NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY POLITEHNICA BUCHAREST

FACULTY OF CHEMICAL ENGINEERING AND BIOTECHNOLOGIES DOCTORAL SCHOOL:

CHEMICAL ENGINEERING AND BIOTECHNOLOGIES

Studies and Research on the Identification of Chemical Markers and Lycopene in Tomato Fruits

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I.INTRODUCTION

Tomato (Solanum lycopersicum, synonym: Lycopersicon esculentum) is one of the most appreciated vegetables worldwide, recognized for its accessibility, nutritional value, and wide range of culinary uses, being a key ingredient in numerous dishes. It belongs to the Solanaceae family, alongside peppers, potatoes, and tobacco. Although today it is a staple crop, about two centuries ago, tomatoes were considered toxic in the United States due to their botanical classification.

Botanically, the tomato is a fruit, but in culinary practice, it is treated as a vegetable. It holds an important place in Romanian agriculture and commerce, being widely cultivated. In the current context, the chemical characterization of tomato fruits and their processing by-products has gained increased importance, as it allows for quality assessment, product authentication, and prevention of food fraud. Identifying chemical markers also contributes to understanding the relationship between chemical composition and sensory properties (taste, aroma, texture), and studies in this field support the importance of tomatoes as a source of nutrients and bioactive compounds with health benefits.

This doctoral thesis aimed to perform a complex analytical characterization of by-products obtained from Romanian tomato varieties (Kristinica, Darsirius, Florina, Hera, Andrada, Flaviola, and Ema de Buzău), considering parameters such as pH, titratable acidity, micro- and macroelement content, dry matter, and lycopene. The research was conducted over two years (2021–2022) and included both the evaluation of the effects of peel and seed removal and the analysis of changes caused by freezing on chemical composition.

The thesis is structured in two parts. The first part presents the theoretical foundations, general characteristics of tomato fruits, analytical methods used (gravimetric, volumetric, electrochemical, ICP-OES), and strategies for valorizing processing by-products. The second part includes four experimental chapters: (II) study of the effect of peel and seed removal on physicochemical parameters, (III) evaluation of changes in micro- and macroelement and carotenoid content at low temperatures, (IV) analysis of the antioxidant capacity of tomato powder using the FRAP test, and (V) data integration for formulating sustainable valorization strategies.

The results highlighted the decisive role of the variety in determining chemical composition, more so than cultivation conditions. The study also confirms that the whole fruit is

an optimal source of nutrients and antioxidants, while the peel and seeds also have high functional value, justifying their use as secondary products.

These conclusions support the development of sustainable solutions for horticultural resource utilization and the transfer of knowledge to the food and nutraceutical industries. The originality and relevance of the research were confirmed by the publication of two articles in specialized journals: two papers in the *Scientific Bulletin. Series B. Chemistry and Materials Science* and one article in *Horticulturae* (Q1, IF: 3), attesting to the scientific and practical value of the results obtained.

II. OWN RESEARCH

This chapter brings together the research conducted to characterize the main physicochemical parameters of tomato fruits—essential indicators for quality, nutritional value, and subsequent technological use. The objective was to obtain a detailed overview of the basic characteristics that can guide both variety selection and the development of sustainable and efficient processing methods.

The chapter presents the physicochemical analysis of Romanian tomato varieties (Kristinica, Darsirius, Florina, Hera, and Andrada), focusing on key parameters for quality and technological valorization. Samples were processed in two variants (with and without peel), then homogenized and stored at −20 °C.

The tomatoes were cultivated at the Buzău Vegetable Research Station under controlled conditions, with drip irrigation and neutral soil. Determinations included: pH, titratable acidity, moisture, dry matter, ash content, nitrates, nitrites, and mineral profile. Analyses were performed using validated methods (gravimetric, volumetric, reflectometric, and ICP-OES), providing precise and reproducible data.

The results contribute to the evaluation of the nutritional and functional value of tomatoes, supporting variety selection and the development of sustainable processing methods.

II.1. EXPERIMENTAL RESULTS ON THE EFFECT OF PEEL AND SEED REMOVAL ON THE PHYSICOCHEMICAL PROPERTIES OF TOMATO FRUITS, COMPARING THE 2021 AND 2022 HARVESTS

This chapter analyzes the influence of peel and seed removal on the physicochemical properties of tomato fruits, comparing the 2021 and 2022 harvests. The study highlights variations in quality parameters depending on fruit processing, offering insight into the impact of climatic and technological conditions on their composition.

pH determination revealed values between 4.59 and 5.29 for both production cycles, confirming the moderate acidity typical of the Solanum lycopersicum species, with implications for microbiological stability and sensory properties (Table 1).

Table 1. pH determination of various tomato fruit samples without seeds and samples without peel and seeds (1 – year 2021, 2 – year 2022) obtained from the studied varieties

Tomato type	pH (seedless sample)	pH (sample without peel and seeds)
$Kristinica_1$	4,75 ± 0,05	4,67 ± 0,20
$Kristinica_2$	4,88 ± 0,03	4,83 ± 0,13
$Darsirius_1$	4,86 ± 0,06	4,88 ± 0,08
$Darisirius_2$	4,79 ± 0,04	4,79 ± 0,09
$Florina_1$	5,29 ± 0,09	4,75 ± 0,05
$Florina_2$	4,60 ± 0,05	4,76 ± 0,06
$Hera_1$	4,59 ± 0,04	4,75 ± 0,05
$Hera_2$	5,29 ± 0,04	4,83 ± 0,06
$Andrada_1$	4,66 ± 0,03	4,76 ± 0,06
$Andrada_2$	4,67 ± 0,02	4,60 ± 0,05

Values expressed as arithmetic means obtained from three measurements per tomato variety.

