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# MODERN AND CURRENT CHEMICAL ANALYZES OF WINES FROM LOCAL AND AUTOCHTHONOUS QUALITY GRAPECULTIVARS IN THE AMPELOGRAPHIC COLLECTION OF SCDVV DRĂGĂŞANI

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***Abstract***

*The research and analyzes were carried out in 2020-2022 at SCDVV Drăgăşani in the ampelographic collection, and at the Cluj Napoca wine analysis laboratory. The wine grape cultivars analyzed and studied were 'Crâmpoşie', 'Romanie', 'Slaviţă', 'Teişor', 'Bătuta neagră', 'Negru mare', 'Negru vârtos', 'Negru Românesc', grape cultivars that are part of the national collection of germplasm of the Drăgăşani unit. The polyphenols, ascorbic acid, tartaric acid and heavy metals present in the wine were determined, both in the treated and untreated wines of these studied cultivars. Statistical calculations were performed for these wines using statistical indices such as: mean, variance (s2), standard deviation (s) and coefficient of variation (CV %). Statistical significance was determined using the "Multiple comparison test-Tukey Multiple Range Test Procedure ($p<0.05$)" method. The analyzes performed have shown that these wines are of high quality, the heavy metals in the wine do not exceed the normal limits, so these wines can be successfully classified as DOC and IG wines.*

***Key words:*** *ampelographic collection, local grape cultivars, polyphenols, wine analysis laboratory, DOC and IG wines.*

## INTRODUCTION

The Research and Development Station for Viticulture and Vinification Drăgăşani is part of the area of the Drăgăşani vineyard, the oldest vineyard in Romania also called the great-grandmother of viticulture. The research station is the first research station in the country founded in 1936.

The most famous and important varieties created at this research station are the varieties for table grapes 'Victoria' and 'Azur', the varieties for white wines 'Crâmpoşie Selecţionată' and 'Vilarom' and for red wines the most important are 'Negru de Drăgăşani', 'Novac' and 'Alutus'.

The viticultural research station owns an Ampelographic Collection which is a national viticultural heritage, in the composition of which there are approximately 300 varieties. The varieties taken in this study are found in this collection, they are autochthonous varieties, some even local, with a very good adaptability to the eco-pedological conditions of the vineyard (Teodorescu et al., 2021).

The qualities of the wine obtained from these varieties were highlighted, through physical-chemical analyses, in order to obtain DOC and IG wines and to promote them on the national and international wine market (Popa, 2019).

The Drăgăşani wines therefore continue their traditional performance even today, that of dominating the market with their famous and unparalleled wines.

The Drăgăşani wines enjoy great fame in the country and abroad, being appreciated among the best red wines in the world (Măcău I. & Gorjan S.Ş., 2016).

## MATERIALS AND METHODS

The research and analyzes were carried out in 2020-2022 at SCDVV Drăgăşani in the Ampelographic Collection, the Wine Analysis

Laboratory within the S.C. Sâmbureşti domains and the Analysis Laboratory come from Cluj-Napoca. The varieties analyzed and studied were 'Cârlogancă', 'Românie', 'Slaviţă', 'Teişor', 'Bătută neagră', 'Negru mare', 'Negru vârtos', 'Negru Românesc', varieties located within the national germplasm collection of the unit from Drăgăşani.

The grapes of these varieties were vinified, obtaining treated and untreated wines. The physico-chemical analyzes of the wine (performed in 3 repetitions in three years) were performed on the untreated wines as well as on the treated wines. During the wine fermentation process, selected yeasts of 0.2 g/liter and enzymes in the amount of 0.03 g/liter were added to the wines proposed for treatment, in order to stabilize and make compare and determinations. The treatment of the wines proposed for treatment was carried out after carrying out the pritroch and filtering it, with sulfur dioxide in the amount of 1 ml/liter. The second step was carried out with the filtration of the wine and the bentonite treatment was carried out in the amount of 2 grams per liter for the white wine and 1 gram per liter for the red wine. After these operations, the wine was filtered and bottled in 0.750 ml bottles for analysis.

