STUDY REGARDING THE IDENTIFICATION OF WINE ADULTERATION

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Abstract
The present paper, presents a study conducted on two wine samples of the commercial network, in order to establish the adulteration methods used, by correlating some physic-chemical parameters determined by laboratory analysis.It is difficult but important to determine the authenticity of wines. One of the most common practices of wine adulteration is the addition of natural or synthetic sweeteners into musts and wines, also by dillution, dillution and alcoholisation, neutralising the fixed acidity. These adulterations influence the balance between the wine's components and so, in the scientific literature correlations have been made between these components, therefore being expressed by oenological parameters, ratios, nomograms. The two wine samples have be analysed in the lab determining certain physic-chemical parameters, the results being correlated with the nomograms of the famous chemist Ghimicescu Ghe., and in this way the adulterations have been identified. The two wine samples, having the same origin and from the same batch, presented different grades of limpidity and solid deposits, and upon opening the bottles presented different smell and taste, not wine related. By analysing the correlation of some physic-chemical parameters determined the conclusion was that the samples were adulterated by dilution, dilution and alcoholisation, neutralising the fixed acidity, addition of sugars and in order to increase the shelf-life sulphur dioxide has been identified in huge amounts. This paper demonstrates that there are technological methods that allowed the manufacturing of a hard to detect adulterated wine product or that there are big gaps regarding the technological regulations of the oenological field.

1. INTRODUCTION

Food adulteration, especially wines is an old technique dating back to ancient Rome, being banned of wine counterfeiting with flavours and colouring agents. If initially wine counterfeiting was made with natural substitutes, not affecting the innocuity, starting with the 18th century the usage of substances harmful to health was widely used. (Bulancea M., 2009, Holmberg L., 2010)

Food counterfeiting, especially drinks represents the illegal techniques that have the goal of:

- total or partial substitute of one or more components of the raw materials.
- the addition of natural or synthetic substances that modifies the chemical composition or the sensorial properties in order to substitute one valuable component with a cheaper one, in this way gaining unworthy benefits.

- the addition of natural or synthetic substances used to hide various defects of the product.
- the usage of ingredients or additives unauthorised or in bigger doses than the recommended ones.
- reconditioning some degraded food products with the purpose of hiding the defects that could evidentiate the product's deficiencies. (Bulancea M., 2009, Savin C., 2011)

Shortly, it can be described that adulteration consists of false labelling and represents the product's counterfeiting in order to sell a cheap merchandise as a more expensive one thus gaining illicitly earnings.

The most frequent wine adulterations, which in most cases do not affect wine's innocuity, but affects the sensorial properties, affecting the image where the consumer's trust in the product's naturalness are:

- adulteration by the addition of natural or synthetic sweeteners to musts or wines. The practice is accepted when the grapes do not accumulate enough sugars due to inappropriate

weather conditions. In our country, the addition of sugars into musts before the fermentation process, it is allowed of a maximum quantity of 35g/L, which enhances the wine's alcohol strength of max. 2% alcohol; these wines can't be classified as protected designation of origin (PDO).

- adulteration by the addition of natural and synthetic sweeteners into wines.

- adulterations by alcoholisation, dilution, neutralising the fixed acidity and glycerol addition. (Bulancea M., 2009, Savin C., 2011, Cotea V., 1985, Tirdea C., 2000).

Natural wines are characterised by a certain balance between its components making possible to establish some correlations that can be expressed as parameters, ratios and nomograms (Cotea V., 1985, Tirdea C., 2000).

The Romanian chemist G. Ghimicescu established some nomograms that reflects the correlation between different laboratory determined parameters and the practice used to adulterate the analysed wine samples. In this way, the present paper proposes to apply these nomograms in order to identify the adulterations of wines (Ghimicescu Gh., 1971, Holmberg L., 2010).

2. MATERIALS AND METHODS

The current paper presents a study performed on two semi-dry white wine samples from the commercial network in order to establish what methods of adulteration can be identified.

The samples where marked as S_1 and S_2, having the same provenience and presented upon sampling different sensorial characteristics regarding the limpidity level, the quantity of solid residue and when the bottles where open a modified, non-characteristic smell and taste was identified.

The following physic-chemical analysis were performed (Rougereau A., 1981, Medina B., 1996, Ana Al., 1980, Gheorghita M., 2002)

- Determining the soluble dry substance by refractometry.

- Determining the whole sugar content, expressed as reducing sugar (g/l) using Schoorl method.

- Determining the total acidity expressed in grams of tartaric acid /l by titrimetric analysis.

- Determining the alcohol concentration by ebulliometry.

- Determining the total dry extract (g/l) by refractometry.

- Determining the total SO_2 content (mg/l) using the iodometric method.

With these values different oenological parameters were calculated correlating them with the nomograms of G. Ghimicescu in order to identify the type of adulterations found within S_1 and S_2 samples.