The pH values for the studied tomato varieties show minor variations between seedless samples and those without peel and seeds. In general, the removal of peel and seeds does not significantly alter acidity, with pH remaining in the range of 4.59–5.29, typical for moderately acidic tomatoes.

Titratable Acidity Determination

Table 2. Titratable acidity determination for various tomato fruit samples without seeds and samples without peel and seeds (1–year 2021, 2–year 2022) obtained from the studied varieties

Tomato type	Fruit weight (g)	Citric acid % (mg/100g) – seedless sample	Citric acid % (mg/100g) – sample without peel and seeds
Kristinica$_1$	10	0,17 ± 0,03	0,18 ± 0,03
Kristinica$_2$		0,07 ± 0.02	0,06 ± 0,02
Darsirius$_1$	10	0,23 ± 0,03	0,18 ± 0,03
Darisirius$_2$		0,07 ± 0,03	0,06 ± 0,03
Florina$_1$	10	0,18 ± 0,02	0,17 ± 0,03
Florina$_2$		0,08 ± 0,03	0,07 ± 0,02
Hera$_1$	10	0,18 ± 0,04	0,13 ± 0,03
Hera$_2$		0,09 ± 0.03	0,06 ± 0,03
Andrada$_1$	10	0,24 ± 0.04	0,16 ± 0,03
Andrada$_2$		0,10 ± 0,03	0,12 ± 0,03

The fruit weight was consistent (10 g) across all tomato varieties. Citric acid content was higher in seedless samples compared to those without peel and seeds. Kristinica, Darsirius, and Florina showed a slight decrease in citric acid after peel removal. Hera exhibited a more noticeable difference between the two types of samples. Andrada maintained the highest level of citric acid, even after the removal of peel and seeds. Overall, removing peel and seeds slightly reduces acidity, but the differences vary depending on the variety.

Determination of Moisture Content and Dry Matter Content

Table 3. Moisture content (U%) and dry matter content (DM%) for various tomato fruit samples without seeds and samples without peel and seeds (1 – year 2021, 2 – year 2022) obtained from the studied varieties

Tomato type	U% – seedless sample	U% – sample without peel and seeds	DM% – seedless sample	DM% – sample without peel and seeds
Kristinica$_1$	94,27 ± 0,07	93,57 ± 0,10	5,73 ± 0,04	6,43 ± 0,05
Kristinica$_2$	93,71 ± 0,12	94,39 ± 0,11	6,29 ± 0,05	5,61 ± 0,06
Darsirius$_1$	93,35 ± 0,08	93,07 ± 0,07	5,65 ± 0,05	6,99 ± 0,10
Darisirius$_2$	94,17 ± 0,09	93,79 ± 0,10	5,83 ± 0,06	6,21 ± 0,06
Florina$_1$	93,91 ± 0,07	94,19 ± 0,11	6,09 ± 0,09	5,81 ± 0,06
Florina$_2$	93,09 ± 0,09	94,17 ± 0,11	6,92 ± 0,10	5,83 ± 0,06
Hera$_1$	93,73 ± 0,12	94,43 ± 0,13	6,28 ± 0,08	5,57 ± 0,07
Hera$_2$	92 ± 0,10	91,60 ± 0,11	8,01 ± 0,12	8,40 ± 0,10
Andrada$_1$	94,43 ± 0,12	93,42 ± 0,12	5,57 ± 0,07	6,58 ± 0,09
Andrada$_2$	94,23 ± 0,12	92,50 ± 0,10	5,77 ± 0,07	7,50 ± 0,10

U% (moisture) varies slightly between samples but remains high (>92%) across all varieties, indicating a high water content.

DM% (dry matter) is higher in samples without peel and seeds for most varieties, suggesting that removing these parts concentrates the dry matter. Hera and Andrada showed the greatest variations in DM%, highlighting a more pronounced influence of processing on composition. Overall, removing peel and seeds slightly reduces moisture and increases dry matter concentration.

Determination of Ash Content (Cd%) The determinations performed on tomato samples revealed notable variations in organic matter and ash content, influenced both by the variety and the type of sample analyzed (seedless vs. without peel and seeds) (Table 4).

Table 4. Ash content (Cd%) for various tomato fruit samples without seeds and samples without peel and seeds (1 – year 2021, 2 – year 2022) obtained from the studied varieties

