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Investigation of Elemental Composition in White Wine Treated with Varying Doses of Bentonite

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Abstract: The mineral composition of wine is affected by numerous factors, including treatments with bentonite to control colloidal hazes. In this study, 10 parallel samples of white wine (Chardonnay, 2021 vintage year) were treated with pre-selected bentonite (activated calcium bentonite) at increasing doses, from 0.3 to 3.0 g/L. Following acid mineralization, the content of some important elements was determined. The elements Al, Ba, Cd, Cu, Cr, Fe, Mg, Mn, P, Pb, and Zn were measured by inductively coupled plasma with optical emission spectrometry (ICP-OES), while flame atomic absorption spectrometry (FAAS) was used for the determination of Ca, K, and Li. Depending on the applied dose, the bentonite changed the concentration of the determined elements in different ways. Results indicated that higher doses of bentonite led to an increase in Al, Ca, and Fe content, while Cu and Zn initially rose with low doses before declining to near-baseline levels with higher doses.

Keywords: wine; bentonite; elements; ICP-OES; FAAS

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1. Introduction

The mineral composition of wines results from various factors. The geographical and soil–climate (terroir) features of the region/microregion where the grapes are grown are of primary importance, followed by the interrelationship in the soil–rootstock–grape variety system. The agro-technical activities carried out in the vineyard during the cultivation of the vines, the method of grape harvesting, the processing of the grapes, and the conditions for the implementation of all technological practices in the pre-fermentative, fermentative, and post-fermentative stages of wine production technology are able to influence its mineral composition in different directions and degrees [1,2].

Certain elements contribute to different forms of wine turbidity. Thus, for example, the salts of tartaric acid with K and Ca cause the appearance of the most common crystal clouding—the so-called tartaric turbidity. Calcium can also interact with other acids (e.g., mucinic acid in rotten grapes) and provoke other crystal opacities. From an oenological point of view, elements from the group of heavy metals (Cu, Fe, Mn, Zn, etc.) can cause the appearance of the so-called chemical or metal hazes—ferriphosphate, ferritanate, and copper [3]. Furthermore, maximum permissible concentrations are established for certain elements [4] given their ability to accumulate in human organs and cause irreversible changes related to their proper functioning, potentially affecting consumer health. All this necessitates clarifying and stabilizing wine treatments in order to regulate the concentrations of these elements.

Such treatment steps will help reduce the possibility of negative impacts on the future quality of win. These treatments significantly alter the concentration of certain elements or groups of elements. The use of bentonite to protect wines from colloidal hazes can indirectly affect the elemental composition of wine in the future [5,6].

Bentonite is a type of clay from the aluminum silicate genus and depending on its nature and/or method of activation, it has a strong capacity to exchange elements with the environment and wine, respectively. Comprising montmorillonite, which has a layered structure, bentonite consists of repeating layers, containing an octahedral structure centered on aluminum and a tetrahedral structure with silicon. Between these layers, significant amounts of water can be sorbed (causing bentonite to swell up to 10–12 times its original volume). The greater separation of the montmorillonite layers probably facilitates the exchange of ions with the medium (the wine) [7]. Depending on the initial degree of wine instability, bentonite must be applied at varying doses for different wines. Its effects on the wine's elemental composition depend on the dosage; however, research in this field (on the interrelationship between the change in the elemental composition according to the applied dose of bentonite) is limited [8–10]. And there are still no studies on the bentonite dosage's influence on the mineral composition of Bulgarian wines. This study's main goal is to fill this gap. Preliminary research examined 16 commonly used bentonites of different natures in Bulgarian winemaking [11,12], namely natural sodium, natural sodium–calcium, natural calcium–sodium, activated sodium, and activated calcium. Based on the research results, the authors selected the one (activated calcium bentonite) which showed the highest sorption and desorption activity of elements from and to the wine. The selection criterion was the increased extractability of elements from the groups of heavy and toxic elements. The content of 14 chemical elements (Al, Ba, Cd, Cu, Cr, Fe, Mg, Mn, P, Pb, and Zn) was determined in the treated wines. Some of them are directly related to the possible development of the wine's metallic or crystalline hazes. Most have maximum permissible concentrations set by the OIV (International Organization of Vine and Wine), as their accumulation in the human body can cause irreversible effects. The OIV also mandates that bentonites used in wine must not contain As, otherwise the product cannot be released in the market. According to the results obtained in previous authors' studies [11,12], the selected activated calcium bentonite does not show any As desorption activity. This is the reason why this study did not include As.

