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Original scientific paper

EXAMINATION OF RADIOACTIVITY AND PRESENCE OF ADDITIVES IN WINES FROM TIKVEŠ REGION

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Abstract

In Republic of North Macedonia, the production of grapes and wine has been known since ancient times. Many grape varieties are grown in this region, but one of the most important and largest regions for wine production is the Tikveš region. The aim of the research was to determine the presence of natural radionuclides, as well as total and free SO_2 that are added as additives in wine during its production. The analyses were performed by gamma spectrometry and the obtained spectra were analyzed by the GENIE 2000 programme. The sulfites were determined using OIV accredited methods after prior validation and verification. The results show that 40K is present in all wine brands with a larger size than the other radionuclides observed. 40K levels ranged from low 24.15 ± 2.30 to 38.22 ± 1.50 Bq/L for white wines and 16.28 ± 3.20 to 22.80 ± 3.50 Bq/L for red. As for sulfites, differences can be noticed in terms of the content of total and free SO_2 in all examined wines. Regarding red wines, the lowest value for the content of both total and free SO_2 is observed in Merlot wine (free SO_2 = 10.20 ± 0.54mg/L and total SO_2 = 51.79 ± 0.55mg/L) and in terms of white wines, the lowest content of total and free SO_2 is observed in Muscat Ottonel wine (free SO_2 = 6.84 ± 0.36mg/L and total SO_2 = 40.24 ± 0.43mg/L).

Key words: *wine, radionuclides, additives, sulfites, quality*

INTRODUCTION

Traceability of wines requires knowledge of their characteristics, which are associated with the geographical origin of grape, soil, water, climate (Fabani et al., 2010) In Republic of North Macedonia viticulture is the most important and most strategic industry in the field of crop production. (Economic chamber of Macedonia, 2005) In this region the process of winemaking is not something new, because it has been made since the ancient times. The wine was cultivated 4,000 years ago and this is confirmed by a number of artifacts found on ancient sites. According to Wine Export Comparative Analysis from 2010-2016, a total of 28 grape varieties are grown in Republic of North Macedonia, and there is a presence of white and black varieties equal to 50%. This country has all the prerequisites for the production of high-quality wines such as favourable climate, moderate amount of water, heat and proper soil with balanced content of all nutrients, which makes it region with great export potential. Tikveš is the most well-known wine region which represents around one third of all grapes grown in Republic of North Macedonia. Tikveš region, has been producing wine since the 4th century BC. Due to the perfect southern Mediterranean climate, full of long and warm summers, Tikveš' local grapes generally retain an ideal sugar concentration (17% to 26%). Over the years it was determined which varieties of grapes are most suitable and possess all the necessary characteristics for producing quality wine (pleasant taste, resistance to various diseases and pests, yielding high yields, etc.). (Angelovska et al., 2022) From the data obtained from the wine industry from 2015, the type of grapes used for production largely determines

both the quality and the specific characteristics of the wine, such as the taste and colour of the wine, the presence of residual sugar, the content of alcohol, acidity and the presence of tannins. Sulphur dioxide (SO_2) and its salts have been added during winemaking since the 17th century. They still remain an essential winemaking additive as there is no one other additive that has the same dual properties of anti-oxidation and preservation. But, used in greater amounts can cause some toxic reaction for wine consumers such as, breathing difficulty, sneezing, hives, migraine and other problems and should be handled with care. Moreover, sulphites are also used as biocide agent in disinfection for sanitation of barrels. (WHO, 2012). If oxygen is present, it will be 'captured' by SO_2. A redox reaction to sulphite and further on to sulphate will take place. Due to this reaction the oxygen concentration reduces and aerobic microorganisms cannot increase anymore e.g., in wine. These properties are very important in the process of winemaking for two reasons: the anti-oxidant effect of SO_2 prevents the alteration of natural aromas of the grapes and wine due to the contact with oxygen and the preservative effect of SO_2 helps inhibiting the development of 'undesirable bacteria' in the wine. When SO_2 is incorporated into a must or a wine, a fraction of it will react with sugars, aldehydes or ketones. The remaining fraction, called free, is the one with the most important properties. So, the total amount of total SO_2 is sum of free and reacted SO_2. (OIV, 2021) More recently, the determination of radionuclide activity in wine has been increasingly used to control the authenticity of wine. Contamination can occur as a result of fruit contamination, which can result from direct deposition on fruit surfaces, absorption from the fruit peel and transport to the pulp, soil deposition, root absorption and fruit transfer. Some researchers have studied the transport of different radionuclides from vines to the wine, but these studies have only dealt with the addition of radioactive traces to the vines to confirm the behaviour and distribution of these radionuclides in the plant and the wine product. (Carini et al., 2005) The consumption of contaminated wines will increase the amount of radioactivity and chemical contamination inside a human being and therefore increases the health risks associated with radiation exposure. (Caridi et al., 2019)

