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Physicochemical and aromatic properties of iron-enriched tomato paste during storage

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tomato paste.

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ARTICLE INFO	A B S T R A C T
A R T I C L E I N F O Keywords: Tomato paste pH TSS Viscosity Acidity	In this study, tomato paste was fortified with iron compounds at 25, 50, and 75 ppm concentrations. The effect of adding these micronutrient iron concentrations on the paste's physical, mechanical, aromatic, and chemical properties was evaluated every 15 days over a 60-day, storage period. The results indicated a gradual decrease in pH, total soluble solids (TSS), and taste index, alongside an increase in total acidity (TA) for all treatments throughout the storage period. The highest lycopene content observed in the Fe-25 % fortified samples at 43.05 mg/kg and the lowest in the control samples at 21.57 mg/kg. Positive values for a* and b* at the beginning and throughout the storage period confirmed the dominance of red and yellow hues in the tomato paste. Viscosity gradually decreased over time. During storage, growth and changes in mold spores and acid-resistant thermophilic bacteria were limited until the 30th day, and total microorganism counts were restricted until the 45th day. The overall accuracy of the support vector machines (C-SVM) and linear discriminant analysis (LDA) method in distinguishing samples into four groups (control, fortified with 25, 50, and 75 ppm iron) were 38 % and 62 % Overall, it can be concluded that increasing the iron micronutrient enhances the nutritional value and positively affects the physical, chemical, and microbial properties and the retention of aromatic compounds in

1. Introduction

Iron is a crucial micronutrient for human health, and its deficiency can lead to anemia, affecting about 30 % of the global population, especially women and adolescents. It can also result in cognitive impairment and decreased immunity (Johnson et al., 2012). Food and food products fortified with iron are the most common and cost-effective strategies to alleviate iron deficiency among humans being (Garcia-Banuelos et al. 2014). Nutrition experts regard food and beverage fortification as one of the best methods for obtaining essential micronutrients. Fortification is the addition of one or more essential nutrients to food products at levels higher than what might naturally occur, aiming to prevent and correct deficiencies affecting entire communities or specific population groups (Stanton et al., 2001). Tomato (Solanum lycopersicum) is among the most popular and significant agricultural products. Due to its diverse functional and technical characteristics, tomatoes can be processed into various products. Among tomato-based products, canned tomatoes, concentrates, sauces, and ketchup are highly demanded, with tomato paste being the most common (Vitalis et al., 2020). Many researchers have reported that tomatoes are rich in bioactive compounds, including polyphenols, lycopene, β -carotene, vitamin C, and dietary fibers (He et al., 2022). Clinical studies have shown that consuming tomato-based products can enhance plasma antioxidant capacity and improve oxidative status and carcinogenic risk (Basu & Imrhan, 2007; Vitaglione et al., 2007). These effects are attributed to the bioactive compounds present, such as carotenoids (lycopene, α - and β -carotene), polyphenols (phenolic acids and flavonoids), and vitamins (ascorbic acid and vitamin A) (Salehi et al., 2019).

Research has been done in the field of food enrichment with iron as well as tomato paste enrichment in recent years, some of which are:

Allen (2002) used amino acid–chelated ferrous bis-glycinate as an iron source in whole maize meal and found that the bisglycinate has higher redox potential and subsequently greater tendency to cause lipid oxidation which causes adverse organoleptic changes. Hilty et al (2009)

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applied iron- and zinc-containing nanostructured powders in banana milk, chocolate milk, and yogurt and result showed these powders are promising for food fortification and other nutritional applications. Soloty (2002) examined the efficacy of Allium sativum (garlic) as a preservative in the tomato paste industry, utilizing fresh garlic and garlic extract at concentrations of 0.125 %, 0.25 %, 0.5 %, 0.75 %, 1 %, 1.5 %, 2 %, 2.5 %, and 3 %. The results indicated that concerning tomato paste's chemical, physical, and taste properties, fresh garlic and chloroformic garlic extract at minimum inhibitory concentrations did not significantly affect the chemical and physical properties. However, taste changes were subjectively assessed as either desirable or undesirable (Soloty, 2002). Jafari et al., (2021) investigated the effects of phenolic olive leaf extracts, in both encapsulated and non-encapsulated forms, and sodium benzoate, a common preservative, on total soluble solids (TSS), pH, color indices, consistency, and the growth rate of Aspergillus flavus mold in tomato paste at concentrations of 500 and 1000 ppm. The results demonstrated that encapsulated olive leaf extract effectively and sustainably preserved tomato paste, improving its shelf life and maintaining its physical, chemical, and microbiological properties over an extended period. Given the factors above and the rising incidence of iron deficiency-related diseases, along with a lack of research, fortifying foods, especially widely consumed ones like tomato paste, appear essential (Jafari et al., 2021).

