# Impact of Grape Pomace Addition on the Mineral Profile of Long-Life Bakery Products

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#### Abstract

The incorporation of grape pomace into the preparation of innovative food products offers a promising strategy for the valorization of wine industry by-products. This study aimed to develop long-life pastry with the addition of grape pomace (Cabernet Franc) at levels of 5%, 10%, 15%, and 20%. The content of micro- and macroelements in the pastries was determined using an atomic absorption spectrophotometer. The concentration of potassium (K), calcium (Ca), magnesium (Mg), and sodium (Na) were observed at concentrations 1692 - 3797 mg/kg, 323 - 5799 mg/kg, 89 - 132 mg/kg, and 317 - 362 mg/kg DM, respectively. Among microelements, copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), chromium (Cr), nickel (Ni), and cobalt (Co) were observed at concentrations of 0.63 - 1.07 mg/kg, 2.40 - 2.66 mg/kg, 3.10 - 3.84 mg/kg, 14.05 - 19.30 mg/kg, 0.10 - 0.41 mg/kg, <LOD - 0.06 mg/kg, and <LOD - 0.08 mg/kg DM, respectively. Lead (Pb) and cadmium (Cd) were detected in the ranges of <LOD - 0.08 mg/kg and <LOD - 0.70 mg/kg DM, respectively. Based on these findings, the addition of grape pomace at a 20% dose in durable bakery products demonstrates significant potential for the sustainable utilization of wine industry waste. It also contributes to enhanced levels of health-beneficial minerals in the final product, offering a valuable approach to producing nutritionally enriched food products.

Key words: grape pomace; biscuits; minerals; heavy metals

#### Introduction

A diet abundant in fruits and vegetables plays a crucial role in preventing diseases associated with oxidative stress. The risk of such diseases can be significantly mitigated by incorporating antioxidant compounds, such as polyphenols, vitamins, and minerals, into the diet<sup>1</sup>.

Grape pomace, a by-product of winemaking and an excellent source of health-promoting bioactive compounds, offers a promising avenue for enhancing the nutritional value of innovative bakery products. Incorporating grape pomace into these products not only supports a healthier diet and reduces the prevalence of lifestyle-related diseases but also aligns with sustainability goals by repurposing waste and minimizing environmental impact. Grape pomace is a valuable source of nutrients, including carbohydrates, minerals, vitamins — particularly vitamin C — and both insoluble (cellulose, hemicellulose) and soluble ( $\beta$ -glucans, pectins, gums) dietary fiber<sup>2</sup>. Castellanos-Gallo et al.<sup>3</sup> report that grape pomace is also rich in dietary fiber and polyphenolic compounds, such as anthocyanins, flavanols, and stilbenes. Similarly, Echave et al.<sup>4</sup> highlight the presence of condensed tannins and resveratrol in grape pomace. These bioactive compounds are associated with a range of potential health benefits, including antioxidant, hypoglycemic, hypolipidemic, and anti-inflammatory activities, among others<sup>5</sup>.

In addition to bioactive compounds, grape pomace is a rich source of essential minerals<sup>6</sup>. Caponio et al.<sup>7</sup> report that it contains a wide range of minerals, predominantly calcium, iron, zinc, potassium, and manganese. Similarly, Machado et al.<sup>8</sup> identify grape pomace as an excellent source of potassium, calcium, iron, manganese, and arachidic acid. Spinei and Oroian<sup>9</sup> also highlight that iron, potassium, calcium, and copper are among the primary minerals present in grape pomace. Minerals play a vital role

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in various biochemical processes within the human body. Potassium, for instance, contributes to protein and glycogen metabolism, regulates the body's water balance, lowers blood pressure, and reduces the risk of osteoporosis<sup>10</sup>. Calcium, another significant mineral in grape pomace, is essential for bone and tooth health, muscle contraction, and blood clotting<sup>11</sup>.

The health-promoting properties of grape pomace make it a valuable ingredient for the development of functional foods, whose consumption may provide specific health benefits to consumers. Therefore, the aim of this study was to incorporate grape pomace into long-lasting bakery products and to evaluate the levels of macro- and micro-elements in the final products.