3. RESULTS AND DISCUSSIONS

The analysis results are shown in the table 1, below:

Table 1 Physic-chemical analysis results

Phisico-chemical analysis	S_1	S_2	Standardized values
Soluble dry substance, %	4	4.2	-
Total sugars expressed as reducing sugar, g/L	21	28	20 – 50
Acidity expressed as tartaric acid, g/L	2.48	0.75	Min. 4.5
Alcoholic concentration, min. % vol.	7.5	7.5	Min. 9
Total dry extract, g/l	15	15.5	Min. 15
Total SO_2, mg/l	316.8	112.64	Max. 200

After obtaining the analysis results and correlating some of the determined physic-chemical parameters, the following results were obtained:

1. Σ alcohol(% vol.)+Total acidity(g/l)= 13-17 (normal value)

$S_1 = 9,97$; $S_2= 8,25$

Because the values of acidity and alcohol content at S_1 and S_2, far below the normal limit, alcohol and acidity amount lies beneath the lower limit.

Analytical data has shown that between alcohol concentration and wine's acidity is a non-linear correlation, where for every alcohol percentage it corresponds a minimum fixed acidity, and their sum has a minimum value, that grows non-linear once with the increase of the alcohol concentration.

The alcohol ratio (% vol.)/fixed acidity (g/l) has a maximum value that increases, non-linear as well, with the increase in alcohol concentration.

2. $$Ratio \frac{Total\ acidity\ \left(\frac{g}{L}\right)}{Alcohol\ (\%\ vol.)} = 0.2 \div 0.8\ (normal\ value)$$

$S_1 = 0{,}33$; $S_2 = 0{,}1$ (this sample has been neutralised more than S_1)

3. $$Ratio \frac{Alcohol\ (\%\ vol.)}{ATotal\ acidity\ \left(\frac{g}{L}\right)} = 1.5 \div 5\ (normal\ value)$$

$S_1 = 3.03$; $S_2 = 10$ (this sample has been neutralised more than S_1)

The correlation values of the two reports, the sample results that fit into the values S_1, S_2 while being neutralizata with 69,75% more than the s1, does not fit in the limit.

4. In figures 1 and 2, two nomograms are presented, showing the correlation between the alcohol and the acidity content. Where the alcohol content, expressed in g%, analytically determined, a vertical line is drawn until this one intersects the horizontal line, where the numbers indicate the value of the sum or alcohol (g%)/fixed acidity (g/l) ratio. Based on the position of the intersection point, wine's authenticity or eventual adulterations can be determined.

The hachured space, between the superior and inferior limits, represents the interval that consists of approximately 90% of natural wines, unadulterated.

In the case of nomogram 1, if the intersection point is situated above the superior limit, wines are suspected to be suffered the following adulterations: alcoholisation (the intersection point may be above or within the hachured space, depending on the amount of added alcohol); the fixed acidity increase can be singular or associated with alcoholisation and dilution.

Sample 1: Alcohol = 7.125 (g%)
Σ (alcohol + fixed acidity) = 9.97
S_1 sample has been adulterated by dillution, dillution with alcoholisation and neutralising the fixed acidity.

Sample 2: Alcohol = 7.125 (g%)
Σ (alcohol + fixed acidity) = 8.25
S2 sample has been adulterated by dillution, dillution with alcoholisation and neutralising the fixed acidity.
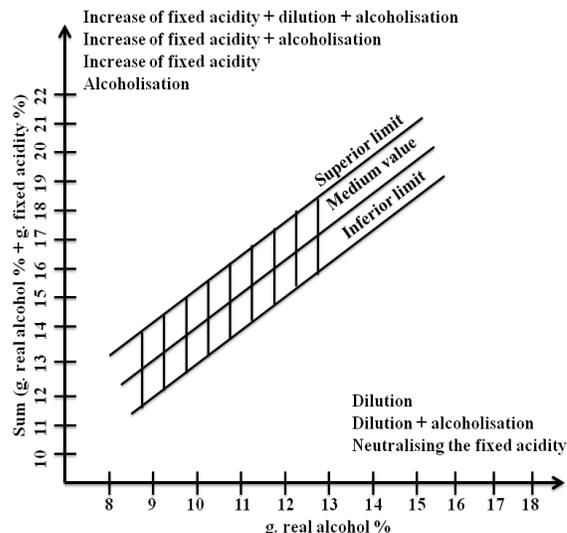

Fig 1. Nomogram - Alcohol (g%) + Fixed acidity (g/L) variation sum (Bulancea & Rapeanu 2009) According to nomogram 1, were obtained the following results:

In the case of nomogram 2 (alcohol/acidity ratio), if the intersection point is situated above the superior limit, the adulteration consists of dilution and alcoholisation, or of neutralising the fixed acidity. When the intersection point is below the hachured space, the adulteration consists of an increase of the fixed acidity, increase of the fixed acidity along with alcoholisation or the increase of the fixed acidity along with alcoholisation and dilution.

According to nomogram 2 were obtained the following results:

Sample 1: Alcohol = 7.125 (g%)
Ratio (alcohol/fixed acidity) = 3.03
S_1 sample has been adulterated by dillution, dillution with alcoholisation and neutralising the fixed acidity.

Sample 2: Alcohol = 7.125 (g%)
Ratio (alcohol/fixed acidity) = 10
S_2 sample has been adulterated by dillution, dillution with alcoholisation and neutralising the fixed acidity.

