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OPC-LIBS for Quantification of Cd and Pb in Tomatoes: A Sustainable Approach to Food Safety Monitoring

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This study shows that laser-induced breakdown spectroscopy (LIBS), combined with one-point calibration (OPC) and a dual-laser system, provides a rapid, cost-effective alternative to conventional methods like atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) for detecting heavy metals in tomatoes. OPC-LIBS quantified cadmium and lead with 93% and 89% accuracy, achieving low limits of quantification (0.03 mg/kg for Cd, 0.08 mg/kg for Pb), complying with ANVISA and EU standards. These results validate OPC-LIBS as a scalable, environmentally friendly approach for real-time contaminant monitoring, offering strong potential for integration into agri-food quality control systems.

Keywords*—LIBS, food safety, determination of heavy metals*

I. INTRODUCTION

The presence of heavy metals such as cadmium (Cd) and lead (Pb) in food is an increasing public health and environmental concern. These metals are toxic, and their ingestion at elevated levels can cause severe health problems, including neurological and kidney damage. Therefore, strict monitoring of these contaminants is essential to ensure food safety.

Conventional techniques such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are widely used for heavy metal quantification. However, these methods present significant drawbacks, including high operational costs, lengthy analysis times, and limitations in large-scale applications [1], [2].

In this context, Laser-Induced Breakdown Spectroscopy (LIBS) emerges as a promising alternative. LIBS provides rapid, versatile, and low-cost elemental analysis [3], [4] by evaluating the plasma generated on the sample surface by a laser pulse. Furthermore, LIBS requires minimal sample preparation and produces no hazardous chemical waste, making it a valuable tool for both environmental analysis and food quality control.

In Brazil, agribusiness represents approximately 24% of the GDP. However, excessive use of fertilizers and pesticides has increased the risk of soil and water contamination with heavy metals, which may accumulate in crops such as tomatoes. This situation highlights the urgent need for faster and more affordable analytical methods to monitor contaminants in food.

The One-Point Calibration Laser-Induced Breakdown Spectroscopy (OPC-LIBS) technique [5] offers an effective solution, combining high sensitivity, precision, and rapid analysis at low cost with zero chemical waste generation. This study aims to explore the use of OPC-LIBS for quantifying cadmium and lead in tomatoes, addressing a critical research gap and offering a more efficient approach for food safety monitoring.

II. QUANTITATIVE MODELS

Calibration-free (CF-LIBS) [6] is a quantitative technique that integrates plasma and emission line parameters. It operates under the assumption of local thermodynamic equilibrium (LTE) [7], [8] within the plasma, where electrons, atoms, and ions share the same temperature. It also requires a sufficient electron density to enable energy exchange through particle collisions and assumes stoichiometric consistency between the sample and the plasma[7].

For CF-LIBS, we use the Boltzmann equation to calculate the emitter density for element α, N_α, as a function of line and plasma parameters:

$$N_\alpha = \frac{I_{ki}^{\alpha}\, L(\lambda)_\alpha\, U_\alpha(T)}{g_k^\alpha A_{ki}^s} \frac{4\pi}{hc} e^{\frac{E_k^\alpha}{K_B T}} \tag{1}$$

In this context, the variables are defined as follows: I_{ki}^s represents the intensity of the emission from transition k to i; $L(\lambda)_\alpha$ denotes the OPC factor; $U_\alpha(T)$ is the α partition function relative to temperature; g_k^α corresponds to the degeneracy of state k; h denotes the Planck constant; c is the speed of light; E_k^α represents the energy of state k; K_B is the Boltzmann constant; and T is the plasma temperature.

One-point calibration (OPC) [5], [9], [10], [11] is an empirical correction method applied to CF-LIBS. Its primary function is to calibrate emission lines while accounting for thermal equilibrium and addressing issues with certain emission line parameters. These issues include the unknown value of the spectrometer function F(λ), which converts arbitrary intensity values to W cm^{-2}; inaccuracies in Einstein's spontaneous emission coefficient; self-absorption; and photon absorption by molecules along the optical path to the collection fiber. Incorrect parameters can lead to erroneous temperature calculations, impacting the accuracy of quantification.

Unlike traditional methods [12], which require multiple calibration samples, CF-LIBS with OPC only needs one sample with a known concentration for calibration. Quantification relies on the concentration of an internal standard element as a reference. Further details are available in [9].

