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## OBSERVATION OF THE CHEMICAL PARAMETERS ON IMPORTED AND DOMESTIC WINES FOUND ON THE MARKET IN THE REPUBLIC OF NORTH MACEDONIA

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#### Abstract

In the Republic of North Macedonia, the production of wine is very well known, but in the markets, there is also a variety of imported wines. Therefore, the aim of our research was to examine the basic parameters which determine the quality of the wine. A total of 106 domestic and imported wines were included in this research. The basic chemical parameters for each of the samples were examined by using standard OIV methods. Verification of the methods was done by determining its accuracy, precision, repeatability and reproducibility using standard reference material and proficiency testing. Depending on the sugar content, wines were divided into 4 groups: dry, semi dry, semi-sweet and sweet wines. The highest alcohol content was observed in dry wines originating from all countries that were subject of this research (up to 13.54 vol %) and the lowest was observed in wines originating from Italy which are mostly used as dessert wines (5.07 vol %). The semi-dry wines originating from France showed the slightest value (min.12.18 mg/L free SO<sub>2</sub> and min.60.20 mg/L total SO<sub>2</sub>), which corresponds to their high quality and price on the market. This research is of great interest for the needs of the market and the price of the wine, due to the wine quality standards under the law of Republic of North Macedonia.

Keywords: wine quality, OIV methods, descriptive analysis, method verification

### INTRODUCTION

As there are several varieties of apple, tomato, etc., there are also several varieties of grapes. But 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.). 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. Recently, mostly used grape varieties for production of red wines are Shiraz, Pinot Noir, Cabernet Sauvignon and Merlo and for white wines, those are Sauvignon Blanc and Chardonnay. But there are other important factors that determine the quality and style of the wine. In order to obtain a healthy harvest, grapes need factors that influence and improve the quality, such as favourable climate, enough sunny days, moderate amount of water,

heat and proper soil with balanced content of all nutrients. Vineyards are very tolerant and grow on all types of soils, but without proper nutrient content in the soil itself, the product obtained will be of lower quality. Also, in the process of winemaking the most important part is the fermentation, where the grape juice changes the flavours into those of wine and knowing when to end the fermentation process determines the type and the quality of the final product. In the Republic of North Macedonia, the production of wine is very well known and it exists more than 4000 years in this area, but in the markets, there is also a variety of imported wines that can be found. Therefore, the aim of our research was to examine the basic parameters which determine the quality of wine, such as total alcohol content, total and free SO<sub>2</sub>, total and volatile acids, reduced sugars, specific gravity and total dry extract, by using standard accredited methods.

## **MATERIAL AND METHODS**

Wine is an alcoholic drink made during the fermentation process from grape juice. The quality of the wine is directly related to the quality of the grape variety and is represented as complex set of interactions, so its quality is easier to detect than define.

A total of 106 samples of red, rose and white imported and domestic wines from different manufacturers were included in this research, originating from Italy (60 samples – 34 white wines, 2 rose wine, 24 red wines), France (20 samples – 8 white wines, 2 rose wines, 10 red wines), Spain (5 white wines), Serbia (16 samples – 7 red wines, 2 rose wines, 7 white wines) and North Macedonia (5 samples – 3 red wines, 2 white wines).

During the research, standard accredited methods were used according to the Law on Wine and Wine Products of the Republic of North Macedonia, as follows: for determining the alcoholic strength in volume percentages OIV-A2 (MA-EAS312-01-TALVOL), (IOVW) method was used by using a pycnometer to measure the distillate density obtained after the distillation of the wine at 20 C. The presence of acids in wine is very important in the process of winemaking and the finished product of wine. They have direct influences on the colour, the balance of the wine and gives fresh and sour taste of the final product. The measurement of the acidity (g/L) in wine is usually known as "total acidity" or "titratable acidity" which originates mainly from the presence of citric, tartaric and malic acid. The method used for determining the content of total acids (such as tartaric acid) was OIV-A10 (MA-EAS313-01-ACITOT), (IOVW). This method includes potentiometric titration with 0.1M NaOH by using standard Titrino Plus titrators. To determine the content of volatile acids (such as acetic acid) the OIV- A11 (MA-EAS313-02-ACITVOL), (IOVW) method was used. This method includes primary distillation of the sample and double titration by using NaOH and lodine standard solutions. The sweetness is a main indicator of how much sugar wine contains (primarily glucose) and depending on that the wines are classified as dry, semi dry, semi-sweet and sweet wines. The residual sugar is the one that remains after the fermentation stops and usually is measured in g/L. So, for

determining the content of reducing sugars the OIV-A4 (MA-EAS311- 01-SUCRED), (IOVW) method was used. This method is based on the reducing characteristics of the sugars present in the grapes by using Fehling solution and then titration with lodine standard solution. The usage of sulphur dioxide is very critical in the process of winemaking. The presence of free sulphur dioxide keeps the wine from spoilage and oxidation, but too much SO<sub>2</sub> can mask the fruity aromas of the wine and gives metallic, sharp and bitter flavour to the wine which has negative effect on the quality. The presence of total sulphur dioxide is the total amount of free sulphur dioxide plus the one that is bound to sugars, pigment, aldehydes. It is very important the concentration (mg/L) of total and free sulphur dioxide to be in balance due to the quality characteristics of the wine. The OIV-A17 (MA-EAS323-04-DIOSOU), (IOVW) official method was used to determine the content of total and free sulphur dioxide. For determination of free SO<sub>2</sub>, standard H<sub>2</sub>SO<sub>4</sub> solution is used and for determining the total SO<sub>2</sub> content, standard solutions of NaOH and  $H_2SO_4$  are used and then the samples are titrated by using standard lodine solution on Titrino plus titrators. The density and specific gravity analysis is used for determining the total alcohol content in g/L and vol. %. For this reason, OIV-A1 (MA-EAS2-01- MASVOL), (IOVW) standard method was used. OIV-A3 (MA-EAS2-03-EXTSEC), (IOVW) method was used to determine the total dry extract content (g/L), by direct evaporation of the volume of the sample.

