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"Smart Bio Wine", a Project for Consumer Information, Business Competitiveness and Environmental Sustainability

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The food label is the first means of communication with which the consumer comes in contact with the product. The same is not limited to hygiene and nutritional value of food, but also extends to environmental, social and ethical.
Italian legislation guiding the labelling was founded in 1974 and aims to ensure on one hand the free circulation of goods in a spirit of fair competition, on the other hand the health protection and the right information for consumers.
Even a well-structured label neglects some important information regarding the consumer's health, such as the presence of harmful elements, making it incomplete for the end user.
The "SBW" project aims to develop a monitoring protocol for the detection of heavy elements (metals) and harmful substances, based on a "voluntary" labelling of food products.
Companies that decide to adopt the control protocol may obtain, in the only case in which the requirements are met, a "certificate of quality", which will be summarized and made evident on the labels through the inclusion of a trademark (easily recognizable logo), connected to remote or in label information.
The aim is twofold: to protect consumers from the point of view of food safety and increase the competitiveness of companies adopting such a system of voluntary labelling. At the same time companies will be stimulated to reduce chemical inputs during the production cycle.
The project, although adaptable to all food products, is tested on a product with a low content of harmful elements: the wine. It has been chosen this product in view of the increasing demand for enhancement of "made in Italy" foodstuffs: in fact, the wine is one of the products that can be sold with a label that is easily reproducible by the market of counterfeit food.
For this purpose a series of tests was carried out on organic wine in two cellars located in central Italy. Results show an average concentration of copper of 39.3 μg/dm^3 (white wine) and 79.9 μg/dm^3 (red wine) in the first winery, and, in the second winery, 5.4 μg/dm^3 (white wine) and 12.3 μg/dm^3 - 482 μg/dm^3 (red wines). The copper concentrations were under the limit of 1000 μg/dm^3: however sensible differences were detected among different wines and this information could be useful for the consumers.

1. Introduction

The European agro-food sector offers several quality products that reflect the producers skills, European traditions and diversity of the regions of the Community.
The agricultural products of the European Union (EU) meet rigorous production requirements and are characterized by specific qualities appreciated by the consumer: so a series of directives have been issued aimed to the protection of producers.
The identification of inorganic substances in foods has always been a taboo for the consumer, hence the introduction of specific marks or codes on labels allow the consumer to know the origin of the product. So the introduction of appropriate identifiers allow the acknowledgment in the product quality, in particular the use of

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specific protocols for analysis, allows to identify the chemicals used for the realization of the products (e.g. the content of copper in organic wines).
Safety and quality of food has always been the basis for the protection of “made in Italy” products, in contrast to producers that put on the market products containing dangerous substances that have a negative impact on people's health.
Especially agricultural products have always been the subject of debate because of the use of chemical compounds which, for their technical and physical characteristics, persist in the raw material and then in the food.
Also the wine sector is not excluded by this problem even though it is reduced by the growing diffusion of the organic production system characterized by the great reduction of the use of chemicals respect to conventional productions.
In Italy the farms with organic orientation are 43,367 units with a territorial extension of 781,489.69 hectares; 9,878 (22.7 %) of these have a viticulture address and occupy an area of 43,999 hectares, equivalent to 5.6 % of all the territory destined to the organic agriculture (ISTAT, 2010).
Farms with organic address follow a specific production disciplinary, which define, in detail, all the agronomic techniques to adopt and particularly outline the types of chemicals that can be used against pathophysiological adversity affecting the *Vitis vinifera*.
All practices implemented by the producers are aimed at achieving a quality product and therefore farms aim at enhancing their wines through appropriate and targeted marketing strategies, such as the food label which is the first form of communication with the buyer. Labels should inform both on hygienic safety and nutritional properties of food, but also on the environmental, social and ethical impact of the product.
Labeling is characterized by an articulated legislative framework composed by constantly revisioned Community and national rules. It was established in Italy in 1974 and aims to ensure the free movement of products in a fair competition framework, the protection of public health and the information right for consumers.
Nowadays either a label that respects the norm shows important gaps referring to the consumer health, such as the absence of information about heavy metals and other harmful chemical compounds contents.
Therefore, the consumer is never in conditions of full knowledge about the presence of extraneous substances in food or drink, especially referring to the residues of pesticides used in agriculture.
All fungal diseases that affect the grapevine, such as *Plasmopara viticola* spp., are immediately contrasted starting from their first manifestation on the plant, by means of the distribution of chemicals, that in compliance with recommendation of the organic disciplinary, introduces, among the main active principles, two very important elements such as copper and sulfur.
The use of certain quantities of chemical products, as in the case of copper (always important in vineyards, as pointed out by Ruyters et al. (2009)), even if controlled in quantity, as shown in the study of Duplay et al. (2014), does not exclude the risk of environmental contamination with effects on the ecosystem, as seen from Boon et al. (1998). A review by Komàrek et al. (2010) summarizes available studies published on the contamination of vineyard soils throughout the world with Cu-based and synthetic organic fungicides. A study from Pitrzak and McPhail (2004), carried out in the state of Victoria, shows that copper can stay active in soils for long periods of time, greater than tens of years, and may result in leaching and transport to deeper soil layers. This is due to the chemical characteristics and physical properties of the active principle that determines also some toxicity for man, as observed by Arnal et al. (2012) in studies of cytotoxicity of copper on the cells, but especially when used with other PA as pointed out by Henandez et al. (2013) or Remore et al. (2009). For this reason, both the distributed quantities of products (containing copper), both the maximum concentrations of the same active principle in the grapes and in the wine, are governed by specific Community regulations and national decrees, allowing, in this way, an analytical control of element through the implementation of conventional laboratory tests as seen from Schiavo et al. (2008) or by stripping potentiometry with medium exchange for the determination of total copper (Clark and Scollary, 2014) or as seen in the study by Provenzano et al. (2010) in wines from organic Mediterranean vineyards.
The "Smart Bio Wine" project, developed by the Department of Agriculture, Forest, Nature and Energy of Tuscia University and SEA Tuscia S.r.l. (Viterbo, Italy), aims at providing producers one more tool to make the company competitive in the global market and to defend it against unfair competition based systems in times of food fraud. It is a system of voluntary labelling based on the indication, directly on the label or remote (easily accessible by the consumer e.g. via QR code) about the content of dangerous chemical elements in the product, but as a characteristic resulting from the production processes related to the product itself. Aim of this study is the identification of one of the most used chemicals in viticulture (also organic viticulture), the copper, in wines from different backgrounds, in order to make a first feasibility study of the project.