Tomato type	Organic matter MO%	Cd% – seedless sample	Organic matter MO%	Cd% – sample without peel and seeds
Kristinica$_1$	86,40 ± 0,40	13,60 ± 0,46	86,18 ± 0,51	13,82 ± 0,45
Kristinica$_2$	93,04 ± 0,37	6,96 ± 0,42	91,27 ± 0,64	8,73 ± 0,51
Darsirius$_1$	86,20 ± 0,79	13,80 ± 0,55	89,54 ± 0,65	10,46 ± 0,55
Darisirius$_2$	91,15 ± 0,48	8,85 ± 0,46	92,38 ± 0,65	7,62 ± 0,46
Florina$_1$	87,44 ± 0,72	12,56 ± 0,46	88,70 ± 0,66	11,31 ± 0,45
Florina2	93,44 ± 0,66	6,56 ± 0,40	90,01 ± 0,66	9,98 ± 0,40
Hera1	90,64 ± 0,76	9,36 ± 0,50	90,71 ± 0,70	9,29 ± 0,50
Hera2	93,45 ± 0,88	6,55 ± 0,48	94,51 ± 0,70	5,50 ± 0,45
Andrada1	92,38 ± 0,47	7,62 ± 0,40	87,91 ± 0,67	12,09 ± 0,45
Andrada2	93,68 ± 0,97	6,32 ± 0,44	93,20 ± 0,70	6,81 ± 0,45

Organic matter (MO%) was predominant in all samples, with values ranging from 86.18% to 94.51%, confirming the nutritional character of tomatoes. **Ash content (Cd%)** was higher in seedless samples, indicating a greater concentration of mineral salts in the pulp portion. The Kristinica and Darsirius varieties showed the most significant differences between sample types, suggesting an uneven distribution of mineral compounds within the fruit structure.

Determination of Nitrate and Nitrite Content

Table 5. Nitrate and nitrite content (mg/kg) for various tomato fruit samples without seeds and samples without peel and seeds (1 – year 2021, 2 – year 2022) obtained from the studied varieties

Tomato type	Nitrates – seedless sample (mg/kg)	Nitrates – sample without peel and seeds (mg/kg)	Nitrites – seedless sample (mg/kg)	Nitrites – sample without peel and seeds (mg/kg)
Kristinica$_1$	0,732	0,85	1,85	1,60
Kristinica$_2$	0,69	0,60	0,62	0,23
Darsirius$_1$	- 0,32	0,40	0,26	0,45
Darisirius$_2$	0,81	0,38	2,50	0,47
Florina$_1$	- 0,37	2,40	0,35	1,44
Florina$_2$	0,18	2,53	2,92	1,52
Hera$_1$	- 0,06	1,77	0,70	3,52
Hera$_2$	6,57	1,86	4,07	3,70
Andrada$_1$	1,14	0,40	0,14	0,29
Andrada$_2$	2,30	0,42	2,97	0,31

Nitrate content varies significantly between varieties and sample types, generally being higher in samples without peel and seeds. **Nitrite levels** are higher in seedless samples, indicating a possible accumulation in the pulp. The **Hera variety** shows the highest concentrations of nitrates and nitrites, especially in samples without peel and seeds. Overall, the removal of peel and seeds influences the content of nitrogen compounds, with variations depending on the variety.

Determination of mineral content. The results obtained from the analyzed samples, comparing the 2021 production with that of 2022, are illustrated in Figures 1, 2, 3, and 4.

