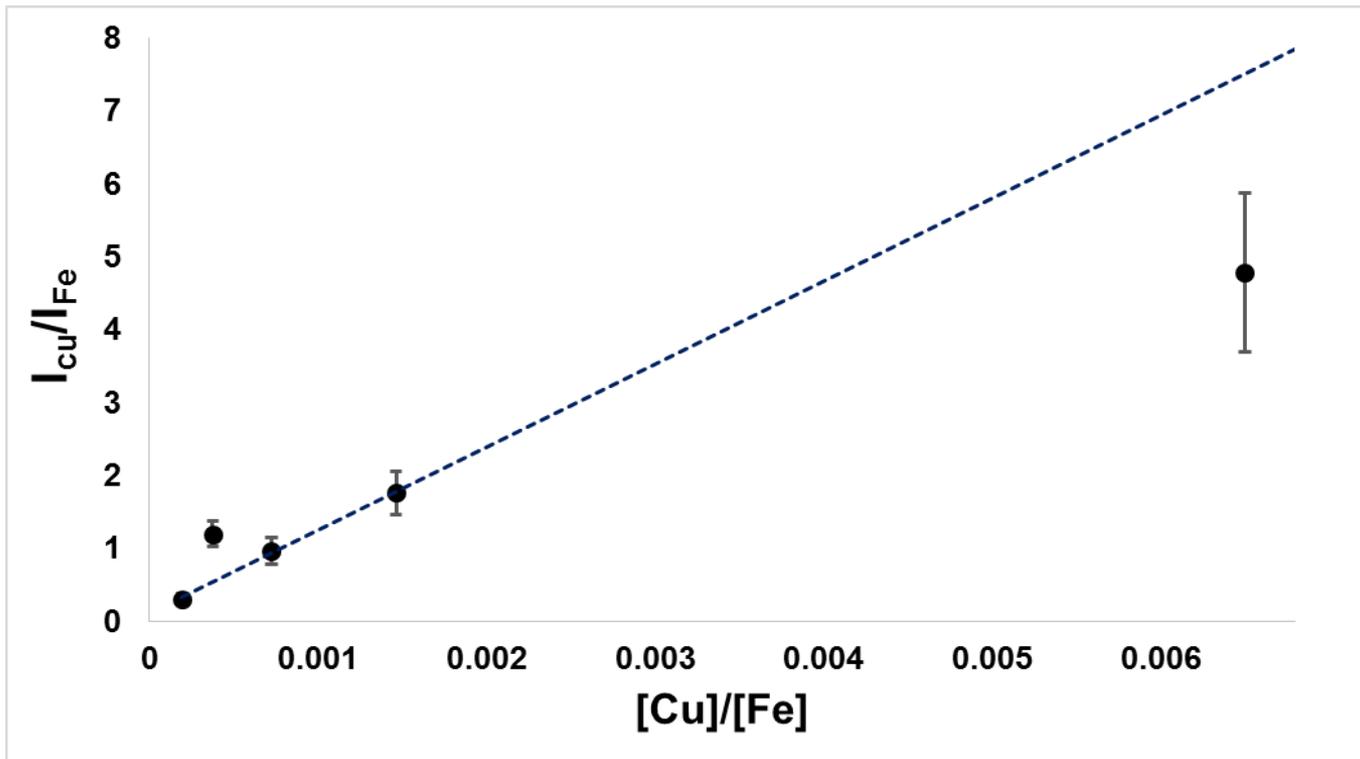
Calibration curve corresponding to the intensity of the Cu line at 327.4 nm



