Data Article

Data on the influence of clarification and stabilization with bentonite clays on the elemental composition of red wines determining their varietal affiliation

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A R T I C L E   I N F O

A B S T R A C T

The research data on the effect of bentonite clays (BT) in the process of clarification and stabilization on the elemental composition determining the varietal affiliation of wines are analyzed in the article. The initial objects were three untreated wine samples produced from Cabernet Sauvignon, Merlot and Moldova grape varieties in the Krasnodar Territory. Clarification and stabilization of untreated wine samples was carried out with 32 samples of BT of various degrees of dispersion and trademarks. The concentrations of metals, i.e., macro- and microelements, in bentonite clays, untreated and treated wine samples were determined by ICP-OES and ICP-MS methods. The results of the influence of stabilization and clarification of various wines with 32 BT on their elemental composition based on the concentrations of 16 micro- and macroelements isolated chemometrically from 39 elements are shown in the article. The elemental composition of the initial wine varieties as well as wine samples obtained after their clarification and stabilization (32 samples per each variety) was established based on the results of three

parallel measurements. The aim of the study was to assess the contribution of macro- and microelements to the formation of the elemental image of wines determining their varietal affiliation. Using discriminant analysis and principal component analysis, the presence of cluster structures in treated and untreated wine samples was established in accordance with their varieties with respect to the concentrations of isolated macro- and microelements. The role of microelements was shown to be higher than that of macroelements in the formation of varietal image of wines. The combination of the most informative macro- and microelements in determining the cluster structure of wine samples increases the possibilities of assessing the intravarietal similarity and intervarietal differences of wines.

Specifications Table

Subject	Food Science: Food Technology
Specific subject area	Chemometric analysis of wine quality
Type of data	Figures, tables
How data were acquired	The ICP-OES and ICP-MS methods were used to quantify 39 elements in treated and untreated wine samples, as well as bentonite clays samples. Statistical analysis of experimental data was performed using the STATISTICA software (v.13)
Data format	Raw
Description of data collection	Raw wine samples produced from grape varieties Cabernet Sauvignon, Merlot and Moldova were clarified and stabilized with 32 bentonite clays samples of various degrees of dispersion and trademarks. The ICP-OES and ICP-MS methods were used to quantify 39 elements in 96 treated and 3 untreated wine samples.
data source location	Center for environmental analysis at the Kuban State University krasnodar russia
Data accessibility	Repository name: Mendeley Data Data identification number: 10.17632/zmyy4fy2hs.3 Direct link to the dataset: https://data.mendeley.com/datasets/zmyy4fy2hs/3
Related research article	Z. Temerdashev, A. Abakumov, M. Bolshov, A. Khalafyan, N. Ageeva, A. Vasilyev, A. Ramazanov, 2022. Instrumental assessment of the formation of the elemental composition of wines with various bentonite clays. Microchem. J. 175, 107,145. 10.1016/j.microc.2021.107145

Value of the Data

- The data provide insight into the interaction of bentonite clays of various nature with wine samples and the procedure for the exchange of elements during the formation of their elemental composition.
- The data allow to assess the contribution of claying agents to the elemental composition of wines and establish marker elements that determine their varietal affiliation.
- The data can be compared with the publications of other authors and/or used by specialists in the selection of bentonite clays that affect the identification and consumer properties of wines.
- The data may be of interest to scientists and oenologists for comparative analysis and expert assessment of the quality of wines.

1. Data Description

The contribution of macro- and microelements to the elemental image formation of wines, which determines their varietal affiliation, considering their stabilization and clarification with bentonite clays (BT) of various degrees of dispersion and trademarks, was assessed by chemometric methods. The cluster structure of the studied wine samples, i.e., the degree of their similarity/difference based on metal concentrations, was determined by the discriminant analysis (DA) using the Fisher criterion (F-criterion); as a result, 16 most informative macro- and microelements were isolated from 39 metals. Statistically significant elements in the discrimination model with a significance level of the F-criterion $p < 0.05$ were selected. Based on the concentrations of 16 isolated metals, DA and principal component analysis (PCA) were used to study the presence of a cluster structure in the treated and untreated wine samples in accordance with their varieties. The sequence of metals in decreasing order of their contribution to the discrimination model, and hence the cluster structure of wine samples, was as follows: Zn, Cu, K, Rb, Ge, Mo, Li, Mg, Ca, Pb, Zr, Na, Cd, Nb, Co, Be. Data on the concentrations of 16 micro- and macroelements in the three initial samples as well as BT-treated wines (32 samples per each variety) considering three parallel measurements are given in the repository.

Changes in metal contents in the untreated and BT-treated wines were assessed by descriptive statistics of the macroelement (Na, K, Ca and Mg) and microelement (Zn, Cu, Rb, Ge, Mo, Li, Pb, Zr, Cd, Nb, Co and Be) concentrations. Descriptive statistics included Mean, Median; Minimum, Maximum, Lower Quartile, Upper Quartile, standard deviation (Std.Dev.). Statistics of macroelement concentrations given in Tables 1–3 show their intra- and intervarietal variability in the untreated and treated samples.

Table 1
Descriptive statistics of macroelements in Cabernet Sauvignon wine.

Variable	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
			Cabernet Sauvignon untreated				
Na	45,000.00	45,000.00	44,000.00	46,000.00	44,000.00	46,000.00	1000.00
K	726,000.00	728,000.00	722,000.00	728,000.00	722,000.00	728,000.00	3464.10
Ca	73,000.00	72,000.00	72,000.00	75,000.00	72,000.00	75,000.00	1732.06
Mg	70,000.00	70,000.00	69,000.00	71,000.00	69,000.00	71,000.00	1000.00
			Cabernet Sauvignon treated with bentonite				
Na	77,062.50	75,500.00	61,000.00	103,000.00	69,000.00	83,500.00	10,463.26
K	630,218.75	634,000.00	595,000.00	676,000.00	622,500.00	638,500.00	16,382.00
Ca	93,625.00	93,000.00	82,000.00	135,000.00	90,000.00	95,000.00	9114.86
Mg	85,343.75	85,000.00	76,000.00	96,000.00	82,500.00	87,000.00	4810.00

Table 2
Descriptive statistics of macroelements in Merlot wine.

Variable	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
			Merlot untreated				
Na	19,000.00	18,000.00	18,000.00	21,000.00	18,000.00	21,000.00	1732.05
K	849,000.00	847,000.00	844,000.00	856,000.00	844,000.00	856,000.00	6244.99
Ca	69,000.00	68,000.00	67,000.00	72,000.00	67,000.00	72,000.00	2645.75
Mg	94,000.00	95,000.00	92,000.00	95,000.00	92,000.00	95,000.00	1732.05
			Merlot treated with bentonite				
Na	41,531.25	40,000.00	27,000.00	62,000.00	34,000.00	48,500.00	9287.47
K	767,843.75	771,000.00	732,000.00	805,000.00	767,000.00	776,000.00	16,240.35
Ca	89,968.75	89,500.00	74,000.00	131,000.00	85,500.00	91,000.00	9620.15
Mg	110,312.50	109,000.00	101,000.00	123,000.00	107,000.00	114,500.00	5468.02

Table 3

Descriptive statistics of macroelements in Moldova wine.

