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CHEMICAL COMPOSITION OF JUICE AND MADZUN (GRAPE MOLASSES) PRODUCED FROM STANUSHINA GRAPE VARIETY BY TRADITIONAL METHOD

SUMMARY

In this study, some chemical characteristics and mineral composition of juice and madzun (grape molasses) produced from the Stanushina grape variety by the traditional method were analysed. Comparative analyses were conducted on one juice sample (S1) and two (S2, S3) madzun samples. Classical, spectrophotometric and HPLC methods were used to determine the basic parameters that determine the quality of madzun. The ICP-MS method was used to determine the content of micro and macro elements. From the obtained results it can be seen that the soluble dry matter content ranges from 29.41 (juice) to 82.98% (madzun), total sugar ranges from 28.04 (juice) to 67.99% (madzun), total phenols 875 (madzun) to 1212 mg/l (juice) and HMF (hydroxymethyl furfural) in the range from 5.25 mg/kg (juice) to 723.05 mg/kg (madzun). The content of the macro elements K, Ca and Mg was determined and ranged from 386-640 mg/kg, 111.7-375 mg/kg, 205.5-297.1 mg/kg respectively. The content of trace elements ranges (Fe 11.26-15.18 mg/kg, Mn 2.42-4.90 mg/kg, Zn 7.34-17.47 mg/kg, B 35.2-39.9 mg/kg and Ba 0.35-0.84 mg/kg). It was also determined that the content of heavy metals (Pb and Ni) in samples S1 and S2 is above the permissible limits for this type of food. This research showed that the composition of the madzun is influenced by the micro region where the grapes are grown, as well as the type and chemical composition of the soil.

Keywords: grape juice, madzun (grape molasses), chemical composition, minerals

INTRODUCTION

Stanushina is an indigenous Macedonian grape variety (Korunoska *et al.*, 2022). It is cultivated on an area of 233 ha (Strategy for Viticulture and Winemaking 2023/2033), with 80% of it in the Tikveš wine region, and a smaller part in other wine regions. Rose and red wines are produced from it, and due to

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its high yield of must, it is very suitable for the production of juice and madzun (grape molasses). Grape molasses is a traditional food that has been produced and used by the local population in North Macedonia for decades (Dimovska *et al.*, 2024). The traditional method that is preferred for molasses production in R. N. Macedonia has remained unchanged for a long time. Commercially are available in the markets with common name “Grape honey”, as well as traditional name “Madzun” (Dimovska *et al.*, 2024). According to the national historical nonformal data the name “Madzun" comes from the Turkish word meaning boiled fruit with a certain density. In North Macedonia, "Madzun" is produced mainly from the Vranec and Stanushina red wine varieties, as well from the table varieties Cardinal, Muscat Hamburg, Afus Ali (Dattier de Beyrouth), or similar.

Grapes and grape products such as juice and molasses represent a potentially important source of carbohydrates, minerals, and phenols, with quantitative differences in their composition depending on the variety, growing conditions, and production technology (Aras, 2020, Aras *et al.*, 2021). Grape juice and molasses are high-value foods due to their distinct flavours, nutritional values, and beneficial effects on human health (Aras, 2020).

Grape molasses is produced primarily from grapes by concentrating juices with a soluble dry matter content up to 70-80% (Cihat *et al.*, 2016). Glucose and fructose account for 50–80% of the sugars present in molasses (Simge *et al.*, 2023). These are simple sugars, which easily pass into the blood through simple diffusion without the prior requirement for breaking down into simpler molecules, thereby enabling rapid energy production in the human body. The average energy value reported for molasses is 293 kcal per 100 g (Batu, 2005; Türkben *et al.*, 2016).

Grape molasses may be classified under different groups based on the production method. According to the most general classification, the following three categories exist—liquid molasses produced using traditional methods, liquid molasses produced using modern methods and white solid molasses (Batu, 2005). Standards, molasses with a pH value of 5.0–6.0 are considered sweet molasses, while molasses with a pH value of 3.5–5.0 are considered sour molasses (Batu, 2020; Tosun *et al.*, 2014).

