

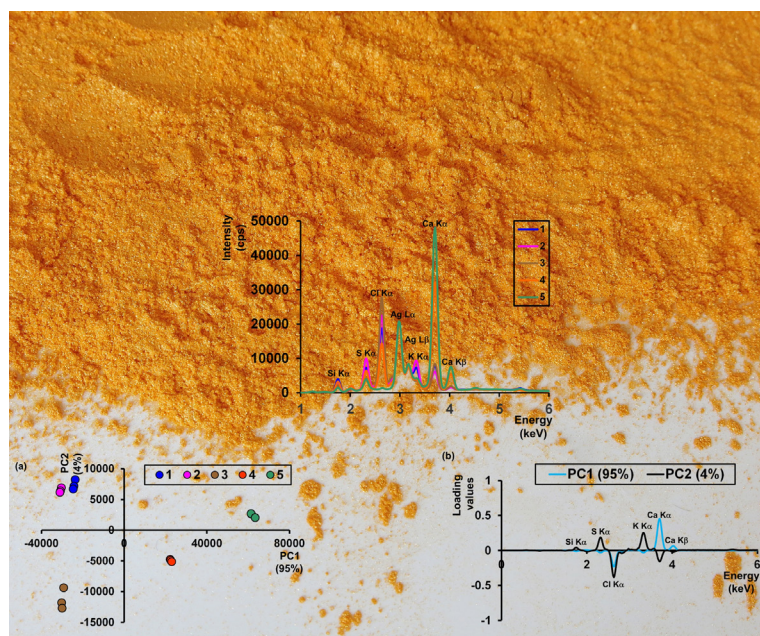
ARTICLE

# Incrustations Formed in Bioelectricity Turbogenerators: An Advanced Evaluation Using Energy Dispersive X-Ray Fluorescence (ED-XRF) and Exploratory Analysis

Érik Geraldo da Silva Souza<sup>1</sup> , Fabiola Manhas Verbi Pereira<sup>1,2\*</sup>  

<sup>1</sup>Group of Alternative Analytical Approaches (GAAA), Bioenergy Research Institute (IPBEN), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, 14800-060, SP, Brazil

<sup>2</sup>National Institute of Alternative Technologies for Detection Toxicological Assessment and Removal of Micropollutants and Radioactive Substances (INCT-DATREM), Araraquara 14800-060, SP, Brazil



This study aims to develop analytical methods that utilize advanced techniques, including x-ray fluorescence (XRF) in conjunction with data science, to monitor samples of incrustations formed in bioelectricity turbogenerators of power plants within the sugar-energy sector. By employing these cutting-edge technologies, valuable information can be generated to enhance bioenergy processes. The proposal to implement direct analysis for this specific type of analytical matrix is innovative as it enables the determination of the chemical composition of incrustations. By conducting analyses with higher frequency, this approach will facilitate informed decision-making regarding the chemical treatments of water used for steam generation, thereby safeguarding the equipment and optimizing the process of electrical energy cogeneration.

**Keywords:** chemometrics, data science, bioelectricity, cogeneration, sugarcane refinery, sustainability

**Cite:** Souza, E. G. S.; Pereira, F. M. V. Incrustations Formed in Bioelectricity Turbogenerators: An Advanced Evaluation Using Energy Dispersive X-Ray Fluorescence (ED-XRF) and Exploratory Analysis. *Braz. J. Anal. Chem.* (Forthcoming). <http://dx.doi.org/10.30744/brjac.2179-3425.AR-41-2024>

Submitted April 1<sup>st</sup>, 2024, Resubmitted June 3, 2024, Accepted June 15, 2024, Available online June 2024.

This article was submitted to the BrJAC special issue celebrating the achievement of a Journal Impact Factor<sub>2022</sub> of 0.7.

