UNIVERSIDADE ESTADUAL PAULISTA
“JÚLIO DE MESQUITA FILHO”
INSTITUTO DE PESQUISA EM
BIOENERGIA

PROGRAMA INTEGRADO (UNESP, USP E UNICAMP) DE PÓS-GRADUAÇÃO EM BIOENERGIA

ADVANCED ANALYTICAL METHODS FOR PREVENTING SCALING AND ENSURING WATER QUALITY IN BIOENERGY GENERATION PROCESSES

ÉRIK GERALDO DA SILVA SOUZA

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Tese apresentada ao Instituto de Pesquisa em Bioenergia de Rio Claro, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Doutor em Ciências.

Orientadora: Dra. Fabiola Manhas Verbi Pereira

Rio Claro – SP
2025

S729a

Souza, Érik Geraldo da Silva
Advanced analytical methods for preventing scaling and ensuring water quality in bioenergy generation processes / Érik Geraldo da Silva Souza. -- Rio Claro, 2025
64 p. : il., fotos

Tese (doutorado) - Universidade Estadual Paulista (UNESP), Instituto de Pesquisa em Bioenergia, Rio Claro
Orientadora: Fabiola Manhas Verbi Pereira

1. Bioelectricity. 2. Scaling. 3. Chemometrics. 4. Cogeneration. 5. Sustainability. I. Título.

Sistema de geração automática de fichas catalográficas da Unesp. Dados fornecidos pelo autor(a).

UNIVERSIDADE ESTADUAL PAULISTA

Unidade Complementar - Rio Claro

IPBEN
Instituto de Pesquisa em Bioenergia

CERTIFICADO DE APROVAÇÃO

TÍTULO DA TESE: Advanced Analytical Methods for Preventing Scaling and Ensuring Water Quality in Bioenergy Generation Processes

AUTOR: ÉRIK GERALDO DA SILVA SOUZA
ORIENTADORA: FABIOLA MANHAS VERBI PEREIRA

Aprovado como parte das exigências para obtenção do Título de Doutor em Ciências, área: Bioenergia pela Comissão Examinadora:

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Prof.ª Dr.ª FABIOLA MANHAS VERBI PEREIRA (Participaçao Virtual)
Departamento de Quimica Analitica Fisico-Quimica e Inorganica / Instituto de Quimica UNESP Araraquara

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Prof. Dr. JONAS CONTIERO (Participaçao Virtual)
Departamento de Bioquimica e Microbiologia / Unesp - IB Rio Claro

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Prof. Dr. DIEGO VICTOR DE BABOS (Participaçao Virtual)
Departamento de Química / Universidade Federal de Uberlândia

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Dr. MARCO AURELIO SPERANÇA (Participaçao Virtual)
Departamento de Pesquisa / SG Soluções Científicas

Rio Claro, 24 de fevereiro de 2025

I dedicate this work to my parents, for their unconditional love.
I also extend my gratitude to everyone who believed in me and cheered for the realization of this dream.
To myself, for the perseverance and determination to overcome every challenge along the way.
Miss you already.

ACKNOWLEDGEMENTS

To the São Paulo State University "Júlio de Mesquita Filho" (Unesp) and the Institute of Chemistry, which served as my foundation throughout this journey, providing the resources and environment necessary for the development of this work.

To the Institute for Research in Bioenergy (IPBEN), for its fundamental contribution to my academic growth and for the inspiration to move forward, overcoming the challenges of research.

To the partner universities of the Bioenergy Graduate Program, the University of São Paulo (USP) and the University of Campinas (UNICAMP), for strengthening this journey with shared knowledge and valuable opportunities.

To the professors and students of the Ph.D. Program in Bioenergy, whose commitment, collaboration, and exchange of knowledge were fundamental in guiding and supporting me at every step of this journey. In particular, to Professor Dr. Fabiola Manhas Verbi Pereira, for her attentive guidance, her belief in my potential, and for welcoming me into the Alternative Analytical Approaches Group (GAAA), where I learned far more than I ever thought possible.

To the Association of Universities of the Montevideo Group (AUGM) and Unesp, for offering me the incredible opportunity to participate in the Graduate Exchange Program. The experience at the Faculty of Exact and Natural Sciences and Surveying (FaCENA) of the National University of the Northeast (UNNE) in Argentina contributed significantly to my learning throughout this course. I am deeply grateful to Professors Dr. Manuel Cáceres and Juán Daniel Ruíz Díaz for their generosity and warm welcome, and to the Argentine friends I made in Corrientes, who brought lightness and joy to this stage of my journey—I will never forget it.

Finally, but no less importantly, I am deeply grateful to everyone who, in one way or another, was part of this journey—whether through words of encouragement, support during difficult moments, or simply believing in me. Every contribution, no matter how small, was essential in making this dream a reality.

This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil. Process Numbers: 2021/10882-7, 2019/01102-8, and 2014/50945-4. The opinions, hypotheses, conclusions, or recommendations expressed in this material are the responsibility of the author(s) and do not necessarily reflect the views of FAPESP.

This study was also supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), under grant numbers 302085/2022-0 and 465571/2014-0.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and grant No. 88887136426/2017/00.

Our greatest glory is not in never falling, but in rising every time we fall.

(Oliver Goldsmith)

ABSTRACT

This study addresses the challenges associated with bioelectricity generation in the sugar-energy industry, focusing on scaling formation and water quality management in the steam generation process. Utilizing water-tube boilers fueled by sugarcane bagasse and straw, these biorefineries produce high-pressure steam to drive turbines and generate electricity for both internal consumption and the national power grid. The thesis is structured into two chapters. The first chapter investigates scaling formation in turbogenerators, employing techniques such as energy-dispersive X-ray fluorescence (ED-XRF) and principal component analysis (PCA). Samples collected from critical points in the turbines and boilers revealed the predominant presence of elements such as silicon (Si), sulfur (S), chlorine (Cl), potassium (K), and calcium (Ca), which contribute to scaling formation. The results emphasize the direct relationship between water quality and scaling, highlighting the importance of rigorous water treatment controls to prevent impacts on equipment efficiency. The second chapter evaluates the quality of boiler feedwater using exploratory methods such as PCA and minimum spanning tree (MST)-based clustering. The analysis of 120 water and steam samples identified patterns and levels of purity, with critical variables including conductivity, SiO_2 content, and pH. These approaches eliminated subjective biases and provided precise information to optimize water management practices in sugarcane biorefineries. The integrated results demonstrate the complementarity of the applied methods, offering a robust foundation for preventive monitoring and cogeneration process optimization. This study contributes to preserving critical equipment, reducing operational costs, and promoting sustainability in industries that use biomass as an energy source.

Keywords: bioelectricity, scaling, chemometrics, cogeneration, sustainability.

RESUMO

Este trabalho aborda os desafios relacionados à geração de bioeletricidade em indústrias sucroenergéticas, com foco na formação de incrustações e na gestão da qualidade da água no processo de geração de vapor. Utilizando caldeiras aquatubulares alimentadas por bagaço e palha de cana-de-açúcar, essas biorrefinarias produzem vapor de alta pressão para mover turbinas e gerar energia elétrica, tanto para consumo interno quanto para o sistema elétrico nacional. A tese foi estruturada em dois capítulos. No primeiro, investigou-se a formação de incrustações em turbogeradores, empregando técnicas como fluorescência de raios X (ED-XRF) e análise de componentes principais (PCA). Amostras coletadas em pontos críticos das turbinas e caldeiras revelaram a presença predominante de elementos como silício (Si), enxofre (S), cloro (Cl), potássio (K) e cálcio (Ca), que contribuem para a formação de incrustações. Os resultados destacam a relação direta entre a qualidade da água e as incrustações, reforçando a importância de controles rigorosos no tratamento de água para evitar impactos na eficiência operacional dos equipamentos. No segundo capítulo, avaliou-se a qualidade da água de alimentação das caldeiras utilizando métodos exploratórios, como PCA e agrupamento baseado em árvore mínima de expansão (MST). A análise de 120 amostras de água e vapor identificou padrões e níveis de pureza, com variáveis críticas sendo condutividade, teor de SiO_2 e pH. Essas abordagens eliminaram vieses subjetivos e ofereceram informações precisas para otimizar práticas de gestão da água em biorrefinarias de cana-de-açúcar. Os resultados integrados evidenciam a complementaridade dos métodos aplicados, oferecendo uma base sólida para monitoramento preventivo e otimização do processo de cogeração. Este estudo contribui para a preservação de equipamentos críticos, redução de custos operacionais e promoção da sustentabilidade em indústrias que utilizam biomassa como fonte de energia.

Palavras-chave: bioeletricidade, incrustações, quimiometria, cogeração, sustentabilidade.

LIST OF ABBREVIATIONS

BrJAC	Brazilian Journal of Analytical Chemistry
CC BY	Creative Commons Attribution
ČSN	*Československá Norma*
E2G	Second-Generation Ethanol
ED-XRF	Energy-Dispersive X-Ray Fluorescence
EPR	Electron Paramagnetic Resonance Spectroscopy
ESB	Ethanol, Sugar, and Bioenergy
JBCS	Journal of the Brazilian Chemical Society
k-NN	K-Nearest Neighbors
MEC	Multi-Energy Calibration
MMC	Matrix-Matching Calibration
MST	Minimum Spanning Tree
OP GSA	One-Point Gravimetric Standard Addition
PC	Principal Component
PCA	Principal Component Analysis
UNICA	*União da Indústria de Cana-de-Açúcar e Bioenergia*
XRF	X-Ray Fluorescence

LIST OF SYMBOLS

°C	Degree Celsius
μA	Microampere
μm	Micrometer
$\mu S\ cm^{-1}$	Microsiemens per Centimeter
Al^{3+}	Aluminum Ion
Ag	Silver
Ba^{2+}	Barium Ion
bar	Unit of pressure
Be	Beryllium
Ca	Calcium
Ca^{2+}	Calcium Ion
$CaCO_3$	Calcium Carbonate
$CaSiO_3$	Calcium Silicate
$CaSO_4$	Calcium Sulfate
Cl	Chlorine
CO_2	Carbon Dioxide
Fe^{2+}	Iron (II) Ion
Fe^{3+}	Iron (III) Ion
g	Gram
GWh	Gigawatt-hour
He	Helium
K	Potassium
keV	Kilo-electronvolt
$kgf\ cm^{-2}$	Kilogram-force per Square Centimeter
kV	Kilovolt
$K\alpha$	K Alpha (X-ray Emission Line)
$K\beta$	K Beta (X-ray Emission Line)
$L\alpha$	L Alpha (X-ray Emission Line)
$L\beta$	L Beta (X-ray Emission Line)
m^3	Cubic meter
$mg\ L^{-1}$	Milligram per Liter

$Mg(OH)_2$	Magnesium Hydroxide
Mg^{2+}	Magnesium Ion
$MgCO_3$	Magnesium Carbonate
$MgSiO_3$	Magnesium Silicate
mL	Milliliter
Mn^{2+}	Manganese Ion
MPa	Megapascal
MW	Megawatt
MWh	Megawatt-hour
nm	Nanometer
pH	Potential of Hydrogen
S	Sulfur
Si	Silicon
SiO_2	Silicon Dioxide
Sr^{2+}	Strontium Ion

LIST OF FIGURES

TABLE OF CONTENTS

1. GENERAL INTRODUCTION

The search for renewable energy sources drives producing organizations to improve their industrial processes, reuse by-products, and increase their energy efficiency (LAWRENCE et al., 2019).

In Brazil, the sugar-energy sector stands out in the production of bioenergy through the Ethanol, Sugar, and Bioenergy (ESB) industries. Ethanol is produced and has various applications but is primarily used as a biofuel due to its plant-based origin and the fact that it emits less carbon dioxide into the atmosphere. Furthermore, bioelectricity can be generated from burning sugarcane straw and bagasse, which is considered biomass. Biogas plants and second-generation ethanol (E2G) also reprocess residues and by-products for bioenergy generation (DUTRA FILHO et al., 2021).

Sugarcane biomass is the primary raw material used in power plants due to its high potential for generating bioelectricity and renewable nature. This highlights the importance of utilizing by-products from the sugarcane processing industry for cogeneration of electricity (MERCANTE, 2020).

