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EFFECT OF THE TEMPORAL INTEGRATION ON THE ACCURACY OF THE MEASURED CONCENTRATION IN LIBS MEASUREMENTS

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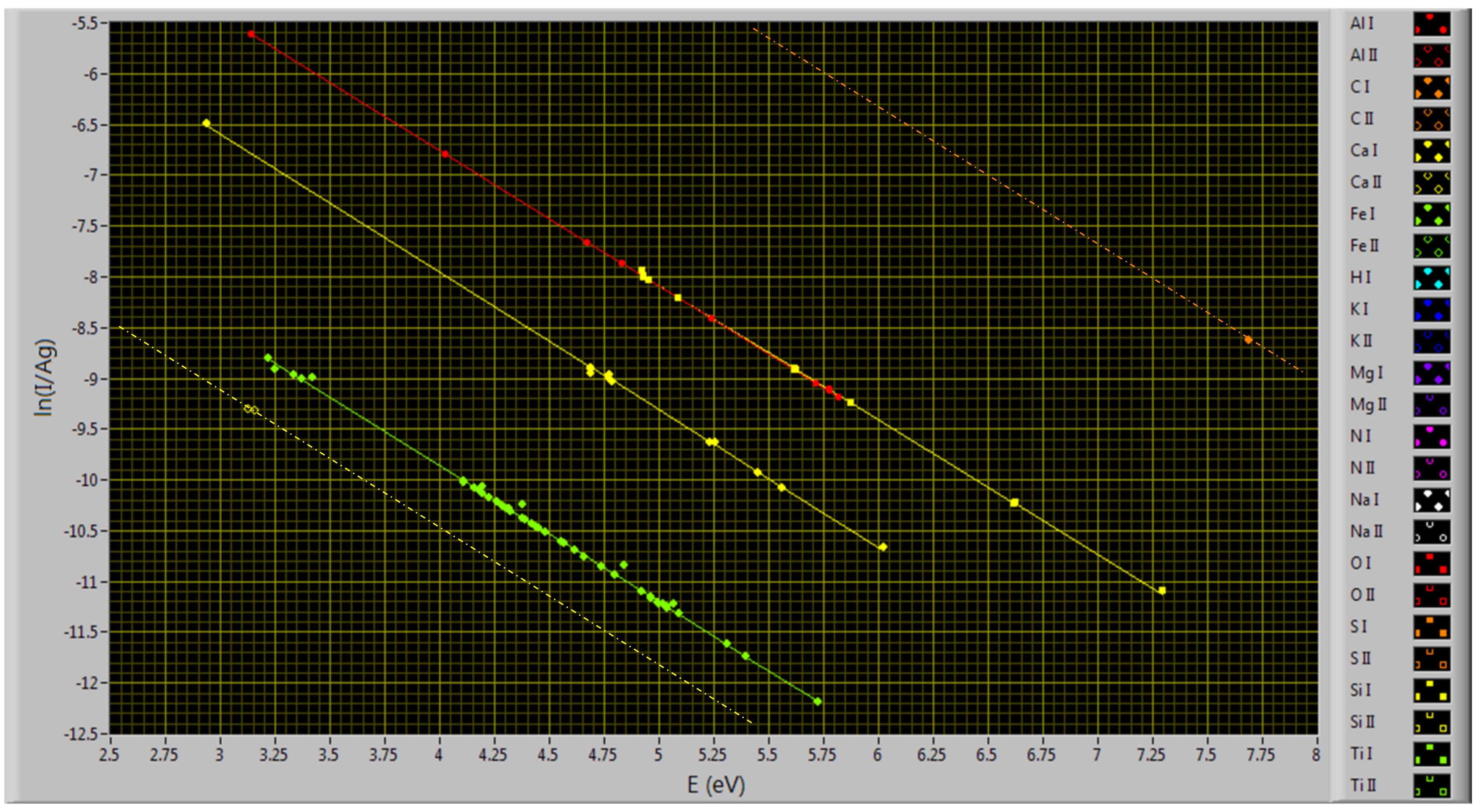
We have developed a simulation program that allows to calculate the plasma emission spectrum of a coal sample in a LIBS experiment. We used the acquired data to evaluate the effect of temporal integration on the accuracy of measured concentration obtained using the calibration free method.

Introduction

The Laser Induced Breakdown Spectroscopy (**LIBS**) is a laser based analytical technique capable of providing both qualitative and quantitative chemical composition of gas, liquid and solid samples. The principle of operation relies on the generation of a **breakdown plasma** by means of high irradiance (>10^{10} W/cm^2) laser pulses. Light contributions emitted by the plasma are collected and **spectrally analyzed** by a properly designed detection unit. To get **quantitative measurements**, this method usually requires the construction of empirical calibration curves, which in many cases (like e.g. in non-homogeneous materials) can hardly be derived. To cope with this problem we are evaluating the use of the so called **calibration free** method. With the present work we intend to estimate the dependence of the measured concentration on the measuring integration time.