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

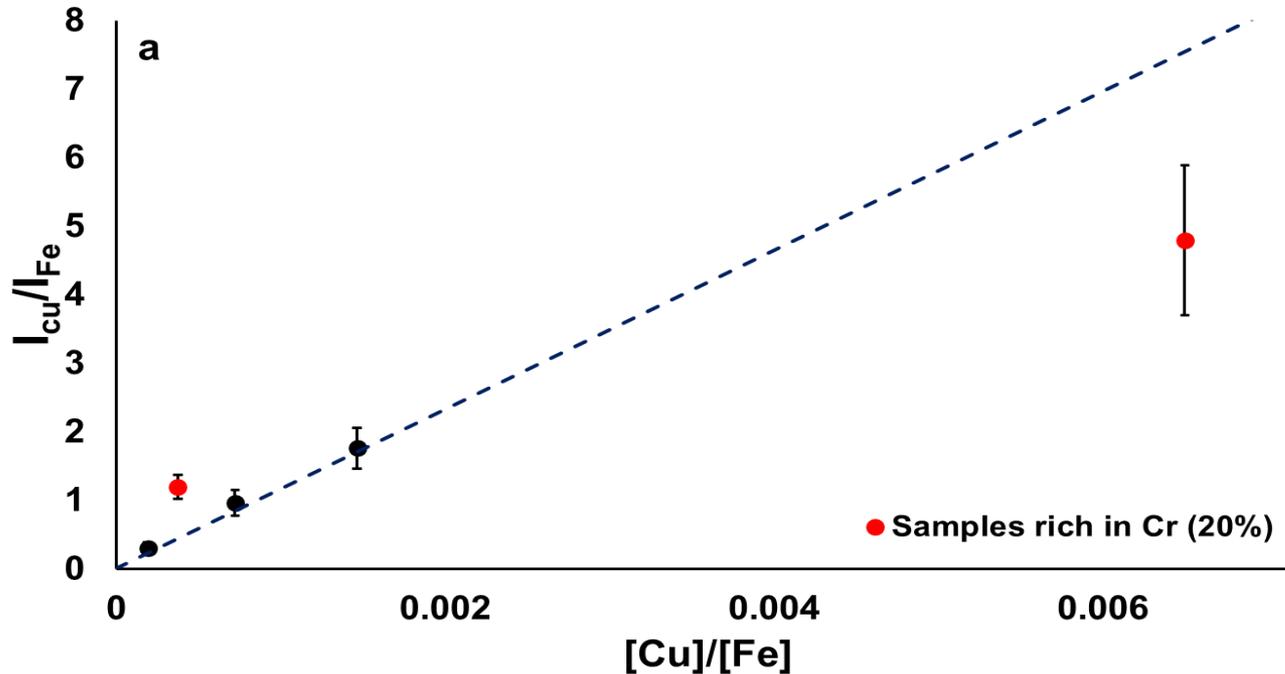


Cu spectral intensity values at 327.4 nm are normalized by Fe spectral intensity values