## INTRODUCTION

The growing demand for renewable energy sources has prompted industrial organizations to enhance their processes, aiming to reuse by-products and improve energy efficiency.<sup>1</sup> Brazil showed 17206 MW for bioenergy capacity and 16702 MW for solid biofuels and renewable waste in 2022.<sup>2</sup>

In Brazil, the sugar-energy sector plays a prominent role in bioenergy generation through the ethanol, sugar, and bioenergy (ESB) industries. These industries produce ethanol from plant sources and utilize it as biofuel due to reduced carbon dioxide emissions. Furthermore, bioenergy is generated by burning sugarcane straw and bagasse, which is considered biomass, to produce electricity. In addition, biogas and second-generation ethanol (E2G) plants, which recycle residues and by-products to generate bioenergy, have emerged.<sup>3-5</sup>

Sugarcane biomass serves as the primary raw material in these plants due to its high potential for bioelectricity generation and renewable nature. Utilizing by-products from the sugarcane processing industry is crucial for cogenerating electric energy.<sup>2,4</sup> The ESB industrial plants have invested in enhancing their efficiency, reducing electricity consumption in production processes, and increasing electricity exports.<sup>3</sup>

Bioelectricity generation begins in steam boilers, where sugarcane bagasse and straw are burned in ESB plants, producing high-pressure steam. This steam drives turbines that convert heat into mechanical energy, generating electricity. It is essential to produce high-quality steam to maintain turbine integrity, maximize usage, and ensure efficiency.<sup>6</sup>

One challenge that can negatively impact the machinery of these industrial plants is the formation of incrustations in pipes and equipment. Incrustations can reduce device efficiency, cause failures, lead to process interruptions, and increase the likelihood of corrosion and premature wear.<sup>5,7,8</sup> Consequently, bioelectricity-producing companies in the ESB sector may face high costs associated with stoppages, equipment damage, failures, and maintenance. Identifying the points of fouling, their chemical composition, and their origins is crucial.<sup>7,8</sup>

Fouling occurs due to the deposition of corrosive products, non-volatile bases, various salts, organic impurities, and other compounds. The accumulation of these materials on surfaces is particularly problematic in steam generator boilers that operate with water steam, as it impairs heat exchange and limits the equipment's steam production capacity.<sup>8,9</sup>

The water used in the process is considered one of the primary causes of incrustation in steam equipment. Therefore, water treatment is vital to prevent this problem and maintain the integrity of the devices. Tavares *et al.*<sup>9</sup> identified incrustations formed by aluminum and sodium silicates on the inner walls of boiler tubes, emphasizing the importance of proper water treatment to avoid incrustation formation.

Given that the sugar-energy sector is one of Brazil's major bioelectricity producers, it is crucial to identify and analyze incrustations in steam devices used in this industry, specifically in turbogenerators responsible for electricity production. Such analysis can help identify the root causes of incrustation and develop methods to prevent its formation, thereby optimizing the machine's productivity and preventing damage, failures, and unplanned shutdowns.<sup>10-14</sup>

To the best of our knowledge, there is a lack of studies to monitor the chemical composition of sample materials in a water steam-driven turbogenerator. Then, x-ray fluorescence and multivariate exploratory analysis<sup>15</sup> were applied to identify and understand the causes of incrustation phenomena.

