POTASSIUM FERROCYANIDE WINE TREATMENT: A CONTROVERSIAL, YET NECESSARY OPERATION

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Abstract: *This paper presents the method of iron removal from wine by using a potassium ferrocyanide treatment, a method implemented in Romania by oenologist Ştefan Teodorescu, which became official in 1973. Potassium ferrocyanide treatment is a controversial operation that poses safety and environmental protection problems, but is absolutely necessary for the efficient removal of iron from wines rich in this cation. Without iron removal, wines with over 10 mg/l of iron become susceptible to fearsome chemical defects, such as turning whiter, darker or bluisher. The paper presents a case study for the white wine Fetească Regală, obtained in the Recaş vineyard, harvested in 2016, in order to establish the theoretical and practical doses of potassium ferrocyanide based on microprobes, to remove the iron up to the safety threshold (4 mg Fe total/l of wine). The conclusions of the paper include some "good practices" for the success of the treatment and the prevention of toxicity problems.*

Keywords: potassium ferrocyanide, wine, microprobes, iron removal.

INTRODUCTION

By mineral nutrition, the wine accrues small amounts of iron in grapes: 2-3 mg/kg. In addition to the mineral substances derived from grapes, wine is enriched with significant amounts of exogenous mineral substances coming from the tanks in which the wine is stored; the materials used to condition wines; the machines with which the wine comes in contact, especially the filters, pumps, hoses, metallic pipes (Ţârdea, 2007). Therefore, the iron in wine can be "biological iron" (coming from the vine), "agronomic iron" (coming from the ferruginous soil through the grapes), and "technological iron" (coming from metal machinery and equipment with which the wine comes in contact) (Cotea *et al.*, 2009).

Prior to stabilization, wine may contain larger quantities of mineral substances than the grapes from which it is made, reaching a level of 18-20 mg/l (Cotrău, 1983).

The prerequisites for iron-related defects (iron precipitations) occur due to increased iron content, aeration conditions, and low storage temperatures. Iron-related defects are physicochemical defects of wine that can take two forms: they can be ferrous-phosphate or discoloration defects, which occur in white wines allowed to breathe, and turning darker and bluisher in color, which occurs both in white and red wines (Gheorghiţă *et al.*, 2002).

In order to prevent the occurrence of these chemical defects and for a better stabilization of the wine, it is necessary to remove the iron from the wine. (Poiană, 2005)

Currently, in Romania, two different methods of iron removal from wine are used: the potassium ferrocyanide treatment, and the treatment with phytic acid and its salts (Mihalca, 2007).

Worldwide, in recent years, the research has begun to establish alternative methods (removal of iron from white wines through ion exchange techniques) that may enable the decrease od the metal content from white wine without altering its organoleptic characteristics (Benîtez *et al*., 2002).

The treatment of musts and/or wines with PVI-PVP for decreasing the levels of metals such as Fe, Cu, Zn and Al, has been under discussion at OIV by experts under both the "Wine Technology" and, also the "Food Security" groups.

In May 2006, the French Agency of Food Security commented in an advice (AFSSA 2006) that utilisation of PVI-PVP at a dosage of 80g/hl did not appear to present any risk to consumer health (Mira *et al*., 2007).

Potassium ferrocyanide treatment poses safety and environmental protection problems, but is absolutely necessary for the efficient removal of iron from wines rich in this cation. The alternative treatment with phytic acid/calcium phytate has the disadvantages that it only removes trivalent iron from the wine, requires oxidation that creates many uncertainties about the evolution of the wine, and last but not least, there remains important amounts of calcium that cause precipitation of calcium tartrate.

The objective of this study was to establish the theoretical and practical doses of potassium ferrocyanide for removing the iron up to reach the safety limit of 4 mg Fe total/l.

MATERIALS AND METHODS

Wine samples

White wine Feteasca Alba coming from Recaş vineyard (Timiş County), harvested in 2016, was used in this study. Wine samples are taken on the day of treatment, in duplicate, in 1 liter glass bottles, from each container (cask or tank). Samples that were not very clear were filtered.

