

## ON CV-AAS DETERMINATION AND SPECIATION OF MERCURY IN WINE

Krste Tašev<sup>1</sup>, Irina Karadjova<sup>2</sup>, Ivan Boev<sup>3</sup> and Trajče Stafilov<sup>4\*</sup>

<sup>1</sup>State Phytosanitary Laboratory, Bul. Aleksandar Makedonski bb, 1000 Skopje, North Macedonia

<sup>2</sup>Faculty of Chemistry, University of Sofia, J. Bourchier 1, 1164 Sofia, Bulgaria

<sup>3</sup>Faculty of Natural and Technical Sciences, Goce Delčev University, Blvd. Krste Misirkov 10A, 2001 Štip, North Macedonia

<sup>4</sup>Institute of Chemistry, Faculty of Science, St. Cyril and Methodius University, POB 162, 1000 Skopje, North Macedonia;

\*corresponding author: [trajcest@pmf.ukim.mk](mailto:trajcest@pmf.ukim.mk)

### ABSTRACT

The possibilities of cold vapor - atomic absorption spectrometry (CV-AAS) for the determination and speciation of mercury in wine samples are critically discussed in the present study. In a first step, the direct determination of Hg using SnCl<sub>2</sub> and NaBH<sub>4</sub> as reducing agents is attempted. The influence of the type of reducing agent and its concentration, as well as the concentration of HCl on the absorbance signal of the different Hg species (Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>1+</sup>) is investigated. The results show that direct determination of both Hg species is possible: inorganic Hg can be selectively determined by using 0.04% NaBH<sub>4</sub> and 1 mol/l HCl directly in an untreated wine sample; both Hg species are determined simultaneously by using 0.9% NaBH<sub>4</sub> and 1 mol/l HCl again directly in an untreated wine sample. The recoveries obtained by using HCl at a concentration below 1 mol/l are lower than 85% which can be considered as evidence that the mercury in the wine sample is bound in some complex compounds. In the second step, a separation and preconcentration method for Hg determination in wine is proposed. The quantitative sorption of both Hg species was achieved by using Chelex 100 at pH 4. Quantitative elution of the Hg retained on the resin is possible with 2 mol/l HNO<sub>3</sub>. The limits of determination of the analytical procedure consist of Hg pre-concentration on Chelex 100 followed by CV-AAS measurement of eluted Hg, allows the determination of total Hg in all types of wine samples with their natural contents.

**Key words:** mercury, wine, determination, speciation, cold vapor - atomic absorption spectrometry

### INTRODUCTION

Mercury and its compounds are considered hazardous to health, and it is known that their toxicity depends strongly on the chemical form: organic mercury species are generally more toxic than inorganic mercury salts. According to the requirements of the Office International de la Vigne et du Vin (OIV), the mercury content in bottled wines should not exceed 5 µg/l. However, the natural Hg content in wines is far below this limit and its determination, even more, its speciation in wine samples is a real analytical challenge. Therefore, several analytical techniques are used for the quantitative determination of mercury in wine, including inductively coupled plasma - mass spectrometry (ICP-MS) (Perez-Jordan et al., 1999; Wu et al., 2007; Gao et al., 2012; Dressler et al., 2012), anodic stripping voltammetry (ASV) (Daniele et al., 1989; Zakharova et al., 1996); atomic fluorescence spectrometry (AFS) (Liang et al., 1994; Li et al., 2006; Han et al., 2007), ratiometric fluorescence sensor (Yang et al., 2020), ultrasound assisted-cloud point extraction with UV-VIS spectrophotometry (Zengin & Gürkan, 2022) or energy-dispersive (EDXRF) and total-reflection X-ray fluorescence

spectrometry (TXRF) with previous selective preconcentration/separation of Hg(II) ions using graphene oxide/thiosemicarbazide in dispersive micro-solid phase extraction (Musielak et al., 2022). Inductively coupled plasma mass spectrometry (ICP-MS) is also used to determine Hg in wine samples, with a prior dilution (1:1) in HNO<sub>3</sub> (1% V/V) (Perez-Jordan et al., 1999; Bianchi et al., 2003). Inductively coupled plasma atomic emission spectrometry (ICP-AES) has also been used to determine Hg in wine samples without sample preparation using calibration with a standard addition (Lee & Lim, 1999).