In addition to traditional experimental methods for assessing the quality of food and agricultural products, which involve evaluating their physical, chemical, and microbial properties, one non-destructive and practical approach is using an electronic nose system. This system simulates the human olfactory system and detects the headspace aroma of samples using an array of sensors (Modupalli et al., 2021). An electronic nose contains various gas sensors that produce signals in response to odor molecules (Kiani et al., 2016). The electronic nose has found numerous applications, from environmental process control (Kashwan & Bhuyan, 2005) to medical uses (Längkvist & Loutfi, 2011), and has been extensively studied in the food industry (Sanaeifar et al., 2017).

Therefore, the objectives of this study are as follows:

Fortification of tomato paste with iron compounds at 25, 50, and 75 ppm concentrations.

Comparing the chemical properties of the samples at time intervals of 0, 15, 30, 45, and 60 days post-preparation, including pH, acidity, Lab^* color values, Brix, viscosity, lycopene, and vitamin C.

Comparing the microbial characteristics of the samples at time intervals of 0, 15, 30, 45, and 60 days post-preparation, focusing on mold spores growth, acid-resistant thermophilic bacterial growth, and total microorganism counts.

Evaluating the aromatic compounds of the samples at time intervals of 15, 30, 45, and 60 days post-preparation using an electronic nose system.

2. Materials and methods

2.1. Sample preparation and fortification

Tomato paste samples with specific characteristics (TSS = 27.9 and pH = 4.15) were obtained on the day of production from Sahar Food Industries, located in Hamedan Province, Iran. On day zero, the samples were transported under controlled conditions (4) °C) to the Pishgaman Part laboratory, where fortification was conducted. The samples were divided into four groups: control and those fortified with 25, 50, and 75 ppm iron. Initially, each paste sample was divided into three 100 g portions, and 25, 50, and 75 mg of ammonium iron(III) sulfate were added and mixed into each portion. Each 100 g portion was then added to a 900 g portion and thoroughly mixed, resulting in 25, 50, and 75 mg/kg (ppm) concentrations. After classification, the fortified samples were packaged in specialized containers and stored for 60 days at 4 °C with 75 % relative humidity. Tests were conducted every 15 days on days 0,

15, 30, 45, and 60 for all treatments.

2.2. Physicochemical tests on tomato paste

2.2.1. Measurement of TA, pH, and TSS

Chemical properties are crucial in determining the quality of food products, such as tomato paste, during production and storage, as they indirectly indicate internal changes, including microbial activity (Ganje et al., 2016). Fundamental chemical properties include pH, TSS, and TA. In this study, the chemical properties were measured during each period in triplicate. pH was measured using a pH meter (model PHS3-W3B, Italy) with a resolution of 0.01. The device was calibrated with pH 4 and 7 buffer solutions before measuring the samples at 25 °C. TSS was measured using an Atago refractometer (model PLA-2, Japan) with a resolution of 0.01 at 25 °C. The refractometer was calibrated with distilled water, and a uniform sample of tomato paste was filtered through filter paper. A few drops of the filtrate were placed on the refractometer for reading.TA was determined using the association of official analytical chemists (AOAC) method (AOAC, 1984). The total acidity was calculated using the following equation:

$$TA(\% ascitricacid) = \frac{Volume of 0.1NNaOH used \times 0.0064 \times 100}{Weight of sample(g)}$$
(1)

The ratio of TSS/TA was considered the samples' taste or maturity index (Shui & Leong, 2002).

2.2.2. Measurement of lycopene and ascorbic acid (Vitamin C)

An extraction solution was first prepared by mixing 5 mL of 95 % ethanol, 5 mL of pure acetone, and 10 mL of hexane to measure the lycopene content. Then, between 0.4 and 0.6 g of the tomato sample was added to the extraction solution. The resulting mixture was combined using a shaker at 180 rpm for 15 min to achieve a homogeneous mixture. Next, 3 mL of distilled water was added to the samples, and they were shaken for an additional 5 min under the same conditions. The samples were then left for 5 min at room temperature to allow phase separation. The hexane phase (upper phase) was carefully collected, and the absorbance was measured using a spectrophotometer (Unico 2100 UV-Vis) at a wavelength of 503 nm (Fish et al., 2002). Ascorbic acid was measured using an iodometric method, expressed as mg/100 mL. First, 1.269 g of iodine was dissolved in ethanol and mixed with 16.6 g of potassium iodide dissolved in distilled water, and the solution was made up to one liter. The normality of iodine in the above solution is 0.01 N. Ten milliliter of the sample was diluted with 20 mL of distilled water, and 2 mL of starch indicator was added. The mixture was titrated with an iodine solution until the color changed to light gray. Each milliliter of iodine equals 0.88 mg of ascorbic acid (Rahmawati & Bundjali, 2012).