The potassium ferrocyanide treatment to remove the iron from wine

Potassium ferrocyanide reacts with ferric iron to form a blue insoluble ferric ferrocyanide precipitate $Fe_4[Fe(CN)_6]_3$, easily separable by flocculation with gelatin or bentonite. Ferric iron in wine is mostly employed in complex combinations with very poorly dissociable organic ferritartrate and ferrimalate acids. When ferrocyanide is added to the wine, free Fe^{3+} ions are immediately made insoluble in the form of ferric ferrocyanide, a blue precipitate (Prussian or Berlin blue). The reaction that takes place is depicted in Scheme 1.

$$3K_4[(CN)_6Fe] + 4Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3 + 12K^+$$

Potassium ferrocyanide — Blue ferric ferrocyanide

Scheme 1. The reaction that lead to the formation of ferric ferrocyanide.

The reaction of potassium ferrocyanide with ferrous ions (Fe^{2+}) is faster and more complete, compared to that with ferric ones (Fe^{3+}). Depending on the conditions, two compounds may be formed: ferro-potassium ferrocyanide $K_2Fe[Fe(CN)_6]$, which is white (Williamson white), and ferrous ferrocyanide $Fe_2[Fe(CN)_6]$, which is blue (Turnbull blue), or a mixture of these two salts according to the reactions from Scheme 2.

$$K_4[(CN)_6Fe] + Fe^{2+} \longrightarrow K_2Fe[Fe(CN)_6] + 2K^+$$

Ferro-potassium ferrocyanide (white)

$$K_4[(CN)_6Fe] + 2Fe^{2+} \longrightarrow Fe_2[Fe(CN)_6] + 4K^+$$

Ferrous ferrocyanide (blue)

Scheme 2. The reaction that lead to the formation of ferrous derivatives.

The white and white-blue divalent iron salts are hard to detect in the dark blue ferric ferrocyanide precipitate formed in wine (Bosso and Castino, 1994).

The stoichiometric method of removing iron from wine (The Ştefan Teodorescu Method)

The Ştefan Teodorescu Method is based on the association of the principle of the classic German Von Der Haide method with Prilinger's stoichiometric calculation. The method consists in determining the amount of potassium ferrocyanide required to remove iron from wine, after the stoichiometric calculation and microprobing. A safety level of 4 mg of iron in total (2 mg Fe^{2+}, and 2 mg Fe^{3+}) is maintained in wine, to avoid the over-clarifying of wine with ferrocyanide (Teodorescu *et al.*, 1960).

The method has been experimented since 1956, and is the official method used in Romania to remove iron from white and rosé wines.

RESULTS AND DISCUSSIONS

The ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) content is determined directly from wine by the colorimetric method by using potassium thiocyanate. Based on the results obtained, the stoichiometric calculation is performed to determine the theoretical quantities of ferrocyanide. A safety level of 4 mg total Fe/l of wine is maintained (2 mg Fe^{2+}, and 2 mg Fe^{3+}).

Case study for the white wine Fetească Regală

We determined the iron content of white wines obtained in the Recaş vineyard (Timiş County), harvested in 2016, and Fetească Regală variety had a content of 7 mg Fe^{3+}/l, and 9 mg Fe^{2+}/l, respectively.

As it is depicted in Scheme 1, 3 potassium ferrocyanide molecules react with 4 trivalent iron ions. By calculating the molecular weight of the ferrocyanide, and the atomic weight of the iron it follows:

422.2 x 3 = 1266.6 for ferrocyanide

55.84 x 4 = 223.4 for iron

The analysis of the figures obtained shows that 1266.6 mg of potassium ferrocyanide is combined with 223.4 mg of trivalent iron. Therefore, 5.6721 mg of ferrocyanide (specific consumption) is needed to precipitate 1 mg of trivalent iron,

- 7 mg Fe^{3+} - 2 mg = 5 mg/l ferric iron to be removed from the wine;
- 5 mg x 5.6721 mg ferrocyanide (specific consumption) = 28.360 mg ferrocyanide/l of wine, to remove Fe^{3+};

According with reactions presented in Scheme 2, it is found that 1 molecule of potassium ferrocyanide reacts with 1 bivalent iron ion.

Considering the molecular weight of the ferrocyanide (422.3 Da), and the atomic mass of the iron (55.84 Da), it results that 7.5643 mg of ferrocyanide (specific consumption) is needed for 1 mg of divalent iron.

- 9 mg Fe^{2+} - 2 mg = 7 mg/l ferrous iron to be removed from the wine;
- 7 mg x 7.5643 mg ferrocyanide (specific consumption) = 52.950 mg ferrocyanide/l of wine, to remove Fe^{2+}.

The theoretical dose of ferrocyanide used is: 28.360 + 52.950 = 81.310 mg/l ≅ 81 mg ferrocyanide/l of wine.