So, the aim of our research was to determine the content of total and free SO_2 in wine samples from Tikveš region as well as radionuclide activity.

MATERIAL AND METHODS

In recent years, many studies have been conducted in which the content of radionuclides as indicators of the origin of the food industry products have been discussed. Wine analysis seems to draw much attention because of its importance in assessing the quality of a food product, possible verification of adulteration and analysis of its position in the production chain in the agriculture and the food industries. (Gajek et al., 2021)

Wine is produced by the fermentation process of wine juice under the action of enzymes such as *Saccharomyces cerevisiae*. SO_2 can be represented as endogenous (which occurs during the fermentation process) and exogenous (which is added during technological processes). Endogenous SO_2 occurs during the process of enzymatic transformation of sulphur-containing substances, such as thiamine acids (cysteine, cystine, methionine, glutathione, elemental sulphur, etc.). It is present in low concentrations from several mg/L up to 30 mg/L (Kubáň et al., 2018). Therefore, before adding exogenous SO_2 during technological processes, it is very important to determine the content of endogenous SO_2.

Wine samples: Total of 31 samples of red and white wine from different manufacturers from Tikveš region were subject of our research. The aim was determination of total and free SO_2 as well as radionuclide activity, by using standard accredited methods according to the Law on Wine and Wine Products of Republic of North Macedonia.

SO_2 determination: The presence of total SO_2 is the total amount of free SO_2 plus the one that is bound to sugars, pigment, aldehydes. It is very important the concentration (mg/L) of total and free SO_2 to be in balance due to the quality characteristics of the wine. The OIV-MA-AS323-04B official method was used to determine the content of total and free SO_2. For determination

of free SO_2, standard H_2SO_4 solution is used and for determination of the total SO_2 content, standard solutions of NaOH and H_2SO_4 are used and then the samples are titrated on Titrino plus titrators by using standard Iodine solution. Before the analysis, verification on each method was performed by determining accuracy, precision (standard deviation and relative standard deviation), repeatability and reproducibility by using standard reference material and proficiency testing.

The measurement of the control reference material (PT FAPAS 1389 - set 1 and 2, Quality indicators in wine) was performed in 10 repetitions for each method separately and for the calculation of the extended measurement uncertainty as a source of uncertainty were taken into account the repetition, bias, as well as errors arising from the equipment used. (Angelovska et al., 2022).

The results for the extended measurement uncertainty for each method are as follows: total SO_2 ± 1.07% and free SO_2 ± 5.33%. (Extended measurement uncertainty for k = 2, 95 % probability level).

Radioactivity: The analyses for the presence of radionuclides in wine were made without prior preparation of the wines. The samples of wine were measured with an instrument - gamma spectrometer (Canbera Packard) with a high purity germanium detector. The measurement was carried out in beakers that were hermetically sealed so that 222Rn produced by the decomposition of 226Ra would not result in gas leakage. After ensuring a time balance between the successors of the 238U and the 232Th series, these sealed samples were prepared for analysis. GENIE 2000 software was used for data acquisition and analysis. The specific activity of 226Ra is calculated for the energy line of 186.1 (keV) and 232Th through its decay descendant 228Ac (second in the decay chain), that is, through its three gamma decay energy lines which occur at 338.4; 911.07 and 968.9 (keV).

The activities of 40K were determined from its γ-line of 1460 keV. The time interval for calculation (counting) was 108000 seconds. (Angeleska et al., 2021).

RESULTS AND DISCUSSION

Table 1 contains results for free and total SO_2 determined in red and white wines from Tikveš wine region.