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.

The results for the extended measurement

uncertainty for each method are as follows: volatile acidity  $\pm$  6.27 %, total dry extract  $\pm$  4.92 %, total SO<sub>2</sub>  $\pm$  1.07 %, total acidity  $\pm$  1.87 %, sugar content  $\pm$  6.06 %, free SO<sub>2</sub>  $\pm$  5.33 %, total alcohol content  $\pm$  6.19 % and specific gravity  $\pm$  0.20 %. (Extended measurement uncertainty for k = 2, 95 % probability level).

#### **RESULTS AND DISCUSSION**

Depending on the content of sugars in the wine, they were first divided into four basic groups as dry (up to 4 g/L), semi dry (up to 12 g/L), semi-sweet (up to 45 g/L) and sweet wines (more than 45 g/L) and also, depending of the country of origin. The results shown that most of the wines included in this research belong to the group of semi dry wines (n=62 or 65.72 %) and least in the group of sweet wines (n=6 or 6.36 %). Residual sugar is one that remains in the wine after alcoholic fermentation. Then, each wine group was examined on the basic chemical parameters that were subject of this research. The results showed differences in almost all examined parameters.

	Type of wine							
Country	Dry	Semi dry	Semi Sweet	Sweet				
Italy	10	32	13	5				
France	2	17	1	/				
Spain	/	/	5	/				
Serbia	2	11	2	1				
North Macedonia	3	2	/	/				
Total number of samples	17= 18.02 %	62 = 65.72 %	21 = 22.26 %	6 = 6.36 %				

The sugar content of the grapes is closely related to the alcohol content of the wine. Fermentation is a process where under the action of the yeast (mostly Saccharomyces cerevisiae) comes to the utilization of the sugar present in the grape juice, which produces alcohol and carbon dioxide, with at least 12 enzymes included in the process. The longer the fermentation, the higher the alcohol and lower the sugar level. So, this is very important step in the process of winemaking because of the different flavours produced which directly affect the taste of the wine. Therefore, from the results shown we can notice that dry wines originating from all countries included in the research, contain the highest alcohol content (up to  $13.54 \pm 0.83$  vol %), with some minor exceptions, such as two samples of semi dry wine originating from North Macedonia, one sample of semi-sweet wine originating from France and one sample of sweet wine originating from Serbia - vermouth wine. The lowest alcohol content was observed in wines

originating from Italy and they are mostly used as dessert wines  $(5.07 \pm 0.31 \text{ vol }\%)$ .

The total acidity in wine usually depends on the presence of non-volatile acids, such as mallic, tartaric or citric acid plus the volatile acids such as acetic acid. These components directly affect the smell and the taste of the wine. Determination of volatile acidity is used routinely as an indicator of wine spoilage. The results shown no significant difference between all groups of wine and the countries of origin such as, for total acidity between  $4.81 \pm 0.09$  g/L -  $6.70 \pm 0.12$  g/L and for volatile acidity between  $0.26 \pm 0.02$  -  $0.39 \pm 0.02$  g/L.

				Dry wines			
Country	Total alcohol content (vol	Total acidity	Volatile acidity	Free SO <sub>2</sub>	Total SO <sub>2</sub>	Total dry extract	Specific gravity
	%0)	(9, 2)	(g/L)	(119/2)	(119/2)	(g/L)	$(MU = \pm 0.0019 \text{ for all} wines)$
Italy	14.55 ± 0.90	4.98 ± 0.09	$0.44 \pm 0.03$	66.75 ± 3.55	150.80 ± 1.61	32.25 ± 1.58	0.9796
	14.00 ± 0.86	5.92 ± 0.11	$0.37 \pm 0.02$	38.16 ± 2.03	90.66 ± 0.97	25.85 ± 1.27	0.9801
	12.50 ± 0.77	4.85 ± 0.09	$0.22 \pm 0.02$	18.85 ± 1.00	88.21 ± 0.94	20.40 ± 1.00	0.9810
	12.78 ± 0.79	$4.46 \pm 0.08$	$0.22 \pm 0.02$	30.41 ± 1.62	98.82 ± 1.05	18.39 ± 0.90	0.9816
	14.12 ± 0.87	4.15 ± 0.08	$0.20 \pm 0.02$	24.68 ± 1.31	68.17 ± 0.72	26.02 ± 1.28	0.9801
	14.55 ± 0.90	4.25 ± 0.08	$0.26 \pm 0.02$	25.70 ± 1.36	75.50 ± 0.80	25.50 ± 1.25	0.9796
	13.55 ± 0.83	5.30 ± 0.10	$0.26 \pm 0.02$	28.15 ± 1.50	69.25 ± 0.74	24.12 ± 1.18	0.9807
	13.30 ± 0.82	5.17 ± 0.10	$0.25 \pm 0.02$	27.03 ± 1.44	68.35 ± 0.73	23.52 ± 1.15	0.9810
	13.50 ± 0.83	5.10 ± 0.10	$0.36 \pm 0.02$	27.20 ± 1.45	60.20 ± 0.64	20.22 ± 0.99	0.9807
	12.55 ± 0.77	6.10 ± 0.11	0.33 ± 0.02	30.20 ± 1.61	105.19 ± 1.12	20.25 ± 0.99	0.9818
	MV=	MV =	MV=	MV=	MV=	MV=	MV=
	13.54 ± 0.83	5.03 ± 0.09	0.29 ± 0.02	31.71 ± 1.69	87.51 ± 0.93	23.65 ± 1.16	0.9806
France	12.55 ± 0.77	6.01 ± 0.11	0.38 ± 0.02	44.80 ± 2.38	97.56 ± 1.04	15.70 ± 0.77	0.9818
	13.00 ± 0.80	5.43 ± 0.10	0.40 ± 0.03	38.71 ± 2.06	132.94 ± 1.42	16.70 ± 0.82	0.9813
	MV=	MV=	MV=	MV=	MV=	MV=	MV=
	12.77 ± 0.79	5.72 ± 0.11	0.39 ± 0.02	41.75 ± 2.22	115.25 ± 1.23	16.20 ± 0.79	0.9815
Spain	1						
Serbia	13.50 ± 0.83	4.78 ± 0.09	$0.25 \pm 0.02$	20.80 ± 1.10	139.52 ± 1.49	17.25 ± 0.84	0.9807
	13.05 ± 0.80	4.85 ± 0.09	$0.35 \pm 0.02$	30.52 ± 1.62	75.90 ± 0.81	19.55 ± 0.96	0.9813
	MV=	MV=	MV=	MV=	MV=	MV=	MV=
	13.27 ± 0.82	4.81 ± 0.09	0.30 ± 0.02	25.66 ± 1.36	107.71 ± 1.15	18.40 ± 0.90	0.9810
North	11.83 ± 0.73	5.62 ± 0.10	$0.25 \pm 0.02$	28.98 ± 1.54	85.20 ± 0.91	21.20 ± 1.04	0.9827
Macedonia	13.77 ± 0.85	5.25 ± 0.10	0.27 ± 0.02	36.66 ± 1.95	101.17 ± 1.08	17.56 ± 0.86	0.9805
	13.86 ± 0.85	5.08 ± 0.09	$0.25 \pm 0.02$	29.57 ± 1.57	84.76 ± 0.90	16.87 ± 0.83	0.9804
	MV=	MV=	MV=	MV=	MV=	MV=	MV=
	13.15 ± 0.81	5.31 ± 0.10	0.26 ± 0.02	31.73 ± 1.69	90.37 ± 0.96	18.54 ± 0.91	0.9812

