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Determination of arsenic and antimony in wine by electrothermal atomic absorption spectrometry

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Abstract. The determination of As and Sb in red and white wines by graphite furnace Zeeman atomic absorption spectrometry is described. The wine can be analyzed directly, provided a matrix modifier is used. Three modifiers have been tested; palladium nitrate was found to be superior to nickel nitrate and nickel sulphate. The sensitivity and detection limits were improved when the wine was decomposed with a mixture of nitric acid and hydrogen peroxide prior to analysis. Two different decomposition systems (Tecator and Bethge) were employed without loss of analyte. The concentration of As and Sb was found to be below 10 μg/L for all the wine samples. The standard addition method was used for the quantitative determination.

Introduction

Little has been published concerning As and Sb in wine, but uncontaminated wine probably contains only a few μg/L of these elements [1]. Therefore, a very sensitive method is required for this analysis. A classical method that has been used for the determination of As in wine is based on the generation of the hydride, followed by the reaction with silver diethyldithiocarbamate and measurement of the As-complex by molecular absorption [2, 3]. The detection limit of this method is about 10 μg/L, which is probably insufficient for most wine samples. In the more recent studies of As in wine, hydride generation atomic absorption spectrometry has been employed [4–7]. There appears to be no recent results published for Sb in wine; Interesse et al. [8] found that the concentration of Sb was below the detection limit of ICP-AES. The hydride technique normally requires a decomposition of the wine sample, which is time consuming and may lead to high blank values or loss of the analyte. Graphite furnace atomic absorption spectrometry (GFAAS) should be an attractive alternative to the hydride generation technique, because the wine can be injected directly in the graphite furnace, as will be shown in this paper. The determination of As in wine by GFAAS has been attempted [9, 10], but few results were reported.

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Experimental

Apparatus, reagents and samples

A Perkin Elmer model 5000 Zeeman atomic absorption spectrometer and a HGA 400 graphite furnace were used. An electrodeless discharge lamp was used for As, and a hollow cathode lamp for Sb. The analytical signal corrected for background and the background signal were recorded with a Perkin Elmer 3600 data system and an Anadex DP 9500 B Printer. Pyrolytically coated graphite tubes from Applied Optics AB (Sweden) were used. The atomization cell was purged with argon. Solutions were transferred to the furnace with plastic-tipped micropipettes. For decomposition of the wine, a Tecator System 6 with six 250 mL borosilicate glass tubes and an Autostep 1012 Controller were used. A laboratory-made Bethge apparatus [11] with heating mantle was also used.

All reagents were of analytical grade. Standard solutions were prepared by dilution of 1000 ± 0.5 mg/L stock solutions (Spectrascan, Norway). Nitric acid (65%) and hydrogen peroxide (31%) were used for decomposition of the wine. The matrix modifiers used were 1 % palladium nitrate solution (Spectrascan), and 1% nickel solutions prepared from nickel nitrate hexahydrate and nickel sulphate hexahydrate, respectively. Deionized water was used throughout.

Most of the method development was done with a red wine, Saint Clement, which was available in a 3 L "bag-in-box". Wine could be poured from this bag without letting air into the bag. The other wine samples were in 0.7 L bottles, which were analyzed shortly after the bottles had been opened.

Direct analysis of the wine

A sample volume of 10 μL and 2 μL 1% palladium modifier were injected in the furnace and heated according to the temperature programme given in Table 1. The areas of the analyte signal and the background were recorded at 193.7 nm for As, and at 217.6 nm for Sb. Deionized water plus palladium modifier was used as the blank. The concentration of As and Sb must be determined by the standard addition procedure. Four aliquots of the sample were spiked with 10, 20, 30 and 40 μg/L of As or Sb, and the respective peak areas were recorded. The regression line was then calculated, and the concentration was determined by extrapolation.

If the values are close to the detection limit, the wine should be decomposed before analysis, as described below.