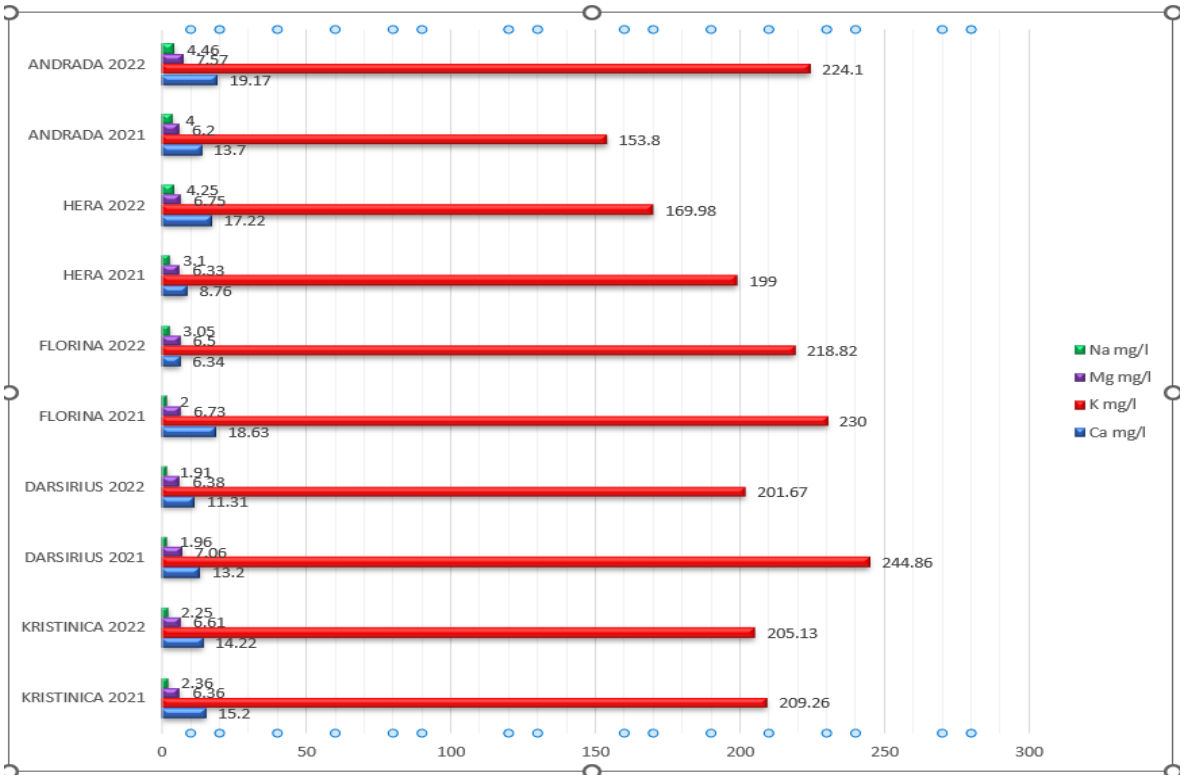


Fig. 1. Macroelement content in various seedless tomato fruit samples

- Calcium (Ca): Values vary significantly between years and varieties. Florina 2021 and Andrada 2022 showed the highest concentrations, suggesting that cultivation conditions influence Ca accumulation.
- Potassium (K): The dominant element in all samples, with peak values in Darsirius 2021 (244.86 mg/l), indicating good ripening and osmotic balance.
- Magnesium (Mg): Remains relatively stable across varieties and years, with slight increases in Andrada 2022 (7.57 mg/l), possibly reflecting intense metabolic activity.
- Sodium (Na): Values increased in 2022 for most varieties, especially Hera and Andrada, suggesting a possible influence of irrigation or soil on Na absorption.

Overall, year-to-year variations reflect the impact of environmental and technological factors on the mineral composition of tomatoes.

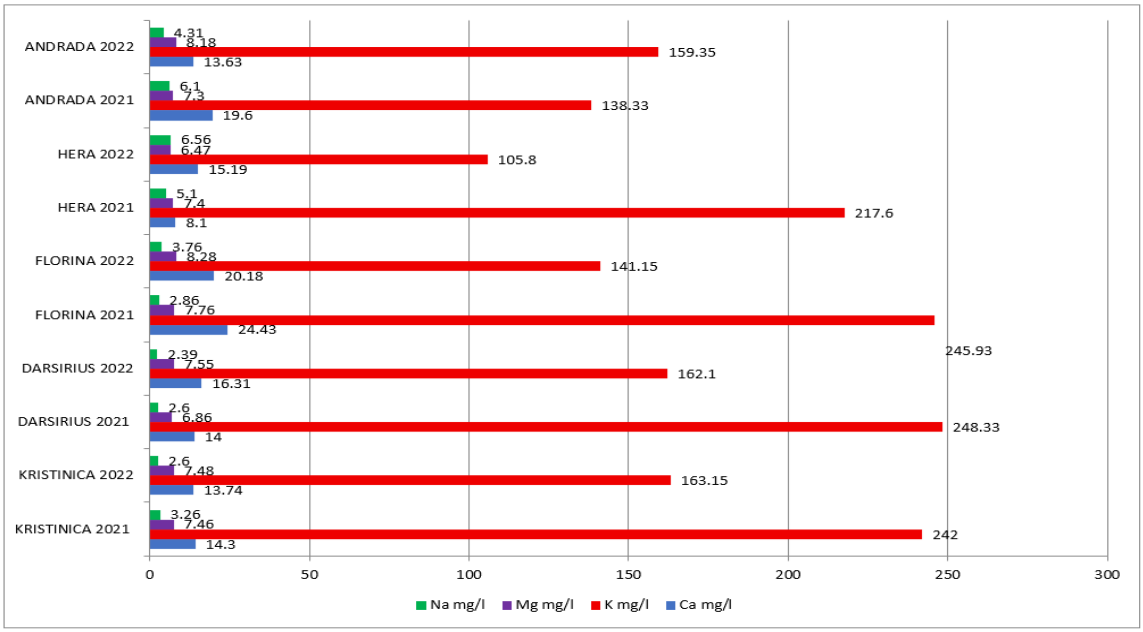


Fig. 2. Macroelement content in various tomato fruit samples without peel and seeds

- Calcium (Ca): Highest in Darsirius and Kristinica, indicating good cellular structure.
- Potassium (K): Consistent across varieties, essential for ripening.
- Magnesium (Mg): Slightly higher in 2022, reflecting metabolic activity.
- Sodium (Na): Increased in 2022, possibly influenced by soil or irrigation.

Year-to-year differences highlight the impact of cultivation conditions on the mineral composition.

