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Determination of Alcohol and Total Dry Extract in Slovenian Wines by Empirical Relations

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Summary

The possibility of fast determination of alcohol and total dry extract from given relative density and refractive index in wine was examined on fifty eight samples of Slovenian white and red still wines. Calculated relation values obtained from literature were compared to values determined experimentally using official methods (pycnometry and hydrostatic balance). Determination of alcohol and total dry extract together by means of calculation was the most accurate for the group of white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} and the least accurate for the group of white wines with over 15 g L^{-1}. For alcohol calculation the standard deviations and coefficients of variation for literature and our relations were different (literature relations: SD = 7.37–8.53, CV = 8.33–9.52 %, our relations: SD = 7.18–13.94, CV = 7.96–16.55 %) and they were higher for the total dry extract (literature relations: SD = 16.39–16.76, CV = 45.14–49.49 %; our relations: SD = 13.70–16.73, CV = 42.68–49.16 %). The most accurate relations for separate groups of wines (white wines with different reducing sugars content or red wines) have already been published (*2–6*). Our own relations for calculation of alcohol level and total dry extract were obtained by means of multiple linear regression analysis. The experiment has shown that none of the results are accurate enough to be obtained using only one relation for different wines.

Key words: wine, alcohol, total dry extract, official method, rapid method, empirical relations

Introduction

Determination of alcohol and total dry extract involves two obligatory types of analyses for certified wine in Slovenia and Europe.

Laboratories should issue suitable certificates in a defined period of time. They are not able to run all the prescribed official methods for all the samples due to the fact that they are time-consuming (sample distillation) and economically extremely demanding (*1*). Most laboratories, especially those running numerous sample tests, apply various rapid methods to determine alcohol and total dry extract. There is a wide choice of rapid methods available. Their advantage is in their precision (0.5–1 %), but the greatest problem concerning their application is the accuracy of results when it comes to such a complex medium as wine. If suitable apparatus is used in a rapid method, the purchase price and maintenance costs are higher. In comparison with official methods the advantages of the rapid ones lie particularly in the simplicity of analysis, and in a large number of measurements carried out in a short period of time.

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In this study we examined the possibility of fast determination of alcohol and total dry extract from relative density given, and from refractive index in wine. Empirical relations to calculate the previously mentioned parameters were first described by Rebelein in 1953, who was later followed by several other authors (*2–6*). Nowadays, various empirical relations represent the basic part of commercial equipment needed to determine alcohol and total dry extract (*6*). The greatest advantage of their use is, besides their precision, the rapidity of analysis (without time-consuming process of distillation). The results were compared to experimental results obtained by official methods and were subject to statistical analysis.

Material and Methods

Material

The measurements were obtained from a group of selected red (17 samples) and white Slovenian wines (41 samples) of vintages from 1995 to 1999. White wines were arranged according to the concentration of reducing sugars: up to 5 g L^{-1} (14 samples), between 5 and 15 g L^{-1} (13 samples) and over 15 g L^{-1} (14 samples).

Methods

The measurements of relative density, refractive index, alcohol concentration (g L^{-1}), total dry extract (g L^{-1}), reducing sugars (g L^{-1}) and total acidity (expressed as g L^{-1} tartaric acid) were carried out by using official methods (*1*).

Alcohol and total dry extract examined according to the official methods – pycnometry and hydrostatic balance (*7*) – were compared to the results obtained by the electronic densimetry using commercial apparatus Centec MDA200 (*6*). This apparatus uses automated method based on the principle of the resonant frequency oscillation of a wine sample in an oscillation cell (resonance U-tube).

Conductivity (χ) measurements were carried out using a conductometer (Conductivity Meter, CDM 83, Radiometer Copenhagen) with cell (CDC, Type 304, Radiometer Copenhagen) at 20 °C.

Viscosity (η) was measured at a temperature of 20 °C using an Ubbelodhe glass capillary viscosimeter, which was calibrated at different temperatures with distilled water. The measured flow time (t) ranged from 175 to 455 s. The estimated error in viscosity determination was $1.0 \cdot 10^{-3}$ Pa s.

