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Mineral element content of some Georgian wines

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## A B S T R A C T

The purpose of this study was to determine mineral element composition in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. All sample wines are made from grapes variety grown in Adjara region and were from 2015 to 2017 vintages. Plasma-atomic emission spectrometer ICPE-9820 has been used for qualitative and quantitative determination of the elements in the required concentration range, because of a high sensitivity, a wide dynamic range and a high sample throughput of this spectrometer. The ICPE-9820 provides axial view plasma observation in a direction coaxial to the plasma, and in addition to axial view, provides radial view plasma observation in the perpendicular direction. This dual view capability allows measurements to switch automatically between high-sensitivity axial view and high-accuracy radial view, enabling analysis of elements across a broad concentration range with a single method. In this study, sixteen mineral elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) were analyzed. The analysis was performed by diluting wine samples 10 times with deionized water, without any prior preparation, followed by sequential determination of the elements by ICPE. The higher concentrations were noted for major elements as follows: potassium, magnesium, calcium, sodium and iron. The lowest concentrations were noted for minor elements: manganese, aluminium, barium, zinc and copper. Such trace elements as nickel, chromium and lithium were found under the limit of quantitation. Plumbum, cadmium and cobalt were under the limit of detection. Analyzing concentration levels of elemental composition, it can be concluded that depending on the color of the wine, the content of the individual element was different. Data obtained showed that none of the wine samples surpassed the toxic levels reported for metals in the literature and were within the allowed metals levels in wines for human consumption.

***Keywords:*** major elements, minor elements, concentration, multielement analysis, wine, ICPE-9820.

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# Introduction

Georgia is one of the oldest winemaking nations in the world and by some experts even considered as the birth-place of wine. This is supported by 8000 years old archeological findings of grape-stones in- side antique clay pots. In Georgia the conditions are well suited for winemaking, as the climate is mod- erate and extreme weather conditions are rare. The summers are not too hot and the winters are mild. Also, the surrounding mountains are full of natural springs, with rivers providing mineral-rich waters into the valleys. Nowadays, approximately 530 na- tive Georgian sorts of grapes are known. More than 425 sorts are preserved today and are kept is special nurseries. 30-35 sort of Georgian grapes are used today in wine production [1].

A lot of scientific researches have been conduct- ed to confirm that the moderate consumption of wine improves good health and longevity when it is combined with a balanced diet [2]. Wine is a com- plex matrix and it contains low level concentration of mineral elements. Determination of the mineral element content of wines is important for many rea- sons. Firstly, the concentration of elements in wine is useful information to vine grower and oenolo- gists for controlling the process of obtaining high and quality wines, also the element content could be used as a wine fingerprint and represents one of the criteria for evaluating the authenticity of wine [3,4]. Secondly, their content should be determined and controlled, because excess is undesirable, and in some cases prohibited, due to potential toxicity. In

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addition, the wine industry does not require control of the metal content in wine, thus, the knowledge of their content in this alcoholic beverage is very im- portant [5-7].The level of the major elements (Ca, K, Na, Mg and Fe) that are related to the grape va- riety and maturity, type of soil in the vineyard, and ecoclimatic conditions, usually ranges between 10 and 1000 mg/L. The minor elements (Al, Cu, Mn, Ba, and Zn) depends on external impurities during the growth of grapes and vinicultural and winemak- ing practices, are present in the range of 0.1 to 10 mg/L. Trace elements (Cd, Co, Cr, Ni, Li and Pb) are in the range of 0.1-1000 μg/L [8]. Some factors, such as application of fungicides, pesticides and fer- tilizers during the growing season, can lead to an increase these elements in wine [9-11]. The allowed levels of metal in wines are prescribed by the Inter- national Organization of Vine and Wine (OIV) [12]. The goal of this study is to measure and ana- lyze the mineral components in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. In- ductively coupled plasma-atomic emission spec- trometer (ICPE-9820) was used for qualitative and quantitative determination of mineral elements in

wine samples [13].

# Materials and Methods

Three samples of wines, including one sample of red wine (Aladasturi), one sample of rose wine (Chkhaveri) and one sample of white wine (Tso- likouri) were analyzed. All sample wines are made from grapes variety grown in Adjara region and were from 2015 to 2017 vintages. Aladasturi is dry red wine made from Aladasturi grapes, cultivated in Western Georgia. Wine has pomegranate color and is characterized with distinctive bouquet and harmo- nious taste. Chkhaveri is dry rose wine made from rare Georgian grape variety – Chkhaveri, harvested in mountainous area of Adjara region. Chkhaveri is described as light and pleasant wine in “Ampelog- raphy of Georgia” – a book issued in 1960, being one of the most valuable books in Georgian wine- making. Nowadays, wine professionals and wine- makers fairly think that such interpretation is not sufficient and Chkhaveri varietal needs further ob- servation and research. Tsolikouri, dry white wine, has been manufactured since 1890. The wine made from grapes variety of the same name cultivated in Western Georgia. Tsolikouri is of pale-straw colour and has strong bouquet, at fresh harmonious taste.