2. Materials and Methods

2.1. Materials

The bentonite with which this research was carried out was chosen based on our previous research. Among a set of 16 bentonites, it showed the greatest sorption and desorption ability of elements from and to model solutions and real wine. In nature, this bentonite is activated calcium. A 5% bentonite slurry was prepared with the selected bentonite. The concentration of the bentonite suspension was chosen based on our many years of scientific and practical experience in the field of wine processing and stabilization. For many of the bentonites offered on the Bulgarian market, it is difficult, and in some cases practically impossible, to prepare a precisely dosed more concentrated bentonite suspension due to its high viscosity. On the other hand, using a suspension with a lower concentration leads to the introduction of more water into the wine, i.e., aromas and flavors are diluted. A portion of 300 mL still unstabilized Chardonnay wine, vintage 2021, from the Danube Plane Region in Bulgaria, was mixed with the prepared 5% bentonite slurry. The suspension was dosed under constant stirring on a magnetic stirrer in increasing amounts, providing bentonite doses from 0.3 g/L to 3.0 g/L in increments of 0.3 g/L. In order to complete the flocculation and sedimentation processes of bentonite sludge, the mixtures rested for 48 h. The clarified wine from each experimental sample was decanted from the sludge and then filtered using a "blue band" filter. From each treated wine, three parallel samples were mineralized using concentrated nitric acid [12]. Based on previous authors' studies [11,12], the number of chemical elements to be determined was selected.

Concentrated HNO_3, ≥69.0%, Trace SELECT (Fluka, Seelze, Germany), was used for wine sample acid mineralization.

A multielement standard solution 1 for ICP TraceCERT (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), containing 10 mg/L Ag, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, Sr, and

Zn; 50 mg/L Al, B, Cr, Li, Mo, Na, Ni, and Tl; and 100 mg/L Bi, K, and Pb was used for ICP-OES calibration standard solution preparation. Phosphorus Standard for ICP TraceCERT, (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) was used for phosphorus ICP-OES calibration standard solution preparation. Single-element standard solutions of elements Ca, K, and Li (Fluka, Seelze, Germany) with initial concentrations of 1000 mg/L were used after appropriate dilution to prepare FAAS calibration standard solutions.

All solutions were prepared with double-deionized water (Millipore purification system Synergy, Darmstadt, Germany).

2.2. Methods

The elemental content of Al, Ba, Cd, Cu, Cr, Fe, Mg, Mn, P, Pb, and Zn in the analyzed wine samples was determined using the instrumental technique of inductively coupled plasma–optical emission spectrometry (ICP-OES) by Varian Vista-MPX CCD Simultaneous. The instrument was equipped with a glass concentric nebulizer and a glass cyclonic spray chamber. The content of the selected elements was measured by the following wavelengths [nm]: Al, 308.215; Ba, 233.527; Cd, 214.439; Cu, 324.754; Cr, 267.716; Fe, 259.940; Mg, 279.800; Mn, 293.305; P, 213.618; Pb, 220.353; and Zn, 213.857.

The content of the elements Ca, K, and Li was determined using the instrumental technique of flame atomic absorption spectrometry (FAAS) via Perkin Elmer AAnalyst 400. An air–acetylene flame was used under recommended optimal instrumental parameters by the manufacturer.

2.3. Statistics

Excel software was used for data processing. The elements' concentration data were obtained as the average from three replicates of each of the three parallel wine samples mineralized. Principal component analysis (PCA) was performed on the analytical data concerning the mineral content of the wine samples treated with increasing bentonite doses. In order to see the changes in the mineral content with the increase in the bentonite, a Kendall's tau-b correlation was run, and statistical analysis was conducted using XLSTAT software (Addinsoft ©, Annual version 2023.3.1.1416, Paris, France) [13].