However, atomic absorption spectrometry (AAS) is the most commonly used technique for the determination of mercury in wine samples (Stafilov & Karadjova, 2009). One of the techniques used is electrothermal atomic absorption spectrometry (ETAAS). Sample preparation was performed by digestion in a microwave oven and extraction with ammonium pyrrolidine dithiocarbamate (ADPC) in methyl isobutyl ketone (MIBK). Palladium is used as a modifier and the detection limit is 0.2 µg/l (Karadjova et al., 2004). Cold vapor generation is widely used for the determination of mercury at trace levels because of its high selectivity, high sensitivity, and simplicity. The most common method for pretreating samples is to mineralize and vaporize them with nitric acid and hydrogen peroxide by heating them on a hot plate, which is both time and labor intensive Ferreira et al., 2015). Capelo et al. (2003) developed the method based on the generation of mercury vapor by cold vapor flow injection atomic absorption spectrometry (FI-CV-AAS) from white wine samples after ozonation as sample pretreatment. The detection limit and quantification limit are 0.5 and 1.7 µg/l, respectively. Non-chromatographic speciation and determination of Hg in wine by CV-AAS was proposed using a new ion-impregnated core-shell sorbent (Dakova et al., 2012). Cold vapor atomic fluorescence spectrometry (CV-AFS) is used for the direct determination of Hg in wine, where the reaction medium is HCl and ethanol is used as the reducing agent, with a detection limit of 0.07 µg/l (Li et al., 2006). CV-AAS was also applied in the speciation analysis of Hg in white and red wines carried out in a column solid-phase extraction scheme, whereby Hg(II) is quantified in column eluates AAS and MeHg is calculated by the difference between total Hg and Hg(II) (Zarco-Fernández et al., 2015).

The aim of this work is to develop a method for the direct determination of two different Hg species (Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>1+</sup>) in wine by applying cold vapor atomic absorption spectrometry (CV AAS) by its direct determination using SnCl<sub>2</sub> and NaBH<sub>4</sub> as reducing agents and by its separation and enrichment by solid phase extraction with Chelex 100 and Dowex 50W.

## MATERIALS AND METHODS

### Instrumentation

Cold vapor atomic absorption spectrometry (CV-AAS) measurements were performed using the Perkin Elmer FIMS 100 (Flow Injection Mercury System) mercury analysis system with AS 93 Plus autosampler and the Varian VGA 77 cold vapor system installed on the Varian 55 AAS. The FIMS 100 system has a mercury-specific light source and detector and does not require the use of a special atomic absorption spectrometer. All measurements are performed on the basis on the peak area. The standard gas-liquid separator (GLS) of FIMS 100 is made of polymethylpentene with an internal volume of 2.15 ml and PTFE membrane. The optimal instrument parameters for FIMS 100 and VGA 77 are given in Tables 1 and 2.

### Standard solutions and reagents

Reagents with analytical grade were used. Basic standard solution for Hg with a mass concentration of 1000 µg/mL Hg<sup>2+</sup> (AAS standard solution), the solution was prepared by dissolving methylmercury chloride, CH<sub>3</sub>HgCl, in water (Sigma-Aldrich Laborchemikalien, Germany). Operating standards were prepared weekly and stored in a refrigerator at 4°C.

The sodium tetrahydridoborate solution, NaBH<sub>4</sub> (Fluka) (0.5% *m/V* in NaOH (0.1% *m/V*) was prepared daily. Tin(II) chloride solution was prepared by dissolving SnCl<sub>2</sub>·H<sub>2</sub>O (1% *m/V*) in 3% (*V/V*) HCl before use.

Table 1. Optimal instrumental parameters FIMS 100 measurements

Parameter	Setup		
Wavelength	253.7 nm		
Signal	AA (peak area)		
Integration	19 points		
Baseline offset correction time (BOC time)	2 s		
Reading delay	0 s		
Reading time	25 s		
The volume of the pits for the sample	500 µL, PTFE tube, 1 mm i.d., 64 cm		
Pipeline for taking on the sample	tygon tube, 1.52 mm i.d., 10.5 ml/min at 120 rpm		
Carrier pipe (acid)	tygon tube, 1.52 mm i.d., 11 ml/min at 120 rpm		
Reduction pipeline	tygon tube, 1.14 mm i.d., 6,5 ml/min at 120 rpm		
Waste from GLS	tygon tube, 3.18 mm i.d., 18.5 ml/min at 120 rpm		
Reactor	PTFE tube, 1.3 mm i.d., 100 cm		
Argon flow	125 ml min <sup>-1</sup>		
Optimization of FIMS <sup>®</sup> programme			
Step	Time/s	Pump speed/rev/min	Valve position
Pre-charge	2	120	Charging
1	15	120	Charging
2	20	120	Injection

i.d.- internal diameter

Table 2. Instrumental parameters for VGA 77 CV-AAC

Parameter	
Lamp	Hg Varian hollow cathode lamp
Wavelength	253.7 nm
Spectral slit	0.5 nm
Integration time	3 s
Reading delay	40 s
Number of repetitions	3
Quartz tube temperature	20-800°C
Flow of the sample	7 ml/min
Flow of the acid solution	1 ml/min
Flow of the solution from the reduction solution	1 ml/min

