Agrovoc descriptors: red wines, white wines, ash content, statistical methods

Agris category code: Q04, F60, U10

University of Ljubljana
Biotechnical Faculty
Department of Food Science and Technology COBISS Code 1.01

Determination of ash content in Slovenian wines by empirical equations

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Received June 17, 2003, accepted September 10, 2003.
Prispelo 17. junija 2003, sprejeto 10. septembra 2003.

ABSTRACT

The possibility of fast determination of ash content from given conductivity, alcohol and total dry extract was examined on 58 samples of Slovenian white and red still wines. Values calculated by literature relations were compared to experimentally determined values obtained by official method (burning in a furnace). The standard deviations and coefficients of variation for literature equations were very different and higher (SD = 0.57-0.72, CV = 24.16-29.25 %) in comparison to our own equations (SD = 0.32-0.56, CV = 14.73-25.74 %) obtained by multiple regression analysis for the separate group of white and red wines as well as for all the samples studied. The differentiation of wines into two groups was statistically confirmed especially for red wines (SD = 0.32, CV = 14.73 %). The experiment has shown that the results to be obtained cannot be accurate enough if only one empirical equation for different types of wines is used.

Key words: wine, ash content, conductivity, official method, empirical equation

IZVLEČEK

DOLOČANJE VSEBNOSTI PEPELA V SLOVENSKIH VINIH Z EMPIRIČNIMI ENAČBAMI

Možnost hitrega določanja vsebnosti pepela na osnovi prevodnosti, alkohola in skupnega suhega ekstrakta smo proučevali na 58 vzorcih slovenskih belih in rdečih mirnih vin. Vrednosti, izračunane z literaturnimi enačbami, smo primerjali z eksperimentalno določenimi vrednostmi, dobljenimi z uradno metodo (žarenje v peči). Standardne deviacije in koeficienti variacije za literaturne enačbe so bile zelo različne in visoke (SD = 0,57-0,72; CV = 24,16-29,25 %) v primerjavi z našimi enačbami (SD = 0,32-0,56; CV = 14,73-25,74 %), dobljenimi z metodo večkratne regresijske analize, tako za posamezne skupine belih in rdečih vin, kot za vse proučevane vzorce skupaj. Razločevanje vin v dve skupini se je statistično potrdilo zlasti za bela vina (SD = 0,32; CV = 14,73 %). Z eksperimentom smo pokazali, da dobljeni rezultati niso dovolj točni, če za izračun vsebnosti pepela uporabimo za različna vina samo eno empirično enačbo.

Ključne besede: vino, vsebnost pepela, prevodnost, uradna metoda, empirična enačba

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1 INTRODUCTION

Ash content is an obligatory analysis for certified wines to be placed on the market place. It is defined as all the products (inorganic matter) remaining after igniting the residue left from the evaporation of must or wine (Commission regulation (EEC), 1990). Determination of the ash, the alkalinity of the ash, and cations and anions is important to the enologist for a variety of reasons: legal, health, taste and regional definition (Ough and Amerine, 1988). Most of the wine producing countries prescribe the minimum amounts of ash content, which are in Slovenia 1.2, 1.4 and 1.6 gL^{-1} for white, rose and red wines, respectively (Pravilnik o spremembah in dopolnitvah pravilnika o kakovosti vina, 1988). It usually comprises potassium, calcium, magnesium and sodium salts, as well as sulphuric, phosphoric, hydrochloric and carbonic acids. It is expected that ash content present about 10 % of the sugar-free extract although it varies between varieties, regions and seasons.

The prescribed official method for determination of ash content is simple but time-consuming (Commission regulation (EEC), 1990). Most laboratories, especially those running numerous sample tests, apply faster methods, based on empirical equations relating ash content with the measurements of conductivity, (as it primarily depends on mineral content in wine), alcohol content and total dry extract. The first efficient experiments were done more than 40 years ago and some excellent results were reported by many authors (Müller and Würdig, 1987; Hupf *et al.*, 1987; Dikanović-Lučan *et al.*, 1993; Operating manual Centec MDA200, 2000). The advantage of conductometric methods is in their precision (1-2 %), but the greatest problem concerning their application is the accuracy of results when it comes to such a complex medium with very different chemical composition as wine. In comparison to the official method the advantage of the rapid one lies in the simplicity of analysis and in a large number of measurements carried out in a short period of time.