Treated and untreated wines were analyzed, performing chemical analyzes to determine polyphenols, ascorbic acid, malic acid, tartaric acid as well as modern heavy metals present in the wine. For the determination of metals, the Perkin Elmer inductively coupled plasma mass spectrometer, type ELAN DRC II, with quadrupole and equipped with a reaction cell for the elimination of interferents, with a mass range of 3-240 m/z, resolution below 1 amu, (IU -36, Series Q1970307H). Calibrate the device using standard calibration solutions prepared from stock solution (Multi-element Calibration Standard 3, Perkin Elmer).

The obtained data were analyzed with the help of statistical indices such as: mean, variance ($s^2$), standard deviation (s) and coefficient of variation (CV %). Statistical significance of differences was analyzed using analysis of variance (ANOVA) and *Tukey Multiple Range Test ($p<0.05$)*.

## RESULTS AND DISCUSSIONS

Analyzes, observations and determinations were made on these wines from these varieties, both treated and untreated, in order to see the existing qualitative differences, regarding the structure of polyphenols and ascorbic acid (acw) existing in wines.

In Figures 1 and 2 for polyphenols and for ascorbic acid (acw) we have the following determinations:

When determining the average polyphenols in wines during the study period 2020-2022, it can be observed that in most wines there are differences between treated and untreated wines, higher values being found in untreated wines, but from the qualitative point of view of the composition of the wines treated shows, as usual, good values in order to obtain quality white and red wines.

Therefore, for the 'Cârlogancă' wine, we have 116.26 mg/ml echiv GAE for the untreated wine compared to 136.10 mg/ml echiv GAE for the treated wine, the average/variety being 126.2 mg/ml echiv GAE.

In 'Românie' wine, the polyphenol values are 250.22 mg/ml echiv GAE in the untreated wine and 81.96 mg/ml echiv GAE in the treated one, with an average/variety of 161.1 mg/ml echiv GAE.

The wine 'Slaviţă' has a value of 68.91 mg/ml echiv GAE for the untreated wine, 67.83 mg/ml echiv GAE for the treated wine, the average/variety being 68.4 mg/ml echiv GAE.

The average value of polyphenols in 'Teişor' wine shows the following values, slightly higher in the untreated wine 43.88 mg/ml echiv GAE compared to the treated wine 43.56 mg/ml echiv GAE with an average/variety of 43.7 mg/ml echiv GAE.

For red wines of the 'Bătută neagră', we have a value of 235.12 mg/ml echiv GAE for the treated wine, compared to 108.71 mg/ml echiv GAE for the untreated wine, so after the treatment of the red wine, the value of the polyphenols in this wine increases. The average/variety is 171.9 mg/ml echiv GAE.

We find the same situation with the 'Negru vârtos' wine, which has a higher value for the treated wine of 122.30 mg/ml echiv GAE compared to the untreated wine, which has a value of 86.27 mg/ml echiv GAE, with an

average/variety of 104.3 mg/ml echiv GAE. The increase in polyphenols in the treated wine is evident in this variety.

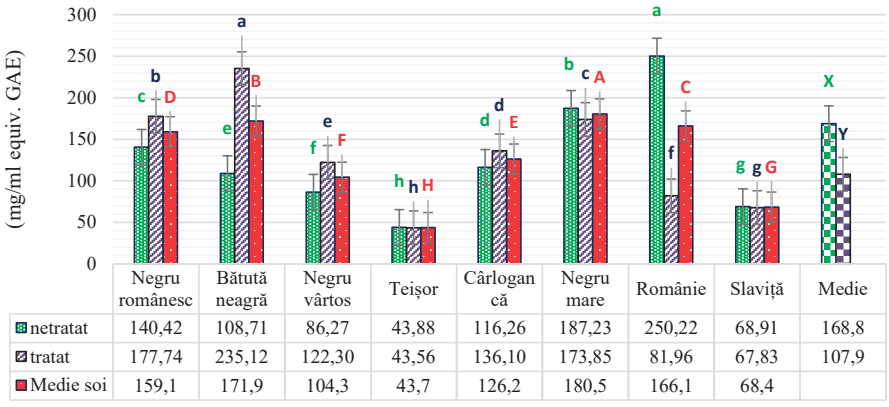
A similar situation as with the 2 varieties of red wine presented above, we also have it at the wine 'Negru Românesc' with a value of 177.74 mg/ml echiv GAE for the treated wine compared to 140.42 mg/ml echiv GAE for the untreated wine, the average/variety being 159.3 mg/ml echiv GAE.