Regarding bioelectricity, these ESB industrial plants have increasingly invested to become more efficient, consuming less electricity in production processes and consequently exporting more electric loads. In 2023, the Brazilian sugar-energy sector produced 21 thousand GWh of bioelectricity, representing 75% of all electricity generated from biomass and 28,919 thousand m^3 of ethanol (UNICA, 2024).

The process required for generating bioelectricity begins in steam boilers, where sugarcane bagasse and straw are burned in ESB plants. This generates high-pressure steam that drives turbines to convert heat into mechanical energy, which then powers electricity generators. Therefore, it is essential that the steam generated is of high quality to maintain the integrity, optimization, and efficiency of the turbines driving the generators. According to Lanzendorf et al. (2020), steam turbines are prone to failures due to the formation of deposits, which cause anomalies such as imbalance, excessive vibrations, unexpected shutdowns, and component damage.

One issue that may arise and cause problems for the machinery of these ESB industrial plants is scaling from the steam generation processes in equipment, which reduces device efficiency, causes failures and process stoppages and increases the likelihood of premature corrosion and wear. Steam generators, boilers, and turbogenerators are the main equipment involved in bioelectricity production, and any issues can compromise their performance and operating characteristics. In the case of electricity generation, scaling also forms on the steam turbine, which is responsible for converting thermal energy into mechanical energy and, subsequently, through generators, into electricity. This scaling can damage the turbine and its internal components—rotor, blades, blade holders, shaft, casing, and bearings. The presence of this material compromises the machine’s operation, reducing energy efficiency and generating costs for the company due to stoppages, failures, damaged equipment, and maintenance (GOUVÊA et al., 2012).

Therefore, it is crucial to identify the points of scaling, their chemical composition, and origin and to carry out chemical analyses since using chemical reagents in the steam generation process to prevent the formation of these impurities depends on the chemical composition of the material in question (MELLO et al., 2022).

The scaling process 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 common in boilers, causing a decrease in heat exchange and preventing the equipment from operating at its maximum steam production capacity (TYAPKOV et al., 2022).

In theory, one of the main causes of scaling in steam equipment is the water used in the process. Although boiler materials follow strict construction standards, the primary factor influencing scale formation is water quality, as the presence of silicates leads to pipe blockages. To address this, the use of polymeric additives and some organic acids to dissolve solid material is widespread in the sugar-energy sector (DEMADIS et al., 2007).

Although measures and procedures for treating and purifying this water are in place, scaling continues to occur. Thus, water treatment significantly prevents this issue and maintains the devices in good condition. In their research, Tavares et al. (2013) identified scale deposits formed by aluminum and sodium silicates on the inner walls of boiler tubes, where the authors state that to prevent scaling, proper water treatment must be carried out.

Given that the sugar-energy sector is one of Brazil's largest bioelectricity generators, it becomes important to identify and analyze scaling in steam devices used in this type of industry, particularly in turbogenerators, which are responsible for bioelectricity production. By doing so, it is possible to identify the root cause and develop methods to eliminate the possibility of scaling formation in this system, thus maximizing the productive performance of the machine and avoiding damages, failures, and unwanted stoppages.

In this way, this study encompasses the application of methods for analyzing materials that have scaled in a turbogenerator powered by water steam so they can be examined and identified to provide answers to the causes of this phenomenon. It will also serve any bioenergy-producing company or studies that need to analyze scaling in processes related to bioelectricity production through biomass.

1.1. General Objective

The general objective of this work is to monitor the chemical composition of scale deposits and investigate their relationship with feedwater quality in bioenergy cogeneration processes. This study employs laboratory chemical analysis techniques and chemometric approaches to evaluate scaling formation and water quality interactions.

1.2. Specific Objectives

a) Characterize the steam and bioelectricity generation process.
b) Identify the chemical composition and sources of scale deposits from an electricity cogeneration turbine.
c) Apply chemometric techniques to analyze scale formation and water quality interactions.
d) Interpret and evaluate the analysis results to assess the impact of water quality on scaling.
e) Develop strategies to optimize water treatment and prevent scaling in steam generation systems.

1.3. Scope of This Thesis

This thesis was developed to address critical challenges in bioelectricity generation within sugarcane biorefineries, focusing on the formation of scaling in critical equipment and the sustainable management of water quality in the steam generation process. By combining advanced analytical techniques with exploratory data analysis, the research aims to propose strategies for improving efficiency, reducing operational costs, and promoting sustainability in this industrial sector.

The thesis is structured into two interconnected chapters:

In Chapter I, the focus is on the formation of scaling in turbogenerators, which are essential for bioelectricity production. Advanced techniques, such as energy-dispersive X-ray fluorescence (ED-XRF) and principal component analysis (PCA), were used to identify the chemical composition of scaling materials. Samples collected from turbines and boiler critical points revealed elements such as silicon (Si), sulfur (S), chlorine (Cl), potassium (K), and calcium (Ca) as major contributors to scaling formation. The analysis highlighted the direct relationship between water quality and scaling, emphasizing the necessity of stringent water treatment protocols to prevent efficiency losses and mechanical failures.

In Chapter II, the study shifts to sustainable water management in the steam generation process. Using exploratory data analysis methods, including PCA and minimum spanning tree (MST)-based clustering, 120 samples of water and steam were examined to assess water quality, purity, and operational impacts. Critical variables, such as conductivity, pH, and SiO_2 content, were identified as key indicators of water quality. These methods provided robust insights into optimizing water treatment practices, reducing subjectivity, and enhancing decision-making in industrial operations.

The integrated findings of this thesis establish a strong foundation for the development of preventive monitoring strategies and cogeneration optimization. By addressing the interplay between scaling formation and water quality, this research contributes to the preservation of critical equipment, minimization of operational costs, and advancement of sustainability in industries that utilize biomass as a primary energy source.

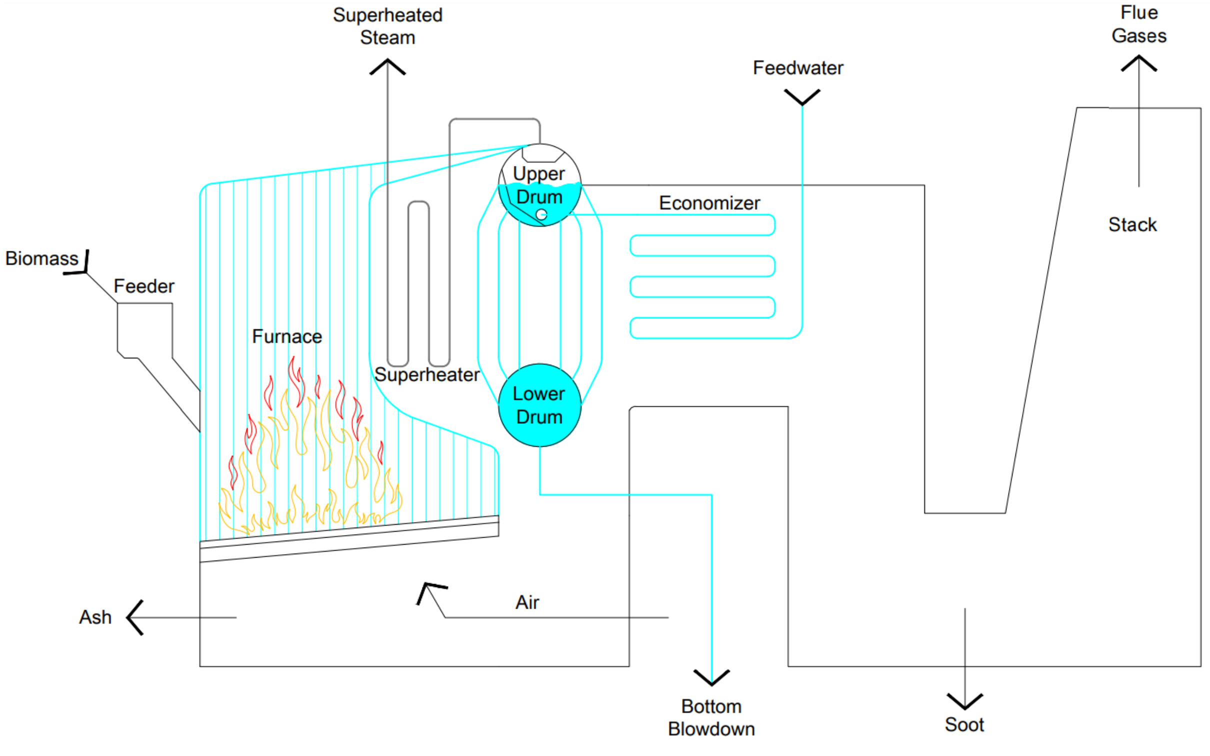
2. THEORETICAL FRAMEWORK

2.1. Steam and Bioelectricity Generation

Industrial processes in various sectors require thermal, mechanical, and electrical energy. To obtain these energies, boilers typically generate steam from water by burning some fuel. The steam generated at high temperature and pressure is used as a heat source in reactors, heat exchangers, evaporators, dryers, and various thermal processes and equipment. It also generates mechanical energy through steam turbines and turbogenerators to produce electrical energy (BIZZO, 2003; SOUZA, 2022).

Boilers are generally classified into two types: fire-tube boilers and water-tube boilers. Fire-tube boilers are used in small installations that require less than 15 tons/hour of steam and pressure below 15 bar. Water-tube boilers are more widely used and are built in small, medium, and large sizes for high pressures and temperatures (PUSTELNIK, 2019). Figure 1 shows a simple diagram of a water-tube boiler.

Figure 1 - Representation of a Biomass-Fired Water-Tube Boiler



Industries in the sugar-energy sector use fire-tube boilers, which burn sugarcane straw and bagasse as fuel. Once considered waste and discarded, bagasse has become the primary energy source for the ESB production process. It was first used to generate enough electricity for industrial production, then optimized to produce an excess that could be exported to the Brazilian power grid. The bioelectricity generated from sugarcane bagasse plays a significant role in Brazil, particularly by providing electricity to the national power system during drought periods when hydropower reserves are low (CAVALCANTI et al., 2020; PAVAN et al., 2021). Moreover, this bioelectricity is considered a sustainable business model, offering excellent environmental, economic, and social performance (FERASSO et al., 2020).

2.2. Scale Formation in Bioenergy Production Devices

Thermal energy production is typically related to steam generated from water at high temperatures and pressures. Boilers are used to generate steam by burning fuel and producing enough energy to turn water into steam. For efficient steam production in industries and biorefineries, it is essential to use ultra-pure water for boiler feed. This reduces the need for chemicals to treat the water and minimizes the number of blowdowns due to the lower concentration of dissolved solids and corrosion marks in the boiler. The fewer impurities present, the fewer problems such as sludge accumulation, scaling, caustic embrittlement, foam formation, and corrosion occur in the boiler. A good example is the reduced wear on turbine blades in thermal power plants when high-purity water is used to generate steam for turbo-generator operation (MELTZER, 1993).

Problems such as corrosion and scaling frequently occur in thermal power plants' turbines and boilers, and to prevent this, boiler feed water treatment is carried out. As a result, water treatment technologies for industries are constantly improved to mitigate equipment failures caused by scaling and corrosion. Compromised water quality signals that serious problems will arise, which can be avoided by data analysis and prompt actions. Thus, it is essential to eliminate impurities in the water before feeding the boilers using water treatment methods. Applying water treatment processes and technologies provides advantages in conservation, availability, efficiency, and environmental preservation. Furthermore, boiler-feed water treatment aims to enhance performance, reliability, and operational safety and reduce maintenance and costs (TSUBAKIZAKI et al., 2013; KISPOTTA et al., 2014; SHOKRI; FARD, 2023).

The topic of boiler feed water treatment has been discussed for a long time. Brownlie (1925) presented treatment techniques to prevent boiler scaling and corrosion. Powell and Wolfe (1925) argued that a scale-free boiler is essential for proper operation since steam generation is a critical step in industrial processes. Brownlie (1929) discussed the scientific advancement of steam generation and the revolution in water treatment principles, emphasizing the need to eliminate scaling to prevent heat transfer reduction, overheating, and damage to metal parts in boilers. Christman et al. (1931) stated that the primary goal of boiler-feed water treatment is to remove the chemical elements that cause scaling, usually calcium and magnesium salts. This hardness in the water forms a silicate scale, which severely impacts boiler operations by reducing heat transfer, leading to losses and burning and warping tubes. SiO_2 and hardness must be removed from the water to prevent silicate scaling.