	Moldova untreated						
Variable	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
Na	22,000.00	22,000.00	21,000.00	23,000.00	21,000.00	23,000.00	1000.00
K	732,000.00	732,000.00	729,000.00	735,000.00	729,000.00	735,000.00	3000.00
Ca	92,000.00	93,000.00	89,000.00	94,000.00	89,000.00	94,000.00	2645.75
Mg	79,000.00	78,000.00	77,000.00	82,000.00	77,000.00	82,000.00	2645.75
	Moldova treated with bentonite						
Na	46,281.25	45,000.00	29,000.00	65,000.00	39,000.00	54,000.00	9580.87
K	650,562.50	655,000.00	612,000.00	690,000.00	642,000.00	660,000.00	16,891.97
Ca	116,562.50	116,000.00	104,000.00	184,000.00	112,000.00	117,000.00	13,167.66
Mg	90,533.02	90,000.00	80,669.09	100,457.30	88,000.00	93,000.00	4765.04
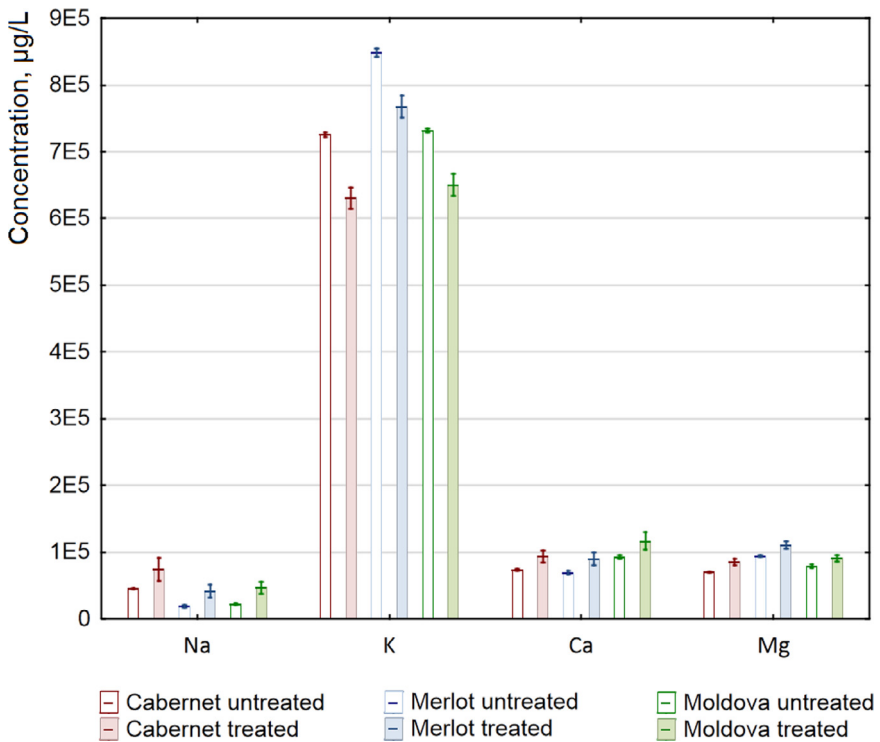
Fig. 1. A bar chart of microelement concentrations in wine samples.

The dynamics of changes in the concentrations of macroelements during the stabilization and clarification using BT can be more clearly represented using a bar chart (Fig. 1). The concentrations of elements in the untreated samples are indicated by horizontal shading, and mean concentrations in treated wine samples are indicated by vertical shading. As can be seen from the presented graph, the concentrations of Na, Ca, Mg averagely increase after the treatment with BT in comparison with the untreated ones, while K concentration decreases.

Descriptive statistics of microelement concentrations in the untreated and BT-treated wines are given in Tables 4–6.

Table 4

Descriptive statistics of microelements in Cabernet Sauvignon wine.

Variable	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
			Cabernet Sauvignon untreated				
Li	23.80	23.60	22.40	25.40	22.40	25.40	1.51
Co	1.60	1.55	1.53	1.73	1.53	1.73	0.11
Zr	4,.30	4.30	4.20	4.40	4.20	4.40	0.10
Mo	0.38	0.36	0.36	0.42	0.36	0.42	0.03
Cd	0.12	0.12	0.11	0.13	0.11	0.13	0.01
Cu	356.00	359.00	348.00	361.00	348.00	361.00	7.00
Zn	271.00	272.00	263.00	278.00	263.00	278.00	7.55
Be	0.15	0.16	0.14	0.16	0.14	0.16	0.01
Ge	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb	0.14	0.14	0.13	0.15	0.13	0.15	0.01
Rb	967.65	969.15	967.63	961.30	967.63	961.30	5.74
Pb	7.10	7.10	690.00	7.30	6.90	7.30	0.20
			Cabernet Sauvignon treated with bentonite				
Li	25.40	25.30	23.50	28.40	24.85	25.80	0.96
Co	2.79	2.48	1.70	7.40	2.12	3.17	1.12
Zr	33.17	30.65	7.60	71.80	18.10	40.25	18.08
Mo	1.11	1.18	0.40	2.00	0.85	1.35	0.36
Cd	0.79	0.75	0.48	1.35	0.62	0.93	0.22
Cu	112.00	114.50	86.00	130.00	102.50	121.50	11.64
Zn	224.50	223.00	194.00	255.00	217.50	230.50	13.43
Be	2.42	1.24	0.17	8.36	0.74	3.69	2.41
Ge	0.07	0.03	0.00	0.28	0.00	0.12	0.09
Nb	0.35	0.35	0.00	0.57	0.27	0.43	0.12
Rb	798.74	800.57	710.88	853.50	787.63	817.82	30.30
Pb	13.63	12.55	8.40	27.50	11.10	14.75	4.17

The dynamics of changes in the concentrations of microelements was also analyzed using bar charts. Since the concentrations of microelements are of different orders of magnitude, for clarity of visualization, trace elements were divided into 3 groups: Cu, Zn and Rb; Li, Co, Zr and Pb; Mo, Cd, Be, Ge and Nb.

Graphical illustrations in Figs. 2–4 and data given in Tables 4–6 confirm that the average values of the contents of Cu, Zn and Rb after treatment with BT are lower than their concentrations in the untreated samples, and the average contents of the remaining 9 trace elements (Li, Co, Zr, Pb, Mo, Cd, Be, Nb and Ge) increase.