In the analysis of the 'Negru mare' wine we have a higher value for the untreated wine of 187.23 mg/ml echiv GAE, compared to the treated wine which has a value of 173.85 mg/ml echiv GAE. The average/variety is 180.5 mg/ml echiv GAE.

We can observe that the average values of polyphenols in the wines studied for these varieties are higher in the case of white wines, in untreated wines compared to treated ones. In the case of red wines, we have higher values of polyphenols in the treated wines compared to the untreated ones, with the exception of the wine from the 'Negru mare' variety, which has a higher value in the untreated wine compared to the treated wine.

We can observe differences in white wines compared to red wines, which have lower values in the constitution of polyphenols, both in treated and untreated wines. The 'Cârlogancă' wine has a higher average value in terms of polyphenols constitution, closer to red wines.

The statistical calculations for these wines, in the determination of polyphenols, indicate that there are significant differences in all the analyzed wines. Measurements are compared to a gallic acid calibration curve (25, 50, 100, 250 ppm) and results are expressed in gallic acid equivalents (Figure 1).




| | Negru românesc | Bătută neagră | Negru vârtos | Teișor | Cârlogancă | Negru mare | România | Slaviță | Medie |
|---|---|---|---|---|---|---|---|---|---|
| netratat | 140,42 | 108,71 | 86,27 | 43,88 | 116,26 | 187,23 | 250,22 | 68,91 | 168,8 |
| tratat | 177,74 | 235,12 | 122,30 | 43,56 | 136,10 | 173,85 | 81,96 | 67,83 | 107,9 |
| Medie soi | 159,1 | 171,9 | 104,3 | 43,7 | 126,2 | 180,5 | 166,1 | 68,4 | |

The difference between any two variants followed by a common letter is not significant, according to the test *post-hoc* Tukey ($p < 0,05$). The vertical lines represent error of the average (±sE).

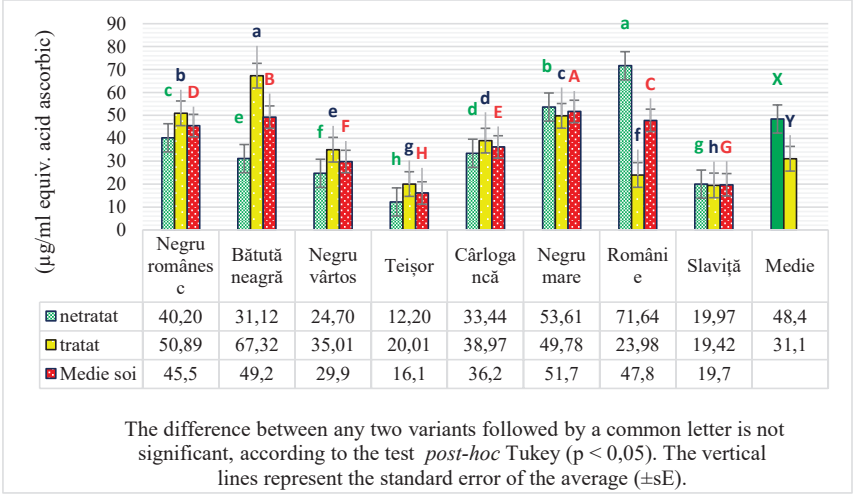
Figure 1. Wine chemical analyzes (2020-2022 average) - Poliphenols

The analyzes and determinations carried out regarding the average ascorbic acid (acw) existing in the wines, during the study years 2020-2022, indicate that in five treated wines out of eight, the content of the wine has more ascorbic acid (acw) compared to the wines untreated.