Osmolality ($\hat{m}$) was measured by the cryoscopic method using a Knauer cryoscope with Cryoscopic Unit,

Table 1. Results of standard physico-chemical analysis of investigated wines

Category of samples	Experimental results (range)							
Category	N (sample)	γ(TA)/(gL^{-1})	γ(RS)/(gL^{-1})	γ(A)/(gL^{-1})	γ(E)/(gL^{-1})	d_{20}^{20}	n_D^{20}	R_D^{20}
Red wines	17	4.96-11.52	0.6-9.4	72.7–105.8	20.2–36.1	0.99275–0.99938	1.3410–1.3442	34.63–43.86
Red wines (up to 5 g/L reducing sugar)	15	4.96-11.52	0.6-4.3	72.7–105.8	20.2–31.2	0.99275–0.99702	1.3410–1.3442	34.63–43.86
White wines	41	5.03-10.67	0.8-72.4	76.7–105.0	16.9–116.1	0.99082–1.02986	1.3413–1.3549	36.18–72.80
White wines (up to 5 g/L reducing sugar)	14	5.03-8.41	0.8-4.5	81.8–104.3	16.9–26.3	0.99082–0.99541	1.3413–1.3436	36.18–41.36
White wines (up to 30 g/L reducing sugar)	22	5.17-10.67	5.8-21.9	77.0–105.0	28.6–52.2	0.99374–1.00603	1.3428–1.3459	40.15–48.40
All wines (red and white)	58	4.96-11.52	0.6-72.4	72.7–105.8	16.9–116.1	0.99082–1.02986	1.3410–1.3549	34.63–72.80

Legend: TA = titratable acidity expressed as tartaric acid concentration; RS = reducing sugar; A = alcohol; E = total dry extract; d_{20}^{20} = relative density (-); n_D^{20} = refractive index (-); R_D^{20} = refractive number

Table 2. Literature relations used for the calculation of alcohol (g.L^{-1})

	Literature relation (A1): $\gamma(A)/(gL^{-1}) = 7756.2 \cdot n_D^{20} - 2865.25 \cdot d_{20}^{20} - 7474.1$							
	Literature relations (A2–A8; A10): $\gamma(A)/(gL^{-1}) = a \cdot R_D^{20} - b \cdot d_{20}^{20} + c$							
Constant	A2	A3	A4	A5	A6	A7	A8	A10
a	2.954	2.64025	2.6282	2.6186	2.6429	2.691789244	2.5532	2.62765
b	2922.182	2680.45675	2606.56	2585.70	2683.73	2701.344779	2604.06	2605.54
c	2879.192	2650.32763	2577.69	2557.19	2655.57	2668.958	2577.68	2576.684
	Literature relation (A9): $\gamma(A)/(gL^{-1}) = 100\ (n_D^{20} - 1.333) \cdot ((n_D^{20} - 1.333) \cdot 25 + 76.9) + 2888 \cdot (1 - d_{20}^{20})$							

Reference: relation (A1): Rebelein. *(2)*; relation (A2): Kovacs-Klement and Petro-Turza. *(3)*; relation (A3): Geiss. Kupka and Nestler. *(4)*; relation (A4): Würdig and Müller. *(5)* – Centec 1; relation (A5): Würdig and Müller. *(5)*; relation (A6): Würdig and Müller. *(5)* – for must; relation (A7): Geiss; relation (A8): Heidger; relation (A9): Lay; relation (A10): Centec 2 type 7312400000. The cryoscope was calibrated with water/ethanol solutions in the concentration range from 7 to 14 vol %.

The measurements mentioned above were carried out in at least three replications, and the results were given as mean value. The results obtained from basic chemical and physical analyses of wine samples are presented in Tables 1 and 11, respectively.

All the results of experimental value and calculations were statistically analyzed by the method of least squares using the GLM Procedure software (*8*).

Results and Discussion

Concentration of alcohol

Literature relations used for calculation of alcohol mass concentration (g L^{-1}) are shown in Table 2. Calculated values obtained by the above mentioned relations were compared to experimental values obtained with official methods. The comparison was made for all the relations in the entire group of wines (N = 58) despite the fact that their use had not been recommended by authors for all groups of wines (*2–6*).

Limitations for relations as recommended by authors:

A1 for dry wines if $40 < \gamma\ (A)/(g\ L^{-1}) < 100$,

A2 for wines with less than 25 g L^{-1} reducing sugars if $100 < \gamma\ (A)/(g\ L^{-1}) < 131$,

A3 for wines if $55 < \gamma\ (A)/(g\ L^{-1}) < 110$,

A4 for wines if $\gamma(E) < 90$ g L^{-1} and $50 < \gamma\ (A)/(g\ L^{-1}) < 100$, and if total alcohol content is not more than 100 g L^{-1},

A5 for wines if $\gamma(E) < 90$ g L^{-1} and $50 < \gamma\ (A)/(g\ L^{-1}) < 100$, and if total alcohol content is not more than 100 g L^{-1},

A6 for must: $2 < \gamma\ (A)/(g\ L^{-1}) < 50$,

The variations for alcohol, which have been defined experimentally and by means of calculated values, were divided into the following three groups:

1. optimal variation: up to 0.2 %
2. still acceptable variation: between 0.2 and 0.5 %
3. unacceptable variation: over 0.5 %

Alcohol content in selected samples of Slovenian wines ranged from 9.2 to 13.4 vol %. For the entire group of wines, the comparison between alcohol determined by experiments (experimental data determined by the official method) and calculations (calculated data obtained by different relations) gave the following results (for all relations together). Most samples resulted in optimal variation (max. 55.2 % – A4; min. 39.7 % – A1) (Fig. 1). Still acceptable variation was found in the smaller number of samples (max. 34.5 % – A9; min. 25.9 % – A3, A7). Least samples resulted in unacceptable variation (max. 27.6 % – A1; min. 15.5 % – A2, A4, A5, A6, A10).

