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| **Author(s):** | **Matthieu Baudelet, Ph.D.** |
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**PI:** Dr. Matthieu Baudelet

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Arlisia Potter

# Purpose and objectives of the project

This project proposed to establish a parameter to quantify the level of confidence that can be given to an elemental analysis by Laser-Induced Breakdown Spectroscopy (LIBS). To that purpose, (1) the parameter will be built considering a LIBS spectrum as a distributed sequence of weighing distributions (the emission peaks with their own profile) over a discrete list of wavelength-ordered emitters. The statistical weight for each emitter line in the list is not equivalent and depends on the emission probability of the transition, the prior knowledge of the sample elemental composition, the parameters of the LIBS plasma. The quality of the spectra and the amount of spectral lines available for decision is also crucial in the confidence for assignment of lines. (2) The parameter will be confronted to different laser conditions as well as detection and analysis conditions.

# Project Design

The elemental analysis starts with the assignment of spectral lines. The reference for spectral line assignment is a database such as the National Institute of Standards and Technology Atomic Spectra Database (NIST)[Kra16], Atomic Line List Harvard-Smithsonian Center for Astrophysics (Kurucz) [Ku95], or Massachusetts Institute of Technology Wavelength tables (MIT) [Har69]. Each database contains information on the experimental or calculated emission lines of ions by their emission wavelength, probability of emission, and energy level involved in the transition.

The spectral line assignment can be tainted by spectral interferences. While high spectral resolution is a first step for confidence in spectral line assignment, it cannot prevent all spectral interferences that occur: spectral line coincidence [Hub11], overlap with a broadened line wing

[Laj04], spectrometer stray light [Lar76], and background continuum [Lar79]. These interferences create uncertainty in the line assignment for elemental analysis.

Quantifying the spectral interference is needed for a more accurate analysis [Rus14] and validation of method [Saf11]. Such quantification being included in the calculation of error rates can lead to reduction of error [Ell12], and quality assurance [And14]. Uncertainty quantification is an assessment of reliability and provides confidence in the method's results.

The evaluation of spectral interference is difficult in LIBS and optical emission spectroscopy in general due to the need for identification and estimation of all parameters involved in the interference [Bou94, Win82]. Boumans *et al.* developed the Q-concept method for quantification of spectral interferences. This method can quantify spectral interferences from coincidence and overlap with the wing of a broadened line. The Q-concept method uses ICP line coincidence tables [Bou90, Bou91] already in existence without the need for specialized software needed for the analysis [Tho06]. The ratios between the analytical line and the interfering line was recognized to possibly be incorrect due to different excitation conditions [Tho06]. Furthermore, a limitation to this method is the correction of only two spectral interferences [Bou88].

The use of correlation analysis between experimental and library spectra has been applied to calculate the composition of a sample using LIBS. This approach uses the differences in spectra and intensity for different materials as a unique identifier. Jurado-Lopez and Luque de Castro applied this method that identified alloys used in jewelry manufacturing by rank correlation [Jur03]. Gornushkin and coworkers identified solid, plastic, and archaeological materials with this method with rank and linear correlation analysis [Gor99, Anz00, Anz02]. A requirement of this method is a library of representative spectrum which can be unrealistic if the samples are unique and/or not completely known. Even if this method can distinguish between similar spectra, only requires small computation times and doesn't need coincidence tables, it cannot quantify the interferences seen in the spectra.

An automatic spectral line assignment method by correlation of model and experimental spectra was proposed by Labutin *et al.*[Lab13]. The method uses the simulation of spectra with different temperature and electron densities that are then compared to the experimental for the best correlation. A steel sample was used for analysis and the certified elements found in that sample were modeled. Two peaks were added manually after the algorithm by the authors because the algorithm did not detect these as being part of the spectral profile. One-line assignment was dependent on a parameter that was not found in the model spectra, which was attributed to the fact that only certified elements were modeled. Spectral α, which was the ratio of the intensity of the *i*th line to the maximum intensity line within the given peak. Although this method allows for simple and fast spectral line assignment there is a requirement of model spectra from the prior knowledge of sample composition.

Yaroshchyk *et al.* established a semi-quantitative analysis software [Yar06] to model LIBS spectra. This approach can only analyze known samples, is based only on neutral and singly ionized emitters and requires the spectral response correction of the detection apparatus to calculate temperature

Mateo *et al.* developed a semi-automatic spectral analysis for element identification called SALIPS [Mat05]. SALIPS combines the use of the NIST Atomic Spectra Database with structured query language sentences for peak and element identification. The sample composition does not need to be known though the authors suggested providing this information to speed up the algorithm and further follow-up treatment. The percentage of confidence defined by the user, if set too high, can result in a lack of element identification for a peak. While this process, requires limited input by the user, the elements are not considered to be producing multiple spectral lines.

Amato *et al.* proposed a method to calculate the probability of an element being present within a sample by text retrieval technique [Ama10]. Although the authors could rank elements by relevance to the sample, misidentification occurred. A limitation to this method was the negligence to identify minor elements that were present in the sample. Another issue with this method was the overestimation of the weights used for quantification purposes.