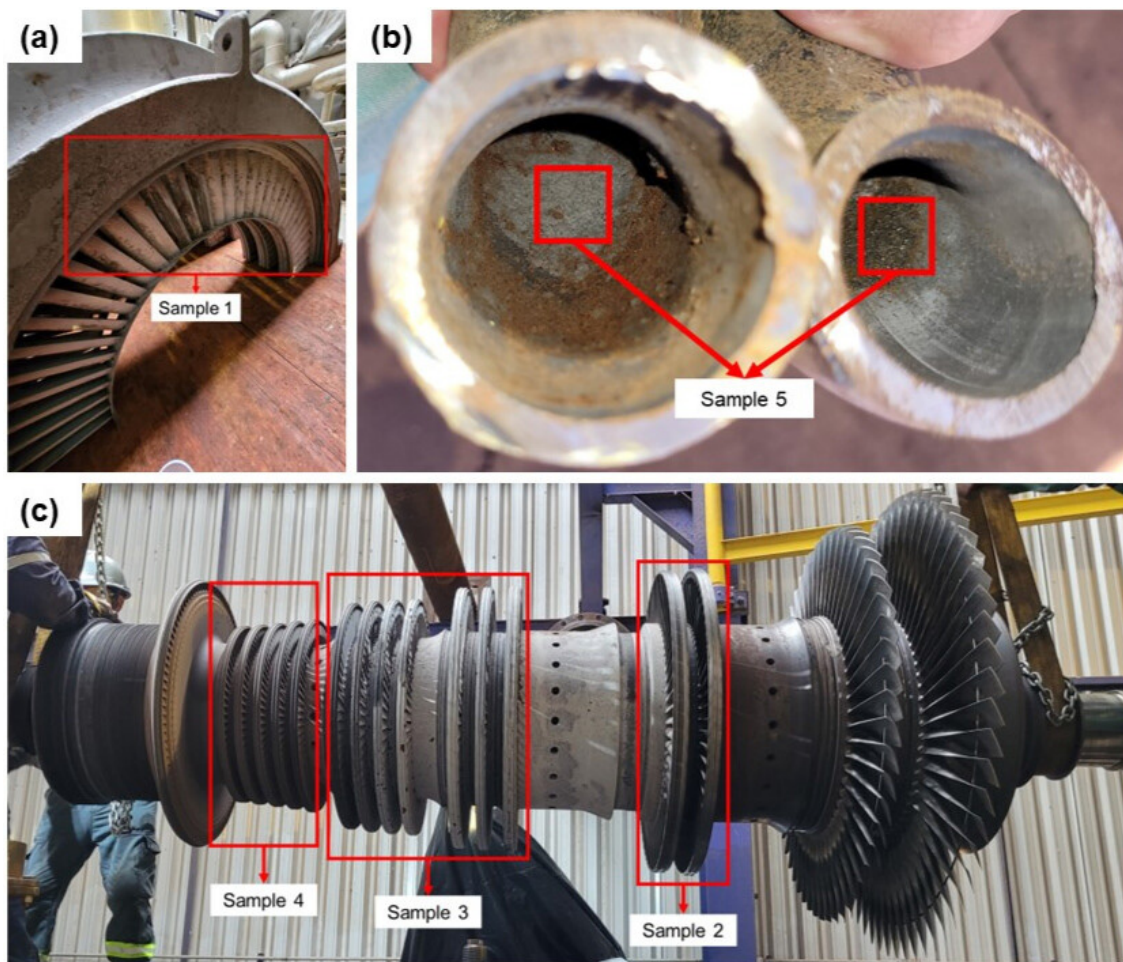
## MATERIALS AND METHODS

### **Samples**

The incrustation samples were collected in a sugarcane biorefinery located in Pitangueiras, São Paulo state, Brazil (21°02'58.3"S 48°15'47.3"W) after a shutdown for cleaning. As a result, a sampling in five positions was collected from different points of the turbine, including the internal (Figure 1a) part of the reed holder and the high-pressure reeds stages of the rotor (Figure 1c). The masses of the formed material vary according to the stage of the process and the collection position, so the material was divided into three replicates for the sampling. Another sample was taken from a different piece of equipment, the boiler



that generates steam for the turbine, this being a sample of the curves from the piping of the second stage of the boiler superheater that supplies steam to the turbine, shown in Figure 1b.



**Figure 1.** Turbine rotor samples of an internal part of the reed holder (a), high-pressure reeds stages of the rotor (b), and boiler superheater second stage curves (c).