LDD=1300ppm
 $R^2 = 0.973$

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

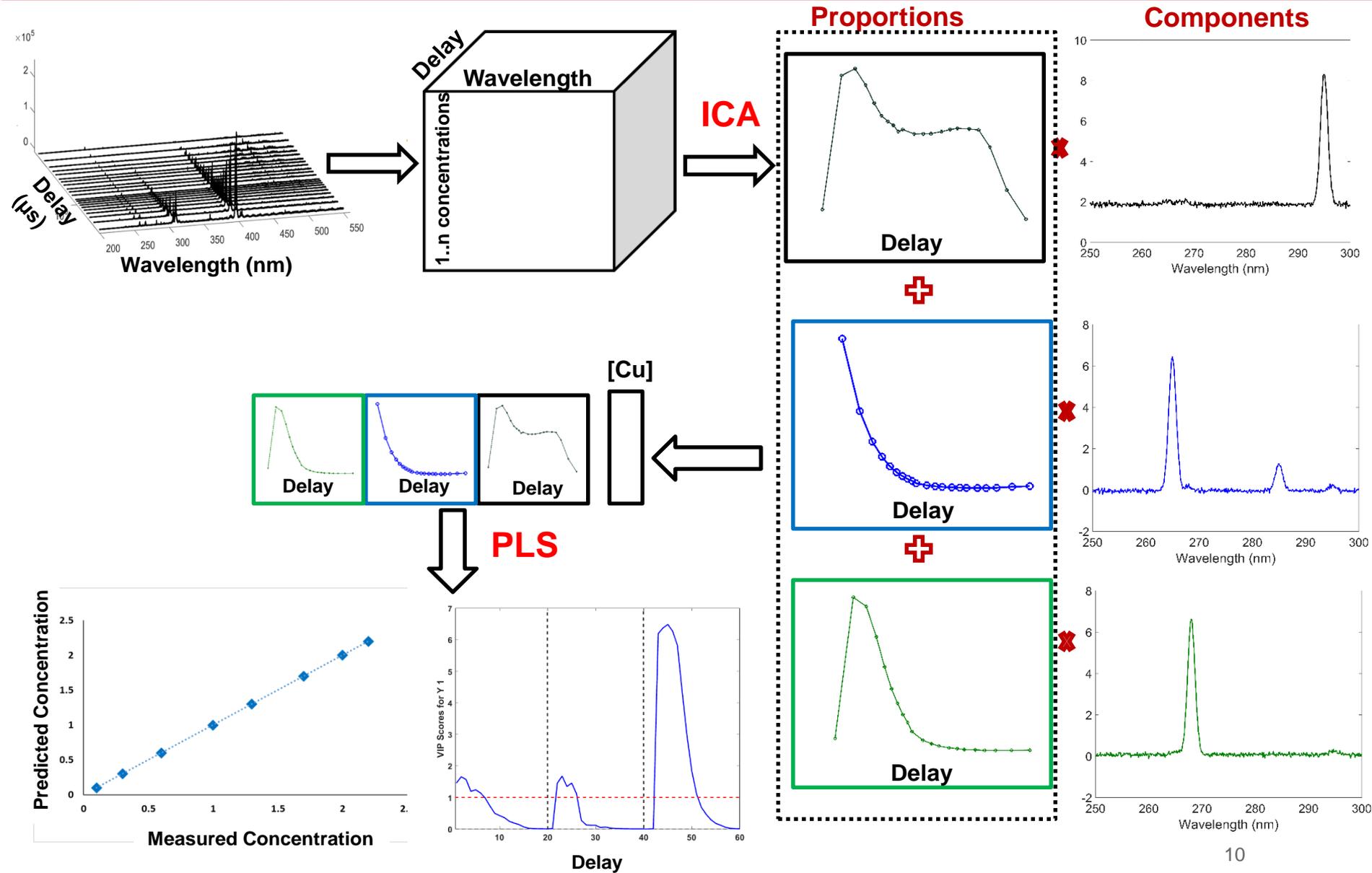


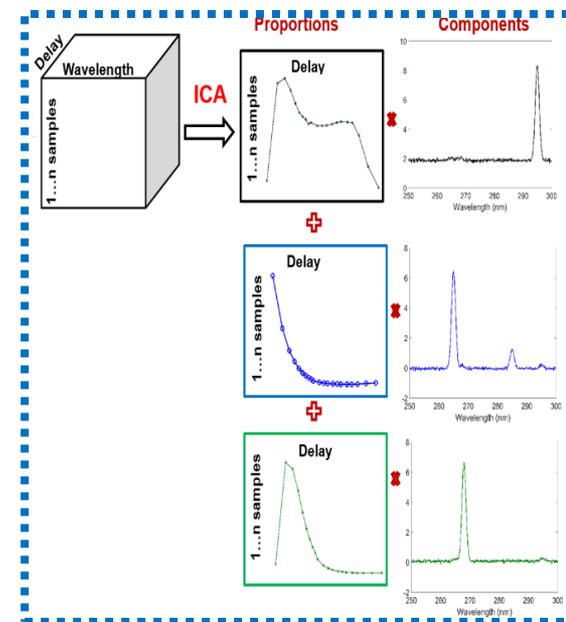
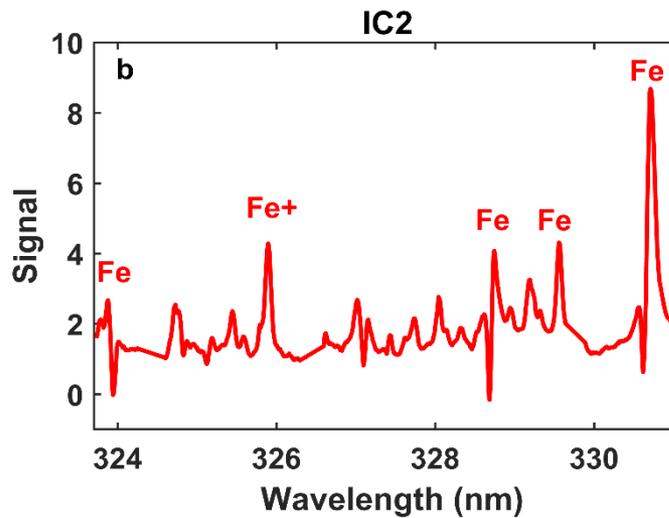
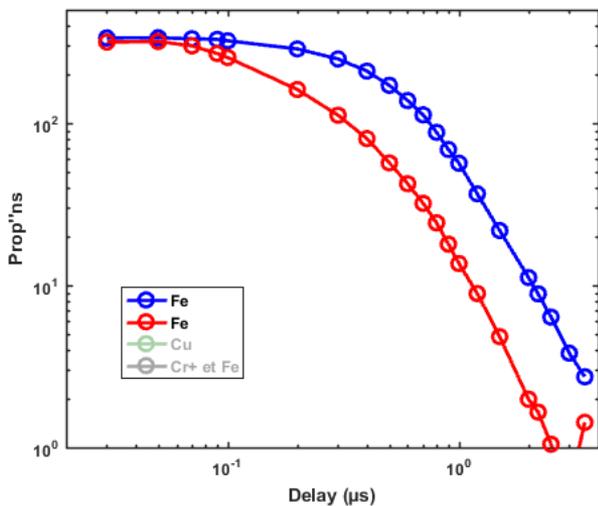