2. Materials and methods

For the determination of concentrations of copper in wine, several samples were taken from bottled, labelled and ready for sale wine, and coming from two wineries located in the Province of Viterbo (central Italy). This experiment has allowed to monitor, through chemical analysis, the real quantity of copper in the wine which could be assimilated by the consumer.
The laboratory instrumentation used in compliance with the implemented protocol is an ICP-OES OPIMA DV (Perkin Elmer, USA) with auto sampler and an Ultrasonic Nebulizer U 5000 AT+ (CETAC, USA).
The first step, regarding chemical analysis in the laboratory, is to prepare the stock solution for the definition of the calibration line; in this process Cu (analytical standard), nitric acid for dilution of samples and yttrium have been used as internal standard.
40 µl of Cu (99.9 % pure), HNO_3 (3 %) and a small amount of yttrium have been introduced and mixed in a flask to arrive at 100 mL. From the stock solution, five different concentrations were obtained: 400 ppb, 200 ppb, 100 ppb, 5 ppb and 10 ppb, which have given an appropriate calibration curve for the definition of the copper concentrations in the analysed samples.
For the determination of copper, three different wavelengths (λ equal to 324.752 nm and 327.393 nm for copper and 371.029 nm for yttrium) were used.
The next step was to prepare the sample to be injected in ICP-OES: 25 mL of wine have been extracted from each bottle; it was thermally treated at 80 °C for 4 h, and then brought, at first to a concentration of 10 mL and then to the final quantity of 25 mL using nitric acid at 3 %. The product to be analyzed was taken, by means of the auto sampler, from this solution. Argon was used as gas carrier. Table 1 shows the test conditions.

Table 1: Argon flow setting

Plasma dm^3/min	Aux dm^3/min	Neb dm^3/min	Power W	View Dist	Plasma view
10	0.3	0.65	1,450	15	Axial reading

3. Results

According to the Italian ministerial decree wines for direct consumption must not contain more than 1 milligram (1,000 µg) of Cu per dm^3 of product, which means that in the bottles on the market (0.75 L) the content of copper must not exceed the threshold of 0.75 mg (750 µg).
The analysis showed a meaningful and important analytical framework, because from the analyzed samples it was found that the wines produced and marketed by the organic farms have a Cu content well below the allowable limit.
Results of the analysis of the wines produced by two different wineries show significant differences between the mean concentrations of Cu, in particular it can be observed that in the second winery values were significantly higher, but still below the threshold limits.

3.1 Winery A

In white wines, the average concentration of copper at a wavelength of 327.393 nm was of 39.5 µg/dm^3, with a minimum value of 27.5 µg/dm^3 and a maximum of 47.95 µg/dm^3; values confirmed also by reading at 324.752 nm, in which the average concentration of copper was of 39.2 µg/dm^3, with a minimum value of 28.6 µg/dm^3 and a maximum of 46.94 µg/dm^3 (Table 2). These results demonstrate that copper concentrations are well below the limits defined by national laws.