Thus, in the white wine from the 'Cârlogancă' variety, we have 38.97 µg/ml echiv acid ascorbic in the treated wine compared to the untreated wine, which has an ascorbic acid (acw) value of 33.44 µg/ml echiv acid ascorbic, the average/variety being 36.2 µg/ml echiv acid ascorbic.

The white wine from the 'Teişor' variety has 20.01 µg/ml echiv acid ascorbic in the constitution of the treated wine, while the untreated wine has a value of 12.20 µg/ml echiv acid ascorbic. The average/variety has the value of 16.1 µg/ml.

We also have a higher ascorbic acid (acw) content in the treated wines than in the untreated wines, as follows:
The wine from the 'Negru Românesc' variety has the value of ascorbic acid (acw) for the treated wine of 50.89 µg/ml echiv acid ascorbic and for the untreated wine of 40.20 µg/ml echiv acid ascorbic, the average/variety being 45.5 µg/ml echiv acid ascorbic.
We find a very large difference in ascorbic acid (acw) in the red wine o the 'Bătută neagră' variety with an ascorbic acid (acw) value of 67.32 µg/ml echiv acid ascorbic in the treated wine, compared to the untreated one with a value of 31.12 µg/ml echiv acid ascorbic and the average years/variety 49.2 ml echiv acid ascorbic In the red wine of the 'Negru vârtos' variety,we have higher value of 35.01 µg/ml echiv acid ascorbic in the treated wine compared to 24.70 µg/ml echiv acid ascorbic in the untreated wine. The average/varieties 29.9 µg/ml echiv acid ascorbic.
We have a higher content of ascorbic acid (acw) found in the constitution of the wine in the untreated red wine from the 'Negru mare' variety with a value of 53.61 µg/ml echiv acid ascorbic compared to the treated wine which indicates a value of 49.78 µg/ml echiv acid ascorbic, the average of the years/variety having the value of 51.7 µg/ml echiv acid ascorbic.
In two white wines, we find a higher value in the untreated wine, in ascorbic acid (acw) compared to the wine treated as follows: The wine from the 'Românie' variety has a value of high ascorbic acid (acw) of 71.64 µg/ml in the untreated wine, the treated wine having the value of 23.98 µg/ml, and the average of the years/variety being 47.8 µg/ml.
A slightly higher value of ascorbic acid (acw) in the untreated white wine is also found in the 'Slaviță' variety, with a value of 19.97 µg/ml compared to the treated wine 19.42 µg/ml. The average of the years/variety has the value of 19.7 µg/ml.
Therefore, a higher content of ascorbic acid (acw) in the composition of treated wines is found in red varieties, where three out of four wines have higher values.In the case of white wines, we have two varieties that have higher values in the constitution of wines treated with ascorbic acid (acw), and two untreated wines have higher values compared to the treated ones. We can observe that red wines generally present higher values of ascorbic acid (acw) in treated and untreated wines compared to white wines, with the exception of wines from the 'Cârlogancă' and 'Românie' varieties.
After carrying out the test on these wines, in the determination of ascorbic acid (acw), we can observe significant differences in all the analyzed wines (Figure 2).