All steam and energy generation system equipment installed in biorefineries must operate efficiently. However, scaling and corrosive destruction of equipment parts hinders proper operation. This occurs when water quality is compromised, causing scaling on tubes and other equipment, impeding heat exchange, and promoting corrosion development. Therefore, proper boiler feed water treatment is crucial, involving various factors such as salt and oxygen content, flow rate, temperature, and volume, which make quality control challenging (GENEROWICZ et al., 2023).

Ziółkowski (2012) identifies four types of scale found in steam boilers:

I. White or beige carbonate scaling: occurs when water-softening systems fail. In addition to carbonates, calcium and magnesium ions also enter the boiler. This scale can contain up to 50% calcium carbonate ($CaCO_3$), with additional magnesium carbonate ($MgCO_3$), $Mg(OH)_2$, and iron oxides.

II. Brown carbonate scale: directly related to the chemical composition of the water (high iron content) and formed by divalent iron (Fe^{2+}).

III. Gray sulfate scaling: Composed of more than 50% $CaSO_4$, it is hard, partially soluble in water, and difficult to remove.

IV. Red silica scaling (SiO_2): Formed by calcium silicates ($CaSiO_3$), magnesium silicates ($MgSiO_3$), and aluminosilicates. It has low thermal conductivity and high hardness.

According to Klyukin et al. (2022), these scaling can be categorized into two general types:

I. Inorganic scaling: Formed by alkaline earth metals (e.g., Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}), metalloids such as silica (SiO_2), and other elements including iron (Fe^{3+}), aluminum (Al^{3+}), and manganese (Mn^{2+}) dissolved in boiler feed water.

II. Organic scaling: Formed by dissolved organic matter, hydrocarbons, and bioorganic compounds, including humic substances, carboxylates, and microbial byproducts, which can contribute to deposit formation in steam systems.

Given that scaling commonly occurs in steam devices, industrial water treatment is essential to prevent it. To achieve high-quality parameters for use in boilers and cogeneration systems, water must undergo a demineralization process, which can be done using either reverse osmosis or ion exchange methods (ČUDA et al., 2006). High-quality water must be clear and colorless, contain no suspended solids, oils, or aggressive chemicals, have low hardness, alkalinity, oxygen, CO_2, and SiO_2 levels, and have a pH above 8.5 (ČSN, 1992).

The continuous nature of steam and energy generation presents challenges that make controlling scale formation in boilers, turbines, and heat exchangers difficult, mainly when boiler feed water is poorly regulated. In this case, solid deposit development is inevitable. Scaling can be easily removed by chemical cleaning in some cases, but some scales are difficult to clean, even mechanically (KUTUM et al., 2023).

These scales cause serious damage to equipment due to corrosion forming on metal surfaces covered by such deposits. A failure in a piece of equipment (boiler, turbine, or heat exchanger) can be enough to halt an entire industrial plant, leading to significant energy generation and production losses, as well as financial losses. Liu et al. (2022) conducted a failure analysis on a boiler tube that ruptured and concluded that the main cause was poor feed water quality, containing high concentrations of dissolved oxygen, Ca^{2+}, and Mg^{2+}. These substances, along with Cl and oxygen, also triggered an electrochemical reaction, forming deposits such as $MgCO_3$, $CaCO_3$, and SiO_2. These scales caused corrosion on the tube surface, leading to rupture. The authors state that to avoid such failures, water quality must be frequently monitored, and appropriate procedures must be followed to maintain optimal water treatment conditions, such as regeneration, backwashing, rinsing, and using thermal and chemical deaeration to reduce the oxygen content in the water.

2.3. Analytical Techniques for Bioenergy Systems

For a better understanding of failures in bioenergy production equipment, especially those related to scaling formations, chemical analyses are used as tools for investigations and solutions. Himarosa et al. (2022) analyzed failures in water-wall tubes, superheaters, and condensers of a boiler, where the results showed that the chemical composition of the internal surface of the tubes was different from the manufacturing materials, leading to steam leaks. Wang and Ye (2023) used ED-XRF to analyze scales removed from tubes of two condensers that showed corrosion. The main elements found were Cu, Cl, O, Ni, Ca, and Si. The authors concluded that the way to eliminate the formation of these scales is to improve the water quality, which would decrease tube corrosion.

Chemometrics is a critical resource as it is a statistical method that allows the analysis of several variables from a single sample. One of its foundations is multivariate methods, which enable an understanding of the chemical variation analyzed in each sample (MALINOWSKI, 2002). Analyzing failures means recognizing the variables that contribute to better equipment performance, which can be used to determine operating conditions. Not using the right tools makes identifying important variables challenging due to the many factors in a system or equipment. An effective way to address this is to use statistical multivariate analysis techniques, specifically PCA (GROENEWALD et al., 2018).

2.3.1. Chemometric Approaches in Failure Analysis

Technological development and advances in chemical analysis methods have increased the amount of analytical data. This is due to using and improving microcomputers in chemical laboratories (BRUNS; FAIGLE, 1985). However, large amounts of information require greater efforts to relate the analyzed variables, making it necessary to use more robust techniques to obtain coherent results. Multivariate statistical models allow the acquisition of many variables and enable simultaneous data analysis and correlation (SENA et al., 2000; FERREIRA, 2015). Therefore, the use of statistical, mathematical, and computational models in the study and interpretation of chemical data is known as chemometrics (PASQUINI, 2003; BARROS NETO et al., 2006).

Chemometrics has been extensively studied in recent years with the aim of boosting data acquisition and promoting better solutions to specific study issues. It is typically applied when the objective is to identify the most important variables in a dataset with many variables. In experimental research, where the investigator may not fully understand the data due to the large amount of information, fast and efficient computational data processing methods are used to obtain results quickly and reliably (PEREIRA FILHO, 2015; PEREIRA, 2018; CHARLES; ALAMSJAH, 2019). The use of software for identifying data trends provides better results, meaning that the recognition of information occurs from the first data set, enabling the verification of similarity between the samples under analysis. Identifying patterns allows a dataset to be analyzed to reveal trends and clusters within those sets (SOUZA; POPPI, 2012; WILLIAMS, 2019).

2.3.2. Principal Component Analysis

Principal Component Analysis is a widely used statistical technique for reducing the dimensionality of multivariate data, transforming correlated variables into orthogonal components that maximize the explained variance. This approach enables the identification of patterns and correlations between variables, facilitating the interpretation of complex datasets, particularly in exploratory analyses (FERREIRA et al., 2023; COSTA et al., 2025).

In applied sciences, PCA is essential for processing spectral data from techniques such as ED-XRF and Electron Paramagnetic Resonance Spectroscopy (EPR), aiding in sample discrimination based on chemical or geographical characteristics. Its application is valuable for visualizing inherent patterns in data and integrating it with chemometric tools, such as heat maps and multivariate classifications (FERREIRA et al., 2023; COSTA et al., 2025).

Despite its effectiveness, interpreting principal components requires careful attention, as the generated axes combine original variables in complex ways. Even so, its use in environmental, agricultural, and chemical studies highlights PCA’s versatility across diverse research areas (ZHOU et al., 2018).

2.3.3. Minimum Spanning Tree-based Clustering

The Minimum Spanning Tree-based Clustering method is widely used for its effectiveness in identifying clusters of arbitrary shapes and sizes in complex datasets. It constructs an MST from an undirected graph, where vertices represent data points and edges correspond to the distances between them. After constructing the MST, high-weight edges are removed, separating the graph into clusters without the need to predefine their number. This approach is particularly useful for datasets with nonlinear relationships, where traditional clustering methods struggle due to complex distributions, irregular patterns, or varying densities among data points. Nonlinear data structures are common in high-dimensional datasets, where relationships between variables do not follow a simple geometric separation, making graph-based clustering techniques, such as MST, more effective in capturing these patterns. To enhance efficiency, MST-based clustering can be combined with optimization techniques, such as sparse graph construction, which preserves essential proximity information while reducing the number of processed edges, significantly decreasing computational complexity in large datasets. Despite its effectiveness, MST-based clustering faces challenges such as sensitivity to parameters for edge removal. However, recent advancements, like leader node selection based on local density, have improved the scalability and accuracy of MST, making it more suitable for high-dimensional and complex datasets (YAO et al., 2024; AKHTER et al., 2025).

2.3.4. Instrumental Techniques for Bioenergy Systems

Instrumental analysis is essential for the advancement of chemistry, enabling the precise and detailed assessment of the composition and properties of various types of samples. These techniques significantly enhance the ability to investigate complex systems, providing fundamental insights that go beyond the capabilities of classical analytical methods. They allow for a deeper interpretation of chemical phenomena, identification of components, determination of their concentrations, and understanding of their interactions. The accuracy and sensitivity of these approaches establish instrumental analysis as a cornerstone of modern chemistry, indispensable for scientific and technological advancements (MCKIBBIN et al., 2024; LASKUS et al., 2018).

2.3.5. Energy-Dispersive X-ray Fluorescence

The energy-dispersive X-ray fluorescence (ED-XRF) technique is widely recognized as a non-destructive method for the elemental analysis of materials, with multi-element detection capabilities. The principle of ED-XRF is based on the excitation of atoms in the target material by an X-ray source, such as an X-ray tube. This excitation induces the emission of characteristic X-rays from the elements present in the material, enabling their identification and quantification based on the energies associated with the spectral lines. This technique applies to elements ranging from magnesium to uranium, covering a broad spectrum of analytical applications (STOLIDI et al., 2023; VISENTIN et al., 2023; FIGUEIREDO et al., 2024a).

One of the main advantages of ED-XRF is its minimal sample preparation requirements, which simplify the analytical process and significantly reduce the time needed to obtain results (MELLO et al., 2022; STOLIDI et al., 2023). In industrial and environmental analyses, ED-XRF stands out as an essential tool for fast and cost-effective characterizations, being widely used in the analysis of metals, recycled materials, food, and electronic waste (VISENTIN et al., 2023; FIGUEIREDO et al., 2024a).

The technique of ED-XRF is based on the fundamental phenomenon of X-ray fluorescence, in which atoms of the analyzed material are excited by high-energy radiation, causing the ejection of inner-shell electrons. This creates vacancies that are filled by electrons from higher energy levels, resulting in the emission of secondary X-rays that are characteristic of each element present in the sample (COSTA et al., 2019). Because each element emits X-rays with distinct energy values, ED-XRF allows for qualitative and quantitative analysis of multiple elements simultaneously without damaging the sample. This capability makes it an attractive technique for analyzing complex solid samples, particularly in industrial and environmental settings.

In applications such as scale deposit characterization in bioenergy processes, ED-XRF has demonstrated effectiveness in identifying both major and trace elements with high precision. This technique is particularly useful for analyzing the composition of scaling materials in boilers and turbines, where the detection of elements such as calcium, silicon, and iron provides critical information on deposit formation mechanisms (BABOS et al., 2019). Recent studies highlight the importance of minimizing matrix effects through matrix-matching calibration (MMC) and multivariate regression techniques, improving the accuracy of elemental quantification in complex materials.

Another key advancement in ED-XRF is the development of alternative calibration strategies, such as one-point gravimetric standard addition (OP GSA) and multi-energy calibration (MEC). These approaches have been successfully applied to improve the precision of elemental analysis in heterogeneous samples, including electronic waste and high-performance industrial materials (CASTRO et al., 2020). These strategies help compensate for matrix-related interferences, enhancing the robustness and applicability of ED-XRF in various scientific and technological fields.

Despite its advantages, ED-XRF faces limitations, such as lower sensitivity to light elements and matrix effects, which require proper calibration to ensure accurate results. However, ongoing research has focused on the development of customized calibration solutions and the integration of chemometric models, which significantly enhance the technique's precision in complex sample matrices (FERREIRA et al., 2024; FIGUEIREDO et al., 2024b; RODRIGUES et al., 2024). These advancements reinforce the role of ED-XRF as a powerful tool for multi-elemental analysis in a wide range of industrial, environmental, and research applications.