For the entire group of wines, the most accurate relation was A4 (55.2 % of samples with optimal variation and 29.3 % with unacceptable variation), closely followed by A2, A5 and A10. The least accurate relations were A1 (39.7 % of samples with optimal variation and 32.8 % with still acceptable variation) and A9 (39.7 % of samples with optimal variation and 34.5 % with still acceptable variation).

For separate groups of wines, the comparison between alcohol determined by experiment (experimental data determined by the official method) and calculation (calculated data obtained by different relations) gave the following results. For white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1}, the most accurate relation proved to be A6, while the least accurate were A7 and A8. For white wines with the value between 5 and 15 g L^{-1} the most accurate relations proved to be A4, A5 and A10, while the least accurate were A1 and A9. For white wines with over 15 g L^{-1} the

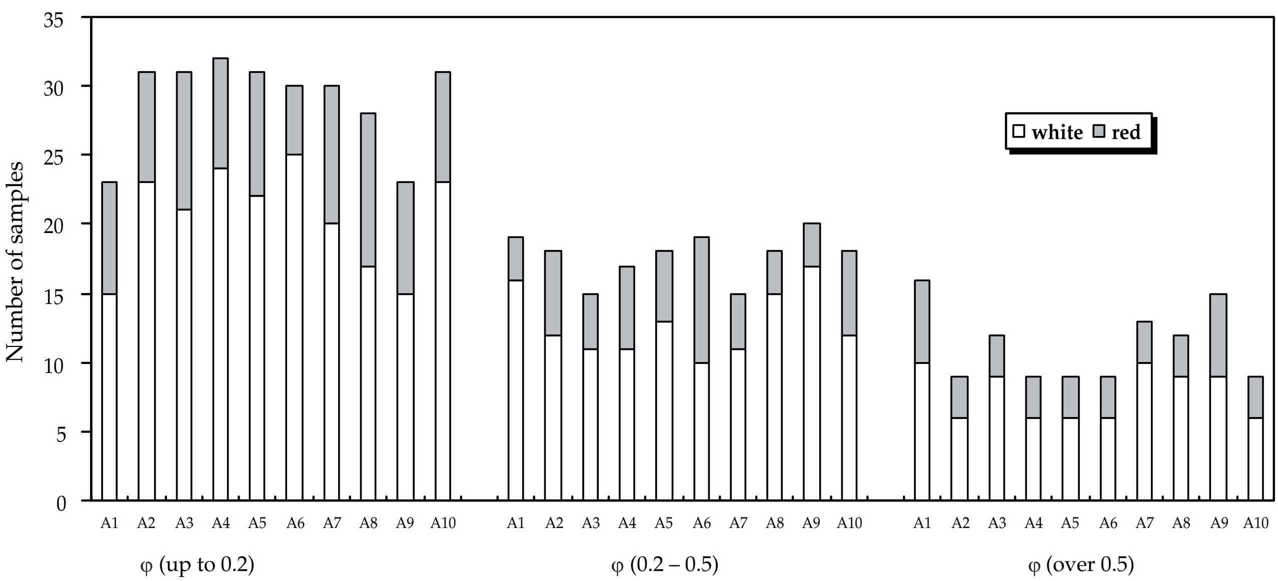

Fig. 1. Variation in alcohol volume fraction (φ/%) between experimantal and calculated values

most accurate relation proved to be A4 while the least accurate was A1. Finally, for red wines the most accurate relation proved to be A8 while the least accurate were A1, A6 and A9.

The calculation of alcohol by given relations was the most suitable for the group of white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} (with the most of optimal and the least of unacceptable variations), and the least suitable for the group of white wines with over 15 g L^{-1} (with the most of unacceptable and the least of optimal variations). The most accurate relations and the least accurate ones varied for each group. A4 proved to be the most accurate for two groups of wines. A1 and A9 were the least accurate for 3 and 2 groups of wines, respectively. While for white wines with up to 5 g L^{-1}, A6 (this relation is suitable only for must as recommended by author) appeared to be the most accurate, it proved to be the least accurate for red wines. The opposite was found for A8 for the above mentioned groups of wines. The relation A8, which was the most accurate for the group of red wines, was never accurate for three groups of white wines.

