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professional paper

Determination of Ash Content in Wines by the Conductometric Method

Određivanje količine pepela u vinima konduktometrijom

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Summary

Ash content is one of the important indicators in wine quality determination. The conventional gravimetric method for ash quantity determination is time consuming.

As conductivity is primarily dependent on mineral content, its value (from 1276 to 3460 μS/cm) was determined in 107 wine samples. Alcohol (53.20–109.35 g/L) and total extract concentration (4.82–24.40 g/L) were also analyzed.

Based on the experimental data the empirical equation for ash concentration calculation is proposed. The results obtained by using this equation were correlated with the results obtained by gravimetric method.

Calculated ash content, according to the proposed equation is found to be satisfactory for 79.4 % of analysed wine samples, while the efficiency of this model is found to be 98.2 %.

Sažetak

Količina pepela važan je pokazatelj pri ocjenjivanju vina. Uobičajena gravimetrijska metoda određivanja pepela je dugotrajna. Budući da provodnost primarno ovisi o količini prisutnih mineralnih tvari, određena je provodnost (1276–3460 μS/cm), koncentracija alkohola (53.20–109.35 g/L) i ukupnog ekstrakta (4.82–24.40 g/L) u 107 uzoraka vina.

Na temelju ovih eksperimentalnih podataka predložena je jednadžba za brže izračunavanje količine pepela. Rezultati dobiveni ovom jednadžbom korelirani su s rezultatima gravimetrijske metode.

Proračuni količine pepela prema predloženoj jednadžbi dali su zadovoljavajuće rezultate za 79.4 % istraživanih uzoraka vina, a djelotvornost ovog modela iznosi 98.2 %.

Introduction

Ash represents a mineral content present both in must and wine. The average ash content in wine ranges from 1.2 to 3 g/L, while its content in must is higher, usually from 3–5 g/L.

Both too high and too low ash content indicate that a wine is not genuine. Minimum ash content in white wines is 1.2 g/L. In rosé and red wines it is 1.4 and 1.6 g/L respectively *(1)*.

Ash content usually comprises calcium, potassium and magnesium salts, as well as sulfuric, phosphoric, hydrochloric and carbonic acids. Traces of chlorine, flourine, copper, iron and manganese are also present.

Analysis of ash content in wine is of great significance from the analytical point of view. As the traditional gravimetric measurements are time consuming, many scientists have been making efforts to find a new method, which would be more accurate and faster. One of the possibilities is conductivity measurement as it primarily depends on mineral content in wines.

In the past this method has been not very often used. Procopio and Laporta *(2)* improved it and corrected it for empirical dependence on conductivity.

Barna and Grill *(3)* have published a method for ash content calculation on the quantitative basis of the sodium, potassium, magnesium and phosphate content in wines. But this method is suitable only in the case when analytical estimation of wine included the determination of these substances.

Müller and Würdig *(4)* suggested the following equation for ash content calculation:

$$\gamma(\text{ash})/(\text{g/L}) = 1.346\ 10^{-3}\ \text{cm}\ \mu\text{S}^{-1}\text{gL}^{-1}\ x_1 + 1.684\ 10^{-2}\ x_2 + 9.706\ 10^{-3}\ x_3 - 2.282 \qquad /1/$$

where x_1 is conductivity (μS/cm) at t = 20 °C
x_2 is alcohol content (g/L)
x_3 is extract content (g/L)

The equation represents mathematical dependence on conductivity, alcohol and extract concentrations. According to the authors the equation can be used for both ash-rich and ash-poor wines, as well as for the dry and sweet wines. The allowed deviation between gravimetrically and mathematically determined ash content is ±10 %, for the wines with ash content less than 2.6 g/L, while for the wines with higher ash content it is up to ±15 %.

Hupf and al. *(5)* made further improvement of Müller and Würdig equation as they found it unsatisfactory during analysis of 222 wine samples. They showed that the ash content determination by using conductivity measurement can be used as the parameter for wine quality control.

The aim of this work was to find out an equation which could be used for quality control of Croatian wines in order to determine ash content by simpler and faster method.

Material and Methods

Material

Analysis of 107 wine samples (55 white, 39 red and 13 rosé wines) were performed.

The wines were obtained from the market (92 samples) and from individual producers (15 samples).

The white wines are classified as the highest quality (3 samples), quality (19 samples) and table (33 samples) wines.

The red wines are the highest quality (6 samples), 16 samples are quality and 17 samples are table wines. The rosé wines are quality (6 samples) and table (7 samples) varieties.

Methods

Determinations of ash, alcohol and extract content were performed by AOAC methods *(6)*.

Conductivity measurements were performed with Pt-electrode (HEK–1213) by means of conductometer »Iskra« 5964.

Based on the experimental results an equation for ash content determination is proposed.