In this study we examined the possibility of determining the ash content in wine samples from the results of conductivity, alcohol content and total dry extract using empirical equations proposed by different authors, and of finding out the new possible equations (one or more) which would be more suitable for determination of ash content in a selected group of Slovenian wines. The calculated results were compared to the experimental ones obtained with the official method and were subject to statistical analysis.

2 MATERIAL AND METHODS

The measurements were obtained from a group of selected white (41 samples) and red (17 samples) Slovenian wines supplied from the market.

The measurements of ash content (gL^{-1}), alcohol (gL^{-1}) and total dry extract (gL^{-1}), were carried out using the official methods (Commission regulation (EEC), 1990) as well as the determination of the following parameters: alkalinity of ash ($meqL^{-1}$), relative density, refractive index, total acidity (gL^{-1} as tartaric acid) and reducing sugars (gL^{-1}). Glycerol was determined by HPLC, minerals (potassium, calcium, sodium, magnesium, copper and iron in mgL^{-1}) were determined directly by atomic absorption spectrophotometry (Commission regulation (EEC), 1990), while total phenols (mgL^{-1} as gallic acid) were spectrophotometrically measured using Folin-Ciocalteu reagent (Zoecklein *et al.*, 1999).

Additionally, we also analysed conductivity (μScm^{-1}), viscosity (Pas) and osmolality (molkg^{-1}). The conductivity measurements were carried out using a conductometer (Conductivity Meter, CDM 83, Radiometer Copenhagen) with cell (CDC, Type 304, Radiometer Copenhagen) at 20°C. The viscosity was measured at temperatures of 20°C using an Ubbelodhe glass capillary viscosimeter that was calibrated at different temperatures with distilled water. The osmolality was measured by the cryoscopic method using a Knauer cryoscope with Cryoscopic Unit, type 7312400000.

The measurements mentioned above were carried out in at least three replications, and the results were given as mean value. All the results of experimental value and calculations were statistically analyzed by the method of least squares using the GLM Procedure software (SAS/STAT, 1999).

3 RESULTS AND DISCUSSION

The results obtained from basic physico-chemical analyses of wine samples are presented. It can be concluded that ash, alcohol and total dry extract content were in a very wide range (Table 1). The ash varied from 1.23 to 3.90 gL^{-1}, the alcohol from 72.7 to 105.8 gL^{-1} and the total dry extract from 16.9 to 116.1 gL^{-1}. The range for conductivity was between 1634.4 and 3473.3 μScm^{-1} for white wines and from 1590.1 to 2262.6 μScm^{-1} for red wines.

Table 1. The results of physico-chemical analysis of investigated wines

	Category (number of samples)		
Parameter (unit)	White wines (41)	Red wines (17)	All wines (58)
titratable acidity (gL^{-1} as tartaric acid)	5.03-10.67	4.96-11.52	4.96-11.52
reducing sugars (gL^{-1})	0.8-72.4	0.6-9.4	0.6-72.4
alcohol (gL^{-1})	76.7-105.0	72.7-105.8	72.7-105.8
total dry extract (gL^{-1})	16.9-116.1	20.2-36.1	16.9-116.1
glycerol (gL^{-1})	4.6-12.2	5.6-8.3	4.6-12.2
total phenols (mgL^{-1} as gallic acid)	168.7-425.7	255.8-2518.8	168.7-2518.8
minerals* (mgL^{-1})	558.1-2039.4	612.8-1537.0	558.1-2039.4
ash (gL^{-1})	1.23-3.90	1.43-2.74	1.23-3.90
alkalinity of ash (meqL^{-1})	10.52-39.96	12.70-26.11	10.52-39.96
conductivity (μScm^{-1})	1634.4-3473.3	1590.1-2262.6	1590.1-3473.3
relative density (-)	0.99082-1.02986	0.99275-0.99938	0.99082-1.02986
refractive index (-)	1.3413-1.3549	1.3410-1.3442	1.3410-1.3549
osmolality (molkg^{-1})	2.203-4.855	1.885-2.899	1.885-4.855
viscosity (Pas)	1.479-1.945	1.456-1.678	1.456-1.945

Legend: minerals* (mgL^{-1}) = sum of concentrations of potassium, calcium, sodium, magnesium, copper and iron

The literature equations (Müller and Würdig, 1987; Hupf *et al.*, 1987; Dikanović-Lučan *et al.*, 1993; Operating manual Centec MDA200, 2000) used for calculation of ash content (gL^{-1}) are shown in Table 2. The calculated values obtained by equations mentioned above were compared to experimental values obtained by the official method. The comparison was made for all equations in the entire group of wines (N = 58). We eliminated the equation proposed by Piracci *et al.* (1990) because of the unfitness of its results for all our selected wines. Only the equation Ash 2 proposed by Hupf *et al.* (1987) draw a distinction between white and red wines.

