

## ELECTROCHEMICAL METHODS DETERMINATION OF HEAVY METALS IN WINE BEVERAGE ACHIEVING ECOSANOGENE

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### Abstract

*In this work, we estimated reproducibility and procedures to improve the selectivity of the method and to determine the influence of different analytical parameters (pH, electrolyte composition, deposition time and potential, presence of ligands). Detection limit of copper in samples of white wine and red Blaj (Romania) is 2.4 ppm, with a deviation of 1.5-2,0%. The results were compared with the results by atomic adsorption classical method. The sensitivity of the method is two times smaller, Daton this Pb<sup>2+</sup> ions.*

**Key words:** wine, heavy metals, electrochemical methods

### INTRODUCTION

In recent years, methods of "stripping" were used increasingly frequently in the food industry for the control of trace metal ions both in food and in wine [2,7].

Lead contamination of wine is a consequence of using the facilities of this metal in wine [3,7]. Normal limit for lead in wine recommended is 200 mg / L [5], considerably higher than the maximum limit for drinking water in different countries, taking into account the relative consumption of water and wine. Regarding the maximum admissible concentration of copper in wine, it must be kept below the 0.3-0.5mg / L [6].

The main source of copper in wine is a consequence of practicing added copper sulphate (II) Removal that emit sulphurous odor. The large amount of residual copper is related to a high degree of damage to oxidants, which eventually lead to the brown coloring of wine, especially white wine [2,3]. Copper (II) may contribute to disorder wine, a phenomenon that becomes visible only after bottling occurs. Knowing the chemical forms of copper in the wine rather than knowing its total concentration may be the best indicator for the extent of damage to wine.

The method involves two steps [4]:

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

### MATERIALS AND METHODS

The work was performed in two stages: in the first part was devised method of "stripping" L71, and the second part was the actual frame analysis of copper concentration in commercial wines from Blaj.

Volt meter control to use a device connected to a computer equipped with 100W BAS Controlled Growth Mercury Electrode (CGME West Lafayette, USA) and a portable analyzer for trace elements (PTEA - WAGTECH) equipped with a glassy carbon electrode (CV), covered a thin film of mercury. To determine the cyclic volt meter was used classical three- electrode cell (El - CV, CE - Pt wire ER Ag / AgCl). Results electrochemical control was made spectro photometric metrically with a UV-VIS device unique computer assisted Helios β.

Before first use and at the beginning of each day of work, CV electrode was cleaned with an aqueous suspension of Al<sub>2</sub>O<sub>3</sub> powder (0.25 μm) on a polishing fabric and cleaned by ultrasonic for 3 minutes. Experimental part for determination concentration of copper ions will be detailed in the following.

## RESULTS AND DISCUSSIONS

To improve selectivity and reproducibility of the method (see right calibration, Fig. 1) The action of mercury droplet size - Fig.2 and storage time - Fig.3, the peak current in synthetic wine solutions. Synthetic wine solution has the following composition: (12% by volume of ethanol solution, saturated Potassium tartrate and brought to pH 3.2 with tartaric acid)

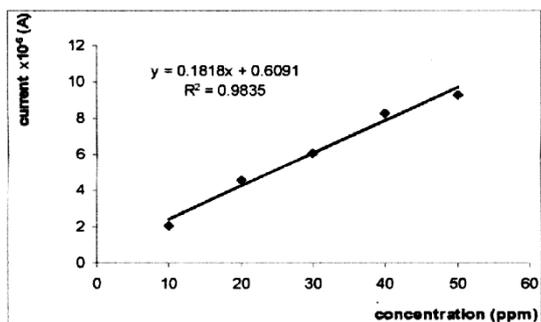


Fig.1. Calibration curve - polarographic data size

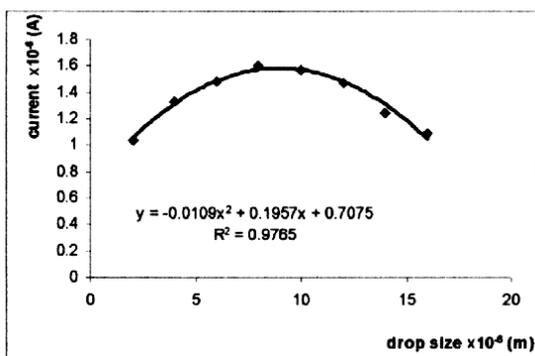


Fig.2. Influence of mercury droplet size

Reproducibility response Volt ( $R_2 = 0.97$ ) corresponds to a standard deviation of 4.5% to 6 determinations. Addition is described the equation  $y = -0,0109x^2 + 0.1957x + 0.7075$  and the current maximum 0,1957x was obtained for the mercury droplet size of 8-10 μm. Regarding storage time, it can work to its

value of 500 s - Fig.3, depending also on the concentration of copper in wine.