Grape polyphenols reduce atherosclerosis and inflammation, regulate blood pressure, activate new proteins (Slavin and Lloyd, 2012). It is stated that regular consumption of grapes and products in the Mediterranean traditional diet may contribute to the reduction of chronic diseases such as cancer, cardiovascular diseases, stroke, nervous disorders and aging (Iriti and Faoro, 2009). The most commonly measured phenolic compounds in grape juice and molasses is gallic acids, its concentrations range usually within 295.82 mg/L (grape juice) and 9823.24 mg/L (grape molasses) (Aktop *et al.*, 2023).

The mineral profile of grapes and grape products (grape juice, molasses) has been considered important not only from the nutritional aspect but also from a technological point of view. Some minerals may influence the production

process, sometimes negatively via an oxo-reduction reaction and/or organoleptic alteration in the grape derivates (Olalla *et al.*, 2004).

The following amounts of most commonly metal ions from purple and white grape juice are usually measured: Fe (2,18–2,23 mg/L), Ca (7,45–12,88 mg/L), Mg (10,38-10,70 mg/L), Mn (0,08-0,36 mg/L), Zn (0,77–1,29 mg/L), Cu (0,58–2,41 mg/L), Si (1,09–1,15 mg/L), Cl (2,77-3,00 mg/L), (C. Dani *et al.*, 2012).

The following quantities were measured in grape molasses produced from 14 different grape varieties in Turkey: Ca (163,12 -4.973,93 mg/kg), Fe (2,27-403,67 mg/kg), K (3.370,98-5.109,56 mg/kg), Mg (191,97-612,83 mg/kg), Na (48,70-344,28 mg/kg, P (226,76-597,81 mg/kg)-Cihat *et al.*, 2016). Some minerals may influence the production process, sometimes negatively via an oxo-reduction reaction and/or organoleptic alteration in the grape products (Olalla *et al.*, 2004). Generally, for producing pekmez (grape molasses), after grape washing and crushing, the obtained grape juice it is recommended heated and some clarifying agents such as bentonite, gelatine, or white soil is added to the juice in order to remove the suspended solids (Roya Peirovi Minaee *et al.*, 2024).

MATERIAL AND METHODS

Samples preparation

The juice and molasses were produced from the indigenous wine grape variety Stanushina (Picture 1) using traditional methods by local producers. In the Republic of Macedonia, the Stanushina variety is grown on an area of 220 hectares, of which 90% are in the Tikvesh wine region. The grapes used for producing grape juice and molasses come from the same locality (Begnishte). The traditional production method includes the following steps (Figure 1): First, the grapes are harvested at technological maturity with a sugar content of 230-240 g/L. They are then washed with clean water, crushed, after which 2.0 ml/100 kg of pectinolytic enzyme is added and left for 3-4 hours for maceration. The pectinolytic enzyme (pectinase) acts by breaking down the pectin found in the structure of the cell wall of the grape berry. Pectin is a substance that represents a physical barrier, preventing all substances from the cells from being fully released, primarily color (anthocyanins) and aromatic compounds (terpenes), which are most abundant in the grape skin.

Then, the grape juice (must) is separated, transferred into a clean stainless-steel container, and an enzyme (2 g/100 L) is added and left to settle for 24 hours at a temperature of 5°C. This prevents the must from starting to ferment. Next, the clear grape juice is separated from the sediment. Part of it is bottled into glass bottles of 250-500 mL and pasteurized at 80°C for 1 hour. For the production of molasses, the grape juice (must) is boiled at a temperature of 100-110°C in a copper or stainless-steel container with a wide opening until it reaches a level of 68-85°Brix of dry matter. Then, it is packed into glass jars and should be stored at a temperature no higher than 25°C. The samples for analysis were: one sample of grape juice (S1) in 250 mL bottles and two samples (S2, S3) of molasses packed in 100 mL glass jars (Picture 2).