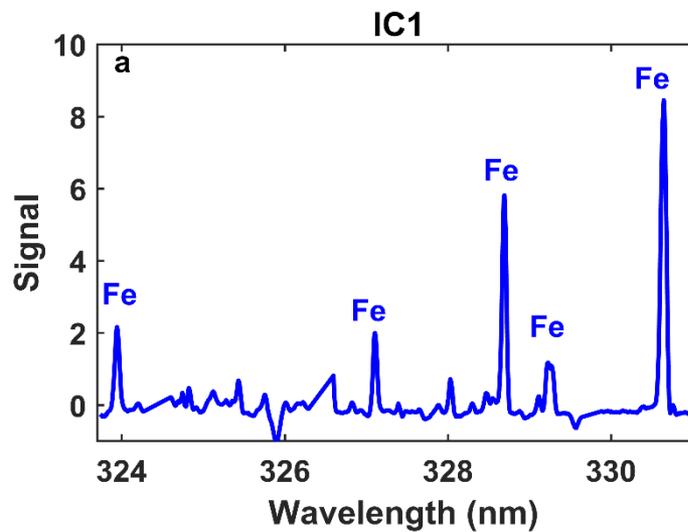
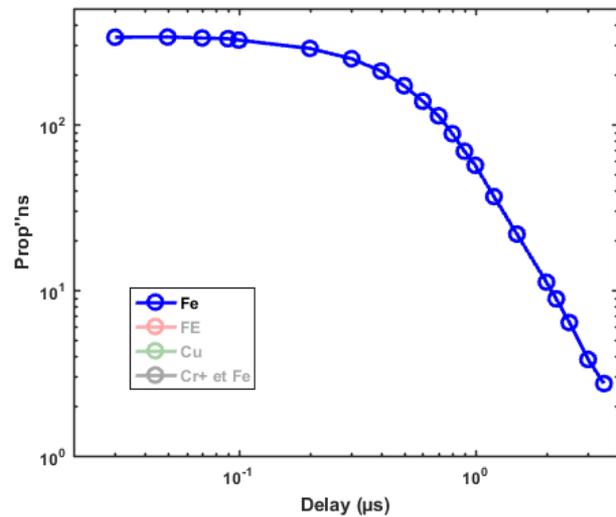
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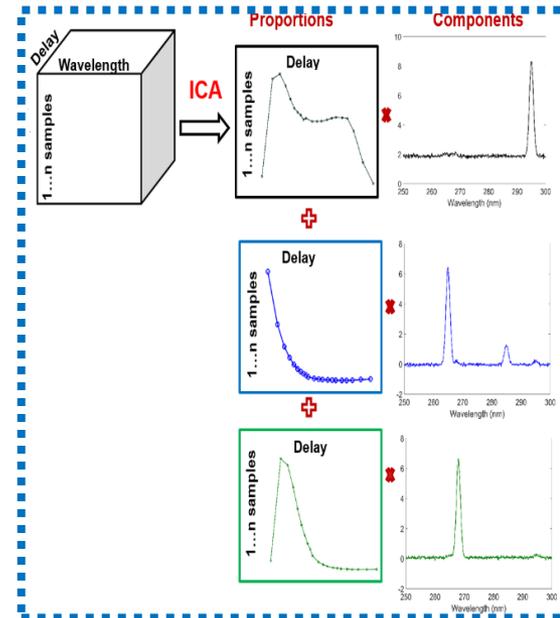
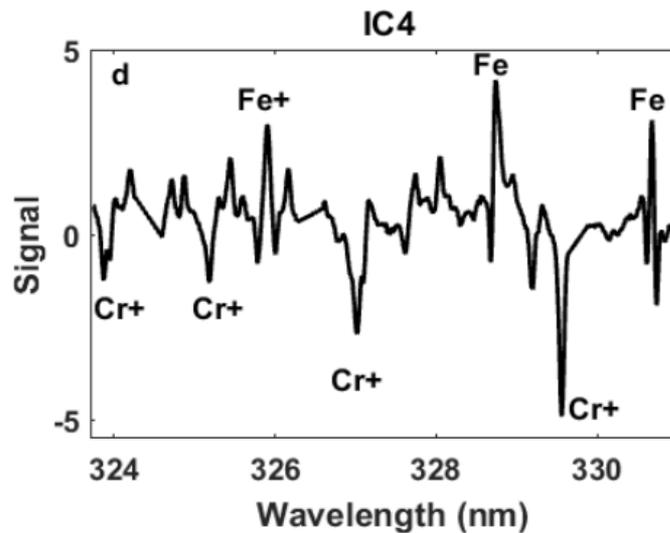