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INCRUSTATIONS FORMED IN BIOELECTRICITY TURBOGENERATORS: AN ADVANCED EVALUATION USING ENERGY DISPERSIVE X-RAY FLUORESCENCE (ED-XRF) AND EXPLORATORY ANALYSIS

ABSTRACT

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

1. 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.[1] Brazil showed 17206 MW for bioenergy capacity and 16702 MW for solid biofuels and renewable waste in 2022.[2]

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.[3-5]

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.[2,4] The ESB industrial plants have invested in enhancing their efficiency, reducing electricity consumption in production processes, and increasing electricity exports.[3]

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.[6]

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.[5,7,8] 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.[7,8]

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.[8,9]

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.[9] 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.[10-14]

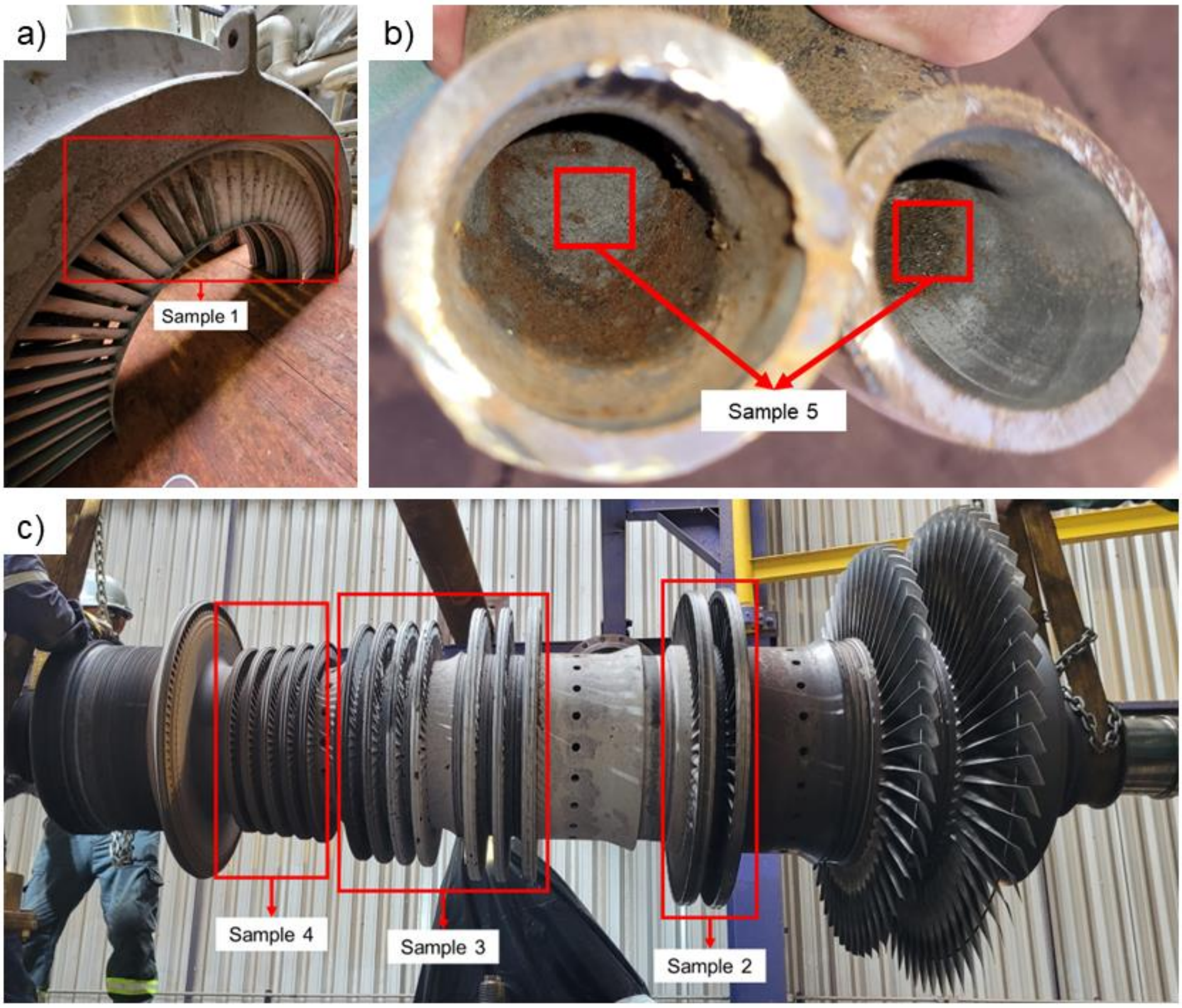
To the best of our knowledge, there is a lack of studies to monitor the chemical composition of sample materials in a water steam-driven turbogenerator. Then, X-ray fluorescence and multivariate exploratory analysis[15] were applied to identify and understand the causes of incrustation phenomena.

2. MATERIALS AND METHODS

2.1. 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. The first sample was collected from the internal part of the reed holder of the turbine (Figure I.1a). Another sample was taken from the piping curves in the second stage of the boiler superheater, part of the boiler that generates steam for the turbine (Figure I.1b). Additional samples were collected from three high-pressure stages of the turbine rotor (Figure I.1c). The masses of the incrustation material varied according to the stage of the process and the collection position; therefore, the material was divided into three replicates for the analysis.

Figure I.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)



2.2. Energy dispersive X-ray fluorescence data collection

The XRF spectra were collected using a benchtop X-ray Fluorescence (XRF) spectrometer, the Rigaku NEX QC^{+} (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 keV, 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 µm thick Mylar® film (Premier Lab Supply, Port St. Lucie, Florida, USA). The analysis was conducted under three sets of instrumental conditions: 1) 50 kV and 10 µA, 2) 30 kV and 10 µA, and 3) 6.5 kV and 50 µA, 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® 2022b (MathWorks, Natick, MA, USA) laboratory codes and Pirouette 5.0 software (Infometrix, Bothell, WA, USA).

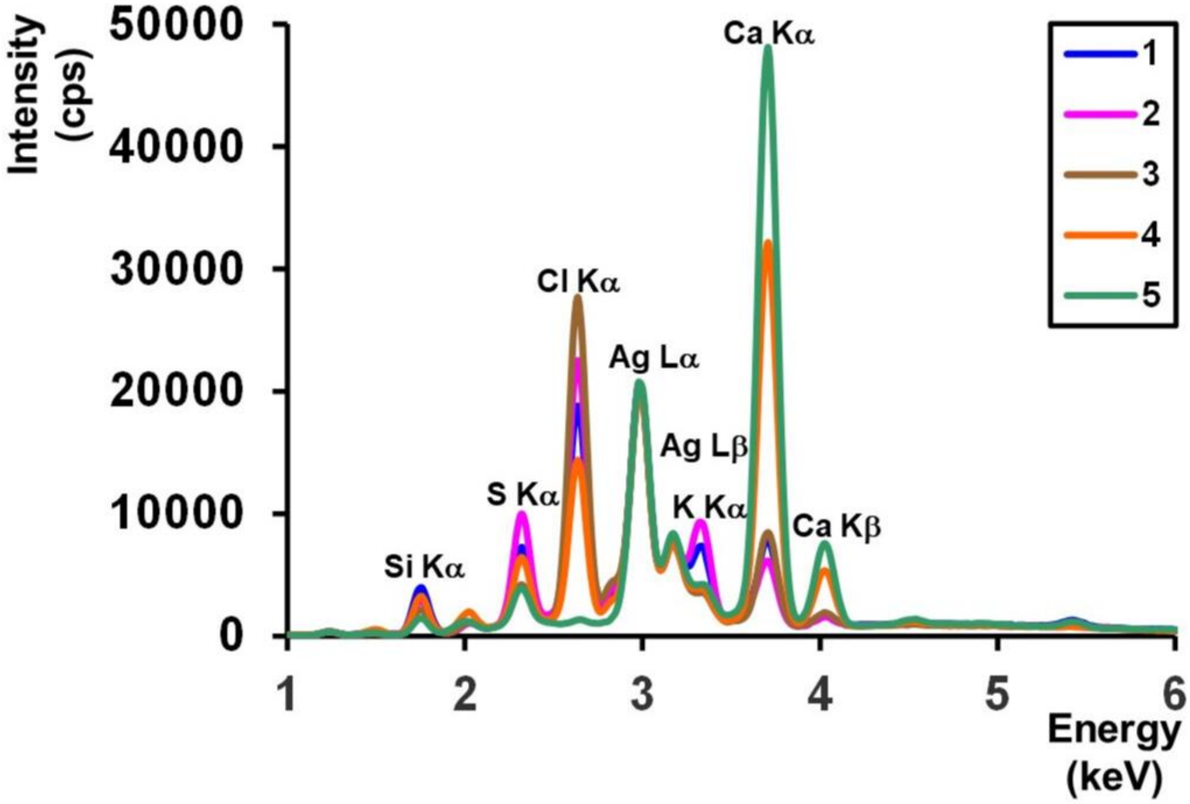
3. RESULTS AND DISCUSSION

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 × 2048 (rows and columns) were generated. Additionally, to enhance the analysis, matrices with increased columns were investigated to explore potential improvements in data resolution and interpretation. Three authentic replicates represented each sample. Figure I.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 Kα 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); Kβ for Ca (4.013) and Lα (2.984) and Lβ (3.151) for silver - Ag from the X-ray source.

Figure I.2 - Spectra of material samples (1 to 5) acquired using ED-XRF under the best condition: the third instrumental condition in air

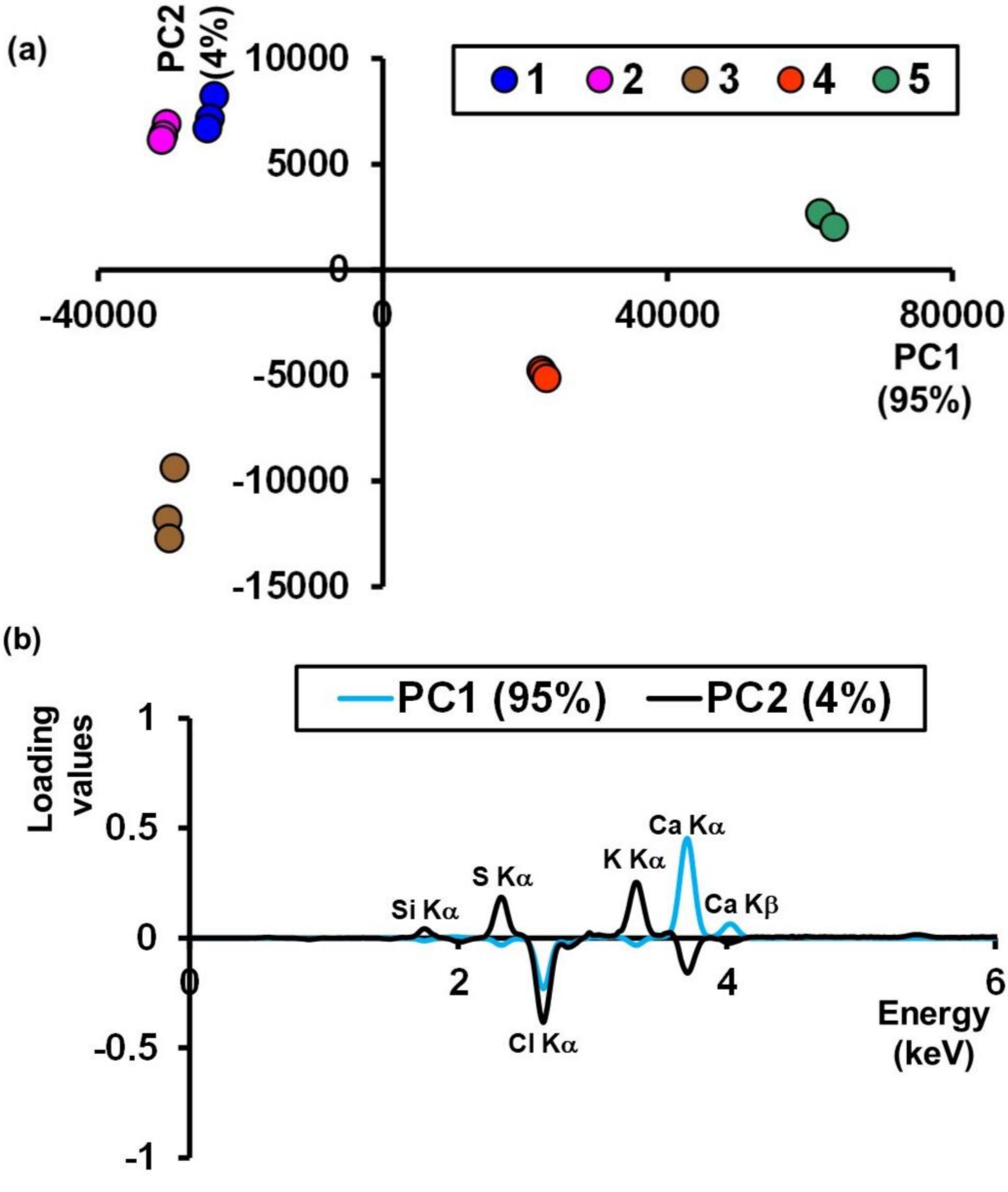


The ED-XRF spectra were mean-centered PCA calculations. PCA aided in confirming patterns within scale samples derived from incrustation, as shown in Figure I.3a, where the scores plot demonstrates the distribution of samples and replicates under instrumental condition 3, the best for data information. 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 I.3b, 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 Kα and Kβ 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 Kα fluorescence line is 2.622 keV

Figure I.3 - Score (a) and loading (b) plots for the five samples and replicates were calculated using PCA



The most significant loading values for PC1 were associated with Ca, explaining 95% of the variance and distinguishing samples 4 and 5 (Figure I.1). For PC2, the descending loading values were Cl, K, S, Ca, and Si, accounting for 4% of the explained variance. These results highlight the specific role of these elements in incrustation formation.