At the International Power, Electronics, and Materials Engineering Conference in 2015, Zhendong Ji presented a method to identify the probability of the presence of an element by calculating the cosine similarity of spectral peak information and NIST database [Ji15]. This method does not consider when a probable element for a peak is missing instead it removes that element from the calculation. The nature of LIBS plasma will affect dynamic shifting and broadening of spectral lines that were not considered in this method.

In this project, we develop a quantitative interference factor (QIF) for each spectral line in an experimental spectrum using a novel algorithm based on an existing database and Bayesian statistics. This approach can be applied with or without knowledge of the plasma and/or the sample. It is experimentally tested on pure silicon as well as a NIST SRM 610 glass sample. The two samples were evaluated with either no prior or qualitative prior knowledge yielding an elemental profile of each sample. We show how the choice for non-interfered spectral lines can be crucial depending on whether this knowledge is available.

## Algorithm development

In this method, the LIBS spectrum is considered a multimodal distribution of emission from elements listed in a database, where each transition has a weigh proportional to its strength. A spectrum is a specific set of weighted distributions which results in the emission peaks having their own profile. The statistical weight attributed to each emitter from the database is not equivalent. The weight is dependent on emission probability of the transition, probability of the population of energy levels, and plasma parameters.

The quantitative interference factor (QIF) is calculated by comparing the detected peaks from the sample spectrum to the emission lines listed in the database. This method only requires the list of extracted peaks and their parameters from the experimental spectrum that are then compared to the expected peaks of each element from the database of choice for the analyst.

The parameters defining each peak from the experimental spectrum are the first input of the QIF algorithm. The distribution of each peak does not assume any instrumental function, resolution, or broadening phenomenon. The position and the width of the peak will respectively define the central wavelength and the range of the sub-section of the wavelength-ordered spectral database that will be used for comparison for each individual peak. The line shape of the peak defines the interpolation values for the emission intensity between experimental data points. The important information from the extracted peaks of the peak position and peak width will be used as input for the QIF calculation.

The database consists in a list of wavelength-ordered emission transition. Each transition is at least characterized by the wavelength characterizing the energy difference between levels, the energy value of these levels, its strength and its emitter. In this paper, the Kurucz database is used because it is available in an electronic format and includes parameters such as the energy levels and emission probabilities even if a great variance for the latter values could be discussed [Kur95]. Only the neutrals and first ions are used in this algorithm for simplicity and speed of calculation, as well as the fact that they have a greater probability of being at the origin of the spectrum compared to higher ionization states in LIBS conditions. Nonetheless, the method could be generalized to higher degrees of ionization.

The level of knowledge about the plasma establishes the strength of the transition. A basic level of knowledge for the QIF uses the probability of the emitter's transition as the value weighing the emission from each line. A second level of the QIF knowledge considers the population of the upper energy level of transition given by the Boltzmann equation. The population of the upper energy level can be defined by an excitation temperature (considered as a parameter) and the assumption of local thermodynamic equilibrium (LTE). Higher levels of knowledge for the QIF can be determined if all parameters relating to the LIBS process are known (i.e. electronic density, ionic densities in the plasma …). Addition of more parameters increases calculation time. In this paper, the level of knowledge used for calculating the QIF is the population of the upper energy level of transition multiplied by the probability of emission. We considered it is a good compromise between accuracy of the results and calculation time. This level of knowledge leads to the strength $S_{i\to j}^{e}$ of the transition $i \to j$ for the emitter $e$ to be defined as

$$S_{i\to j}^{e} = \frac{g_i^e A_{i\to j}^{e}}{Z^e(T)} \exp\left(\frac{E_i^e}{T}\right) \qquad (1)$$

with $g_i^e$ the degeneracy of the upper energy level (energy $E_i^e$) involved in the transition, $A_{i\to j}^{e}$ the emission probability (in s$^{-1}$), $Z^e(T)$ the partition function of the emitter $e$ at the excitation temperature $T$.

The first step in the establishment of the QIF is an overview of the spectrum and a semi-quantitative evaluation of the emission of each ion in the database. This evaluation consists in a matching factor comparing how many lines are detected in the spectrum for each emitter in comparison to the theoretical amount of lines that are found in the database for the spectral range defined by the overall analyzed spectrum. This factor is defined as the ratio between the sum of the strength of the detected peaks by the sum of the strength of the theoretical number of peaks this emitter should have in this spectral range. The larger the number of peaks to explain the spectrum found within the database, the higher the matching factor value will be. The reverse holds true also.