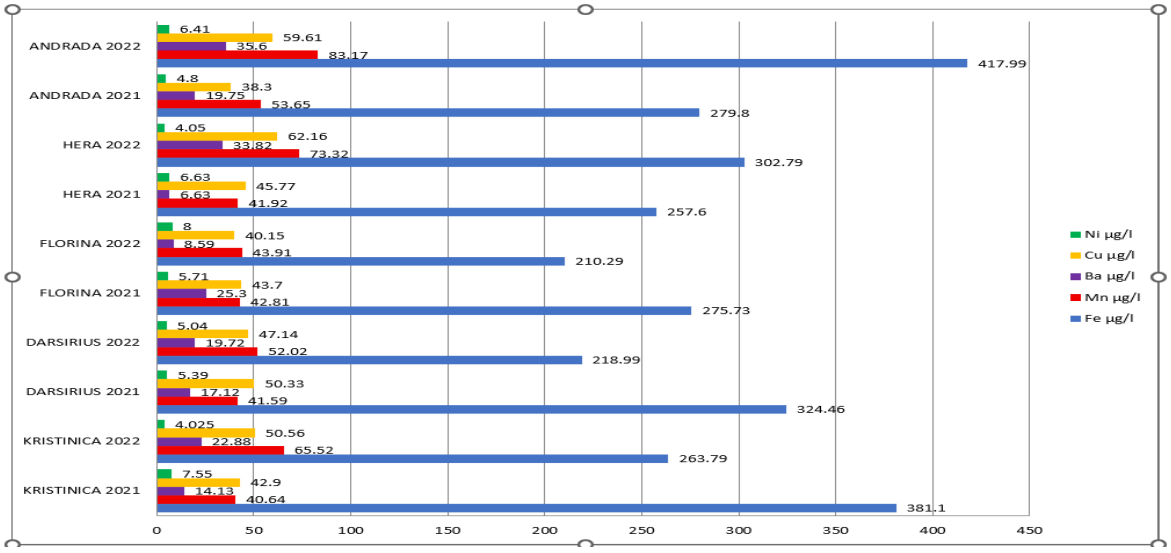


Fig. 3. Microelement content in various seedless tomato fruit samples

- Manganese (Mn): The dominant element in all samples, with the highest values in Kissintzos 2021 and Andrada 2022, indicating significant accumulation.
- Copper (Cu) and Zinc (Zn): Elevated levels found only in Andrada samples, while other varieties show uniformly low concentrations.
- Nickel (Ni): Remains constant across all samples, with no significant variations.

Overall, Andrada 2022 exhibits the highest total metal concentration, which may reflect the influence of environmental or technological conditions during that year.

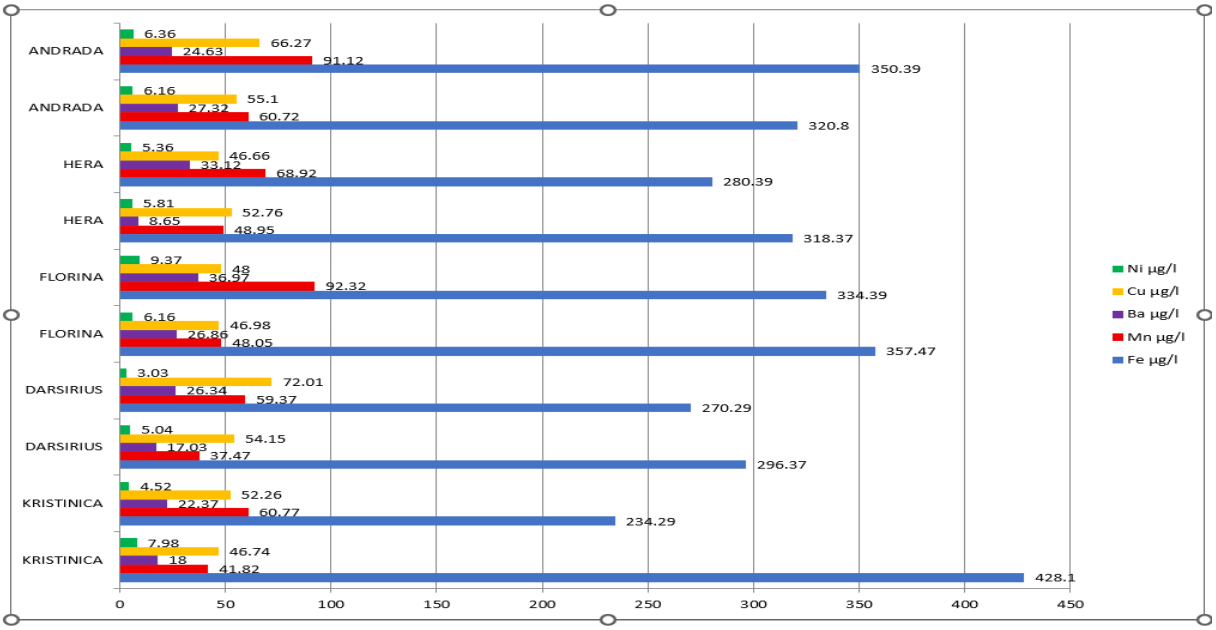


Fig. 4. Microelement content in various tomato fruit samples without peel and seeds

- Iron (Fe): The dominant element in all samples, with peak values in Kristinica (428.1 μg/g), indicating significant accumulation and high nutritional potential.
- Barium (Ba) and Nickel (Ni): Show moderate and consistent values across samples, with no significant variations.
- Copper (Cu): Evenly distributed in all samples, with stable values (~4.16 μg/g).
- Manganese (Mn): Has the lowest concentrations but is present in all samples, with slight variations.

Overall, Fe is the main contributor to total metal load, and differences between samples reflect the influence of environmental conditions and soil composition on element absorption.

II. Research on Changes in Micro- and Macroelement Content and Carotenoids (Lycopene and β-Carotene) in Tomato Fruits Exposed to Low Temperatures

Tomatoes (*Lycopersicum*) are botanically classified as fruits but legally considered vegetables. Due to their short growing season, freezing is a common method used to preserve their nutritional qualities. This study analyzes the effects of 12-month freezing on the physical and chemical properties of cherry tomatoes (*Flaviola* and *Ema*), extending beyond the duration of previous research. Low temperatures reduce microbial activity, prolonging shelf life. They also influence the texture and chemical composition of the fruit, with variable effects on nutrients. Analyses included the determination of micro- and macroelement content using ICP-OES, as well as lycopene and β-carotene levels using the Nagata & Yamashita method. Comparison of fresh and frozen samples revealed significant changes in physicochemical parameters, relevant for assessing quality and improving tomato varieties.