The predominance of Ca in PC1 reflects the findings of Christman, Holmes, and Thompson[16], who identified calcium and magnesium as key contributors to boiler scaling. These elements form silicate scales that reduce heat transfer efficiency and damage tubes. The removal of Ca^{2+} and SiO_2 from water is essential to prevent this issue, consistent with recommendations for low hardness and reduced SiO_2 levels in high-quality water[17].

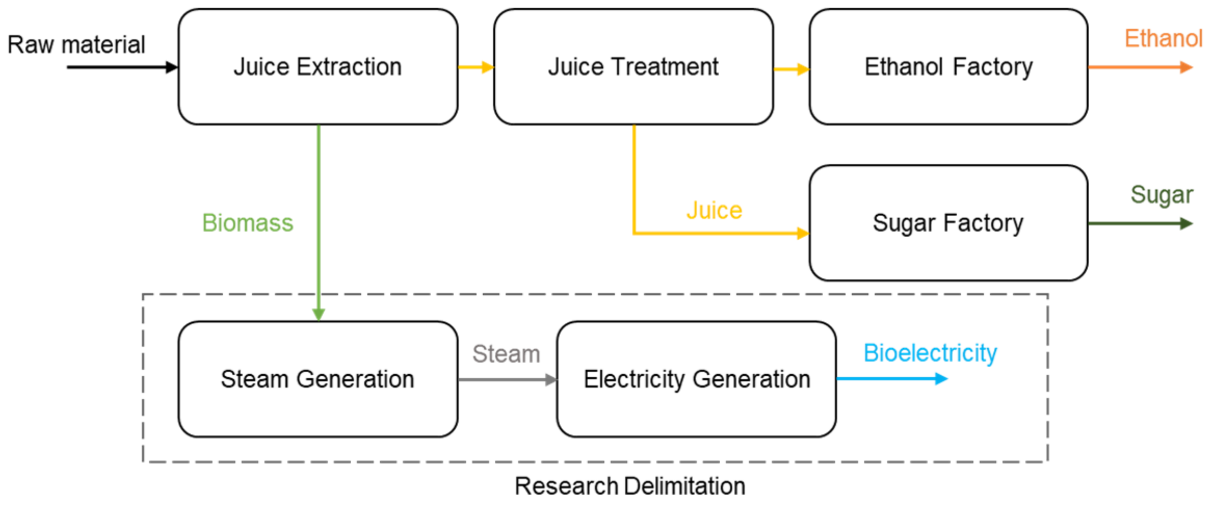
Liu et al.[18] reported that Ca^{2+}, Mg^{2+}, Cl, and oxygen form deposits such as $MgCO_3$, $CaCO_3$, and SiO_2, causing corrosion and tube ruptures. In this study, these elements were also associated with PC2, indicating similar mechanisms of incrustation formation. Himarosa et al.[19] identified failures in water-wall tubes, superheaters, and condensers due to differences in the chemical composition of internal surfaces compared to the manufacturing materials, leading to steam leaks. These findings underscore the importance of controlling water composition to prevent structural damage.

Additionally, Wang and Ye[20] found Cu, Cl, O, Ni, Ca, and Si in incrustations on condenser tubes. As the authors noted that the tubes were made of copper, it is likely that the detected Cu and Ni originated from the tube material. This suggests that, beyond water quality, the composition and degradation of construction materials may influence the chemical composition of scale deposits. The interaction between metallic surfaces and water chemistry can accelerate scaling and corrosion processes, particularly in environments where Cl, Ca, and Si are present. The presence of Cl, Ca, and Si, observed both in this study and by Wang and Ye, highlights the importance of these elements in forming deposits that promote corrosion.

The results presented align with the existing literature and emphasize the importance of robust water treatment and monitoring practices. In addition, material selection for steam system components plays a role in deposit formation, as corrosion and degradation can contribute additional elements to the incrustation process. Controlling water chemistry is essential to minimize incrustations, reduce corrosion, and ensure the efficiency and reliability of steam generation systems.

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.[9] The investigated materials were acquired in an ESB industry during the disassembly of a turbogenerator for off-season inspection. It is important to emphasize that the purpose of this study is limited to the cogeneration of bioelectricity and steam generation, excluding other processes of this type of industry, as represented in Figure I.4.

Figure I.4 - Contextualization of research delimitation



The exploratory analysis of ED-XRF data enhanced the evaluation of the elemental composition of the incrustations, 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.

4. 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.

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SUSTAINABLE WATER MANAGEMENT FOR STEAM GENERATION IN SUGARCANE BIOREFINERIES: APPLYING PCA AND MST CLUSTERING IN SAMPLE ANALYSIS

ABSTRACT

Our study on sustainable water management in sugarcane biorefineries, which utilizes water as a primary resource for generating bioenergy through steam production, has employed a novel approach. High water quality is crucial for optimal efficiency, particularly in boiler operations. We have utilized unsupervised methods, such as principal component analysis (PCA) and minimum spanning tree (MST), alongside instrumental analysis data, to assess water quality in steam production. The PCA exploratory analysis identified three distinct clusters, with the relevant variables being conductivity and SiO_2 content, to differentiate the purity of a dataset of 120 samples. MST-based clustering corroborated the PCA findings, forming three clusters: sample 1 represented the purest water, while samples 3 and 6 were in different clusters, indicating less purity in boiler feedwater. These unsupervised methods are highly effective, providing accurate and reliable data analysis and significantly benefiting sugarcane biorefineries by eliminating subjective biases. The findings of this study promise to improve water management practices in sugarcane biorefineries, leading to more efficient and sustainable operations.

Keywords: purity water, boilers, bioenergy, chemometrics, sustainability

1. INTRODUCTION

Water quality throughout the process is crucial for sugarcane biorefineries since compromised water can influence the parameters of the sugarcane juice extracted. Furthermore, water quality guarantees the best efficiency, especially for boilers and other instruments used throughout the steam generation and use process. Sugarcane biorefineries can also produce energy using water as a primary source, generating condensed and steamed water.[1-5]

Analyzing data derived from reactions, processes, synthesis, and industrial plants across various sectors is extremely helpful in establishing standards, references, and concepts regarding uncertainties, analysis errors, and improving quality parameters.[6] For instance, one of these strategic non-supervised techniques is an exploratory analysis using principal component analysis (PCA), which can project the multidimensional data into a reduced number of variables known as principal components (PCs), as illustrated in equation 1:

$$\mathbf{X} = \mathbf{T_a L_a^T} + \mathbf{E} \qquad \text{Equation (1)}$$

Matrix **X** contains the data of interest, decomposed into two matrices: score matrix **T** and orthonormal loading matrix **L**, with a matrix **E** representing errors for a specific number of principal components denoted as “a”. The scores and loadings provide information about the samples and variables, respectively. Through exploratory analysis and data mining, it is possible to better understand the data, identify correlations between variables, and uncover underlying information. This approach allows for the identification of the main characteristics of the data, facilitating informed decision-making.[7,8]

Another technique is the minimum spanning tree (MST), which uses a graph where nodes represent stimuli and edges represent potential links, with weights typically employed to predict or reconstruct empirical dissimilarities data. The goal is to find the tree that spans the graph (ensuring a path exists between each pair of nodes without any cycles) such that the sum of the edge weights is minimized or maximized for dissimilarities or similarities, respectively. Solving the MST problem is formally equivalent to performing single-link clustering, and the relationship between clustering and spanning trees has proven highly valuable. However, it is assumed that interest in the MST first arose in engineering (e.g., in the layout of telephones, powerlines, and other networks). The main advantage over the different techniques is the application in Phyton,[9] which means there is no need for expensive software to run the code.[10-13]

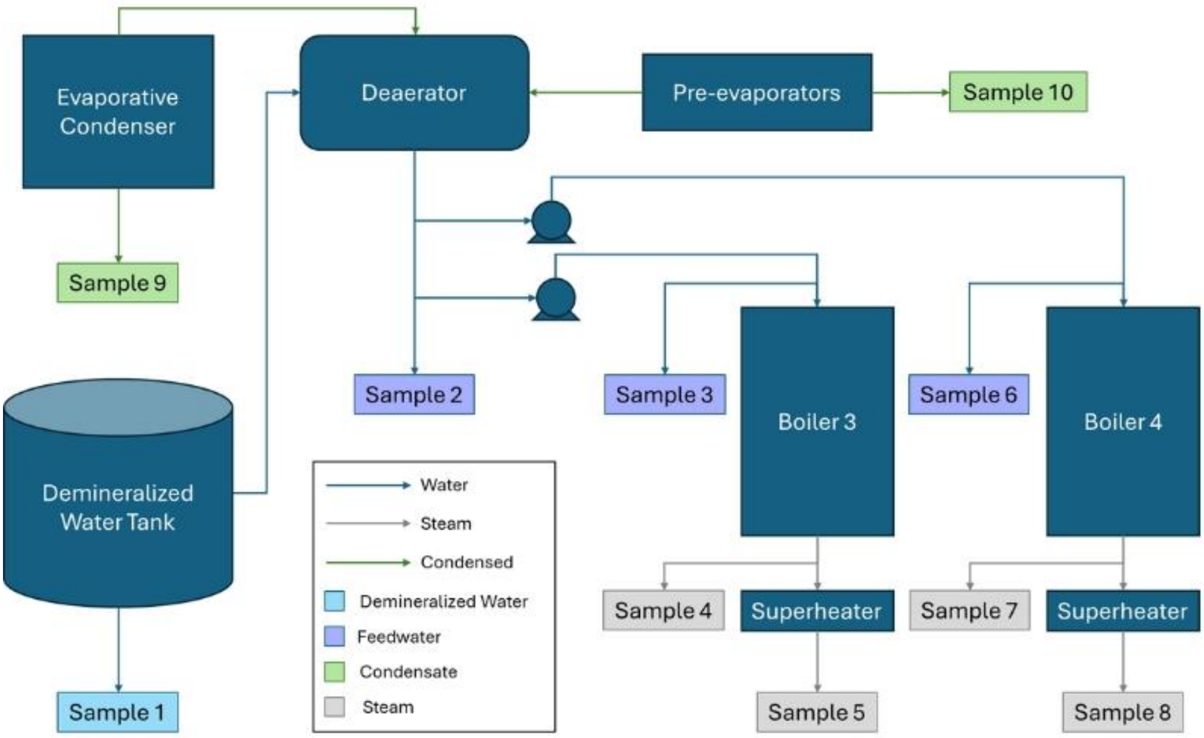
This study uses mathematical and statistical techniques and instrumental analysis data[14] to evaluate the water quality in different steps of a power-generating plant dedicated to a biorefinery.

2. EXPERIMENTAL

2.1. Samples

Four water samples, four steam samples, and two condensed water samples were collected from April to June 2023, as shown in Figure II.1. The number of analyses for each sample type was determined based on the requirements of the process. An average was calculated for each type, resulting in twelve replicates representing each sample, comprising 120 data samples.