### ***Energy dispersive x-ray fluorescence data collection***

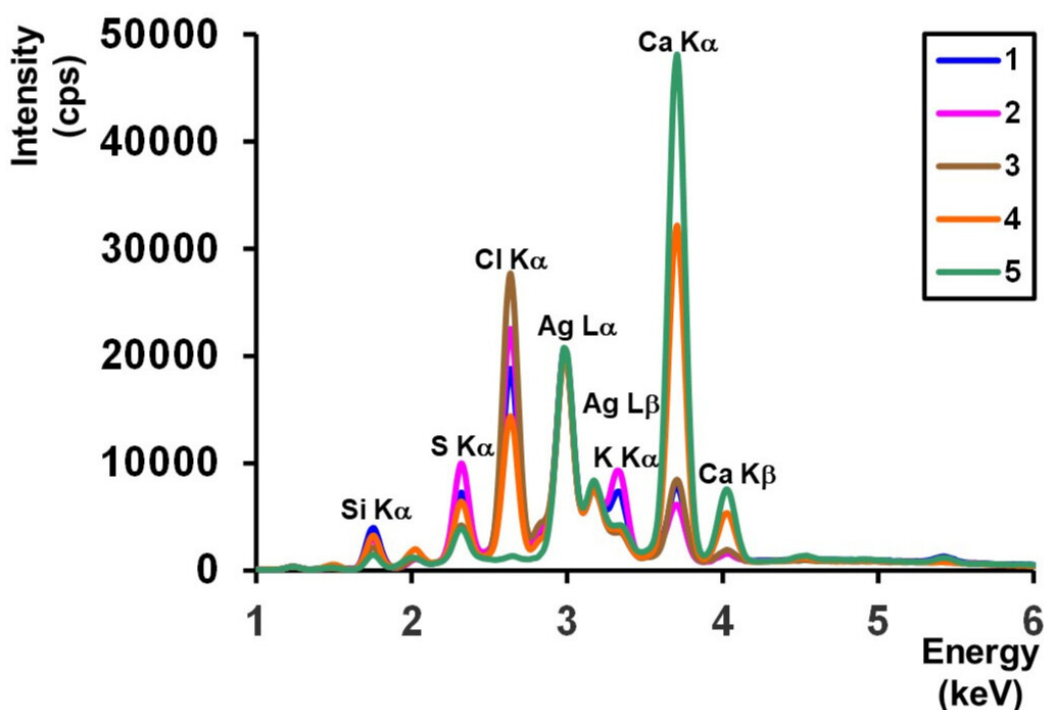
The XRF spectra were collected using a benchtop x-ray fluorescence (XRF) spectrometer, the Rigaku NEX QC<sup>+</sup> (Austin, TX, USA), equipped with an Ag-target x-ray tube and a Be detector. This spectrometer can operate at up to 50 kV, with a resolution of 0.024 keV, from 0 to 49.937, totaling 2048 energy channels. To prepare for the tests, samples ranging from 1 to 4 g were weighed and placed in polypropylene cuvettes, sealed with 6  $\mu\text{m}$  thick Mylar<sup>®</sup> film (Premier Lab Supply, Port St. Lucie, Florida, USA). The analysis was conducted under three sets of instrumental conditions: 1) 50 kV and 10  $\mu\text{A}$ , 2) 30 kV and 10  $\mu\text{A}$ , and 3) 6.5 kV and 50  $\mu\text{A}$ , with the spectra acquired in atmospheres of both air and helium. Each set of conditions had a measurement duration of 30 seconds. Data analysis was carried out using MATLAB<sup>®</sup> 2022b (MathWorks, Natick, MA, USA) laboratory codes and Pirouette 5.0 software (Infometrix, Bothell, WA, USA).

## **RESULTS AND DISCUSSION**

The samples were taken from a steam turbine responsible for mechanically driving an electrical power generator that produces an average of 35 MWh. This turbine-generator set is responsible for electricity production for export, resulting in financial gains for the company and, therefore, is an essential piece of the equipment.

Collecting samples was only possible due to operational issues with the turbine, which required the equipment to be dismantled for necessary repairs. According to the manufacturer, a turbine like this should be able to operate for ten years without the need for maintenance. However, in this case, the turbine operated for only four years, each consisting of seven consecutive months of operation followed by five months of hibernation.

The data obtained through ED-XRF were evaluated considering the three instrumental conditions and the atmospheres of air and He. In the case of instrumental conditions, six matrices of 15 x 2048 (rows and columns) were generated. Three authentic replicates represented each sample. Figure 2 shows the spectra of the material samples from 1 to 5 for the best condition, denoted as 3 in the atmosphere of air. The x-ray fluorescence  $K\alpha$  lines detected for them were in keV, as follows: silicon - Si (1.740), sulfur - S (2.308), chlorine - Cl (2.622), potassium - K (3.313) and calcium - Ca (3.691);  $K\beta$  for Ca (4.013) and  $L\beta$  (3.151) for silver - Ag from the x-ray source.