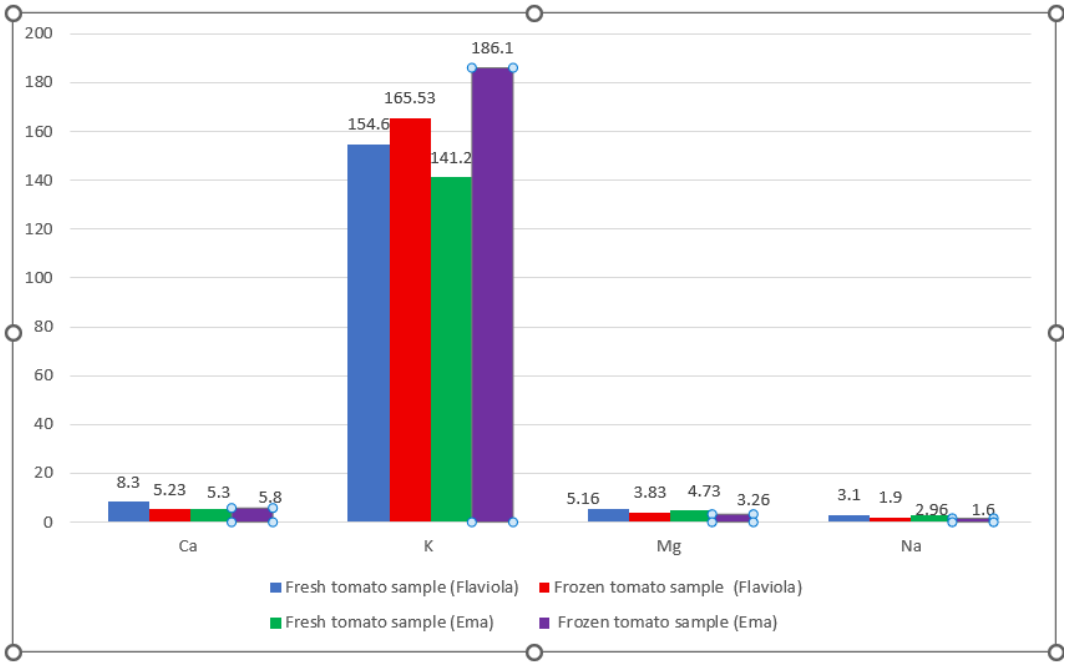


Fig. 5. Macroelement content (mg L^{-1}) in fresh and frozen tomat samples, Ema and Flaviola varieties

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Calcium (Ca): Decreases significantly after freezing, especially in Flaviola, indicating a possible loss of cellular structure.

Potassium (K): Increases in both varieties after freezing, suggesting internal redistribution of ions during the process.

Magnesium (Mg): Drops following freezing, which may affect enzymatic activity and nutritional value.

Sodium (Na): Shows a visible reduction after freezing, particularly in Ema, possibly due to loss through exudate.

Overall, freezing influences the mineral composition of tomatoes, with variety-specific variations**.**