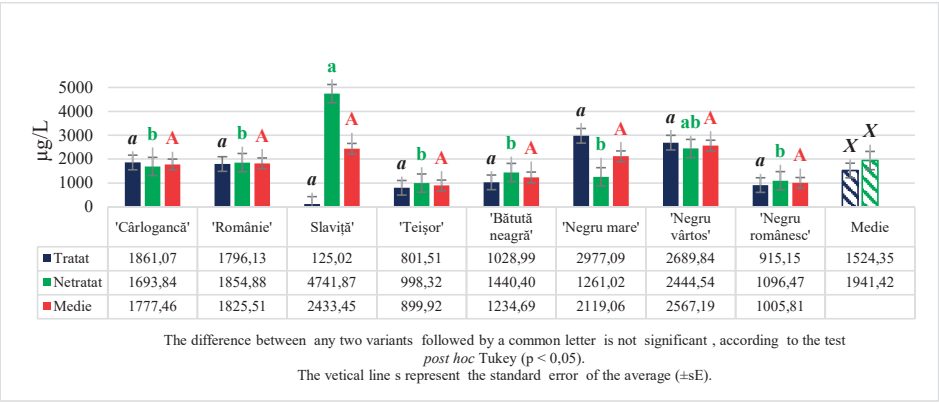



| | Negru românesc | Bătută neagră | Negru vârtos | Teișor | Cârlogancă | Negru mare | Românie | Slaviță | Medie |
|---|---|---|---|---|---|---|---|---|---|
| netratat | 40,20 | 31,12 | 24,70 | 12,20 | 33,44 | 53,61 | 71,64 | 19,97 | 48,4 |
| tratat | 50,89 | 67,32 | 35,01 | 20,01 | 38,97 | 49,78 | 23,98 | 19,42 | 31,1 |
| Medie soi | 45,5 | 49,2 | 29,9 | 16,1 | 36,2 | 51,7 | 47,8 | 19,7 | |

The difference between any two variants followed by a common letter is not significant, according to the test *post-hoc* Tukey ($p < 0,05$). The vertical lines represent the standard error of the average (±sE).

Figure 2. Ascorbic acid ACW (2020-2022 average)

Following the analyzes and determinations made regarding malic acid in the composition of treated and untreated wines, we can observe a higher content of malic acid in five untreated wines. In the treated wines, in number of three we have a higher content of malic acid, in the white wine variety 'Cârlogancă' and in the red varieties 'Negru mare' and 'Negru vârtos' respectively. We generally observe a higher content of malic acid in red wines than white wines, treated or untreated. Through the *Tukey post-hoc* test ($p<0,05$- means >95% probability) for these wines, treated and untreated, we can observe insignificant differences regarding the malic acid content of the wines according to statistical calculations (Figure 3).

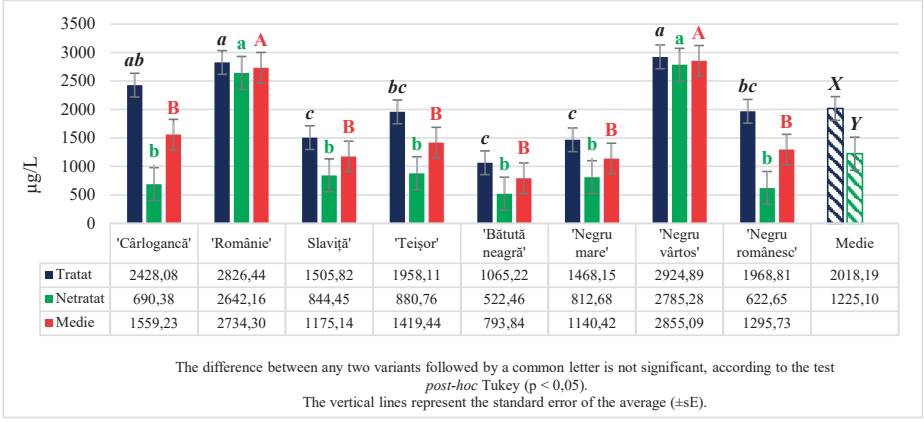



| | 'Cârlogancă' | 'Românie' | Slaviță' | 'Teișor' | 'Bătută neagră' | 'Negru mare' | 'Negru vârtos' | 'Negru românesc' | Medie |
|---|---|---|---|---|---|---|---|---|---|
| Tratat | 1861,07 | 1796,13 | 125,02 | 801,51 | 1028,99 | 2977,09 | 2689,84 | 915,15 | 1524,35 |
| Netratat | 1693,84 | 1854,88 | 4741,87 | 998,32 | 1440,40 | 1261,02 | 2444,54 | 1096,47 | 1941,42 |
| Medie | 1777,46 | 1825,51 | 2433,45 | 899,92 | 1234,69 | 2119,06 | 2567,19 | 1005,81 | |

The difference between any two variants followed by a common letter is not significant , according to the test *post hoc* Tukey ($p < 0,05$).
The vetical line s represent the standard error of the average (±sE).