Picture 1. Stanushina grape variety

Picture 2. The samples for analysis (S1, S2, S3)

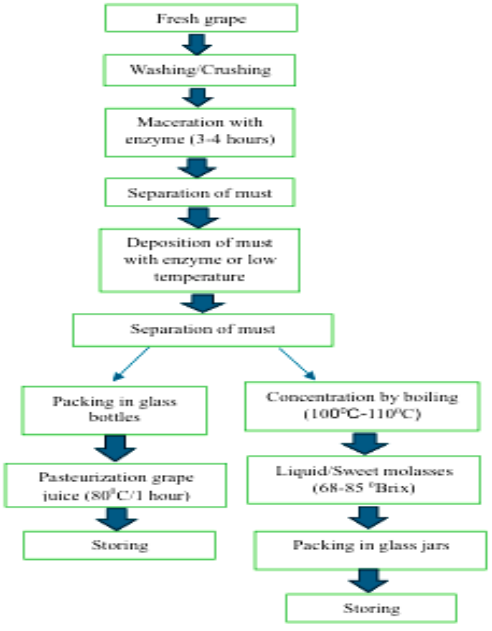

Figure 1. Schematic illustration for to produce of traditional grape juice and grape molasses in R. North Macedonia

The total sugar content of grape molasses samples was determined according to Official Method 929.09 (AOAC 2005).

Identification and quantification of individual sugars (glucose, fructose, sucrose and maltose) were performed by High-Performance Liquid Chromatography (HPLC) according to harmonized methods of the International Honey Commission (Bogdanov *et al.*, 1997), adapted for grape-derived products. Analyses were carried out using an Agilent 1260 Infinity HPLC system (Agilent Technologies, Santa Clara, CA, USA) equipped with a refractive index detector (RID). Chromatographic separation was performed on an Agilent Hi-Plex Ca carbohydrate column (300×7.7 mm, 8 μm particle size) maintained at 80 °C. Ultrapure water was used as the mobile phase under isocratic elution conditions at a flow rate of 0.6 mL/min. The injection volume was 20 μL. Prior to analysis, samples were diluted with ultrapure water, homogenized and filtered through a 0.45 μm membrane filter. Identification of individual sugars was based on comparison of retention times with authenticated external standards, while quantification was performed using calibration curves prepared from standard solutions of glucose, fructose, sucrose and maltose. Results were expressed as percentage content (%). Similar chromatographic approaches for carbohydrate profiling in honey and grape-derived products have been previously reported by Terrab *et al.*, (2002); Sanz *et al.*, (2004)

The soluble dry matter content of the grape juice and molasses (madzun) samples was determined according to the Official Method SOP 345 (Institute for Standardization of the Republic of Macedonia, 2010).

The content of total phenols (TPC) was determined using Folin-Ciocalteu method by spectrophotometer (model Paro 300 Merck Germany). The content of total phenols was expressed as mg equivalents of gallic acid per g of dry matter (mg GAE/g).

Titratable acidity was determined by titration with 0.1 N NaOH to the titration point of pH 8.3, monitored with a pH meter and expressed as tartaric acids content (g/L). The pH was measured by pH meter (model Mettler Toledo Seven Compact pH/ion S220, Switzerland).

Hydroxymethyl furfural (HMF) was determined according to the official method 890.23 (AOAC 2005), based on the colorimetric reaction between barbituric acid, p-toluidine and HMF, which forms a red-colored complex. The intensity of the red color was measured using a UV-Vis-NIR-5000 spectrophotometer (analytical wavelength of 550 nm was used).

Multi-element characterization: Inductively coupled plasma with mass spectrometry (ICP-MS, model 7500cx Agilent Technologies, USA) with a glass concentric nebulizer was used for analyses of the elements content. In this study, five step set or combination of power, pressure, and time conditions for microwave-assisted digestion were applied (Table 1). Microwave-assisted digestion conditions involved the digestion of 0.5 g of the sample with 5 mL HNO_3 and 2 mL of H2O2 in the microwave digestion system CEM model MARS 5 (CEM Corporation, Matthews, NC, USA).

After digestion, the vessels were allowed to cool until the pressure of the vessel was reduced to below 50 psi and temperature was below 40 °C. The caps of each vessel were then carefully removed, and the contents were filtered using 2 µm filter paper diluted to 25 mL in a volumetric flask using deionized water and stored in polyethylene vial prior to the final determination of the elements' concentration. Total of 35 elements were analyzed using the ICP-MS technique (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Ti, V and Zn). The ICP-MS system was optimized under typical tuning conditions for high and variable sample matrices.