In CF-LIBS, the concentration of an element α, denoted as C_α, is determined based on the total emitter density N_α in relation to other parameters, as given by the following expression:

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$$C_\alpha = N_\alpha A_\alpha \chi_p \qquad (2)$$

where A_α is the α atomic mass, and χ_p is the plasma normalization constant, typically determined using an element with a known concentration as an internal reference (In this work, it was Ti).

III. MODEL EVALUATION

The prediction of the models was evaluated using the accuracy, the root mean relative error, RMSRE, and, the coefficient, r^2, defined as

$$Accuracy = 100\%\left(1 - \frac{1}{N}\sum_{i=1}^{N}\frac{|C_i-\tilde{C}_i|}{C_i}\right) \qquad (3)$$

$$RMSRE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{C_i-\tilde{C}_i}{C_i}\right)^2} \qquad (4)$$

$$r^2 = \left[\frac{\sum_{i=1}^{N}(C_i-\underline{C})(\tilde{C}_i-\underline{\tilde{C}})}{\sum_{i=1}^{N}(C_i-\underline{C})^2\sum_{i=1}^{N}(\tilde{C}_i-\underline{\tilde{C}})^2}\right]^2 \qquad (5)$$

where C_i and $\tilde{C}_i$ are, respectively, the sample i nominal concentration, and the concentration predicted with CF-LIBS and the OPC method.

We also employed the definition of the limit of detection (LOD) and limit of quantification (LOQ) described in [13] for further data analysis.

IV. SAMPLE PREPARATION

For this study, fifteen samples portions of grape tomatoes from local markets in São Carlos, SP, Brazil, were selected, sourced from different batches to introduce matrix variability. The tomatoes were freeze-dried for 72 hours, ground, and sieved to 100 mesh (particle size <149 µm). After drying, the remaining mass represented about 5% of the original.

Solutions of lead nitrate ($Pb(NO_3)_2$) and cadmium nitrate ($Cd(NO_3)_2$) were added at varying concentrations. Samples were dried at 40°C for 120 hours. Metallic copper with 1% titanium dioxide (TiO_2) was added to aid OPC-LIBS calculations, since Ti was used as the internal reference. The mixture was ball-milled for 120 seconds at 30 Hz, pressed at 2.4 kBar into 500 mg pellets (12.5 mm diameter), and stored in plastic bags under refrigeration.

V. LIBS MEASUREMENTS

Samples were analyzed using a pulsed Nd:YAG laser (Quantel Brilliant) at 532 nm (4 ns pulse, 60 mJ energy, 950 J/cm² fluence), combined with a second Nd laser (Quantel Ultra) at 1064 nm (8 ns pulse, 50 mJ, 510 J/cm², 20 Hz repetition rate).

An LTB Echelle spectrometer (Arielle model) with a 21–37 pm resolution (275–770 nm range) and ICCD detector collected the spectra (100 ns delay, 500 ns interpulse delay, 1 µs gate width). Two hundred laser shots were fired at multiple positions on each pellet using an XY automatic stage.

Emission lines were identified using the NIST database, and LIBS data were processed using RStudio software. Data processing involved outlier removal (based on cosine similarity), averaging of spectra, baseline correction around the peak, and peak fitting to determine peak area. CF-LIBS and OPC method calculations were performed using Excel spreadsheets with the assistance of OriginLab.

VI. RESULTS AND DISCUSSION

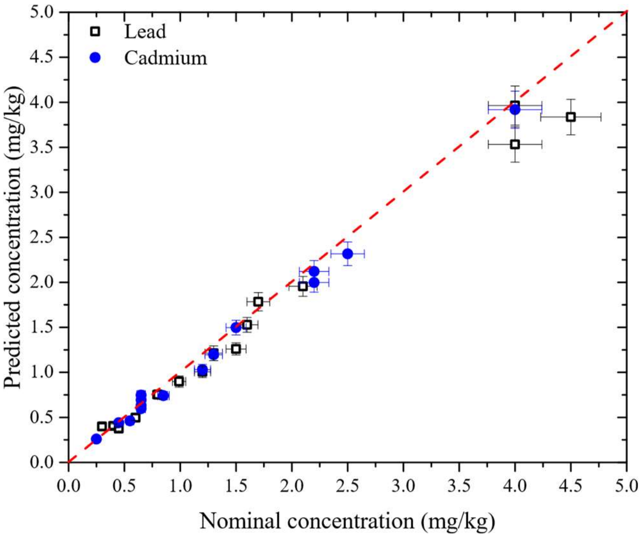
The analysis of tomato samples using the LIBS technique produced significant results that highlight its effectiveness and applicability for quantifying heavy metals, specifically cadmium (Cd) and lead (Pb). The findings demonstrate that the One-Point Calibration Laser-Induced Breakdown Spectroscopy (OPC-LIBS) technique is a viable and efficient alternative to traditional analytical methods such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