Table 1.1. Mean values of physical-chemical parameters in dry wines from different countries

	Semi dry wines							
Country	Total alcohol content (vol %)	Total acidity	Volatile acidity	Free $SO_2$	Total $SO_2$	Total dry extract	Specific gravity	
		(g/L)	(g/L)	(IIIg/L)	(IIIg/L)	(g/L)	$(MU = \pm$	
							all wines)	
Italy	$11.00\pm0.68$	5.46 ± 0.10	$0.28 \pm 0.02$	30.14 ± 1.60	90.20 ± 0.96	26.55 ± 1.30	0.9836	
	$11.10 \pm 0.68$	5.95 ± 0.11	0.31 ± 0.02	26.50 ± 1.41	86.65 ± 0.92	27.66 ± 1.36	0.9836	
	$11.00\pm0.68$	5.87 ± 0.11	$0.30 \pm 0.02$	27.18 ± 1.44	89.76 ± 0.96	28.20 ± 1.38	0.9836	
	$11.50 \pm 0.71$	5.82 ± 0.11	$0.25 \pm 0.02$	42.15 ± 2.24	140.55 ± 1.50	25.15 ± 1.23	0.9830	
	$12.00\pm0.74$	5.82 ± 0.11	0.41 ± 0.03	30.25 ± 1.61	150.94 ± 1.61	33.75 ± 1.66	0.9824	
	$12.50\pm0.77$	$5.12 \pm 0.10$	$0.25 \pm 0.02$	22.84 ± 1.21	98.50 ± 1.05	21.71 ± 1.06	0.9810	
	$15.95\pm0.98$	5.49 ± 0.10	0.31 ± 0.02	30.11 ± 1.60	151.01 ± 1.61	38.86 ± 1.91	0.9781	
	$12.00\pm0.74$	$5.18 \pm 0.10$	$0.29 \pm 0.02$	28.20 ± 1.50	120.82 ± 1.29	23.65 ± 1.16	0.9824	
	$12.17 \pm 0.75$	$5.28 \pm 0.10$	$0.30 \pm 0.02$	21.40 ± 1.14	100.53 ± 1.07	21.12 ± 1.03	0.9823	
	$11.74 \pm 0.72$	5.57 ± 0.10	$0.32 \pm 0.02$	19.84 ± 1.05	$73.58 \pm 0.78$	24.62 ± 1.21	0.9828	
	$13.05 \pm 0.80$	$4.90 \pm 0.09$	$0.34 \pm 0.02$	26.76 ± 1.42	78.10 ± 0.83	27.18 ± 1.33	0.9813	
	11.95 ± 0.73	4.95 ± 0.09	$0.30 \pm 0.02$	28.16 ± 1.50	119.40 ± 1.27	23.76 ± 1.16	0.9824	
	$12.45 \pm 0.77$	5.10 ± 0.10	$0.25 \pm 0.02$	22.85 ± 1.21	98.42 ± 1.05	21.70 ± 1.06	0.9810	
	$12.50 \pm 0.77$	7.77 ± 0.14	$0.40 \pm 0.03$	13.11 ± 0.69	74.75 ± 0.79	27.21 ± 1.33	0.9819	
	$13.00\pm0.80$	$4.80 \pm 0.09$	$0.28 \pm 0.02$	25.60 ± 1.36	60.75 ± 0.65	24.95 ± 1.22	0.9813	
	$12.00\pm0.74$	5.15 ± 0.10	$0.30 \pm 0.02$	28.85 ± 1.52	120.80 ± 1.29	24.50 ± 1.20	0.9824	
	$15.23 \pm 0.94$	6.18 ± 0.11	$0.32 \pm 0.02$	25.55 ± 1.36	98.00 ± 1.04	33.37 ± 1.20	0.9789	
	$14.06\pm0.87$	$4.90 \pm 0.09$	$0.30 \pm 0.02$	27.18 ± 1.44	60.75 ± 0.65	26.60 ± 1.30	0.9801	
	$12.50\pm0.77$	$4.90 \pm 0.09$	$0.22 \pm 0.02$	20.22 ± 1.07	85.16 ± 0.91	20.16 ± 0.99	0.9818	
	$13.05\pm0.80$	4.85 ± 0.09	$0.28 \pm 0.02$	25.55 ± 1.36	59.62 ± 0.63	25.18 ± 1.23	0.9813	
	$12.00\pm0.74$	$5.12 \pm 0.10$	$0.30 \pm 0.02$	29.00 ± 1.54	123.98 ± 1.32	24.78 ± 1.21	0.9824	
	$12.54\pm0.77$	4.87 ± 0.09	$0.20 \pm 0.02$	19.87 ± 1.05	90.52 ± 0.96	19.21 ± 0.94	0.9818	
	$14.00\pm0.86$	$4.78 \pm 0.09$	$0.29 \pm 0.02$	24.66 ± 1.31	58.80 ± 0.62	25.88 ± 1.27	0.9801	
	$13.50\pm0.83$	$5.10 \pm 0.10$	$0.33 \pm 0.02$	30.16 ± 1.60	80.02 ± 0.85	26.68 ± 1.31	0.9807	
	$12.00\pm0.74$	5.90 ± 0.11	$0.42 \pm 0.02$	31.25 ± 1.66	152.80 ± 1.63	33.80 ± 1.66	0.9824	
	$14.56 \pm 0.90$	4.63 ± 0.09	$0.26 \pm 0.02$	30.69 ± 1.63	81.10 ± 0.86	27.20 ± 1.33	0.9796	
	$14.00\pm0.86$	4.95 ± 0.09	$0.22 \pm 0.02$	25.80 ± 1.37	80.10 ± 0.85	25.38 ± 1.24	0.9801	
	$13.56\pm0.83$	5.07 ± 0.10	$0.20 \pm 0.02$	27.60 ± 1.47	65.59 ± 0.70	26.35 ± 1.29	0.9807	
	$11.00 \pm 0.68$	5.13 ± 0.10	$0.23 \pm 0.02$	23.32 ± 1.24	142.08 ± 1.52	25.12 ± 1.23	0.9836	
	$11.05 \pm 0.68$	6.00 ± 0.11	$0.34 \pm 0.02$	32.87 ± 1.75	108.50 ± 1.16	26.30 ± 1.29	0.9836	
	$9.50\pm0.58$	4.87 ± 0.09	$0.30 \pm 0.02$	27.58 ± 1.47	112.75 ± 1.20	28.10 ± 1.38	0.9854	
	$11.50\pm0.71$	5.55 ± 0.10	$0.42 \pm 0.03$	40.16 ± 2.14	133.00 ± 1.42	35.18 ± 1.73	0.9830	
	MV=	MV=	MV=	MV=	MV=	MV=	MV=	
	$12.50 \pm 0.77$	$5.34 \pm 0.10$	$\textbf{0.30} \pm \textbf{0.02}$	27.04 ± 1.44	99.61 ± 1.06	26.55 ± 1.30	0.9818	