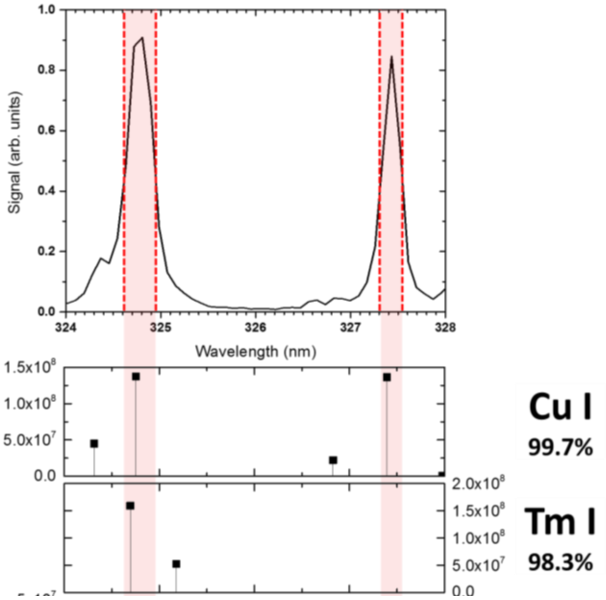

***Figure 1.*** *Measurement of the matching factor of several ions for the spectral range [324 nm - 328 nm] of copper emission*

For example, Figure 1 shows the typical spectrum of copper emission between 324 and 328 nm. Copper has two strong emission lines at 324.7 nm and 327.4 nm (resp. $3d^{10}4s\ ^2S_{1/2} \leftarrow 3d^{10}4p\ ^2P°_{3/2}$ and $3d^{10}4s\ ^2S_{1/2} \leftarrow 3d^{10}4p\ ^2P°_{1/2}$). Considering only these two lines as the spectrum input and the list of transitions belonging to each peak width (shown as the shaded areas in Fig. 1), the matching factor is calculated for all ions in the database and some values are shown in the figure.

A second step for the analysis is the listing and evaluation of the probability of all the transitions within the width of each peak individually. Each peak is considered a probability distribution of emission over a series of wavelength-ordered transitions. Each transition has its own strength as explained above. In this paper, we use the population of the upper energy level of transition multiplied by the probability of emission as described in Equation 1. Every transition is characterized by its strength which is then multiplied by the interpolated experimental value of the emission for this particular wavelength and the matching factor of the corresponding ion. The list of transitions and their individual weight before and after multiplication by the experimental emission as shown in Figure 2 for the example of the 324.7 nm line of Cu I.

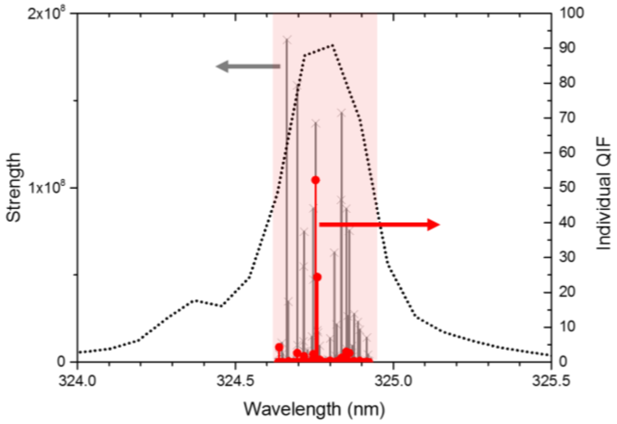

***Figure 2.*** *List of transitions for the individual 324.7 nm line of Cu I. The experimental spectrum is shown as a dotted line. The shaded area represents its full-width at half-maximum. The light grey lines (symbol ×) represents the Strength for each transition from the database. The bold red lines (symbol ●) represents the individual QIF of each transition for this spectral line only.*

It can be seen here that in this example that two transitions are theoretically the main contributors to the emission: Cu I (324.754 nm) and Th II (324.759 nm). The contribution from copper for this spectral line is explained by its large probability of emission as well the large population of its upper level in LIBS conditions and the large matching factor in the spectral range [324 nm – 328 nm] in which the analysis is performed. The contribution from Th II is explained by its large probability of emission ($A = 1.83 \times 10^7\ s^{-1}$) and large matching factor. The ionic aspect of Th II is not taken into account here because the calculation of the strength is not using electronic density as a parameter. The QIF information for each individual peak is then compiled into a matrix with the rows representing the ion from the database and the column the individual QIF.

A Bayesian approach [Les12] is then used to combine the information obtained for each peak in order to explain the whole experimental spectrum and include any available prior knowledge of model parameters. In this case, these parameters are the ions found in the Kurucz database and their QIF for each individual peak. The ions are first ordered in decreasing order of their contribution to the spectrum, based on the sum of their individual QIF for each peak. This ordering is performed by a greedy search of the largest sum of the QIFs for all peaks and then the subsequent ions with the next largest likelihood sum[42]. In order to avoid unnecessary calculation that would not provide useful information, a Bayesian Information Criterion (BIC) is then used to weigh the different possible models to be evaluated by the Bayesian approach. This selection is made by determining which set of emitters should be chosen over another to explain the combination of all peaks in the spectrum. The BIC is calculated according to the following equation:

$$BIC = -2\ln(I) + K\ln(n) \quad (2)$$

where $I$ is the maximum QIF estimate of each parameter, $K$ is the number of parameters in the model and $n$ is the number of observations in the data [Sch78]. Once all ions are ordered, the set of ions with the optimized BIC is the smallest number of ions needed to explain the whole spectrum. Because each ion is treated separately, a singly ionized emitter could be chosen for the optimal model without its neutral counterpart. Since the emission of an ion without its neutral is very rare in LIBS, the neutral ion of any chosen ion that were not already present are added to the optimal ions. More ions could be added to the optimum calculated by the Bayesian Information Criterion to explain the experimental spectrum, but it would increase computational times with little to no information about the QIF added to the analysis. An example for the copper spectrum example is given in Figure 3. Once the optimal number of emitters to explain the spectrum is chosen, any prior information we have access to about the sample can be used. In our case, we focused on the plasma composition. Either this composition is known or not. In the latter case, every emitter in the database is given the same probability of emission. In the prior case, a restriction is made to the emitters contained in the sample's composition and background gas for the LIBS analysis (since it could be excited and contribute to the emission spectrum), still with an equal probability of emission for each of them. The comparison between the two models will show the amount of prior knowledge of a sample that would be required to evaluate interferences for an unknown sample.

