

# PARAFAC Analysis for IBIL Spectra Interpretation

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## INTRODUCTION

Ion Beam Induced Luminescence (IBIL) is a spectroscopic technique based on the detection of UV, visible and IR radiation from a solid sample excited by an ion beam (typically H<sup>+</sup> or He<sup>+</sup>) at energy up to a few MeV. Due to the high energy of the probe, the spectra collected during the irradiation undergo a modification related to the damaging of the luminescent molecules. Then, the output of this spectroscopic analysis is an intensities matrix (emission wavelength \* time) for each probed sample.

In the last few years some statistical tools such as Principal Components Analysis (PCA) were used for the identification and characterization of the spectral features in IBIL spectra of natural and anthropogenic matrices [1-4]. The main trouble related to these analysis was the choice of the best pre-normalization procedure of the two dimensional IBIL spectra for the subsequent comparison of different samples.

In this work we introduce the potentialities of PARAllel FACtor analysis (PARAFAC), a statistical technique used to decompose data arranged in three or higher order arrays (about IBIL spectra: sample \* emission wavelength \* time) that facilitate the identification and quantification of independent underlying signals termed 'components' [5], without special pre-normalization procedures of data. Specifically, we show the preliminary results of the data decomposition of Ag<sup>+</sup>-Na<sup>+</sup> exchanged silicate glasses (with or without subsequent annealing) IBIL spectra which will help us to better understand the evolution of silver ions and silver complex with the changing of the annealing temperature around the threshold value evidenced by [6].

Referring to IBIL spectra, PARAFAC analysis decompose the original three-way dataset ( $X_{ijk}$ ) into a set of trilinear terms ( $a_{if}b_{jf}c_{kf}$ ) and a residual array ( $e_{ijk}$ ) as shown in equation 1:

$$X_{ijk} = \sum_{f=1}^F a_{if}b_{jf}c_{kf} + e_{ijk} \quad (1)$$

where  $x_{ijk}$  is the spectral intensity corresponding to the  $i^{\text{th}}$  sample at the  $j^{\text{th}}$  wavelength at the  $k^{\text{th}}$  time and  $e_{ijk}$  is the residual representing the variability not accounted for by the model characterized by  $F$  components. Each component is characterized by: i) an  $\mathbf{I}_f$  a-values (scores)

, one for each sample; ii) an  $\mathbf{J}_f$  b-values, one for each emission wavelength; iii) an  $\mathbf{K}_f$  c-values, one for each time. In this paper the  $F$  components have the following interpretations: the vectors  $\mathbf{J}_f$  are a scaled estimate of the emission spectrum of the  $f^{\text{th}}$  analyte; the vectors  $\mathbf{K}_f$  are a scaled estimate of the intensity decreasing rate of the  $f^{\text{th}}$  analyte; the parameter  $a_{if}$  is directly proportional to the concentration of the  $f^{\text{th}}$  analyte in the sample  $i$ .

## EXPERIMENTAL

Silver doped silicate glasses were realized by performing ion exchange process on commercial soda-lime optical glass (SLG) slides. The ion exchange was obtained by immersing the glass slides in a molten salt bath of AgNO<sub>3</sub>:NaNO<sub>3</sub> (two different silver molar concentration bath mixture were used: 0.1% and 1%) at the temperature of 320°C for 20 minutes. Subsequently, samples were annealed in air at the temperature of 380°C, 410°C and 440°C; for each temperature three different annealing duration were explored: 1h, 4h and 16h.

Samples were irradiated with a 2.0 MeV H<sup>+</sup> ion beam, with a current density of about 1.6  $\mu\text{A}\times\text{cm}^{-2}$  on an area of 3×2 mm<sup>2</sup>. The spectra were collected by a UV graded silica fibre (600  $\mu\text{m}$  of diameter) aligned in front of the sample and recorded by an Ocean Optics QE 65000 spectrometer. All the spectra were acquired with 1 s of integration time and for each sample 200 spectra were collected. The total irradiation charge was measured with a Faraday cup, which was the scattering chamber itself. Spectra were normalized as a function of the electric parameters and the intensities at each wavelength were expressed as: counts Coulomb<sup>-1</sup> cm<sup>-2</sup>. Then the dimensions of the tensor to characterize with PARAFAC analysis are: 21 samples, 1044 wavelength (number of detector channels), 200 spectra.

The numerical procedure for the PARAFAC analysis was performed with Matlab R2013a; specifically by using drEEM (version 0.1.0) and N-way (version 3.20) toolbox.