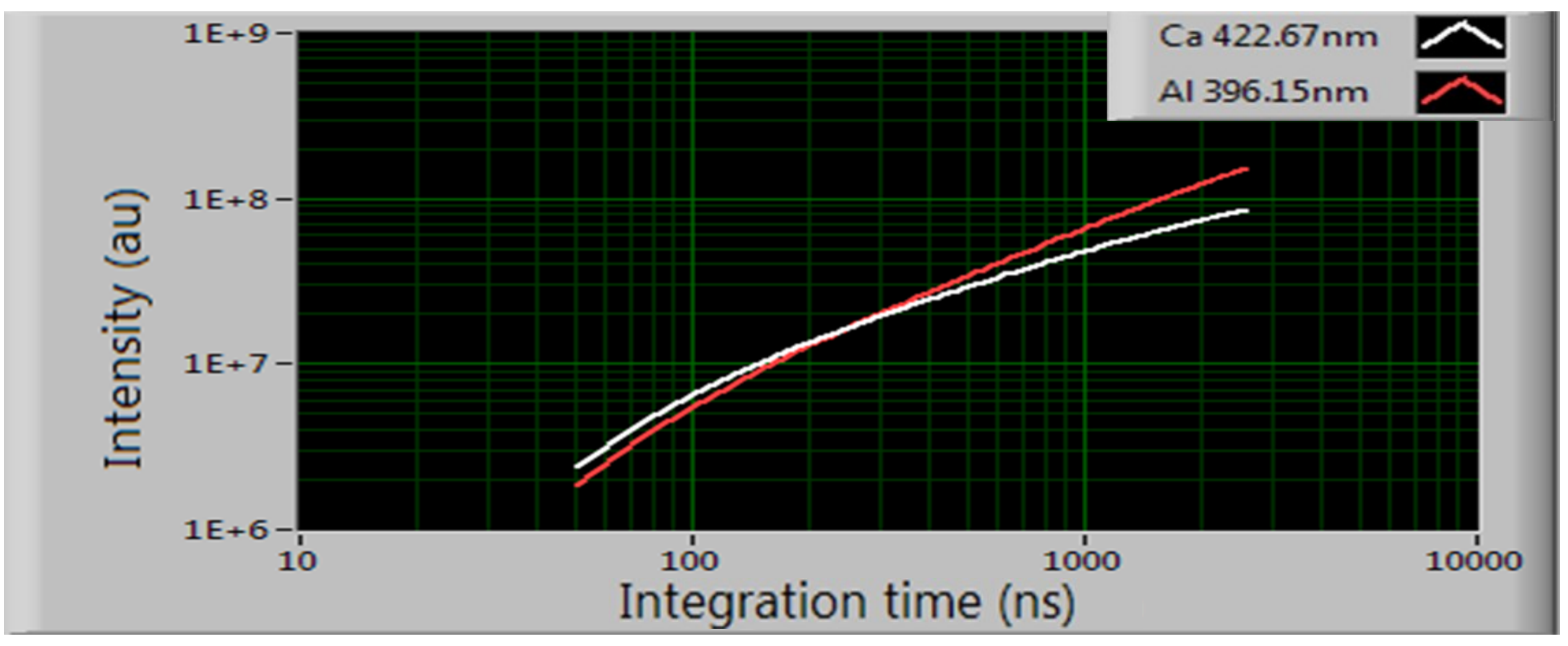
$$I_{ki} = \alpha C \frac{A_{ki} g_k}{U(T)} e^{-\frac{E_k}{k_B T}} \tag{1}$$

$$ln\left(\frac{I_{ki}}{A_{ki} g_k}\right) = -\frac{1}{k_B T} E_k + ln\left(\frac{\alpha C}{U(T)}\right) \tag{2}$$