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The alcohol in each wine samples ranges from 10 to 12.5%vol, sugar - from 18 to 22% and titratable acidity - from 7 to 9‰ [1].

For the determination of elemental composition of wines, it is required to properly prepare the sam- ples. Taking into consideration that wine is a com- plex water-ethanol mixture, containing various in- organic and organic substances at different levels, the sample preparation stage is very important in the analysis of particular wine components. The wine samples have been simply diluted 10 times with deionized water, without any prior prepara- tion. It was sufficient for the elimination of matrix effects, especially the amount of salts and organic components introduced into the ICP plasma. Low- er dilution factors significantly hindered determi- nation of elements in wine samples. The similar observation was found in the study of wine anal- ysis by A.Gonzálvez [14]. The containers used for storage or treatment of the samples were cleaned to avoid contamination with any metals. The contain- ers were treated with nitric acid and washed with deionized water [14,15].

The ICPE-9820 spectrometer (Shimadzu, Ja-

pan) was used for the analysis of sixteen elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) in selected wine samples.

The Shimadzu ICPE-9820 is a simultaneous spectrometer with CCD (charge-coupled device) detector, which has been used for all determina- tions. The ICPE-9820 provides axial view plasma observation in a direction coaxial to the plasma, and the radial view plasma observation in the perpen- dicular direction. This dual view capability allows measurements to switch automatically between high-sensitivity axial view and high-accuracy radial view, enabling analysis of elements across a broad concentration range with a single method. This se- ries features Shimadzu’s mini-torch system and Eco mode, which reduces argon gas consumption and power consumption during measurement standby by approximately half in comparison to previous mod- els. Furthermore, performance is ensured even with

99.95 % pure argon gas, not the 99.999 %, or purer gas generally used for ICP systems which helps to reduce operating costs. In addition, a vertically-ori- ented torch reduces memory effects and shortens rinse time. The adoption of this torch and vacuum spectrometer enables highly stable, high-throughput analysis. ICPE solution control software features intuitive operation for easy creation and optimiza- tion of complicated methods, allowing for a smooth

analysis process from the start [14,16,17]. Table 1 shows a summary of the system parameters and the analytical lines for each element are shown in table 2. For spectrometry measurements, series of calibra- tion solutions with proper concentrations were made. For calibration solution preparations following stan-

dards (Sigma-Aldrich, Switzerland) were used:

-Multielement Standard Solution 6 for ICP, 100mg/L each element in 5% HNO3;

-Internal Yttrium Standard (Y) for ICP, 1001 mg/L±4mg/L in 2% HNO3.

1% HNO3 was used to prepare calibration stan- dards immediately before usage. Concentrations of calibrations were from 5µg/L to 5 mg/L for every el- ement and 0.1mg/L for an internal yttrium standard.

Deionized water with the maximum resistivity of 18.2 MΩ/cm obtained from the Purity Labwa- ter system D340 (Oxfordshire, United Kingdom) were used for sample pretreatment and dilution. All the solutions were prepared in high-density poly- ethylene containers and were of analytical reagent grade [14].

### **Table 1.** ICPE-9820 instrumental parameters for determination of elements in wine

|  |  |
| --- | --- |
| Parameters | Setting |
| Radio frequency power | 1.20 kW |
| Gas Type | Argon |
| Argon | 6 L/min |
| Gas purity | 99.95% |
| Auxiliary gas | 0.60 L/min |
| Plasma gas | 7.00 L/min |
| Carrier gas | 0.70 L/min |
| Nebulizer | Coaxial |
| Plasma observation | Axial/Radial |
| Detector | CCD (charge coupled device) |
| Spectral range | 167 – 800 nm |
| Exposure time | 15 sec. |
| Attached Instrument | Mini-torch |

**Table 2.** *The analytical lines for determination of each element*

|  |  |
| --- | --- |
| Elements | Detection wavelength (/nm) |
| Aluminium | 396.153 |
| Barium | 455.403 |
| Calcium | 315.887 |
| Copper | 327.396 |
| Iron | 259.940 |
| Potassium | 766.490 |
| Magnesium | 383.231 |
| Manganese | 344.297 |
| Sodium | 589.592 |
| Zinc | 213.856 |
| Nickel | 231.604 |
| Plumbum | 220.353 |
| Cadmium | 226.502 |
| Cobalt | 237.862 |
| Chromium | 206.149 |
| Lithium | 610.364 |