Our own relations (Table 4) to calculate alcohol (g L^{-1}) for the separate group of the investigated wine were calculated by means of multiple linear regression analysis. The parameters (a, b, c) were obtained by the least square method. Analysis of variance for the calculation of alcohol was presented in Table 5. The comparison of experimental and calculated alcohol values showed that the average deviations for all wines were very small, they varied from 0.1 to 0.2 %, while the standard deviation for all wines was 2.7 % (for white wines: SD = 2.2–2.3 %; for red wines: SD = 3.5 %).

For our relations, the comparison between alcohol determined by experiment and calculation gave the following results. Most samples resulted in optimal variation (max. 85.7 % – rel. 4; min. 41.1 % – rel. 1). Still acceptable variation was found in a smaller number of samples (max. 47.1 % – rel. 1; min. 0.0 % – rel. 4). Least samples resulted in unacceptable variation (max. 20.0 % – rel. 2; min. 7.3 % – rel. 3).

Concentration of total dry extract

Literature relations used for the calculation of total dry extract (g L^{-1}) are given in Table 3. Calculated values obtained by the above mentioned relations were compared to experimentally determined values obtained by the official method. The comparison was made for all relations in the entire group of wines (N = 58) despite the fact that their use was not recommended by authors for all groups of wines (*2–6*).

Limitations for relations as recommended by authors:

E1 for dry wines if $40 < \gamma\,(A)/(g\,L^{-1}) < 100$,

E2 for wines with less than 25 g L^{-1} reducing sugars if $81 < \gamma\,(A)/(g\,L^{-1}) < 105$,

Table 3. Literature relations used for the calculation of total dry extract mass concentration (γ)

	Literature relations (E1-E7): $\gamma(E)/(gL^{-1}) = a \cdot R_D^{20} + b \cdot d_{20}^{20} - c$						
Constant	E1	E2	E3	E4	E5	E6	E7
a	3164.54	1.139	1.02356	1.00	1.2095	1.0451	1.00024
b	1431.43	1463.052	1555.00738	1581.04	1374.18	1540.7992	1579.995
c	5647.4	1475.158	1562.46255	1587.41	1387.04	1549.232	1586.38

Reference: relation (E1): Rebelein. *(2)*; relation (E2): Kovacs-Klement and Petro-Turza. *(3)*; relation (E3): Geiss. Kupka and Nestler. *(4)*; relation (E4): Würdig and Müller. *(5)*; relation (E5): Würdig and Müller. *(5)* – for must; relation (E6): Geiss; relation (E7): Centec

Table 4. Our relations used for the calculation of alcohol and total dry extract mass concentration (γ)

	Our relations: $\gamma(A)/(gL^{-1}) = a \cdot R_D^{20} - b \cdot d_{20}^{20} + c$					
Constant	1	2	3	4	5	6
a	2.50608	2.31654	2.55304	2.83479	2.49916	2.62189
b	3025.51149	3760.15603	2544.20068	2399.76909	2518.78075	2590.24769
c	3000.15996	3738.20495	2520.26778	2365.98362	2497.26527	2562.95468
R	0.87551	0.86239	0.92059	0.94031	0.91755	0.89885
SD	3.3291	3.41627	2.11544	1.87986	2.17739	2.51951
	Our relations: $\gamma(E)/(gL^{-1}) = a \cdot R_D^{20} + b \cdot d_{20}^{20} - c$					
Constant	1	2	3	4	5	6
a	0.96927	0.86622	0.97844	0.98934	0.96064	1.00132
b	1513.45484	1277.71741	1623.96616	1587.94360	1633.29496	1610.69874
c	1518.68735	1280.27897	1628.60741	1593.32958	1637.13107	1616.47285
R^2	0.92829	0.88578	0.99825	0.92339	0.99312	0.99718
SD	1.10969	1.02023	0.81466	0.77756	0.83243	0.90534

Legend: relation 1: red wines; relation 2: dry red wines (up to 5 gL^{-1} reducing sugars); relation 3: white wines; relation 4: dry white wines (up to 5 gL^{-1} reducing sugars); relation 5: white wines (up to 30 gL^{-1} reducing sugars); relation 6: all wines (red and white); SD = standard deviation

Table 5. Analysis of variance by multiple linear regression analysis for the calculation of alcohol ($g \cdot L^{-1}$) in all the investigated wine samples