Table 2: Winery A: copper concentration in white wines

		Cu λ 327.393 nm	Cu λ 324.752 nm
n. wine - n° bottle	Sample	µg/dm^3	µg/dm^3
Wine 1-1	1	28.00	28.60
		27.50	29.00
	2	47.95	46.91
		47.79	46.94
Wine 1-2	1	36.20	35.10
		36.10	35.00
	2	46.19	46.52
		45.97	45.77

In red wines (Table 3) results show that in some samples there are higher copper levels than in white wine samples: at the wavelength for Cu identification of 327.393 nm the average is about 81.6 μg/dm^3, with a minimum value of 32.75 μg/dm^{3}and a maximum value of 133.28 μg/dm^3. Referring to the second wavelength the average value is 78.2 μg/dm^3, with a minimum of 32.3 μg/ dm^3 and a maximum of 125.53 μg/ dm^3.

Table 3: Winery A: copper concentration in red wines

n. wine – n. bottle	Sample	Cu λ 327.393 nm μg/dm^3	Cu λ 324.752 nm μg/dm^3
Wine 2-1	1	126.30	121.90
		126.60	120.10
	2	130.17	125.53
		133.28	125.32
Wine 2-2	1	34.90	32.30
		35.70	32.30
	2	32.75	33.67
		32.85	34.15

3.2 Winery B

In white wines from the second winery (Table 4), the average concentration of copper at a wavelength of 327.393 nm was of 5.6 μg/dm^3, with a minimum value of 3.6 μg/dm^3 and a maximum of 11.23 μg/dm^3; values are also confirmed by the reading to 324.752 nm, in which the average value is 5.2 μg/dm^3, with a minimum of 3.3 μg/dm^3 and a maximum of 10.94 μg/dm^3.

Table 4: Winery B: copper concentration in white wines

n. wine – n. bottle	Sample	Cu λ 327.393 nm μg/dm^3	Cu λ 324.752 nm μg/dm^3
Wine 3-1	1	5.80	5.30
		5.90	5.30
	2	11.21	10.94
		11.23	10.61
Wine 3-2	1	3.70	3.50
		3.60	3.30
	2	1.62	1.44
		1.69	1.43

In red wine (Table 5), results show that in some samples there are higher copper levels than in white samples; at the wavelength for Cu identification of 327.393 nm the average value is 12.7 μg/dm^3 for the first red wine and 479.7 μg/dm^3 for the second, with a minimum values of 11.3 μg/dm^3 and 431.1 μg/dm^3 respectively; the maximum values are 13.63 μg/dm^3 for the first sample and 584.09 μg/dm^3 for the second.
For the second wavelength, the average values are 11.9 μg/dm^3 for the first sample and 483.3 μg/dm^3 for the second red wine, with a minimum value of 10.0 μg/dm^3 for the first sample and 443.7 μg/dm^3 for the second. Maximum value are of 13.48 μg/dm^3 for first sample and 588.57 μg/dm^3 for the second.

4. Conclusions

Copper levels defined by laboratory analysis showed that wine from organic agriculture is characterized by copper concentrations significantly under the Ministerial limits but these wines contain chemical products that manifest a certain direct toxicity for humans and, because of its ability to persist in soils, for the environment.
The comparison between different farms, although characterized by a quantitative difference of copper in wine, has highlighted the qualitative aspect of all organic wines that are characterized by values well below the limits set by the national rules.
The observation of the average amounts of copper obtained from analysis at two different wavelengths, shows that the values (in the first winery 39.3 μg/dm^3 for white and 79.9 μg/dm^3 for red wine; in the second winery 5.4 μg/dm^3 for white and 12.3 μg/dm^3 for the first red and 482 μg/dm^3 for the second red wine) are well below the limit of 1,000 μg/dm^3.

Table 5: Winery B: copper concentration in red wines

n. wine – n. bottle	Sample	Cu λ 327.393 nm µg/dm^3	Cu λ 324.752 nm µg/dm^3
wine 4-1	1	12.90	12.20
		12.90	12.10
	2	13.63	12.89
		13.34	13.48
Wine 4-2	1	11.30	10.00
		11.30	10.30
	2	12.88	12.30
		12.94	12.09
Wine 5-1	1	431.10	446.80
		437.90	461.20
	2	583.95	588.57
		584.09	586.83
Wine 5-2	1	453.50	443.70
		449.20	458.20
	2	450.11	443.92
		447.46	445.43

This should be an incentive for companies that want to enhance their product, highlighting the fact that a farm not based on a organic system has a great negative incidence both on the environment and on humans, which also means a greater amount of chemicals on the tables of consumers.

For this reason, the application on labels of systems for the identification and classification of chemicals used in fields, has a dual purpose: to protect the consumer from the point of view of food security and to increase the competitiveness of companies adopting such a system of voluntary labeling.

Use of a label or a specific logo is an effectiveness communication tool, both for the intuitiveness by all consumers, which thanks to the modern communication systems are capable to "read" any information, both for the producers that can put in prominence the seriousness with their transparency but above all the guardianship of the quality, hinge of their business politics.

Some aspects of this research, such as those related to sampling (e.g. minimum number of bottles to have a significant figure), should be deepened in the future.

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