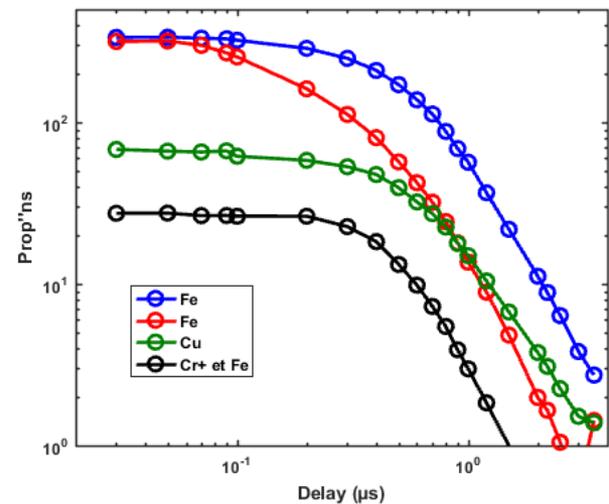
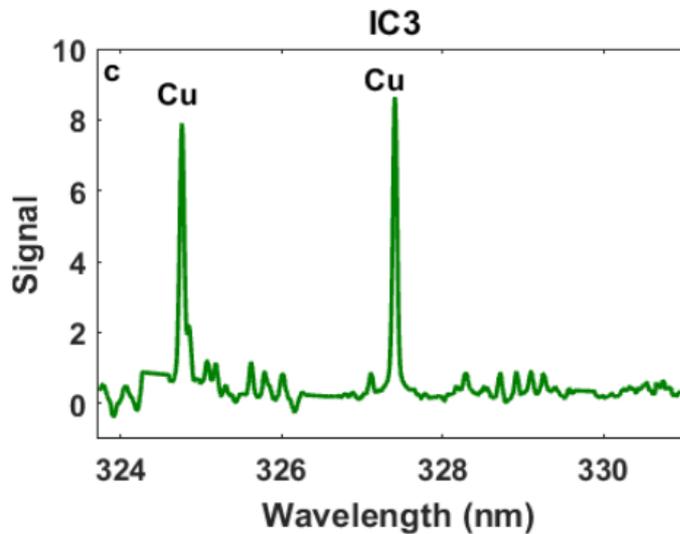
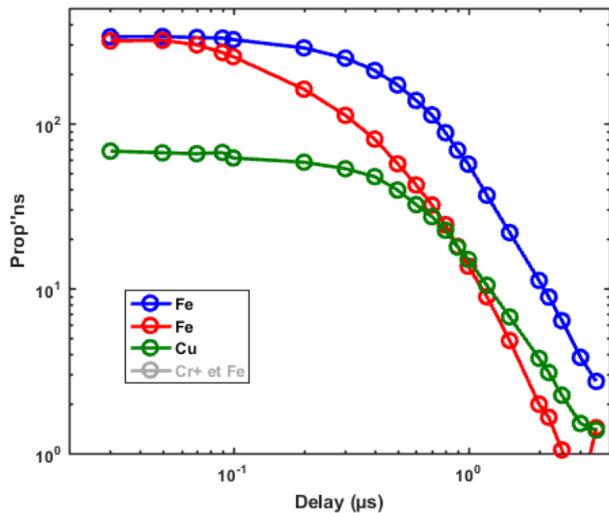
Improved calibration curve is observed by standardizing but analytical performance still insufficient.