Summarizing the results of graphical analysis for 16 micro- and macroelements, it can be concluded that the clarification and stabilization of wines with BT of various groups is accompanied by an increase in the concentrations of Na, Ca, Mg, Li, Co, Zr, Pb, Mo, Cd, Be, Nb, Ge and a decrease in the concentrations of K, Cu, Zn, Rb in treated wine samples. The data given in Tables 1–6 and Figs. 1–4 show a small variance in microelement concentrations in the treated wine samples of the same variety, which also allows to draw an equally important conclusion about the presence of small intra-varietal and significant inter-varietal differences in the concentrations of micro- and macroelements in the untreated and treated wine samples.

Using DA and PCA methods, it was established that intravarietal similarity and intervarietal differences of 16 micro- and macroelements form a cluster structure of treated wine samples, which is evident in their division into homogeneity groups in accordance with varieties. Therefore, it seems relevant to assess the role of macro- and microelements in the preservation of intervarietal differences and intravarietal similarity of wines after their treatment with BT.

The role of macroelements in the preservation of varietal differences was assessed by DA and PCA methods based on the concentrations of 4 macroelements from 16 previously isolated elements. The quality of discrimination is related to the configuration of wine samples as objects

Table 5
Descriptive statistics of microelements in Merlot wine.

Variable	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
				Merlot untreated			
Li	15.27	15.20	14.80	15.80	14.80	15.80	0.50
Co	1.20	1.30	1.00	1.30	1.00	1.30	0.17
Zr	2.47	2.49	2.38	2.53	2.38	2.53	0.08
Mo	1.20	1.20	1.10	1.30	1.10	1.30	0.10
Cd	0.11	0.10	0.08	0.15	0.08	0.15	0.04
Cu	271.00	269.00	266.00	278.00	266.00	278.00	6.24
Zn	375.33	375.00	370.00	381.00	370.00	381.00	5.51
Be	0.07	0.07	0.07	0.08	0.07	0.08	0.01
Ge	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rb	870.33	868.00	863.00	880.00	863.00	880.00	8.74
Pb	4.87	4.60	4.60	5.40	4.60	5.40	0.46
				Merlot treated with bentonite			
Li	16.93	16.90	15.30	19.40	16.30	17.30	0.89
Co	2.62	2.50	1.80	6.30	2.00	2.90	0.92
Zr	23.33	20.40	7.83	62.10	15.68	25.47	13.02
Mo	2.06	1.75	1.20	3.50	1.50	2.85	0.70
Cd	0.74	0.72	0.50	1.41	0.59	0.85	0.20
Cu	134.97	133.50	115.00	156.00	126.00	142.50	11.36
Zn	260.94	260.50	227.00	291.00	251.00	270.00	13.75
Be	2.30	1.62	0.14	7.38	0.61	3.33	2.16
Ge	0.05	0.00	0.00	0.27	0.00	0.10	0.08
Nb	0.05	0.00	0.00	0.30	0.00	0.06	0.10
Rb	688.00	691.15	631.41	714.80	683.61	696.96	16.68
Pb	9.80	9.15	6.40	20.60	8.50	11.10	2.54

of a multidimensional space, i.e., with its increase, their cluster structure becomes more pronounced. Characteristics of wine samples discrimination given in Table 7, namely, Wilks' Lambda close to 0 (0.002), the significance level of the F-criterion of $p < 0.00$ and significance levels of all 4 metals (p-value) less than 0.05, indicate the successful discrimination of samples – the presence of a cluster structure in wine samples. Metals are listed in the table in a descending order of their contribution to the discrimination pattern, as determined by the Wilks' Lambda value in column 1.

A graphical confirmation of the presence of a cluster structure of wine samples is a scatter diagram of canonical values, which allowed to transfer wine samples as objects of a space of dimension 4 (by the number of macroelements) into a space of dimension 2 (on a plane), while maintaining the order of the distances between them (Fig. 5). Untreated and BT-treated wine samples are displayed as geometric figures. According to the diagram, it is possible to assess the degree of similarity/difference, both between wine samples and between their varieties by means of the distances between their graphical images according to the principle: the greater the distance, the less the similarity, i.e., the greater the difference.

The diagram shows the formation of groups of homogeneity by treated wine samples, namely, clusters in accordance with their varietal affiliation, since treated samples of one variety are localized in a certain part of the plane in close proximity to each other. A certain difference is also noticeable between untreated wine samples; they are separated from each other. Nevertheless, the insufficiently high density of the location of samples of one variety on the graph, the contact of the location areas of treated wines of Cabernet and Moldova varieties, the erroneous classification of 2 samples of Cabernet as Moldova, indicate insufficient intravarietal similarity and intervarietal differences of wines, i.e., the weakness of their cluster structure.

Table 6
Descriptive statistics of microelements in Moldova wine.

| Variable | Merlot untreated | | | | | | |
	Mean	Median	Minimum	Maximum	Lower Quartile	Upper Quartile	Std.Dev.
Li	12.49	12.54	12.12	12.80	12.12	12.80	0.34
Co	2.42	2.41	2.39	2.47	2.39	2.47	0.04
Zr	0.51	0.53	0.44	0.56	0.44	0.56	0.06
Mo	1.69	1.68	1.66	1.72	1.66	1.72	0.03
Cd	0.02	0.02	0.02	0.03	0.02	0.03	0.01
Cu	158.67	158.00	156.00	162.00	156.00	162.00	3.06
Zn	860.33	863.00	855.00	863.00	855.00	863.00	4.62
Be	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ge	1.16	1.14	1.13	1.20	1.13	1.20	0.04
Nb	0.30	0.30	0.29	0.30	0.29	0.30	0.01
Rb	662.10	661.20	659.00	666.10	659.00	666.10	3.63
Pb	19.17	19.10	18.30	20.10	18.30	20.10	0.90
	Moldova treated with bentonite						
Li	14.64	14.49	12.79	17.94	13.85	15.16	1.17
Co	5.30	4.28	2.97	9.16	3.64	7.02	2.00
Zr	21.74	17.80	5.73	55.92	12.85	24.23	13.77
Mo	3.68	3.77	1.70	4.98	2.88	4.54	0.90
Cd	0.72	0.72	0.35	1.50	0.48	0.89	0.27
Cu	68.79	67.10	43.38	91.95	57.87	82.48	14.40
Zn	589.85	589.12	555.25	621.07	575.72	603.73	18.84
Be	3.86	3.07	0.29	12.67	1.29	5.10	3.42
Ge	2.68	2.61	1.46	4.00	2.24	3.10	0.62
Nb	0.69	0.59	0.23	1.28	0.47	0.91	0.27
Rb	485.17	488.35	465.34	500.29	477.28	493.89	10.51
Pb	33.11	31.34	26.46	48.82	29.48	36.69	5.51