Table 1. Wines from Tikveš region, free and total SO_2 content (mg/L)

Red wine	**Free SO_2 (mg/L)**	**Total SO_2 (mg/L)**
Merlot 1	10.20 ± 0.54	51.79 ± 0.55
Merlot 2	39.88 ± 2.12	119.30 ± 1.27
Merlot 3	39.96 ± 2.12	125.90 ± 1.34
Aleksandar	36.53 ± 1.94	141.67 ± 1.51
Tempranillo	36.30 ± 1.93	151.30 ± 1.61
Vranec 1	30.18 ± 1.60	113.77 ± 1.21
Vranec 2	43.62 ± 2.32	119.09 ± 1.27
Vranec 3	20.32 ± 1.08	88.60 ± 0.95
Vranec 4	32.30 ± 1.72	123.33 ± 1.31
Cabernet Sauvignon 1	43.19 ± 2.30	162.76 ± 1.74
Cabernet Sauvignon 2	44.29 ± 2.36	106.11 ± 1.13
Cabernet sauvignon 3	38.04 ± 2.02	84.35 ± 0.90
Mekedonsko crveno trpezno vino	33.05 ± 1.76	69.32 ± 0.74
Red cuvee	38.88 ± 2.07	145.20 ± 1.55
mean value (MV)	**34.77 ± 1.85**	**114.46 ± 1.22**

White wine	**Free SO_2 (mg/L)**	**Total SO_2 (mg/L)**
Traminec	66.41 ± 3.53	179.81 ± 1.92
Temjanika 1	38.40 ± 2.04	124.19 ± 1.32
Temjanika 2	27.88 ± 1.48	108.85 ± 1.16
Muscat Temjanika	38.35 ± 2.04	131.00 ± 1.40
Chardonay 1	40.80 ± 2.17	214.42 ± 2.29
Chardonay 2	25.80 ± 1.37	118.16 ± 1.26
Chardonay Aristokrat	27.01 ± 1.43	114.15 ± 1.22
Riesling 1	29.98 ± 1.60	133.35 ± 1.42
Riesling 2	29.90 ± 1.59	128.23 ± 1.37
Pinot Grigio	21.89 ± 1.16	90.50 ± 0.96
Muscat Ottonel	6.84 ± 0.36	40.24 ± 0.43
Zilavka 1	23.48 ± 1.25	122.70 ± 1.31
Zilavka 2	21.91 ± 1.16	87.12 ± 0.93
Smederevka 1	22.73 ± 1.21	125.26 ± 1.34
Smederevka 2	16.56 ± 0.88	68.79 ± 0.74
Smederevka 3	32.23 ± 1.71	112.03 ± 1.19
Sauvignon blanc	40.16 ± 2.14	150.20 ± 1.60
mean value (MV)	**27.75 ± 1.48**	**120.53 ± 1.29**

Table 2. Wines from Tikves region, radionuclide activity

Red wine	**^{40}K(Bq/L)**	**^{226}Ra(Bq/L)**	**^{232}Th(Bq/L)**	**^{137}Cs(Bq/L)**
Merlot 1	31.20 ± 5.00	0.47 ± 0.20	0.36 ± 0.20	<0.10
Merlot 2	37.12 ± 5.20	0.92 ± 0.50	0.52 ± 0.45	<0.07
Merlot 3	34.00 ± 5.00	0.94 ± 0.50	0.46 ± 0.33	<0.10
Aleksandar	31.23 ± 2.50	1.71 ± 1.55	0.92 ± 0.90	<0.09
Tempranillo	31.20 ± 2.00	1.22 ± 1.00	0.97 ± 0.85	<0.07
Vranec 1	32.78 ± 1.50	1.81 ± 1.22	1.22 ± 1.00	<0.10
Vranec 2	33.12 ± 1.50	1.96 ± 1.22	1.35 ± 1.10	<0.08
Vranec 3	33.75 ± 1.05	1.95 ± 1.00	0.89 ± 0.75	<0.10
Vranec 4	32.50 ± 1.50	1.23 ± 1.20	1.07 ± 1.00	<0.10
Cabernet Sauvignon 1	28.33 ± 2.50	0.95 ± 0.55	0.47 ± 0.32	<0.08
Cabernet Sauvignon 2	24.15 ± 2.30	0.83 ± 0.70	0.33 ± 0.25	<0.08
Cabernet sauvignon 3	24.50 ± 2.00	0.91 ± 0.75	0.55 ± 1.52	<0.10
Mekedonsko crveno trpezno vino	31.25 ± 1.00	0.77 ± 0.75	0.26 ± 0.20	<0.10
Red cuvee	38.22 ± 1.50	0.75 ± 0.65	0.62 ± 0.64	<0.10
mean value (MV)	**31.66 ± 2.46**	**1.17 ± 0.84**	**0.64 ± 0.58**	
White wine	**^{40}K(Bq/L)**	**^{226}Ra(Bq/L)**	**^{232}Th(Bq/L)**	**^{137}Cs(Bq/L)**
Traminec	29.17 ± 3.50	0.96 ± 0.50	0.38 ± 0.22	<0.10
Temjanika 1	25.40 ± 4.00	0.40 ± 0.32	0.38 ±0.20	<0.07
Temjanika 2	21.18 ± 4.50	0.41 ± 1.22	0.40 ± 0.15	<0.09
Muscat Temjanika	27.22 ± 4.04	1.22 ± 1.40	0.92 ±0.55	<0.09
Chardonay 1	22.80 ± 3.50	0.58 ± 1.50	0.51 ±0.30	<0.10
Chardonay 2	20.44 ± 3.50	0.65 ± 1.20	0.55 ±0.20	<0.10
Chardonay Aristokrat	26.01 ± 3.90	0.80 ± 1.25	0.58 ±0.33	<0.10