By using the least square method the A, B, C and D coefficients in the following equation are established *(7)*:

$$y = Ax_1 + Bx_2 + Cx_3 + D \qquad /2/$$

Based on the results obtained the following equation is proposed:

$$\gamma(\text{ash})/(\text{g/L}) = 1.02\ 10^{-3}\ \text{cm}\ \mu\text{S}^{-1}\text{gL}^{-1}\ x_1 + 9.98\ 10^{-3}\ x_2 + 2.76\ 10^{-2} x_3 - 1.38 \qquad /3/$$

N = 107

where x_1 is conductivity (μS/cm) at t = 20 °C

x_2 is alcohol content (g/L)

x_3 is extract content (g/L)

According to this equation, the ash content was calculated for all investigated samples.

Results and Discussion

Analysis of 107 wine samples yielded the results discussed below.

The alcohol concentration is from 53.20 to 109.35 g/L, which is in good accordance with literature data *(8-11)*. Wine samples supplied from the individual producers have an alcohol content from 73.40 to 109.35 g/L, while those from the market showed slightly lower values (53.20–103.8 g/L).

Experimentally determined total extract content is between 4.82 and 24.20 g/L. These values are slightly lower compared to literature data *(1,12-14)*.

Ash content for the investigated 107 wine samples determined by gravimetric method is from 0.83 to 3.08 g/L.

Wines supplied from the market (92 samples) showed higher ash content (0.91–3.08 g/L) than those obtained from individual producers (0.83–2.30 g/L).

Experimentally determined ash content for the wine samples obtained from the market, was greater for the red wines (N = 37). The reason for this is higher mineral content (from 1.59 to 3.08 g/L). Lower ash content was found for rosé wines (N = 8), with values from 1.39 to 2.30 g/L, while for the white wines (N = 47) ash content is the lowest (0.91–2.57 g/L).

Among the 107 samples, 38 samples (35.5 %) have ash content above 2.0 g/L and 8 samples (7.5 %) less than 1.0 g/L.

Table 1. Conductivity, extract and alcohol content and experimental and calculated ash content in white wines

Tablica 1. Rezultati određivanja provodnosti, ekstrakta, alkohola te eksperimentalne i izračunane količine pepela u bijelim vinima

Wine samples, number, year Uzorci vina, broj, godina	Conductivity Provodnost μS/cm	γ (alcohol / alkohol) g/L	γ (extract / ekstrakt) g/L	gravim. γ (ash / pepeo) g/L	eq. /3/; jedn. /3/ γ (ash / pepeo) g/L
Graševina (1) 1985	2050	85.90	19.50	2.11	2.10
Križevačka graševina (2) 1987	2100	78.50	20.00	2.06	2.09
Rizling (3) ----	2045	91.35	13.15	1.98	1.98
Istarska malvazija (4) 1985	1900	91.90	16.30	1.98	1.92
Panonski rizling (5) ----	2307	62.60	15.99	1.89	2.03
Moslavac (6) 1986	1820	85.20	19.70	1.79	1.87
Rizling (7) ----	1710	93.30	16.80	1.75	1.75
Ribar (8) 1989	1953	56.30	12.15	1.46	1.50
Bilikum (9) 1988	1656	75.50	9.80	1.38	1.33
Burgundac (10) 1985	1970	98.70	21.10	2.22	2.16

Table 2. Conductivity, extract and alcohol content and experimental and calculated ash content in red wines
Tablica 2. Rezultati određivanja provodnosti, ekstrakta, alkohola te eksperimentalne i izračunane količine pepela u crnim vinima

Wine samples, number, year Uzorci vina, broj, godina	Conductivity Provodnost μS/cm	γ(alcohol/alkohol) g/L	γ(extract/ekstrakt) g/L	gravim. γ(ash/pepeo) g/L	eq. /3/; jedn. /3/ γ(ash/pepeo) g/L
Slovin (1) 1987	2826	94.70	23.61	2.85	3.09
Pelješac (2) 1986	2253	102.90	19.62	2.45	2.48
Babić (3) 1985	1620	100.80	24.40	2.10	1.95
Klikun (4) 1989	2020	65.55	14.37	1.71	1.73
Barrique 85 (5) 1985	1898	76.05	10.37	1.82	1.79
Ribar (6) 1989	2010	65.70	15.69	1.71	1.75
Benkovački grenaš (7) 1987	2122	76.60	10.37	1.42	1.41

Table 3. Conductivity, extract and alcohol content and experimental and calculated ash content in rosé wines
Tablica 3. Rezultati određivanja provodnosti, ekstrakta, alkohola te eksperimentalne i izračunane količine pepela u ružičastim vinima

Wine samples, number, year Uzorci vina, broj, godina	Conductivity Provodnost μS/cm	γ(alcohol/alkohol) g/L	γ(extract/ekstrakt) g/L	gravim. γ(ash/pepeo) g/L	eq. /3/; jedn. /3/ γ(ash/pepeo) g/L
Benkovački rosé (1) 1987	1667	83.30	9.42	1.42	1.41
Šibenski opolo (2) 1986	1484	96.80	12.38	1.39	1.44
Plavac (3) -----	2020	103.80	12.64	2.01	2.06

Müller and Würdig *(4)* found ash content between 1.28 g/L and 4.50 g/L. Hupf et al. *(5)* reported values of 1.0–4.0 g/L for white and red wines, while for the red wines Palić et al. *(15)* found ash content from 1.9 to 2.7 g/L.