The two curves in Figure 3 show the importance of providing prior information to optimize the number of ions that explain the spectrum. In the case of a prior knowledge of a copper plasma in air, the optimum set of ions was {Cu I, Cu II, N I, O I}. In the case of no prior knowledge at all, all ions that contributed at least once in the individual QIF were considered and as such the list of ions that could explain the spectrum is large: {Fe II, Cu I, Fe I, Th II, Ni II, Th I, N I, K I, Ba I, Si I, Rh I, Cu II, Na I, Os I, Sn I, Eu I, Co I, Ag I, Ge I, U I, Al I, Ca II, Gd II, Sc I, Tl I, Te I}. Neutral and singly-ionized copper are part of this list while many other emitters that could have contributed to only one line are not discarded.

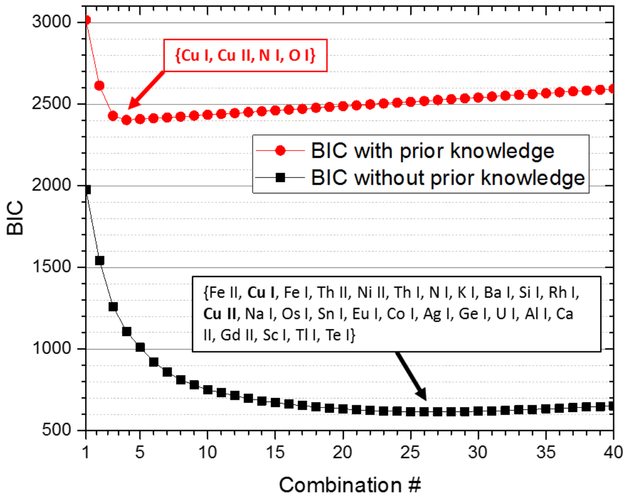

***Figure 3.*** *Bayesian Information Criterion for the example of the copper spectrum above. Two cases of prior knowledge are represented.*

After the optimal number of emitters are determined, their individual peak QIF values are used as the input for the Bayesian calculation of the QIF taking into account all the detected peaks. To find this factor, combinations of emitters with their individual QIFs are found and the best solutions to the experimental spectrum are determined by Bayes likelihood.

For each combination, its likelihood is determined by following equation:

$$\text{Bayes Likelihood} = \exp\left[\sum \ln L + \ln\big(p(n)\big)\right] \qquad (3)$$

where $L$ is the QIF of the parameters and $p(n)$ is the probability of the number of observations in the data [Rus95]. This algorithm is explained in the following figure 4.

- Draw a number of elements, *k*
- Draw the specific collection of *k* elements in the sample, the set ***c***
  - A collection of elements has likelihood proportional to the product of the probabilities of existence ***q***
- Draw a set the elemental activations for each peak, ***e***
  - A peak assignment has probability proportional to the LOC, ***p***

$$k \sim \boldsymbol{\pi}$$

$$\mathbf{c} \sim \mathcal{S}\left(\mathbf{c}|k,\mathbf{q}\right)$$

$$\mathbf{e} \sim \mathcal{A}\left(\mathbf{e}|\mathbf{c},\mathbf{p}\right)$$

$$\mathcal{S}\left(\mathbf{c}|k,\mathbf{q}\right) = \frac{1}{Z_{\mathcal{S}}\left(k\right)}\prod_{j=1}^{k} q_{c_j} \qquad \mathcal{A}\left(\mathbf{e}|\mathbf{c},\mathbf{p}\right) = \frac{1}{Z_{\mathcal{A}}\left(\mathbf{c},\mathbf{p}\right)}\prod_{i=1}^{P} p_{ie_i}$$

- The posterior for any possible assignment of elements to peaks has log-likelihood

$$\begin{aligned}\mathcal{L}\left(k,\mathbf{c},\mathbf{e}|\boldsymbol{\pi},\mathbf{q},\mathbf{p}\right) &= \pi_k \mathcal{A}\left(\mathbf{e}|\mathbf{c},\mathbf{p}\right)\mathcal{S}\left(\mathbf{c}|k,\mathbf{q}\right) \\ &= \frac{\pi_k}{Z_{\mathcal{A}}\left(\mathbf{c},\mathbf{p}\right)Z_{\mathcal{S}}\left(k\right)}\prod_{j=1}^{k} q_{c_j}\prod_{i=1}^{P} p_{ie_i}\end{aligned}$$

- Normalization gives a probability

$$Pr\left(k,\mathbf{c},\mathbf{e}\right) = \frac{1}{Z_{\mathcal{L}}}\mathcal{L}\left(k,\mathbf{c},\mathbf{e}|\boldsymbol{\pi},\mathbf{q},\mathbf{p}\right)$$

***Figure 4.*** *Algorithm for fusion of LOC of multiple lines in a spectrum.*

The combination with the largest likelihood is then chosen as the optimum one, defining what contribution from each ion of the model to each peak explains the spectrum.