Figure II.1 - Locations of sampling points for water, steam, and condensed water in the steam generation process



The samples were collected in a sugarcane biorefinery located in Pitangueiras, São Paulo State, Brazil (-21.048431, -48.262912), where sugar, ethanol, yeast (*Saccharomyces cerevisiae*), and electrical energy are processed. Steam must be produced for this process, as all production stages require this resource. Therefore, water quality is essential for all systems to operate correctly. Thus, all samples are part of the steam generation process using high-pressure boilers at 67 kgf cm^{-2}.

2.2. Instrumental Analysis

Several instrumental techniques were employed to monitor the water quality and composition of the samples. For pH and conductivity measurements, a mPA-210 pH meter (MS Tecnopon, Piracicaba, São Paulo State, Brazil) and a TEC-4MP digital conductivity meter (Tecnal, Piracicaba, São Paulo State, Brazil) were used, both at a controlled laboratory temperature of 25 ± 0.5 °C. For samples with pH values above 9.4, a preliminary adjustment was performed using a commercial conductivity neutralizing solution (Sinergia Científica, Campinas, São Paulo, Brazil), added dropwise under continuous stirring until a color change from pink to colorless was observed. This color change indicates the neutralization of pH; however, the exact composition of the neutralizing solution, including the presence of pH indicators, is proprietary and not disclosed by the manufacturer. Conductivity results were reported in µS cm^{-1}.

Two methods were used to determine the SiO_2 content based on sample composition, employing a DR 5000™ UV-Vis spectrophotometer (Hach, London, UK). The first method was used on most samples, while the second was explicitly applied to sample 9 (evaporative condenser).

Method 1

The sample was split into two 50 mL portions (sample and blank test). After adding specific reagents (molybdate 3, citric acid F, and amino acid F), the reaction progressed for set intervals before measurement. The spectrophotometer was set to the Silica ULR program, zeroed with the blank, and the absorbance of the sample was measured at 815 nm in a 10 mL cuvette, yielding results in mg L^{-1}.

Method 2

For sample 9, additional preparation was performed by adding specific reagents sequentially (2% hydrochloric acid, 10% oxalic acid, 10% ammonium molybdate, and

17% sodium sulfite), allowing the solution to rest for 10 min before analysis. The silica program on the UV-Vis spectrophotometer was zeroed with a prepared blank test, and the absorbance of the sample was measured at 460 nm, with results recorded in mg L^{-1}.

This combined approach using UV-Vis spectrophotometry and other complementary instrumental techniques comprehensively analyzed water quality parameters, including pH, conductivity, and SiO_2 content.

2.3. Data processing

The recorded data were evaluated using the Matlab® 2023b (MathWorks, Natick, MA, USA)[15] routines developed in our research group and Pirouette 5.0 (Infometrix, Bothell, WA, USA) software.[16,17] The variables pH, conductivity, and SiO_2 content were pre-processed by autoscaling, i.e., mean equals 0 and standard deviation equals 1, for PCA calculations. Python codes were prepared to calculate the MST data evaluation.[18]

3. RESULTS AND DISCUSSION

3.1. Exploratory analysis

PCA projects the multidimensional spectral information into compact matrices, termed scores (**T**) and loadings (**L**), arranged in descending order of explained variance, as shown in equation 1.[7,8]

The PCA exploratory analysis revealed three distinct clusters with 100% explained variance for three principal components (PCs), 62% for PC1, and 28 and 10% for PC2 and PC3, respectively.

Figure II.2a presents the score plots, revealing three main clusters. The first cluster, shown as blue circles, represents sample 1, corresponding to the demineralized water tank. In pink circles, the second cluster includes samples 3 and 6, representing the feedwater of boilers 3 and 4, respectively.

The remaining samples form the third cluster, represented by gray circles. This group includes:

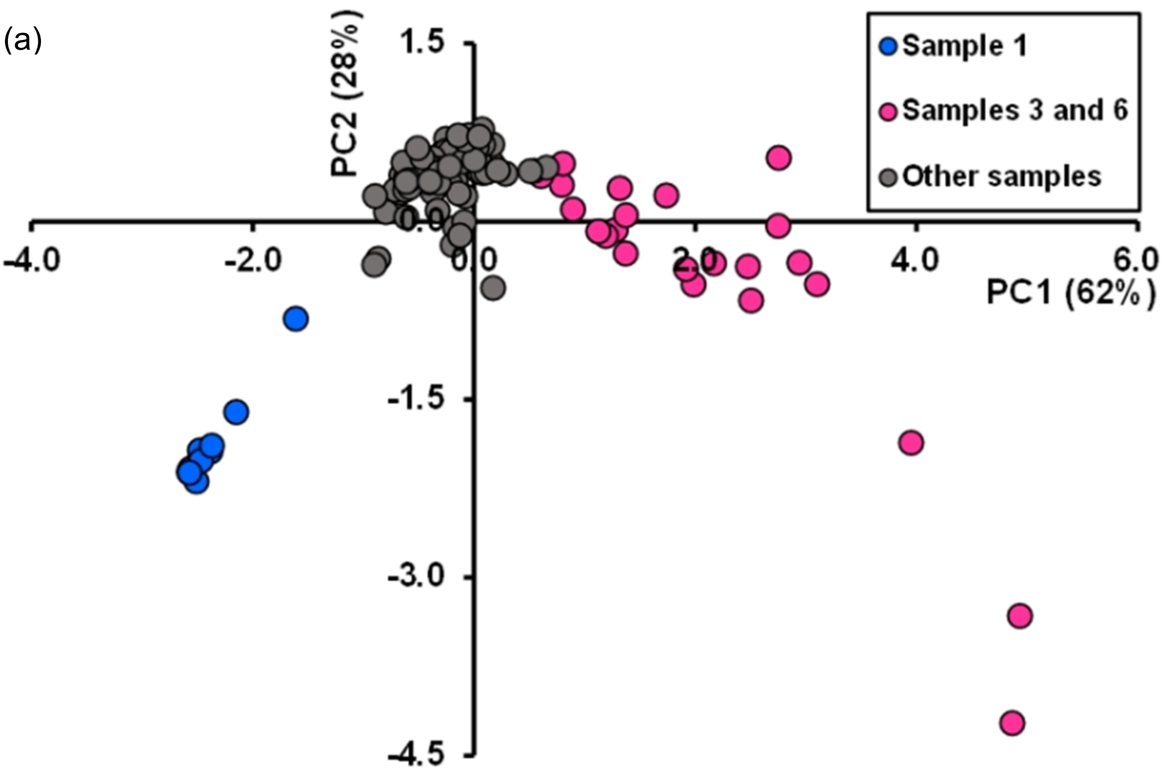
(*i*) Sample 2, from the feedwater deaerator,

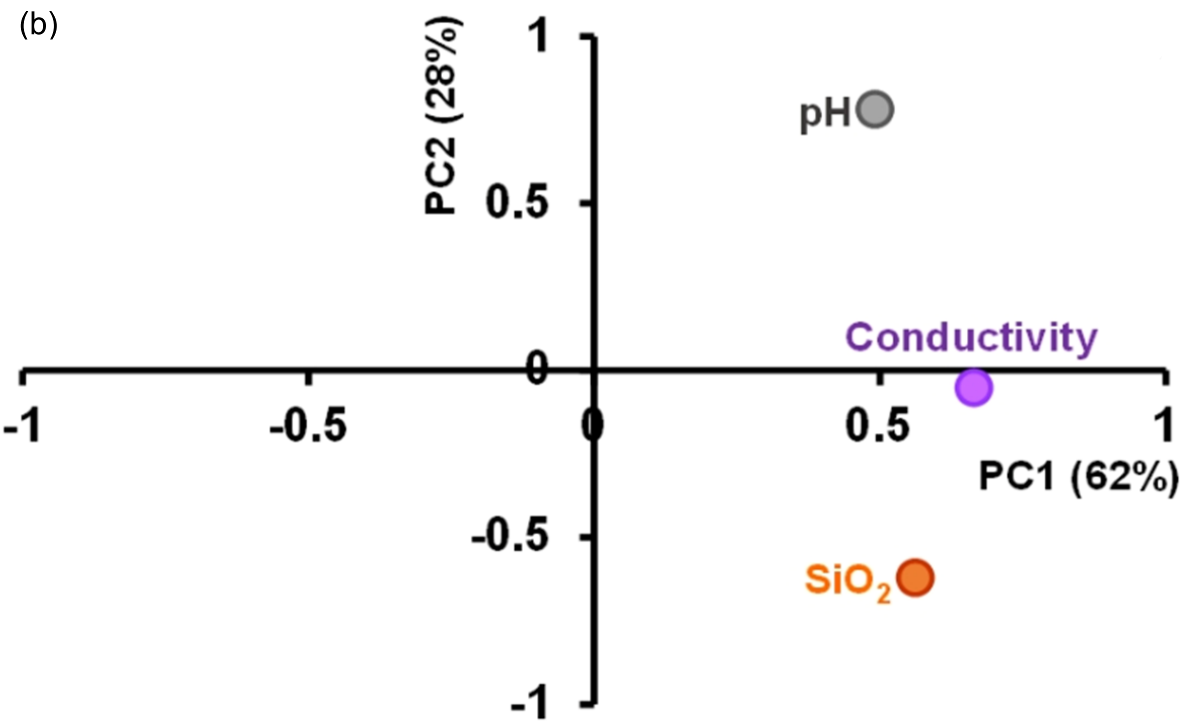
(*ii*) Sample 4, representing saturated steam from boiler 3,
(*iii*) Sample 7, representing saturated steam from boiler 4,
(*iv*) Samples 5 and 8, representing superheated steam from boilers 3 and 4, respectively,
(*v*) Sample 9, corresponding to the evaporative condenser and
(*vi*) Sample 10 represents the condensate from the pre-evaporators.

Figure II.2a shows the relationships among these clusters based on their water or steam sources. In Figure II.2b, the loading plots revealed that the PC1 was responsible for its differentiation, with 62% explained variance visualized in the scores plot (Figure II.2a). The essential variables were conductivity and SiO_2 content to differentiate the most (sample 1) to least (samples 3 and 6) pure samples. The pH parameter was associated with the differentiation of the cluster of other samples (gray circles) and 3 and 6 (pink circles) concerning the cluster of samples 1 (blue circles), with 28% of explained variance along PC2, shown in Figure II.2b.

Figure II.2 - Score (a) and loading (b) plots calculated using PCA for data matrix samples (120 x 3)

(a)





Samples 3 and 6 showed vast differences in conductivity, 16-fold higher than sample 1 (μS cm^{-1}), and SiO_2 content, 201-fold compared to sample 1 (mg L^{-1}). Analogize to other samples (2, 4, 5, 7-10), the conductivity is 8-fold (μS cm^{-1}), and SiO_2 content is 23-fold (mg L^{-1}) over sample 1. It is emphasized that the sample 1 cluster (blue circles) had the lowest values for conductivity, from 1.1 to 3.5 μS cm^{-1}, SiO_2 content, 0.002 to 0.008 mg L^{-1}, and pH, between 5.5 and 7.5. The cluster for samples 3 and 6 (pink circles) ranged from 12.6 to 54.9 μS cm^{-1} (conductivity), 0.1 to 1.5 mg L^{-1} (SiO_2 content), and 9.0 to 10.4 (pH), respectively. The cluster for other samples (gray circles) had values from 4.7 to 26.2 μS cm^{-1}, 0.002 to 0.2 mg L^{-1}, and 8.2 to 9.8 (pH) for the same parameters, respectively.

3.2. Minimum spanning tree-based clustering

A k-nearest neighbors (k-NN) graph connecting each sample to its k-nearest neighbors in the input space was created, as shown in Figure II.S1 (Supplementary Information (SI) section). With the help of Figure II.S1, the resulting k-NN graph for the samples, considering k = 5, showed the clustering tendency for the replicates of sample 1 (from 1 to 12, except for 3), which differ because they are positioned in distinct parts of the k-NN graph.

