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ON THE PROBLEMS OF THE ETAAS DETERMANATION OF ARSENIC IN WINE

J. CVETKOVIC[1], S. ARPADJAN[2], I. KARADJOVA[2], T. STAFILOV[3]

[1] *Institute of Agriculture, Blvd. A. Makedonski b.b., 1000 Skopje, Macedonia*
[2] *Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*
[3] *Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia*

Abstract: The problems for ETAAS determination of arsenic in wines arise due to its different thermal behavior in the graphite furnace in different wines. The heating program conditions, the absorbance signal profiles, the amount of different chemical modifiers and the sample pretreatment procedure were optimized to perform the calibration with aqueous standard solutions independent on the type of the analyzed wine. Best recovery and repeatability were obtained for 5 μg Pd as matrix modifier and atomization from wall. On using this amount of Pd modifier, the pyrolysis and atomization temperatures are 1300 and 2600 °C, respectively. The white wines can by analyzed directly, for red wines a preliminary wet mineralization with a mixture of HNO_3 and H_2O_2 is necessary. The proposed method permits the determination of 5 μg l^{-1} As (n = 12, 6SD). The relative standard deviation ranged between 3 and 9% (10–50 μg l^{-1} As wine). The arsenic content in Macedonian and Bulgarian wines ranged between 6 and 50 mg l^{-1} for white and between 8 and 85 mg l^{-1} for red wines.

Keywords: wine, arsenic, ETAAS, determination.

INTRODUCTION

Many papers concerning the determination and speciation of arsenic have been published because of its high toxicity and the efforts to clarify its toxicity and sub-lethal effects. Arsenic is found in its various forms (inorganic As, methylated species of As, arsenobetaine, arsenocholine, arsenosugars) in food products, in biological and environmental materials at trace and ultratrace levels [1–11]. Traditionally, the hydride generation atomic spectrometry is the official method for determining As in wines and

beverages [10, 12, 13]. However, only arsenic species that form volatile hydrides can be measured in this manner. To insure the availability of As for hydride generation a combination microwave digestion-dry ash sample preparation is proposed [7].

Although the extensive use of the inductively coupled plasma mass spectrometry (ICP-MS) for determining As in a wide range of materials including wines [8, 14], the electrothermal atomic absorption spectrometry (ETAAS) is still advantageous because of the sensitivity, easy operation, and availability in many laboratories. The wine sample can be injected direct into the graphite furnace, but the quantitative detection of arsenic by ETAAS is prone to errors owing to uncontrolled matrix interferences in spite of the use of matrix modifiers. These interferences observed depend on many factors as type of wine, applied wine processing protocol, ETAAS instrumentation. It is therefore of interest to study the conditions under which ETAAS gives quantitative recovery for total arsenic in all kind of wines independent on the used viticultural and manufacturing processes. The aim of this paper is to optimize the experimental conditions for reliable ETAAS determination of total arsenic in wines with satisfactory high recovery, high sensitivity, interference free measurement, calibration against aqueous standard solutions, simplified sample preparation procedure. A Varian instrument for ETAAS determination of As in wine was investigated in detail because this instrument is more sensitive to wine matrix interferences in comparison to Perkin-Elmer instruments.

EXPERIMENTAL

Instrumentation. A SpectrAA-880 Varian atomic absorption spectrometer with a GTA-100 graphite furnace was used. A hollow cathode lamp was applied to take measurements at the 193.7 nm As line. Pyrolytic graphite coated graphite tubes and pyrolytic graphite L'vov platform were used as atomizers. Peak areas of the absorption signals were used for quantification.

Reagents. All reagents used were of analytical-reagent grade or higher purity. Arsenic stock solution (arsenic acid in nitric acid 0.5 mol l^{-1}, Merck) with concentration 1g l^{-1} As was used for daily preparation of working standard solutions by appropriate dilution. As matrix modifier 10 g l^{-1} Ag as $AgNO_3$ (purified by recrystallization) and 1 g l^{-1} Pd (palladium standard solution, Merck) were used. Doubly distilled water was used throughout.

Commercially available 0.7 l bottled wines from Macedonia and Bulgaria were analyzed.

Sample preparation. To validate the results obtained by direct analysis of wine samples, a 10.0 ml portion of the sample was treated with 1 ml of 65 % (v/v) HNO_3 and 2 ml of H_2O_2 in a borosilicate beaker, covered with a watch glass. Than the samples were heated at 120 °C on a sand bath till clearness. If necessary, for red wines aliquots of H_2O_2 were additionally added until the solution remained transparent and clear. The watch glass was removed and the sample was evaporated near to dryness. The residue was dissolved in 10.0 ml 0.2 % HNO_3 .