$$X = Vi \times 0.88Vs \times 100 \tag{2}$$

Where:

- X is the mg of ascorbic acid per 100 mL of sample
- $\bullet\ V_i$ is the volume of iodine solution used
- Vs is the volume of the sample in mL

2.2.3. Measurement of color indices

Color is one of the most important physical factors influencing the quality and marketability of food products. Primary color indices such as L (lightness), a (red-green), and b (yellow-blue), and secondary indices such as color change (Δ E) and browning index (BI) are critical for determining the visual quality of agricultural products during storage. The a/b ratio is also significant in assessing the color quality of tomato paste (Katırcı et al., 2020). For this purpose, primary indices were measured using a colorimeter (model HP-200, Shenzhen Handsome Technology Co., Ltd.), and secondary indices were calculated using the following formulas (Gholami et al., 2023; Gholami et al., 2017):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{3}$$

Where x is calculated as:

$$BI = \frac{100(x - 0.31)}{0.172} \tag{4}$$

$$x = \frac{a + 1.75L^*}{5.645L^* + a^* + 3.01b^*}$$
(5)

These indices help assess color changes, which are vital for evaluating the product's quality over time.

2.3. Microbiological tests

2.3.1. Measurement of mold spores

The Howard test (AOAC, 1965) measured mold spores in tomato paste samples.

2.3.2. Examination of thermophile acid resistant bacteria

The growth of thermophilic acid-resistant bacteria was examined using the pour plate method with a 1:10 dilution prepared with sterile physiological serum in plate count agar (PCA) medium. The samples were incubated at 55 $^{\circ}$ C for 96–120 h.

2.3.3. Total microorganism count

The total microorganism count was determined using the pour plate method with a 1:10 dilution prepared with sterile physiological serum in PCA medium. The samples were incubated at 30 °C for 48–72 h (ISO 4833-1:, 2013).

2.4. Mechanical tests

2.4.1. Measurement of viscosity

The viscosity and consistency of the fortified and control samples were measured using the Bostwick method. This method allows a specific fluid volume to flow under its weight within a given time frame. It is considered reliable for viscosity measurement, although it is unsuitable for very thick materials (Bayod et al., 2008). To measure consistency, the tomato paste samples were diluted with distilled water to a Brix level of 12, and their consistency was measured at 25 °C using a Bostwick viscometer. The results are reported as the distance traveled in centimeters over 30 s (Barrett et al., 1998).

2.5. Electronic nose system

The electronic nose system uses metal oxide semiconductor (MOS) sensors. The system components include a sensor chamber, a sample chamber, a micropump, three two-way solenoid valves, a data acquisition system (USB), 5 V and 12 V power supplies, an inlet air filter (activated carbon), and a graphical interface. The procedure involved placing each sample in a sealed chamber directly connected to the olfactory device for 10 min for odor detection. After a specified time, sampling commenced. The total sampling time was 250 s (100 s for sensor cleaning and baseline stabilization, 100 s for sample odor injection into the sensor chamber, and 50 s for sensor cleaning). Data preprocessing was performed to extract features. Data preprocessing aims to enhance sensor response detection and increase accuracy in pattern recognition analysis. A fractional method is used for baseline correction in metal oxide semiconductor sensors (Arshak et al., 2004):

$$Y(t) = \frac{X(t) - X(0)}{X(0)}$$
(6)

Where Y(t) is the dimensionless-preprocessed response, X(0) is the baseline, and X(t) is the sensor response.

3. Data analysis

Data obtained from the experiments (Physicochemical properties) were analyzed using SPSS 19 for analysis of variance (ANOVA) and mean comparison (Duncan's test). Preprocessed data (aromatic properties) were analyzed using C-SVM and LDA with Unscrambler V. 9.7 and MATLAB 2015a software. LDA creates a linear combination of all features, resulting in classification across a series of samples. This function maximizes the ratio of between-group variance to within-group variance. Transformations are conducted so that when new observations are made, the prediction of differences between groups is maximized (Esteki et al., 2017; Varmuza and Filzmoser, 2009). SVM are supervised learning methods based on statistical learning theory, widely used for regression and classification problems. In SVM, C-SVM and NU-SVM methods are primarily used for data classification, each employing different approaches to minimize the error function (Sanaeifar et al., 2017). The evaluation of the accuracy and performance of recognition patterns is based on sensitivity, specificity, and accuracy indices, which are calculated as detailed in previous work by the authors (Gholami et al., 2023).

