

METHOD OF ANALYSIS FOR THE DETERMINATION OF HEAVY METALS FROM WINE

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Abstract

In this paper, the procedures were estimated to improve the reproducibility and selectivity of the method and determine the influence of different analytical parameters (pH, electrolyte composition, deposition time and potential, this ligands). Detection limit of copper in samples of white wine and red Blaj (Romania) was 2-4 ppm, reflecting a deviation of 1.5-2,0%. The results mentioned in this paper were compared with the results obtained using the classical method of atomic adsorption. The sensitivity of the method is twice smaller than the detection of Pb²⁺ ions.

Key words: analysis, heavy metals, products, wine

INTRODUCTION

Lead contamination is a consequence of wine with use of facilities of this metal in wine production [8,9]. The normal limit recommended for lead in wine is 200 mg/L [7], considerably higher than the maximum limit for drinking water in different countries, given the relative consumption of water and wine. Regarding the maximum admissible concentration of copper in wine, it must be kept below 0.3-0.5 mg / L [3].

In the recent years, the methods of "stripping" were increasingly and frequently used in the food industry for the control of trace metal ions both in food and in wine [1,4].

The main source of copper in wine is a consequence of the practice of adding copper sulphate (II) sulfide odor remover that emit. The large amount of residual copper is linked to an increased degree of oxidative be damaged, leading finally to brown coloring in wine, especially white wine [2,3]. Copper (II) may contribute to the wine disorder phenomenon which becomes visible only after bottling. Knowing the chemical forms of copper into the wine rather than knowledge of its total concentration may be the best indicator for the degree of deterioration of the wine.

The method involves two steps [4]:

- Stripping when oxidation occurs free ions or metal ions on the surface of mercury; current oxidation is proportional to the concentration of metal ions.
- Preconcentration, which consists of applying a constant reduction potential for a while, when there is accumulation of metal on the electrode surface adsorption of mercury: $Me^{n+} + e^{-} \rightarrow Me$ (Hg).

MATERIALS AND METHODS

To control ammeters can use a device connected to the computer, BAS 100W equipped with Controlled Growth Mercury Electrode (CGME West Lafayette, USA) and a portable analyzer for trace elements (PTEA-WAGTECH) equipped with carbon electrode vitreous (CV), covered with a fine film of mercury. For the determination of cyclic voltammetry it is necessary to use a classic three-electrode cell (E1-CV; EC-wire Pt ER Ag/AgCl). The results of the spectrophotometric and electrochemical control have been made with a UV-VIS device unique computer assisted β Helios.

The work was performed in two stages: in the first part was devised method stripping L71 and the second part was heel proper analysis

of the concentration of copper in commercial wines from Blaj.

Before the first use and at the beginning of each workday, the CV electrode was cleaned with an aqueous suspension of Al_2O_3 powder ($0.25 \mu m$) on a fabric polished and cleaned by sonication for 3 minutes. The experiments determined the concentration of copper ions which will be presented in details in the next paragraph.

RESULTS AND DISCUSSIONS

The optimization of the stripping method on synthetic solutions.

To improve the selectivity and reproducibility of the method (see right calibration Fig. 1) it is needed to follow the influence of mercury droplet size - Fig.2 and time of accumulation - Fig. 3, the current bit in synthetic wine solutions. The wine synthetic solution has the following composition: volume 12% ethanol solution, saturated potassium tartrate and brought to pH 3.2 with tartaric acid.

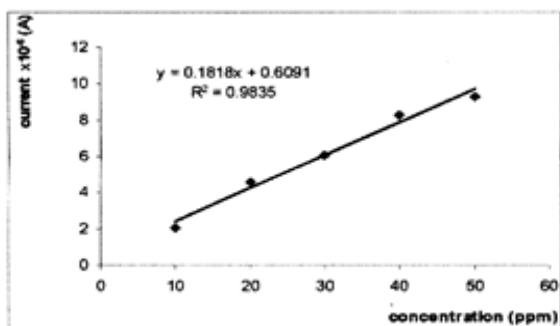


Fig. 1. The right calibration - Dimension Data polarography

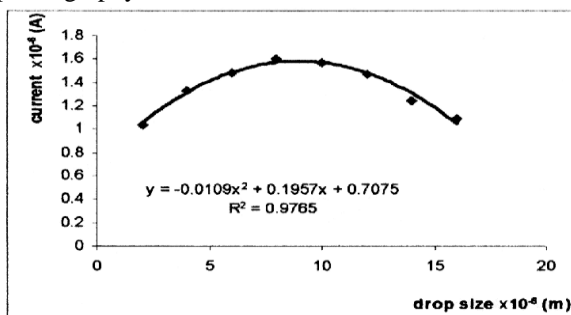


Fig. 2. Influence of mercury droplet size mercury droplet 6 microns; v 10 mVsec-1.

Reproducibility response of ammeters ($R_2 = 0.97$) corresponding to a standard deviation of 4.5% for 6 determinations. Addition is

described by the equation $y = + 0.7075 - 0,0109x^2 + 0,1957x$ and maximum current was obtained for mercury droplet size 8-10 μm .