## RESULTS

Figure 1 shows representative IBIL spectra of each sample, while Figure 2 shows the three components of PARAFAC model. Vectors  $\mathbf{I}_f$  (panel a) is directly

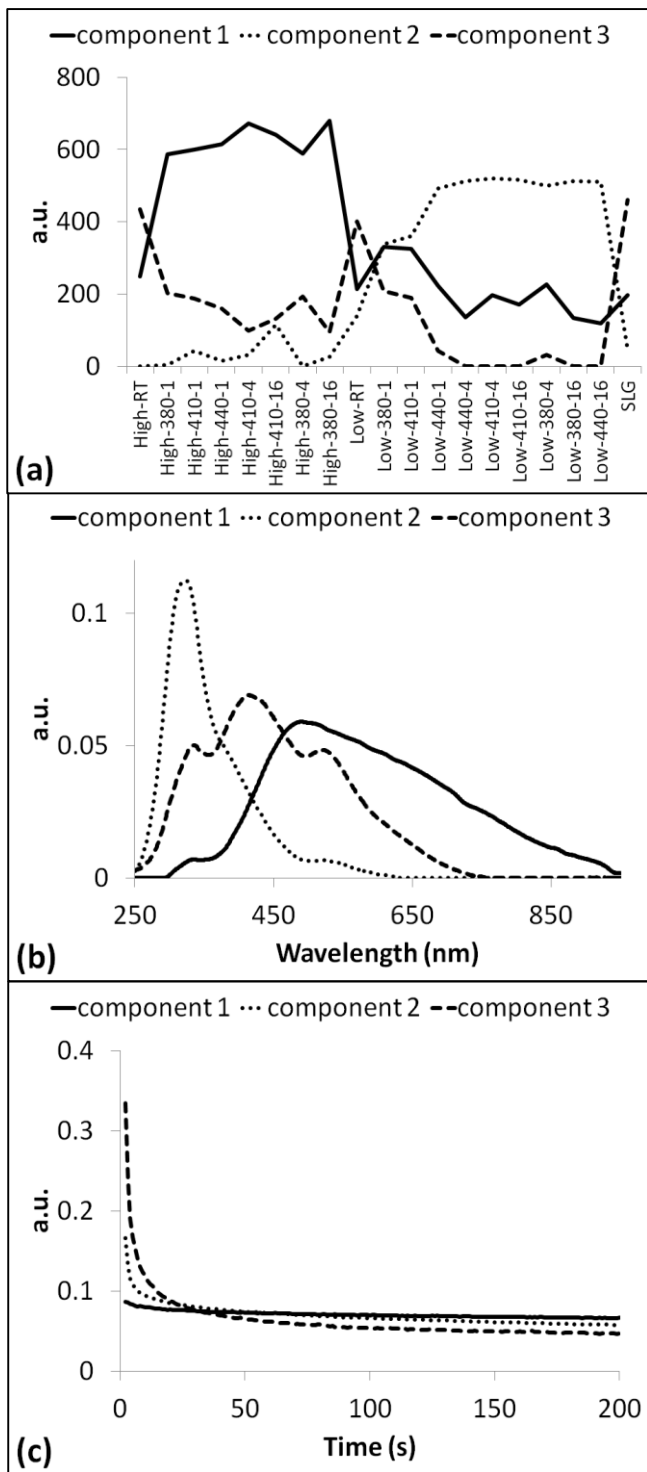


Fig 2: PARAFAC components of IBIL spectra

proportional to the normalized concentrations of the different components in the samples reported in abscissa; vectors  $\mathbf{J}_r$  (panel b) and  $\mathbf{K}_r$  (panel c) are a scaled estimate of the emission spectrum and a scaled estimate of the intensity decreasing rate of the respective components, respectively.

The three components show the typical features of silver doped glasses, a UV peak ascribed to  $\text{Ag}^+$ , a blue component at around 430 nm assigned to  $\text{Ag}^+$  embedded into a depolymerized network, a green band around 530 nm attributed to  $\text{Ag}^+-\text{Ag}^+$  pairs [7], and a broad red band at 620-650 nm due to silver trimers which are the seeds for the formation of metallic nanoclusters [8].

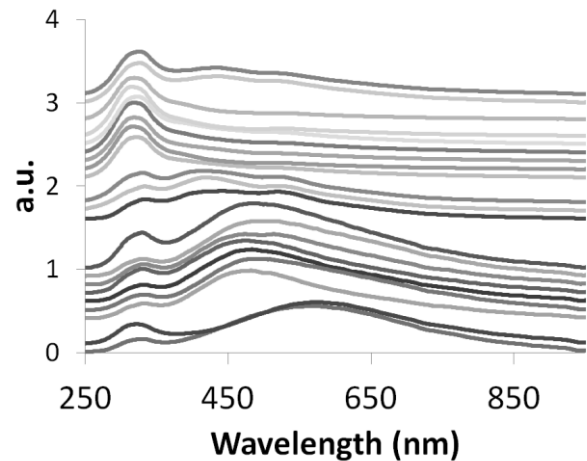


Fig. 1: Representative IBIL spectra of each sample

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