Table 1. Microwave digestion program for digestion of madzun (grape molasses)

Step	Initial T (^{0}C)	Final T (^{0}C)	Power (W)	Time (min.)
1	25	150	800	15
2	150	150	800	10
3	150	180	1600	5
4	180	200	1600	10

Statistical analysis

All analytical determinations were performed in triplicate (n=3), and results were expressed as mean ± standard deviation (SD). Descriptive statistical parameters, including minimum, maximum, arithmetic mean, standard deviation and coefficient of variation (CV, %), were calculated to assess data dispersion and relative variability among samples. Pearson's correlation coefficients (r) were calculated to evaluate linear relationships among selected chemical quality parameters (total sugars, soluble dry matter, total phenols, total acidity, pH and HMF), as well as among mineral elements quantified above the limit of detection. Principal Component Analysis (PCA) was applied to identify dominant sources of variance and to explore underlying multivariate patterns within the compositional dataset. Prior to PCA, all variables were standardized to eliminate scale effects and ensure comparability among parameters expressed in different units. Components with eigenvalues greater than 1 were retained according to the Kaiser criterion. Descriptive statistical calculations were performed using Microsoft Excel (Microsoft Corp., Redmond, WA, USA), while correlation analysis and PCA were conducted using IBM SPSS Statistics for Windows, Version 26.0 (IBM Corp., Armonk, NY, USA). Due to the limited number of samples (n=3), statistical results were interpreted as exploratory and indicative rather than inferential.

RESULTS AND DISCUSSION

The basic chemical parameters that determine the quality of grape juice and madzun (grape molasses) include total sugars, particularly those originating from fresh grapes (glucose and fructose), soluble dry matter, total phenolic content, total acidity and pH value (Dimovska *et al.*, 2024). Glucose and fructose are the

predominant carbohydrates in grapes, whereas sucrose and maltose are mainly present in other vine tissues (shoots, leaves and perennial parts) in considerably lower amounts. Consequently, the carbohydrate profile of grape pekmez is dominated by glucose and fructose, which represent primary energy sources and are rapidly absorbed in the small intestine (Narkabulova and Jabborov 2023). The average reported energy value of grape pekmez is approximately 293 kcal per 100 g (Batu 2005; Türkben *et al.,* 2016).

The contents of total sugars, individual simple carbohydrates and soluble dry matter are presented in Table 2. Among the analyzed samples, fructose and glucose contents were significantly lower in grape juice (S1) than in madzun samples (S2 and S3), reflecting the lower temperature and shorter duration of pasteurization applied during juice production.

Table 2. Content of total sugars, simple carbohydrates and soluble dry matter in samples

Sample	Fructose (%)	Glucose (%)	F/G* ratio (%)	Sucrose (%)	Maltose (%)	Total sugars (%)	Soluble dry matter (%)
S1	14.56	13.48	1.09	<0.1	<0.15	28.04 ± 1.21	29.42 ± 1.27
S2	30.99	28.36	1.09	<0.1	0.25	59.70 ± 2.58	84.98 ± 3.67
S3	35.17	32.82	1.07	<0.1	<0.15	67.99 ± 2.94	80.98 ± 3.49
Mean (S2–S3)	33.08	30.59	1.08	–	–	63.84 ± 2.58	82.98 ± 3.11

*Values are expressed as mean ± standard deviation (n=3); *F/G ratio represents the fructose-to-glucose ratio; Values below the detection limit are reported as <LOD*

In grape juice, fructose and glucose contents were 14.56% and 13.48%, respectively. In madzun samples, fructose ranged from 30.99% (S2) to 35.17% (S3), while glucose ranged from 28.36% (S2) to 32.82% (S3). Despite this pronounced increase in absolute sugar concentration, the fructose/glucose (F/G) ratio remained remarkably stable (1.07–1.09), indicating that thermal processing primarily causes sugar concentration through water evaporation rather than selective degradation of individual monosaccharides. In all samples, sucrose content was below the detection limit (<0.1%), confirming that no additional sugar was added during processing. Total sugar content increased from 28.04% in grape juice to an average of 63.84% in madzun samples (S2/S3), in agreement with previously reported trends (Aras and Göktürk, 2021).

Soluble dry matter in grapes is mainly composed of sugars and organic acids such as citric and malic acid (Cemeroğlu 2010). In the present study, soluble dry matter increased from 29.42% in grape juice to 84.98% in madzun, confirming the strong effect of thermal concentration. According to Regulation (EU) No 1169/2011, samples S2 and S3 can therefore be classified as solid grape molasses.