### Sample preparation

Wine samples were analysed directly for Hg and CH<sub>3</sub>HgCl, i.e., known volumes of Hg and CH<sub>3</sub>HgCl solutions ranging from 0.2–1 µg/l were added (spiked) to different types of wine samples. Inorganic Hg species were determined by using 0.04% NaBH<sub>4</sub> and 1 mol/l HCl directly in untreated wine samples. The two Hg species were determined simultaneously using 0.9% NaBH<sub>4</sub> and 1 mol/l HCl again in untreated wine samples. The same procedures were repeated using a 1% SnCl<sub>2</sub> solution. In a second step, the separation and preconcentration of As was performed using two types of sorbents, Chelex 100 and Dowex 50W. Twenty-five

milliliters of wine were preconcentrated and the two Hg species were quantitative separated using Chelex 100 at a pH close to the original pH 4 of the wine.

## RESULTS AND DISCUSSION

### Direct determination of Hg

#### *Effect of acid*

In the development of the method for the determination of Hg and CH<sub>3</sub>HgCl in wine samples with CV-AAS, optimization of the reaction medium (the concentration of HCl) and the reducing agents (NaBH<sub>4</sub> and SnCl<sub>2</sub>) was performed. The optimization was performed with a standard aqueous solution with an Hg concentration of 1 ng/l and with wine samples (red and white wine) with a standard addition of 1 ng/l. The HCl concentration ranged from 0.005 mol/l to 2 mol/l (Figure 1). As can be seen from Figure 1, the absorbance signal of the wine samples at low HCl concentrations is slightly lower than of the water standard, but at concentrations of 0.5 mol/l and 1 mol/l the signals are equal to that of the water standard of 1 ng/l Hg. It should be emphasized that the HCl concentration is very critical for the determination of Hg in wine. The analytical yield obtained with HCl at a concentration below 1 mol/l is less than 85%, which can be considered as an evidence that the mercury in the wine samples is bound in complexes (together with proteins, polyphenols, organic acids, etc.).

#### *Effect of the reducing agent (NaBH<sub>4</sub>)*

The effect of the content of NaBH<sub>4</sub>, used as a reducing agent was studied at 0.004%; 0.02% and 0.1%, with a concentration of 0.1 mol/l; 0.5 mol/l, 1 mol/L and 2 mol/l HCl (Figure 2). From Figure 2, it can be seen that a relatively low absorbance signal for the standard of 1 ng/l Hg was obtained at a low content of NaBH<sub>4</sub> at HCl concentrations of 0.1 mol/L; 0.5 mol/l, 1 mol/l, and 2 mol/l. With increasing NaBH<sub>4</sub> content (0.1%), the signals increase significantly. Therefore, HCl concentration of 0.5 mol/l and NaBH<sub>4</sub> content of 0.4% were chosen as the optimal parameters for further work. Under these conditions, the influence of the matrix effects was determined.

#### *Effect of the matrix*

To assess the influence of the matrix, the slope of the calibration curves of the water standard of 1 ng/l Hg and 1 ng/l CH<sub>3</sub>HgCl is compared with different types of wine with a standard addition of 1 ng/l Hg and 1 ng/l CH<sub>3</sub>HgCl (Table 3). From the slope of the curves (Table 3), it can be concluded that the determination of Hg<sup>2+</sup> in wine at an HCl concentration of 0.5 mol/l and 1% SnCl<sub>2</sub> can be performed with CV-AAS, and the determination of CH<sub>3</sub>HgCl at 0.5 HCl mol/l and 0.4% NaBH<sub>4</sub> can be performed with CV-ICP-AES.