3. Results

3.1. Changes in Macroelement Content

The content of the elements Ca, K, Mg, and P in the raw wine untreated with any bentonite was found as 69 ± 7 mg/L, 470 ± 46 mg/L, 95 ± 8 mg/L, and 115 ± 10 mg/L, respectively. Figure 1 presents the tendency of Ca, Mg, and P concentration changes in wine samples after their treatment with different doses of bentonite. The potassium content was found to be between 445 ± 43 mg/L and 510 ± 50 mg/L. This means that as a result of adding bentonite in the treated wines, the concentration of K did not change significantly, even with the highest treatment dose.

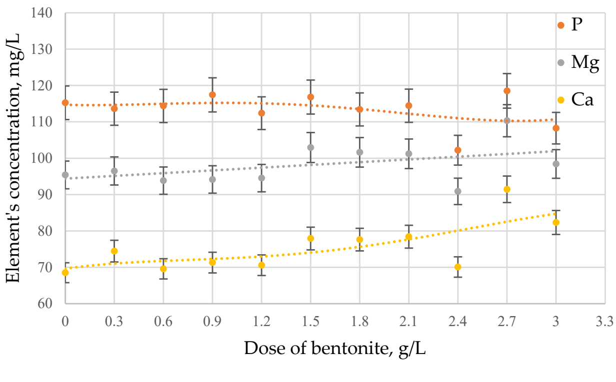

Figure 1. Changes in Ca, Mg, and P concentration in wine after treatment with bentonite in increasing doses.

3.2. Changes in Oligoelement Content

The concentrations of Al, Fe, Mn, and Zn in the analyzed wine samples are presented in Figure 2. Initially, the addition of bentonite resulted in a smooth increase in Al concentration; as its dose increased and for the highest doses of the selected treatment range, the increase was almost abrupt. The initial iron concentration in the sample without imported bentonite was 0.92 ± 0.08 mg/L. The addition of increasing amounts of bentonite led to its gradual sorption from the wine composition. In the wines with the highest doses of bentonite imported, a reverse trend was reported, namely its resorption. The Mn content of the raw wine was 0.67 ± 0.07 mg/L. Its treatment with the bentonite used did not significantly change the presence of this element in the analyzed wines, even with the highest dose applied. The change in Zn content with an increasing amount of bentonite added did not correspond to any of the trends discussed so far. Its content in the blank wine sample was 0.31 ± 0.04 mg/L. Once the first dose of imported bentonite (0.3 mg/L) was added, its concentration increased to 1.76 ± 0.15 mg/L; afterwards the increase in the dose led to its recovery to the same concentration as in the untreated wine. With a further increase in the bentonite dose, its concentration in the investigated dose range hardly changed.

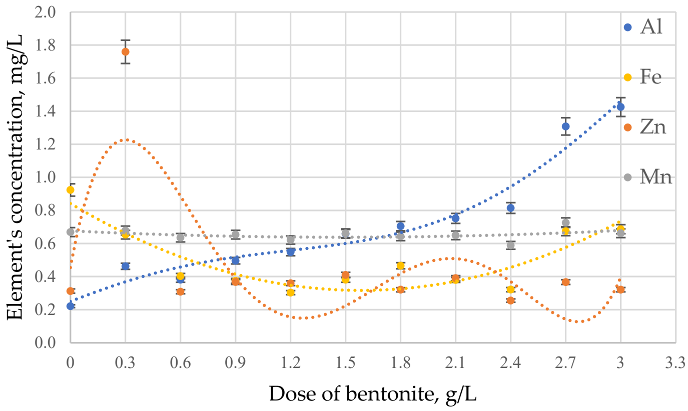

Figure 2. Changes in Al, Fe, Mn, and Zn concentration in wine after treatment with bentonite in increasing doses.

The Ba and Cu contents in the untreated wine sample were 0.079 ± 0.009 mg/L and 0.044 ± 0.006 mg/L, respectively, (Figure 3). The trend in the deviation of these elements slightly follows the one already discussed for Zn. A sharp increase in their concentrations was reported as a result of the first dose of bentonite applied for treatment, followed by the recovery of the concentration to approximately the initial value at the next step of increasing the amount of bentonite and maintaining this concentration until the end of the range of doses of the stabilizer applied.