Table 7
DA results for wines based on macroelement concentrations.

| | Discriminant Function Analysis Summary (Bentonites1–1) No. of vars in model: 4; Grouping: Sort (6 grps) Wilks' Lambda: 0.002 approx. F (20.319) = 82.439 $p < 0.00$ | | | | | |
$N = 105$	Wilks' Lambda	Partial Lambda	F-remove (5.96)	p-value	Toler.	1-Toler. (R-Sqr.)
K	0.013	0.181	86.642	0.000	0.847	0.153
Mg	0.009	0.258	55.284	0.000	0.923	0.077
Na	0.006	0.433	25.186	0.000	0.892	0.108
Ca	0.005	0.484	20.457	0.000	0.826	0.174

Reducing the dimensionality of space in PCA is achieved by selecting the principal components of factors and depicting each object on the factor plane with coordinates Factor1, Factor2 (Fig. 6).

As can be seen from Fig. 6, treated wine samples, in accordance with their varieties, also form groups of homogeneity with an insufficiently pronounced cluster structure, since according to one sample, Merlot and Moldova are outside the cluster boundaries and the distance between Cabernet and Moldova wines is insignificant.

The role of microelements in the preservation of intervarietal differences was assessed based on the concentrations of 4 microelements in order to provide a comparative analysis of the role of macro- and microelements in the formation of the cluster structure of wine samples in approximately equal conditions of their quantitative ratios. For this, according to column 1 of Table 8 constructed using DA, 4 out of 12 trace elements were selected, namely, Zn, Cu, Li,
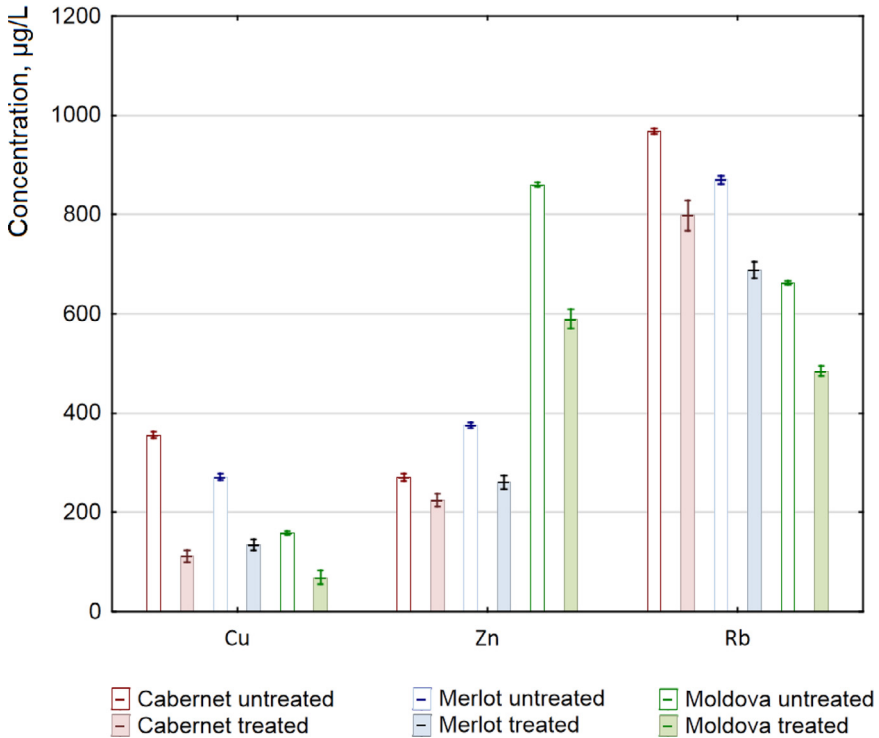
Fig. 2. A bar chart of Cu, Zn, Rb concentrations in wine samples.

Table 8
DA results for wines based on microelement concentrations.

	Discriminant Function Analysis Summary (Bentonites1–2) No. of vars in model: 12; Grouping: Sort (6 grps) Wilks' Lambda: 0.000001 approx. F (60.415) = 143.89 $p < 0.000$					
$N = 99$	Wilks' Lambda	Partial Lambda	F-remove (5.88)	p-value	Toler.	1-Toler. (R-Sqr.)
Zn	0.00001357	0.040	420.799	0.000	0.647	0.353
Cu	0.00000276	0.197	71.685	0.000	0.793	0.207
Li	0.00000204	0.266	48.456	0.000	0.665	0.335
Rb	0.00000137	0.398	26.602	0.000	0.767	0.233
Ge	0.00000103	0.530	15.603	0.000	0.602	0.398
Pb	0.00000089	0.611	11.224	0.000	0.705	0.295
Co	0.00000074	0.732	6.443	0.000	0.421	0.579
Zr	0.00000073	0.743	6.079	0.000	0.593	0.407
Mo	0.00000072	0.754	5.757	0.000	0.593	0.407
Cd	0.00000069	0.793	4.581	0.001	0.399	0.601
Be	0.00000059	0.917	1.585	0.173	0.589	0.411
Nb	0.00000058	0.933	1.273	0.283	0.715	0.285

Rb, with the greatest contribution to the discrimination of wine samples and therefore to the formation of their cluster structure.

DA results for 4 selected microelements are shown in Table 9 and Fig. 7.

Comparison of DA results presented in Tables 7 and 9 and in Figs. 5 and 7, made it possible to claim that the role of microelements in the separation of wine samples by varieties is higher than that of macroelements. Thus, Wilks' Lambda = 0.00001 in the informational part
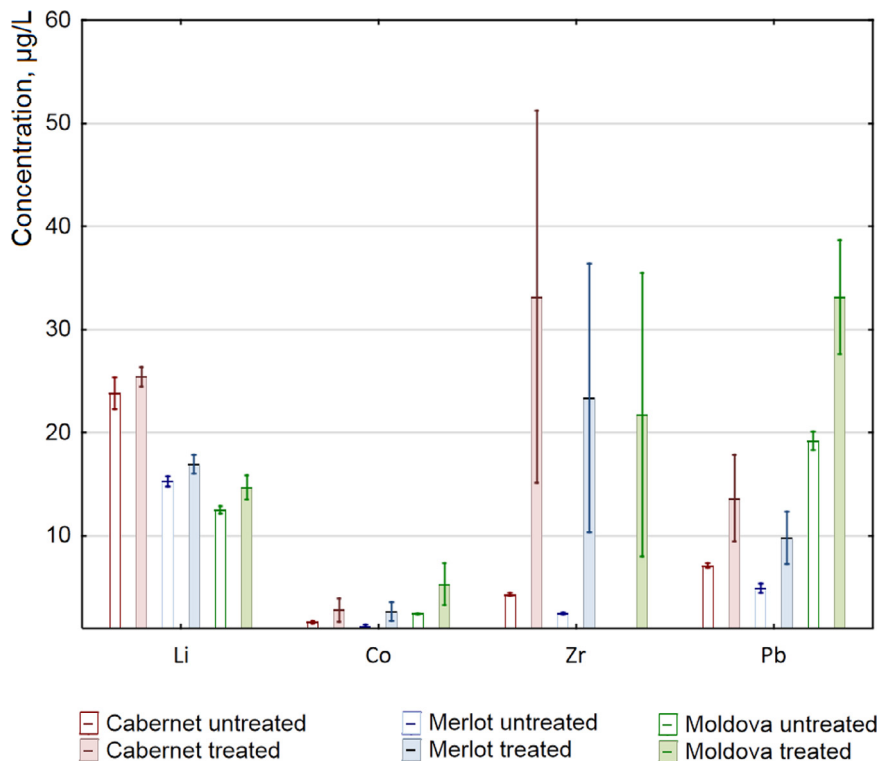
Fig. 3. A bar chart of Li, Co, Zr, Pb concentrations in wine samples.