Table 2. Literature equations used for the calculation of ash (gL^{-1})

	Literature equation: $\gamma(\mathbf{ash}) = \mathbf{a} \cdot \chi + \mathbf{b} \cdot \gamma(\mathbf{A}) + \mathbf{c} \cdot \gamma(\mathbf{E}) - \mathbf{d}$				
Constant	Ash 1	Ash 2 (white wines)	Ash 2 (red wines)	Ash 3	Ash 4
a	0.001346	0.001346	0.001346	0.00102	0.00136628
b	0.01648	0.01648	0.01648	0.00998	0.001679
c	0.009706	0.009706	0.009706	0.0276	0.0671
d	0.0282	2.107	1.948	1.38	2.26011

Reference: equation (Ash 1): Würdig and Müller, 1987; equation (Ash 2): Hupf, 1987; equation (Ash 3): Dikanović and Lučan, 1993; equation (Ash 4): Centec, 2000

Legend: γ = concentration in gL^{-1}; A = alcohol; E = total dry extract; χ = conductivity (μScm^{-1})

Table 3. Our equations used for the calculation of ash (gL^{-1})

	Our equation: $\gamma(\mathbf{ash}) = \mathbf{a} \cdot \chi + \mathbf{b} \cdot \gamma(\mathbf{A}) + \mathbf{c} \cdot \gamma(\mathbf{E}) - \mathbf{d}$		
Constant	1	2	3
a	0.00117	0.00206	0.00121
b	0.00745	0.01390	0.00691
c	0.00459	- 0.00260	0.0036
d	0.94953	2.3815	0.93599
R	0.88957	0.69496	0.84502
SD	0.20698	0.23241	0.21885

Legend: equation 1: white wines; equation 2: red wines; equation 3: all wines (white and red); R = R-Square (COD);
SD = standard deviation; γ = concentration in gL^{-1}; A = alcohol; E = total dry extract; χ = conductivity (μScm^{-1})

The differences in ash content between the experimental and the calculated values were divided into three groups:
1. optimal difference: up to 5 %
2. still acceptable difference: between 5 and 10 %
3. unacceptable difference: above 10 %

The comparison between the experimental data (determined by the gravimetric method) and the calculated data (obtained by different equations) are presented in Fig.1. Most samples (white and red wines together) resulted in unacceptable difference (34 samples or 58.6 % with the equation Ash 3 and 28 samples or 48.3 % with the equation Ash 2). The optimal difference range was found in 31 samples or 53.4 % with the equation Ash 4, and 28 samples or 48.3 % with Ash 1. Still acceptable difference was found in the smaller number of samples (20 samples or 34.5 % – Ash 2 and 14 samples or 24.1 % - Ash 1). The equation Ash 4 appeared to be the most accurate with the determination of ash content by means of calculation

(72.4 % of samples with optimal and still acceptable difference), while the calculation with the equation Ash 3 gave the highest number of unacceptable differences (58.6 %). It can be clearly seen that the calculation of ash content in white wines with equation Ash 3 (as well as Ash 2) is not accurate enough in comparison with the equations Ash 4 and Ash 1 (Fig. 1).