# Table 1.2. Mean values of physical-chemical parameters in semi dry wines from different countries

	$12.00 \pm 0.74$	$733 \pm 0.14$	$0.32 \pm 0.02$	13 20 + 0 70	66 65 + 0 71	21 00 + 1 07	0.9824
Trance	$12.00 \pm 0.74$	$7.55 \pm 0.14$	$0.32 \pm 0.02$	$13.20 \pm 0.70$	$60.00 \pm 0.71$	$21.90 \pm 1.07$	0.9024
	$12.00 \pm 0.74$	$7.59 \pm 0.14$	$0.30 \pm 0.02$	12.16 ± 0.04	$00.20 \pm 0.04$	$22.20 \pm 1.09$	0.9624
	$12.00 \pm 0.74$	$7.00 \pm 0.14$	$0.55 \pm 0.02$	$15.10 \pm 0.00$	$02.10 \pm 0.00$	$23.10 \pm 1.13$	0.9624
	12.54 ± 0.77	$0.75 \pm 0.12$	$0.24 \pm 0.02$	$15.20 \pm 0.81$	78.80 ± 0.84	$24.18 \pm 1.18$	0.9818
	$12.50 \pm 0.77$	6.90 ± 0.13	$0.28 \pm 0.02$	$16.18 \pm 0.86$	79.92 ± 0.85	$23.75 \pm 1.16$	0.9818
	14.//±0.91	4.50 ± 0.09	$0.28 \pm 0.02$	26.27 ± 1.40	83.48 ± 0.89	27.28 ± 1.34	0.9794
	$15.05 \pm 0.93$	$4.33 \pm 0.09$	$0.26 \pm 0.02$	$27.21 \pm 1.45$	96.69 ± 1.03	27.96 ± 1.37	0.9791
	13.55 ± 0.83	5.06 ± 0.10	0.40 ± 0.03	37.48 ± 1.99	118.66 ± 1.26	26.53 ± 1.30	0.9807
	13.50 ± 0.83	4.27 ± 0.08	$0.38 \pm 0.02$	45.52 ± 2.42	90.78 ± 0.97	29.82 ± 1.46	0.9807
	13.00 ± 0.80	4.70 ± 0.09	0.41 ± 0.03	38.15 ± 2.03	107.20 ± 1.14	25.20 ± 1.23	0.9813
	15.05 ± 0.93	4.68 ± 0.09	0.35 ± 0.02	38.78 ± 2.06	132.94 ± 1.42	29.71 ± 1.46	0.9790
	12.50 ± 0.77	6.86 ± 0.13	0.37 ± 0.02	19.76 ± 1.05	105.65 ± 1.13	23.09 ± 1.13	0.9818
	12.50 ± 0.77	4.19 ± 0.08	$0.44 \pm 0.03$	31.95 ± 1.70	79.87 ± 0.85	23.05 ± 1.13	0.9818
	12.52 ± 0.77	4.33 ± 0.09	$0.42 \pm 0.03$	32.20 ± 1.71	81.15 ± 0.86	24.80 ± 1.22	0.9818
	12.55 ± 0.77	4.58 ± 0.09	0.30 ± 0.02	50.18 ± 2.67	105.16 ± 1.12	30.88 ± 1.51	0.9818
	11.00 ± 0.68	6.60 ± 0.12	$0.40 \pm 0.03$	44.59 ± 2.37	125.77 ± 1.34	25.65 ± 1.26	0.9836
	11.00 ± 0.68	5.90 ± 0.11	$0.39 \pm 0.02$	40.90 ± 2.17	120.15 ± 1.28	32.82 ± 1.61	0.9836
	MV=	MV=	MV=	MV=	MV=	MV=	MV=
	12.82 ± 0.79	5.65 ± 0.11	0.33 ± 0.02	29.70 ± 1.58	93.83 ± 1.00	25.99 ± 1.27	0.9777
Spain	1						
C 1 :							
Serbia	12.50 ± 0.77	4.48 ± 0.09	0.28 ± 0.02	28.31 ± 1.50	53.79 ± 0.57	24.42 ± 1.20	0.9818
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$	$4.48 \pm 0.09$ $5.41 \pm 0.10$	$0.28 \pm 0.02$ $0.32 \pm 0.02$	28.31 ± 1.50 18.48 ± 0.98	$53.79 \pm 0.57$ $127.82 \pm 1.36$	$24.42 \pm 1.20$ $22.12 \pm 1.08$	0.9818 0.9824
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \end{array}$	$0.28 \pm 0.02$ $0.32 \pm 0.02$ $0.29 \pm 0.02$	28.31 ± 1.50 18.48 ± 0.98 20.80 ± 1.10	$53.79 \pm 0.57$ 127.82 ± 1.36 110.50 ± 1.03	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$	0.9818 0.9824 0.9830
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$	$4.48 \pm 0.09$ 5.41 ± 0.10 4.90 ± 0.09 5.89 ± 0.11	$0.28 \pm 0.02$ $0.32 \pm 0.02$ $0.29 \pm 0.02$ $0.35 \pm 0.02$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$	0.9818 0.9824 0.9830 0.9808
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$	0.9818 0.9824 0.9830 0.9808 0.9824
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \\ 6.23 \pm 0.12 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \\ 6.23 \pm 0.12 \\ 5.02 \pm 0.09 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \\ 6.23 \pm 0.12 \\ 5.02 \pm 0.09 \\ 4.80 \pm 0.09 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \\ 0.28 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831 0.9824
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \\ 6.23 \pm 0.12 \\ 5.02 \pm 0.09 \\ 4.80 \pm 0.09 \\ 5.20 \pm 0.10 \end{array}$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.30 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831 0.9824 0.9819
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$ <b>MV=</b>	$\begin{array}{c} 4.48 \pm 0.09 \\ 5.41 \pm 0.10 \\ 4.90 \pm 0.09 \\ 5.89 \pm 0.11 \\ 7.03 \pm 0.13 \\ 6.76 \pm 0.12 \\ 5.62 \pm 0.10 \\ 6.23 \pm 0.12 \\ 5.02 \pm 0.09 \\ 4.80 \pm 0.09 \\ 5.20 \pm 0.10 \\ \textbf{MV=} \end{array}$	$0.28 \pm 0.02$ $0.32 \pm 0.02$ $0.29 \pm 0.02$ $0.35 \pm 0.02$ $0.40 \pm 0.03$ $0.39 \pm 0.02$ $0.33 \pm 0.02$ $0.37 \pm 0.02$ $0.31 \pm 0.02$ $0.28 \pm 0.02$ $0.30 \pm 0.02$ <b>MV=</b>	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$ <b>MV=</b>	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$ <b>MV=</b>	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$ <b>MV=</b>	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831 0.9831 0.9824 0.9819 <b>MV</b> =