#### **Experimental part**

The grape pomace, consisting of skins, pulp, and seeds, used in this study was derived from the Cabernet Franc variety, sourced from the Slovak wine producer Tajna, s.r.o., whose vineyards are situated in the Nitra wine-growing region of Slovakia. The grape marc was dried at 50 °C for four days using a Memmert SF 110 dryer (Memmert GmbH, Schwabach, Germany) and subsequently homogenized for 60 seconds at 25,000 rpm with an IKA A10 batch mill to achieve a particle size of 0.7 mm (20 mesh).

Durable pastry (control sample) was prepared using wheat flour, sugar, butter, and vanilla. Variants of the pastry were then formulated by incorporating 5%, 10%, 15%, and 20% of the dried, homogenized grape pomace. Baking was conducted at 150°C for 20 minutes. After cooling, the biscuits were homogenized and prepared for subsequent analyses.



Figure 1: Biscuits with addition of grape pomace powder

Content of mineral elements was determined as described by Lidiková et al.<sup>6</sup>. A 1 g of sample was mineralized in 10 ml of concentrated HNO<sub>3</sub> and 5 ml of concentrated HCIO using a MARS X-press mineralization device (CEM Corp., Matthews, NC, USA). The mineralized sample was filtered through quantitative filter paper (Filtrak 390, Munktell, GmbH, Bärenstein, Germany). For the determination of K, Ca, P, and Mg content, 2 ml of the filtered sample was diluted with distilled water to a final volume of 50 ml and analyzed against a blank solution using an atomic absorption spectrophotometer (VARIAN AASpectra DUO 240FS, Varian Ltd., Mulgrave, VIC, Australia).

To measure P content, 1 ml of the filtered sample was diluted with 8 ml of a reagent solution containing  $C_6H_8O_6$ ,  $H_2SO_4$ ,  $(NH_4)_2MoO_4$ , and  $C_4H_4KO_7Sb\cdot 5H_2O$ , and deionized water was added to a final volume of 50 ml. The solution was analyzed against a blank using a UV/Visible Scanning Spectrophotometer (Shimadzu UV-1800, Shimadzu, Kyoto, Japan).

For the determination of Fe, Cu, Zn, Mn, Co, Cr, and Ni, a 1 g sample was mineralized in 5 ml of concentrated  $HNO_3$  and 5 ml of redistilled water using the MARS X-press mineralization device. The mineralized sample was filtered (Filtrak 390) and diluted to 50 ml with distilled water. Elemental concentrations were analyzed against a blank using an atomic absorption spectrophotometer (Varian 240FS, Varian Inc., Mulgrave, VIC, Australia). The contents of Pb and Cd were determined using the Varian 240Z atomic absorption spectrophotometer.

Mercury was analyzed using cold-vapor atomic absorption spectroscopy with a selective Hg analyzer (AMA254, Al-tec, Prague, Czech Republic).

Statistical analysis was performed using XLSTAT software. To asses the normality of the data, Shapiro-Wilk test was performed. Based on the normality of the data, analysis of variance (ANOVA) with post hoc Tukey test, and Kruskal-Wallis test with post hoc Dunn test for was performed to determine the differences between samples. Spearman correlation was performed to assess relationships between individual mineral element contents. All analyses were performed in quadruplicate.

#### Results and discussion

The valorization of wine industry by-products, such as grape pomace, represents an effective strategy for recovering bioactive compounds and minerals while reducing the environmental impact of industrial waste. Due to its rich mineral profile, grape pomace can serve as a sustainable alternative source of both macro- and micronutrients, enabling the development of novel functional foods with potential health benefits for consumers<sup>12</sup>. Abouelenein et al.<sup>13</sup> reported that grape production by-products exhibit high concentrations of essential minerals, including calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na).

Samples	Dry matter (%)	K (mg/kg DM)	Na (mg/kg DM)	Ca (mg/kg DM)	Mg (mg/kg DM)
Control	94.58±1.55	1692.8±88.5 <sup>a</sup>	317.3±18.2 <sup>a</sup>	325.3±22.5 <sup>a</sup>	89.20±5.11 <sup>a</sup>
5 %	94.06±1.98	2030.2±114.3 <sup>ab</sup>	<b>345.4</b> ±29.9 <sup>bc</sup>	323.1±12.8 <sup>a</sup>	89.20±6.63 <sup>a</sup>
10%	94.35±0.38	2805.5±155.8 <sup>ab</sup>	323.6±33.3 <sup>ab</sup>	360.5±21.8 <sup>ab</sup>	94.40±9.11 <sup>ab</sup>
15%	94.50±1.02	<b>3792.5</b> ±412.11 <sup>b</sup>	<b>346.3</b> ±29.8 <sup>bc</sup>	457.1±33.5 <sup>ab</sup>	113.9±7.54 <sup>ab</sup>
20%	94.22±0.87	<b>3797.0</b> ±285.4 <sup>b</sup>	<b>362.6</b> ±14.8 <sup>c</sup>	<b>579.0</b> ±39.5 <sup>b</sup>	<b>132.8</b> ±8.6 <sup>b</sup>