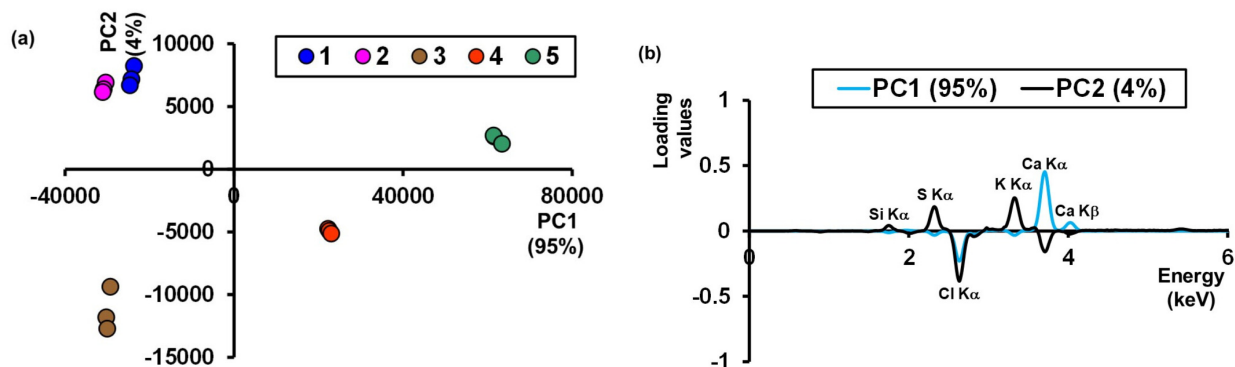
**Figure 2.** Spectra profiles were acquired using an energy-dispersive x-ray spectrometer (ED-XRF) for the incrustation of five types of samples.

The ED-XRF spectra were mean-centered for principal component analysis (PCA) calculations. PCA aided in confirming patterns within scale samples derived from encrustation, as shown in Figure 2, where instrumental condition 3 was the best for data information. The instrumental condition criteria were the most informative chemical element ED-XRF spectra and the explained variance of PCA calculations. Therefore, the cluster separations with a 95% explained variance were obtained for PC1 and 4% for PC2.

Analyzing the loadings as shown in Figure 2b, it is understood that the positive part of PC1 and the negative part of PC2 for the samples denoted as 4 and 5 are composed of Ca revealed by the  $K\alpha$  and  $K\beta$  fluorescence lines in 3.691 and 4.013 keV, respectively.

The negative loading values of PC1 and positive for PC2 are linked to the cluster of samples 1 and 2; Si, S, and K are predominant over these samples.

For the negative part of PC1 and PC2, sample 3 differs from the others, and the element Cl highlighted with the K $\alpha$  fluorescence line is 2.622 keV.