Decomposition in Tecator apparatus

25 mL of the wine sample was transfered to each decomposition tube (250 mL), and the tube was placed in the heating block. 2 mL nitric acid

and 3 mL hydrogen peroxide were added and the temperature programme started. The temperature was increased from 20 to 125 °C in 1 h; the tubes were then heated for 4 h at 125 °C. Heating to dryness should be avoided. The remaining 1 mL sample was cooled, transfered to a 25 mL volumetric flask and diluted to volume. The blank was prepared by carrying out the decomposition procedure with deionized water instead of the wine.

Decomposition in Bethge apparatus

25 mL of the wine was transfered to the flask, and 2 mL nitric acid plus 3 mL hydrogen peroxide were added. After 10 min of boiling with reflux, the collection of the evaporated liquid in the reflux collector was started. After about 40 min the remaining 1 mL sample was cooled, transfered to a 25 mL volumetric flask and diluted to volume. The blank was prepared by carrying out the decomposition procedure with deionized water instead of the wine.

Analysis of decomposed wine

A sample volume of 20 µL was injected in the furnace. The volume of the palladium modifier (1%) was 10 µL for As, and 2 µL for Sb. The temperature programme is given in Table 1; see the direct analysis procedure for subsequent steps.

Results and discussion

Atomization parameters

The use of a matrix modifier was found to be essential for the determination of As and Sb in wine. Even in the presence of palladium, the sensitivity, i.e. slope of the standard addition curve, was lower for the wine samples than for simple aqueous solutions of the elements. The sensitivity for As was about 60% lower for untreated wine, and 30% lower for decomposed wine than for a standard solution of As; for Sb the corresponding values were 50 and 20%, respectively.

The optimum ashing and atomization temperatures for As and Sb were determined by recording the appropriate ashing and atomization curves for both untreated and decomposed wine. Using direct injection of the wine and palladium modifier, the optimal ashing and atomization temperatures were found to be 1200 and 2400 °C, respectively, for both elements (Table 1). For decomposed wine, the corresponding values were 1400 and 2300 °C for both elements (Table 1). The stabilizing effect of the palladium modifier is illustrated by the fact that for standard solutions of the elements in absence of palladium, the maximum ashing temperature was found to be 400 °C for As, and 600 °C for Sb.

The optimum amount of palladium to be used was established by injecting different volumes of the modifier; both red wine, white wine and decomposed red wine were analyzed. As can be seen from Table 2, 2 µL of 1% palladium solution gave the largest peak area in most cases. For As in decomposed red wine, the largest peak area was obtained using 10 µL of the modifier. When a 20 µL volume of modifier was used, a negative baseline dip in front of the Sb signal was observed, in addition to an enhanced background and delayed atomization of the analyte. The negative baseline dip close to the Sb signal may be related to the large amount of acid introduced with the modifier (see below).

In the last years, palladium has been the preferred chemical matrix modifier for As and Sb [12, 13]. Before that, nickel salts were frequently used for this purpose [14]. The results of a comparison between palladium nitrate, nickel nitrate and nickel sulphate are shown in Table 3, for untreated and decomposed wine and standard solutions of the elements (the experimental conditions were not identical for the three sample types). For the wine samples, it can be seen that the highest peak area is obtained in the presence of palladium. In addition, the height and symmetry of the peak were best in this case. In contrast, palladium appears to offer no advantage over the nickel salts for simple standard solutions of the elements.

Table 1. Temperature programme for As and Sb using direct injection of wine in the graphite furnace, and palladium modifier. The values in parenthesis were used for decomposed wine.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (mL/min Ar)
Drying	100	10	40	300
Ashing	1200 (1400)	10	40	300
Atomization	2400 (2300)	0	3 (4)	0
Cool down	20	1	2	300
Clean out	2700	0	3	300

Decomposition procedures

The wine was analyzed either directly, or after decomposition with acids. Two types of decomposition equipment

Table 2. Effect of the amount of palladium modifier on the atomic absorption signals of As and Sb for spiked (100 µg/L) wine samples; 1% palladium solution; n = 3