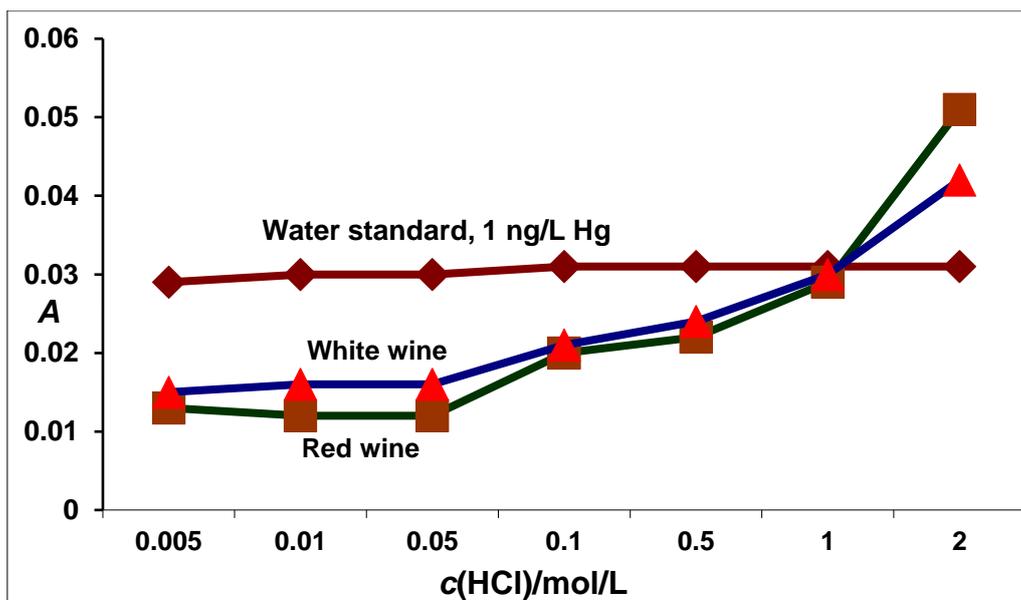


Figure 1. The effects of HCl concentration (at 0.4 % NaBH<sub>4</sub>) on the absorption signals in water solution containing 1 ng/l Hg, and wine (red and white).

(■) – red wine with 1 ng/l Hg, (▲) – white wine with 1 ng/l Hg and (◆) – water solution with 1 ng/l Hg

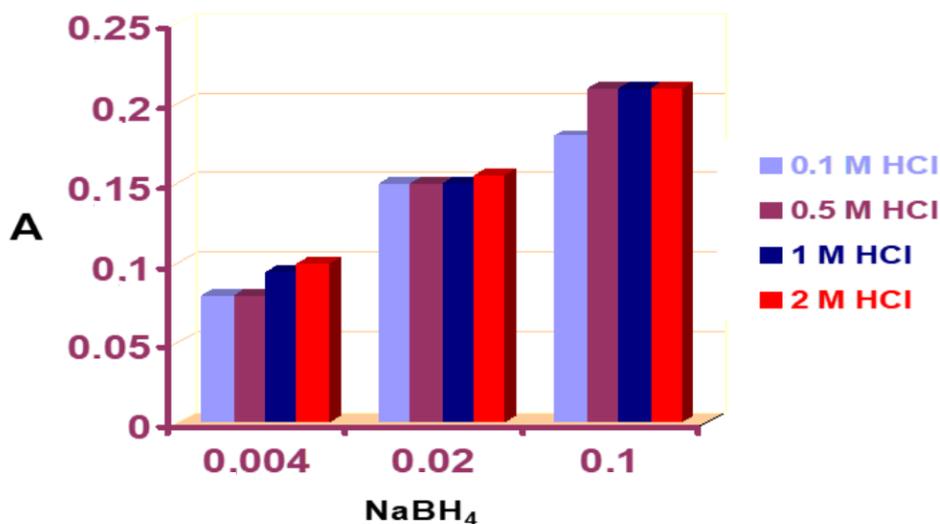


Figure 2. Effect of the content of NaBH<sub>4</sub> (in %, *m/V*) mol/l) in different concentrations of HCl on the absorbance of Hg in wine samples containing 1 ng/l Hg.