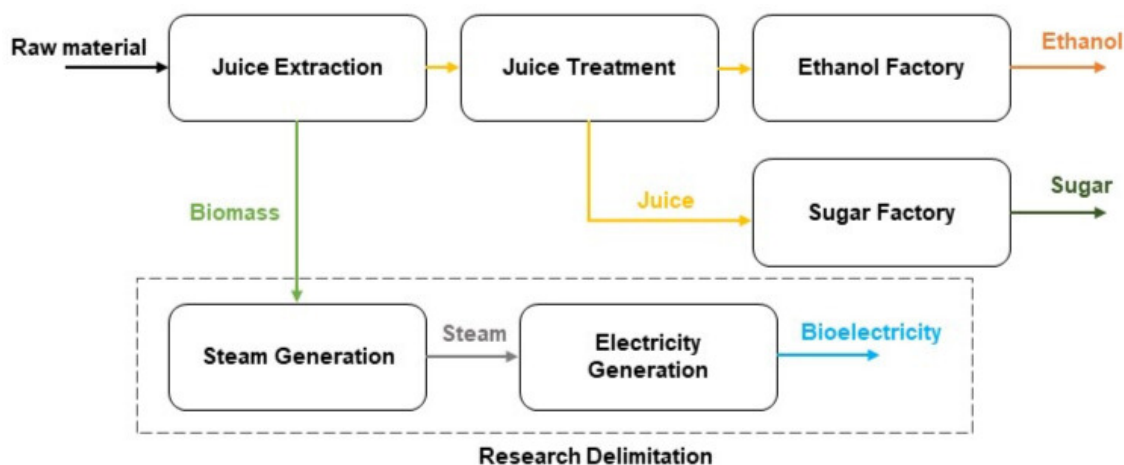


**Figure 3.** Score (a) and loading (b) plots for the five samples and replicates were calculated using principal component analysis (PCA).

The most significant loading values for PC1 were predominant for Ca with a more explained variance of 95%, responsible for the differentiation of samples 4 and 5 (Figure 1). The other elements in PC2 have the decreasing order of loading values, Cl, K, S, Ca, and Si comprising 4% of the explained variance.

The PCA results indicate that the formation of these encrustations is primarily linked to the following chemical elements: Si, S, Cl, K, and Ca. Hence, this study suggests that the analyzed samples have chemical composition elements indicating that they were formed from the steam used in the turbine. This is because they are related to the water treatment process for steam generation in boilers.

This study aims to solve problems by collecting data to comprehensively understand the case, thereby enabling a broader perspective for interpreting and clarifying the issue.<sup>9</sup> The investigated materials were acquired in an ESB industry during the disassembly of a turbogenerator for off-season inspection. It is also important to emphasize that the purpose of this study is only the cogeneration of bioelectricity and steam generation, excluding the other processes of this type of industry, thus being limited to these two stages, as represented by Figure 4.



**Figure 4.** Contextualization of research delimitation.

The exploratory analysis of ED-XRF data enhanced the evaluation of the elemental composition of the encrustations, potentially providing crucial information to the bioenergy sector. This is significant because monitoring and assessing the chemical composition of these types of samples can aid ESB plants.

## CONCLUSIONS

In conjunction with ED-XRF, the exploratory data analysis allowed for identifying the elements present in the encrustations formed on the turbine rotor during the steam and bioelectricity generation process. The detected chemical elements were Si, S, Cl, K, and Ca. The findings will benefit companies involved in bioenergy production and contribute to any research or industry seeking to analyze incrustations in processes related to bioelectricity generation from biomass. It is very relevant to emphasize that these elements cannot be present in those turbines and must be a warning for the companies.

## Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This study was supported by the São Paulo Research Foundation (FAPESP) under grants No. 2021/10882-7, 2019/01102-8, and 2014/50945-4; National Council for Scientific and Technological Development (CNPq) grants No. 302085/2022-0 and 465571/2014-0; and the Coordination for the Improvement of Higher Education Personnel (CAPES) grant No. 88887136426/2017/00 and Finance Code 001.

