

Evaluation of the wines adulteration from Cotesti vineyard

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Abstract

The adulteration of wine is usually accomplished by addition of alcohol, water, dyes and aromas to wine of minor commercial value. As these wines are usually produced with inadequate conditions of hygiene, they become of high risk for the human health. Another risk for the consumer of adulterated wines is the ingestion of products not elaborated with raw materials controlled by control organs. The aim of this study was to identify the adulterated wines obtained in Cotesti vineyard by the private and local producers during the time period of 2007 - 2009. From the 219 wine samples analyzed it was noticed that the cheap wines are frequently adulterated. The trend of wine adulterations from Cotesti vineyard had a decreasing value from 2007 (88.3%) to 2009 (48.5%). The decreasing of the adulterated wines from 2007 to 2009 is probably due to the application of Romanian legislative regulations on wine quality level.

Keywords: yeasts, fermentation, multiplication, ethanol yield

1. Introduction

Wine is one of the most complex alcoholic beverages. Due to the high economic value of the wine-product for some worldwide typical geographical areas and for further socio-cultural reasons, the development of analytical methods for wine classification is extremely important, mainly for the assignment of a trade mark such as protected designation of origin (PDO), controlled denomination of origin (CDO), protected geographic indication (PGI) for quality wines. In this context, useful analytical methods serve to wine identification and, consequently, to protect the trade-mark quality wines and to prevent their illegal adulteration [1].

Wine fraud occurs in many different forms. Often counterfeiters target the more expensive and older wines. Not only are sales of these wines financially profitable, but few people are familiar with the labels and other markings on these bottles so the fraud is harder to detect.

Auctioneers and resellers sell expensive wines in large quantities, so the contents of a bottle or a case can be tampered with without anyone noticing for some time. One of the easiest scams involves replacing the contents of a case of expensive wine with bottles of less expensive wine. The cases are sold without ever being opened and then stored for years in warehouses before being sold again [2]. Another common type of fraud involves replacing the contents of an expensive bottle of wine with a wine of a lesser quality. Using a two-prong wine opener, corks can be removed and replaced with little damage. The adulteration of wines consists in the addition of regulated amounts of alcohols, e.g. methanol or ethanol, in order to artfully increase the alcoholic content of wine. This induced increase of the wine alcoholic degree producing a commercial enhancement with sales at higher costs of the wine, but the addition of an adulterant agent (alcohol) to the wine is an illegal fraud because the adulterated increase of the wine alcoholic degree is not due to a normal fermentation process of the grapes.

The addition of beet or cane sugar or concentrated rectified must to the grape must or wine before or maybe during fermentation is often used in order to increase the natural ethanol content in wine and, therefore, the value of wine for reaching higher prices in the market. This leads to deceiving of the consumers, since sugar addition is not declared on the product [3].

Glycerol is a natural ingredient of wines, normally the second most important product of glucose fermentation by yeast after ethanol. The compound is a major part of the sugar-free extract of wine and, due to its sweet taste, contributes largely to the sensory qualities of wine. This is the reason for attempts to “improve” wines with a low concentration of glycerol by the addition of glycerol from other sources, which is, however, not permitted by the Romanian law.

The proof that wine has been adulterated by the addition of glycerol has been based on conventional analytical methods, and especially the defined norm for the ratio between the concentrations of glycerol and ethanol. However, this ratio is quite variable (6 to 10% glycerol relative to ethanol), because it depends on the yeast strain, the concentrations of nutrients in the must, the fermentation temperature, and the grade of fermentation. However, the high natural variability of the concentrations of all wine ingredients limits the analytical power of this method.

Because the glycerol and the gluconic acid content and also the ratio glycerol/alcohol of wine is known to be highly variable may be the reason for the systematic adulteration of wine with glycerol within the natural range of this compound in wine. Thus attempts are being made to develop new methods for the detection of glycerol addition to wine, which are more accurate and sensitive than the existing techniques [4,5].

A variety of testing methods can be used to ensure the authenticity of wine. Along with more traditional methods of inspection, chemical assays such as stable isotope analysis, chromatography, mineral content analysis, and DNA fingerprinting are being used by various wineries. A novel method that incorporates unique DNA codes into the label of wine bottles is also used to avoid counterfeiting.

The authenticity of wine is guaranteed by strict guidelines laid down by the responsible national authorities that include official sensory evaluation, chemical analyses and examination of the register kept by the wine producer. Commission Regulation (EC) [6] lays down certain rules for applying Council Regulation (EC) No 1493/1999 regarding the description, designation, presentation, and protection of certain wine sector products. Regulation EC 753/2002 governing the designation, naming and protection of wines has been amended by regulation [7] and by Commission Regulation (EC) [8].

The aim of this study was to identify the adulterated wines obtained in Cotesti vineyard by the private and local producers during the time period of 2006-2008.