Figure 3. The malic acid content of the analyzed wines, 2020-2022

Regarding the average content in tartaric acid µg/L in these studied wines, we observe that in all the wines treated both in the white and red varieties, a higher content of tartaric acid.
From the analyzes carried out, we find that white and red wines from these varieties have a similar µg/L tartaric acid content. The treated wines from these varieties have a higher content of tartaric acid µg/L compared to the untreated ones. After performing the *Tukey post-hoc* test ($p<0.05$) we find that there are significant differences between the varieties, namely in the varieties 'Românie', 'Negru vârtos' with a higher content in tartaric acid µg/L compared to the other varieties (Figure 4).




| | 'Cârlogancă' | 'Românie' | Slaviță' | 'Teișor' | 'Bătută neagră' | 'Negru mare' | 'Negru vârtos' | 'Negru românesc' | Medie |
|---|---|---|---|---|---|---|---|---|---|
| Tratat | 2428,08 | 2826,44 | 1505,82 | 1958,11 | 1065,22 | 1468,15 | 2924,89 | 1968,81 | 2018,19 |
| Netratat | 690,38 | 2642,16 | 844,45 | 880,76 | 522,46 | 812,68 | 2785,28 | 622,65 | 1225,10 |
| Medie | 1559,23 | 2734,30 | 1175,14 | 1419,44 | 793,84 | 1140,42 | 2855,09 | 1295,73 | |

The difference between any two variants followed by a common letter is not significant, according to the test *post-hoc* Tukey ($p < 0,05$).
The vertical lines represent the standard error of the average (±sE).

Figure 4. The tartaric acid content of the analyzed wines, 2020-2022

Following the determination of the heavy metals in the wines of the analyzed varieties, we observe that they do not exceed the legal norms of major risk in this food.

After carrying out this study we can observe in general that these wines present higher values of heavy metals in untreated wines, these values decreasing after treatment (Table 1).

For the chemical element Pb (µg/L) we find a higher value in the treated wine of the 'Negru Românesc' variety compared to the untreated one, the other wines analyzed showing higher values before the treatment.

In the red wines of the varieties studied, the chemical element Na (µg/L) has higher values in the treated wines than in the untreated ones, which indicate higher values in the white wines.

For the chemical element Ni (µg/L), the untreated wines show higher values than the treated wines, except for the treated wine of the 'Bătută neagră' variety, which shows a higher value.

The chemical element Al (µg/L) has a higher content in treated white wines, and a higher content in untreated wines in red wines.

Table1. Determination of heavy metals in wines analyzed by the ICP-MS method in the period 2020-2022