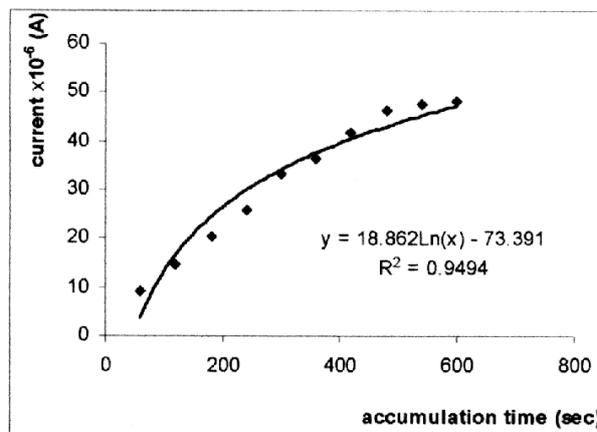


Fig.3. Influence of accumulation time on the peak current

Detection limit for copper ion is 0.05 ppm ( $R = 0.9992$ ), but in the presence of Pb<sup>2+</sup> detection limit increases to 1.5 ppm.

### Control of copper concentration in wines from Blaj

Potentiometric stripping was used to measure the concentration of labile and total copper in wine and tomatoes have.

Conditions were optimized for a supporting electrolyte having the following composition: 1 mol / L hydrochloric acid and 0.5mol / L CaCl<sub>2</sub>. It was observed that mercury is a convenient oxidant than oxygen, and to determine the labile copper concentration was necessary exchange agent.

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

A similar effect was observed intrication white wine, but the degree of Pb complexity was lower than in red wine.

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

### Determination of labile copper wine

Striped curve was recorded as described above the total concentration of copper. Quantification was performed from a right calibration generated by the introduction of incremental additions of copper to a model base wine as the test sample.

*Determination of total copper in white wine*

Dilute wine (20 mL) containing about 50 mg / L copper was mixed with electrolyte - 2.0 mol / L HCl, 1.0 mol / L CaCl<sub>2</sub> and 600 mg / L Hg (II) - in electrochemical cell (Table 1).

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

After execution stripedului electrode is at a potential of 100 mV for 15 seconds to clean and stabilize the new film of mercury. Potentiostatic stops and striped curve is recorded in the potential range of 900-100 mV.

Table 1. Total copper and white wine labile striped analyzed by potentiometer and controlled by flam photometric

Wine	AAS (mg/L)	Total cooper (mg/L)	Dilution factor	Labile cooper (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	

Note: We give the mean and 95% confidence limit. Number of determinations is given in parentheses

Detection limit for copper ion is 0.05 ppm (R = 0.9992), but the results are given in Table 1 to determine total copper in many wines have, using optimized enrichment potential of 700 mV to 500 seconds. From the table it is observed that the sample dilution factor is an essential parameter of determination.

For a high dilution factor, total copper concentration is underestimated by potentiometer flam photometric striped compared with AAS (Atomic Adsorption Spectrophotometry). Varying the enrichment and use of additional cycles of enrichment / striped with shorter enrichment times have not improved results.

To overcome this dilemma, the dilution factor was changed so that the concentration of copper in test sotutia always be greater than 50 mg / L. In these conditions, for all wines, no significant differences at the 5% mtre

results by potentiometer striped and the obtmute by flamfotometne.

**CONCLUSIONS**

Striped potentiometric analysis is a simple analytical procedure for monitoring copper in wines.

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

Striped volt meters was used for the anode (VSA) as the decomposition of the sample is often necessary to remove interfering substances prior to the measuring step.

Application of striped potentiometers to determine speciation is still limited, mainly because the usual method requires the addition of high concentrations of Hg (II) as a chemical oxidant.

The concentration of copper in Traminer, Pinot Gris and Riesling exceeds recommended limits (0.3-0.5mg / L [1]).

As the need monitoring other metals in wine will probably increase in the future, we need simple analytical methods that can simultaneously determine the content of lead and cadmium.

Preliminary determinations (unpublished results) have shown this to be possible.

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