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METHODOLOGY FOR ACIDITY CORRECTION OF DEFICIENT MUSTS BASED ON GRAPE MATURATION INDICES AS PART OF PRECISION OENOLOGY

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Abstract

Acidity corrections are one of the most important pre-fermentative operations, with significant consequences on wine quality. The proposed methodology is based on the study of two grape maturation indices, °Brix/%TA and °Brix x pH^2, which were determined and evaluated before and after the application of acidity correction. This paper proposes a methodology in agreement with the principles of precision oenology for acidity corrections of deficient musts, especially those from areas located in European zones CII.

Keywords: precision oenology, maturation indices, quality assurance, acidity corrections

Introduction

Harvesting of grapes is one of the most critical decisions of oenologists with influences on the quality of the future wine. The best moment to harvest may be determined using various physico-chemical parameters such as Brix degrees, total titratable acidity (TA), pH and, last but not least, sensory analisys.

Oenologists may encounter two difficult situations during the harvest period: the first one when the grapes are underripen (high acidity, low sugar level, "green" flavors and harsh tannins) and the second one when the grapes are overripen (low acidity, high sugar level and off- or uncharacteristic flavours) (Zoecklein *et al*., 1999). When the second situation occurs and some times even in the case of normally ripen grapes, there is a need for acidity corrections. The acidity correction is always advisable due to the positive effect of TA and pH on solubility of tartrates and proteins (Boulton *et al*., 1998), on color stability (Brise Maria Josephine, 2007), on selectivity of microorganisms during fermentation and aging (Guzzo *et al*., 2009), on oxidation-reduction reactions (Zoecklein *et al*., 1999), on production of fine flavours (Boulton *et al*., 1998) and finaly, but most importantly, on the taste balance (Zoecklein *et al*., 1999) that has to be in concordance with the desired wine style intended by the oenologist and desired by the consumers.

Taste balance of grapes at harvest time can be quantified by some maturation indices such as °Brix/%TA and °Brix x pH^2, which aim to show the optimal equilibrium between sugar and acidity in the berry, which will lead in the end to an optimum balance of ethanol and acidity in wine (Zoecklein *et al*., 1999). The application of °Brix/%TA index was suggested by Amerine and Winkler (1940), and subsequently, the introduction of °Brix x pH^2 was suggested by Coombe *et al*. (1980) pointing out the faults of °Brix/%TA index, caused by the lack of reliability of total titratable acidity as measurable parameter. The titratable acidity does not necessarily measures the total acidity, while the pH is a much reliable parameter.

°Brix/%TA index (Amerine, M. *et al*., 1940; Gallander, 1983) was evaluated by various authors and it was suggested that it should range between 30 and 32 (Gallander.,

1983), 30 to 35 (Cox, 1999) or 37 to 38 in the case of overripen grapes (Amerine *et al*., 1970; Amerine *et al*., 1980).

°Brix x pH² index (Coombe *et al*., 1980; Amerine *et al*., 1970) was evaluated by various authors and it was suggested that it should be around 220 for white wines and 260 for reds (Cox, 1999). Overripen grapes may reach values over 260 for this index (value of 311 in case of 24 °Brix and 3.6 for pH, for example), which places them beyond the optimum values which usually indicate taste balance. In these cases the oenologists should take into consideration the acidification of the resulted must.

By reviewing several works (Amerine *et al*., 1940; Amerine *et al*., 1970; Amerine *et al*., 1980; Gallander, 1983; Cox, 1999), we derived the following normal range values and optimal values for these indices (Table 1).

Table 1. Normal range and optimal values of maturity indices of grapes for the production of balanced wines

Index	Normal range values		Optimal values	
	White grapes	Black grapes	White grapes	Black grapes
˚Brix/%TA	27-32	32-35	28	33
˚Brix x pH²	200-240	245-280	220	260

It should be mentioned that some black grape cultivars grown in warm climates usualy achieve these optimal values before reaching full phenolic maturity or development of flavor compounds and for this reason this methodology has its limitations. As mentioned before, ˚Brix x pH² index may have values in excess of 260, as, for example, 350 in the case of a red variety grown in a warm climate (Bisson, 2001).

Materials and methods

Raw materials: The maturity indices were analyzed for five different grape varieties harvested in a vineyard located in the south of Romania, classified as a CII European zone, where the climate conditions determine a sharp drop in acidity during the normal maturation period. The indices were calculated in the must, before and after acidification with various amounts of tartaric acid, done to adjust these indices and bring them inside the desirable ranges. Grape varieties analyzed were: Crâmpoşie (ID 1, 2, 3), Sauvignon blanc (ID 4), Royal Feteasca (ID 5), Italian Riesling (ID 6) and Merlot (ID 7). The first six varieties are white and the last one red.