Minimum spanning tree-based clustering pertains to graph theory, which involves mathematical structures representing binary relationships among elements of a finite set. Typically, a graph comprises a set of vertices connected pairwise by edges. When an edge connects two vertices, they are considered neighbors, as shown in Figure II.S2 (SI section). Given G = (V, E, w), where w: E → R^+ is the edge weighting function, obtain the spanning tree T that minimizes the following criterion as shown in equation 2. Note that finding the MST of a graph is an optimization problem.[10-12]

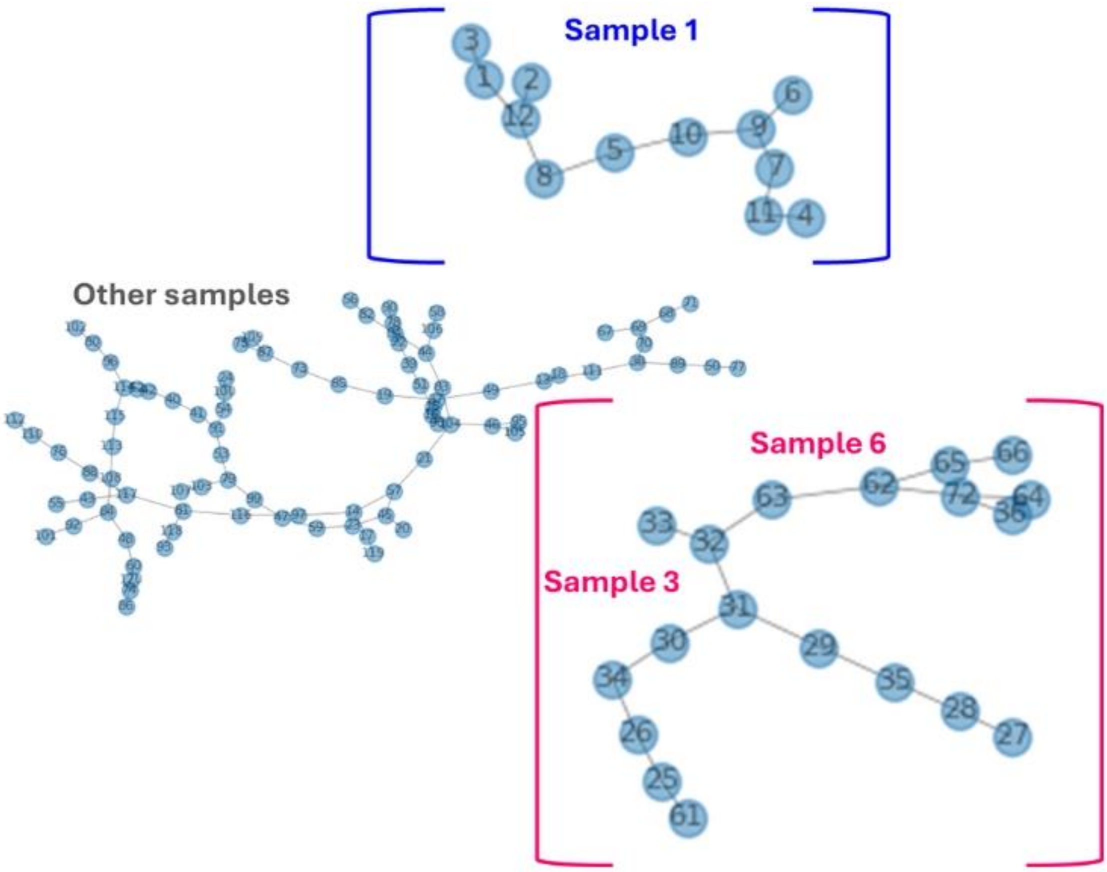
$$\mathbf{w(T)} = \sum_{\mathbf{e \in T}} \mathbf{w\,(e)} \qquad \text{Equation (2)}$$

Kruskal's algorithm[13] constructs the MST of an arbitrary graph in a computationally efficient manner. The algorithm begins with a tree consisting of n vertices and no edges. Each iteration adds the lowest cost edge to the tree, ensuring no cycles are formed, as trees are acyclic structures. The following section presents Kruskal's algorithm for obtaining an MST.

The divisive MST-based algorithm was applied to the dataset to find clusters in the samples. The most well-known class of MST-based clustering algorithms are the divisive algorithms that employ the single linkage strategy. In this approach, the distance between two clusters is determined by the closest pair of elements from each cluster. The main idea of this algorithm is to remove edges from the MST to minimize the sum of the intra-cluster spreads of the partitions, a criterion similar to that used in the K-means algorithm. Figure II.S3 (SI section) shows the results for two clusters when the first largest edge was removed.

Figure II.3 shows that the second largest edge was removed, resulting in three clusters, a pattern consistent with the clustering observed in the PCA data analysis. In that analysis, sample 1 was identified as the purest water, while samples 3 and 6 formed separated clusters, representing the least pure feedwater from boilers 3 and 4. Figure II.3 highlighted the clusters for samples 1, 3, and 6, and Figure II.S4 (SI section) showed the original graph.

Figure II.3 - The divisive MST-based clustering found in the three clusters. Note that the first smallest cluster comprises the replicates of samples 1 (1-12), the second for samples 3 (25-36), and 6 (62-66 and 72)



4. CONCLUSIONS

The outcomes of the PCA and MST analyses highlighted the differentiation among the water samples, mainly their purity based on an unsupervised pattern. Sample 1 from the demineralized water tank was the purest, with a conductivity ranging from 1.1 to 3.5 μS cm^{-1}, SiO_2 content between 0.002 and 0.008 mg L^{-1}, and pH values between 5.5 and 7.5. In contrast, samples 3 and 6, which were the least pure, exhibited significantly higher conductivity (12.6 to 54.9 μS cm^{-1}), increased SiO_2 content (0.1 to 1.5 mg L^{-1}), and pH values ranging from 9.0 to 10.4. These findings reinforce the importance of controlling water quality, as the presence of dissolved ions and suspended solids plays a critical role in scaling formation. The use of ultra-pure (demineralized) water in steam generation systems significantly reduces the risk of deposits, improving operational efficiency and minimizing equipment maintenance needs.

The differentiation was evident based on these physicochemical parameters and was verified through a comprehensive data analysis approach. By applying PCA and MST in an integrated manner, this study demonstrated the potential of unsupervised multivariate techniques for detecting and understanding water quality patterns in biorefineries. These methods objectively reveal relationships between variables without introducing subjective bias, providing a robust framework for data-driven decision-making in industrial water treatment. Furthermore, the approach adopted here highlights how exploratory data analysis can support predictive maintenance strategies and long-term process optimization.

While this study focused on sample differentiation, industrial standards define acceptable concentration limits for elements present in feedwater. Future research could further explore these thresholds in relation to heat transfer efficiency, scaling prevention, and corrosion control, aligning process monitoring with industry best practices.

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SUPPLEMENTARY INFORMATION

Figure II.S1 - k-NN graph for the samples with k = 5. Each edge (I, j) is weighted with the Euclidean distance between samples i and j

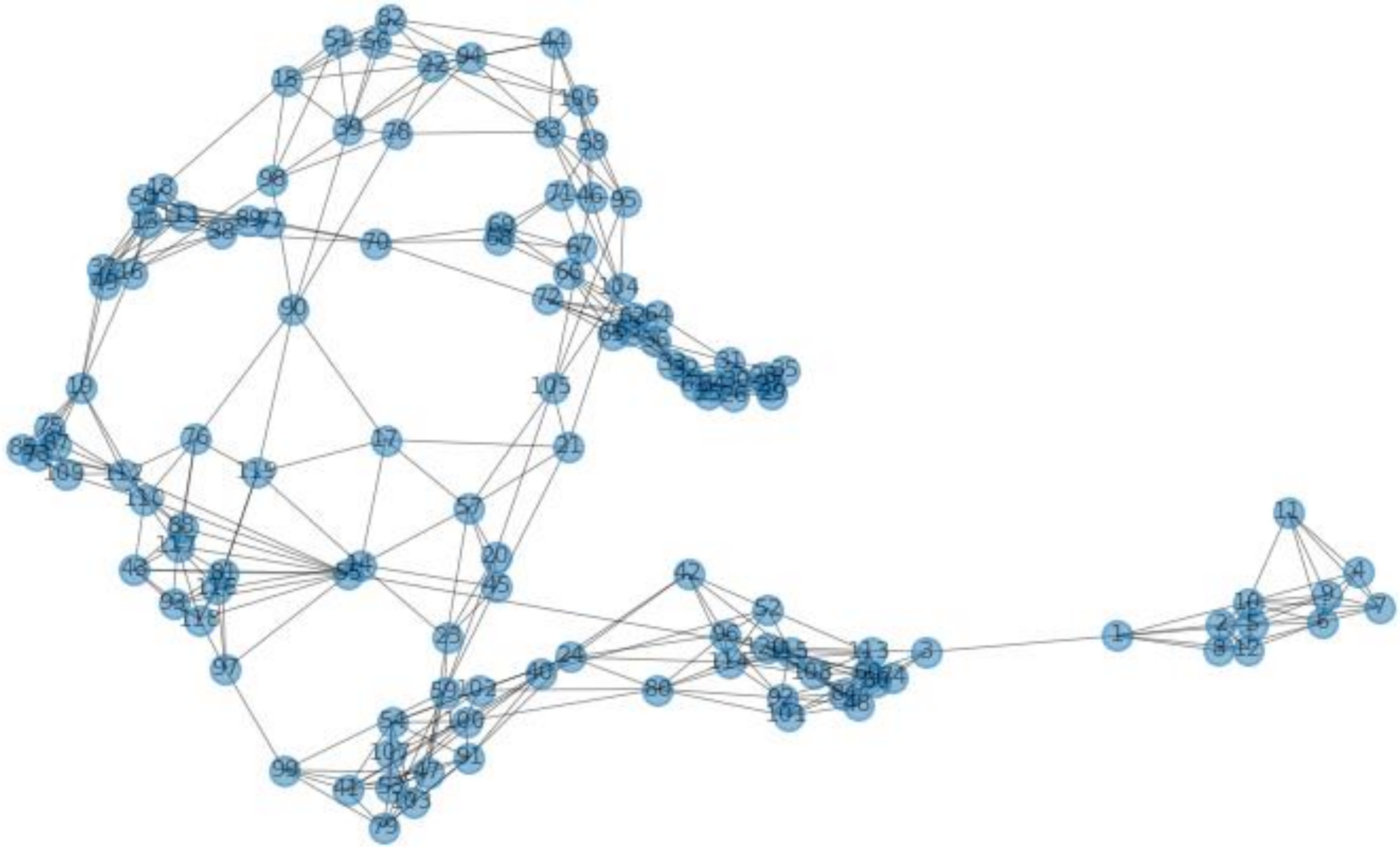


Figure II.S2 - MST obtained by Kruskal's algorithm for the samples' k-nearest neighbors (k-NN) graph