Our relations: $\gamma(A)/(gL^{-1}) = a \cdot R_D^{20} - b \cdot d_{20}^{20} + c$				
Constant	Value	Error	t-Value	P > |t|
a	2.62189	0.12933	20.27295	<0.0001
b	2590.24769	117.19483	22.10206	<0.0001
c	2562.95468	111.97502	22.88863	<0.0001
ANOVA table				
Item	DF	SS	MS	F
Model	2	3102.53384	1551.26692	244.37293
Error	55	349.13719	6.34795	
Total	57	3451.67103		

Legend: P = Probability (significance level); DF = Degrees of freedom; SS = Sum of squares; MS = Mean square; F = Fisher ration

E3 for wines if $20 < \gamma(E)/(g\ L^{-1}) < 110$,

E4 for wines if $15 < \gamma(E)/(g\ L^{-1}) < 160$ and if total alcohol content is not more than 160 g L^{-1},

E5 for must: $2 < \gamma(A)/(g\ L^{-1}) < 50$

The variations for total dry extract, which were defined experimentally and by means of calculated values, were divided into the following three groups:

1. optimal variation: up to 0.5 g L^{-1}
2. still acceptable variation: between 0.5 and 0.8 g L^{-1}
3. unacceptable variation: over 0.8 g L^{-1}

Total dry extract in selected samples of Slovenian wines ranged from 17.7 to 114.4 g L^{-1}. The calculation of total dry extract by given relations was not as successful as the calculation of alcohol content. In continuation we eliminated the relation E5 because of the unfitness of its results for our selected group of wines (this relation is suitable only for the must as recommended by author). For the entire group of wines, the comparison between total dry extract determined by means of experiment (experimental data determined by the official method) and calculation (calculated data obtained by different relations) gave the following results (for all the relations together, E5 excluded). Most samples resulted in optimal variation (max. 53.4 % – E7, min. 27.6 % – E1) (Fig.2). Unacceptable variation was found in a smaller number of samples (max. 53.4 % – E1, min. 31.0 % – E7). Least samples resulted in still acceptable variation (max. 19.0 % – E1, E2, min. 12.1 % – E3, E4, E6).

For the entire group of wines, the most accurate relation was E7 (53.4 % of samples with optimal variation and 15.5 % of samples with still acceptable variation) followed by E4 (53,4 % of samples with optimal variation and 12.1 % of samples with still acceptable variation) and E2 (48.3 % of samples with optimal variation and 19.0 % of samples with still acceptable variation). The least accurate was relation E1 (27.6 % of samples with optimal variation and 19.0 % of samples with still acceptable variation).

For separate groups of wines, the comparison between total dry extract determined by experiment (experimental data determined by the official method) and calculation (calculated data obtained by different relations) gave the following results (for all the relations together, E5 excluded). For white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} the most accurate relations found were E4 and E7, while the least accurate was E1. For white wines with the value between 5 to 15 g L^{-1} the most accurate relation proved to be E4 while the least accurate was E1. For white wines with over 15 g L^{-1} the most accurate relation proved to be E2 while the least accurate was E1. Finally, for red wines the most accurate relations proved to be E3 and E6, while the least accurate was E1.

The calculation of total dry extract from given relations was the most suitable for the group of white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} and the group of red wines (the most of optimal variations and the least of unacceptable ones),