Methods of analisys and equipments: *Brix degree* was determined with a portabile ATC Brix refractometer and the *pH* with an Ino Lab pH 720 (AOAC, 960.19). *Total titratable acidity* (TA) was determined with TitroLine easy Schott Instruments until the end point of titration at pH 8.2 was reached (AOAC, 962.12), while the *buffer capacity* (β) was determined with the same equipment by titration with HCl 0.1 N until 1 pH unit was dropped. The *alcalinity of the ash* (AA) was calculated based on titratable acidity and buffer capacity, in accordance to the mathematical relations presented hereafter.

Calculations: In order to achieve practical goals, it will be considered that a single monoprotic acid HV is present in the must. For this case acid dissociation constant can be easily calculated based on the laboratory determinations of pH, total titratable acidity (TA) (Moreno *et al*., 2012). Thus, the equilibrium reaction can be represented as: $HV \leftrightarrow H^+ + V^-$.

As shown in this chemical equilibrium, the acids present in musts are partly dissociated. The anions formed in this reaction are neutralized by cations [M^+] from the must

leading to electrochemical neutrality. Thus, the following relations, can be established (Moreno J. *et al*., 2012): $[V^-] = [M^+] = AA$ and $[HV] = TA$, where: $[V^-]$ - anions from musts; $[M^+]$ - cations from musts (alkali metals); AA - ash alkalinity; $[HV]$ - undissociated acid from must; TA - total titratable acidity of the must;

In accordance to the Mass Action Law and Henderson Hasselbalch equation (Ţârdea, 2007; Usseglio Tomasset 1992; Moreno J. *et al*., 2012), the value of the acid dissociation constant (Kv) of the above equillibrum can be calculated as:

$$Kv = \frac{[V^-] \times [H^+]}{[HV]}, \text{where: } pKv = pH - \log_{10}\frac{[V^-]}{[HV]} = pH - \log_{10}\frac{[AA]}{[TA]}$$

Because the determination of the alkalinity of the ash (AA) is very laborious, it can be indirectly calculated by taking into account the buffer capacity and applying the following equation (Ţârdea C., 2007; Usseglio Tomasset 1992; Moreno J. *et al*., 2012):

$$\beta = \frac{L}{\Delta pH} = \ln(10) \times \frac{TA \times AA}{TA + AA}, \text{where: } AA = \frac{\beta \times TA}{\ln(10) \times TA - \beta}, \text{where:}$$

$\Delta pH = pH_i - pH_f$ pH_i pH_f

β - buffer capacity of must, meq/l; ; - initial pH value of must; - final pH value of must; L - titre of HCl 0.1 N, in ml; ln (10) - natural logarithm of 10 = 2.3026; TA - total titratable acidity in meq/l, determined by physicochemical analysis; AA – alkalinity of ash in meq/l, calculated indirectly from physicochemical analysis of β;

According to the Henderson Hasselbalch equation the *pKv* value for hypothetical monoprotic acid in musts (equivalent to the combination of each acid present) and the pH value can be calculated (Moreno J. *et al*., 2012):

$$pKv = pH - \log_{10}\frac{[AA]}{[TA]}, \text{where: } pH = pKv + \log_{10}\frac{[AA]}{[TA]}$$

After the addition of tartaric acid, precipitation phenomena of potassium bitartrate will occur, due to the abundence of potassium and low saturation point of this salt in musts. Also, salt precipitation has an effect on the total titratable acidity (TA) and the alkalinity of ash (AA). Thus, the measurement or calculation of TA and pH after acidification is also necessary. In order to calculate them we go through two stages (Moreno *et al*., 2012):

Stage I. Effects of acidification on AA and TA can be calculated using the following relations (Moreno J. *et al*., 2012): $Stage\ I\ AA = AA - H_2T + H_2T$ and $Stage\ I\ TA = TA + 2 \times H_2T$.

Stage II. Effects of bitartrate precipitation on AA and TA can be calculated using the following relations (Moreno J. *et al*., 2012): $Stage\ II\ AA = Stage\ I\ AA - H_2T$ and $Stage\ II\ TA = Stage\ I\ TA - H_2T$, where: H_2T – meq/l of tartaric acid added.

Results and discussion

For our grapes harvested in a vineyard affected by a hotter than usual climate, located in a CII viticultural zone, a series of physico-chemical analyses were preformed to the resulted musts, prior to their acidification. The results are shown in Table 2.

As it can be seen in Table 2, maturity indices of analyzed musts have much higher values than the optimal ones from Table 1. This is due to the obtainment of musts from grapes with very

low acidity and normal to medium-high levels of sugar, specific for the vineyard where we conducted the study. These musts need an acidification in order to achieve a good taste balance between sugar and acid which will finally have an impact on the ethanol/acidity balance of wine.