| Element | Variety/Variant/Year | Wine Treat | | | Wine Untreated | | |
|---|---|---|---|---|---|---|---|
| | | *Average* | *Standard deviation (SD)* | *Coefficient of variation (CV %)* | *Average* | *Standard deviation (SD)* | *Coefficient of variation (CV %)* |
| **Pb (µg/L)** | 'Cârlogancă' | 3.4 | 0.0 | 0.00 | 5.6 | 0.1 | 1.79 |
| | 'Românie' | 1.8 | 0.1 | 5.56 | 2.5 | 0.1 | 4.00 |
| | Slaviță' | 2.2 | 0.1 | 4.55 | 3.4 | 0.1 | 2.94 |
| | 'Teișor' | 2.7 | 0.1 | 3.70 | 4.4 | 0.1 | 2.27 |
| | 'Bătută neagră' | 2.8 | 0.1 | 3.57 | 3.6 | 0.1 | 2.78 |
| | 'Negru mare' | 2.4 | 0.1 | 4.17 | 3.2 | 0.1 | 3.13 |
| | 'Negru vârtos' | 2.9 | 0.0 | 0.00 | 3.1 | 0.0 | 0.00 |
| | 'Negru românesc' | 2.2 | 0.1 | 4.55 | 1.2 | 0.1 | 8.33 |
| **Na (µg/L)** | 'Cârlogancă' | 4106 | 1.0 | 0.02 | 5831 | 1.0 | 0.02 |
| | 'Românie' | 4622 | 1.0 | 0.02 | 5278 | 1.0 | 0.02 |
| | Slaviță' | 4806 | 1.0 | 0.02 | 5252 | 1.0 | 0.02 |
| | 'Teișor' | 4522 | 1.0 | 0.02 | 5678 | 1.0 | 0.02 |
| | 'Bătută neagră' | 4372 | 1.0 | 0.02 | 4250 | 1.0 | 0.02 |
| | 'Negru mare' | 5222 | 1.0 | 0.02 | 5620 | 1.0 | 0.02 |
| | 'Negru vârtos' | 5458 | 1.0 | 0.02 | 5952 | 1.0 | 0.02 |
| | 'Negru românesc' | 5015 | 1.0 | 0.02 | 4448 | 1.0 | 0.02 |
| **Ni (µg/L)** | 'Cârlogancă' | 5.1 | 0.1 | 1.96 | 9.4 | 0.1 | 1.22 |
| | 'Românie' | 9.8 | 0.1 | 1.02 | 14.2 | 0.1 | 0.70 |
| | Slaviță' | 19.4 | 0.1 | 0.52 | 22.2 | 0.1 | 0.45 |
| | 'Teișor' | 7.8 | 0.0 | 0.00 | 10.6 | 0.1 | 0.94 |
| | 'Bătută neagră' | 16.8 | 0.0 | 0.00 | 16.1 | 0.0 | 0.00 |
| | 'Negru mare' | 17.8 | 0.1 | 0.56 | 20.6 | 0.1 | 0.56 |
| | 'Negru vârtos' | 17.8 | 0 | 0 | 19.1 | 0 | 0 |
| | 'Negru românesc' | 17.4 | 0.1 | 0.57 | 20.4 | 0.1 | 0.49 |
| **Al (µg/L)** | 'Cârlogancă' | 537.5 | 0.1 | 0.02 | 443.5 | 0.1 | 0.02 |
| | 'Românie' | 522.4 | 0.1 | 0.02 | 514.6 | 0.1 | 0.02 |
| | Slaviță' | 490.6 | 0.1 | 0.02 | 422.5 | 0.1 | 0.02 |
| | 'Teișor' | 524.9 | 0 | 0 | 482.8 | 0 | 0 |
| | 'Bătută neagră' | 58.5 | 0.1 | 0.17 | 72.5 | 0.1 | 0.14 |
| | 'Negru mare' | 82.5 | 0.1 | 0.12 | 98.4 | 0.1 | 0.10 |
| | 'Negru vârtos' | 89.5 | 0.1 | 0.11 | 104.5 | 0.1 | 0.10 |
| | 'Negru românesc' | 28.6 | 0.1 | 0.35 | 39.5 | 0.1 | 0.25 |

## CONCLUSIONS

The wines obtained from these varieties of a certain value meet all the conditions for obtaining quality white and red wines.

The polyphenols, ascorbic acid, malic acid and tartaric acid have a decisive role in obtaining the quality of these wines.

Heavy metals existing below the legal norms in these wines prove that they are not a danger to human health and thus, a moderate consumption of wine does not have a negative impact on human health.

In the future, the aim is to promote these old, local wines from the ampelographic collection of SCDVV Drăgăşani on the wine market.

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