4. Results and discussion

4.1. Chemical properties

4.1.1. Changes in pH, TA, TSS, and taste index

The values of pH, TSS, TA, and taste index (TSS/TA) during the storage period are shown in Fig. 1. Statistical analysis (ANOVA and mean comparison) results indicate a significant effect (at the 99 % level) of storage duration and fortification, as well as their interaction with all four chemical factors (Tables 1 and 2). The data showed a gradual decrease in pH, TSS, and taste index and an increase in TA for all treatments during storage. The initial values for pH, TSS, TA, and taste index were 4.15 \pm 0.1, 27.80 \pm 0.01, 1.55 \pm 0.01, and 17.97 \pm 0.1, respectively. The suitable pH range for tomato paste is reported to be less than 4.4, and the suitable range for TSS is between 25 and 30 °Brix (Katırcı et al., 2020), with all samples in this study remaining within these ranges at the end of storage. At the end of the storage period, the most significant decrease in pH and increase in TA occurred in the Fe-75 % fortified samples, with changes of 4.9 % and 38.79 %, respectively, and the slightest change was observed in the control samples, with changes of 3.45 % and 13.79 %, respectively. The decreasing trend in pH in this study contrasts, while the decreasing trend in TSS aligns with previous research findings (Jafari et al., 2021). A decrease in pH increases acidity, creating an acidic environment that controls enzymatic activity and microbial growth in food and agricultural products. Therefore, adding substances like iron fortifies the product and potentially extends its shelf life.

4.1.2. Changes in lycopene and ascorbic acid

This section evaluates and statistically analyzes the results of lycopene and ascorbic acid measurements in control and iron-fortified samples. At the beginning of the storage period, the average lycopene and ascorbic acid contents in the control samples were 141.13 \pm 1 mg/ kg and 131.93 \pm 1 mg/100 g, respectively. The trend decreased from start to end of the storage period (Fig. 2), with the highest lycopene content observed in Fe-25 % fortified samples at 43.05 mg/kg (a 69.5 % reduction from day one) and the lowest in the control samples at 21.57 mg/kg (an 84.72 % reduction from day one). Additionally, the highest ascorbic acid content at the end of storage was 5.13 mg/100 g in Fe-75 % fortified samples (a 96.1 % reduction from day one), and the lowest was 4.8 mg/100 g in the control samples (a 96.4 % reduction from day one). Overall, the Fe-fortified samples showed less variation in lycopene and ascorbic acid, likely due to iron's role in stabilizing tomato paste and limiting oxidation by controlling enzymatic activity. Statistical analysis (Table 1) showed that changes in lycopene and ascorbic acid were





Fig. 1. Changes in pH, TSS, TA, and taste index (TSS/TA) during the storage period.

Table 1	
Analysis of variance of physical and chemical properties of tomato pas	te.

	Model	Day	Fe%	Day*Fe%
рН	53.738**	69.764**	70.485**	13.803^{**}
TA	37.455**	72.379**	33.127^{**}	15.019^{**}
TSS	257.052^{**}	988.971**	11.682^{**}	4.551**
Favor	74.073**	196.871^{**}	40.299**	14.215^{**}
Viscosity	93.551**	361.217^{**}	11.378 ^{ns}	5.357*
Lycopene	1201.805^{**}	4770.564**	53.374**	14.303^{**}
Ascorbic	1337.408^{**}	5270.659**	30.245**	20.778^{**}
Mold	60.818^{**}	231.944**	7.822^{**}	4.045**
Microorganism	2708.062^{**}	5087.347**	1108.116^{**}	2264.246^{**}
Bacteria	704.916**	1336.230^{**}	509.533**	481.313^{**}
L*	126.690^{**}	461.382^{**}	26.604*	19.104**
a*	46.952**	179.204^{**}	26.428^{**}	3.113^{**}
b*	25.852^{**}	97.533**	10.271 ^{ns}	1.811 ^{ns}
a*/b*	5.231**	18.656**	6.595**	0.515 ^{ns}
ΔE	213.389^{**}	806.791**	72.934**	19.230^{**}
BI	3.987**	11.761^{**}	0.933 ^{ns}	1.328 ^{ns}