Table 2. Quality parameters and maturity indices determined in musts prior to acidification

ID	Grape colour	˚Brix	pH	TA, %	β, meq/l	AA, meq/l	pKv	˚Brix/%TA	˚Brix x pH²
1	white	21.6	3.51	0.56	72.03	53.85	3.652	38.57	266.11
2	white	22.4	3.54	0.55	72.26	54.88	3.666	40.73	280.71
3	white	22.8	3.59	0.54	71.01	53.97	3.715	42.22	293.85
4	white	24.4	3.85	0.47	80.88	79.99	3.744	51.91	361.67
5	white	21.8	4.12	0.38	70.00	76.07	3.943	57.37	370.04
6	white	23.6	3.53	0.55	75.19	58.89	3.625	42.91	294.08
7	black	23.0	3.99	0.42	67.15	60.89	3.953	54.76	366.16

Due to the high drop in grape acidity before harvest, the quantities of tartaric acid needed to be added for correction in musts are sometimes even higher than the maximum allowed by the legislation, i.e. 1.5 g/l tartaric acid for European CII zones (Order 645, 2005). The addition of very large amounts of tartaric acid prior to fermentation is not only limited by law, but it should be avoided also because of the negative effect of this acid on the flavor of the wine. In this particular case, oenologists should also rely on sensory analysis when they acidify these kinds of musts.

In order to bring the maturity indices closer to the optimum values presented in Table 1, the musts were acidified with certain amounts of tartaric acid (Table 3), decided by a panel of 3 oenologists in accordance to the best sensory taste balance achieved in laboratory samples corrected with various levels of acidity. The results of the physicochemical analyses performed after acidification are shown in Table 3.

Table 3. Quality parameters and maturity indices determined in musts after acidification

ID	Grape colour	Amount of tartaric acid used (g/l)	Brix, %	pH	TA, %	˚Brix/%TA	˚Brix x pH²
1	white	2	21.6	3.12	0.69	31.30	210.26
2	white	2	22.4	3.13	0.71	31.75	219.45
3	white	2	22.8	3.15	0.69	32.85	226.23
4	white	3.5	24.4	3.34	0.74	32.98	272.20
5	white	4	21.8	3.35	0.77	28.31	244.65
6	white	4	23.6	3.30	0.67	35.38	257.00
7	black	1.75	23.0	3.68	0.59	38.70	311.48

As it can be seen, the values obtained for the maturity indices after acidity correction are much more close to the normal range of values for these type of wines. However, in order for these musts to be corrected satisfactorily, in all the cases the legal limit of acid addition had to be exceeded. For these situations, in practice, even though the sugar accumulation might not be optimal, an early harvest should be considered.

In order to propose a methodology to adjust the maturity indices by acidification without having to make other physico-chemical determinations after the correction, for the added acid concentrations used in Table 2 we calculated the parameters pH, TA, β, AA and maturity indices. The calculated parameters are called „predicted quality indicators” and are shown in Table 4.

Table 4. Predicted quality parameters and maturity indices of musts after acidification

ID	Grape colour	Amount of tartaric acid (g/l)	β, meq/l	AA, meq/l	pH	TA, %	˚Brix/%TA	˚Brix x pH²
1	white	2	49.38	27.20	3.08	0.76	28.42	204.91
2	white	2	50.68	28.22	3.12	0.75	29.87	218.05
3	white	2	49.26	27.32	3.16	0.74	30.81	227.67
4	white	3.5	58.84	33.35	3.23	0.82	29.76	254.56
5	white	4	43.01	22.77	3.28	0.78	27.95	234.53
6	white	4	56.13	32.24	3.13	0.75	31.47	231.21
7	black	1.75	58.70	37.57	3.63	0.60	38.66	303.07

Comparison of results (Fig. 1 and 2) were performed for the determined maturity indices against the predicted maturity indices by using correlation matrices of the software package Statistica 10.0. As it can be seen, the correlation coefficients in both cases are very high, and we can conclude that, for the adjustment of the maturity indices through acidity correction we only need to determine the initial pH, titratable acidity (TA) and the buffer capacity (β) and calculate for the intended amount of acid to be used the predicted maturity indices. The amount of acid to be used will be decided by the oenologist when the predicted maturity indices are satisfactory as compared to the normal range and optimum values and must also not exceed the legal limits.