Initial test

We started from the theoretical dose of ferrocyanide of 81 mg/l, determined by the stoichiometric calculation. We used introduced 10 ml of wine in 5 glass tubes with the same sizes to which we added the potassium ferrocyanide solution. The calculation is depicted in Scheme 3.

81 mg ferrocyanide .... 1000 ml of wine
x .... 10 ml of wine

$x = \frac{81 \text{ x } 10}{1000}$ = 0.81 mg ferrocyanide for 10 ml of wine

100 ml solution ....500 mg ferrocyanide
x.....................................0.81 mg ferrocyanide

$x = \frac{0.81\text{x}100}{500}$ = 0.16 ml ferrocyanide solution for 10 ml of wine (theoretical dose)

Scheme 3. Calculation for initial test.

For the practical application of the treatment, the practical dose is calculated by compiling two series of microprobes according to Table 1.

Table 1. Microprobes for the treatment with potassium ferrocyanide

	Tube no.	**1**	**2**	**3**	**4**	**5**
1st series	Wine (ml)	10	10	10	10	10
	0.5% potassium ferrocyanide solution (ml)	0.13	0.16	0.19	0.22	0.25
	Tube no.	**1**	**2**	**3**	**4**	**5**
2nd series	Wine (ml)	20	20	20	20	20
	0.5% potassium ferrocyanide solution (ml)	0.26	0.32	0.38	0.44	0.50

In the tubes of both series we added 3-4 drops of gelatin solution, and 7-8 drops of tannin solution. The content of the tubes are shaken vigorously after each addition of reagents, and filtered at the end.

For the first series, we looked in the filtrate for the presence of iron remaining in the wine. To this end, we took 5 ml of the filtrate, added a drop of ferro-ferric mixed reagent, and 0.5 ml of HCl (1/1).

For the second series, we looked in the filtrate for potassium ferrocyanide excess, by adding one drop of alum solution (double iron and ammonium sulphate). The 5th test tube showed a blue-green coloration (strong ferrocyanide excess), and the 4th test tube showed a grayish color, therefore the practical ferrocyanide dose will be the one in the third tube.

0.19 ml of ferrocyanide solution x 5 = 95 mg of potassium ferrocyanide/l of wine is the practical ferrocyanide dose, higher than the theoretical dose of 81 mg/l.

Practical application of the ferrocyanide treatment

The amount of ferrocyanide determined for each individual container is dissolved in distilled water, 1:4 (v/v), at 20-25 °C (ferrocyanide is not dissolved directly in the wine because organic acids decompose it).

After 8-10 days following the application of the treatment, clear wine is drawn from the ferrous ferrocyanide deposit into another clean tank. The wine is then filtered through filters to retain fine ferric ferrocyanide suspensions. The efficiency of filtration is verified by passing the wine through a paper filter; if, after filtration and drying, the paper filter is colorless or has the color of the wine, the wine has been well filtered; if, after filtration and drying, the paper filter turns blue, then the wine was not well filtered, having a residual amount of ferrocyanide. In this case, it is recommended to repeat the filtration through filter plates with a lower porosity (0.45 μm).

Ferric ferrocyanide residue disposal

Ferric ferrocyanide residues have a high toxicity. Their management to avoid the pollution of surface waters and the environment remains an unresolved problem, cyanide ion having a long-lasting resistance over time. Presently, ferric ferrocyanide residues are collected in special containers, and deposited in deep caves (deserted salt mines) (Țârdea, 2007).

CONCLUSIONS

The results of this study have revealed that the potassium ferrocyanide treatment has good results if some conditions are fulfilled, as follows:

- it is a pretentious treatment to be applied only by authorized oenologists;
- microprobes should be taken for each batch of wine, and the theoretical and practical doses of potassium ferrocyanide should be rigorously calculated;
- longer contact (over 10 days) of wine with the ferrocyanide deposit should be avoided, as it decomposes under the action of organic acids in wine, releasing cyanide acid;
- particular importance should be given to filtration after the treatment, in order to separate fine ferric ferrocyanide suspensions;
- the ferric ferrocyanide residue must be disposed of in compliance with the environmental protection legislation;
- potassium ferrocyanide treatment does not apply to wines with an iron content lower than 5 mg/l; in order to obtain wines with low iron content, it is advisable to keep mash and wines in metallic containers protected with acid-resistant materials, so that the proportion of technological iron in wine is as low as possible.

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