2. Materials and Method

Materials. The analyzed samples (219 samples) have been collected from private and local producers during the time period of 2007-2009. The wine samples were obtained the Cotesti vineyards, Vrancea County.

In 2007 a number of 34 samples were collected and studied.

During the year 2008 and 2009, a number of 78 and 107 samples, respectively, were analyzed.

Methods. To characterize wine authenticity, the determination of the alcoholic degree (% v/v) (picnometric method STAS 184/2-87), total acidity and volatile acidity (g/l H₂SO₄) (SR184-5:1997), free and total SO₂ (mg/l) (STAS 6182-12:2009), total sugar (g/l) (STAS 6182-18:2009), sugar free extract (g/l) (STAS 6182-25:2009), glycerol (g/l) (enzymatic method E 0148270, Darmstadt, Germany), citric acid (g/l) (STAS 6182-26:2009), presence of natural and synthetic colorants or flavors by using official methods (OIV) have been done.

Since natural wines are characterized by a balance between its components, among them we were able to establish correlations that may be expressed by oenological indices.

Although they have large variations for wines from different vineyards and not always correspond to mathematical rigor, they are use to assess at least a first phase of wine authenticity and the detection of possible fraud.

The correlation between alcohol concentration and acidity is expressed by the calculation of the following indices:

Gautier sum - Alcohol (% v/v) + Total Acidity (g/L), with values between 13-17;

If the wines are diluted with water when this indicator is below 13, the degree of wine dilution can be estimated by using the following relationship:

$$\text{Water, \%} = \frac{13 - (A + T)}{13} \cdot 100$$

where: A – fixed acidity of wine, (g/l); T – alcoholic degree of wine, (%v/v).

Blarez rules - Alcohol (%v/v) + Fixed acidity (g/L), ranging from 11-17;

Alcohol (%v/v)/Fixed acidity (g/L), with values between 1.75-1.65 (for an alcoholic degree of 7-14% v/v).

Halphen ratio - Total acidity (g/l)/Alcohol (%v/v), with values between 0.2 - 0.8.

The correlation between alcohol concentration and extract

The correlation between the alcoholic degree and extract is expressed as the ratio R: $R = \frac{\text{Total alcohol (g/L)}}{\text{sugar free extract (g/L)}}$ with values between 3.6 - 5.5.

Overcoming these values indicate the adulteration of wine by alcohol addition.

The correlation between alcohol concentration and glycerol

Between the amount of glycerol and the alcoholic concentration of wine there is a linear correlation, the amount of glycerol increased with increasing the alcohol concentration. Normally, the amount of glycerol is 6.5-10% by weight of ethyl alcohol. If the obtained values are not in within these limits, an ethanol or glycerol fraudulent intervention addition is required.

The value of ratio $\frac{\text{glycerol (g/L)} \cdot 10}{\text{alcohol (g\%)}}$ for the

Romanian wines varies within the limits of 5,5-13,5, with an average of 8.5.

To detect sugar addition, the presence of glucose and sucrose was necessary as in the case of sweet wines only fructose is present. The addition of synthetic sweeteners is noticed when the sample is sweet and no reducing sugars are present in the sample.

All determinations were carried out in triplicate, and the relative standard deviations were less than $\pm 1\%$.

3. Results and Discussion

Taking into consideration the label conformity a number of 13 samples from 34 samples analyzed in 2007 weren't in conformity with their labels. For example, a number of wine samples had a lower alcohol concentration (% v/v) (3 samples) and a higher total and volatile acidity, in the case of 7 samples.

Samples analyzed in 2007 were adulterated with water and a decreased alcohol concentration was observed. Wines adulterated with water became watery of less consistency and after swallowing do not produce a nice and warm sensation in the superior part of the oral cavity and stomach. The wines color is also diluted and flavor and bouquet are diminished related to the water percentage substitution.

Also, the samples collected during the time period of 2007 were adulterated by sugar addition and synthetic sweeteners in case of 7 samples and the presence of synthetic colorants was detected in 9 samples.

The adulterated wines were 88.30% of the total number of samples collected (Figure 1).

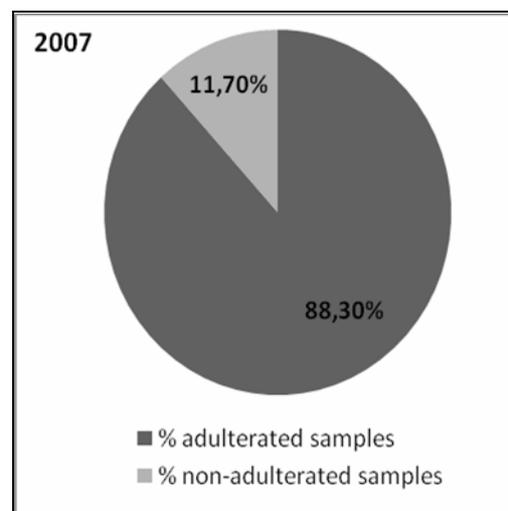


Figure 1. Adulterated wines during the period of year 2007

During the year 2008 a number of 78 samples were analysed and the percentage of adulterated wines had a slight decrease from 88.30% to 50.1% (Figure 2).