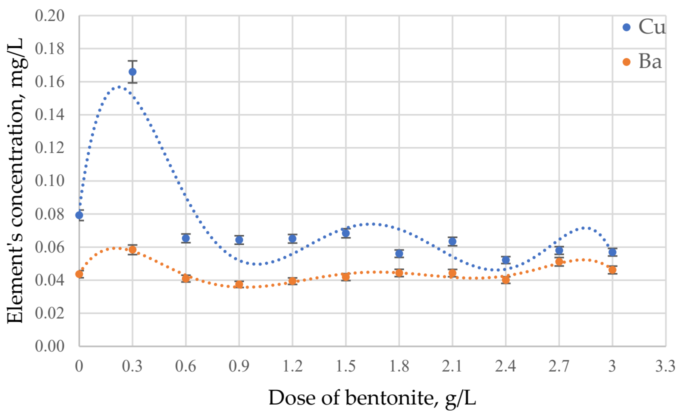

Figure 3. Changes in Ba and Cu concentration in wine after treatment with bentonite in increasing doses.

3.3. Changes in Microelement Content

For this group of elements, we report the deviations in Cd and Cr content (Figure 4). The content of Cd and Cr in the wine untreated with bentonite was 0.007 ± 0.001 mg/L and 0.011 ± 0.002 mg/L, respectively. Bentonite, regardless of the applied dose, did not significantly change the presence of Cd. The concentration of Cr decreased slightly with the very first dose of bentonite, it remained at almost unchanged levels, and with the highest applied doses, a slight increase was reported but not enough to reach the initial concentration of the element. Probably the reason for this decrease in chromium concentration is its sorption by the bentonite. The increase in the applied processing dose leads to a gradual decrease in the concentration of this element in the processed wine. In the experimental samples with the highest concentrations of bentonite imported, an increase in the concentration of this element was reported, probably due to release (desorption) from the bentonite to the wine.

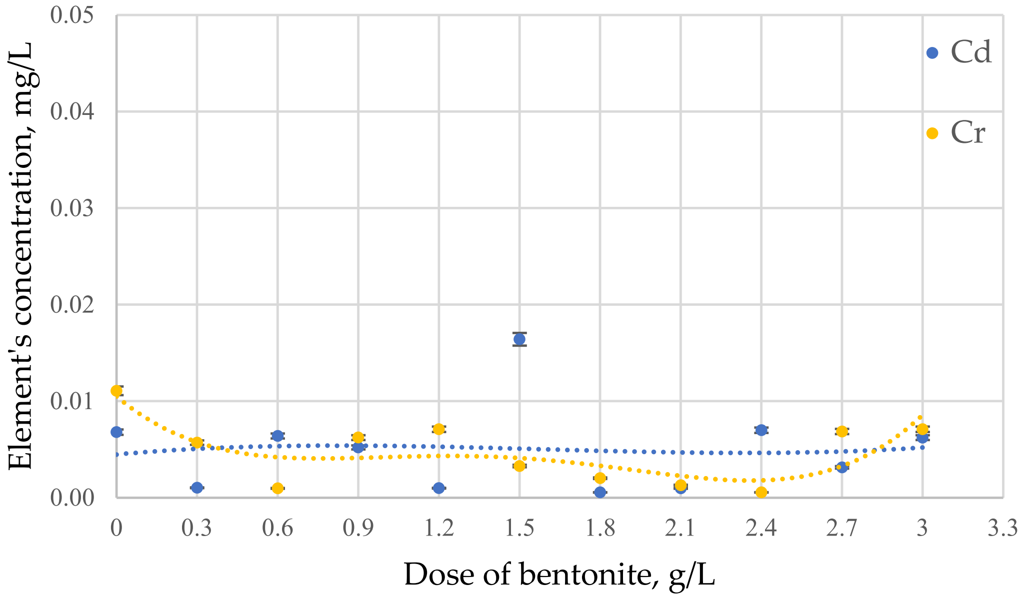

Figure 4. Changes in Cd and Cr concentration in wine after treatment with bentonite in increasing doses.