## Experimental evaluation

For verification of the QIF algorithm, a pure Silicon wafer (UniversityWafer Inc., South Boston, MA) and NIST S610 glass standard reference sample were analyzed using a J200 LIBS system (Applied Spectra Inc., Fremont, CA). The J200 consisted of a 266 nm Nd:YAG laser (8 ns) focused to a 100-µm-diameter spot and an energy of 21 mJ, a 6-channel spectrometer covering the spectral range from 185 to 1040 nm (acquisition delay of 1 µs for 1 ms acquisition duration). Five spectra of ten shots from five locations of each sample were taken and averaged for quantitative evaluation of the spectral interferences of each sample.

The first evaluation of the QIF algorithm was performed on LIBS spectra obtained from a silicon wafer (Figure 5).

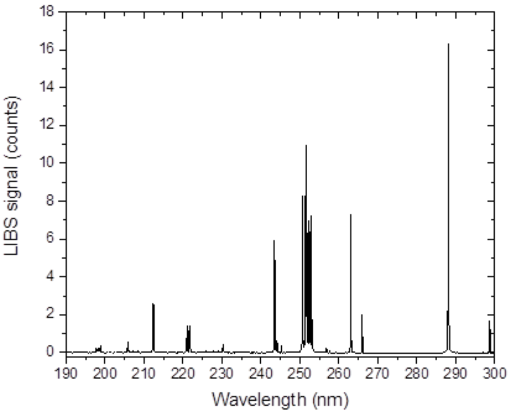

***Figure 5.*** *Experimental LIBS spectrum from a silicon wafer.*

Silicon has most of its emission lines (thirty-five (35) peaks were detected) below 300nm in our conditions. As an example of individual QIFs for each spectral line, Table 2 lists the five most intense peaks with their top 10 contributors based on their individual QIF emitters. The major contributors for each line were expected to be Si I and Si II. Si I was only the second contributor for the peak at 252.85 nm because of the large interference from Sb I, which is known as an interference from its line at 252.853 nm [Kub65]. Neutral Si had the highest or second highest individual QIF for 27 of the 35 most intense peaks while Si II had the highest individual QIF for 2 of these peaks. The seven other peaks were showing spectral interference.

The elemental profile of the best set of ions to explain the Silicon spectrum was calculated with and without prior knowledge of the sample composition. The Silicon wafer sample was analyzed in air so nitrogen (N I, N II), oxygen (O I, O II), and hydrogen (H I) from moisture were added to the prior knowledge of the sample composition due to the ionization of these elements from the LIBS plasma. Posterior QIFs of all sixty peaks in the spectrum were calculated from the 400,000 combinations of prior elemental data.

**Table 2**. Five peaks from the silicon spectrum with each peak's top emitters and individual QIF values

| **Peak 250.69nm** | | **Peak 251.61nm** | | **Peak 252.41nm** | | **Peak 252.85nm** | | **Peak 288.15nm** | |
|---|---|---|---|---|---|---|---|---|---|
| ION | QIF | ION | QIF | ION | QIF | ION | QIF | ION | QIF |
| Si I | 0.9019 | Si I | 0.9666 | Si I | 0.9465 | Sb I | 0.5530 | Si I | 0.9785 |
| Ru II | 0.0388 | Co II | 0.0049 | Bi I | 0.0105 | Si I | 0.4080 | Ni II | 0.0039 |
| Co II | 0.0186 | Fe II | 0.0030 | Pt I | 0.0072 | Co II | 0.0164 | Th II | 0.0034 |
| Co I | 0.0107 | Ti II | 0.0029 | Sn I | 0.0062 | Co I | 0.0069 | Mn II | 0.0025 |
| Os II | 0.0083 | Mn II | 0.0028 | Mn II | 0.0058 | Mn II | 0.0028 | Cr II | 0.0024 |
| Fe II | 0.0043 | Cr II | 0.0024 | Fe II | 0.0056 | Fe II | 0.0027 | Fe II | 0.0024 |
| Mn II | 0.0041 | Cl II | 0.0023 | Cr II | 0.0050 | Cr II | 0.0022 | Co I | 0.0024 |
| Tm II | 0.0037 | Th II | 0.0023 | Mn I | 0.0030 | Cl II | 0.0015 | Mn I | 0.0013 |
| Cr II | 0.0031 | Bi I | 0.0014 | Cr I | 0.0029 | Mn I | 0.0014 | Cr I | 0.0012 |
| Mn I | 0.0021 | Cr I | 0.0014 | Mg I | 0.0023 | Cr I | 0.0013 | Fe I | 0.0008 |