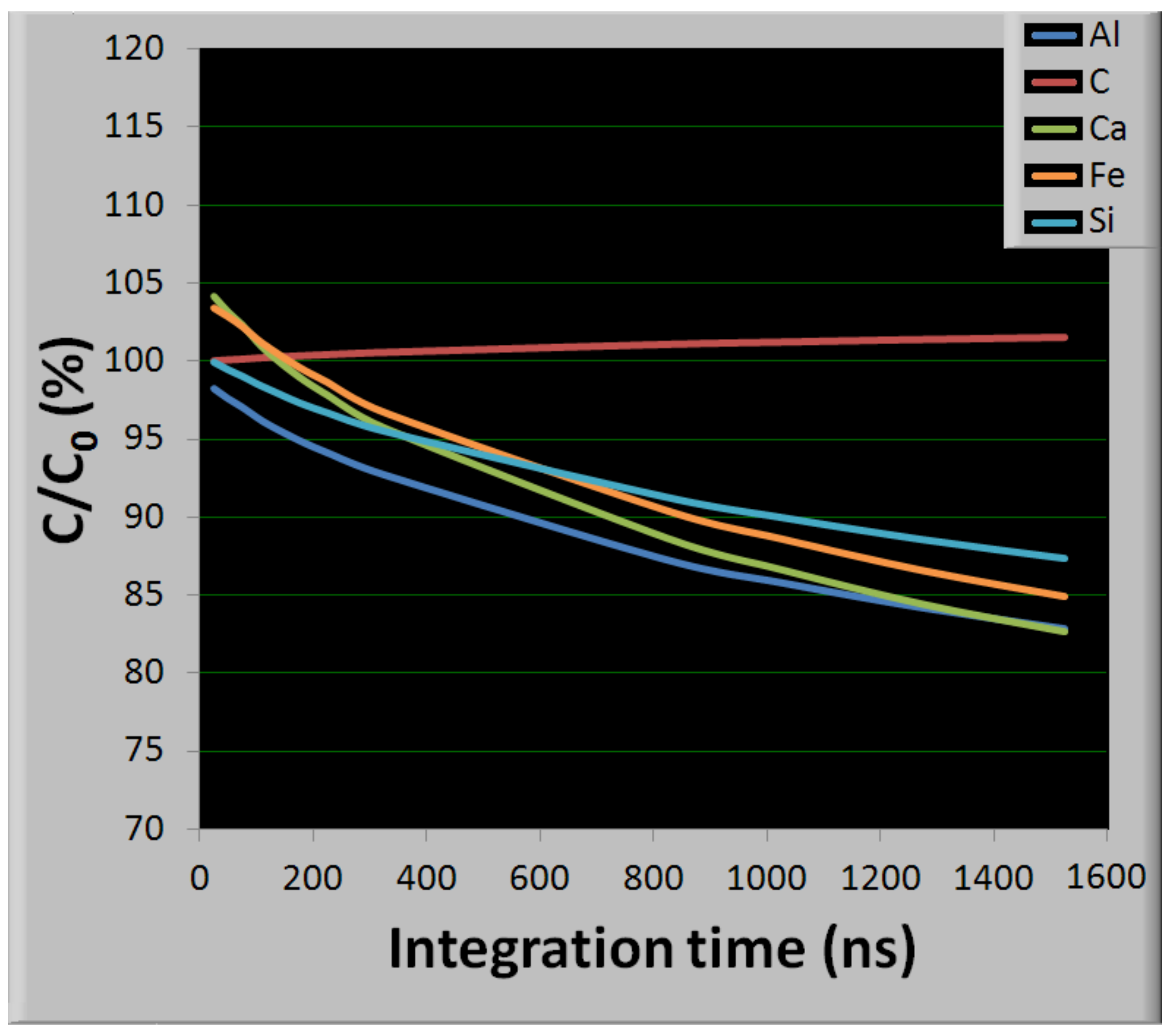
Calibration free method

Using Local Thermal Equilibrium approximation, the intensity of a spectral line due to a transition between the atomic level *k* and *i* is given by the Eq. 1, where *C* is the concentration of the atomic species of interest, *U(T)* is its partition function at temperature *T*, A_{ki} is the Einstein transition probability of $k \rightarrow i$ transition, g_k and E_k are respectively the statistical weight and the energy of the *k-th* level, while K_b is the Boltzmann constant. As shown in Eq. 2, derived from Eq. 1, a **linear relationship** exists between the upper energy *k* and the quantity $\ln(I/Ag)$. By means of a linear fit it is possible to obtain both the temperature *T* and the quantity αC_n for every atomic species. The α factor can thus be determined by normalizing to the unit the sum of the species concentration $\sum_n C_n = 1$. In this way the **relative concentration** of the sample's component can be derived



Simulation program

Utilizing data taken from the NIST database, we developed an algorithm that allows to calculate the emission spectrum generated by a sample of **chosen composition**. We also used the values of temperature and electron numerical density measured by Dong *et al.* (*J. Anal. Act. Spectrom.*, ***27***, *2066, 2012)* to simulate the evolution of the spectra as a function of time. By summing up a number of these spectra it was possible to reproduce the effect of **time integration**. As shown in the figure, the ratio between line intensities of different elements changes as a function of the integration time, thus preventing a correct measure of the concentration.



Results

By means of the simulation program, we have calculated the LIBS spectra of samples with different elemental composition and for each one we have evaluated the elemental concentrations for different integration times. As an example we show the result relevant to a sample with the following composition: 90.5% of carbon, 5% silicon, 3% aluminum, 1% iron and 0.5% calcium. As it can be noticed, the calculated carbon concentration does not significantly change as a function of the integration time, while the concentration of the other elements vary up to 25% with respect to the input original concentration. We have also observed that the concentration of more abundant species changes more slowly than concentration of the less abundant ones and that concentration of elements with stronger emission lines usually changes faster than concentration of elements with lower intensity line. Furthermore, it seems that concentration changes faster in samples made by few elements. The only evident exception we have found so far is the case of samples with a high content of hydrogen. In fact, in spite of the fact hydrogen lines are weak, the measured hydrogen concentration can vary up to 60% of the input value. The same anomalous behavior is observed for other elements of the sample.

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