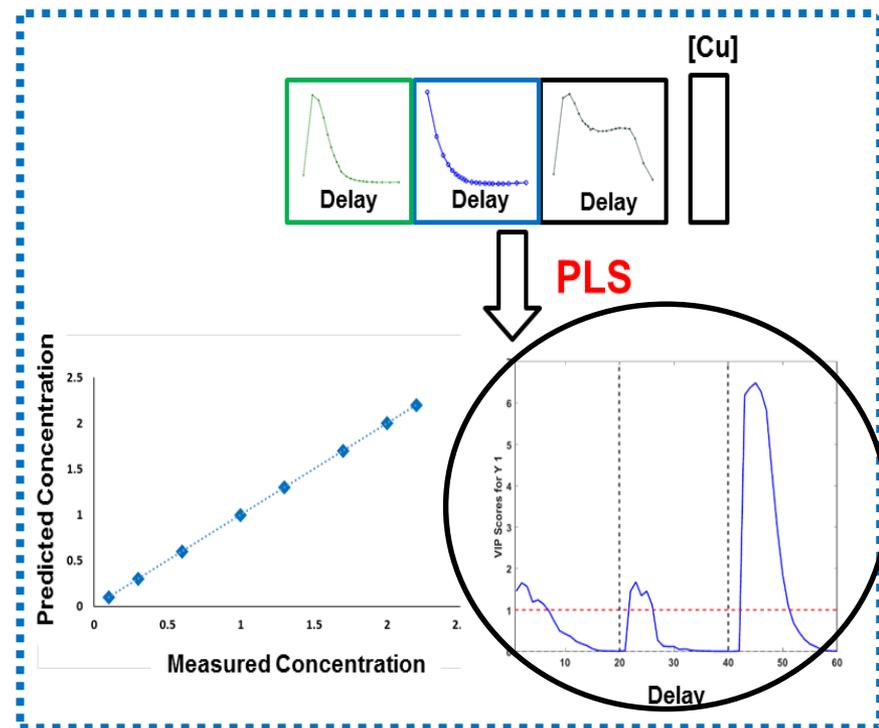
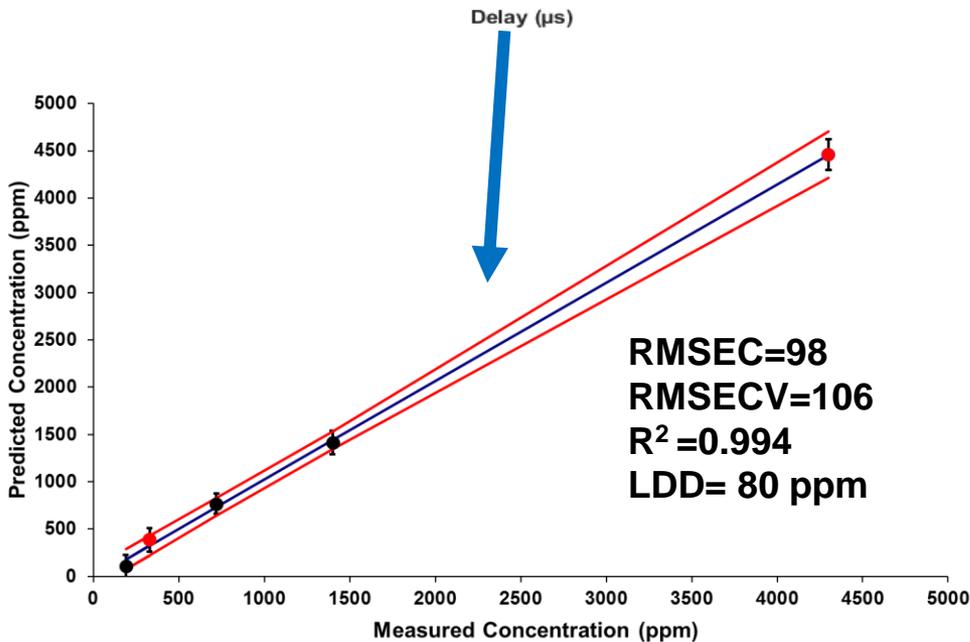
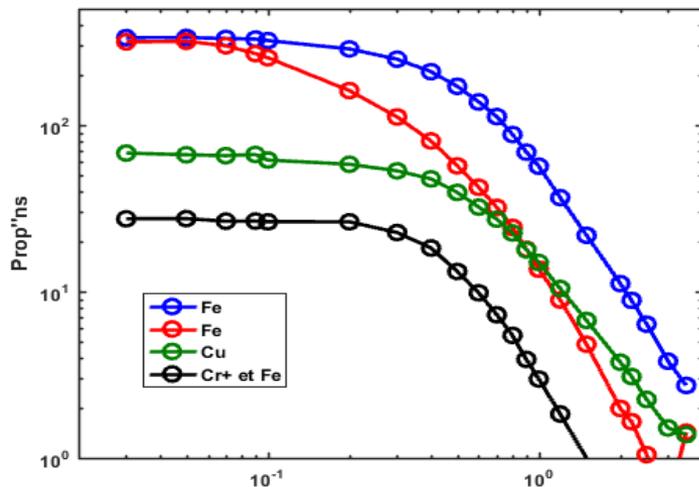


