

## **Spectrophotometric Determination of Free and Labile Iron(II) Concentration in White and Red Wines**

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**Abstract:** On the storage and treatment of wines it is of crucial importance to know as much as possible about the distribution of the total dissolved iron content among its different oxidation forms and their transformation process into one another. The applied method is suitable for the fast and simple determination of the wine's iron(II) content and it offers the possibility to investigate the circumstances of the iron(II) and iron(III) transformations.

### **Introduction**

One of the most significant fields of speciation analysis is food investigation with a special regard on the determination of the quantity of metal compounds which have different toxicities. Wine analyses require an exceptional circumspection, as wine compounds whose estimated number even exceeds ten thousand, form a complex system dissolved in water and alcohol whose equilibrium is permanently changing (Eperjesi et al. 1998).

The greatest number of previous measurements refer to the most examined lead. One of the trends deals with the determination of the especially toxic ethyl and methyl derivatives (Lobinski 1995), the other one deals with the so-called physical speciation (e.g. the separation of coarse disperse-, bound to colloids-, and dissolved lead compounds) (Eschnauer 1996). Similar investigations could easily be extrapolated to metals of crucial importance from the viewpoints of both physiology and enology (Murányi 1998).

The examination of iron distribution by the means of speciation analysis is of great importance from another aspect too. Only a small proportion (3-5 mg/L) out of the total metal content (10-50 mg/L) comes from the grape into the wine in a natural way, the rest might be considered as the result of the

enological technology (Murányi 1997a). Wines with high iron content (above 20 mg/L) show a tendency of precipitation which is a significant quality destroying factor. The above mentioned phenomenon is only caused by the separation of iron(III)-precipitate (Eperjesi et al. 1998). This is the reason why the proportion of iron(II) occurring in wines and the factors which influence their equilibrium are very important for us. Under the circumstances characteristic of wine the greatest amount of the dissolved iron is most likely to be present in the lower oxidation state, dissociated to a high extent. (Eperjesi et al. 1998). On the basis of what is already established, the determination could directly be carried out, by the means of photometry - without enrichment and separation from the matrix, provided that we can find a complex-forming reagent which complies with the following requirements:

- it should selectively form a complex with iron(II)
- the formed complex should be coloured
- the complex should have a high stability under the circumstances occurring in wines.

The well-known 2,2'-dipyridyl used for the determination of iron(II) proved to meet the above requirements, thus its application seemed to be obvious (Murányi 1997b).

## **Experimental part**

### **Sampling and sample preparation**

At speciation a problem of crucial importance is the constancy of the sample between sampling and measurement. It is especially advantageous in this case, that the applied complex-forming reagent maintains unchanged the iron(II), after the addition of 2,2'-dipyridyl its concentration does not decrease (Murányi 1997b).

Samples were taken from a depth of 100 mm under the surface of the liquid through a pipe made of silicone into two plastic bottles. 1 mL of 1% 2,2'-dipyridyl reagent solution was added to 10 mL of wine. Untreated wine sample was also collected. (This second fraction was essential for the determination of the total iron concentration as well as it is reference sample for photometric measurement.) Before further treatments both sample fractions were filtrated.

For the determination of the total iron concentration 25 mL of wine sample was evaporated on a water bath and afterwards it was atmospherically digested with the a mixture of 5 mL of cc nitric acid and 1 mL of 30% hydrogen peroxide solution. (This treatment with nitric acid and hydrogen-

peroxide had in most of the cases to be repeated in order to make the digestion complete.) After the digestion, the samples were dissolved in 0.1 M nitric acid solution and filled to 25 mL in volumetric flasks.

### Measurement parameters

Determination of iron(II) concentration was carried out by means of a Jasco V-530 UV/VIS spectrophotometer named at 522 nm. Reference solution was prepared by the addition of 1 mL abs. alcohol to 10 mL of wine. Calibration solutions (1 mg/L - 25 mg/L) were produced from freshly made iron(II) solution by setting pH value to 3 and the alcohol content to 10%.

The determination of the total iron concentration was carried out with a Pye Unicam SP 192 FAAS instrument at 248.3 nm in acetylene/air flame.

### Results, conclusions

Table 1 shows that the ratio of iron(II) to total iron concentration can be an indicator of the art of wine making (oxidative or reductive).

*Table 1. The ratio of iron(II)- to total iron concentration in wines made with different technologies*

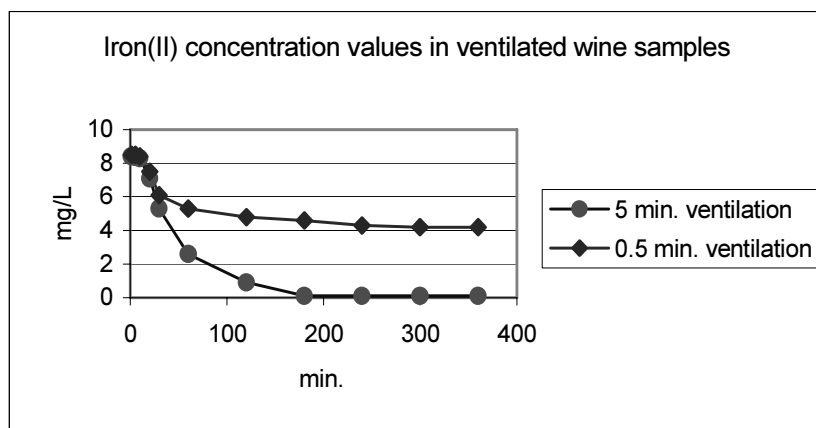
art of samples	Fe(II) (mg/L)		total Fe (mg/L)		Fe(II) (%)	
	min-max	average	min-max	average	min-max	average
Eger wines (reductive) n=10	4.5-12.6	8.3	4.7-13.2	8.6	95-98	96.5
Eger wines (oxidative) n=18	2.8-16.8	10.7	3.2-20	12.4	82-90	85
Tokay wines (oxidative) n=25	5.2-16.6	9.3	7.5-25.8	12.9	46-86	77

The above method seems to be suitable for the investigation of the factors influencing the equilibrium of iron in wines between its two oxidation states. Due to the fact that the system is so complex there is a need to carry out a large number of well-planned and controlled series of measurements.

The previous experiments show the air contact decreases the iron(II) proportion in wines to a great extent. This process has been attempted to be modelled under laboratory circumstances in order to refine the notions concerning the alterations of iron(II) concentration. Investigations have been performed with Zweigelt of Eger wine.

The ventilation of the wines was accomplished in a gaswasher, constant air current was produced with a pump. The duration of this treatment varied between 0.5 and 5 minutes, samples of 4 mL each were taken with an automatic pipette from the treated wine. Iron(II) concentration values in ventilated wine samples are shown in Figure 1.

Figure 1.



After a treatment longer than three or five minutes the concentration curve vs. time does not change to a considerable extent, i.e. this is the approximate time length needed to saturation with oxygen. As it is observable through a ventilation of adequate duration the iron(II) content of wines can totally be transformed into iron(III). This process proved to be completed in three to four hours.

Knowledge of this sort might turn out to be extremely useful to enologists, since these might lend a hand in predicting any changes occurring in wines during ventilation both in short and long run. The proportion of iron(II) and iron(III), on the other hand, is a good indicator of the oxidation state of wines, thus the obtained results may be expected to be successfully applicable in the research of this sort.

## References

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