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Determination of cadmium in wine by electrothermal atomic absorption spectrometry

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A method is described for direct electrothermal atomic absorption spectrometric (ETAAS) determination of cadmium in untreated samples of wine. Pyrolytic graphite tubes and graphite tubes with standard L'vov pyrolytic platforms were tested as atomizers. The detection limit achieved was 0.08 μg L^{-1} Cd in wine. The relative standard deviation for the concentration range from 0.2 to 10 μg L^{-1} Cd ranged from 1 to 7%. The accuracy of the method was confirmed by comparing the current results with those found for wet digested wine samples and by the analysis of spiked samples. By applying the proposed method it was found that the cadmium concentration in Macedonian wines ranges from 0.10 to 0.90 μg L^{-1}.

Keywords: cadmium, wine, ETAAS

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The main sources of cadmium pollution are the nonferrous metal production, waste incineration, phosphate fertilizer manufacture, wood, coal, oil and gasoline combustion, iron and steel production, industrial Cd applications and nonferrous metals mining. In industrialized areas, Cd in air varies from 1 to 50 ng m^{-3} *vs*. 0.1 to 6 ng m^{-3} in rural air.

Cadmium lands on agricultural soil via air deposition (41%), phosphate fertilizers (54%), sludge application (5%) and in unusual conditions via liquid effluents and solid wastes from Cd-processing plants (1). In highly contaminated soils, Cd level may reach values of up to 800 μg g^{-1}, while the least polluted soils contain 0.2 to 0.6 μg g^{-1}. The residence time of Cd in soils is up to 300 years.

Cadmium enters the human body via plants and animal food products. It is more readily absorbed by plants than Pb. Fruit and seeds contain less Cd than leaves. The body burden of Cd increases with age. In adults it is estimated to be between 9 and 40 mg, with marked geographic and smoking habit dependencies (about twice as high in smokers). Widely consumed wine could contribute an important fraction of the dietary intake of Cd. The maximum allowable concentration of Cd in drinking water is 5 μg L^{-1},

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whereas for wine this concentration limit is 10 μg L^{-1} (1) or 100 μg L^{-1}, according to Macedonian legislation. Therefore, accurate and reliable control of the whole wine making process is required.

Electrothermal atomic absorption spectrometry (ETAAS) is probably the most used technique for the determination of low concentrations of trace elements expected in wine samples (1–16), and some methods are proposed for determination of Cd as well (4, 10, 12). The main analytical problems are connected with the wine matrix influence on the atomization of Cd and with the volatility of Cd in organic media. To overcome these problems, the proposed methods include preliminary acid digestion of the wine sample. The official method proposed by OIV (17) for Cd determination in wine is direct ETAAS, but in the presence of H_3PO_4 as modifier. However, in some wines with high Ca and Mg contents and in some cases with a naturally high content of phosphate in wine this modifier causes high nonspecific absorption values and is especially not appropriate for atomic absorption instruments without a Zeeman background corrector.

The aims of the present work are: (*i*) to develop a method for direct ETAAS determination of Cd in wines, *i.e.*, without preliminary treatment of the sample, (*ii*) to propose a more universal modifier, like Pd, appropriate for atomic absorption instruments without a Zeeman background corrector and for all types of wines, (*iii*) to apply the proposed method to analysis of Macedonian wines.

EXPERIMENTAL

Instrumentation

A Varian (USA) model SpectrAA 880 atomic absorption spectrometer with deuterium arc background correction, GTA 100 graphite furnace and autosampler were used. Pyrolytically coated tubes and graphite tubes with standard L'vov pyrolytic platforms were employed as atomizers. The atomization cell was purged with argon. Optimum temperature programs for ETAAS measurements are given in Table 1.

Reagents

Standard solutions were prepared from 1000 mg L^{-1} of cadmium atomic absorption standard (Merck, Germany). Working standard solutions were prepared daily by diluting appropriate aliquots of the stock solution in doubly-distilled water. The matrix modifiers used were palladium solutions of different concentrations prepared from palladium standard solution (1000 mg L^{-1}, Merck). Suprapure hydrogen peroxide and nitric acid, provided by Merck, were used for decomposition of the wine matrices.

Procedure

Cadmium was directly determined by ETAAS in different types of wine (red, white, rosé) by injections of 10–20 μL samples together with 5–10 μL of modifier solutions. The accuracy of the direct ETAAS determination of Cd was proved by the analysis of decomposed wine samples. The decomposition procedure was performed with a mixture of hydrogen peroxide and nitric acid.