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# Result and discussion

This research was intended to characterize the wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region and made from different types of grapes, in terms of metals content. Sixteen elements were analyzed by plasma-atomic emission spectrometer (ICPE-9820). The method proposed

is simple and sensitive, allowing the adequate and simultaneous determination of major and minor elements by ICPE. Depending on the elements, their quantity varied in wine from µg/L to mg/L. It needs to be noted that all metals content in the analyzed wine samples was much smaller than the maximum concentrations permitted according to the OIV [12].

Major elements like potassium, magnesium, cal- cium, sodium and iron were abundant in our wine samples (Table 3). The concentration levels of these elements in our study were close to the values found in other researches [18,19,20,21].

Potassium exhibited higher concentrations (255 to 425 mg/L) than the rest of the elements in our wine samples. The highest level of K (425 mg/L) was detected in the white wine (Tsolikouri). Po- tassium is the main positive ion in wine. A number of factors affect the amount of potassium in wine, including the variety of grapes, soil and climatic conditions, time of harvest, the temperature of fer- mentation and storage, and the pH and he use of ion-exchange resins. The high level of potassium in wine has great nutritional values.

Magnesium was detected in concentrations be- tween 77.2 mg/L to 110 mg/L in our wines. Red wine (Aladasturi) contents higher concentration of mag- nesium (110 mg/L). Magnesium content in wines correlates with the natural Mg content of grapes, its content also can be attributed to a number of factors

and winemaking process. Iron play an important role in chemical processes with acetaldehyde, it catalyzes acetaldehyde combination with phenol compounds. Minor elements such as manganese, aluminium, barium, copper and zinc were found in lowest concen- trations (0.48 to 1.07 mg/L, 0.42 to 1.22 mg/L, 0.42 to

0.57 mg/L, 0.14 to 0.46 mg/L, and 0.14 to 0.38 mg/L, respectively) that were under Maximum Permissible Limits (MPL). The results revealed the trace elements concentration such as nickel, chromium, lithium to be extremely low, under the limit of quantitation (ULOQ) (<0.0105µg/L, <0.0162µg/L, <0.0792µg/L, respec- tively) in our wines. Plumbum, cadmium and cobalt were under the limit of detection (ULOD) (Table 3). This can be explained by the limited industrialization in the area grapes were cultivated.

Figures 1-5 demonstrate the calibration curves of major and minor elements (K, Mg, Ca, Na, Fe, Mn, Al, Ba, Zn and Cu). The calculated calibration curves show good linearity range for all tested analytes with coefficient of determination in the range from 0.974 to 0.999; limit of quantity (LOQ) and the limit of de- tection (LOD) for each element were obtained.

Figures 6-9 show the spectral lines of major and minor elements in selected wines (Aladasuri, Ch- khaveri and Tsolikouri).

The results of quantitative analysis of elemen- tal concentrations in different wine samples deter- mined by ICPE-9820 are listed in Table 3.

500

K 766.490 nm (2)

r = 0.97490

450

400

350

300

Intensity

250

200

150

100

50

0

including the soil composition, pH, the time and tem-

perature of storage, and the rate of pressing.

0 25 50 75 100

Concentration (mg/L) Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.3514225

Weight: None

Calcium, sodium and iron were 57.7 to 80 mg/L,

b = 0.0000000

d = -48.90168

Origin: None

1.77 to 5.51 mg/L, 1.43 to 4.26 mg/L, respectively, in wine samples. High concentration levels of these elements were in rose wine sample (Chkhaveri). Vineyard soil is a natural source of calcium in musts, however, wines with a calcium level above 80 mg/L are considered to be at risk of instability. However, calcium leads to no problems under normal circum- stances, and the fining process can be a pathway for calcium entry in wine. Sodium is the main extracellu-

2500

2000

1500

1000

500

0

Detection Limit (3s) = 2.100298 Limit of Quantity (10s) = 7.000992

0 25 50 75 100



Mg 383.231 nm (2)

r = 0.99980

Intensity

Concentration (mg/L)

lar cation. It participates in the maintenance of the ac-

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor: a = 0.0000000 c = 0.0454339

Weight: None

id-base balance and in osmotic regulation. This prin-

b = 0.0000000

d = 0.2055085

Origin: None

cipal component can be related to soil composition

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Detection Limit (3s) = 2.078815 Limit of Quantity (10s) = 6.929384

