

Avoiding Misunderstanding Self-Absorption in Laser-Induced Breakdown Spectroscopy (LIBS) Analysis

Vincenzo Palleschi

In a recent article published in this journal (1), I discussed seven common errors that may affect the results of laser-induced breakdown spectroscopy (LIBS) analysis. Among these errors, one of the recurring ones is related to misunderstanding the process of self-absorption in LIBS plasmas. Because many people working in LIBS still consider self-absorption as a problem yet to be solved, I am dedicating a full article to this topic. The physics and chemistry of the phenomenon have been well known for many years, and this knowledge can tell us how self-absorption can be not only “corrected,” but also tuned to our advantage in analytical applications of LIBS.

Self-absorption occurs in spectro-chemistry when part of the radiation emitted by an extended source is re-absorbed before exiting the source and eventually reaching the detector. In LIBS quantitative analysis, the measurement of the radiation intensity determines the number concentration of the emitting analyte. When the effects of self-absorption are negligible, a linear relationship is typically obtained between the measured intensity and the analyte number concentration. Dealing with linear relations makes life easier for the analyst because it allows for

the building of (linear) calibration curves from which limits of detection (LOD) and limits of quantification (LOQ) of the analyte being studied can be determined.

In most spectro-analytical techniques, self-absorption effects can be considered negligible; however, in LIBS analysis, we often make measurements involving large concentrations of the analyte (percent level). In this case, the probability for a photon emitted by an atom or ion in the plasma to be reabsorbed by another atom or ion before exiting the plasma could be quite high, and definitely higher than that for the same analyte diluted at sub-ppm concentration in, for example, inductively coupled plasma–optical emission spectroscopy (ICP-OES) analysis.

The result of a strong self-absorption in LIBS is a nonlinear saturation effect, which is observed in the calibration curve; when the number concentration of the analyte increases, the measured intensity of the emission line does not grow proportionally. At large concentrations, the calibration curve saturates; it is well-known in the literature that in a log–log scale, the slope of the calibration curve changes from 1 to $\frac{1}{2}$ with the increase of the analyte concentration and the effect of self-absorption.

Don't Mistake Self-Reversal for Self-Absorption

Two observations should be made at this point, both correlated to frequent analytical errors. The first error that is often made in dealing with self-absorption in plasmas is mistaking this effect with the self-reversal phenomenon. Self-reversal manifests as a narrow dip on top of the emission line. Its presence is related to self-absorption, but self-reversal shows up only in the presence of spatial gradients of the plasma temperature and electron number density, which usually occur at the periphery of the plasma. Therefore, although the presence of self-reversal is an indication that the self-absorption phenomena in the emitting source are not negligible, as well as the spatial inhomogeneities in the plasma, its absence does not mean that self-absorption can be considered negligible.

Understand What Is Really Happening in a “Correction”

The second error that is, in my opinion, more subtle and substantial is associated to the need that some people working in LIBS feel to “correct” the effects of self-absorption. Although the term “correction” can be used at a colloquial level, it is nev-

ertheless important to know that this term does not correspond to the true nature of the phenomenon.

An emitting source is also an absorbing source. There is no problem to be solved unless we insist on using an unrealistic treatment of the emission process in which each emitter is considered independent from the others. Instead, what we could do is take into account the physical processes occurring during the propagation of the radiation in the plasma (spontaneous emission, absorption, and stimulated emission, with the latter being in general negligible). In the approximation of homogeneous plasma in local thermal equilibrium, the number of photons emitted by the laser-induced plasma at a given wavelength along the line of sight of the detector can be easily determined by solving a simple differential equation:

$$\frac{dn_p(\lambda, x)}{dx} = \varepsilon(\lambda) - k(\lambda)n_p(\lambda, x) \quad [1]$$

In the above equation, the ε coefficient is proportional to the number of emitters and to the spontaneous emission coefficient A_{ki} of the transition (see Figure 1). Following the Einstein treatment of the propagation of radiation in a two-level atomic system (the same which is used to model the laser effect), it's easy to demonstrate that the absorption coefficient, k , and the emission coefficient, ε , are linked by the relation:

$$B(\lambda)k(\lambda) = \varepsilon(\lambda) \quad [2]$$

where $B(\lambda)$ is the Planck black body radiation function at the plasma temperature (T). The radiation propagation equation can be easily solved, at each wavelength, along the line of sight of the detector.