Riesling 1	22.65 ± 4.05	0.88 ± 1.50	0.76 ±0.55	<0.10
Riesling 2	22.90 ± 4.50	1.20 ± 1.35	1.28 ±1.20	<0.10
Pinot Grigio	20.10 ± 3.00	0.90 ± 0.95	0.66 ±0.50	<0.09
Muscat Ottonel	19.14 ± 3.80	1.70 ± 1.50	1.55 ±1.00	<0.10
Zilavka 1	16.28 ± 3.20	0.96 ± 1.00	0.92 ±0.65	<0.10
Zilavka 2	19.20 ± 3.33	0.98 ± 1.00	0.95 ±0.70	<0.10
Smederevka 1	22.50 ± 2.50	1.70 ± 1.33	0.92 ±0.50	<0.09
Smederevka 2	21.97 ± 2.55	1.75 ± 1.70	0.92 ±0.50	<0.10
Smederevka 3	21.13 ± 3.10	1.22 ± 1.20	1.30 ±0.95	<0.10
Sauvignon blanc	27.34 ± 3.30	1.50 ± 1.60	1.28 ±1.00	<0.08
mean value (MV)	**22.66 ± 3.56**	**1.04 ± 1.25**	**0.83 ± 0.57**	

*The results are average value after 5 repetitions for each sample and each analyte ± MU (measurement uncertainty)

From the results obtained, differences can be noticed in terms of the content of total and free SO_2 in all examined wines. Regarding red wines, the lowest value for the content of both total and free SO_2 is observed in Merlot 1 wine (free SO_2 =10.20 ± 0.54mg/L and total SO_2=51.79 ± 0.55mg/L) and the highest in Cabernet Sauvignon 2, for free SO_2 (44.29 ± 2.36mg/L) and Tempranillo for total SO_2 (151.30 ± 1.61mg/L). In terms of white wines, the lowest content of total and free sulphur dioxide is observed in Muscat Ottone wine (free SO_2 =6.84 ± 0.36mg/L and total SO_2=40.24 ± 0.43mg/L). If a comparison is made between the same types of wine, but from different producers, we notice differences in the content of total and free SO_2. Thus, there is a significant difference between Merlot 1 and Merlot 2 and 3 both in terms of total SO_2 and free SO_2 content. Compared to Vranec and Cabernet Sauvignon, no significant differences were observed in the content of free SO_2 (from 20.32 ± 1.08mg/L to 44.29 ± 2.36mg/L), but higher differences were observed in the content of total SO_2 (from 88.60 ± 0.95mg/L to 162.76 ± 1.74mg/L). Regarding white wines, the most significant differences were observed in the content of total SO_2 in Chardonnay 1 and 2 wines from different producers, where the content is significantly lower in Chardonnay 2 (118.16 ± 1.26mg/L), compared to Chardonnay 1 (214.42 ± 2.29mg/L). Due to the quality standards prescribed in the Law of wine and wine products of Republic of North Macedonia and in accordance with the Rulebook published in Official Gazette of the Republic of Macedonia, No.16 of 02.02.2012, the amount of total SO_2 should not be higher than 200mg/L for white and rose wines and 150mg/L for red wines. The results show that some of the samples does not meet the requirements of the rulebook and exceed the value of the allowed presence of total SO_2, such as red wines Tempranillo (total SO_2=151.30 ± 1.61mg/L) and Cabernet Sauvignon 1 (total SO2=162.76 ± 1.74mg/L) and white wine Chardonnay 1 (total SO2=214.42 ± 2.29mg/L). All wines contain sufficient amount of free and total SO2 that protects wines from oxidation, the main role of this additive. According to previously published data on determination of total and free SO_2 in Macedonian wines, we can notice that in Vranec wine there are no significant differences in the concentration in terms of free SO_2 content, but there are differences in terms of total SO_2 content compared to our results. (Ivanova-Petropulos et al., 2014)40K is present in all wine brands with a size larger than the other radionuclides observed. 40K levels ranged from 24.15 ± 2.30 to 38.22 ± 1.50 Bq / L for white wines and 16.28 ± 3.20 to 22.80 ± 3.50 Bq / L for red. Potassium is a mineral element present in grapes and wine, it is also used as a fertilizer in vineyards. To a large extent, potassium in wine comes from the potassium in the soil where the vines are grown and at the same time the K content can be increased in the vineyard and from potassium sorbate which is often added to preserve certain types of wine. Thus, the vinification process will directly affect the amount of potassium stored in the alcoholic beverage. The radionuclide values of radium and thorium were significantly lower than those of K, which is consistent with other studies and the anthropogenic radioactive contamination of the examined samples.