Table 1: Dry matter (%) and macro-element content (mg/kg) of biscuits with added grape pomace

Values marked with different letters are statistically significantly (p < 0.05) different; values marked with bold are statistically significantly (p < 0.05) higher than control

As shown in Table 1, the addition of 20% grape pomace to durable bakery products led to a statistically significant increase in calcium (Ca) content. Cormick et al.<sup>14</sup> have also highlighted the reutilization of wine by-products, particularly based on their Ca content. Calcium is a vital mineral required for several physiological functions, including blood coagulation, cell division, and muscle function.

When monitoring potassium (K) content, values ranged from 1692.8 to 3797.0 mg/kg, with the highest level observed following the incorporation of 20% grape pomace. Similarly, the magnesium (Mg) content reached its peak value (132.8 mg/kg) after the addition of 20% grape pomace. Magnesium is an essential nutrient that plays a critical role in energy production, muscle contraction, protein synthesis, bone growth, and blood pressure regulation<sup>15</sup>.

Sodium (Na) content in the bakery products enriched with grape pomace ranged from 317.3 to 362.6 mg/kg. The higher levels of potassium compared to sodium promote mineral balance and contribute to the control of hypertension, as reported by Sousa et al.<sup>16</sup>.

Incorporation of grape pomace into durable bakery products also led to an increase in the content of microelements (Cu, Zn, Mn, Fe, Cr, Ni and Co). The results are presented in Table 2.

Samples	Cu (mg/kg DM)	Zn (mg/kg DM)	Mn (mg/kg DM)	Fe (mg/kg DM)	Cr (mg/kg DM)	Ni (mg/kg DM)	Co (mg/kg DM)	Pb (mg/kg DM)	Cd (mg/kg DM)
Control	0.63±0.03ª	2.40±0.03 <sup>a</sup>	3.10±0.19ª	15.45±1.11⁵	0.10±0.01ª	<lodª< td=""><td><lod<sup>a</lod<sup></td><td><lodª< td=""><td><lod<sup>a</lod<sup></td></lodª<></td></lodª<>	<lod<sup>a</lod<sup>	<lodª< td=""><td><lod<sup>a</lod<sup></td></lodª<>	<lod<sup>a</lod<sup>
5 %	0.89±0.05 <sup>ab</sup>	2.58±0.02 <sup>ab</sup>	3.28±0.31ª	16.13±0.98⁵	0.27±0.02 <sup>ab</sup>	<lodª< td=""><td><lodª< td=""><td><lodª< td=""><td><lodª< td=""></lodª<></td></lodª<></td></lodª<></td></lodª<>	<lodª< td=""><td><lodª< td=""><td><lodª< td=""></lodª<></td></lodª<></td></lodª<>	<lodª< td=""><td><lodª< td=""></lodª<></td></lodª<>	<lodª< td=""></lodª<>
10%	0.91±0.08 <sup>ab</sup>	<b>2.66±</b> 0.15 <sup>b</sup>	3.68±0.31b	14.05±1.61ª	0.30±0.03 <sup>abc</sup>	<lodª< td=""><td><lodª< td=""><td><lodª< td=""><td><lodª< td=""></lodª<></td></lodª<></td></lodª<></td></lodª<>	<lodª< td=""><td><lodª< td=""><td><lodª< td=""></lodª<></td></lodª<></td></lodª<>	<lodª< td=""><td><lodª< td=""></lodª<></td></lodª<>	<lodª< td=""></lodª<>
15%	0.92±0.05 <sup>ab</sup>	<b>2.65±</b> 0.21 <sup>b</sup>	<b>3.73±</b> 0.25 <sup>b</sup>	<b>19.30</b> ±1.11°	<b>0.35</b> ±0.21 <sup>bc</sup>	0.05±0.01 <sup>ab</sup>	<b>0.08±</b> 0.05 <sup>b</sup>	<b>0.28±</b> 0.05 <sup>b</sup>	0.20±0.01 <sup>ab</sup>
20%	<b>1.07±</b> 0.09 <sup>b</sup>	<b>2.60±</b> 0.15 <sup>b</sup>	<b>3.84±</b> 0.28 <sup>b</sup>	<b>19.20±</b> 0.78℃	<b>0.41</b> ±0.21℃	<b>0.06±</b> 0.01 <sup>b</sup>	0.07±0.03 <sup>ab</sup>	0.27±0.02 <sup>ab</sup>	<b>0.70±</b> 0.09 <sup>b</sup>