The range for conductivity values is between 1276 and 3460 μS/cm. Wines supplied from the individual producers have conductivity values from 1303 to 2454 μS/cm, while those from the market range between 1276 and 3460 μS/cm.

The highest conductivity values are recorded for red wines (1303–3460 μS/cm) supplied from the market.

Rosé and white wines cover the range of 1276–2433 and 1312–2307 μS/cm, respectively.

Comparing conductivity and ash content one can say that the wines with greater ash content show higher conductivity. This relationship is not directly proportional as the conductivity of samples depends on many factors, i.e. the amount of free and partially neutralized acids, viscosity, temperature, and hydrodynamic resistance of transported media.

Statistic interpretation of the results showed the correlation coefficient $r = 0.80$ between conductivity and ash content. The correlation coefficient ($r = 0.41$) shows statistically unsignificant correlation between the extract content and conductivity. From the statistic analysis it is evident that conductivity strongly depends an ash content, i.e. mineral rather than extract content.

In this research 107 wine samples were analysed.

Conductivity, alcohol and extract content, as well as ash content determined experimentally and calculated by the equation are presented in Table 1 (for white wines), Table 2 (for red wines) and Table 3 (for rosé wines).

The presented samples showed the best agreement (±8 % deviation) between conductometric and gravimetric method used for ash content determination.

By applying equation /3/ the following results are obtained: among the 107 wine samples, 59 samples are in the range of tolerance of ±8 %, 26 samples within ±15 % and 22 samples are above ±15 %.

This means that for 85 out of 107 samples (79.4 %) satisfactory results were obtained.

As the investigated samples showed deviation of less than ± 8 %, this value is proposed as allowed deviation for Croatian wines.

Among the investigated samples, 58.9 % ($N=107$) were found to be satisfactory by applying Müller and Würdig *(4)* equation when comparing experimentally obtained and calculated ash content.

Modification of Müller and Würdig equation *(4)* done by Hupf et al. *(5)* was found unsatisfactory. In this case only 22.7 % samples ($N = 79$) showed satisfactory results as they showed differences between ±10 and ±15 %, which is in the range of the allowable deviation.

According to statistic analysis, better results are obtained by using the equation proposed in this paper (eq. 3) then those calculated using Müller and Würdig equation (eq.1). Thus the proposed equation could be used for ash content determination, with conductometric method, for Croatian wines.

The efficiency of stochastic relationships for the calculated models was proved by experimental and calculated variance.

The results of analysis of variance by multiple linear regression are presented in Table 4.

Table 4. Analysis of variance by multiple linear analysis of regression
Tablica 4. Analiza varijance metodom mnogostupanjske analize regresije

The source of variation Izvor varijacija	DF	SS	MS	F	p
Regression/ Regresija	3	22.3673	7.455774	119.998	0.05
About regression / Oko regresije	103	6.3374	0.062132	–	–
Total / Ukupno	106	28.7047	–	–	–

DF = Degrees of freedom / stupnjevi slobode
SS = Sums of squares / suma kvadrata odstupanja
MS = Mean squares / prosjeci kvadrata
F = Fisher ratio / Fišerov kvocijent
p = Significance level / razina značajnosti

The difference between calculated and experimental values was represented by so called »variance about regression«.

The difference between the sum of the squares of deviation of total experimental data and the sum of the squares of deviations estimated by regression, represents the basis for testing the model efficiency *(16)*. The efficiency of calculated equation was 98.2 %.

Conclusion

In this paper 107 wine samples were analysed. The samples were obtained from the market (by random sampling method) and individual producers. These samples showed differences not only in grape variety but in cultivation area, maturity and quality as well.

Based on the experimental results an empirical equation for ash content determination is proposed:

$$\gamma(\text{ash})/(\text{g/L}) = 1.02\ 10^{-3}\ \text{cm}\ \mu\text{S}^{-1}\text{gL}^{-1}\ x_1 + 9.98\ 10^{-3}\ x_2 + 2.79\ 10^{-2}\ x_3 - 1.38$$

According to the proposed equation the satisfactory result for 79.4 % samples (N = 107) is obtained, meaning that conductivity method can be applied as a fast and reliable method for ash content determination.

By applying Müller and Würdig equation it was found to be 58.9 % satisfactory for 107 investigated samples.

Hupf et al.'s equation was only 22.7 % satisfactory (N = 79).

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