Phenolic compounds, organic acids and HMF are key quality indicators because they reflect both the nutritional value and the technological impact of thermal processing. The results for total phenols, total acidity, pH and HMF are presented in Table 3.

Total phenolic content was significantly higher in grape juice (S1) than in madzun samples (S2 and S3), with values ranging from 875 mg/L (S3) to 1212 mg/L (S1). The observed decrease in phenolic content in madzun can be attributed to prolonged exposure to high temperatures, which accelerates oxidation, polymerization and degradation of phenolic compounds, particularly anthocyanins. Although concentration effects could theoretically increase phenolic levels, degradation processes clearly dominated under traditional boiling conditions.

The pH values ranged from 3.45 to 4.43, while total acidity (expressed as tartaric acid) varied from 3.92 to 9.50 g/L. Titratable acidity showed an inverse relationship with pH, confirming matrix acidification during processing. According to the grape pekmez Notification (2007), all analyzed samples fall within the category of sweet grape products. Comparable pH and acidity ranges have been reported in previous studies (Cihat *et al.*, 2016; Dimovska *et al.*, 2024; Arslaner and Salık, 2020).

HMF exhibited the most pronounced variation among all parameters. Only trace levels were detected in grape juice, whereas very high concentrations were measured in madzun samples. HMF is formed during heating through acid-catalyzed dehydration of reducing sugars and is widely used as an indicator of thermal severity (Cemeroğlu 2010; Türkben *et al.*, 2016). The elevated HMF levels observed in madzun samples reflect traditional open-vessel boiling at high temperatures.

Table 3. Total phenols, total acids, pH and HMF in samples

Sample	Total phenols (mg/L)	Total acids (g/L)	pH	HMF* (mg/kg)
S1	1212 ± 6.66	4.63 ± 0.04	3.45 ± 0.01	5.24 ± 0.41
S2	1114 ± 2.89	3.92 ± 0.02	4.43 ± 0.03	640.72 ± 51.25
S3	875 ± 5.20	9.50 ± 0.01	3.73 ± 0.03	805.38 ± 64.43
Mean (S2–S3)	994.5	6.35	4.08	723.05

*Values are expressed as mean ± standard deviation (n=3); Total acidity is expressed as g/L tartaric acid equivalents; *HMF: hydroxymethylfurfural*

Descriptive statistical parameters are summarized in Table 4. Parameters directly associated with thermal processing, particularly HMF and total acidity, exhibited the highest coefficients of variation, indicating strong sensitivity to processing conditions. In contrast, pH and total phenols showed lower variability, suggesting partial buffering by the grape matrix.

Table 4. Descriptive statistical parameters of key chemical indicators (n = 3)

Parameter	Minimum	Maximum	Mean	SD	CV* (%)
Total sugars (%)	28.04	67.99	51.94	20.48	39.43
Soluble dry matter (%)	29.42	84.98	65.79	30.15	45.83
Total phenols (mg/L)	875	1212	1067	173.35	16.25
Total acids (g/L)	3.92	9.50	6.02	3.04	50.48
pH	3.45	4.43	3.87	0.50	13.04
HMF (mg/kg)	5.24	805.38	483.78	422.53	87.34

*Descriptive statistical parameters were calculated using all samples (n = 3); *CV- coefficient of variation; Due to the limited number of samples, results should be interpreted as indicative trends.*

The descriptive statistical parameters clearly illustrate the different sensitivities of individual chemical indicators to thermal processing. Total sugars and soluble dry matter exhibited relatively high coefficients of variation (39.43% and 45.83%, respectively), reflecting the pronounced concentration effect caused by water evaporation during madzun production. These parameters increase proportionally with processing intensity and therefore show substantial variability among samples subjected to different heating conditions.

Total acidity showed similarly elevated variability (CV=50.48%), indicating that organic acid composition is strongly influenced by thermal treatment. In addition to concentration effects, acid degradation, volatilization and possible salt formation may contribute to the observed dispersion. The inverse relationship between total acidity and pH is further supported by the relatively low variability of pH values (CV=13.04%), suggesting that the grape matrix partially buffers pH changes despite significant alterations in titratable acidity.

In contrast, total phenolic content displayed comparatively low variability (CV=16.25%), indicating a degree of structural stability of phenolic compounds within the grape matrix. Although thermal degradation of phenolics occurs during processing, the relatively narrow range of values suggests that degradation and concentration effects partially compensate each other. This buffering behavior is consistent with the complex chemical nature of phenolic compounds and their interactions with sugars and organic acids.