Spectro-temporal approach using chemometrics

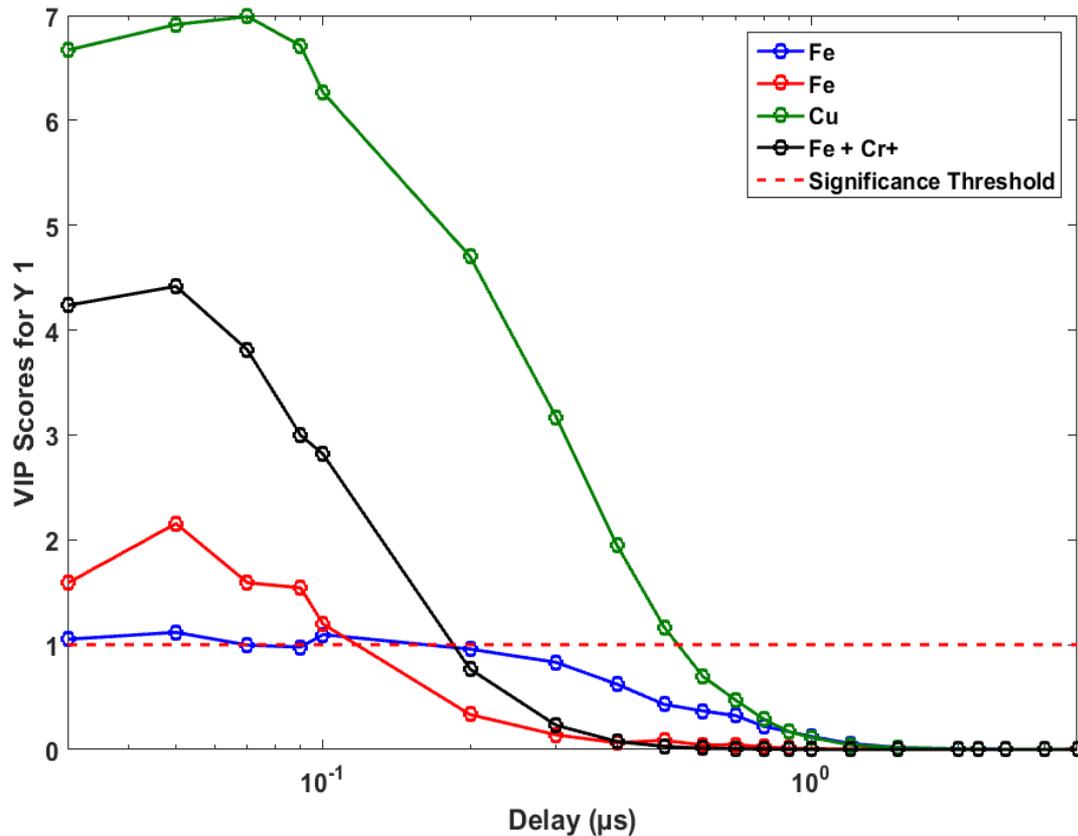






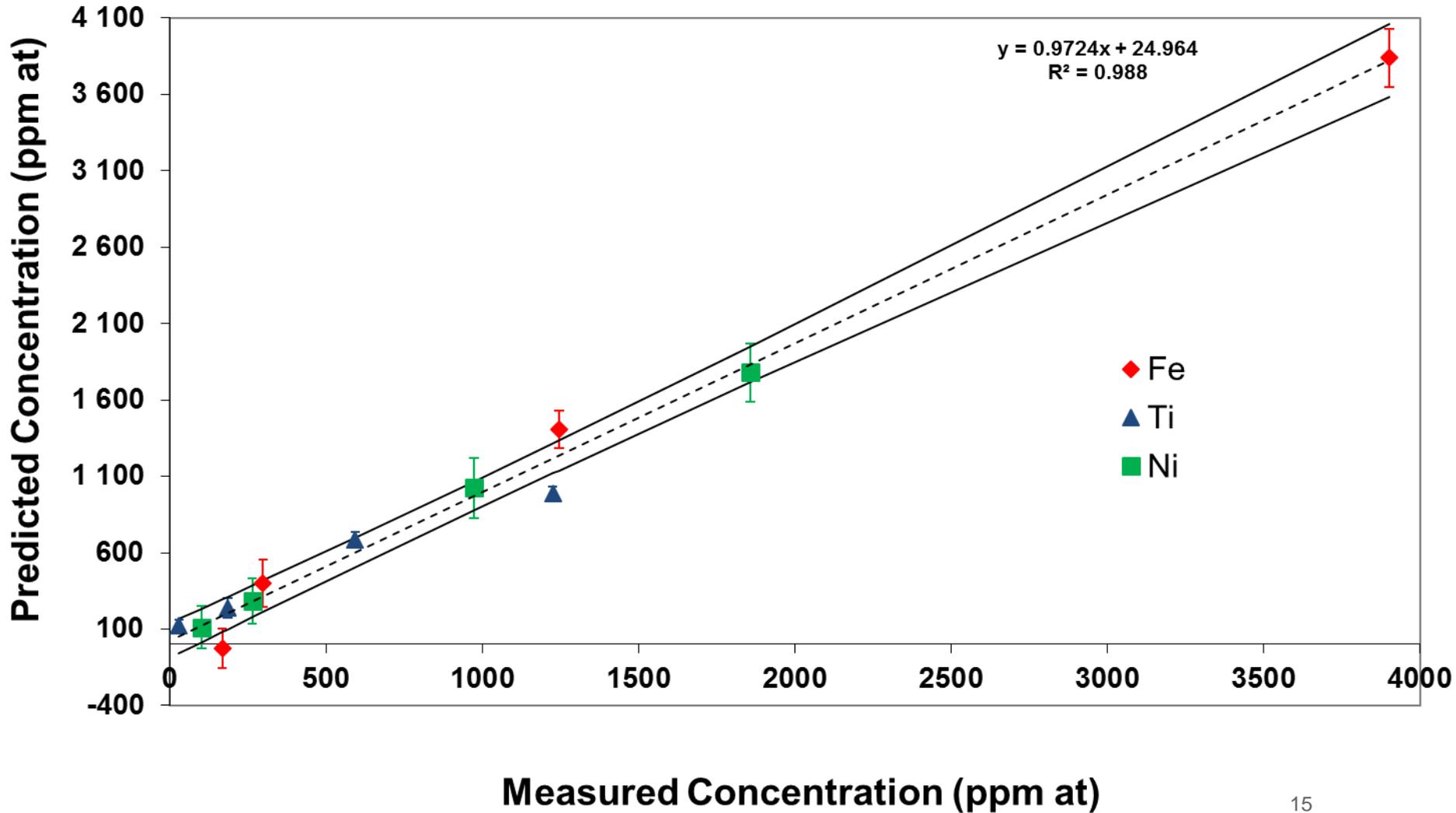


Variable Importance in Projection (VIP) scores estimate the importance of each variable in the projection used in a PLS model and is often used for variable selection. A variable with a VIP Score close to or greater than 1 (one) can be considered important in given model.