The changes in Li and Pb were also evaluated. The results showed values below 0.001 mg/L and below 0.10 mg/L, respectively, in all analyzed experimental wines.

3.4. Principal Component Analysis (PCA)

A PCA biplot, presented in Figure 5, shows how the wine samples are characterized by some chemical element content. The sum of the main two components is 65.33%. The W1 wine sample has the highest content of Ba, Cu, Fe, and Zn and a low Cd content. The W9 sample has the highest content of Ca, Mg, Mn, and P and a low content of K. On the other hand, W8 has the highest K content but very low or the lowest concentrations of Ba, Ca, Cr, Cu, Fe, Mg, Mn, P, and Zn. The other samples are in the middle of the plot and prove to be more balanced in the change in mineral content.

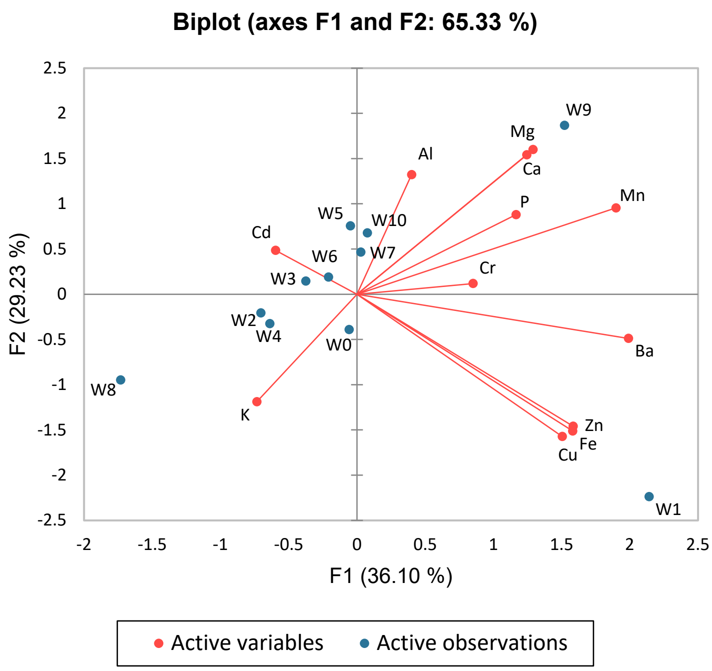

Figure 5. Principal component analysis (PCA) biplot of the wine sample mineral content. W0—blank wine sample; W1–W10—wine samples with increasing bentonite dose.

4. Discussion

The values obtained for the Ca and Mg concentrations in the analyzed wines treated with different doses of bentonite are in agreement with previous studies and the results published in various literary sources in the field of oenology [14]. With an increase in the dose of the bentonite added, a slight and gradual increase in Mg and Ca levels after treatment was observed. More specifically, for Ca, some of the literature sources [3] mention an increased risk of turbidity due to the formation of calcium tartrate at concentrations around and above 80 mg/L. This concentration is reached and even exceeded in the wine variants treated with the highest doses of bentonite. The P content showed a tendency towards a very slight decrease but only for the wines with the highest bentonite doses. Lower doses did not affect the content of this element in the wine.

The concentration of Al increased from 0.22 $\pm$ 0.02 mg/L in the untreated wine to 1.43 $\pm$ 0.12 mg/L in the sample treated with the highest dose. Despite this increase, its concentration does not exceed the maximum permissible value in wine regarding the OIV (3 mg/L). As is well known, bentonite is a type of hydrated aluminum silicate. These results are probably due to the substitution of Al from the crystal lattice by other elements. Similarly to Al, the reported values for Fe are below its maximum limit (10 mg/L) in wine regarding the OIV. Furthermore, the Fe concentration found, even in the sample with the highest dose of bentonite added, is too far from being able to provoke iron haze after treatment with this bentonite.