Pd volume (µL)	As; mean peak area/(AU·s)			Sb; mean peak area/(AU·s)		
	Red wine[a]	White wine[a]	Decomposed[b]	Red wine[a]	White wine[a]	Decomposed[b]
2	0.184 ± 0.005	0.191 ± 0.005	0.227 ± 0.011	0.210 ± 0.005	0.195 ± 0.008	0.251 ± 0.003
5	0.171 ± 0.006	0.203 ± 0.004	0.334 ± 0.005	0.179 ± 0.007	0.188 ± 0.015	0.247 ± 0.008
10	0.138 ± 0.005	0.198 ± 0.004	0.356 ± 0.006	0.154 ± 0.006	0.170 ± 0.017	0.239 ± 0.007
20	0.131 ± 0.013	0.185 ± 0.007	0.322 ± 0.008	0.144 ± 0.004	0.139 ± 0.016	0.196 ± 0.006

[a] Direct analysis
[b] Red wine, decomposed in Bethge apparatus

Table 3. Effect of palladium and nickel modifiers on the atomic absorption signals (mean ± s; n = 4) of As and Sb, for spiked (100 μg/L) red wine and standard (100 μg/L) solutions. 2 μL of 1% modifier was used

Sample	As; mean peak area/(AU · s)			Sb; mean peak area/(AU · s)		
	$Pd(NO_3)_2$	$Ni(NO_3)_2$	$NiSO_4$	$Pd(NO_3)_2$	$Ni(NO_3)_2$	$NiSO_4$
Red wine, direct	0.185 ± 0.003	0.121 ± 0.003	0.090 ± 0.004	0.147 ± 0.004	0.115 ± 0.005	0.117 ± 0.003
Red wine, decomp.[a]	0.294 ± 0.003[b]	0.231 ± 0.004[b]	0.146 ± 0.004[b]	0.251 ± 0.003	0.198 ± 0.006	0.174 ± 0.004
Standard solution	0.208 ± 0.003	0.219 ± 0.004	0.218 ± 0.005	0.246 ± 0.004	0.258 ± 0.007	0.247 ± 0.006

[a] Tecator apparatus
[b] 10 μL of 1% modifier

were tested: open borosilicate tubes heated in a heating block with a temperature controller (Tecator), and heating with reflux in a closed system according to Bethge [11]. In both the Tecator and the Bethge procedures, the sample was heated until about 1 mL of the solution remained. This took about 5 h with the Tecator system, but only 40 min with the Bethge apparatus. However, many Bethge apparatus are required if a number of samples are to be decomposed simultaneously, whereas a single Tecator unit can accommodate many samples.

Three acid mixtures were studied: pure nitric acid, nitric acid plus hydrogen peroxide, and nitric acid with repeated additions of hydrogen peroxide. The peak areas increased slightly (< 10%) when hydrogen peroxide was used in addition to nitric acid. Hydrogen peroxide (3 mL) was added either at the start of the decomposition, or the acid was added in 1 mL portions; 1 mL at the start, and then again after 1 and 2 h, respectively. The resulting peak areas, using the two ways of adding hydrogen peroxide, were not significantly different. Both the Tecator and Bethge systems were used for all three digestion mixtures; the atomic absorption signals obtained were not significantly different for the two systems. Since the Tecator system can digest many samples simultaneously, equipment similar to this system is recommended for routine analysis.

The Bethge apparatus was useful for checking any loss of As and Sb during the decomposition. In this apparatus, any evaporated analyte can be collected above or below the reflux system. The corresponding solutions in the top part and in the reflux collector were analyzed for As and Sb, after decomposition of a spiked (100 μg/L) red wine. The values obtained for the solutions above and below the reflux system were not significantly different from the blank values, indicating that As and Sb are not volatilized when the wine is decomposed by heating with nitric acid/hydrogen peroxide.