Analyzing the 35 peaks found within the 185nm and 300nm region, the ions needed to explain that part of the experimental spectrum with no prior knowledge of the sample composition were Bi I, Fe I, Fe II, Ni I, Ni II, Pb I, Rh I, Rh II, Si I, and Th I (Figure 6). The peaks at 205.482nm, 207.25nm, 208.43nm, 226.01nm, 228.98nm, 243.89nm, and 298.75nm have large spectral interferences where there is not any emitter with a QIF greater than or equal to 90%, resulting in uncertainty in elemental assignment of those peaks. Some of these peaks are known in the literature to be very easily interfered. An example is the one at 205.48 nm for which Fe was seen as an interferent for ICP-OES [Das99]. Small interferences mean that one emitter has a QIF greater than or equal to 90% and that all other interfering elements' QIF only add together to 10% or less. The peak at 205.48nm had three possible emitters of Fe II, Ni I, and Ni II with large spectral interferences. Peaks 197.70nm, 198.26nm, 244.33nm, 245.21nm, and 253.25nm have small spectral interferences. The highest QIF for these peaks are Si I but there are small probabilities that the Si I contribution is interfered by additional emission from other emitters. Nonetheless, twenty-four (24) of the peaks in this spectral region were judged not to be interfered.

The same 35 peaks were analyzed with prior knowledge of the sample's composition (Figure 5). Four ions (N I, O I, Si I, and Si II) were needed to best explain the spectrum with prior knowledge of the sample composition. Thirty-two of the peaks contained no spectral interferences and have 100% certainty of elemental assignment. Peaks 206.13nm and 243.89nm have small spectral interferences. There was large spectral interference in peak 205.48nm with equiprobability of the four best ions being the emitter of the peak. This peak was then judged non-reliable for Si analysis in any case.

Depending on the prior knowledge used for the analysis, the set of ions are not the same due to optimization of the ordering of ions to best explain the experimental spectrum. Nonetheless, Si I was a common (and only) ion to both cases. It was considered the main emitter (highest QIF) of spectral lines for half of them. This demonstrate that some spectral lines in this spectrum could be used as silicon signal without the worry of spectral interference even in the case the sample was unknown.