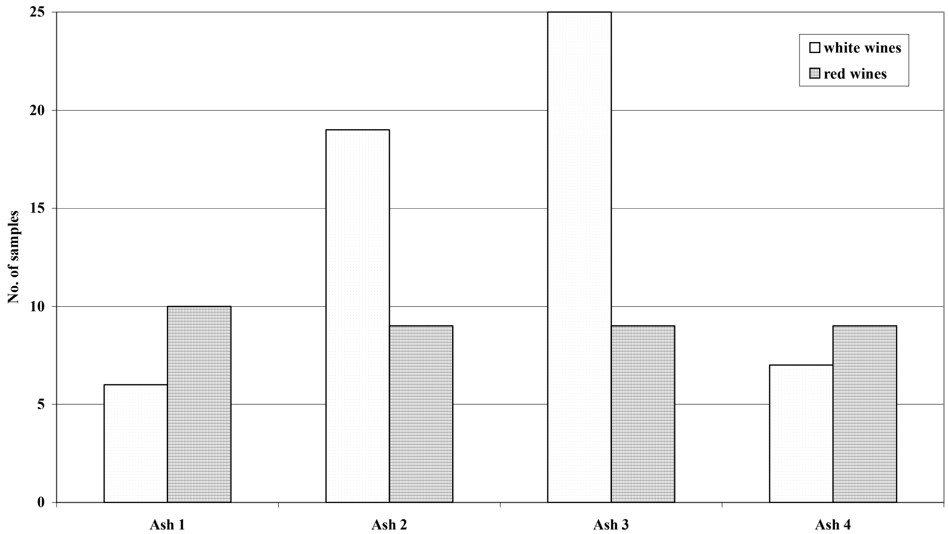

Figure 1. Difference in ash content above 10 % between the experimental and calculated values (γ / gL^{-1}) by literature equations

Our own equations for the calculation of ash content (gL^{-1}) were calculated by means of multiple linear regression analysis for the separate groups (white and red) of the wine investigated as well as for all the samples together. The parameters (a, b, c, d) obtained by the least square method are presented in Table 3, while the analysis of variance for the calculation of ash content was shown in Table 4. For our equations, the comparison between ash content determined by means of experiment and by means of calculation gave the following results (Figs. 2 and 3). Most samples resulted in an optimal difference (56.1 % for white wines, 47.1 % for red wines, 50.0 % for all wines). Still acceptable difference was found in a smaller number of samples (29.3 % for white wines, 23.5 % for red wines and 24.1 % for all wines). Least of the samples resulted in an unacceptable difference (14.6 % for white wines, 29.4 % for red wines and 25.9 % for all wines). From the results we could conclude that separate equations for white and red wines resulted in a significantly smaller number of samples with unacceptable difference from the experimental data (especially in the case of red wines).

Table 4. Analysis of variance by multiple regression analysis for the calculation of ash (gL^{-1}) in all wine samples investigated

Our equation 3: $\gamma(\mathbf{ash}) = \mathbf{a}\cdot\chi + \mathbf{b}\cdot\gamma(\mathbf{A}) + \mathbf{c}\cdot\gamma(\mathbf{E}) - \mathbf{d}$				
Constant	Value	Error	t-Value	P>|t|
a	0.00121	8.65E-05	14.0206	<0.0001
b	0.00691	0.00417	1.65577	0.10357
c	0.0036	0.00193	1.86349	0.06784
d	0.93599	0.46144	-2.02844	0.04746
ANOVA table (P>F <0.0001)				
Item	DF	SS	MS	F
Model	3	14.10142	4.70047	98.14328
Error	54	2.58628	0.04789	
Total	57	16.6877		

Legend: P = Probability (significance level); DF = Degrees of freedom; SS = Sum of squares; MS = Mean square; F = Fisher ration; γ = concentration in gL^{-1}; A = alcohol; E = total dry extract; χ = conductivity (μScm^{-1})

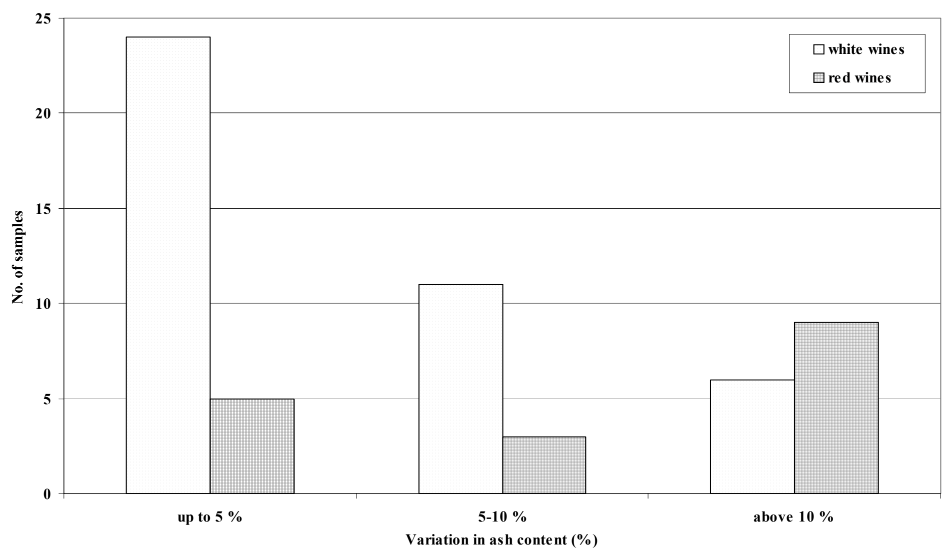

Figure 2. Difference in ash content between the experimental and calculated values (γ / gL^{-1}) by our equation 1 for the white wines and equation 2 for the red ones