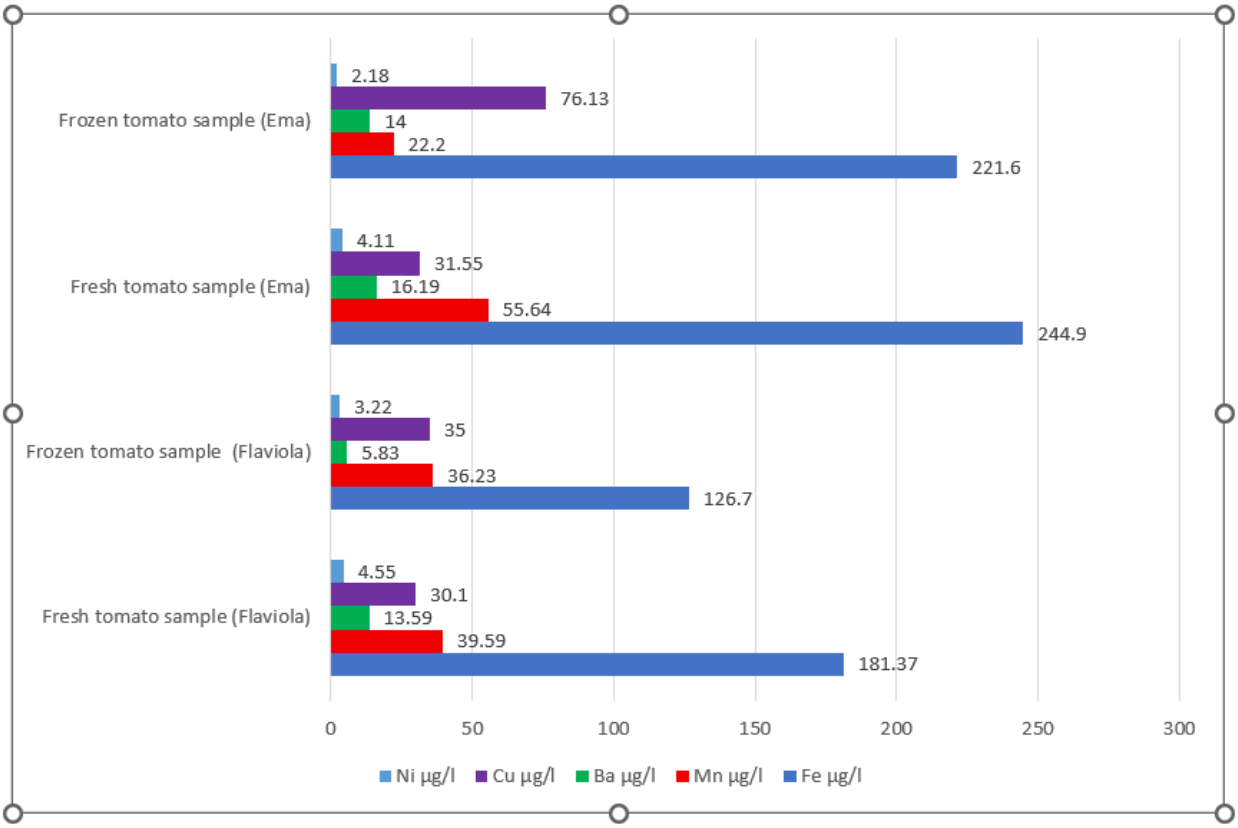


Fig. 6. Microelement content (µg L^{-1}) in fresh and frozen tomato samples, Ema and Flaviola varieties

Fe (Iron), Mn (Manganese), Ba (Barium), and Ni (Nickel) decrease after freezing in both varieties.

Cu (Copper) increases significantly after freezing, especially in Ema.

Additionally, Ema shows higher values for most elements in its fresh state.

Freezing affects each element differently, possibly due to structural changes in the tissue.

Table 6. Effect of the freezing method on the physicochemical properties of tomatoes (1 – fresh sample, 2 – frozen sample**)**

Tomato type	Lycopene mg (100 mL)$^{-1}$	β-carotene mg (100 mL)$^{-1}$
Ema_1	0,76 ± 0,01	0,14 ± 0,04
Ema_2	0,26 ± 0,01	0,35 ± 0,02
$Flaviola_1$	0,98 ± 0,03	0,11 ± 0,01
$Flaviola_2$	0,60 ± 0,01	0,22 ± 0,02

The values represent the average of three repetitions ± standard deviation (p ≤ 5 ppb)

Conclusion: The tomato varieties analyzed here can be considered good sources of certain mineral elements, some of which possess antioxidant properties. These results may contribute to the conservation of a significant part of agricultural biodiversity, and the high content of minerals and trace elements detected in these varieties is potentially useful for tomato breeders working on developing new cultivars with improved composition.

IV. Evaluation of the Antioxidant Capacity of Tomato Powder Using the FRAP Test – An Ecological Approach to Valorizing Tomato Fruits

The study analyzes powder obtained from three local tomato varieties (*Hera*, *Andrada*, *Kristinica*) as an ecological solution for valorizing by-products and reducing food waste. Antioxidant capacity was evaluated using the FRAP test, highlighting the role of bioactive compounds (lycopene, polyphenols) in neutralizing free radicals. *Hera* stood out with the highest dry matter content, making it ideal for processing, while *Kristinica* showed a balanced profile. Although limited, the FRAP method provides an effective assessment of antioxidant potential, supporting technological optimization and sustainable use of tomatoes.

Table 7. Physicochemical characterization of different tomato varieties

Tomato type	Moisture (%)	Dry matter (%)
KRISTINICA	93,71	6,29
ANDRADA	94,23	5,77
HERA	91,99	8,01

The values are expressed as the arithmetic mean obtained from five determinations for each tomato

variety. Hera – lowest moisture and highest dry matter content; ideal for industrial processing, retaining a high concentration of bioactive compounds. Andrada – highest moisture and lowest dry matter content; suitable for fresh consumption, but less efficient for processing. Kristinica – intermediate values; versatile, balancing nutritional properties and texture, making it suitable for both consumption and processing.

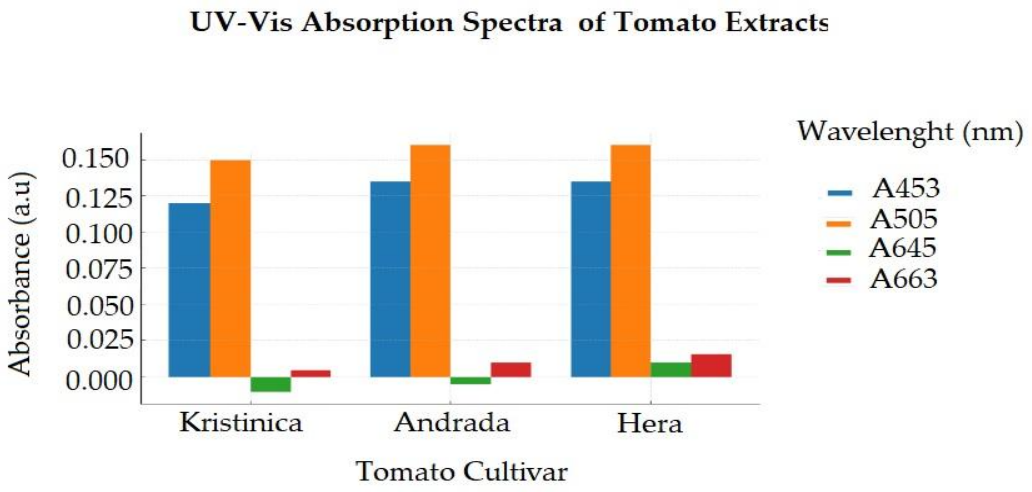


Figure 7. UV-Vis Absorption Spectra of Tomato Extracts.