Table 9
DA results for wines based on the concentrations of 4 selected microelements.

	Discriminant Function Analysis Summary (Bentonites1–2) No. of vars in model: 4; Grouping: Sort (6 grps) Wilks' Lambda: 0.00001 approx. F (20.319) = 591.51 $p < 0.0000$					
$N = 96$	Wilks' Lambda	Partial Lambda	F-remove (5.93)	p-value	Toler.	1-Toler. (R-Sqr.)
Zn	0.000285	0.020	934.345	0.000	0.991	0.009
Cu	0.000037	0.156	103.680	0.000	0.960	0.040
Li	0.000032	0.179	88.313	0.000	0.958	0.042
Rb	0.000027	0.212	71.530	0.000	0.996	0.004

of Table 9 is 200 times less than Wilks' Lambda = 0.002 in the informational part of Table 7; the distance between the treated wine samples of the same variety, characterizing the intravarietal differences in the scatter diagram in Fig. 7, is less than in Fig. 5; the distances between the treated samples of different varieties, characterizing the intervarietal differences in Fig. 7, are greater than in Fig. 5. The high geometric manifestation of the cluster structure, determined by microelements, is proven by the fact that all 96 treated samples were classified correctly according to their varieties by the discrimination model.

A similar result regarding the dominant role of microelements in the formation of the cluster structure of treated wine samples was obtained by PCA when imaging wine samples on the factor plane (Fig. 8). The density of the arrangement of samples of the same variety in Fig. 8 is higher than in Fig. 6, clusters of varieties are more clearly expressed, there are no Merlot and Moldova samples outside the clusters.
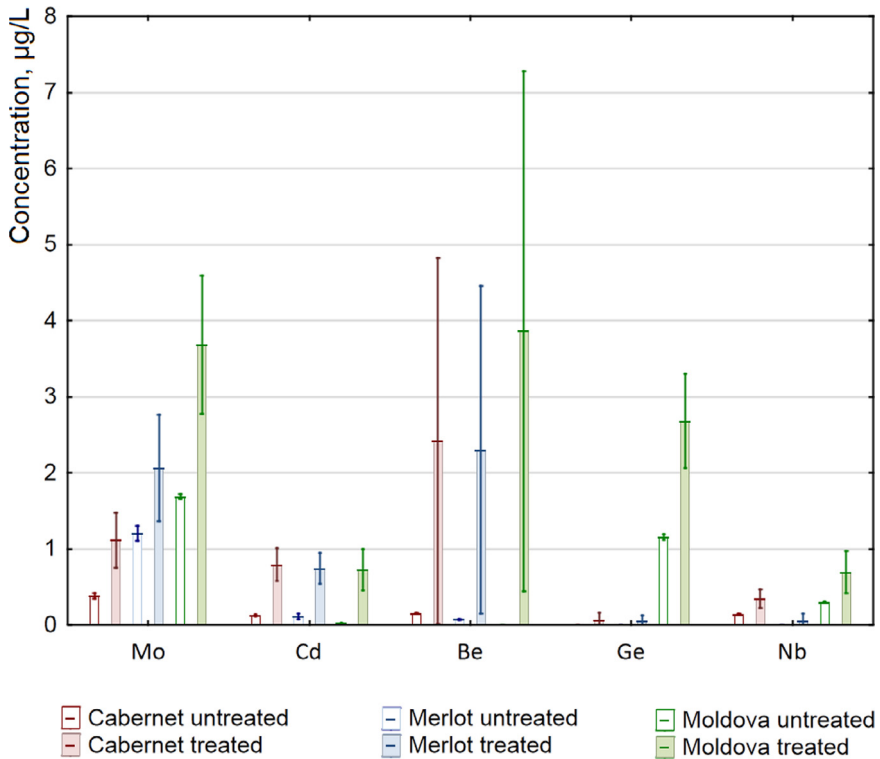
Fig. 4. A bar chart of Mo, Cd, Be, Ge, Nb concentrations in wine samples.

It is noteworthy that the elemental images of treated wine samples retain the character of varietal differences in the elemental image of untreated wine samples. Figs. 7 and 8 show that the varietal difference between untreated Cabernet Sauvignon and Merlot wines, determined by the distance, became smaller than between them and Moldova; the same character was retained after wine treatment with BT. In the case of the formation of the elemental image of wine samples by macroelements, a less pronounced character of varietal differences was observed – the difference between Cabernet Sauvignon and Moldova varieties was less than between them and Merlot (Figs. 5 and 6).

The scattering diagram of the canonical DA values (Fig. 9) and the PCA factorial plane graph (Fig. 10), plotted by the sum of the contents of 4 macro- and microelements, show that, in comparison with the graphical presentation of wine samples separately for macro- and microelements, the cluster structures of samples are more pronounced, e.g., the distance between them within the classes significantly decreased and the distance between the classes determining the variety increased. This means that the sum of the contents of macro- and microelements led to an increase in intravarietal similarity and intervarietal differences in wine samples. The dominance of microelements in the separation of wine samples by varieties was manifested in the character of varietal differences in the elemental images of wine samples, namely, the difference between the untreated and treated Cabernet Sauvignon and Merlot samples is less than between them and Moldova.