The shape of the lines emitted by an optically thin plasma ($k(\lambda)l \ll 1$) is usually well approximated by a Lorentzian function, peaked at the wavelength of the transition. However, because the absorption coefficient is proportional

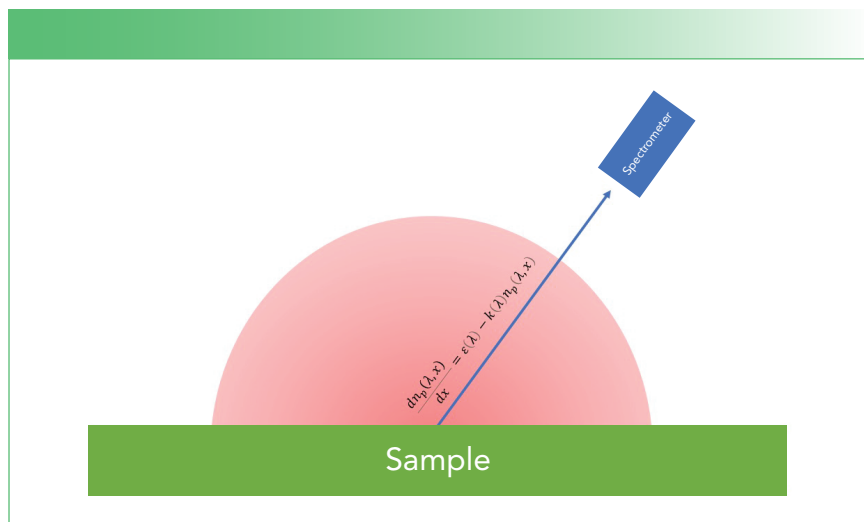


FIGURE 1: Schematic representation of the phenomena occurring within an emitting plasma.

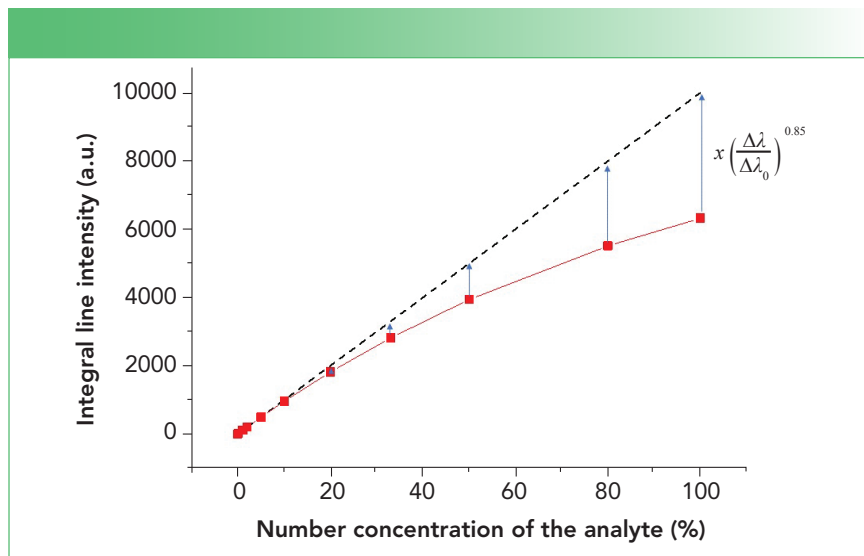


FIGURE 2: Linearization of the calibration curve for a given analyte by multiplying the measured integral line intensity by $(\frac{\Delta\lambda}{\Delta\lambda_0})^{0.85}$. The dotted black line is the optical thin limit, and the dotted red line is the measured intensity.

to the emission coefficient, the effect of self-absorption is more evident where the emission is stronger (at the peak of the line). This deformation of the shape of the emission lines makes the calculation of their integral intensity slightly more complex, but it can be demonstrated that, at least for low to moderate self-absorption, the integral intensity of the line would be given by:

$$I \cong I_0 \left(\frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l} \right)^{\frac{1}{2}} \quad [3]$$

where $k(\lambda_0)$ is the absorption coefficient calculated at the peak of the emission line, and I_0 is the integrated intensity (total number of photons emitted) that would have been measured on the detector if the plasma was optically thin.