Statistical data for ash content (gL^{-1}) calculated using literature equations (Table 5) and our equations (Table 6) were presented in comparison with the experimental data. The literature equations (Ash 1 and Ash 4) and all our equations (Eqs. 1-3) were not significantly different (P>0.05). We could see that the standard deviations and coefficients of variation for literature equations and our equations were very different (literature equations: SD = 0.57-0.72, CV = 24.16-29.25 %; our equations: SD = 0.32-0.56, CV = 14.73-25.74 %). The maximal value of statistical parameters mentioned in the literature equations corresponded to the equation Ash 3. We were surprised that its minimal value in our equations corresponded to the group of red wines (Eq. 2).

Table 5. Statistical data for the concentration of ash (gL^{-1}) calculated by literature equations in comparison with the experimental data

	Literature equations					
Parameter	Experimental data	Ash 1	Ash 2	Ash 3	Ash 4	P-value
Mean	2.18^{b}	2.19^{b}	2.41^{a}	2.45^{a}	2.15^{b}	<0.0001
N	58	58	58	58	58	
MIN	1.23	1.23	1.41	1.39	1.22	
MAX	3.90	4.30	4.48	5.14	4.23	
SD	0.54	0.59	0.58	0.72	0.57	
CV (%)	24.82	26.86	24.16	29.25	26.37	

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)

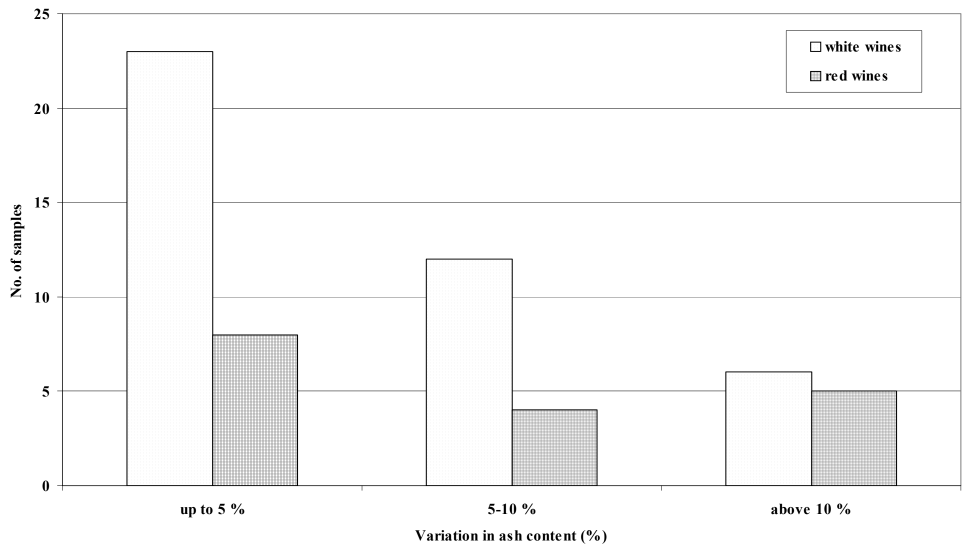

Figure 3. Difference in ash content between the experimental and calculated values (γ / gL^{-1}) by our equation 3 for all the wines

Table 6. Statistical data for the concentration of ash (gL^{-1}) calculated by our equations in comparison with the experimental data

	Our equations				
Parameter	Experimental data	1	2	3	P-value
Mean	2.18^{a}	2.20^{a}	2.14^{a}	2.18^{a}	<0.0001
N	58	41	17	58	
MIN	1.23	1.39	1.45	1.40	
MAX	3.90	3.98	2.60	4.04	
SD	0.54	0.56	0.32	0.50	
CV (%)	24.82	25.74	14.73	22.82	

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)

For separate samples, even the least acceptable variation could not be established by any of the equations applied in comparison to the official method (six white wine samples and six red wine samples in alcohol determination). It was found that the values of physico-chemical parameters (reducing sugars, total dry extract, total phenols, minerals, conductivity, osmolality and viscosity) of all these samples were either minimal or maximal (Table 1). It became evident that the ratio of ash content to sugar-free extract was also very important parameter. The ash content presented from 6.7 to 13.6 % (average = 9.5 %) of the sugar-free extract in white wines and from 5.8 to 11.4 % (average = 9.2 %) in red wines. The same samples were also problematical at the determination of alcohol and total dry extract concentrations by empirical equations (Bavčar and Košmerl, 2002). The correlations between ash content and several physico-chemical parameters of investigated wines were presented in Table 7.