Serbia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$ <b>MV=</b> $12.61 \pm 0.78$	$4.48 \pm 0.09$ $5.41 \pm 0.10$ $4.90 \pm 0.09$ $5.89 \pm 0.11$ $7.03 \pm 0.13$ $6.76 \pm 0.12$ $5.62 \pm 0.10$ $6.23 \pm 0.12$ $5.02 \pm 0.09$ $4.80 \pm 0.09$ $5.20 \pm 0.10$ <b>MV=</b> $5.57 \pm 0.10$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.30 \pm 0.02 \\ \textbf{MV=} \\ \textbf{0.33 \pm 0.02} \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$ <b>MV=</b> $36.28 \pm 1.93$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$ <b>MV=</b> $105.77 \pm 1.13$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$ <b>MV=</b> $27.30 \pm 1.34$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831 0.9824 0.9819 MV= 0.9817
North	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$ <b>MV=</b> $12.61 \pm 0.78$ $14.57 \pm 0.90$	$4.48 \pm 0.09$ $5.41 \pm 0.10$ $4.90 \pm 0.09$ $5.89 \pm 0.11$ $7.03 \pm 0.13$ $6.76 \pm 0.12$ $5.62 \pm 0.10$ $6.23 \pm 0.12$ $5.02 \pm 0.09$ $4.80 \pm 0.09$ $5.20 \pm 0.10$ <b>MV=</b> $5.57 \pm 0.10$ $5.71 \pm 0.11$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.30 \pm 0.02 \\ \textbf{MV=} \\ \textbf{0.33 \pm 0.02} \\ 0.28 \pm 0.02 \\ 0.28 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$ <b>MV=</b> $36.28 \pm 1.93$ $40.24 \pm 2.14$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$ $MV=$ $105.77 \pm$ $1.13$ $90.29 \pm 0.96$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$ <b>MV=</b> $27.30 \pm 1.34$ $33.99 \pm 1.67$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9801 0.9801 0.9831 0.9824 0.9819 <b>MV=</b> 0.9817 0.9796
Serbia North Macedonia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$ <b>MV=</b> $12.61 \pm 0.78$ $14.57 \pm 0.90$ $15.61 \pm 0.96$	$4.48 \pm 0.09$ $5.41 \pm 0.10$ $4.90 \pm 0.09$ $5.89 \pm 0.11$ $7.03 \pm 0.13$ $6.76 \pm 0.12$ $5.62 \pm 0.10$ $6.23 \pm 0.12$ $5.02 \pm 0.09$ $4.80 \pm 0.09$ $5.20 \pm 0.10$ <b>MV=</b> $5.57 \pm 0.10$ $5.71 \pm 0.11$ $5.99 \pm 0.11$	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.39 \pm 0.02 \\ 0.39 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.31 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.30 \pm 0.02 \\ \textbf{MV=} \\ \textbf{0.33 \pm 0.02} \\ 0.28 \pm 0.02 \\ 0.38 \pm 0.02 \\ 0.38 \pm 0.02 \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$ <b>MV=</b> $36.28 \pm 1.93$ $40.24 \pm 2.14$ $42.55 \pm 2.26$	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$ $MV=$ $105.77 \pm$ $1.13$ $90.29 \pm 0.96$ $92.24 \pm 0.98$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$ <b>MV=</b> $27.30 \pm 1.34$ $33.99 \pm 1.67$ $38.67 \pm 1.90$	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9810 0.9801 0.9831 0.9824 0.9819 <b>MV=</b> 0.9817 0.9796 0.9785
Serbia North Macedonia	$12.50 \pm 0.77$ $12.05 \pm 0.74$ $11.53 \pm 0.71$ $13.43 \pm 0.83$ $12.00 \pm 0.74$ $14.05 \pm 0.86$ $13.30 \pm 0.82$ $14.00 \pm 0.86$ $11.40 \pm 0.70$ $12.00 \pm 0.74$ $12.45 \pm 0.77$ <b>MV=</b> $12.61 \pm 0.78$ $14.57 \pm 0.90$ $15.61 \pm 0.96$ <b>MV=</b>	$4.48 \pm 0.09$ $5.41 \pm 0.10$ $4.90 \pm 0.09$ $5.89 \pm 0.11$ $7.03 \pm 0.13$ $6.76 \pm 0.12$ $5.62 \pm 0.10$ $6.23 \pm 0.12$ $5.02 \pm 0.09$ $4.80 \pm 0.09$ $5.20 \pm 0.10$ <b>MV=</b> $5.57 \pm 0.10$ $5.71 \pm 0.11$ $5.99 \pm 0.11$ <b>MV=</b>	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.32 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.02 \\ 0.40 \pm 0.03 \\ 0.39 \pm 0.02 \\ 0.33 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.37 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.30 \pm 0.02 \\ \textbf{MV=} \\ \textbf{0.28 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.38 \pm 0.02 \\ \textbf{MV=} \end{array}$	$28.31 \pm 1.50$ $18.48 \pm 0.98$ $20.80 \pm 1.10$ $44.24 \pm 2.35$ $61.49 \pm 3.27$ $48.97 \pm 2.61$ $43.65 \pm 2.32$ $51.61 \pm 2.75$ $28.22 \pm 1.50$ $30.13 \pm 1.60$ $23.20 \pm 1.23$ <b>MV=</b> $36.28 \pm 1.93$ $40.24 \pm 2.14$ $42.55 \pm 2.26$ <b>MV=</b>	$53.79 \pm 0.57$ $127.82 \pm 1.36$ $110.50 \pm 1.03$ $139.11 \pm 1.48$ $136.52 \pm 1.46$ $115.02 \pm 1.60$ $130.79 \pm 1.39$ $136.78 \pm 1.46$ $73.16 \pm 0.78$ $70.88 \pm 0.75$ $69.20 \pm 1.55$ $MV=$ $105.77 \pm$ $1.13$ $90.29 \pm 0.96$ $92.24 \pm 0.98$ $MV=$	$24.42 \pm 1.20$ $22.12 \pm 1.08$ $21.60 \pm 1.06$ $21.32 \pm 1.04$ $22.56 \pm 1.10$ $27.49 \pm 1.35$ $32.41 \pm 1.59$ $33.04 \pm 1.62$ $30.78 \pm 1.51$ $31.85 \pm 1.56$ $32.80 \pm 1.61$ <b>MV=</b> $27.30 \pm 1.34$ $33.99 \pm 1.67$ $38.67 \pm 1.90$ <b>MV=</b>	0.9818 0.9824 0.9830 0.9808 0.9824 0.9801 0.9801 0.9801 0.9831 0.9824 0.9819 MV= 0.9817 0.9796 0.9785 MV=