Thus, during the clarification and stabilization of untreated wine samples with BT, the concentrations of macro- and microelements in the wines of Cabernet Sauvignon, Merlot and Moldova varieties noticeably changed. The contents of K, Cu, Zn and Rb decrease, while for Na, Ca, Mg, Li, Co, Zr, Pb, Mo, Cd, Be, Nb and Ge they increase. Despite the revealed change in the
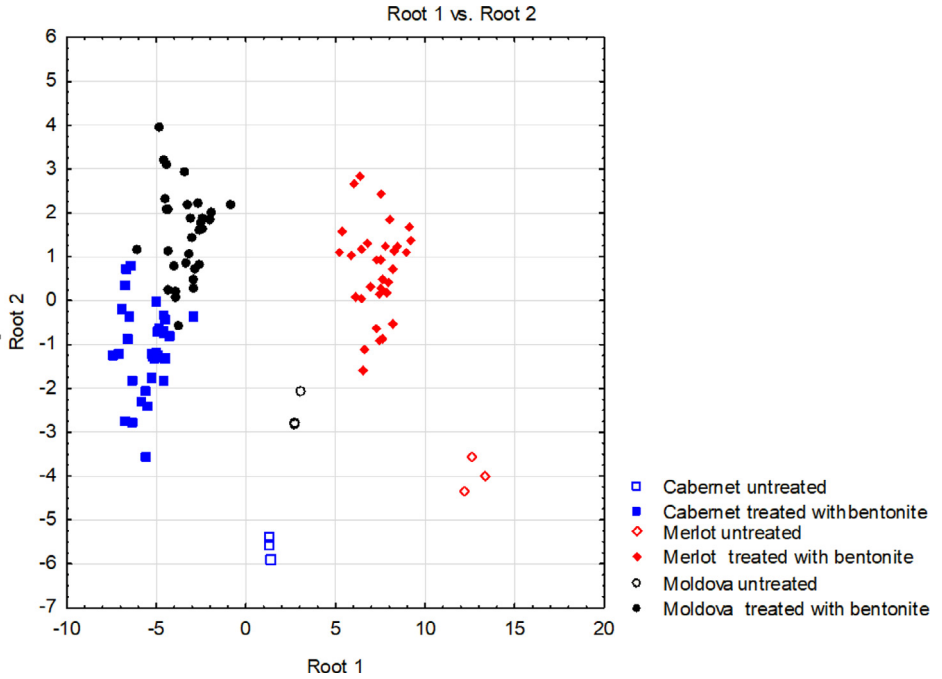
Fig. 5. Scatter diagram of canonical values of wine samples based on the concentrations of macroelements.
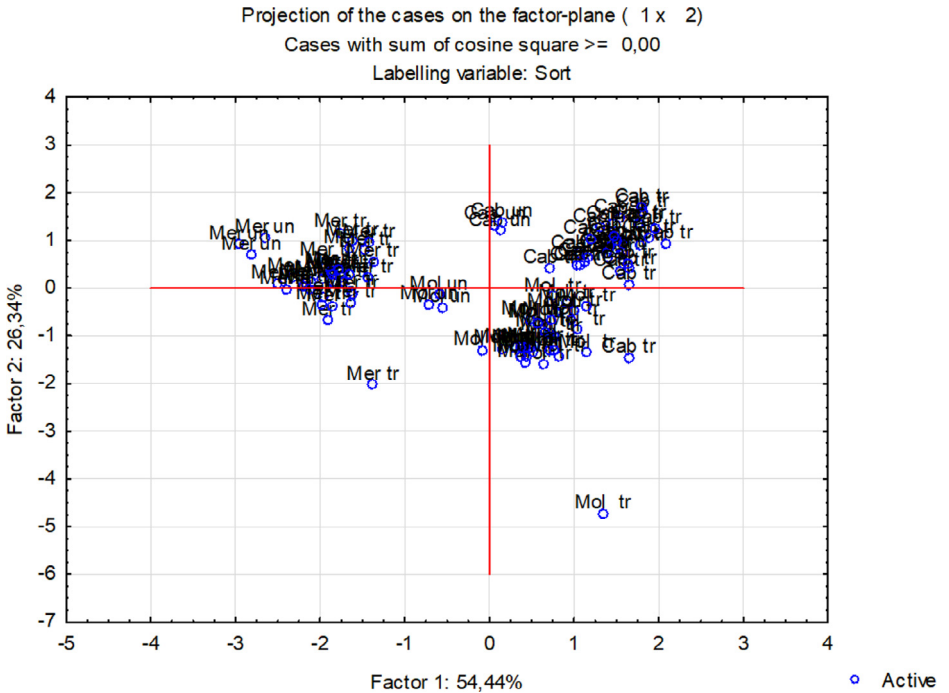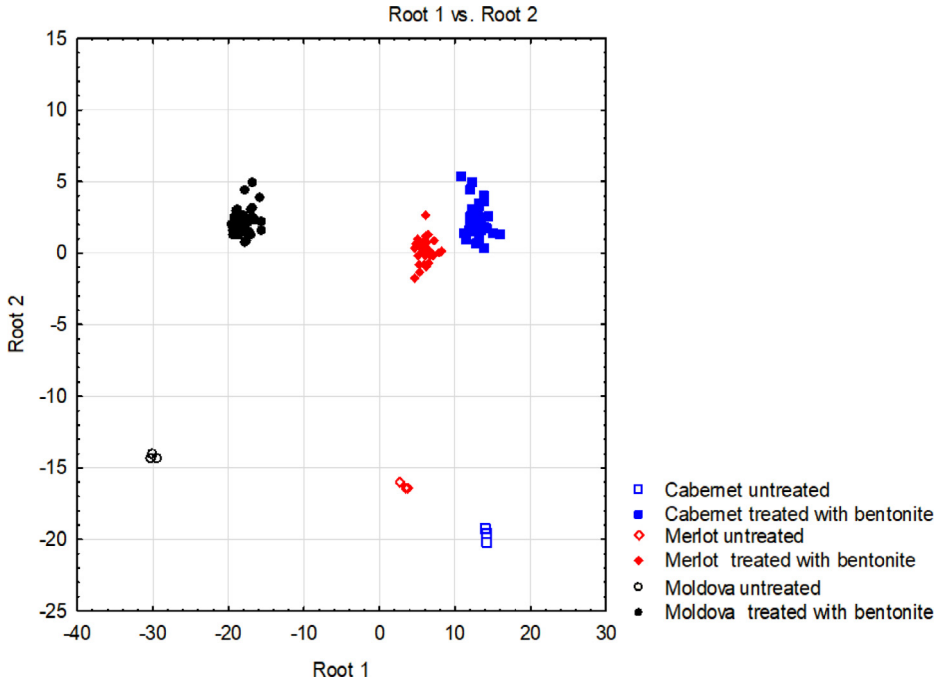

Fig. 6. Graphical illustration of wine samples on the factor plane based on the concentration of macroelements: Cabernet Sauvignon – Cab, Merlot – Mer, Moldova – Mol; untreated – un; treated – tr.