RESULTS AND DISCUSSION

MATRIX MODIFICATION

Palladium and silver in various concentrations were studied as chemical modifiers for determination of arsenic in wine. Aliquots of different wine samples were spiked with 10—50 mg l^{-1} of As. A sample volume of 10 ml together with 10 ml modifier solution were injected in the furnace and the respective peak areas for unspiked and spiked samples were recorded starting the temperature program given in Table 1.

Table 1

Temperature programs for ETAAS determination of As in wine

Step	Temperature, °C	Time, s	Argon flow, l min^{-1}
Drying			
1	85	5	3
2	95	40	3
3	120	10	3
Pyrolysis			
4	vary (900—1500)	5	3
5	vary (900—1500)	2	3
6	vary (900—1500)	2	0
Atomization			
7	vary (2300—2700)	1	0
8	vary (2300—2700)	2	0
Cleaning			
9	2700	2	3

The recovery (R, %) was calculated from:

$$R(\%) = \frac{A_{wine+As} - A_{wine}}{A_{As}} \cdot 100 \ .$$

where:

$A_{wine + As}$ — the absorption signal for As for spiked wine sample;

A_{wine} — the absorption signal for As in wine;

A_{As} — the absorption signal for As in aqueous solution with the same concentration for As as the added one to the wine sample.

The effect of the masses of palladium and silver on the arsenic recovery for white and red wines is shown in Fig. 1. As long as for white wines the addition of 5 μg Pd leads to quantitative recovery of As independent on the wine type, for red wines the maximum recovery achieved is about 50%. The recovery for As when red wines are directly injected into the graphite furnace depends on the type of the analyzed wine (recovery range 15–50%) and even the matrix modification does not help to overcome the matrix interferences problems. The accurate quantitative determination of As in red wines

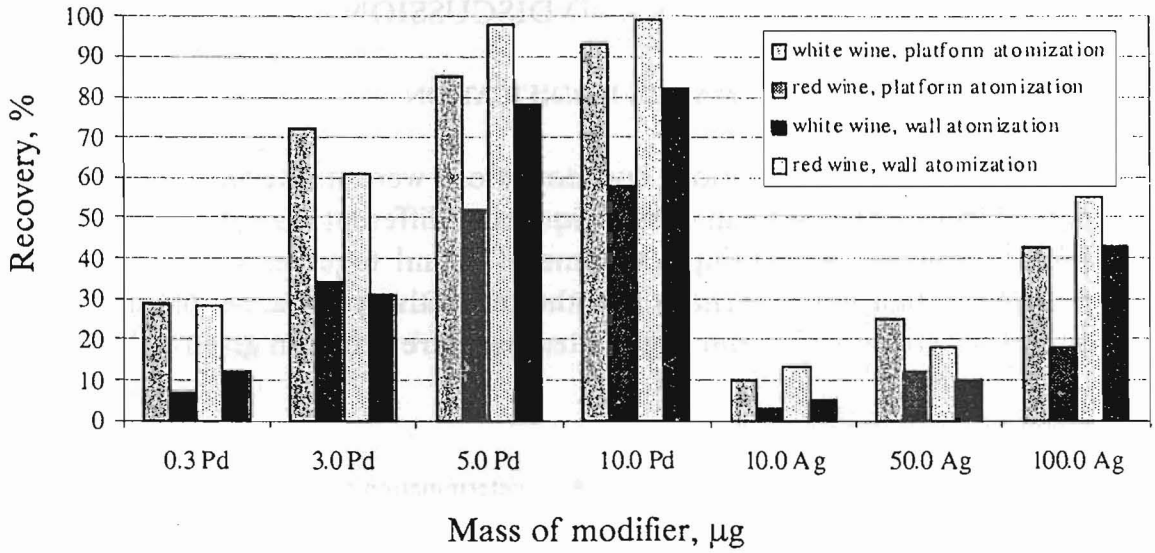

Fig. 1. The recovery for As in dependence of the mass of the matrix modifier applied

requires preliminary sample digestion with HNO_3-H_2O_2 mixture as described in sample preparation procedure. After this wet mineralization and matrix modification with 5 µg Pd recoveries higher than 95% can be achieved for As independent on the type of the analyzed red wine.