	Semi sweet wines								
Country	Total alcohol content (vol %)	Total acidity (g/L)	Volatile acidity	Free SO <sub>2</sub> (mg/L)	Total SO <sub>2</sub> (mg/L)	Total dry extract	Specific gravity (MU = +		
			(9, 2,			(9/2)	0.0019 for all wines)		
Italy	11.50 ± 0.71	5.55 ± 0.10	0.41 ± 0.03	40.22 ± 2.14	120.55 ± 1.28	34.88 ± 1.71	0.9830		
	11.60 ± 0.71	6.19 ± 0.12	0.40 ± 0.03	55.20 ± 2.94	140.10 ± 1.49	31.20 ± 1.53	0.9904		
	11.50 ± 0.71	6.12 ± 0.12	0.35 ± 0.02	38.15 ± 2.03	140.16 ± 1.49	38.20 ± 1.87	0.9831		
	9.65 ± 0.59	6.80 ± 0.13	0.36 ± 0.02	12.50 ± 0.66	128.66 ± 1.37	55.60 ± 2.73	0.9850		
	11.00 ± 0.68	5.80 ± 0.11	$0.40 \pm 0.03$	30.10 ± 1.60	150.75 ± 3.08	35.15 ± 1.72	0.9836		
	10.05 ± 0.62	6.50 ± 0.12	$0.38 \pm 0.02$	29.50 ± 1.57	130.88 ± 1.40	76.15 ± 3.74	0.9848		
	$10.02 \pm 0.62$	5.94 ± 0.11	$0.40 \pm 0.03$	29.20 ± 1.55	180.14 ± 1.92	66.80 ± 3.28	0.9848		
	12.03 ± 0.74	5.07 ± 0.10	0.30 ± 0.02	28.67 ± 1.52	100.53 ± 1.07	29.33 ± 1.44	0.9813		
	11.00 ± 0.68	5.66 ± 0.11	$0.40 \pm 0.03$	30.15 ± 1.60	154.18 ± 1.64	35.20 ± 1.73	0.9836		
	9.55 ± 0.59	5.07 ± 0.09	0.35 ± 0.02	26.88 ± 1.43	130.20 ± 1.39	60.80 ± 2.99	0.9804		
	10.85 ± 0.67	5.37 ± 0.10	0.22 ± 0.02	16.36 ± 0.87	109.29 ± 1.16	28.01 ± 1.37	0.9845		
	18.10 ± 1.12	4.10 ± 0.08	0.15 ± 0.02	15.22 ± 0.81	58.18 ± 0.62	55.18 ± 2.71	0.9850		
	7.55 ± 0.46	5.38 ± 0.10	$0.40 \pm 0.03$	40.60 ± 2.16	128.16 ± 1.37	34.65 ± 1.70	0.9878		
	MV=	MV=	MV=	MV=	MV=	MV=	MV=		
	11.10 ± 0.68	5.65 ± 0.10	$0.34 \pm 0.02$	30.21 ± 1.61	128.59 ± 1.37	44.70 ± 2.19	0.9844		
France	13.40 ± 0.82	6.70 ± 0.12	0.36 ± 0.02	32.10 ± 1.71	110.28 ± 1.17	41.25 ± 2.02	0.9808		
Spain	11.53 ± 0.71	5.24 ± 0.10	0.22 ± 0.02	18.12 ± 0.96	115.69 ± 1.23	36.55 ± 1.79	0.9830		
	11.50 ± 0.71	5.11 ± 0.10	$0.32 \pm 0.02$	$14.49 \pm 0.77$	103.53 ± 1.10	52.51 ± 2.58	0.9830		
	11.50 ± 0.71	$5.24 \pm 0.10$	$0.32 \pm 0.02$	16.30 ± 0.86	103.53 ± 1.10	52.50 ± 2.58	0.9830		
	11.50 ± 0.71	5.11 ± 0.10	$0.22 \pm 0.02$	$14.49 \pm 0.77$	115.68 ± 1.23	36.54 ± 1.78	0.9830		
	11.50 ± 0.71	5.17 ± 0.10	0.27 ± 0.02	18.12 ± 0.96	109.60 ± 1.17	44.52 ± 2.19	0.9830		
	MV=	MV=	MV=	MV=	MV=	MV=	MV=		
	$11.50 \pm 0.70$	5.17 ± 0.10	$\textbf{0.27} \pm \textbf{0.02}$	$16.30\pm0.86$	109.60 ± 1.17	44.52 ± 2.19	0.9830		
Serbia	12.16 ± 0.75	6.65 ± 0.12	0.38 ± 0.02	72.83 ± 3.88	145.92 ± 1.56	27.53 ± 1.35	0.9823		
	12.03 ± 0.74	6.38 ± 0.12	0.36 ± 0.02	63.67 ± 3.39	123.34 ± 1.31	24.16 ± 1.18	0.9824		
	MV=	MV=	MV=	MV=	MV=	MV=	MV=		
N - utla	12.10 ± 0.75	6.51 ± 0.12	0.37 ± 0.02	68.25 ± 3.63	134.63 ± 1.44	25.84 ± 1.27	0.9824		
North	/								
Macedonia									