Table 3. Slope of calibration curves for the determination of Hg<sup>2+</sup> and CH<sub>3</sub>HgCl in wine and water samples using CV-AAS and CV-ICP-AES

Species (sample)	0.5 HCl mol/l; 0.4 % NaBH <sub>4</sub>		0.5 mol/l HCl; 1% SnCl <sub>2</sub>	
	CV-AAS	CV-ICP-AES	CV-AAS	CV-ICP-AES
Hg <sup>2+</sup> (wine)	0.025±0.003	48.7±0.5	0.025±0.002	49.3±0.3
Hg <sup>2+</sup> (water)	0.029±0.002	51.7±0.4	0.028±0.003	52.4±0.4
CH <sub>3</sub> HgCl (wine)	0.016±0.002	47.6±0.5	0.002±0.001	11.7±0.7
CH <sub>3</sub> HgCl (water)	0.019±0.002	50.7±0.4	0.003±0.003	12.7±0.7

The results of CV-AAS are compared with those obtained with CV-ICP-AES. The ratios of the slopes of the calibration curves for the determination of  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{HgCl}$  using CV-AAS and CV-ICP-AAS are given in Table 4. From the results in Table 4, it can be seen that there are no significant obstacles in the determination of Hg under the reaction conditions of 0.5 HCl mol/l and 0.4%  $\text{NaBH}_4$ , from which it can be concluded that the calibration can be performed with water standards.

Table 4. Ration of the slopes of the calibration curves (*b*) for the determination of  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{HgCl}$  using CV-AAS and CV-ICP-AAS

Ratio	0.5 HCl mol/l; 0.4 % $\text{NaBH}_4$		0.5 mol/l HCl; 1% $\text{SnCl}_2$	
	CV-AAS	CV-ICP-AES	CV-AAS	CV-ICP-AES
$b[\text{Hg}^{2+}(\text{wine})]/b[\text{Hg}^{2+}(\text{water})]$	0.86	0.94	0.89	0.94
$b[\text{CH}_3\text{HgCl}(\text{wine})]/b[\text{CH}_3\text{HgCl}(\text{water})]$	0.84	0.93	-	0.92

### Determination of Hg after preconcentration with solid phase adsorption

Two types of adsorbents were used in the enrichment of Hg in wine: Chelex 100 and Dowex 50W. 25 mL of wine with a standard addition of 1 ng/mL was passed through the columns containing the listed Hg sorbents and a water standard for comparison, and the Hg concentration in the eluent was 1 ng/mL. Several different acids with different concentrations were used as eluents and very good results were obtained by using 4 mol/l nitric acid solution (Table 5).

Table 5. The influence of the eluent concentration on the elution recovery

Eluent	4 mol/l HCl	2.5 mol/l $\text{HNO}_3$	4 mol/l $\text{HNO}_3$	1 % thiourea in 2 mol/l HCl
Elution recovery, %	40±3	84±2	> 100	11±5

Quantitative elution of the two forms of mercury ( $\text{Hg}^{2+}$  and  $\text{CH}_3\text{HgCl}$ ) was achieved using aqueous solutions for both adsorbents. The columns filled with Chelex 100 as adsorbent were found to be more successful than the columns filled with Dowex 50W-X8 in the determination of  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{HgCl}$  in the wine matrix. The degree of adsorption is directly dependent on the pH of the medium (Table 6). It was found that the conditioning of the column was well recovered using acetate buffer with pH 4.5.

Table 6. The influence of pH on the recovery of adsorption

pH	3.0	4.0	4.5	5.0
Adsorption recovery for water sample, standard addition of 1 ng/ml of Hg, %	90±2	95±2	>99	>99
Adsorption recovery for wine sample, standard addition of 1 ng/ml Hg, %	80±3	85±3	99±2	-

### Influence of Fe, Cu and $\text{HNO}_3$ on the absorption signal after elution

Among the heavy metals in wine, iron and copper are the most abundant (Stafilov & Karadjova, 2009). In order to investigate the possible influence of the presence of these two elements in the wine samples on the Hg signal in the determination with CV-AAS, the determination of the Hg absorption signal was performed with two reducing reagents 0.04%  $\text{NaBH}_4$  and 1%  $\text{SnCl}_2$  at different concentrations of Fe and Cu. Thus, Fe concentration ranged

from 2 mg/mL to 50 mg/mL, Cu concentration ranged from 0.5 to 20 mg/mL, and HNO<sub>3</sub> concentration ranged from 0.5 to 4 mol/l. The absorption signal was monitored at an Hg concentration of 1 µg/mL obtained after elution (Tables 7 and 8). From the results presented in Tables 7-9, it can be concluded that there is no effect on the Hg absorption signal when the concentration of Fe, Cu, and HNO<sub>3</sub> is below 10 mg/mL, 1 mg/mL, and 2 mol/l, respectively, when both reduction agents are used.