It can also be demonstrated that the full width at half maximum (FWHM) of the self-absorbed line will increase with respect to the corresponding FWHM in optically thin plasma conditions following the same square root behavior:

TUTORIAL

$$\Delta\lambda \cong \Delta\lambda_0 \left(\frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l} \right)^{\frac{1}{2}} \quad [4]$$

Therefore, if we can estimate the FWHM of the line in the optically thin limit, it would be possible, by measuring the FWHM of the self-absorbed line, to estimate the value of the factor:

$$\left(\frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l} \right) \quad [5]$$

Substituting it in the relation for the line intensity, the simple relation is obtained:

$$I_0 \cong I \frac{\Delta\lambda}{\Delta\lambda_0} \quad [6]$$

A more precise calculation leads to the formula $I_0 \cong I (\Delta\lambda/\Delta\lambda_0)^{0.85}$, which is valid also in case of strong self-absorption. I_0 is, by definition, proportional to the number of emit-

ting atoms or ions in the plasma; therefore, the above equation allows recovering a linear relation between the measured intensity, I , and the concentration of the analyte (see Figure 2).

Conclusions

In conclusion, we can safely say that the self-absorption effect in LIBS is not a problem anymore. On the contrary, the simple treatment of the plasma as a homogeneous emitter at a temperature T makes it possible to recover the linear dependence between signal intensity and number concentration of the analyte, which characterizes an optically thin plasma. Moreover, knowledge of the physics of the phenomenon contributes to improving the precision of the determination of fundamental plasma parameters as transition probabilities and Stark coefficients of non-optically thin emission lines (2). The numerical simulation of the radiation propagation equation has

also demonstrated that the approximation of homogeneous plasma is not critical for the determination of the Stark coefficients of self-absorbed LIBS emission lines (3).

References

- (1) V. Palleschi, *Spectroscopy* **34**(8), 16–17 (2019).
- (2) S.M. Aberkane, A. Safi, A. Botto, B. Campanella, S. Legnaioli, F. Poggialini, S. Raneri, F. Rezaei, and V. Palleschi. *Appl. Sci.* **10**(14), 4973 (2020). <https://doi.org/10.3390/app10144973>
- (3) V. Palleschi, *J. Quant. Spectrosc. Radiat. Transf.* **271**, 107714 (2021). <https://doi.org/10.1016/j.jqsrt.2021.107714>

Vincenzo Palleschi is a Senior Researcher at the National Research Council of Italy in Rome, Italy, and a professor with Pisa University in Pisa, Italy. Direct correspondence to: vincenzo.palleschi@cnr.it ●

● Continued from Page 53

Internal standards are elements that are not present (or present at very low levels) in samples. They are added, at a fixed concentration, to all blanks, calibration solutions, and samples, either on-line via a mixing tee or valve port (easy), or off-line, by manual addition (tedious). When a sample contains high concentrations of sodium, potassium, and calcium, the internal standard signals are suppressed compared to what they are in the blank or matrix-free solutions. Many regulated methods specify how much internal standard suppression is permitted in a sample, which is typically between 75–80% of the signal observed in a sample matrix-free blank (usually the first calibration blank in the analysis). In general, if internal standard recovery is less than 75–80% in any sample, dilution and re-analysis is required. The most common reason for internal standard recoveries being greater than 120% is often attributed to the ICP-MS interface not being conditioned properly. *Conditioning* is the process of running a dummy sample containing similar matrix to the samples to be

analyzed through the instrument for approximately 30 min before you start the actual analysis, which causes the interface cones to become coated and helps to stabilize ion signals and minimize drift. It remains somewhat unclear as to why cone conditioning helps improve signal stability, but it is a well-documented fact that it does and conditioning in this way is standard practice. Cone conditioning is especially important after cleaning the interface cones or when they are replaced. In general, cleaning the interface cones should only be considered when signs of blockage or unremovable contamination are observed or if the instrument performance has significantly dropped.

Finally, The Route to Success

Finding the right configuration of the sample introduction system for a specific sample type is easy once a few questions are answered up front. The most important questions are related to the sample matrix: is it aqueous or organic? What is the amount of total dissolved solids? And what is the approximate composition?

Figure 1 summarizes a few of the crucial aspects that should be considered when setting up an instrument (either ICP-OES or ICP-MS) for analyzing a new sample type.

If a method is defined and validated but does not perform up to expectations, it is important to know which key areas of the system configuration to focus on and to understand how the different components of the sample introduction system are working together. As a general rule, instability is usually caused by problems upstream of the sample introduction system, whereas drift and suppression are rather caused downstream (injector tube, torch, and interface cones [in the case of ICP-MS]). In some cases, effects that may be attributed to the hardware may also originate from unexpected interferences from the sample, but that is a subject for another tutorial.

Simon Nelms and **Daniel Kutscher** are with Thermo Fisher Scientific. Direct correspondence to: daniel.kutscher@thermofisher.com ●