Table I. Instrumental conditions for cadmium determination by ETAAS

	Condition			
	Wavelength		228.8 nm	
	Slit		0.5 nm	
	Lamp current		4 mA	
	Calibration mode		Absorption, peak area	
	Background correction		D_2	
	Cd in aqueous solution		Cd in wine	
	m_{Pd} = 1 μg	m_{Pd} = 3 μg	m_{Pd} = 1 μg	m_{Pd} = 3 μg
	Platform atomization	Wall atomization	Wall atomization	Platform atomization
Drying				
Temperature (°C)	95	95	95	95
Ramp time (s)	40	40	40	40
Temperature (°C)	120	120	120	120
Ramp time (s)	10	10	10	10
Pre-treatment				
Temperature (°C)	300	600	300	400
Ramp time (s)	5	5	5	5
Hold time (s)	1	5	1	5
Atomization				
Temperature (°C)	1800	1800	1800	1800
Ramp time (s)	1	1	1	1
Hold time (s)	2	2	2	2
Cleaning				
Temperature (°C)	2500	2500	2500	2500

Decomposition procedure was performed as follows: Portions of 50 mL wine samples were placed in 100-mL beakers with conc. HNO_3 (2 mL) and 30% H_2O_2 (5 mL), covered with watch glass and heated on a hot water-bath until a transparent and clear solution was obtained. Watch glasses were then removed and the samples were further heated to a wet residue. Heating to dryness should be avoided. The residue was cooled, dissolved in distilled water, transferred to a 50-mL volumetric flask and diluted to the volume with doubly distilled water. The blank was run through the whole decomposition procedure.

RESULTS AND DISCUSSION

Optimization

The furnace program was optimized owing to the pretreatment and atomization curves for aqueous standard solution of Cd (5 μg L^{-1}) and diluted wine sample (1:1) enriched with 5 μg L^{-1} Cd, using pyrolytically coated tubes and graphite tubes with standard L'vov pyrollytic platforms, with and without modifier.

The results obtained on pyrolytically coated tubes indicate an identical thermal behavior of Cd for aqueous standard solutions and wine samples (Fig. 1). Maximum loss-free pretreatment temperature by using wall atomization was 200 °C. Palladium, proposed as a modifier, had a stabilizing effect on Cd in the aqueous standard solution as well as in wine samples. The optimal pre-treatment temperature in this case is 300 °C, and the optimal atomization temperature is 1800 °C.

The effect of the different masses of palladium, used as a modifier, on the absorbance signal of Cd in aqueous solution and in wine was also investigated and the results obtained are shown in Fig. 2. It is obvious that with 1 μg Pd as modifier the wine matrix interferences are practically eliminated and the absorbance signal for Cd in aqueous solution equalizes with that for Cd in wine. The difference in integrated absorbance for 5 μg L^{-1} Cd in aqueous and wine matrix is less than 1%. This allows the application of a simple calibration procedure with aqueous standard solutions.

Similar investigations were run with the standard L'vov pyrolytic platform. The pretreatment and atomization curves are presented in Fig. 3. As expected, the sensitivity of the measurements is increased. Also, the optimal pretreatment temperature in this case is 400 °C for aqueous solution and for wine samples, even in the absence of modi-