Wines analyzed during this time period were adulterated with water (16 samples), sugar (13 samples) and citric acid (19 samples) addition.

Finally, in the year 2009, only 52 samples were adulterated (with water 12 samples, with synthetic colorants 4 samples, with sugar and synthetic sweeteners 4 samples and with citric acid 32 samples) when a total number of 107 samples were controlled (Figure 3).

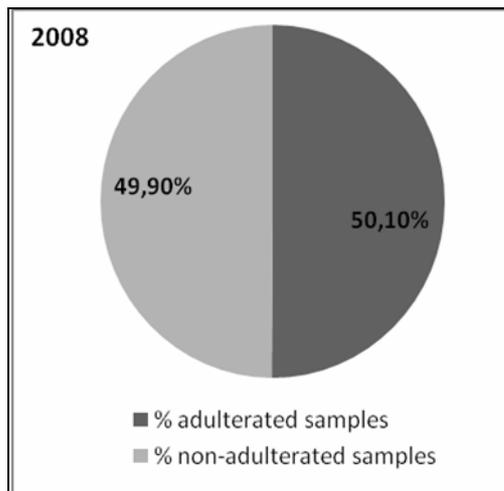


Figure 2. Adulterated wines during the period of year 2008

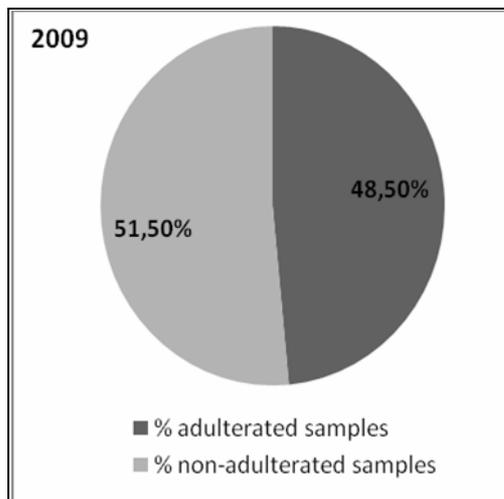


Figure 3. Adulterated wines during the period of year 2009

Some misleading-labeled wines, by including them in a higher quality level class of wines were being noticed.

Moreover, the whole label is not in agreement with the wine content. The grape variety

mentioned on the label has to be minimum 85% and a minimum alcohol concentration of 11% v/v.

Even if the wine contains more than 88-90% of a single grape variety but the synthetic colorants and flavors are detected, it cannot be named according to the controlled denomination of origin (CDO). In this case, the wine is considered misleading labeled.

Both governments and manufacturers have started to impose their own anti-counterfeiting, anti-diversion and anti-smuggling control mechanisms for wine authentication and supply chain security. These mechanisms include secure alcohol excise tax stamps and secure banderols, product authentication features and secure alcohol track and trace technology.

To be effective, they must comply with certain requirements: to offer solutions against all forms of alcohol and soft drink illicit trade; not to interfere with manufacturing and trade processes; to be flexible, and to practice an acceptable cost share and to allow for international collaboration in tackling alcohol illicit trade.

4. Conclusion

The number of adulterated wines decreased gradually from 2007 (88.3%) to 2009 (48.5%). From the total number of 219 wine samples analysed it was observed that usually the cheap wines (the table wines) are frequently adulterated.

This decreasing in fraudulent practices is probably due to the application of legislative regulations on wine quality. Today, state regulations, increasingly those of the EU, create basic conditions to protect specific wine qualities. This way, the consumer is meant to be protected a certain minimum wine quality is to be guaranteed.

At the same time, wine producers are obliged to keep up with specific wine criteria. Against that background, a multitude of factors decide over the wine quality, the modern quality protection being obviously always able to regulate some elements which are decisive for the quality of a wine assortment.

At the moment, quite a few are under the impression of an over regulation and demand - also with regard to the globalisation of the wine markets - a larger self responsibility for the wine producers and to leave the decision on wine qualities mainly up to the market as well as to competition.

Others insist on state standardization wine-growing policies which lay down a minimum quality level and punish violations of these regulations. Just the current discussion makes it clear that no durable agreement exists on the numerous elements of qualitative wine production.

With regard to the wine scandals, this means that are violations of state standardisation exposed and punished regarding wine-growing that cannot refer to constant and also always valid quality criteria.

Acknowledgements

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