According to the nomograms 1 and 2 interpretations both samples have been

adulterated by dillution, dillution with alcoholisation and neutralising the fised acidity.
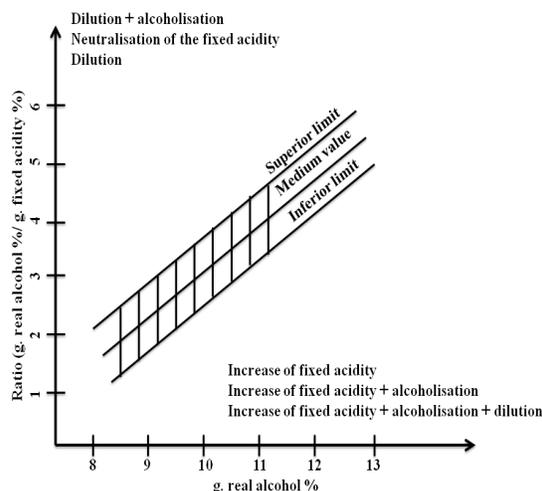

Fig. 2. Nomogram - Alcohol (g%)/Fixed acidity (g/l) variation ratio(Bulancea & Rapeanu 2009)

Neutralising the acidity for both samples can be evidentiated by the value of the acidity/alcohol ratio and alcohol/acidity ratio, described below:
S_1 it is found between the normal limits because it was less neutralised in comparisson with S_2, both samples having the total acidity value below the minimum normal limit of 5 g/l according to current standards.

5. To find out the alcohol amounts added, the nomogram 3 are used, as it follows:

The minimum degree of alcoholisation can be obtained by drawing a straight line that intersects the point corresponding to the alcohol concentration found at the analysis of scale II with the point corresponding to the reduced extract from scale IIIS, until it intersects scale I. When scale IIIM is used the maximum degree of alcoholisation is obtained.

According to nomogram 3 the samples alcoholisation degree considering the alcohol content and total dry extract, the following results were obtained:

S_1 – alcohol = 7.125% (g%)

Extract = 15 g/l

S_1 sample has beed alcoholised with 0.3g %, up to max. 1%, but not sufficiently to fit the min. allowed limit of 9%.
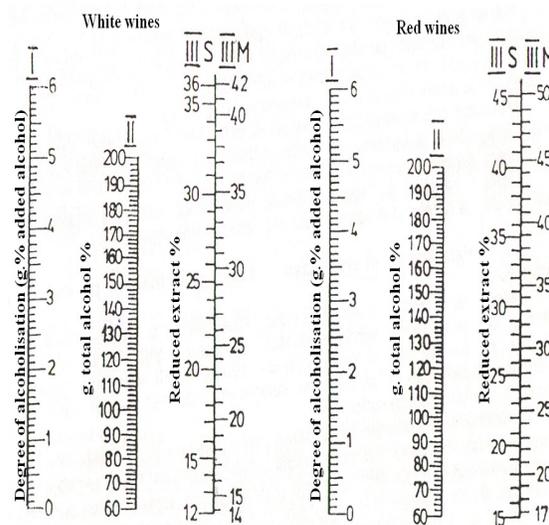
S_2 – alcohol = 7.125% (g%)

Extract = 15.5 g/l

Fig 3. Nomogram - used to calculate the amount of alcohol added (after Ghimicescu Ghe. 1971)

S_2 sample has beed alcoholised with 0.1g %, up to max. 0.8%, but not sufficiently to fit the min. allowed limit of 9%.

6.Analysing the results regarding the dry extract content, both samples have the values at the inferior limit of the normal value for the semy-dry white wine of min. 15 g/l, being in a close correlation with the dry substance value and the residual sugar content.

7.S_1 sample has a total SO_2 content of 316.8 mg/l, 58.4% higher than the standard value (max 200 mg/l).

S_2 sample has a total SO_2 content of 112.64 mg/l, found within normal limits.

3. CONCLUSIONS

The two samples, apparently having the same provenience and the same batch, with sensorial and physic-chemical properties completly different and not having the specific characteristics of semi-dry white wines.

Comparing the data from the scientific literature (nomograms, ratios, parameters), these samples present the characteristics of adulterated wines bu dillution, dillution and alcoholisation and neutralising the fixed acidity.(*Pomohaci N., 2000, Gheorghita M., 2002, Holmberg L., 2010, Bulancea M., 2009*)

Also, having these in mind, the value of the total dry extract is also liable to be adulterated by sugar addition (the dry extract value can't keep it's normal values without the addition of dry substance from sugar addition).

Regarding the high SO_2 content of S_1 sample, a conclusion can be made that S_1 contained large doses of sulphur dioxide, perfect to hide turbidity and deposits, that were also identified in sample S_2.

The study demonstrates that there are technological methods that allowed the production of hard to notice forgeries in some cases or that there are huge gaps in the manufacturing technical regulations of the product. Additionally, when there are no ways to evidentiate or to measure a forgery, tehnique of adulteration is unnoticeable.

4. REFERENCES

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