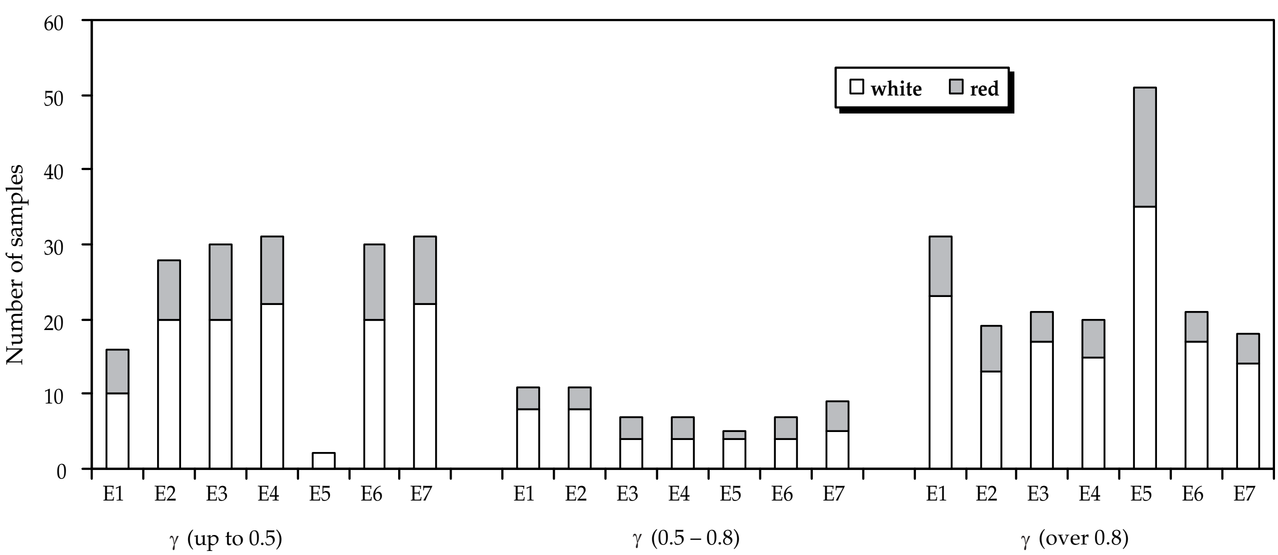

Fig. 2. Variation in total dry extract mass concentration (γ/gL^{-1}) between experimantal and calculated values

and the least suitable for the group of white wines with over 15 g L^{-1} (the most of unacceptable variations and the least of optimal ones). E4 and E7 proved to be the most accurate for two groups of wines, while E1 was the least accurate for all groups of wines. The relations E3 and E6, which were the most accurate for the group of red wines, were never the most accurate for three groups of white wines. Relation E2 was the most effective for the group of white wines with over 15 g L^{-1} (this relation is suitable for the wines with up to 25 g L^{-1} as recommended by author).

Our own relations (Table 4) to calculate total dry extract (g L^{-1}) for the separate group of the investigated wine were calculated by means of multiple linear regression analysis. The parameters (a, b, c) were obtained by the least square method. Analysis of variance for the calculation of total dry extract is included in Table 6. Comparison of experimental and calculated total dry extract values showed that there was a slight average deviation only in the case of white wines and it varied from 0.0 to 0.5 % (for white wines: average = 0.0–0.2 %; for red wines: average = 0.1–0.5 %). Standard deviation for all wines was 3.3 % (for white wines: SD = 2.6–3.8 %; for red wines: SD = 4.2–4.3 %).

For our relations, the comparison between total dry extract determined by experiment and calculation gave the following results. Most samples resulted in optimal variation (max. 64.3 – rel. 4; min. 41.2 % – rel. 1). Unacceptable variation was found in the smaller number of samples (max. 35.3 % – rel. 1; min. 14.3 % – rel. 4). Least samples resulted in still acceptable variation (max. 26.7 % – rel. 2; min. 19.0 % – rel. 6).

Table 6. Analysis of variance by multiple linear regression analysis for the calculation of total dry extract mass concentration (γ) in all the investigated wine samples

Our relations: $\gamma(E)/(gL^{-1}) = a \cdot R_D^{20} + b \cdot d_{20}^{20} - c$				
Constant	Value	Error	t-Value	P > |t|
a	1.00132	0.04647	21.54678	<0.0001
b	1610.69874	42.11154	38.24839	<0.0001
c	1616.47285	40.23591	40.17488	<0.0001
ANOVA table				
Item	DF	SS	MS	F
Model	2	15962.6025	7981.30125	9737.66769
Error	55	45.07974	0.81963	
Total	57	16007.68224		

Legend: P = Probability (significance level); DF = Degrees of freedom; SS = Sum of squares; MS = Mean square; F = Fisher value

Conclusions

The comparison between total dry extract and alcohol content by experiment and calculation was carried out on 58 samples of Slovenian wines. A wide range of total dry extract and alcohol content was from 9.2 to 13.4 vol. % for alcohol content and from 17.7 to 114.4 g L^{-1} for total dry extract.

If we consider all wine samples, the relation A4 appeared to be the most accurate with the determination of alcohol content by calculation (84.5 % of samples with optimal and still acceptable variation). For different groups of wines, the most accurate relations proved to be the following: for white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} - A6, for white wines with the value between 5 and 15 g L^{-1} – A4, A5 and A10, for white wines with over 15 g L^{-1} – A4, A1 and for red wines – A8.

Statistical data for the concentration of alcohol (g L^{-1}) calculated by literature relations (Table 7) and by our relations (Table 8) were presented in comparison with the experimental data. The literature (A1, A6, A9) and our relations (rels. 3, 5 and 6) are not significantly different (P>0.05). We could see that the standard deviations and coefficients of variation for literature and our relations were very different (literature relations: SD = 7.37–8.53, CV = 8.33–9.52 %; our relations: SD = 7.18–13.94, CV = 7.96–16.55 %). The maximal value of statistical parameters mentioned in our relations corresponded to the group of dry red wines.