significantly affected by storage duration, Fe fortification, and their interaction at the 99 % level. Duncan's mean comparison (Table 2) also showed significant changes in both factors on days 0, 15, 30, 45, and 60, although the concentration analysis revealed a significant difference in ascorbic acid content between fortified samples and controls but not between 25, 50, and 75 ppm concentrations. Other researchers have reported similar findings on the impact of storage and processing or additives on lycopene changes (Ordóñez-Santos et al., 2009). Lycopene preservation can occur due to enzymatic activity control during storage. Previous research has shown that lycopene directly affects the color of tomatoes and tomato paste, as discussed in this study's color evaluation

section and compared with lycopene data. There is a direct correlation between ascorbic acid, lycopene, and the antioxidant properties of tomatoes and tomato paste (Kelebek et al., 2017). Thus, the results indicate that iron fortification at different concentrations can preserve lycopene and ascorbic acid and maintain the product's antioxidant properties throughout storage.

Control Fe-25ppm Fe-50ppm Fe-75ppm

5. Physical properties

5.1. Color indices

In all agricultural and even food products, color is the first factor customers evaluate and serves as the primary criterion for determining quality and selecting these products. Color significantly influences consumer choice in tomatoes, tomato extract, and tomato paste. The lightness index (L*), red-green index (a*), and yellow-blue index (b*) were measured throughout the storage period. The a*/b* ratio, as well as color change indices (ΔE) and browning index (BI), were calculated using the formulas (Fig. 3). Positive values for a* and b* at the beginning and throughout the storage period confirm the dominance of red and yellow colors in tomato paste. Due to the presence of carotenoids, especially lycopene, the red color is predominant in tomato paste (Ghasemi Baghabrishami & Goli, 2023). The a*/b* ratio is a factor in determining the color quality of tomato paste. Values of 2 and above for this factor indicate superior color, while values between 1.8 and 2 are classified as acceptable (Katırcı et al., 2020). At the beginning of the storage period, the average values of a and the a*/b* ratio for the initial samples were 9.39 \pm 0.27 and 1.90 \pm 0.12, respectively, indicating the acceptable quality of the paste at the start of storage.

Results for a* and the a*/b* ratio throughout the storage period

Table 2

Duncan's Mean Comparison.

Day Properties	0	15	30	45	60	0	Fe Fe-25	Fe-50	Fe-75
pН	4.15 ^a	4.02 ^b	4.01 ^b	4.02 ^b	3.99 ^c	4.07 ^a	4.00 ^b	4.01 ^b	3.99 ^c
TA	1.54 ^d	1.72^{c}	1.75 ^c	$1.90^{\rm b}$	1.99 ^a	1.69 ^b	1.87 ^a	1.89 ^a	1.89 ^a
TSS	27.80 ^a	27.38^{b}	27.15 ^c	25.63 ^d	25.20 ^e	26.63 ^a	26.47 ^b	26.21 ^d	26.30 ^c
Flavor	17.97 ^a	15.89^{b}	15.52^{b}	13.47 ^c	12.70 ^d	15.87 a	14.34b	13.85c	14.06 bc
Viscosity	6.00 ^a	5.94 ^a	5.72^{b}	5.60 ^c	4.84 ^d	5.53 a	5.57 a	5.58 a	5.54 a
Lycopene	141.13 ^a	142.46 ^a	123.57^{b}	95.60 ^c	36.67 ^d	100.88 bc	100.18 ^c	103.36 ^a	101.45 ^{bc}
Ascorbic Acid	131.93 ^a	133.29 ^a	57.97 ^b	35.99 ^c	4.96 ^d	68.29 ^a	59.48 ^b	59.55^{b}	60.80^{b}
Mold	2.66 ^d	5.33 ^d	12 ^c	33.33^{b}	42.66 ^a	22.13 ^{ab}	24 ^a	20.66 ^c	19.66 ^c
Microorganism	0 ^c	3.33 ^c	31.66 ^c	967 ^b	2348 ^a	988 ^b	1130 ^a	776 ^c	207 ^d
Bacteria	0 ^c	0 ^c	2.5 ^c	63.33 ^b	293 ^a	59.06 ^a	48.08 ^b	20 ^d	37.05 ^c
L*	13.84 ^a	13.96 ^a	9.76 ^c	10.34^{b}	7.02 ^d	10.23^{b}	10.46 ab	10.71 ^a	10.59 ^{ab}
a*	9.39 ^a	7.65 ^b	5.67 ^c	5.32 ^c	4.24 ^d	5.72^{b}	5.79 ^b	6.05 ^a	6.15 ^a
b*	4.95 ^a	4.71 ^a	3.83^{b}	3.77 ^b	3.03 ^c	3.81 ^a	3.82 ^a	3.98 ^a	4.01 ^a
a*/b*	1.89 ^a	1.62^{b}	1.48 ^c	1.40 ^c	1.39 ^c	1.45 ^b	1.75 ^a	1.65 ^a	1.50^{b}
ΔE	0.00 ^d	2.45 ^c	6.52^{b}	6.42 ^b	9.64 ^a	6.09 ^a	6.05 ^a	5.65^{b}	5.72^{b}
BI	10.63 ^a	5.22 ^b	3.39 ^{bc}	2.69 ^c	2.38 ^c	4.55 ^a	4.35 ^a	3.00 ^a	4.45 ^a