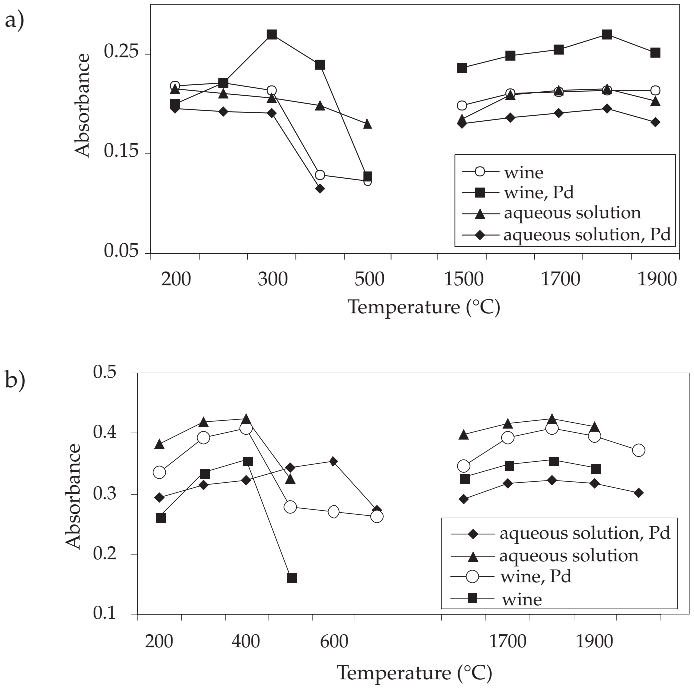

Fig. 1. Thermal pretreatment and atomization curves using: a) pyrolytically coated tubes and b) using graphite tubes with standard L'vov pyrolytic platforms (matrix modifier 1 μg Pd).

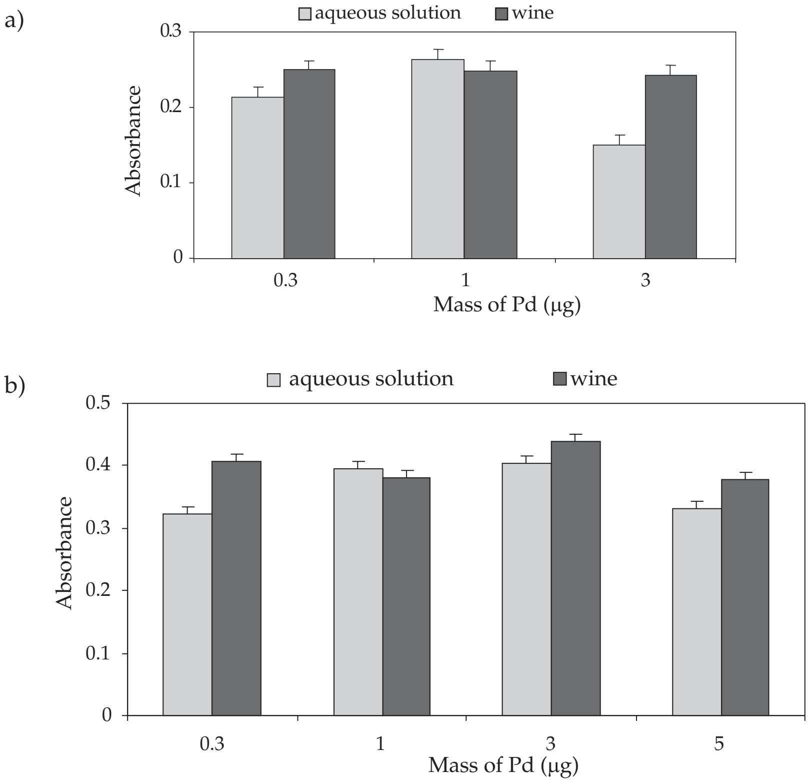

Fig. 2. Effect of Pd mass as a modifier on 0.05 ng Cd using: a) pyrolytically coated tubes and b) graphite tubes with standard L'vov pyrolytic platforms (mean ± SD, *n* = 5).

fier. In the presence of Pd, the maximum loss-free pretreatment temperature for aqueous solution is 600 °C while for wine samples palladium has no additional stabilizing effect and temperatures higher than 400 °C lead to losses of Cd. The optimal atomization temperature is 1800 °C for both aqueous solutions and wine samples.

The effect of the modifier mass on the absorbance signal of Cd in the case of platform atomization is shown in Fig. 4. Equalization between the absorbance signals for Cd in aqueous solutions and Cd in wine is achieved again with 1 μg Pd as matrix modifier. Probably palladium as modifier equalizes the thermal behaviour of the different chemical species of Cd in wine samples and thus reduces the matrix interferences (10, 12, 18). Consequently, aqueous standard calibration curve could be used for quantitative determination.

Analytical figures of merit

It is conventionally accepted that matrix digestion will remove most of the interferences in the analysis of such a complicated sample as wine and will ensure accurate and reliable results for Cd content in wine camples. Therefore, the results obtained by the

Table II. Comparative analyses of Cd in wine[a]

Sample	Direct determination	Determination after mineralization	$t_{(0.95,\ 4)}$[c]
	Cd (μg L^{-1})[b]	Cd (μg L^{-1})[b]	
White wine	2.28 ± 0.04	2.36 ± 0.05	1.78
Rosé	3.36 ± 0.05	3.25 ± 0.05	2.20
Red wine	1.54 ± 0.03	1.47 ± 0.04	2.00

[a] Optimal instrumental parameters (see Table I).
[b] Mean ± SD, $n = 4$.