Table 2: Micro-element content (mg/kg) of biscuits with added grape pomace

Values marked with different letters are statistically significantly (p < 0.05) different; values marked with bold are statistically significantly (p < 0.05) higher than control; LOD – limit of detection

While certain minerals, such as potassium, calcium, and magnesium, showed clear increasing trends, others did not follow a uniform pattern. This highlights the complexity of mineral behavior in food matrices and suggests the need for further investigations into processing effects and interactions affecting mineral retention. The observed increase in trace elements in durable bakery products is a positive outcome, as the trace elements present in grape pomace have the potential to contribute to meeting daily intake requirements<sup>17</sup>. The incorporation of wine industry by-products into bakery products has been widely explored<sup>4,18,19</sup>, though the focus has predominantly been on enhancing the phenolic compound content in the final innovative products.

In contrast, fewer studies have specifically addressed the impact of grape-derived products on the mineral content of biscuits. Our findings align with those of Theagarajan et al.<sup>20</sup> who reported that the 8% addition of grape pomace to biscuits increased mineral content from 1.71 to 3.04%. Similar observations were made by Poiana et al.<sup>21</sup> who stated that the 25% addition of grape pomace led to increases in the ash content of the products: from 1.84% (control) to a maximum of 2.29%. Giosuè et al.<sup>22</sup> documented elevated mineral levels in biscuits enriched with grape pomace (from 1.2% in control samples to 2.1 and 2.0% in samples with addition of 30 and 20% of grape pomace respectively). Likewise, Oprea et al.<sup>23</sup> reported a significant increase in K, Ca, Mg, Cu, Fe, and Zn content when flour enriched with grape pomace powder was incorporated into bakery products.

The addition of grape pomace may also influence the toxicological profile of the biscuits. Incorporating 15% and 20% grape pomace increased the lead (Pb) content to 0.28 and 0.27 mg/kg, respectively, while cadmium (Cd) levels rose to 0.27 and 0.70 mg/kg at these concentrations. However, when considering the average yearly consumption of biscuits and the tolerable weekly intake levels for Pb (1.750 mg/person/week) and Cd (0.175 mg/person/week), the consumption of such biscuits can be considered safe. Nonetheless, careful monitoring of the heavy metal content in grape pomace and its potential cumulative effects is essential to ensure long-term food safety.

	к	Na	Са	Mg	Р	Cu	Zn	Mn	Fe	Cr	Ni	Со	Pb	Cd	Hg
к	1														
Na	0.62	1													
Ca	0.88	0.72	1												
Mg	0.89	0.76	1.00	1											
Р	-0.61	0.11	-0.41	-0.38	1										
Cu	0.80	0.79	0.76	0.76	-0.38	1									
Zn	0.58	0.68	0.38	0.42	-0.29	0.72	1								
Mn	0.91	0.68	0.79	0.80	-0.63	0.87	0.82	1							
Fe	0.75	0.80	0.81	0.85	0.02	0.57	0.36	0.58	1						
Cr	0.89	0.72	0.79	0.79	-0.47	0.97	0.67	0.88	0.62	1					
Ni	0.90	0.66	0.94	0.95	-0.34	0.66	0.30	0.70	0.91	0.75	1				
Со	0.90	0.61	0.87	0.88	-0.33	0.60	0.32	0.68	0.92	0.72	0.98	1			
Pb	0.91	0.63	0.89	0.91	-0.34	0.62	0.32	0.69	0.92	0.73	0.99	1.00	1		
Cd	0.74	0.66	0.96	0.94	-0.29	0.70	0.18	0.63	0.74	0.70	0.88	0.76	0.80	1	
Hg	0.91	0.72	0.97	0.96	-0.51	0.88	0.50	0.87	0.72	0.89	0.88	0.80	0.83	0.92	1

Table 3: Correlations between contents of individual elements

Values in bold are statistically significant (p < 0.05)