Quantitative results

Since the sensitivity for As and Sb was significantly lower for untreated and decomposed wine than for standard solutions of the elements (see above), the standard addition procedure must be used for the quantitative determination of As and Sb in wine. At least four points were used in the standard addition procedure.

The accuracy of the present method is not easily established, since there is no standard wine with reference values for As and Sb available. However, the results obtained for As by direct analysis could be compared with those obtained after acid decomposition. For Saint Clement red wine, the mean As value obtained for triplicate analyses was 8.9 ± 0.7 μg/L for untreated wine, and 8.6 ± 0.2 μg/L for decomposed wine (Tecator). For Pinot Noir red wine, the corresponding As values were 7.8 ± 1.0 μg/L (untreated) and 7.8 ± 0.6 μg/L (decomposed). Thus, a good agreement was obtained between direct analysis and analysis of decomposed wine for As.

Recovery tests were also performed, using both analytical procedures. A previously analyzed red wine (Saint Clement) was spiked with 10 μg/L of each element and then analyzed again. For As, the recovery was 99.4 ± 3.1% for untreated wine and 101.3 ± 2.3% for decomposed wine (Tecator). For Sb, the recovery was 101.1 ± 4.1% for decomposed wine. The results indicate complete recovery of the elements by the two procedures.

The detection limit was calculated from the standard deviation of replicate peak area measurements of an unspiked red wine (Saint Clement); both untreated and decomposed wine were analyzed. The standard deviation was multiplied by three; the detection limit in μg/L was then obtained from the standard addition curve. For As, the detection limit was found to be 1.8 μg/L for untreated wine (21 replicates), and 0.5 μg/L for decomposed wine (12 replicates; Tecator). For Sb, the corresponding values were 5.0 (untreated) and 2.6 μg/L (decomposed). Thus, somewhat better detection limits were obtained for decomposed wine, partly because the sensitivity was improved when the wine was decomposed. The detection limit for As in decomposed wine can be improved further by a factor of 2.5, by diluting the decomposed sample to 10 mL instead of 25 mL. However, the resulting higher acid concentration prevented the determination of Sb in this solution, owing to a negative baseline dip in front of the Sb signal. The difference in the detection limits of As and Sb is partly due to the fact that an electrodeless discharge lamp was used for As, whereas a hollow cathode lamp was used for Sb.

The relative standard deviation of replicate peak area measurements was usually of the order of 2–4% for both untreated and decomposed wine. However, when the standard addition method was used for the quantitative determination, the calculated standard deviation of the

Table 4. Concentration of As and Sb in red and white wines; As was determined by direct analysis, Sb after acid decomposition (Tecator); n = 3

Wine	As		Sb	
	Mean (μg/L)	s[a] (μg/L)	Mean (μg/L)	s[a] (μg/L)
Paul Masson, California	9.7	1.1	< 2.6	
Pinot Noir, Makedonia	7.8	1.0	9.4	0.8
Medoc, France	5.9	0.6	< 2.6	
Saint Clement, Le Cep, France	8.9	0.7	< 2.6	
Castel del Monte, Italy	3.4	0.4	8.1	0.9
Bordeaux Blanc, France (white)	2.7	1.0	< 2.6	
Reiler vom Heissen Stein, Germany (white)	7.5	1.0	3.1	0.5

[a] s = standard deviation

extrapolated concentration [15] was 8–13% (except for Bordeaux Blanc), as can be seen from Table 4.

In Table 4, the results for As and Sb in five red wines and two white wines are given. The As concentration was determined by direct analysis, whereas Sb was determined in decomposed wine (Tecator), to assure the best detection limit for this element. Even so, Sb was below the detection limit for four of the wine samples. For five of the wines, the concentration was lower for Sb than for As, which is supposed to be the normal situation [16].

The results for As agree well with the more recent values obtained by other workers [4–6]. For Sb, it appears to be very few reliable values published [1, 8]. The concentrations of As and Sb shown in Table 4 are far below 0.2 mg/L which is specified by a number of countries as the maximum permitted concentration in wine [17].

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