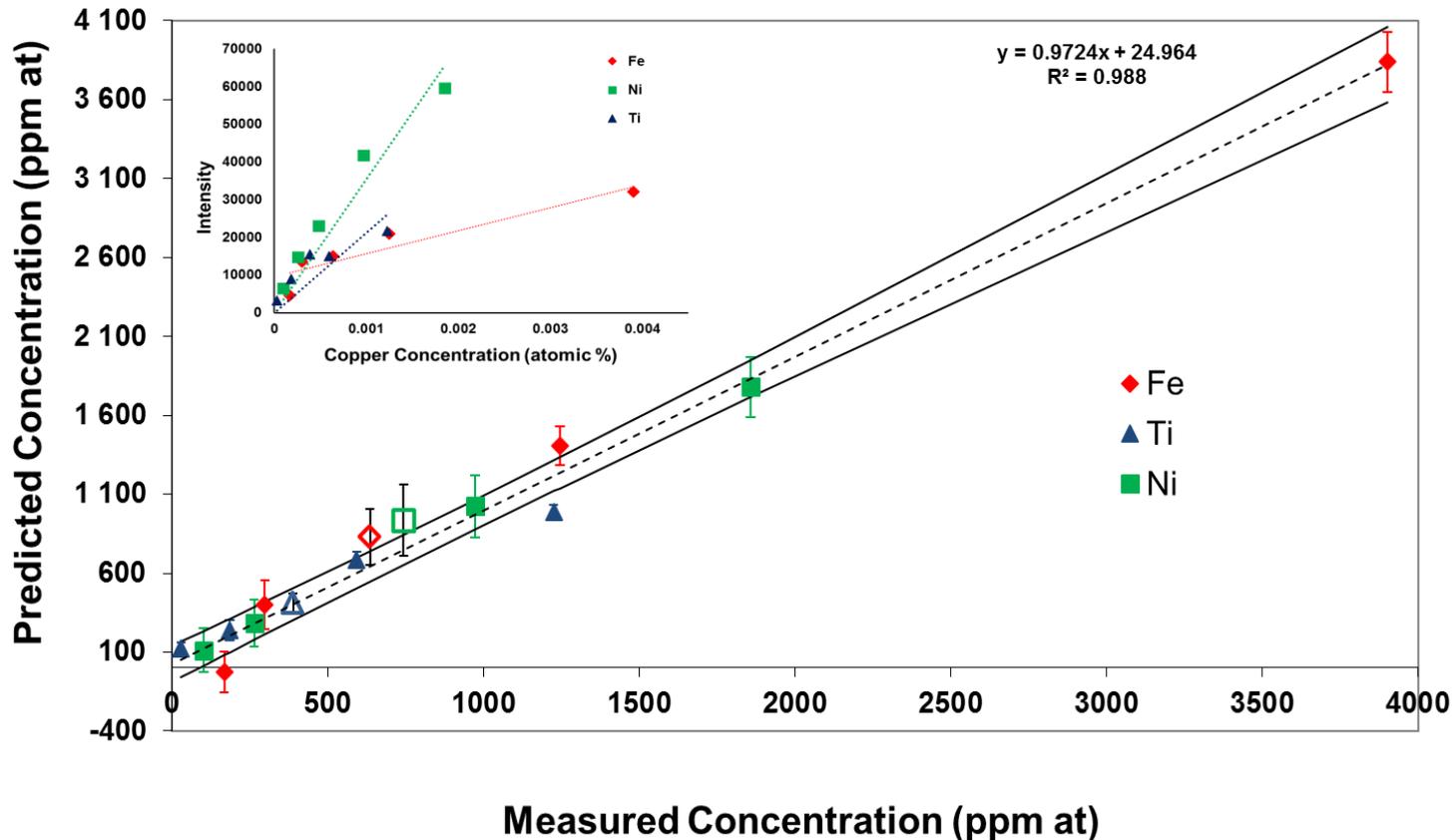


The copper concentration is determined from the intensity of that element at short delay and corrected in the first place by the intensity of the interferent (Cr) and secondly by the intensity of the matrix (Fe).

Multi materials



Multi materials



Measured Values	Predicted values	Relative Bias
Cu dans Ti (513 ppm)	430 ppm ($\pm 15\%$)	(-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**