Fig. 7. Scatter diagram of the canonical values of wine samples based on the concentrations of 4 microelements – Zn, Cu, Li, Rb.

contents of elements, the groups of macroelements (Na, K, Ca and Mg) and microelements (Zn, Cu, Li and Rb) are able to reproduce varietal elemental images of wine samples, retaining the character of varietal differences before and after treatment with BT. At the same time, microelements represent the varietal image of wines better than macroelements. It should be noted that when macro- and microelements were combined, the elemental images were significantly improved, and intra-varietal similarity and inter-varietal differences of wine materials increased. The 4 trace elements identified by discriminant analysis as well as 8 macro- and microelements in total can be markers of the varietal affiliation of the BT-treated red wines of Cabernet Sauvignon, Merlot and Moldova varieties.

2. Experimental Design, Materials and Methods

2.1. Wine clarification and stabilization using BT

The objects of the study were red table wines produced from Cabernet-Sauvignon, Merlot and Moldova grape varieties grown in the Krasnodar Territory, Russia. A traditional technology was used to treat the grapes, which included crushing the grapes, followed by the separation of the pulp and its fermentation by a floating cap technique [1]. The experiments were carried out on the basis of a scientific center "Winemaking" in FGBSO "North Caucasian Region Research Institute of Horticulture and Viticulture" (Krasnodar). The pulp fermentation was carried out using the "Cabernet 5" yeast race at 24–26 °C for 7 days. After the fermentation, wine samples were clarified and stabilized with 10% BT wine-water suspensions prepared according to a generally accepted technology [2]. 32 BT varieties of various degrees of dispersion and trademarks were used: Electra (Italy); Azerbaijan, Bentovin (Azerbaijan); Claris P, Claris P70, ClarisP70
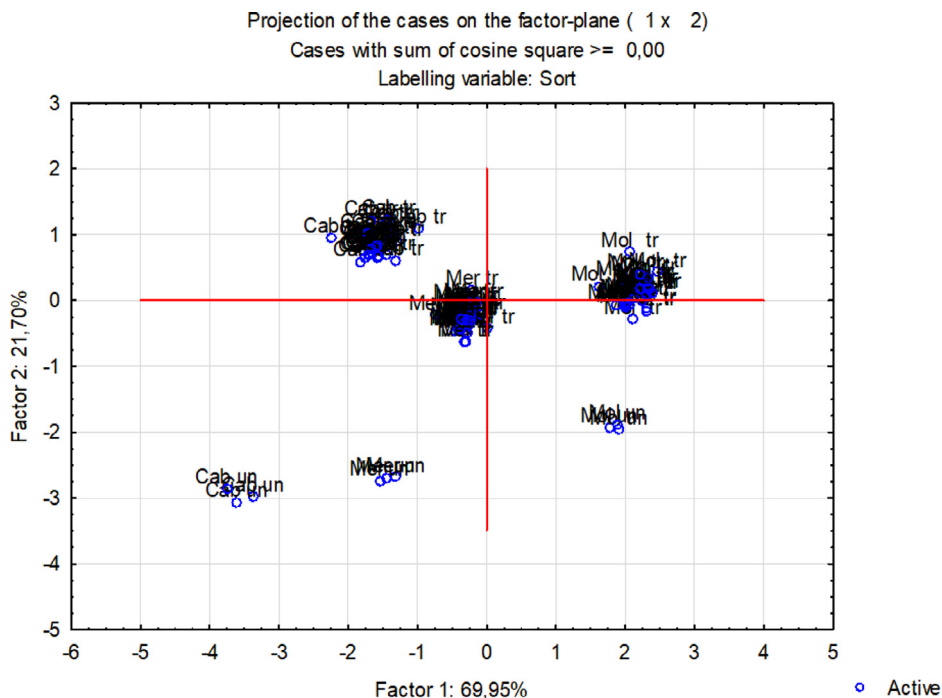
Fig. 8. Graphical illustration of wine samples on the factor plane based on the concentrations of 4 microelements– Zn, Cu, Li, Rb.

«Meridian» (Bosnia and Herzegovina); GranuBent Pore-Tec, Aktivit, Ca-Granulat, NaCalitPore-Tec, KaliNat Erbslöh, Aktivit Erbslöh, Seporit Pore-Tec (Germany); Gumbrin, Askangel (Georgia); Granula, Extrabent, Inobent, Extrabent Super (France); Ijevan bentonite (Armenia); BentoVinumGold (Kazakhstan); Khakass field, Khakassia Sigma-Trade, Dagestan field, Vinobent field "10 Khutor", Crimean bentonite, Kurtsevskoe field (Russia). BT Khakass field, Dagestan field and Crimean bentonite were obtained separately from deposits in the republics of Dagestan, Khakassia, Crimea and prepared taking into account the requirements for the production of wines [2].

2.2. X-ray diffraction and elemental analysis of BT

The interaction of wines with BT of various fineness and brands was assessed by X-ray diffraction analysis, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