Among all investigated parameters, HMF exhibited the highest coefficient of variation (87.34%), confirming its strong sensitivity to processing severity. The wide concentration range reflects the transition from minimal formation in grape juice to intensive formation in madzun samples subjected to prolonged heating. These results support the use of HMF as a reliable indicator of thermal history and processing intensity in grape molasses products.

Pearson correlation coefficients were calculated to evaluate relationships among key chemical parameters Table 5. A strong negative correlation was observed between total phenols and HMF, indicating intensified phenolic degradation with increasing thermal severity. Total acidity showed a positive correlation with HMF and a negative correlation with pH, reflecting acidification during prolonged heating.

Table 5. Pearson correlation matrix for selected chemical parameters

Parameter	Total phenols	Total acids	pH	HMF
Total phenols	**1.00**	−0.92	−0.04	**−0.85**
Total acids	**−0.92**	1.00	−0.35	0.57
pH	−0.04	−0.35	1.00	0.57
HMF	−0.85	0.57	0.57	**1.00**

The Pearson correlation matrix (Table 5) reveals clear relationships among chemical parameters that are directly linked to thermal processing intensity and matrix transformations during madzun production. The strongest negative correlation was observed between total phenols and HMF (r=−0.85), indicating that increasing thermal severity promotes the formation of HMF while simultaneously accelerating the degradation of phenolic compounds. This relationship confirms that prolonged heating favors Maillard-type reactions at the expense of thermally sensitive phenolic structures, particularly anthocyanins and low-molecular-weight phenols.

A pronounced negative correlation was also observed between total phenols and total acidity (r=−0.92), suggesting that acid-catalyzed reactions contribute to phenolic degradation during processing. Organic acids not only enhance the rate of Maillard reactions but also promote oxidative and hydrolytic pathways that destabilize phenolic compounds. This behavior is consistent with the observed reduction of total phenols in madzun samples compared to grape juice.

Total acidity showed a moderate positive correlation with HMF (r=0.57), supporting the role of acidic conditions in facilitating HMF formation through dehydration of reducing sugars. At the same time, the negative correlation between total acidity and pH (r=−0.35) reflects the expected inverse relationship between these parameters and confirms progressive matrix acidification during prolonged heating. The positive correlation between pH and HMF (r=0.57) further indicates that pH alone does not directly control HMF formation, but rather interacts with total acidity and sugar concentration within the complex grape matrix.

In contrast, the weak correlation between total phenols and pH (r=−0.04) suggests that pH variations within the observed range have a limited direct influence on phenolic stability. Instead, phenolic degradation appears to be driven predominantly by thermal exposure and acid-mediated reactions rather than by pH changes alone.

Overall, the correlation analysis demonstrates that HMF formation, phenolic degradation and acid evolution are tightly interconnected processes governed by thermal processing intensity. These relationships corroborate the descriptive statistical results and provide a mechanistic basis for the multivariate patterns observed in the PCA analysis.

Principal Component Analysis (PCA) was applied to integrate the compositional and statistical information and to identify the dominant processes governing the chemical variability among samples. PCA was performed on standardized variables in order to eliminate the influence of different measurement units. Eigenvalues greater than 1 were considered significant. The eigenvalues and explained variance are presented in Table 6, while variable loadings are shown in Table 7.

Table 6. Eigenvalues and explained variance of principal components

Principal component	Eigen value	Explained variance (%)	Cumulative (%)
PC1	14.13	58.87	58.87
PC2	9.87	41.13	100.00

Principal Component Analysis (PCA) was performed on standardized variables. Eigenvalues >1 were considered significant

The first principal component (PC1) explained 58.87% of the total variance, indicating that more than half of the overall variability among samples can be attributed to a single dominant process. PC1 was strongly associated with HMF, total sugars and soluble dry matter, as indicated by their relatively high absolute loading values. These parameters are directly linked to thermal concentration and processing severity, suggesting that PC1 represents the intensity of heat treatment applied during madzun production. The strong contribution of HMF to PC1 confirms its role as a sensitive marker of thermal history, while the concurrent influence of total sugars and soluble dry matter reflects water evaporation and concentration effects.