# Table 1.3. Mean values of physical-chemical parameters in semi-sweet wines from different countries

	Sweet wines							
Country	Total alcohol content (vol %)	Total acidity (g/L)	Volatile acidity (g/L)	Free SO <sub>2</sub> (mg/L)	Total SO <sub>2</sub> (mg/L)	Total dry extract (g/L)	Specific gravity (MU = ± 0.0019 for all wines)	
Italy	15.00 ± 0.92	5.60 ± 0.10	0.27 ± 0.02	20.20 ± 1.07	98.18 ± 1.05	61.10 ± 3.00	0.9790	
	12.34 ± 0.76	4.93 ± 0.09	0.21 ± 0.02	12.62 ± 0.67	70.94 ± 0.75	185.76 ±9.13	0.9821	
	$7.38 \pm 0.45$	6.43 ± 0.12	0.38± 0.02	33.74 ± 1.79	146.56 ± 1.56	78.03 ± 3.83	0.9881	
	12.03 ± 0.74	$5.10 \pm 0.10$	0.31 ± 0.02	28.66 ± 1.52	100.51 ± 1.07	79.35 ± 3.90	0.9813	
	5.07 ± 0.31	5.83 ± 0.11	$0.22 \pm 0.02$	38.78 ± 2.06	181.09 ± 1.93	177.26 ±8.72	0.9911	
	MV=	MV=	MV=	MV=	MV=	MV=	MV=	
	10.36 ± 0.64	5.57 ± 0.10	0.27 ± 0.02	26.80 ± 1.42	119.45 ± 1.27	116.30 ±5.72	0.9843	
France	1							
Spain	1							
Serbia	16.09 ± 0.99	4.88 ± 0.09	0.30 ± 0.02	9.11 ± 0.48	91.19 ± 0.97	170.55 ± 8.39	0.9779	
North	/							
Macedonia								

Table 1.4. Mean values of physical-chemical parameters in sweet wines from different countries

# **Table 2.** The mean values, standard deviation and relative standard deviation were calculated for eachphysical-chemical parameter depending on the type of wine