X-ray diffraction analysis of the BT samples was conducted on a Shimadzu XRD-7000 X-ray diffractometer (Japan). Analysis conditions were as follows: Cu K_α radiation (1.54 Å), Ni filter, operating voltage of 40 kV, 30 mA, angle range of 3–70°, scan speed of 1°/min. According to the results of X-ray diffraction analysis, the BT samples were conventionally divided into four groups, considering their qualitative and quantitative composition. The first BT group was represented by clays based on sodium montmorillonite containing up to 3% of calcite $CaCO_3$; the second is sodium-calcium montmorillonite with 3% of quartz; the third – various forms of montmorillonite, containing more than 5% of quartz and calcite; the fourth – two samples of bentonite, one of which is a mixture of sodium-calcium montmorillonite and quartz (10%), the other, in addition to sodium-calcium montmorillonite, contains about 4% of a non-clay mineral – albite and silicon oxide in the form of cristobalite.
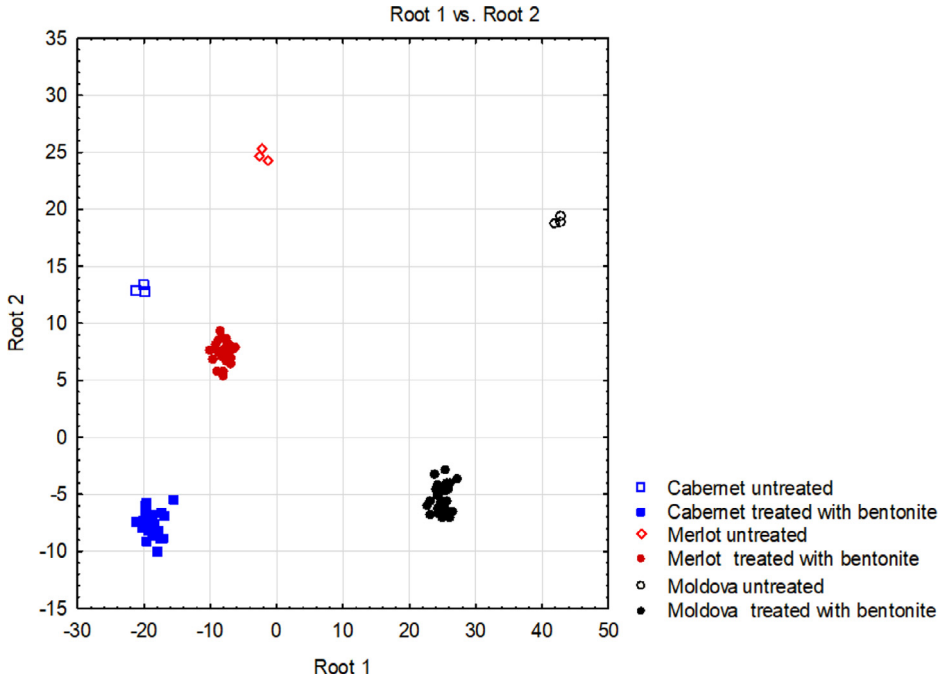
Fig. 9. Scatter diagram of the canonical values of wine samples based on the sum of the contents of macro- and microelements.
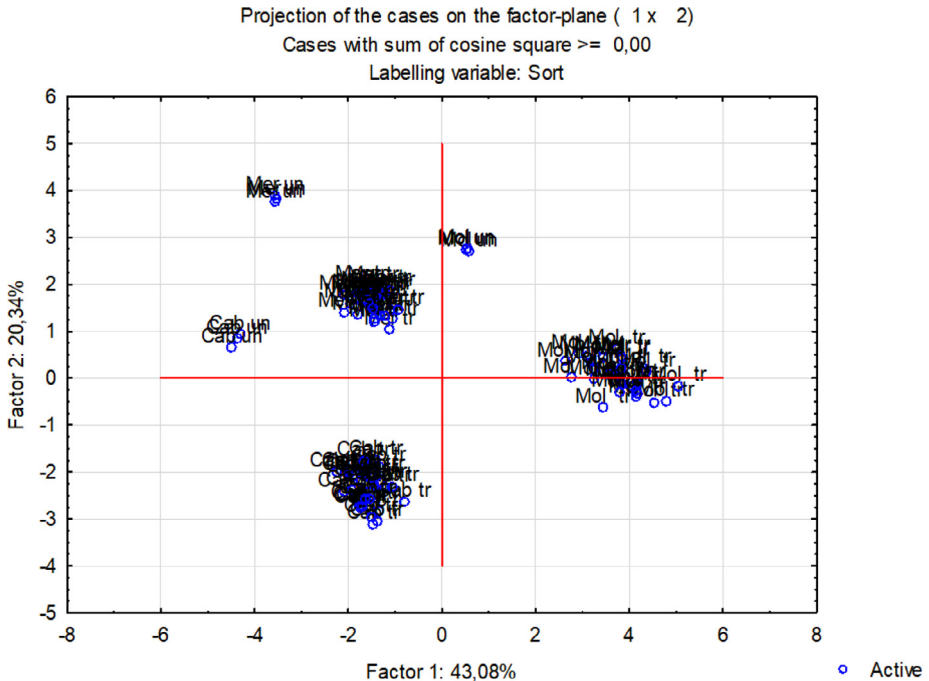

Fig. 10. Graphical illustration of wine samples on the factor plane based on the sum of the contents of macro- and microelements.

To determine the total content of elements in BT, they were subjected to a microwave-assisted decomposition using a MARS 6 system (CEM, USA). BT mineralization was conducted using the scheme given in [3]. Nitric, hydrochloric and hydrofluoric acids of reagent grade or higher were applied in the analysis of BT samples. The samples were prepared and diluted using deionized water.

2.3. Elemental analysis of wines

To assess the influence of BT treatment on the exchange of elements, the elemental composition of the untreated and treated wine samples was established. Li, Be, Ti, V, Co, Ga, Ge, As, Y, Zr, Mo, Ag, Cd, Sn, Sb, Cs, Nb, Hf, Ta, W, Tl, Pb, Bi, Th and U were determined by ICP-MS using an iCAP RQ spectrometer (Thermo Scientific, USA); Zn, Ni, Si, Mn, Fe, Mg, Cu, Al, Sr, Ca, Ba, Na, K and Rb – by ICP-OES using an iCAP 7400 instrument (Thermo Scientific, USA). To decrease the influence of matrix components (organic and inorganic) on the analytical signal of target elements, simplify the procedure and reduce sample preparation time, the wines were diluted with water. The sample dilution factor was selected based on the literature and experimental data on multi-element analysis of various wines as well as the analytical resolution capabilities of the applied instrumentation [4,5]. To prepare the samples and construct calibration curves for the evaluation of elemental composition, standard multicomponent solutions for ICP-MS from the NIST SRM 3100 series (ICP-MS-68A Solution A, ICP-MS-68A Solution B) with metal concentrations of 10 mg/L as well deionized water and nitric acid of reagent grade or higher were used.

2.4. Statistical analysis

Statistical analysis of experimental data was performed using the STATISTICA software (v.13) [6]. The dynamics of changes in the concentrations of macro- and microelements during the clarification and stabilization of BT was presented using a bar chart. The cluster structure of treated and untreated wine samples, determined by varietal differences based on a combination of metal concentrations, was studied by the supervised DA and unsupervised PCA methods, which are widely used in chemometric data processing. DA allows to build predictive models for establishing the belonging of objects to given classes, but it can also be used to identify and demonstrate trends, similarities and differences between classes of objects by reducing the dimension of space by calculating canonical scores and then building a scatterplot of canonical scores in the Root1, Root2 coordinate system. In PCA, there is a different principle of reducing the dimensionality of the object representation space, which is achieved by isolating the factors and calculating the coordinates of each object on the factor plane (Factor1, Factor2) by the principal component analysis. Owing to the possibility of reducing the dimension of space and graphical representation, these methods allowed to determine intergroup differences between wine samples, which are displayed on a plane, depending on belonging to a particular variety.

Ethics Statements

This study doesn't use experiment on human or an animal.

Declaration of Competing Interest

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

Data Availability

Content of elements in untreated and treated with bentonite clays wines (Original data) (Mendeley Data).

CRediT Author Statement

Zaual Temerdashev: Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration; **Aleksey Abakumov:** Investigation, Conceptualization, Writing – review & editing; **Mikhail Bolshov:** Conceptualization, Writing – review & editing; **Alexan Khalafyan:** Software, Formal analysis, Writing – original draft; **Natalia Ageeva:** Resources, Writing – review & editing; **Alexander Vasilyev:** Investigation, Writing – original draft.

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