Fig. 2. Changes in ascorbic acid and lycopene during the storage period.

showed a decline in these factors for all treatments. The most significant reduction in the a and the a*/b* ratio during storage occurred in the control samples, with decreases of 64.50 % and 34.11 %, respectively. The slight increase on the 45th day could be because the conditions of the packaging used on this day may have been affected by the environment during the storage period. If this increase was out of the general trend (for example, the values related to the 45th day were higher than the 0th day), it would need to be investigated and more discussed. Conversely, the most minor decrease in both factors was observed in the Fe-25 % fortified samples, with reductions of 49.45 % and 19.28 %, respectively. Analysis of variance (Table 1) showed that storage duration and fortification significantly affected changes in both factors (at the 99 % level). The mean comparison results indicated significant differences among all days during storage except between days 30 and 45 (Table 2). The effect of concentrations is reported in detail in Table 1. Other researchers have reported similar findings regarding examining the index and the a*/b* ratio in tomato paste fortified with various materials during storage (Ganje et al., 2016; Jafari et al., 2021; Katırcı et al., 2020), which supports the present results. The results also indicated a decrease in L* and b* indices throughout the storage period for all treatments. At the end of the storage period, the most significant reductions in L* and b* indices were observed in control samples (without additives) and the minor reductions in Fe-75 % samples, with decreases of 50.05 % and 48.15 % for L* and 38.59 % and 34.41 % for b*, respectively. Analysis of variance (Table 1) demonstrated a significant effect of storage duration (at the 1 % level) on these two indices. At the same time, the Fe concentration did not significantly affect changes in the b^{*} index statistically. Finally, the analysis of the ΔE index showed an increase in color change for all treatments throughout the storage period. At the end of storage, the most significant color change was observed in control samples at 10.36, and the slightest change was seen in Fe-75 % fortified samples at 9.3. Statistical analysis also indicated a significant storage duration and fortification effect on the color change index. The control of changes in all color indices in fortified samples can be attributed to the effect of Fe concentration (additives) on color stabilization during storage. The changes in color indices, especially the redness index (a*), were consistent with those reported in the previous section for lycopene. Samples with less variation in lycopene and ascorbic acid also showed less variation in the redness index, demonstrating lycopene's direct impact on the red color in products such as tomatoes and their derivatives. Like some previous studies, this result indicates that lycopene and ascorbic acid are influential factors in maintaining the quality and red color of tomatoes and tomato paste.

5.2. Viscosity

Viscosity is a crucial physical–mechanical factor in agricultural and food products. The sample's viscosity was measured at 6 cm on the first day. Over time, the viscosity gradually decreased so that by the end of the storage period, the values for the control, Fe-25 %, Fe-50 %, and Fe-75 % samples were 4.57 cm, 4.93 cm, 4.93 cm, and 4.93 cm, respectively. Analysis of variance showed that the storage duration significantly affected viscosity changes (at the 95 % level). The final day's data indicated that viscosity changes were controlled through fortification, as fortified samples exhibited less reduction in viscosity; however, these changes were not statistically significant. Overall, maintaining and preserving the textural properties of the product throughout the storage period can be considered a positive effect.

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Fig. 3. Changes in color indices of tomato paste during the storage period.