CONCLUDING REMARKS

Based on the results, we came to the conclusion that almost all types of white and red wine from Tikveš region satisfy the standards prescribed in the Law of wine and wine products of Republic of North Macedonia in terms of total and free SO_2 content. When it comes to the radiological activity, the values obtained in this study, regardless of the type of wine, did not exceed the safety limits, which highlights the insignificant danger of radiation arising from radionuclides that are naturally or artificially present in the examined wines most often used by the population in the Republic of North Macedonia. Prevention may be the continuous monitoring of the levels of natural and artificial radionuclides in wines in order to provide useful information on unwanted risks to human health. Many imported as well as domestic wines can be noticed in the markets across the country. In terms of quality, Macedonian wines belong to the group of high-quality wines among other wines with high quality characteristics and market price.

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ОПРЕДЕЛУВАЊЕ НА РАДИОАКТИВНОСТ И ПРИСУСТВО НА АДИТИВИ ВО ВИНАТА ОД ТИКВЕШКИОТ РЕГИОН

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Резиме

Во Република Северна Македонија производството на грозје и вино е познато уште од античко време. Во овој регион се одгледуваат поголем број сорти на грозје, но еден од најважните и најголемите региони за производство на вино е Тиквешкиот регион. Целта на истражувањето беше да се утврди присуството на природни радионуклиди, како и вкупен и слободен SO_2 кои се додаваат како адитиви во виното при неговото производство. Анализите се направени со гама спектрометрија и добиените спектри се анализирани со програмата GENIE 2000. Сулфитите беа утврдени со употреба на OIV акредитирани методи по претходна валидација и верификација. Од добиените резултати се забележува дека 40K е присутен во сите видови на вино во поголема концентрација од останатите радионуклиди. Нивоата на 40K се движеа од ниски 24,15 ± 2,30 до 38,22 ± 1,50 Bq/L за бели вина и 16,28 ± 3,20 до 22,80 ± 3,50 Bq/L за црвени вина. Што се однесува до сулфитите, може да се забележат разлики во однос на содржината на вкупниот и слободен SO_2 кај сите испитани вина. Во однос на црвените вина, најниска вредност за содржината и на вкупниот и на слободниот SO_2 е забележана кај виното Мерло (слободен SO_2 = 10.20 ± 0.54 mg/L и вкупен SO_2 = 51.79 ± 0.55 mg/L), а во однос на белите вина, најмала содржина на вкупен и слободен SO_2 е забележана во виното Muscat Ottonel (слободен SO_2 = 6.84 ± 0.36 mg/L и вкупен SO_2 = 40.24 ± 0.43 mg/L).

Клучни зборови: *вино, радионуклиди, адитиви, сулфити, квалитет*