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ELABORATION OF A METHOD TO DETERMINE THE DRY WHITE WINE FALSIFICATION WITH SUCROSE

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Abstract: *A standard method of reducing sugars determination using Fehling-Muller reagent has been modified and applied to control the presence of sucrose in white dry wine that can be considered as an indication of its falsification. Natural dry wine should not contain any significant amounts of sucrose since its content in regular grape is below 0.9 wt % and it would be fermented almost completely in the course of wine maturing and manufacturing. However, some sucrose can be added by fraudulent producers to the source wine materials in order to accelerate its fermentation. This results in a higher content of residual sucrose in dry wine that can exceed its maximum permissible level of 4 g/l. The modified method of the reducing sugars determination has shown good durability and reproducibility and can be used to determine the residual sucrose concentration above 1.33 g/l. However, excessive sulfites and other reducing preservatives present in some wines (especially in the low-grade samples) can distort the analysis results and should be removed in advance. Potentially, this method can also be applied to analyze wine blending samples and to control their affinity by the ratio between reducing and non-reducing sugars contents.*

Keywords: *white wine; wine falsification; sucrose; modified Fehling-Muller method; reducing sugars*

1. Introduction

Residual sugars content in dry white wine is limited by the value 4 g/l, which should consist of almost no sucrose [1]. This requirement is based on a low content of sucrose in the raw grapes, where glucose and fructose represent almost all the sugars in the berries. Those insignificant amounts of sucrose coming with grape should be completely fermented during maturing of wine. Therefore, any considerable amount of sucrose found in the dry wine can be considered as an evidence of its possible falsification by fraudulent producers through adding of the 'extra' sucrose to accelerate the fermentation [2, 3].

It is known that an estimated amount of falsified wines coming to the world markets is very large. This fraudulent practice started as long as wine has been made in antiquity and it is still popular [4]. There are numerous methods of wine manipulation and adding of disaccharides is one of them.

Technically, there are several approaches to determination total sugars content in wine, which involve photometry, HPLC or traditional chemical methods using oxidation of the monosugars by Fehling-Muller reagent [2].

However, only the latter one is recognized as the official method of determination the sugar content in wines [1, 5].
Both reagents are in fact same complex compound – ditartratocopper (II) hydroxide with the only difference in their preparation methods.
Following both methods, any sugars present in wine should be previously converted into the monosugars (glucose, fructose) and then the concentration of the latter can be determined according to the reagent amount used for their oxidation [1].
An idea beyond our experimental method is following. Theoretically, disaccharides are not subject of oxidation by Fehling-Muller reagent since they do not undergo any chemical transformation under the conditions set for the monosaccharides transformation. In reality, it is not true and disaccharides can be partially oxidized as well, bringing some experimental errors in the results. On the other hand, the value of this error is comparatively low and can be neglected in preliminary investigations.
Therefore, we can establish two parallel determinations with two samples of the same wine. One sample would remain untreated preserving all sugars in their original form (monosaccharides remain monosaccharides while disaccharides also remain unconverted). Another sample would be treated according to the standard sugar inversion method that converts all present sugars into monosaccharides. Then both samples should be analyzed according to the Fehling-Muller method [1, 2] followed by cross-comparison between the results obtained. Any difference between them would indicate presence of some disaccharides in the source material. More exact results can be obtained from the advanced method including parallel idle experiments taking into account unavoidable natural decomposition of the reagents and other factors beyond our control.
It is important to check if this method can work in reality for the samples of white wines available in regular stores and understand if its sensitivity would be sufficient to find disaccharides concentrations expected for the fraudulent wines.
Due to massive amounts of reducing agents present naturally in the red wines and their intense color, our investigations were restricted by the white brands only.