Determination of total dry extract by means of calculation was less successful than determination of alcohol concentration. For the group with all wines, E7 (69 % of samples with the optimal and still acceptable variations) and E4 (65.4 % of samples with the optimal and still acceptable variations) were the most accurate relations to determine total dry extract. For separate groups of wines, the most accurate relations proved to be the following: for white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} – E4 and E7, for white wines with the value between 5 and 15 g L^{-1} –

Table 7. Statistical data for the mass concentration of alcohol (γ) calculated by literature relations in comparison with the experimental data

		Literature relations										
Parameter	Exp. data	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	P-value
Mean	89.76[a]	89.67[a]	88.90[b]	87.88[d]	88.49[c]	88.40[c]	89.97[a]	87.87[d]	87.77[d]	89.63[a]	88.48[c]	<0.0001
N (sample)	58	58	58	58	58	58	58	58	58	58	58	
MIN	72.70	74.17	73.01	73.87	74.67	74.30	75.95	73.50	74.25	74.09	74.36	
MAX	105.76	109.03	107.78	105.13	105.32	105.11	107.24	105.28	104.50	109.03	105.30	
SD	7.78	8.50	8.32	7.64	7.42	7.37	7.65	7.69	7.42	8.53	7.42	
CV/%	8.67	9.48	9.36	8.69	8.39	8.33	8.50	8.76	8.46	9.52	8.39	

Legend: MIN = minimal value; MAX = maximal value; SD = standard deviation; CV/% = coeficient of variation. Means with the same letter in index are not significantly different (P>0.05)

Table 8. Statistical data for the mass concentration of alcohol (γ) calculated by our relations in comparison with the experimental data

		Our relations						
Parameter	Exp. data	1	2	3	4	5	6	P-value
Mean	89.76b	87.57c	84.24d	90.09b	94.02a	90.16b	89.77b	<0.0001
N (sample)	58	58	58	58	58	58	58	
MIN	72.70	66.75	34.41	76.41	75.64	76.84	75.65	
MAX	105.76	106.52	107.06	106.51	107.97	106.38	106.50	
SD	7.78	9.20	13.94	7.25	7.33	7.18	7.38	
CV/%	8.67	10.51	16.55	8.04	7.97	7.96	8.22	

Legend: MIN = minimal value; MAX = maximal value; SD = standard deviation; CV/% = coeficient of variation. Means with the same letter in index are not significantly different (P>0.05)

Table 9. Statistical data for the mass concentration of total dry extract (γ) calculated by literature relations in comparison with the experimental data

		Literature relations							
Parameter	Exp. data	E1	E2	E3	E4	E5	E6	E7	P-value
Mean	34.04b.c	34.20b	33.88c	33.42d	33.45d	36.31a	33.39d	33.44d	<0.0001
N	58	58	58	58	58	58	58	58	
MIN	16.91	17.70	17.58	17.19	17.14	20.14	17.16	17.14	
MAX	116.12	114.41	114.50	113.49	113.64	116.22	113.66	113.61	
SD	16.76	16.76	16.56	16.49	16.53	16.39	16.53	16.52	
CV (%)	49.23	49.02	48.89	49.35	49.42	45.14	49.49	49.40	

Legend: N = number of samples; MIN = minimal value; MAX = maximal value; SD = standard deviation; CV (%) = coeficient of variation, Means with the same letter in index are not significantly different (P>0.05)

Table 10. Statistical data for the mass concentration of total dry extract (γ) calculated by our relations in comparison with the experimental data

		Our relations						
Parameter	Exp. data	1	2	3	4	5	6	P-value
Mean	34.04a	33.41b	32.10c	34.17a	34.20a	34.20a	34.04a	<0.0001
N	58	58	58	58	58	58	58	
MIN	16.91	17.75	18.65	17.65	17.70	17.70	17.51	
MAX	116.12	110.55	98.65	115.08	114.87	114.87	115.22	
SD	16.76	15.90	13.70	16.69	16.65	16.65	16.73	
CV (%)	49.23	47.57	42.68	48.84	48.68	48.68	49.16	

Legend: N = number of samples; MIN = minimal value; MAX = maximal value; SD = standard deviation; CV (%) = coeficient of variation; Means with the same letter in index are not significantly different (P>0.05)

E4 and E7, for white wines with over 15 g L^{-1}– E2 and for red wines – E3 and E6.

Determination of alcohol and total dry extract together by calculation was the most accurate for the group of white wines (according to the concentration of reducing sugars) with up to 5 g L^{-1} and the least accurate for the group of white wines with over 15 g L^{-1}. For separate samples, even the least acceptable variation could not be established by any of the relations applied in comparison with the official method (three white wine samples and two red wine samples in alcohol determination). The same problem was found for three white wine samples and two red wine samples in the determination of total dry extract (the samples were not the same as those mentioned above). It was found that the values of physical parameters (electrolytic conductivity, viscosity, osmolality) of all these samples were either minimal or maximal (*9*) (Table 11). The differences of relative density measured by pycnometry, hydrostatic balance or by resonance U-tube were $\pm 5 \times 10^{-5}$ (*10*). This value is comparable with other published data (*11*).