The second principal component (PC2) accounted for the remaining 41.13% of the variance and was primarily influenced by total phenols and pH. This component reflects matrix-related quality attributes rather than processing intensity. The positive loading of pH and total phenols on PC2 indicates that variations in acidity and phenolic stability are governed by intrinsic grape matrix properties and buffering effects, rather than by thermal concentration alone. The contrasting behavior of total acids, which showed a negative loading on PC2, further highlights the acid–base balance within the grape matrix as a secondary source of variability.

The clear separation of variables between PC1 and PC2 demonstrates that the chemical transformation of grape juice into madzun is controlled by two main mechanisms: (i) thermal processing intensity, which dominates the overall variability and drives sugar concentration, soluble dry matter increase, acidification and HMF formation, and (ii) matrix-related characteristics, which modulate phenolic stability and pH response during heating. The multivariate structure revealed by PCA is fully consistent with the descriptive statistics and correlation analysis, confirming that processing-driven effects dominate the chemical profile, while matrix properties act as secondary modulators of product quality.

Overall, PCA provides a coherent multivariate framework that supports the conclusion that optimization of thermal regimes is essential to balance technological efficiency with preservation of nutritionally and sensorially important compounds in grape molasses.

Table 7. PCA loadings for key chemical parameters

Variable	PC1	PC2
Total sugars	−0.29	−0.21
Soluble dry matter	−0.27	−0.24
Total phenols	0.30	0.14
Total acids	−0.23	− 0.27
pH	−0.13	0.36
HMF	−0.32	0.07

Loadings indicate the contribution of each variable to the principal components; Higher absolute values represent stronger influence

The elemental composition of grape juice and madzun was investigated to provide complementary information on raw material characteristics and product safety, distinct from the thermally driven transformations observed for organic quality parameters. Elemental concentrations determined by ICP analysis are presented in Table 8.

Table 8. Elemental composition of grape juice and madzun samples (mg/kg)

Element	S1	S2	S3
B	36.4	39.9	35.2
Na	170	299	126
Mg	297.1	205.5	242.5
Al	53.6	133.7	147.8
K	386	398	640
Ca	375	228.7	111.7
Cr	0.460	0.215	0.366
Mn	4.90	2.42	2.67
Fe	15.18	14.12	11.26
Cu	2.64	1.53	0.44
Zn	17.47	13.34	7.34
Ba	0.84	0.49	0.35
Pb	0.0395	0.0775	0.0350
Cd	0.0021	0.0185	<0.0001
Ni	0.343	<0.0001	<0.0001
Hg	<0.0001	<0.0001	<0.0001

Elemental concentrations were determined by ICP analysis; LOD = 0.0001 mg/kg; Values below the limit of detection are reported as <LOD.

Table 9. Descriptive statistical parameters of selected elements (mg/kg, n = 3)

Element	Min	Max	Mean	SD	CV* (%)
K	386	640	474.7	143.2	30.2
Ca	111.7	375	238.5	132.1	55.4
Mg	205.5	297.1	248.4	45.9	18.5
Fe	11.26	15.18	13.52	2.03	15.0
Mn	2.42	4.90	3.33	1.36	40.8
Zn	7.34	17.47	12.72	5.05	39.7
Cu	0.44	2.64	1.54	1.11	72.1
Ba	0.35	0.84	0.56	0.25	44.6
Pb	0.035	0.078	0.050	0.022	43.4

*Descriptive statistics were calculated only for elements quantified above the limit of detection; Elements detected entirely below LOD were excluded from statistical evaluation; *CV- coefficient of variation.*

Among microelements, iron concentrations ranged from 11.26 to 15.18 mg/kg (CV=15.0%), demonstrating low variability and suggesting limited sensitivity to thermal processing. In contrast, manganese and zinc exhibited higher coefficients of variation (40.8% and 39.7%, respectively), reflecting partial redistribution during concentration and possible interactions with phenolic compounds and proteins. Copper showed the highest variability (CV=72.1%), with concentrations decreasing from 2.64 mg/kg in grape juice to 0.44 mg/kg in madzun (S3), which may be attributed to complexation and precipitation phenomena rather than contamination.