PYROLYSIS AND ATOMIZATION TEMPERATURE CURVES

The thermal behavior of As in white wine, directly injected into the atomizer is identical to that for As in red wine after wet mineralization of the sample. The pretreatment and atomization curves for As in wine in the case of wall and platform atomization are presented in Fig. 2 (5 µg Pd and 100 µg Ag as modifier). The maximum loss-free pyrolysis temperature for As when atomized from wall is 1300 °C with Pd modifier and 1100 °C with Ag modifier. In the case of platform atomization pretreatment tempera-

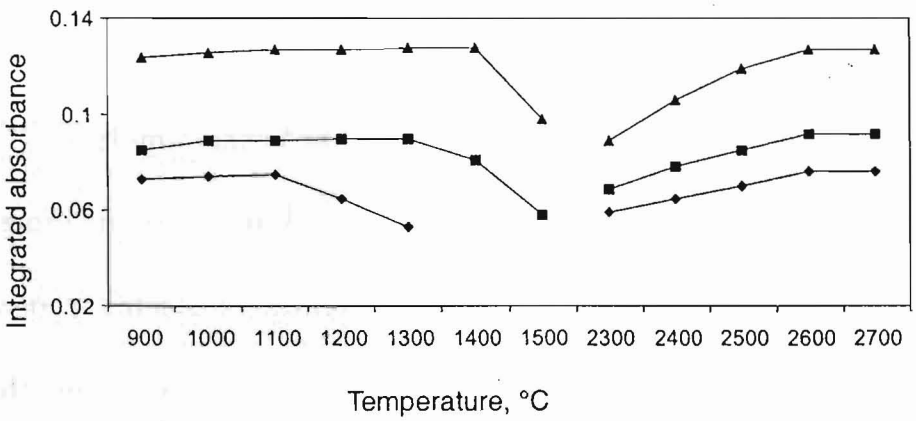

Fig. 2. Pretreatment and atomization curves for As: • — 100 µg Ag, wall atomization; ■ — 5 µg Pd, wall atomization; ▲ — 5 µg Pd or 100 µg Ag, platform atomization

ture of 1400 °C can be used for loss free determination of arsenic with the both modifiers. The optimum atomization temperature in all cases is 2600 °C.

WINE ANALYSIS

The proposed method was applied to the determination of total arsenic content in different white (12 samples) and red (28 samples) wines produced in Macedonia and Bulgaria. The optimized experimental conditions can be summarized as follows:

Atomizer:	pyrolytic graphite coated graphite tube
Injected volume:	10 ml
Modifier:	10 ml 500 ppm Pd
Sample pretreatment:	
White wine	direct measurement
Red wine	digestion with $HNO_3 + H_2O_2$
Pretreatment temperature:	1300 °C
Atomization temperature:	2600 °C
Calibration:	aqueous standard solutions

The calibration was performed against aqueous standard solutions for As in the concentration range 5–100 μg l^{-1} As. Recovery studies for 10 and 50 μg l^{-1} of As added to different wine samples showed acceptable results (95–100%). The comparison between the results obtained for white wines analyzed direct and after wet mineralization showed no significant difference. Comparing the results obtained for five different wine samples with those from hydride generation AAS after $HNO_3 - H_2O_2$ digestion tested the accuracy of the method in addition. The comparative results are presented in Table 2. Comparison by the *t*-test of the results provided by the two methods (ETAAS and HG-AAS) revealed no significant differences at the 95 % confidence level. The quantification limit calculated according to the IUPAC guidelines is 5 μg l^{-1} As in wine. The relative standard deviation ranged from 3% to 9% for the concentration range 10–50 μg L^{-1} As.

Table 2

Comparative results for As in wine determined by ETAAS (n = 4) and HG-AAS (n = 4); SD-standard deviation; w — white wine, r — red wine; n — number of parallel determinations.

$t_{(P=0.95;\, f=6)} = 2.45$

Sample	ETAAS	SD, μg l^{-1} As	HG-AAS	SD, μg l^{-1} As	t
Rajnski Rizling Bovin (w)	53	1	51	2	1.89
Rizling Bitola (w)	27.1	0.8	25.3	1.8	1.96
Muskat Hamburg Bitola (r)	16	0.6	16.8	0.9	1.51
Alexander Bovin (r)	12.5	0.9	12.2	0.6	0.57
Venus (r)	10.1	0.9	9.8	0.7	0.53

The arsenic content in the analyzed 20 Macedonian and 20 Bulgarian wines varied as follows:

White wines Macedonia:	7–53 μg l^{-1} As
White wines Bulgaria:	6–24 μg l^{-1} As
Red wines Macedonia:	8–85 μg l^{-1} As
Red wines Bulgaria:	8–42 μg l^{-1} As

The results for As agree well with the most recent values obtained by other workers [15]. The concentrations are far below 0.2 mg l^{-1} that is specified by a number of countries as permitted concentration in wine.

CONCLUSION

The problems in the ETAAS determination of As in wine could be overcome using 5 μg Pd as matrix modifier, atomization from wall and aqueous standard solutions for calibration. The white wines can be analyzed directly, in the case of red wines a preliminary digestion of the samples with a HNO_3 — H_2O_2 mixture is necessary.

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