2. Experimental

All experiments were carried out using three randomly selected Ukrainian-made wine samples: a cheap unbranded table wine in the tetrapack-type carton box (1); and two other bottled wines of Chardonnay (2) and Sauvignon (3) types. All beverages were declared by their producers as the table dry wines and were purchased in local grocery stores. Each wine was opened right before the investigation and then two equal samples were taken from each bottle/pack. One of them was left **untreated** while the other sample underwent the acidic sugars **inversion** according to [1]. All dilution ratios were kept similar for the both samples. Fehling-Muller reagent and other working solutions were prepared not longer than 6 hors prior usage according to detailed description [1,6].
Then the samples were analyzed and the sugars contents were determined in such a way that the first (untreated) sample result corresponded to the monosaccharides content only while the second sample result corresponded to the total sugars content. A difference between the second and the first values gave us a possible content of disaccharides in the wine.
In order to understand if the method's sensitivity is sufficient for determination of the disaccharides content that can be expected in case of wine falsification, we repeated all the above procedures with

another set of samples after intentional adding of 1,33 g/l (4 mmole/l) of sucrose before investigation. Since this concentration is three times lower than the maximum permissible sugar content for the dry wine, it was considered as an indicator of wine falsification that can be expected in real conditions.

3. Results and discussion

All results of the sugars contents determination in the source and intentionally falsified wine samples are shown in Table 1.

Table 1.
Determined sugars contents (X, mmole/l) in different wine samples

Sample 1	X (source wine) 2	X (intentional falsification) 3
(1), inverted	1.8	19.7
(1), untreated	1.7	12.9
(2), inverted	2.2	4.8
(2), untreated	1.4	4.2
(3), inverted	2.3	5.0
(3), untreated	1.2	4.5

As seen from the data of Table 1, column 2, almost no sucrose was found in the sample 1 (its inverted and untreated X values were 1,8 and 1,7 or almost identical) while in two other samples the concentration of sucrose was about 1 mmole/l (0,34 g/l). Indeed, comparing the X values for the inverted and untreated samples of the wines (2) and (3), one can see that the difference between them was 0.8 for the wine (2) and 1,1 for the wine (3). This content is rather insignificant and it can be considered as a residue of the initial natural sucrose remained in the source blend after its fermentation. Absence of sucrose in the sample (1) can be caused by a comparatively lower content of the compound in the source blend or by a deeper fermentation of the source material. Therefore, it can be initially concluded that there is no any signs of forgery with sucrose in the wine samples taken for this investigation.

On the other hand, the suitability of any analytical method proposed for identification of the food falsification should be tested for the falsified samples in order to assess general qualification and sensitivity of the method. In this context, the data of the column 3, Table 1, which is related to the intentionally falsified samples should be analyzed and discussed.

As seen from the table, the results for the samples (2) and (3) are quite predictable: sugar contents rise approximately by 4 mmole/l after adding extra 4 mmole of sugar. For instance, the total content of all sugars in the sample (2) was 2,2 mmole/l initially and then it increased to 4,8 mmole/l after intentional adding of sucrose. Same data for the sample (3) are 2,3 and 5,0 mmole/l simultaneously. One can notice some deficiency in the sugar contents since 2,2 initial mmole/l plus 4 mmole/l (added) had to result in the content 6,2 mmole/l while in reality it was only 4,8 mmole/l (sample(2)).

This deficiency in the total sugar content can be caused by partial sucrose decomposition and presence of some impurities in the sucrose used for 'falsification'. As a result we added lesser amount of sucrose and some more products of its hydrolysis during the process of intentional forgery.

The result of falsification of the sample (1) is paradoxical as the sugar content in the inverted sample has risen for approximately 18 mmole/l and for ~11 mmole/l in case of untreated wine. In our opinion, this result may be caused by considerable amounts of reducing preservatives (for instance, sulfites) present in this sort of the cheap wine. These compounds may distort results of the sugars content determination by Fehling-Muller method since they also consume copper tartratic complex actively

for the reactions of own reduction. This assumption seems real taking into account lower price category of this wine. That is why potential applicability of the proposed method for the dry wines falsification with sucrose should be limited by the low-preservatives containing wines.

4. Conclusion

The proposed modification of the well known and reliable Fehling-Muller method makes feasible its utilization in the wine genuineness/falsification control. This method ensures determination of disaccharides presence in wine even with contents below their maximum permissible level.

On the other hand, the presence of wine preservatives, sulfites or other reducing agents may cause serious distortion of the results. The method can not be applied directly to red and some other wines with intense color and/or containing considerable amounts of natural reducing agents and tannin-like compounds. Extra attention should be given to application of this method in the case of analysis of low-grade wines.

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