Heavy metals were detected at very low concentrations. Lead ranged from 0.035 to 0.078 mg/kg, yielding a mean value of 0.050 mg/kg, which is well below the maximum allowable limits set by European regulations (Table 9). Cadmium, mercury and nickel were either present at trace levels or below the limit of detection, confirming the absence of significant environmental or technological contamination sources. The relatively high CV for lead (43.4%) is primarily a consequence of low absolute concentrations and analytical variability at trace levels rather than true compositional heterogeneity.

Correlation analysis (Table 10) further supports these interpretations. Strong negative correlations between potassium and calcium ($r = -0.89$), potassium and iron ($r=-0.92$), and potassium and zinc ($r = -0.97$) indicate divergent behavior during thermal concentration, consistent with the solubility-driven enrichment of potassium and the partial removal or redistribution of calcium and transition metals. Conversely, strong positive correlations among calcium, iron and zinc ($r=0.85–0.95$) suggest a shared geochemical origin and coordinated matrix behavior. Lead exhibited weak correlations with all other elements ($r<0.42$), reinforcing the conclusion that its presence is not associated with processing conditions or elemental co-enrichment patterns.

In contrast to organic quality parameters such as total sugars, HMF and acidity, which showed pronounced variability and strong dependence on thermal processing intensity, the elemental profile remained comparatively stable and primarily governed by raw material characteristics. The combined statistical evidence confirms that while thermal treatment strongly modifies the organic composition of madzun, the mineral fraction is largely conserved and reflects the natural geochemical signature of the grapes, supporting both the technological interpretation of processing effects and the chemical safety of the final product.

Table 10. Pearson correlation matrix for selected elements (n=3)

Element	**K**	**Ca**	**Fe**	**Zn**	**Cu**	**Pb**
K	1.00	**−0.89**	−0.92	**−0.97**	−0.86	−0.31
Ca	−0.89	1.00	**0.85**	0.88	0.74	0.42
Fe	**−0.92**	0.85	1.00	**0.95**	0.69	0.28
Zn	−0.97	0.88	0.95	1.00	0.73	0.34
Cu	−0.86	0.74	0.69	0.73	1.00	0.19
Pb	−0.31	0.42	0.28	0.34	0.19	1.00

Pearson correlation coefficients are shown for selected elements quantified above LOD; Correlations are presented for exploratory purposes due to the limited number of samples (n = 3)

CONCLUSIONS

This study provides an integrated chemical and multivariate assessment of grape juice and traditionally produced grape molasses (madzun) derived from the indigenous Stanushina grape variety, offering new insight into processing-induced transformations within grape-based products.

Thermal concentration was identified as the primary driver of compositional variability. The significant increase in total sugars and soluble dry matter confirms water evaporation as the dominant technological mechanism, while the stability of the fructose-to-glucose ratio indicates preservation of the intrinsic carbohydrate profile. In contrast, total phenolic content decreased following prolonged heating, reflecting oxidative and acid-catalyzed degradation processes that accompany high-temperature treatment.

Hydroxymethylfurfural (HMF) emerged as the most sensitive indicator of thermal severity, exhibiting the highest coefficient of variation and strong inverse correlation with total phenols. The statistical relationships observed among HMF, acidity and phenolic content confirm that Maillard-type reactions and acid-mediated transformations are tightly interconnected during madzun production.

Multivariate analysis (PCA) clearly distinguished two dominant dimensions of variability: (i) a processing-driven axis associated with sugar concentration, soluble dry matter increase, acid evolution and HMF formation, and (ii) a matrix-driven axis related to phenolic stability and pH buffering capacity. This dual-structure model demonstrates that while thermal intensity

governs the overall chemical transformation, intrinsic grape matrix characteristics modulate product quality outcomes.

The elemental profile remained comparatively stable and primarily reflected the geochemical signature of the raw material rather than technological impact. Macro-elements (K, Ca, Mg) dominated the mineral composition, and concentrations of potentially toxic elements were below regulatory thresholds, confirming product safety.

Collectively, these findings demonstrate that traditional madzun production induces substantial modifications in organic quality parameters while largely preserving mineral integrity. The integration of classical analytical techniques with multivariate statistical modeling provides a robust framework for optimizing thermal regimes in order to balance technological efficiency with preservation of nutritionally and sensorially relevant compounds. This approach may serve as a scientific basis for the standardization and quality control of traditional grape molasses production.

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