6. Microbial properties

6.1. Examination of mold spores, thermophilic acid-resistant bacteria, and total microorganism count

At the beginning of the storage period, the residual mold spores, total microorganism count, and thermophilic acid-resistant bacteria in the tomato paste samples were 5.33 %, 0, and 0, respectively. During the storage period, up to day 30, the mold spores and thermophilic acid-resistant bacteria, and up to day 45, the total microorganism count remained very limited. This limitation was due to the thermal processing conducted during paste production, which can control product conditions for several days of storage. However, over time, all three factors increased in all treatments. At the end of the storage period, the levels of mold spores in the control, Fe-25 %, Fe-50 %, and Fe-75 % samples were 54.67 %, 45.33 %, 37.33 %, and 33.33 %, respectively. The total

microorganism count was 4435.33, 4393.33, 3066.67, and 720, and the aerobic thermophilic acid-resistant bacteria levels were 222, 119, 293.33, and 106.67, respectively (Fig. 4). It was found that for both factors-mold spores and total microorganism count-the most significant changes during storage occurred in the control samples, and the most minor changes occurred in the Fe-75 % samples. Additionally, in examining thermophilic acid-resistant bacteria, the most significant change was reported in the Fe-50 % samples and the slightest change in the Fe-75 % samples. The growth of fungal and mold species in agricultural and food products, especially tomatoes and tomato paste products, will reduce vitamin C levels (Oladiran & Iwu, 1992). Using substances like iron in fortifying processed products provides essential nutrients and stabilizes the product during storage, preventing mold formation and microorganism growth, thereby maintaining the initial nutritional and chemical quality. Analysis of variance (Table 1) also indicated a significant effect of storage duration, fortification, and their







Fig. 4. Changes in the levels of mold spores, thermophilic acid-resistant bacteria, and total microorganism count.

interaction on all three parameters (at the 99 % level). Duncan's mean comparison for different days (0, 15, 30, 45, and 60) and various fortification levels was also evaluated, with complete results provided in Table 2, indicating a significant impact in some subgroups. Up to day 15, no significant changes were observed in mold spores; up to day 30, no significant changes were observed in microorganisms and resistant bacteria. However, from approximately day 45, sudden and significant changes were observed in all three factors.

6.2. Electronic nose results

Fig. 5 shows the changes of aromatic compounds at the beginning and end of the storage period in each dosage for all sensors. As can be seen in Fig. 5, increasing the iron dosage led to an increase in variation of aromatic compounds of the tomato paste samples, with the nonfortified paste having the lowest changes in aromatic compounds content. Additionally, the aromatic compounds increased with extended storage, likely due to sample thickening or increased concentration of aromatic compounds in the sealed sample containers.

Moreover, aromatic compounds can differentiate and classify samples based on iron dosage (0, 25, 50, and 75 ppm) and storage duration (15, 30, 45, and 60 days). The confusion matrix for classifying samples with different iron dosages using the LDA method is shown in Table 3. This method correctly identified 23, 18, 19, and 19 out of 32 samples for iron dosages of 0, 25, 50, and 75 ppm, respectively. The highest accuracy of this method was 83 % for samples containing 0 ppm iron. The overall accuracy of this method in distinguishing and classifying samples into four groups (control, fortified with 25, 50, and 75 ppm iron) was 62 %. Table 3 shows the confusion matrix for classifying the storage duration of the tomato paste samples. The overall accuracy of this method in classifying samples into five categories (0, 15, 30, 45, and 60 days) was 99 %. All 32 samples were correctly classified on days 15, 30, and 60, with zero misclassification. These results demonstrate that the LDA method distinguishes samples based on different storage durations. Karami et al. (2021) classified the shelf life of edible oil over 150 days using an electronic nose, reporting classification accuracy of 95 % and 94.4 % for QDA and LDA methods, respectively (Karami et al., 2021). Lin et al. (2013) separated different Apiaceae species using electronic nose data combined with the LDA method. In another study, apple classification based on storage time was conducted using frequency response and diagnostic analysis methods (LDA and QDA), showing classification accuracies of 80.56 % and 83.33 % for linear and quadratic models, respectively (Lin et al., 2013). The frequency response method demonstrated high capability for detecting apple tissue (Lashgari &

Table 3

Confusion matrix of LDA for identifying different iron dosages and storage days.

iron dosages	0	25	50	75	SENSIVITY	SPECIFICITY	ACCURACY
0	23	5	1	1	0.72	0.89	0.83
25	9	19	0	6	0.59	0.71	0.68
50	0	5	18	6	0.56	0.68	0.65
75	0	3	13	19	0.59	0.63	0.62
storage days	15	30	45	60	SENSIVITY	SPECIFICITY	ACCURACY
15	32	0	0	0	1.00	1.00	1.00
30	0	32	0	0	1.00	1.00	1.00
45	0	0	31	0	0.97	1.00	0.99
60	0	0	1	32	1.00	0.99	0.99

MohammadiGol, 2016). In a study, researchers used ANN, LDA, and SVM to classify contaminated and healthy mushrooms over 28 days of storage, with LDA showing the best performance (Makarichian et al., 2022).