Table 7. Influence of the iron and copper concentrations on the absorbance signal for 1 µg/mL Hg using different reducing agents (0.04 % NaBH<sub>4</sub> and 1 % SnCl<sub>2</sub>)

Fe, mg/mL	Reduction agent		Cu, mg/mL	Reduction agent	
	0.04 % NaBH <sub>4</sub>	1 % SnCl <sub>2</sub>		0.04 % NaBH <sub>4</sub>	1 % SnCl <sub>2</sub>
0	0.031	0.030	0	0.031	0.031
-	-	-	0.5	0.031	0.031
-	-	-	1	0.030	0.029
2	0.031	0.030	-	-	-
5	0.031	0.029	5	0.029	0.027
10	0.030	0.028	-	-	-
-	-	-	20	0.028	0.020
50	0.029	0.020	-	-	-

Table 8. Influence of the concentration of HNO<sub>3</sub> on the absorbance signal for 1 µg/mL Hg using different reducing agents (0,04 % NaBH<sub>4</sub> and 1 % SnCl<sub>2</sub>)

HNO <sub>3</sub> , mol/l	Reduction agent	
	0.04 % NaBH <sub>4</sub>	1 % SnCl <sub>2</sub>
0.5	0.031	0.029
1	0.031	0.029
2	0.032	0.028
2.5	0.031	0.026
3	0.029	0.022
4	0.028	0.020

Table 9. Analytical figures of merit in the determination of Hg in wine

Procedure	LOD, µg/l	LOQ, µg/l	RSD, %
Direct CV-AAS	0.08	0.20	2-5
SFE-CV-AAS	0.02	0.05	4-10

The results for the limit of detection (LOD) and limit of quantification (LOQ) for direct Hg determination in wine samples by CV-AAS, as well as by concentration with solid phase extraction and CV-AAS (SPE-CV-AAS), are shown in Table 9. In order to determine the precision (both within a determination series and between the different series with three consecutive measurements), parallel measurements of Hg concentration in wine samples were also performed. The relative standard deviation (RSD) was found vary between 2% and 5% for indirect determination with CV-AAS and between 4% and 10% for Hg determination after solid phase extraction and CV-AAS.

### Analysis of real wine samples for the determination of Hg with CV-AAS

In the analysis of real wine samples from the market in North Macedonia (Tikveš vinery) and Bulgaria (Menada vinery), the Hg concentration in more than 50% of the samples was below than the LOD for direct determination with CV-AAS. In all samples analysed, the concentration of CH<sub>3</sub>HgCl was below the detection limit. Table 10 shows comparative results for the determination of total Hg concentration using solid phase preconcentration (SPE-CV-AAS) and with CV-AFS in 5 white and red wines from North Macedonia (Tikveš vinery) and one from Bulgaria (Menada vinery). From these results, it can be seen that the mercury concentration in the wine samples ranged from 0.11 µg/l to 0.31 µg/l which is far from the OIV allowable limit for Hg in wine of 5 ng/ml.

Table 10. The comparative Hg concentration determined by SPE-CV-AAS and CV-AAS in different wine samples from North Macedonia and Bulgaria

Wine	Total content of Hg, µg/l	
	SPE-CV-AAS	CV-AFS
Cabernet Sauvignon (black)*	0.22±0.04	0.21±0.01
Sauvignon Blanc (white)*	0.15±0.02	0.12±0.02
Chardonnay (white)*	0.11±0.02	0.13±0.01
Pinot Noir (black)*	0.29±0.03	0.31±0.02
Merlot (black)*	0.18±0.02	0.19±0.01
Menada (white)**	0.28±0.03	0.26±0.02

\* Tikveš vinery, North Macedonia

\*\* Menada vinery, Bulgaria

## CONCLUSION

It was found that direct determination of both Hg species (Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>1+</sup>) in an untreated wine sample is possible: inorganic Hg can be selectively determined by using 0.04 % NaBH<sub>4</sub> and 1 mol/l HCl; both Hg species are determined simultaneously by using 0.9 % NaBH<sub>4</sub> and 1 mol/l HCl. In the second step, a separation and preconcentration method is used for the determination of Hg in wine. It was also found that quantitative sorption of both Hg species was achieved by using Chelex 100 at an almost natural pH 4 in wine after elution with 2 mol/l HNO<sub>3</sub>. The limits of determination of the analytical procedure consist of a preconcentration of Hg on Chelex 100 followed by a CV-AAS measurement of eluted Hg, which allows the determination of total Hg in all types of wine samples at their natural content.

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