## REFERENCES

- (1) Lawrence, A.; Thollander, P.; Andrei, M.; Karlsson, M. Specific energy consumption/use (SEC) in energy management for improving energy efficiency in industry: meaning, usage and differences. *Energies* **2019**, *12* (2), 247. <https://doi.org/10.3390/en12020247>
- (2) International Renewable Energy Agency – IRENA. *Renewable Energy Statistics 2023*. Available online at: <http://www.irena.org> (accessed on 29 January 2024).
- (3) Romera, J. P. R.; Barsanelli, P. L.; Pereira, F. M. V. Expeditious prediction of fiber content in sugar cane: an analytical possibility with libs and chemometrics. *Fuel* **2016**, *166*, 473-476. <https://doi.org/10.1016/j.fuel.2015.11.029>
- (4) Dutra Filho, J. A.; Gomes-Silva, F.; Souto, L. S.; Souza, A. S.; Luna, R. G.; Moreira, G. R.; Cunha Filho, M.; Silva, M. C. C.; Porto, A. C. F.; Brito, C. C. R.; et al. Energy cane x sugarcane microregion interaction in the state of Pernambuco: Sugarcane for production of bioenergy and renewable fuels. *Agronomy* **2021**, *11* (6), 1046. <https://doi.org/10.3390/agronomy11061046>
- (5) Mello, M. L.; Sperança, M. A.; Pereira, F. M. V. Mineral scale formed during the evaporation in biorefineries — characterization using x-ray fluorescence and exploratory analysis. *Food Anal. Methods* **2022**, *15* (9), 2436-2439. <https://doi.org/10.1007/s12161-022-02308-0>
- (6) Demadis, K. D.; Mavredaki, E.; Stathouloupoulou, A.; Neofotistou, E.; Mantzaridis, C. Industrial water systems: problems, challenges and solutions for the process industries. *Desalination* **2007**, *213* (1-3), 38-46. <https://doi.org/10.1016/j.desal.2006.01.042>
- (7) Mello, M. L.; Barros, N. Z.; Sperança, M. A.; Pereira, F. M. V. Impurities in Raw Sugarcane Before and After Biorefinery Processing. *Food Anal. Methods* **2022**, *15*, 96-103. <https://doi.org/10.1007/s12161-021-02105-1>
- (8) Tyapkov, V. F.; Smykov, V. B.; Legkikh, K. G. Experience Gained with Chemically Cleaning the Evaporators of the Beloyarsk NPP BN-600 Reactor Plant Sodium–Water Steam Generators from Deposits. *Therm. Eng.* **2022**, *69* (4), 279-287. <http://dx.doi.org/10.1134/s0040601522040061>
- (9) Tavares, S. S. M.; Scandian, C.; Macêdo, M. C. S.; Pardal, J. M.; Silva, F. J. Failure of tube used in high pressure steam generator due to incrustation deposits. *Eng. Fail. Anal.* **2013**, *35*, 25-32. <http://dx.doi.org/10.1016/j.engfailanal.2012.10.026>
- (10) Andrade, D. F.; Guedes, W. N.; Pereira, F. M. V. Detection of chemical elements related to impurities leached from raw sugarcane: use of laser-induced breakdown spectroscopy (libs) and chemometrics. *Microchem. J.* **2018**, *137*, 443-448. <http://dx.doi.org/10.1016/j.microc.2017.12.005>



- (11) Guedes, W. N.; Pereira, F. M. V. Classifying impurity ranges in raw sugarcane using laser-induced breakdown spectroscopy (LIBS) and sum fusion across a tuning parameter window. *Microchem. J.* **2018**, *143*, 331-336. <http://dx.doi.org/10.1016/j.microc.2018.08.030>
- (12) Guedes, W. N.; Pereira, F. M. V. Raw sugarcane classification in the presence of small solid impurity amounts using a simple and effective digital imaging system. *Comput. Electron. Agric.* **2019**, *156*, 307-311. <http://dx.doi.org/10.1016/j.compag.2018.11.039>
- (13) Guedes, W. N.; Santos, L. J.; Filletti, E. R.; Pereira, F. M. V. Sugarcane stalk content prediction in the presence of a solid impurity using an artificial intelligence method focused on sugar manufacturing. *Food Anal. Methods* **2020**, *13*, 140-144. <https://doi.org/10.1007/s12161-019-01551-2>
- (14) Sperança, M. A.; Nascimento, P. A. M.; Olivieri, A. C.; Pereira, F. M. V. XRF-based analytical methods for supporting sustainability in sugarcane biorefineries. *Biofuels, Bioprod. Bioref.* **2022**, *16*, 758-765. <https://doi.org/10.1002/bbb.2336>
- (15) Araújo, A. S.; Andrade, D. F.; Babos, D. V.; Castro, J. P.; Garcia, J. A.; Sperança, M. A.; Gamela, R. R.; Machado, R. C.; Costa, V. C.; Guedes, W. N.; Pereira-Filho, E. R.; Pereira, F. M. V. Key information related to quality by design (QbD) applications in analytical methods development. *Braz. J. Anal. Chem.* **2021**, *8* (30), 14-28. <https://doi.org/10.30744/brjac.2179-3425.RV-27-2020>