**Fig. 1.** *The calibration curves of major and minor elements*

100000



Ca 315.887 nm (2)

r = 0.99997

75000

50000

Intensity

25000

0

0 25 50 75 100

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.0011753

Weight: None

b = 0.0000000

d = -0.0402528

Origin: None

Detection Limit (3s) = 0.0595058 Limit of Quantity (10s) = 0.1983526

3000



Na 589.592 nm (2)

r = 0.99911

2500

2000

1500

Intensity

1000

500

0

0 25 50 75 100

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.0411979

Weight: None

b = 0.0000000

d = -7.969392

Origin: None

Detection Limit (3s) = 2.088058 Limit of Quantity (10s) = 6.960195

### **Fig. 2.** The calibration curves of major and minor elements

365

125000



Fe 259.940 nm (2)

r = 0.99997

100000

75000

Intensity

50000

25000

0

0 25 50 75 100

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 9.712104e-004

Weight: None

b = 0.0000000

d = 0.0190317

Origin: None

Detection Limit (3s) = 0.0215505 Limit of Quantity (10s) = 0.0718350

200



Mn 344.297 nm (1)

r = 0.99999

175

150

125

Intensity

100

75

50

25

0

0.0 0.5 1.0 1.5 2.0

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.0114759

Weight: None

b = 0.0000000

d = 0.0100922

Origin: None

Detection Limit (3s) = 8.859409e-004 Limit of Quantity (10s) = 0.0029531

### **Fig. 3**. The calibration curves of major and minor elements

366

175



Al 396.153 nm (1)

r = 0.99976

150

125

100

Intensity

75

50

25

0

0.0 0.5 1.0 1.5 2.0

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.0125266

Weight: None

b = 0.0000000

d = 0.0000000

Origin: Passed

Detection Limit (3s) = 0.0350671 Limit of Quantity (10s) = 0.1168905

250000



Ba 455.403 nm (2)

r = 0.99997

200000

150000

100000

Intensity

50000

0

0 25 50 75 100

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 4.928026e-004

Weight: None

b = 0.0000000

d = 0.0933523

Origin: None

Detection Limit (3s) = 0.0277817 Limit of Quantity (10s) = 0.0926056

### **Fig. 4.** The calibration curves of major and minor elements

367

12500



Zn 213.856 nm (2)

r = 0.99270

10000

7500

5000

Intensity

2500

0

0.0 2.5 5.0

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 4.755525e-004

Weight: None

b = 0.0000000

d = -0.0579668

Origin: None

Detection Limit (3s) = 0.0092475 Limit of Quantity (10s) = 0.0308248

450



Cu 327.396 nm (1)

r = 0.99997

400

350

300

250

Intensity

200

150

100

50

0

0.0 0.5 1.0 1.5 2.0

Concentration (mg/L)

Equation: Conc = a \* I ^ 3 + b \* I ^ 2 + c \* I + d

Factor:

a = 0.0000000 c = 0.0051703

Weight: None

b = 0.0000000

d = -0.0047623

Origin: None

Detection Limit (3s) = 6.711194e-004 Limit of Quantity (10s) = 0.0022371

### **Fig. 5.** The calibration curves of major and minor elements

368

K 766.490 Best

Cond 2

1000

750

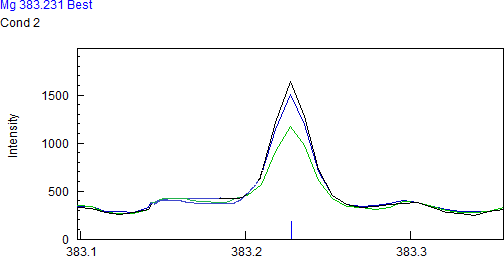
Intensity

500

250

0

766.4 766.6



Ca 315.887 Best

Cond 2

50000

40000

30000

Intensity

20000

10000

0

315.8 315.9

### **Fig. 6.** The spectral lines of major and minor elements in wine samples ( Aladasturi, Chkhaveri, Tsolikouri)

369

Na 589.592 Best

Cond 2

400

300

Intensity

200

100

0

589.5 589.6 589.7

Fe 259.940 Best

Cond 2

3000

2000

Intensity

1000

0

259.9 260.0

Mn 344.297 Best

Cond 1

500

250

Intensity

0

344.2 344.3 344.4

### **Fig. 7.** The spectral lines of major and minor elements in wine samples ( Aladasturi, Chkhaveri, Tsolikouri)

370



Ba 455.403 Best

Cond 2

500

400

Intensity

300

200

100

0

455.3 455.4 455.5

Zn 213.856 Best

Cond 2

750

500

Intensity

250

0

213.80 213.85

213.90

**Fig. 8.** *The spectral lines of major and minor elements in wine samples ( Aladasturi, Chkhaveri, Tsolikouri)*

371

Cu 327.396 Best

Cond 1

4000

3000

Intensity

2000

1000

0

327.3 327.4 327.5

### **Fig. 9.** The spectral lines of major and minor elements in wine samples ( Aladasturi, Chkhaveri, Tsolikouri)

**Table 3.** *Element content of wine samples*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| № | Element | Aladasturi  (red wine) | Chkhaveri  (rose wine) | Tsolikouri  (white wine) |
| Concentration (mg/L) | | |
| 1 | Al | 0.45 | 1.22 | 0.42 |
| 2 | Ba | 0.42 | 0.43 | 0.57 |
| 3 | Ca | 57.7 | 80.0 | 64.1 |
| 4 | Cu | 0.14 | 0.46 | 0.17 |
| 5 | Fe | 1.43 | 4.26 | 2.63 |
| 6 | K | 318 | 255 | 425 |
| 7 | Mg | 110 | 101 | 77.2 |
| 8 | Mn | 1.06 | 0.48 | 1.07 |
| 9 | Na | 1.77 | 5.51 | 5.35 |
| 10 | Zn | 0.38 | 0.33 | 0.14 |
|  |  | Concentration (µg/L) | | |
| 11 | Ni | <0.0524 | <0.0105 | <0.0496 |
| 12 | Pb | ULOD | ULOD | ULOD |
| 13 | Cd | ULOD | ULOD | ULOD |
| 14 | Co | ULOD | ULOD | ULOD |
| 15 | Cr | <0.0162 | <0.0172 | <0.0243 |
| 16 | Li | <0.0792 | <0.1250 | <0.0938 |

ULOD –under the limit of detection

372

450

400

350

300

250

200

Aladasturi (red wine)

Chkhaveri (rose wine) Tsolikouri (white wine)

150

100

50

0

K Mg Ca Na Fe Mn Al Ba Zn Cu

### **Fig.10.** Results for element concentration in the wine samples (in mg/L)

Figure 10 clearly shows the ratio of major and minor elements in determined wines.

If relative abundances of the mineral elements in Aladasturi are compared, the tendency at the ranking is as follows: K>Mg>Ca>Na>Fe>Mn>Al>Ba>Zn>Cu;

in Chkhaveri – K>Mg>Ca>Na>Fe>Al>Mn>Cu>Ba>Zn;

in Tsolikouri – K>Mg>Ca>Na>Fe>Mn>Ba>Al>Cu>Zn.

These relations are similar in all selected wines: K>Mg>Ca>Na>Fe.

The following general conclusions can be made from data in Table 3:

-Magnesium and zinc content of red wine is higher than those of rose and white wines;

-Calcium, sodium, iron, aluminium and copper content of rose wine is higher than those of red and white wines;

-Potassium, manganese and barium content of white wine is higher than those of red and rose wines.

Analyzing concentration levels of determined mineral elements, it can be concluded that depending on the color of the wine, the content of the individual element is different.

Based on the amount of concentration in wine,

the elements were classiﬁed into four categories:

* K, Mg, Ca, Na and Fe – elements in the high concentrations;
* Mn, Al, Ba, Zn and Cu - elements in the low concentrations;
* Ni, Cr and Li - under the limit of quantitation;
* Pb, Cd and Co - under the limit of detection.

# Conclusion

Inductively coupled plasma-atomic emission spectrometer (ICPE-9820) has been used for qualitative and quantitative determination of sixteen mineral elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. The results show that ICPE-9820 is preferable for elemental determination in wine, for its fastness and simplicity of analysis. Moreover, multielement analysis using this spectrometer requires little sample preparation and gives good precision analysis with low detection limits.

Potassium, magnesium, calcium, sodium and iron quantitatively dominate in all determined wine samples. Manganese, aluminium, barium, zinc and copper have been under Maximum Permissible Limits (MPL). A remarkable ﬁnding of this study was that in all wine samples the heavy metals nickel, chromium and lithium have been under the limit of quantitation. Plumbum, cadmium and cobalt have been under the limit of detection. The established content of metals showed that none of our wine samples surpassed the toxic levels of metals as published by the OIV. Analyzing concentration levels of elemental composition, it can be concluded

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that depending on the color of the wine, the content

of the individual element was different.

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