As showed in the Table 3, the correlation analysis revealed several strong relationships between mineral contents in long-life bakery products with grape pomace addition. A highly positive correlation was observed between potassium and magnesium (r = 0.89), calcium (r = 0.88), and manganese (r = 0.91), suggesting that grape pomace is a rich source of these elements and contributes significantly to their increased presence in the final product. Similarly, copper correlated strongly with chromium (r = 0.97), indicating similar distribution patterns within the matrix. Interestingly, phosphorus showed a weak and negative correlation with potassium (r = -0.61), calcium (r = -0.41), and magnesium (r = -0.38). This suggests potential interactions or competitive binding effects that may influence phosphorus retention in the bakery matrix. In terms of safety considerations, lead, cadmium, and mercury exhibited strong positive correlations with key minerals such as calcium (r = 0.89, r = 0.96, r = 0.97, respectively) and magnesium (r = 0.91, r = 0.94, r = 0.96, respectively). This indicates that while grape pomace enhances the nutritional profile, it may also introduce heavy metals that require careful monitoring to mitigate potential health risks.

These findings underscore the need for further investigation into mineral bioavailability and potential mitigation strategies for heavy metal accumulation in bakery products enriched with grape pomace.

#### Conclusion

This study demonstrated that incorporating grape pomace into long-life bakery products significantly enhances their mineral profile. Among the macroelements, potassium, calcium, and magnesium exhibited the most substantial increases, while microelements such as copper, zinc, and iron also improved. However, developing food products with unconventional ingredients requires balancing sensory appeal with nutritional benefits to meet consumer expectations. A key concern identified in this study is the observed increase in heavy metals, particularly lead and cadmium, after grape pomace addition. This finding highlights the need for careful selection, monitoring, and processing of grape pomace to ensure food safety. While moderate inclusion levels appear promising, for industrial applications, it is essential to investigate in more detail how to manage potential toxic effects associated with long-term consumption. Addressing these concerns is crucial to ensuring regulatory compliance and consumer safety.

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For food producers, optimizing the level of grape pomace inclusion is critical to maximizing nutritional benefits while minimizing sensory and safety concerns. Future research should focus on improving the bioavailability of beneficial minerals, refining processing techniques to reduce heavy metal content, and conducting long-term risk assessments to support the safe and sustainable application of grape pomace in food products.

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## Vplyv prídavku hroznových výliskov na minerálny profil trvanlivých pekárenských výrobkov

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#### Súhrn

Začlenenie hroznových výliskov do prípravy inovatívnych potravinárskych výrobkov ponúka sľubnú stratégiu zhodnocovania vedľajších produktov vinárskeho priemyslu. Cieľom tejto štúdie bolo vyvinúť trvanlivé pečivo s prídavkom hroznových výliskov (Cabernet Franc) v množstve 5 %, 10 %, 15 % a 20 %. Obsah mikro- a makroprvkov v pečive sa stanovil pomocou atómového absorpčného spektrofotometra (VARIAN AASpectra DUO 240FS/Z). Koncentrácia draslíka (K), vápnika (Ca), horčíka (Mg) a sodíka (Na) sa pohybovala od 1692 do 3797 mg/kg, 323 do 5799 mg/kg, 89 do 132 mg/kg a 317 do 362 mg/kg sušiny. Z mikroprvkov sa zistili koncentrácie medi (Cu), zinku (Zn), mangánu (Mn), železa (Fe), chrómu (Cr), niklu (Ni) a kobaltu (Co) v rozmedzí 0,63 – 1,07 mg/kg, 2,40 – 2,66 mg/kg, 3,10 – 3,84 mg/kg, 14,05 – 19,30 mg/kg, 0,10 – 0,41 mg/kg, <LD – 0,06 mg/kg a <LD – 0,08 mg/kg DM. Olovo (Pb) a kadmium (Cd) boli zistené v rozmedzí <LD-0,08 mg/kg a <LD-0,70 mg/kg sušiny. Na základe týchto zistení prídavok hroznových výliskov v 20% dávke do trvanlivého pečiva preukazuje významný potenciál pre udržateľné využitie odpadu z vinárskeho priemyslu. Prispieva tiež k zvýšenému obsahu zdraviu prospešných minerálnych látok v konečnom výrobku, čím ponúka cenný prístup k výrobe nutrične obohatených potravinárskych výrobkov.

Kľúčové slová: hroznové výlisky; sušienky; minerálne látky; ťažké kovy