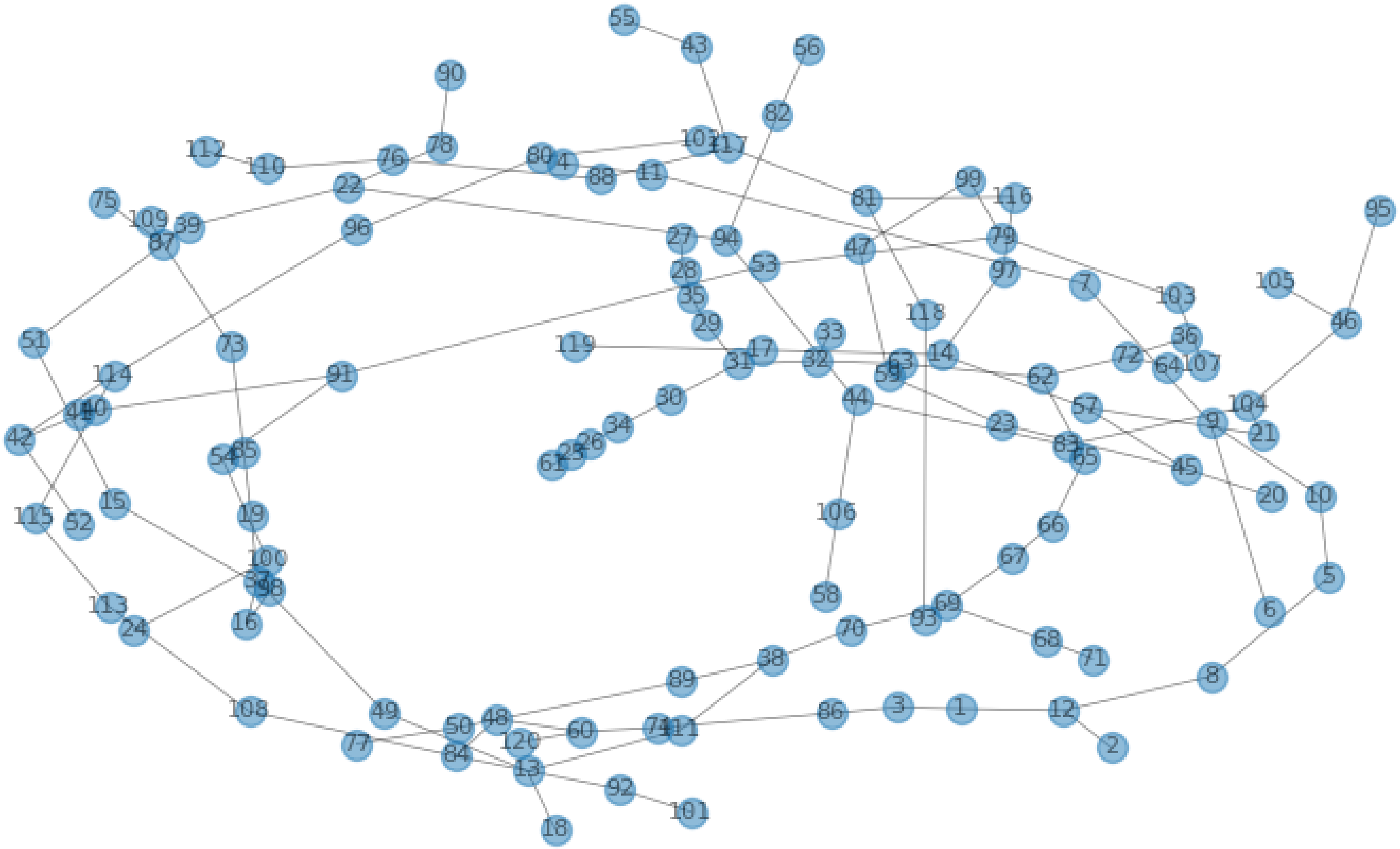


Figure II.S3 - The divisive MST-based clustering found in the two clusters. Note that the smaller cluster contains the replicates of samples 3 (25-36) and 6 (62-66 and 72)

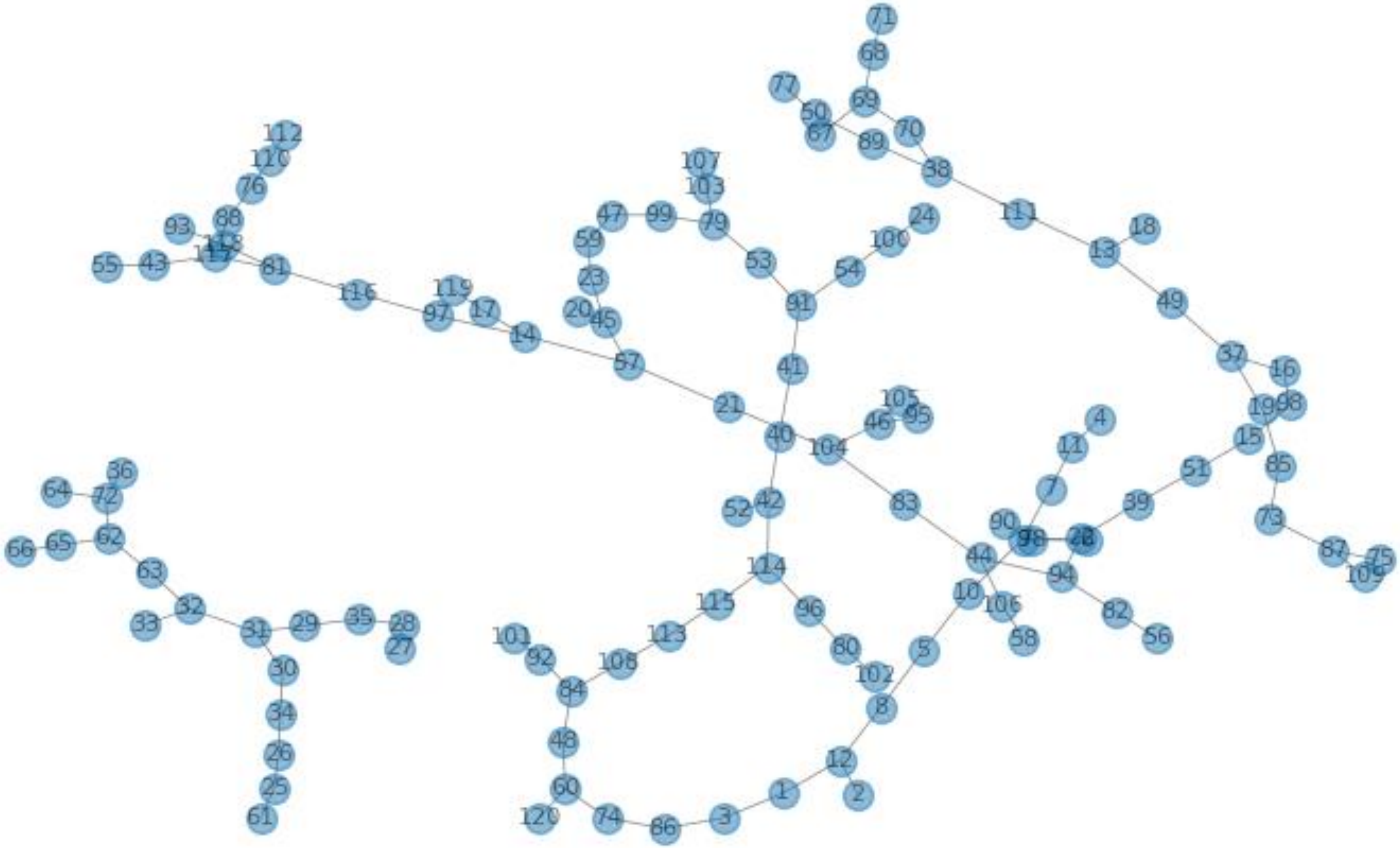
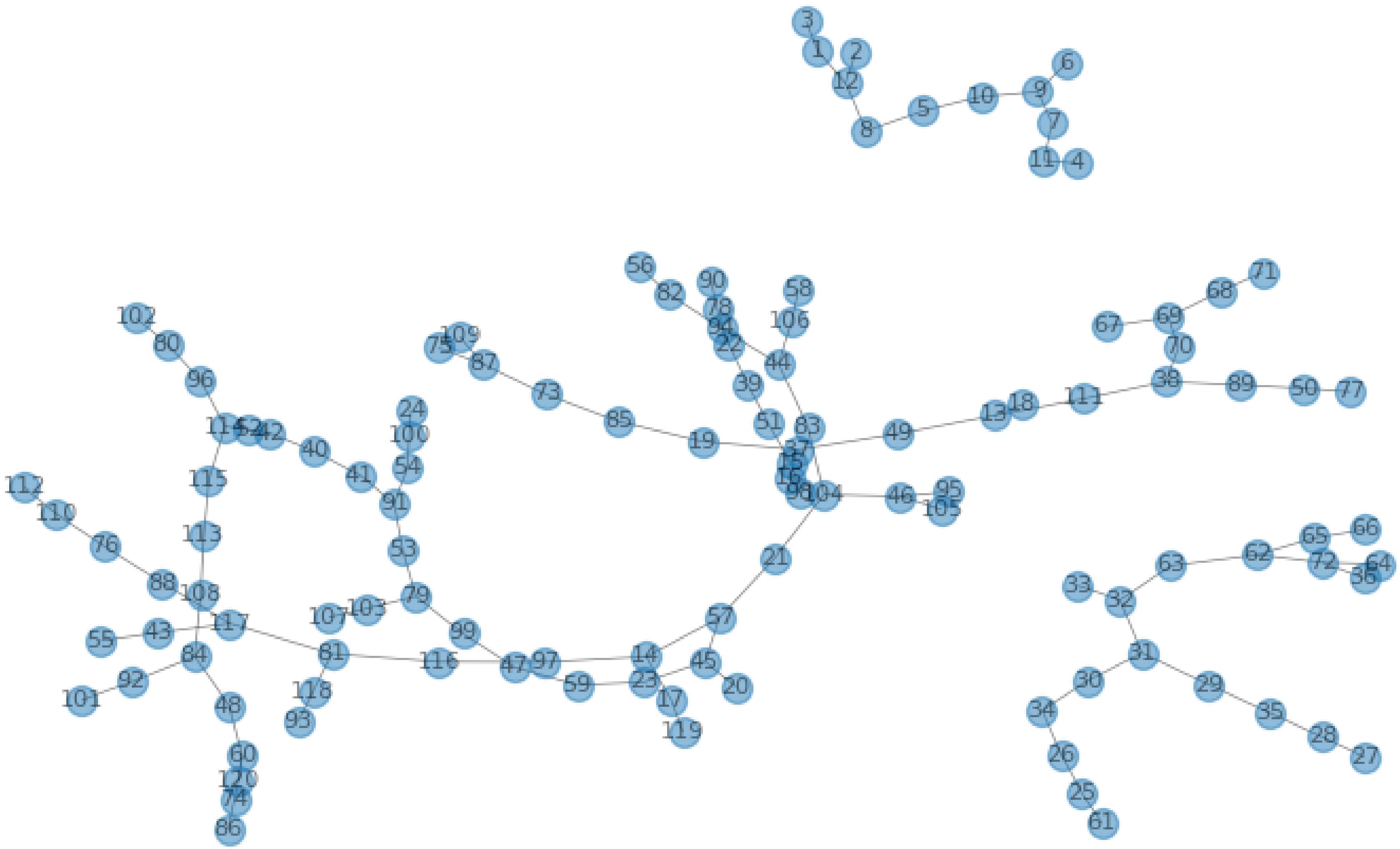


Figure II.S4 - The divisive MST-based clustering found in the three clusters. Note that the first smallest cluster comprises the replicates of samples 1 (1-12), the second for samples 3 (25-36), and 6 (62-66 and 72)



GENERAL CONCLUSION

The findings of this thesis demonstrate the relevance of advanced analytical and statistical techniques in addressing critical challenges in bioenergy generation within the sugar-energy sector, particularly in scaling control and water quality management. The integration of laboratory instrumental methods and robust statistical tools enabled the identification of patterns, critical variables, and preventive solutions to optimize industrial processes and minimize negative impacts.

In Chapter I, the use of ED-XRF was essential in characterizing the chemical composition of scaling deposits in turbogenerators, revealing the predominance of elements such as Ca, Si, S, Cl, and K. This instrumental technique allowed for rapid and reliable analyses, contributing to a detailed understanding of the causes of scaling. The application of PCA to the ED-XRF spectra data identified the main components related to each sample type. Although the analysis was not performed directly on water, the hypothesis, supported by existing literature, suggests that the formation of scaling is associated with the chemical composition of the water used in the processes.

In Chapter II, the study advanced the application of statistical tools to process and interpret data obtained from laboratory analyses. Chemometric methods, including PCA and MST, were employed to evaluate 120 water and steam samples, identifying purity patterns and critical variables such as conductivity, SiO_2 content, and pH. These exploratory approaches eliminated subjective biases, providing a solid scientific foundation for informed decision-making in water treatment.

The integrated use of instrumental techniques and advanced statistical tools not only reinforced the accuracy of the results but also allowed for the visualization of trends and the identification of underlying causes of operational problems. These complementary methodologies highlighted the importance of preventive practices, such as continuous monitoring and the improvement of water treatment protocols, to ensure operational efficiency and sustainability.

As a practical contribution, this work offers well-grounded guidelines for preventive monitoring and water treatment in biorefineries. Additionally, it promotes the preservation of critical equipment, such as boilers and turbogenerators, reduces operational costs, and supports industrial sustainability. The presented results also provide a replicable model for other industries that generate bioelectricity through steam production.

In summary, this thesis integrates laboratory techniques, statistical tools, and chemometric analyses to propose sustainable and comprehensive solutions for managing industrial processes. The contributions presented here strengthen the competitiveness and sustainability of the sugar-energy sector while offering a solid foundation for the development of more innovative and responsible industrial practices.

APPENDIX A

CHAPTER I

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APPENDIX B

CHAPTER II

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