Table 11. Additional physical parameters of investigated wines

Category and number of samples		Experimental results (range)		
Category	N	κ/(μS/cm)	η/(Pa s)	$\hat{m}$/(mol/kg)
Red wines	17	1590.1–2262.6	1.456–1.678	1.885–2.899
White wines	41	1456.8–3473.3	1.479–1.945	2.203–4.855

Legend:
κ = conductivity at 20 °C;
η = viscosity at 20 °C;
$\hat{m}$ = osmolality

For separate groups of wines, white wines with different reducing sugars content or red wines the most accurate relations proved to be those issued by different authors. The limitations in alcohol content, total dry extract and reducing sugars concentration given by the authors of these relations did not prove necessary in case of our wines, due to the fact that relations outside and inside the prescribed limits gave similar results (except for the E5 relation). Relation A6, which one of the authors suggested for must, gave the most accurate results for white wines with up to 5 g L^{-1} while relation E2 appeared to be most successful for the group of white wines with over 15 g L^{-1} (in our case for 14 samples with reducing sugars concentration of 15 – 47 g L^{-1}), although it was meant only for wines with up to 25 g L^{-1} of reducing sugars.

Statistical data for the concentration of total dry extract (g L^{-1}) calculated by literature relations (Table 9) and our relations (Table 10) have been compared with experimental data. The literature (E1, E2) and our relations (rels. 3, 4, 5 and 6) are not significantly different ($P > 0.05$). We found big differences in standard deviations and coefficients of variation between literature and our relations, and they were higher in comparison with the alcohol calculation (literature relations: SD = 16.39–16.76, CV = 45.14–49.49 %; our relations: SD = 13.70–16.73, CV = 42.68–49.16 %).

Based on experimental data, we proposed the empirical relations for alcohol and total dry extract calculation. The results calculated by these relations correlated with the experimental results obtained by official methods. The experiment has shown that enough accurate results cannot be obtained by using only one relation for different wines. To be able to get greater accuracy for all wines, empirical relations should be carried out for separate groups. The minimum condition of separate red and white wines should be satisfied. In addition, groups of white wines need different relations regarding their content of reducing sugars. According to statistical analysis, better results for investigated Slovenian wines were obtained by different relations for calculation of alcohol and total dry extract proposed in our scientific work (for red wines, dry white wines, and white wines up to 30 g L^{-1} reducing sugars) than those calculated by literature relations.

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Određivanje alkohola i ukupnog suhog ekstrakta u slovenskim vinima mjerenjem relativnog odnosa gustoće i refrakcije

Sažetak

Ispitivana je mogućnost brzog određivanja alkohola i ukupnog suhog ekstrakta u 58 uzoraka slovenskih bijelih i crvenih nepjenušavih vina, na osnovi relativne gustoće i indeksa refrakcije. Izračunati odnosi vrijednosti, koji su dobiveni iz literature, uspoređeni su s eksperimentalno utvrđenim vrijednostima dobivenim korištenjem službenih postupaka (piknometrija i hidrostatska ravnoteža). Izračunavanje udjela alkohola zajedno s ukupnim suhim ekstraktom bilo je najtočnije za skupinu bijelih vina s koncentracijom reducirajućih šećera do 5 g/L, a manje točno za skupinu bijelih vina s udjelom preko 15 g/L. Pri izračunavanju alkohola standardna devijacija i koeficijenti varijacije razlikovali su se u literaturi i u našim podacima (literaturni podaci: SD = 7,37–8,53, CV =8,33–9,52 %; naši odnosi: SD = 7,18–13,94, CV = 7,96–16,55 %), a bili su viši za ukupni suhi ekstrakt (literaturni podaci: SD = 16,39–16,76, CV = 45,14–49,49 %; naši podaci: SD = 13,10–16,73, CV = 42,68–49,16 %). Najtočniji odnosi za pojedine skupine vina (bijela vina s različitim udjelom reducirajućih šećera ili crvenih vina) već su objavljeni u literaturi. Naši vlastiti rezultati dobiveni izračunavanjem udjela alkohola i ukupnog suhog ekstrakta za pojedine skupine vina, dobiveni su multiplom linearnom regresijskom analizom. Pokusima je potvrđeno da ni jedan od rezultata nije dovoljno točan ako se koristi samo jedan relativni odnos za različita vina.