These results obtained for Ba and Cu are of great importance from an oenological point of view, as Fe and Zn, like Cu, belong to the group of heavy metals in wine. According to the resolutions of the OIV, there is not only a maximum permissible concentration for them, but under certain conditions, they can also cause the wine to become cloudy. Even the highest concentrations found in the experimental samples are by no means critical, both from a legal point of view and in terms of impairing the wine's clarity.

Results obtained for the microelements Cd, Cr, Li, and Pb show that the content of these elements is also far from the maximum permissible levels in which they can be present in wines.

Kendall's tau-b values, presented in Table 1, show that there is a very strong, positive, and statistically significant association between the contents of bentonite and Al (τ_b = 0.96), a strong, positive, and statistically significant association between the contents of bentonite and Ca (τ_b = 0.56), and a weak, positive, and statistically not significant associations between the contents of bentonite and Ba (τ_b = 0.2) and bentonite and Mg (τ_b = 0.23). On the other hand, an increase in bentonite leads to a decrease in Cu (τ_b = −0.64).

Table 1. Values of Kendall's tau-b.

Sample	Element Content, mg/L													
	Al	**Ba**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Mn**	**P**	**Pb**	**Zn**
W0	0.22	0.044	69	0.007	0.011	0.079	0.92	470	<0.001	95	0.67	115	<0.100	0.31
W1	0.46	0.058	74	0.001	0.006	0.166	6.5	495	<0.001	96	0.68	114	<0.100	1.76
W2	0.38	0.041	70	0.006	0.001	0.065	0.40	450	<0.001	94	0.64	114	<0.100	0.31
W3	0.50	0.037	71	0.005	0.006	0.064	0.37	445	<0.001	94	0.65	117	<0.100	0.37
W4	0.55	0.039	71	0.001	0.007	0.065	0.30	465	0.151	95	0.62	112	<0.100	0.36
W5	0.66	0.042	78	0.016	0.003	0.068	0.38	455	<0.001	103	0.66	117	<0.100	0.41
W6	0.71	0.044	78	0.001	0.002	0.056	0.47	480	<0.001	102	0.64	113	<0.100	0.32
W7	0.75	0.044	78	0.001	0.001	0.063	0.38	450	<0.001	101	0.65	114	<0.100	0.39
W8	0.81	0.040	70	0.007	0.001	0.052	0.32	510	<0.001	91	0.59	102	<0.100	0.26
W9	1.31	0.051	91	0.003	0.007	0.058	0.67	450	<0.001	110	0.73	119	<0.100	0.37
W10	1.43	0.046	82	0.006	0.007	0.057	0.69	465	<0.001	98	0.66	108	<0.100	0.32
τ_b	0.96	0.2	0.56	−0.09	−0.12	−0.64	−0.09	0.02	-	0.23	−0.05	−0.16	-	−0.09

The reported trends in the concentration changes in the studied elements are largely consistent with findings from previous studies in this field [8–10]. However, some authors report much more significant changes in concentrations (sometimes many times higher than the baseline in untreated wines). The changes found in the present study followed the trends but with smaller differences compared to the control sample. This is probably due to the different objectives that were the focus of the different researchers in their scientific work, the uniqueness in the physicochemical composition of the processed and studied wines, the different nature, composition, and properties of the bentonites used, the different dosages with which the wines were treated, and last but not least, the various analytical techniques used to carry out the research.

5. Conclusions

In our previous studies cited above, we have shown that the choice of bentonite for colloidal stabilization matters in the context of its influence on the elemental composition of wine. The results of the present study show that the applied dose of selected bentonite has a different effect on the wine's elemental composition. As the dose of bentonite increases, the changes in the elemental composition of the wine become more significant. For some elements, sorption in the direction from the bentonite side is observed, for others, a release from the bentonite to the wine is observed. And for some elements, both sorption and desorption phenomena were reported with the increase in the dose. The most significant was the influence of the applied dose on Al and Cu content. The applied dose itself depends primarily on the initial degree of instability of the wine. These results are of great importance for the wine practice. Changes in the elemental composition of the wine can cause clouding or affect consumer health.

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Data Availability Statement: The data presented in this study are only available upon request from the corresponding author due to the absence of a data repository for this specific dataset.

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