By employing both the calibration-free (CF-LIBS) model and the OPC-LIBS method, the system was able to quantify Cd and Pb with accuracies of 93% and 89%, respectively (Fig. 1). These results are particularly noteworthy given that the limits of quantification (LOQ) were 0.03 mg/kg for Cd and 0.08 mg/kg for Pb (Table I). These LOQ values are well below the maximum permissible levels established by the Brazilian National Health Surveillance Agency (ANVISA) and the European Union, which set the limits at 0.05 mg/kg for Cd and 0.1 mg/kg for Pb. Moreover, the root mean square error (RMSE) of 7% for Cd and 11% for Pb is also acceptable within the regulatory tolerances defined by these authorities.

The ability of LIBS to meet these regulatory thresholds with high accuracy confirms its suitability for detecting low concentrations of contaminants—an essential requirement for ensuring food safety.

The LIBS technique offers several advantages over traditional methods. Its primary benefit is the simplicity and speed of analysis, which requires minimal sample preparation and provides results in a reduced timeframe. Additionally, LIBS is a low-cost and environmentally friendly technique, as it generates no harmful chemical waste. These characteristics are vital for large-scale implementation, particularly in continuous monitoring and quality control contexts.

Fig. 1: Validation of the OPC-LIBS model: predicted versus nominal concentrations for Pb and Cd in tomate samples.



When compared with other commonly used techniques for heavy metal quantification, such as AAS and ICP-MS, LIBS presents clear advantages in terms of speed and operational cost. Although AAS is highly sensitive, it requires extensive sample preparation and longer analysis times. ICP-MS, while extremely sensitive and precise, involves high operational costs, complex instrumentation, and significant maintenance requirements.

TABLE I. STATISTICAL METRICS OF PREDICTED RESULTS

Element	Accuracy (%)	RMSRE (%)	r^2	LOD (mg/kg)	LOQ (mg/kg)
Pb	89	11	0.97	0.03	0.08
Cd	93	7	0.98	0.01	0.03

Moreover, both AAS and ICP-MS generate chemical waste, posing additional handling and disposal challenges. In contrast, LIBS is a clean technology, requiring no chemical reagents and producing no hazardous by-products. In terms of time resolution, LIBS provides almost real-time results, whereas AAS and ICP-MS often require several hours to days, depending on sample preparation and analysis queues.

It is important to note that the slight increase in deviation observed in Fig. 1 at higher contaminant concentrations is primarily a graphical scaling artifact and does not indicate a reduction in method accuracy. In fact, the accuracy of the LIBS technique remained consistent across the entire tested concentration range.

Overall, these results validate the effectiveness of the LIBS technique in quantifying heavy metals in tomato samples. Furthermore, the study highlights LIBS's potential for broader applications in detecting other metals of public health concern. Its adaptability for various elements and sample types makes LIBS a robust and versatile tool for food quality assurance.The technique's scalability also opens new opportunities for its integration into large-scale agricultural product monitoring systems, improving both food safety and consumer protection.

In summary, the findings of this study underscore the potential of LIBS as an innovative, fast, and efficient method for heavy metal analysis in food products. Its practicality and environmental benefits make it a promising solution for addressing current challenges in food contamination control and public health safety.

VII. CONCLUSION

The results of this study demonstrate that the laser-induced breakdown spectroscopy (LIBS) technique, combined with a one-point calibration (OPC) approach and dual-laser excitation, is a reliable and efficient method for quantifying heavy metals in food matrices. Specifically, the methodology enabled accurate determination of cadmium and lead in tomato samples, with limits of quantification well below regulatory thresholds established by ANVISA and international food safety standards.

The OPC-LIBS system showed strong performance in terms of analytical precision, operational speed, and environmental sustainability, requiring minimal sample preparation and generating no hazardous waste. These attributes underscore its suitability for large-scale applications, including routine screening of contaminants in agricultural products.

These findings support the adoption of OPC-LIBS as a rapid, scalable, and environmentally responsible solution for detecting heavy metals in food products. Its potential for on-site deployment and integration into continuous monitoring systems represents a major advancement in food safety and public health protection.

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