Table 4 presents the confusion matrix for identifying different iron dosages using the C-SVM method. The overall accuracy of this method in classifying samples was 38 %. Thus, compared to the LDA method, LDA had better accuracy and was more suitable for detecting different iron dosages. Table 4 shows the performance of C-SVM in identifying sample storage durations. According to the results, all 32 samples were correctly classified on the 15th day. Results showed that C-SVM performed much better in distinguishing storage durations with 90 % accuracy than iron dosage discrimination with 38 % accuracy. However, LDA outperformed C-SVM in classifying tomato paste samples across different storage

Table 4

Confusion matrix of C-SVM for identifying different iron dosages and storage days.

iron dosages	0	25	50	75	SENSIVITY	SPECIFICITY	ACCURACY
0	5	1	0	0	0.16	0.98	0.63
25	25	28	24	17	0.88	0.23	0.41
50	0	1	0	0	0.00	0.98	0.59
75	2	2	8	15	0.47	0.73	0.62
storage days	15	30	45	60	SENSIVITY	SPECIFICITY	ACCURACY
15	32	2	0	2	1.00	0.95	0.97
30	0	28	5	1	0.88	0.93	0.92
45	0	1	26	1	0.81	0.98	0.93
60	0	1	1	28	0.88	0.98	0.95



Fig. 5. Sensor changes in each sample during the storage period.

durations.

In one study, researchers evaluated mushroom quality over 28 days of storage using an electronic nose, demonstrating that the SVM method had higher classification accuracy than ANN (Gholami et al., 2023). Another study used an electronic nose and the SVM method to classify seven saffron types collected from Iran, Morocco, and Syria with 100 % accuracy based on geographical origin (Taheri-Garavand et al., 2015). Another study used a semiconductor sensor-based electronic nose to assess meat freshness, dividing meat into fresh and spoiled categories, with SVM as the classification algorithm (Balasubramanian et al., 2004).

7. Conclusions

In this study, tomato paste was fortified with iron compounds at concentrations of 25, 50, and 75 ppm, and the effects of adding iron micronutrients at different levels on the physical, mechanical, and chemical properties of the paste were evaluated over a 60-day storage period. After preparation, the tomato paste samples were packaged in specialized containers and stored for 60 days at 4 °C with 75 % relative humidity. Tests were conducted every 15 days on days 0, 15, 30, 45, and 60 for all treatments. The results showed that at the end of the storage period, the most significant decrease in pH and increase in TA occurred in the Fe-75 % fortified samples, with changes of 4.9 % and 38.79 %, respectively, and the minor changes were observed in the control samples, with changes of 3.45 % and 13.79 %, respectively. Overall, the Fefortified samples showed less variation in lycopene and ascorbic acid. The examination of the ΔE index indicated an increase in color change across all treatments during storage. At the end of the storage period, the most significant color change was observed in the control sample at 10.36, and the slightest change was in the Fe-75 % fortified samples at 9.3. For both mold spore levels and total microorganism count, the most significant changes during storage occurred in the control samples, and the most minor changes were in the Fe-75 % samples. Additionally, in the examination of thermophilic acid-resistant bacteria, the most significant changes were reported in the Fe-50 % samples and the least in the Fe-75 % samples. The overall accuracy of the LDA method in distinguishing and classifying samples into four groups (control, fortified with 25, 50, and 75 ppm iron) was 62 %. At the same time, it showed excellent performance in distinguishing samples based on different storage durations (accuracy of 99 %). The results demonstrated that C-SVM performed much better in distinguishing storage durations with 90 % accuracy than in discriminating iron dosages with 38 % accuracy. However, the LDA method outperformed C-SVM in classifying tomato paste samples across storage durations. Overall, it can be concluded that increasing the iron micronutrient enhances the nutritional value and positively affects the physical, chemical, and microbial properties and the retention of aromatic compounds in tomato paste.

CRediT authorship contribution statement

Nahid Aghilinategh: Writing – review & editing, Software, Methodology, Data curation. Rashid Gholami: Supervision, Conceptualization. Vajiheh Dayyani: Data curation, Conceptualization. Paolo Gay: Supervision. Alessandro Biglia: Writing – review & editing.

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Declaration of competing interest

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

Data availability

Data will be made available on request.

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