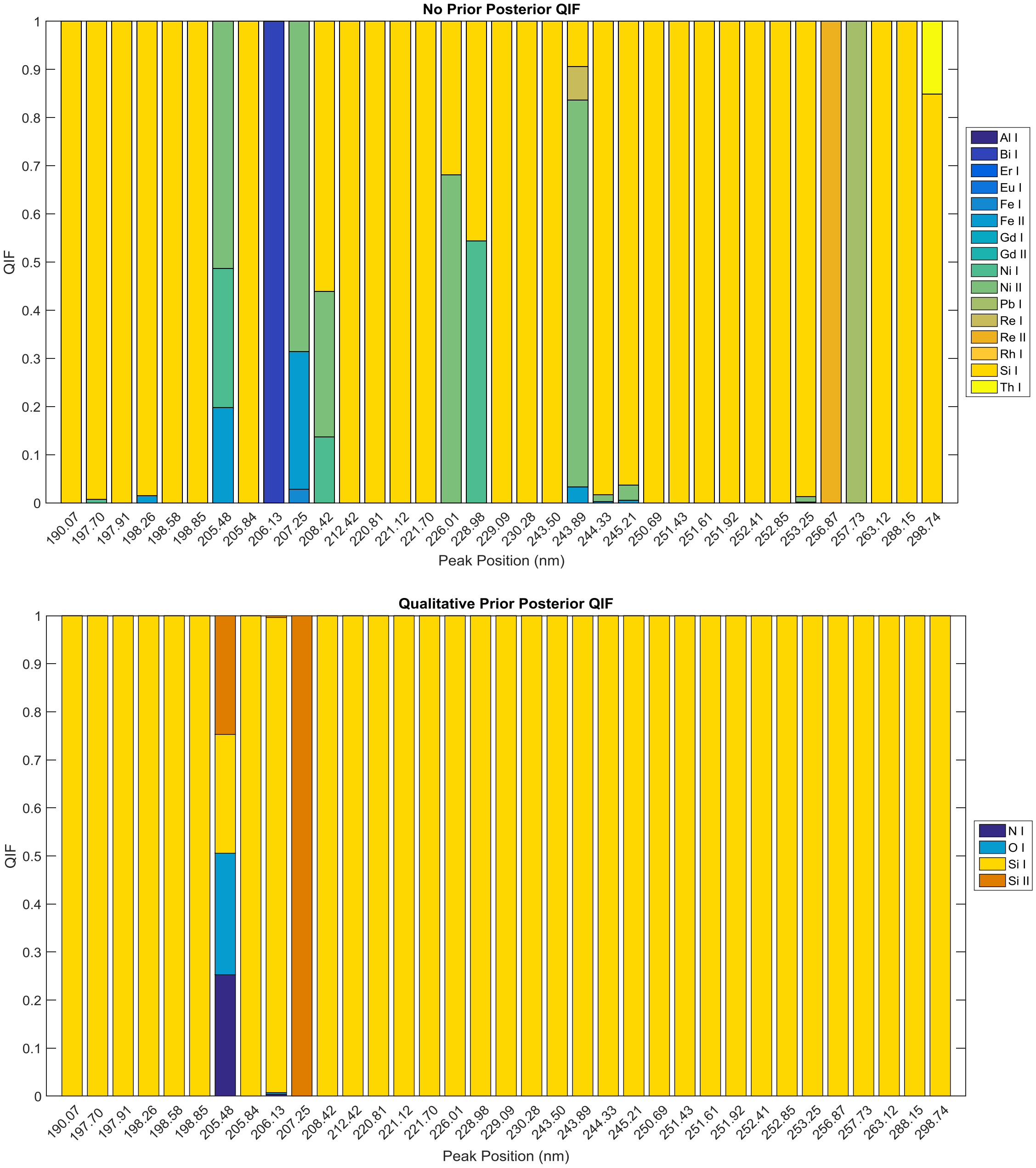

*__Figure 6.__ Posterior QIF for the silicon experimental spectrum*

A more complex sample (NIST SRM610 glass) was analyzed, whose spectrum is shown in Figure 7. The analysis was done using the 205 peaks of the spectrum.

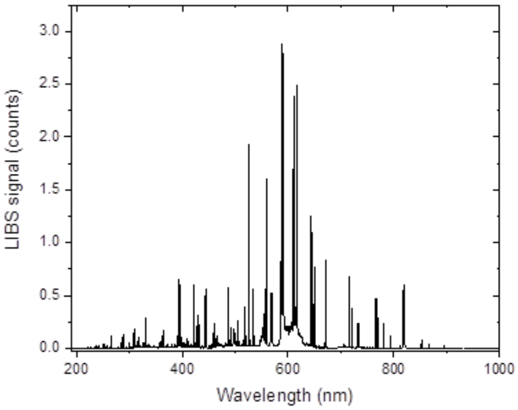

***Figure 7.*** *LIBS spectrum of NISR SRM610*

Prior knowledge of the sample composition (evaluated from the NIST certificate of analysis) resulted in 26 ions needed to best explain the spectrum while 25 ions were needed if no prior knowledge was introduced in the analysis. These two levels of prior knowledge had 24 ions in common. Os I was needed with the low level of prior knowledge but not in the qualitative level, this ion not being in the sample composition. The two ions needed with the qualitative prior knowledge that were different from the no prior knowledge were Cu I and Yb I. Figure 8 shows how knowing the sample's composition assigns peak emitters differently for 15 peaks of interest. This restricted set was used for clarity and conciseness of the discussion. The results for both cases for all the other lines were similar and were not considered here for the discussion.

Six of the peaks showed a single emitter in both levels of knowledge. The other peaks showed different contributions. Both peaks at 226.81 nm and 234.82 nm showed a main contribution from Os I if the analysis was done without prior knowledge. Once prior knowledge was input, these two peaks were found to originate from Si I with a small interference from Ca I and Al I with a small interference of Si I. The same behavior was seen for the peak at 452.74 nm, attributed to Mo I, Th II, and Y I. Os I was a large interference to Ca I for the peak at 237.02nm without prior knowledge, which disappeared when qualitative knowledge was introduced. The same behavior was seen to a milder amplitude for the peaks at 421.14 nm, attributed to Ag I, and 337.15 nm, attributed to Th II. Peaks at 520.57nm and 534.92nm showed highly interfered in both cases. Overall, the highest QIF being attributed to the same ion for no prior and qualitative prior knowledge occurred for 90% of the peaks. This common analysis was the result of the having 24 ions in common to explain the spectrum in both cases.