Parameters	Dry wine	Semi dry	Semi	Sweet	Standard	Relative
		wine	sweet	wine	deviation	standard
			wine		(SD)	deviation
						(RSD)
Total alcohol content (vol %)	12.77-	12.50-	11.10-	10.36 –	0.38 %	3.09 %
	13.54	12.82	12.10	16.09		
		15.09*	13.40*			
Total acidity (g/L)	4.81-5.72	5.34-5.85	5.17-6.70	4.88-5.57	0.03 g/L	0.68 %
Volatile acidity (g/L)	0.26-0.39	0.30-0.33	0.27-0.37	0.27-0.30	0.01 g/L	3.12 %
Free SO, (mg/L)	25.66-	27.04-	16.30-	9.11-	0.19 mg/L	0.56 %
2 -	41.75	41.39	68.25	26.80	_	
Total SO, (mg/L)	87.51-	91.26-	109.60-	91.19-	0.22 mg/L	0.38 %
L	115.25	105.77	134.63	119.45		
Total dry extract (g/L)	16.20-	25.99-	25.84-	116.30-	0.58 g/L	2.42 %
	23.65	36.33	44.70	170.55		
Reduced sugar content (g/L)	up to 4	up to 12	up to 45	more	0.04 g/L	1.74 %
	g/L	g/L	g/L	than 45		
				a/L		

\* exceptions from the mean values

The usage of sulphur dioxide (SO<sub>2</sub>) as preservative in the winemaking industry is known for a long time. It has a direct impact on the wine quality and is used to ensure microbial, oxidative and antiseptic stability. The presence of total SO<sub>2</sub> in wine is usually the total amount of free and bound SO, and also there is a molecular form of SO, Molecular SO, has broadspectrum of antimicrobial properties (Divol du Toit et al., 2012), so it can kill or inhibit most of the spoilage yeast and bacteria that could affect wine. The free SO<sub>2</sub> concentration is defined as molecular SO, plus bisulphites and gives oxidative stability in concentrations between 20-40 mg/L. But its use is of crucial importance and must be regulated because too much SO, can mask the fruity aromas and gives metallic, sharp and bitter flavour to the wine which has negative effect on the quality. In our research, the concentrations of free and total sulphur dioxide in all samples are in balance, but there were semi-dry wines originating from France which showed the slightest value (min.12.18  $\pm$ 0.64 mg/L free SO<sub>2</sub> and min.60.20  $\pm$  0.64 mg/L total SO<sub>2</sub>), which corresponds to their high quality and price on the market.

In the past, the content of the total dry extract was considered as a basic parameter for determining the possible falsification of the wine, or it's dilution with water. But nowadays it is generally accepted that the content of the total dry extract depends mostly on the variety of grapes, seasonal variations as well as the method of wine production. The composition of the total dry extract represents all nonvolatile matter which in specific conditions do not volatilize (Florin Dumitru BORA et al., 2015). From the chemical aspect, the total dry extract consists of: sugars, tannins and dyes, organic acids such as (tartaric, malic, succinic acid, lactic acid), glycerol, 2,3 butylene glycol, nitrogen, pectin, gums, etc. The higher the extract, the fuller the body and greater aroma and flavour of the wine. In ideal conditions, the dry extract should be in balance with the sugar, acidity and alcohol levels in wine. In our research, we can notice that the content of the total extract is continuously growing as the content of sugars in the samples increases. So, the lowest content is observed in the dry wines originating from all countries (16.20  $\pm$  0.79 g/L) and the highest in the sweet wines (up to  $170.55 \pm 8.39 \text{ g/L}$ ).

## **CONCLUDING REMARKS**

Based on the results from the research, we came to the conclusion that all types of white, rose and red imported and domestic dry, semi dry, semi-sweet and sweet wine, satisfy the quality standards prescribed in Law of wine and wine products of the Republic of North Macedonia and the Regulations of wine of the European Commission.

In the markets across the country, many types of wine of different quality, price, and

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different countries of origin, can be found.

Our research included wines commonly found

on the market and by examining their basic

parameters that determine the quality, we

managed to establish that most of the imported

and domestic wines satisfy the quality standards

prescribed in the Law of wine and wine products

of the Republic of North Macedonia, although

some have a lower, and others have a higher

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## ОПРЕДЕЛУВАЊЕ НА ХЕМИСКИТЕ ПАРАМЕТРИ НА УВЕЗЕНИ И ДОМАШНИ ВИНА НА ПАЗАРОТ ВО РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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#### Резиме

Во Република Северна Македонија производството на вино е многу добро познато, но на пазарите има и разновидни увозни вина. Значи, целта на нашето истражување беше да ги испитаме основните параметри кои го одредуваат квалитетот на виното. Во ова истражување беа опфатени вкупно 106 домашни и увозни вина. Основните хемиски параметри за секој од примероците беа испитани со користење на стандардни OIV методи. Верификацијата на методите беше направена со одредување на точноста, прецизноста, повторливоста и репродуктивноста со користење на стандарден референтен материјал и тестови на оспособеност. Во зависност од содржината на шеќер, вината беа поделени во 4 групи: суви, полусуви, полуслатки и слатки вина. Највисока содржина на алкохол е забележана кај сувите вина со потекло од сите земји кои беа предмет на ова истражување (до 13,54 вол.%), а најниска е забележана кај вината со потекло од Италија кои најчесто се користат како десертни вина (5,07 вол.%). Полусувите вина со потекло од Франција покажаа најмала вредност (min.12,18 mg/L слободен SO<sub>2</sub> и мин.60,20 mg/L вкупен SO<sub>2</sub>), што одговара на нивниот висок квалитет и цена на пазарот. Ова истражување е од голем интерес за потребите на пазарот и цената на виното, поради стандардите за квалитет на виното според законот на Република Северна Македонија.

Клучни зборови: квалитет на вино, OIV методи, описна анализа, верификација на метод.