The results indicate that tomato powder retains significant antioxidant activity, suggesting its potential as a functional ingredient in various fields. This confirms the effectiveness of the processing method used in preserving active compounds.

II.1.1. Values determined by the FRAP test

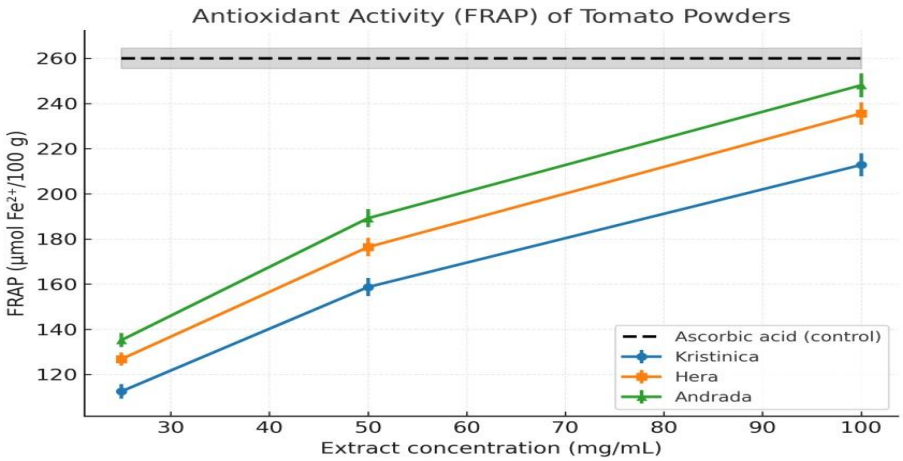


Fig. 8. Antioxidant activity (FRAP) of tomato powder at different concentrations.

The results indicate a concentration-dependent increase in reducing power, with the Andrada variety showing the highest activity, followed by Hera and Kristinica. The values obtained in this study suggest that the drying techniques applied, along with the choice of varieties and harvest timing, contributed to the production of powders with antioxidant activity comparable to that of ascorbic acid, a reference antioxidant.

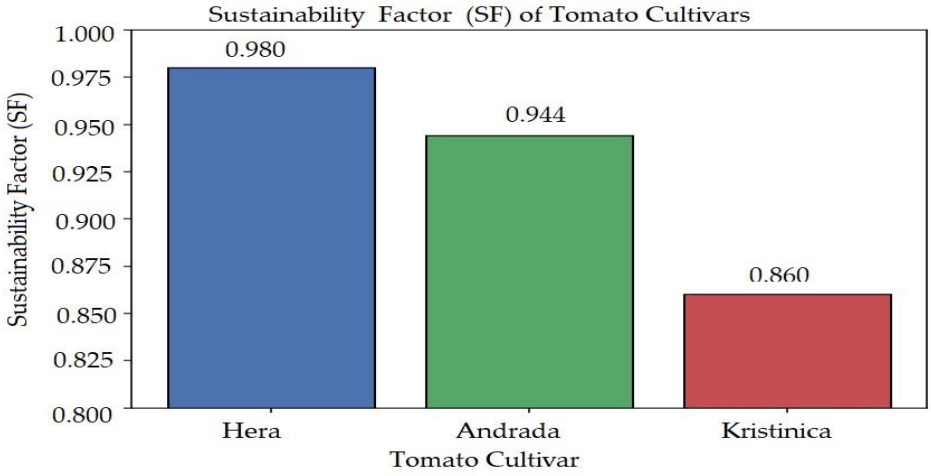


Fig. 9. Sustainability Factor (SF) of Tomato Powders.

Hera stood out as the optimal variety, with the highest lycopene content, elevated FRAP

values, and the highest AEI (0.975) and IENSI (0.983) indices, highlighting the balance between antioxidant activity and processing efficiency. Tomato powders retain the bioactive properties of fresh fruit and can be used both functionally and industrially, supporting the ecological valorization of tomato by-products.

CONCLUSIONS AND RECOMMENDATIONS

This study highlights the potential for valorizing tomatoes and their by-products in industrial, ecological, and nutritional contexts. Powders obtained from the Hera, Andrada, and Kristinica varieties stand out for their high lycopene content and antioxidant activity, making them promising ingredients for functional food products such as beverages, instant soups, or fortified snacks. From an ecological perspective, reusing by-products (pulp, peels, seeds) significantly contributes to reducing agri-food waste and supports the principles of circular agriculture. Valorizing non-compliant tomatoes and processing residues represents a sustainable strategy for combating food waste, facilitating the transition to a more efficient and less polluting food system. The physicochemical analysis of tomato fruits highlighted the structural role of peels and seeds in determining overall composition, as well as the influence of low-temperature storage on the stability of bioactive compounds.

Recommendations from this research include:

- Optimizing processing technologies for full fruit utilization
- Implementing controlled storage to maintain nutritional quality
- Exploring innovative nanoparticle treatments for post-harvest protection
- Developing ecological methods for extracting bioactive compounds

These directions can support both future research and practical applications in horticulture and the food industry, contributing to sustainable development and reducing environmental impact.