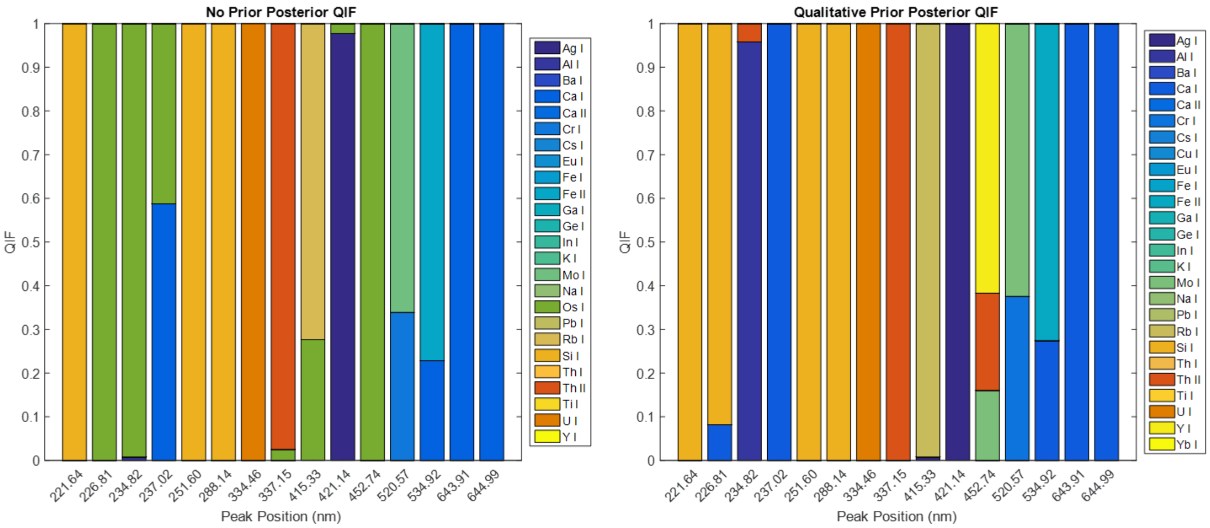

***Figure 8.*** *Posterior QIF for NIST SRM610*

## Conclusion

A novel approach to the evaluation of spectral interferences in the line assignment in LIBS was developed. By combining fundamental knowledge of the plasma emission, eventual prior knowledge of the sample as well as the information a full spectrum can provide, this algorithm provides a quantitative measurement of how much a line is interfered for its assignment. The approach was demonstrated on spectra from a pure silicon sample as well as a more complex NIST SRM610 glass.

The prior knowledge used for the analysis was discussed in two cases: (i) none is available as well as (ii) a qualitative list of elements is known for the eventual composition of the plasma. It showed that obviously more knowledge leads to a better attribution of the spectral lines but that in many cases, the ion assignment for spectral lines is not sensitive to the prior knowledge for a given spectrum. These lines could then be considered reliable signal for elemental analysis.

The algorithm is used here for LIBS data but could be applied to other types of elemental emission techniques such as ICP-OES. The need for only a single spectrum and a database for analysis makes this approach a strong candidate for the analysis of unknown samples where plasma modeling is not possible. Nonetheless, its versatility leaves room for improvement if more knowledge is available such as plasma conditions and exact plasma composition.

# Implications for Criminal Justice Policy and Practice in the U.S.

The algorithm developed under this project provides forensic experts with a complete quantitative evaluation of the input data either they just need to provide a qualitative list of elements present in a sample or they need to establish a comparison between samples. This analysis could become a

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standard for forensic use of LIBS and any optical emission spectroscopy (ICP-OES, GD-OES, Arc, ….). Its main strength resides in the ability to provide a line-by-line evaluation of the spectral interference and the ability to input as much prior knowledge as available on the spectral conditions and/or the sample. A reliable algorithm is currently unavailable in any commercial software or any lab-made algorithm. Its development, which needs more evaluations, can provide for the first time a quantitative measurement of the quality of spectral lines used in optical emission, answering some of the needs established by the NRC Report "Strengthening Forensic Science in the United States".

# Scholarly products

## PUBLICATIONS

1. Jessica Chappell, Mauro Martinez, Matthieu Baudelet, "Quantitative evaluation of spectral interferences in LIBS", submitted to Spectrochimica Acta part B

## PRESENTATIONS

1. Jessica Chappell, Mauro Martinez, Matthieu Baudelet, "Quantitative Line Assignment in Optical Emission Spectroscopy", Pittcon 2018; Orlando, FL, USA; 02/28, 2018. *Poster presentation*
2. Jessica Chappell, Brandon Seesahai, Mauro Martinez, Martin Richardson, Michael Sigman, Matthieu Baudelet, "Fundamentals and statistics: the great marriage for the LIBS analysis of trace evidence", LIBS 2016; Chamonix, France; 09/15, 2016. *Invited*
3. Jessica Chappell, Brandon Seesahai, Martin Richardson, Michael Sigman, Matthieu

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Baudelet, “Quantitative evaluation of spectral interference in Atomic Emission Spectroscopy”, Pittcon 2016; Atlanta, GA, USA; 03/07, 2016.

4. Jessica Chappell, Brandon Seesahai, Martin Richardson, Michael E. Sigman, Matthieu Baudelet, “Spectral line assignment: a statistical approach for forensic applications”, Winter Conference on Plasma Spectrochemistry; Tucson, AZ, USA; 01/12, 2016
5. Jessica Chappell, Brandon Seesahai, Martin Richardson, Michael Sigman, Matthieu Baudelet, “Quantitative evaluation of spectral interference in LIBS”, SciX 2015; Providence, RI, USA; 09/30, 2015. *Invited paper*.
6. Matthieu Baudelet, Jessica Chappell, Brandon Seesahai, Martin Richardson, Michael E. Sigman “Quantitative Evaluation of Interferences in Optical Emission Spectroscopy: Towards Quantitative Line Assignment”; Pittcon 2015; New Orleans, LA; 03/09, 2015.
7. Baudelet, Matthieu; Seesahai, Brandon; Liu, Yuan; Jeon, Cheonha; Richardson, Martin; Sigman, Michael; Chappell, Jessica, “Quantitative line assignment in optical emission spectroscopy”, SciX 2014; Reno, NV; 09/29,2014; *Invited paper*
8. Jessica Chappell, Brandon Seesahai, Yuan Liu, Cheonha Jeon, Martin Richardson, Michael E. Sigman, Matthieu Baudelet, “Quantitative line assignment in optical emission spectroscopy”, Florida Annual Meeting and Exposition 2014; Palm Harbor, FL; 05/10, 2014. *Invited*

PATENT

1. Matthieu Baudelet, “Quantitative Elemental Profiling in Optical Emission Spectroscopy”, *US Patent Application 20150025847 A1*

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