Table 7. Correlation between the ash concentration (experimental data) and some of physico-chemical parameters for the white and red wines investigated by linear or multiple regression analysis

	White wines (41)		Red wines (17)	
Parameter	R	SD	R	SD
conductivity	0.93757	181.754	0.88554	93.282
minerals	0.95490	0.111	0.90208	0.135
alkalinity of ash	0.91673	3.260	0.87116	1.936
minerals + alkalinity of ash	0.92280	0.183	0.86831	0.839
minerals + alkalinity of ash + total phenols	0.92435	0.185	0.86858	0.819
conductivity + minerals + alkalinity of ash	0.92999	0.178	0.89168	0.851
conductivity + alcohol + total dry extract	0.88840	0.874	0.82124	0.754

Legend: R = R-Square (COD); SD = standard deviation

It was found out that the best correlation existed between ash and mineral content for both white and red wines. Additionally, the ash of white wines was well correlated with the conductivity, while the ash of red wines was better correlated with the sum of conductivity, minerals and alkalinity of ash. In continuation (Table 8), the conductivity of white wines was significantly correlated to the sum of minerals, alkalinity of ash and total phenols by means of multiple regression analysis as well as to the minerals and ash by means of linear regression analysis, while for red wines better correlation was found out with ash content and the sum of ash, alcohol and total dry extract.

Table 8. Correlation between the conductivity and some of physico-chemical parameters for the white and red wines investigated by linear or multiple regression analysis

	White wines (41)		Red wines (17)	
Parameter	R	SD	R	SD
ash (experimental data)	0.93757	0.225	0.88554	0.209
minerals	0.94137	0.127	0.84902	0.165
alkalinity of ash	0.90691	3.438	0.80235	2.353
minerals + alkalinity of ash	0.89852	0.890	0.75672	0.703
minerals + alkalinity of ash + total phenols	0.99115	0.900	0.77450	0.690
ash + minerals + alkalinity of ash	0.90798	0.896	0.79989	0.725
ash + alcohol + total dry extract	0.89133	0.878	0.86246	0.811

Legend: R = R-Square (COD); SD = standard deviation

4 CONCLUSIONS

The comparison of ash content determinations by means of experiment and calculation was carried out on 58 samples of Slovenian wines. The ash content was ranged between 1.23 to 3.90 gL^{-1}. From four equations proposed by different authors the equation Ash 4 appeared to be the most accurate with the determination of ash content by means of calculation (72.4 % of samples with optimal and still acceptable difference), while the calculation with the equation Ash 3 gave the highest number of unacceptable differences (58.6 %). The calculation of ash content with the equations Ash 2 and Ash 3 was not accurate enough, especially for white wines.

We proposed our own equations for the calculation of ash content for separate groups (white wines, red wines), and a single equation for all wines together by means of multiple linear regression analysis. The results obtained with our equation for all wines were even better than the results with the equation Ash 4 (74.1 % of samples with optimal and still acceptable difference), while separate equations for white and red wines gave a significantly smaller number of samples with unacceptable difference from the experimental data, especially in the case of red wines.

On the basis of experimental data, we proposed the empirical equations for ash content calculation. The results calculated by these equations correlated with the experimental results obtained by official method. The experiment has shown that the results to be obtained cannot be accurate enough by using only one equation for Slovenian wines with very wide range of principal physico-chemical parameters. To be able to get greater accuracy for all wines, empirical equations should be carried out; the minimum condition of separate white and red wines should be satisfied. In addition, there is a possibility to divide the wines into two groups according to their conductivity, mineral content, alkalinity of ash and total phenols. According to statistical analysis, better results for investigated Slovenian wines were obtained by different equations for the calculation of ash content proposed in our scientific work (for white and red wines) than those calculated by literature equations.

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