Regarding the storage time, it can work at a value of 500 s thereof - Fig.3, depending also on the concentration of copper in wine.

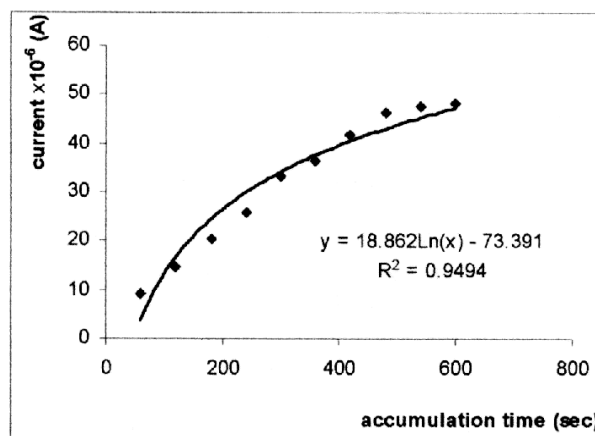


Fig. 3. The influence of time accumulation on the current

The detection limit for copper ion is 0.05 ppm ($R = 0.9992$), but in the presence of Pb^{2+} detection limit increases to 1.5 ppm.

Control of copper concentration in wines from Blaj

The potentiometers stripper was used to measure the concentration of labile and total copper in wine and tomatoes [5,6].

The conditions were optimized for a supporting electrolyte having the following composition: 1 mol / L HCl and 0.5 mol / L $CaCl_2$. It was noted that mercury oxidizes more convenient than oxygen, and to determine labile copper concentration it was necessary to change the agent.

It was observed that red wine "bind" added lead quickly, demonstrating that the wine has a great capacity to lead complex.

A similar effect was observed in case of white wine, but the degree of lead complexity was lower than for red wine.

The aim of this study was to examine the ability of stripping potentiometers as direct technique for determining in-situ labile copper concentration in wine.

Determination of copper in labile wine

The stripping curve was recorded as described above the total concentration of copper.

Quantification was achieved from a right calibration generated by introducing incremental additions of copper from a base model coming as the test sample.

Determination of total copper in white wine

The dilute wine (20 mL) containing about 50 mg/L copper was mixed with the electrolyte- 2.0 mol/L HCl, 1.0 mol/L CaCl₂ and 600mg/L Hg (II) - in the electrochemical cell.

An enrichment of 700 mV potential was applied 300-500 seconds, depending on the concentration of copper in the tested sample. There was no need for venting (removal of oxygen) as the oxidant was used major Hg (II).

After stripping, the electrode is at a potential of 100 mV for 15 seconds to clean and stabilize the new film of mercury. The potentiostatic stops and the stripping curve is recorded to the potential range of 900-100 mV.

Table 1. Total copper and labile white wine stripping analyzed by potentiometer and controlled via flam photometer

Wine type	AAS (mg/L)	Total Copper (mg/L)	The dilution factor of total	Labile Copper (mg/L)
Feteasca Alba	0.28+0.01 (5)	0.23 +0.01 (8)	8	0.18 +0.01(3)
Sauvignon		0.27 + 0.01 (7)	4	
Traminer	0.27+0.01 (8)	0.23 +0.01 (9)	20	0.18 ± 0.01 (2)
Riesling	0.69 + 0.05 (3)	0.65 + 0.02 (10)	20	
Pinot gris	0.64 + 0.01 (6)	0.53 + 0.03 (4)	8	0.52 ± 0.01 (3)
		0.67 + 0.01 (5)	4	

Table 1 presents the results for total copper determined in various wines using the optimized enrichment potential of 700 mV for 500 seconds. From the table it is observed that the sample dilution factor is an essential parameter of determination.

For a high dilution factor, the total copper concentration is underestimated by potentiometer stripping compared to the flam photometric AAS (Atomic Adsorption Spectrophotometry). Varying the use of additional cycles enrichment and enrichment/stripping for a short time, there were obtained improved results.

To overcome this dilemma, the dilution factor

was changed so that the concentration of copper in the test solution always be greater than 50 mg/L.

Under these conditions, for all wines, no significant differences at 5% results by potentiometer stripping and by flam photometer.

CONCLUSIONS

The methodology can be applied also for beer and other alcoholic beverages.

The stripping potentiometric analysis is a simple analytical procedure to monitor copper in wine.

The application of stripping potentiometers to determine the speciation is still limited, especially because the usual methodology requires the addition of high concentrations of Hg (II) as a chemical oxidant.

The stripping voltammetry was used for the anode (VSA) because the decomposition of the samples is often necessary to remove the interfering substances before the measurement step.

The concentration of copper in Traminer, Pinot Gris and Riesling exceeds the recommended limits (0.3-0.5 mg / L [2]).

As the need to monitor other metals in wine will probably increase in the future, it needs a simple analytical method that can simultaneously determine the content of lead and cadmium. The preliminary determinations (unpublished results) showed that this is possible.

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