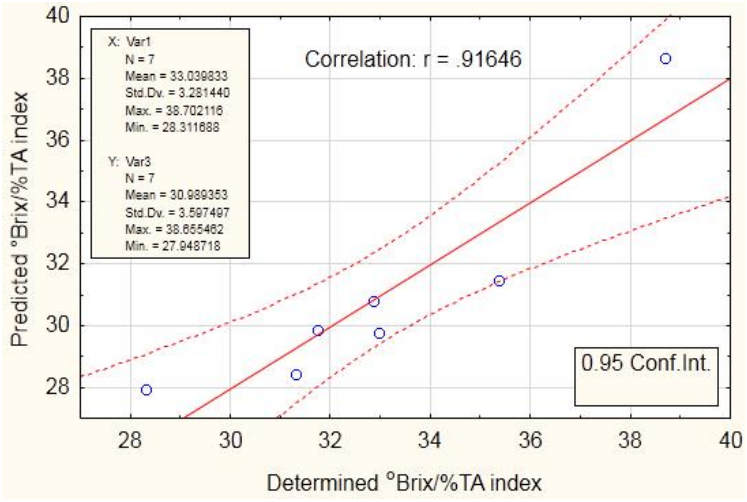

Fig. 1. Correlation between determined ˚Brix/%TA index against its predicted values

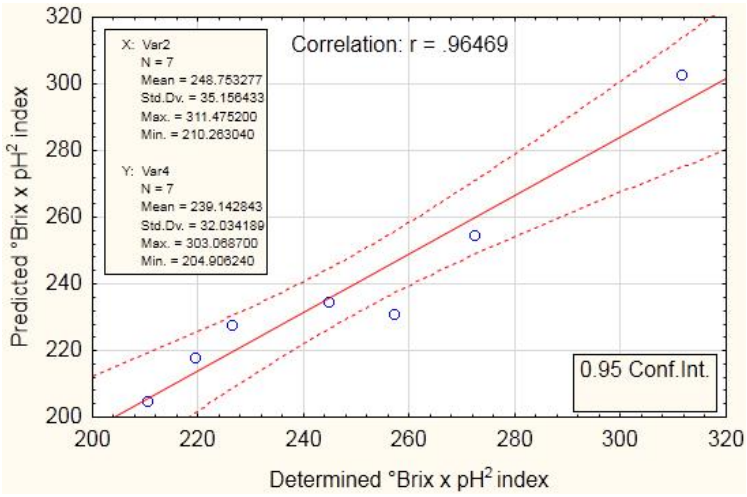

Fig. 2. Correlation between determined ˚Brix x pH² index against its predicted values

Modeling ˚Brix/%TA and ˚Brix x pH² indices through acidification with tartaric acid seems to be a good compromise to achieve the taste balance between sugar and acid and finally between ethanol and acid in wines, especially in European CII zones where the aromatic and phenolic ripeness is achieved when the maturity indices are out of ranges, due to the imbalance of ˚Brix with TA and pH.

It is well known that the acidification of musts is beneficial in case of low TA and high pH, providing a better stabilization of salts and proteins in wines, more color extraction and stabilization for red wines and increased effect of sulfur dioxide on microorganisms during all stages of winemaking process. Moreover, the most important effect of acidity correction is to be encountered in the wine taste balance.

In hot climates, relatively high sugar musts come along with such a lack in acidity, that the maturity indices cannot be brought into the desired normal ranges, irrespective of the acidity corrections. In those cases, the grapes should be harvested before this happens, so that the high alcohol content resulted from all that sugar should not seem imbalanced in a wine with acidity corrected only as much as the legislation permited and not as much as needed from a sensorial viewpoint. Moreover, with late harvest grapes, over 26 °Brix, it is even harder to find a good compromise, especially as such musts normally do not ferment completely, and the remaning sugar will also have a sensory impact on the final wine, along with the high alcoholic content and low acidity. Conversely, addition of high amounts of acid for correction make some wines seem tart and harsh, while impairing their normal aging, even though some of the apparent harshness decreases in time due to the production of ethyl acid tartrate (Edwards *et al*., 1985).

Conclusion

Often, as also acknowledged by the legislation, in European CII zones the acidification of musts is an indispensable operation. To simplify the work of the oenologists, the application the ˚Brix/%TA and ˚Brix x pH² indices and their adjustment to desired values by addition of tartaric acid appears to be a good and rapid option. By using several theoretical acid correction values, the oenologist can calculate the predicted indices based only on the determinations of the initial pH, titratable acidity (TA) and the buffer capacity (β). By taking into account the predicted values and the the legal limits, the oenologist can select the most suitable amount of acid to be added in the must for correction. By making these calculations during the maturation period of grapes, the optimum harvest period can also by determined, by pushing the harvest day as far as possible for the achievement of phenolic maturity, but taking also into account the limitations of the acidity corrections.

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