Table III. Analytical recovery from a spike experiment for direct ETAAS determination of Cd in wine

Sample	Determined value	Added value	Found value	t_{exp}[b]	Recovery (%)
	Cd (μg L^{-1})[a]	Cd (μg L^{-1})	Cd (μg L^{-1})[a]		
White wine	1.52 ± 0.04	1.0	2.60 ± 0.05	1.78	103.2 ± 1.9
Rosé	1.45 ± 0.04	2.0	3.38 ± 0.04	1.75	98.0 ± 1.2
Red wine	2.48 ± 0.05	2.0	4.59 ± 0.05	2.20	102.4 ± 1.1

proposed direct ETAAS determination were compared with the results achieved for previously HNO_3/H_2O_2 decomposed samples, using the optimal furnace conditions, respectively, for aqueous solutions and wine samples (as presented in Table I) in the presence of 1 μg Pd as matrix modifier. Comparative results showing very good agreement are depicted in Table II. For all three types of wine, the calculated *t*-value was lower than the theoretical *t*-value at 95% confidence level. This can be accepted as a proof that the simple and fast ETAAS procedure developed for direct determination of Cd in wines is characterized by good accuracy.

Since no standard reference wine with reference values for Cd is available, the accuracy and the precision of the proposed method was evaluated using the »added-found« method. The results are presented in Table III.

The detection limit ($\bar{x}_{\mathrm{blank}} + 3\ \mathrm{SD}_{\mathrm{blank}}$) achieved is 0.08 μg L^{-1} Cd in wine. The relative standard deviation (RSD) for the concentration range 0.1–10.0 μg L^{-1} Cd is 1–7%. The linear range is between 0.2 and 10.0 μg L^{-1} Cd.

Cadmium concentration in Macedonian wines

A total of 31 wine samples were analyzed by the described direct ETAAS procedure. Cadmium content ranged from 0.21 to 0.97 μg L^{-1} in red wines and from 0.12 to 0.79 μg L^{-1} in white wines.

Table IV shows the average concentration of Cd found in wine samples from different vineries and different regions in Macedonia. It is obvious that Cd levels were higher in red wines (from 0.21 µg L^{-1} in Bovin Vinery to 0.97 µg L^{-1} in Lozar Vinery). These values are in agreement with those obtained by ETAAS for Brazilian (10) (from 0.03 to 55 µg L^{-1}), Spanish (4) (from 0.1 to 15.5 µg L^{-1}) and Slovenian wines (12) (from 0.2 to 0.5 µg L^{-1}), or with Argentinian wines (from 0.37 to 2.16 µg L^{-1}) obtained by atomic emission spectrometry with inductively coupled plasma (19).

Table IV. ETAAS data on concentration of Cd in wine samples from different vineries in Macedonia

Vinery, location	Average concentration of Cd (µg L^{-1})	
	White wines	Red wines
Tikveš, Kavadarci	0.38	0.44
Povardarie, Negotino	0.23	0.50
Bovin, Negotino	0.27	0.28
Lozar, Veles	0.65	0.67
Lozar, Bitola	0.10	0.90

CONCLUSIONS

The optimal conditions for direct ETAAS determination of Cd in wines are: L'vov platform as atomizer, total Pd modifier in the furnace of 1 µg, pretreatment temperature of 400 °C, atomization temperature of 1800 °C and calibration against aqueous standards. The direct method proposed in this study for cadmium determination in wines is fast, reliable and suitable for routine laboratories dealing with wine quality control. It allows determination of total cadmium content directly in a wine sample without any preliminary sample pretreatment. As the next step analytical procedure for cadmium speciation, *e.g.* examination of exact cadmium species in wines, should be developed in order to clarify cadmium bioavailability and toxicity in such a widely consumed beverage as wine.

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SAŽETAK

Određivanje kadmija u vinu atomskom apsorpcijskom spektrometrijom

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Opisana je izravna metoda određivanja kadmija u uzorcima vina elektrotermičkom atomskom apsorpcijskom spektrometrijom (ETAAS). Za atomizaciju su upotrebljene pirolitičke grafitne cjevčice i grafitne cjevčice sa standardnom pirolitičkom platformom po L'vovu. Granica određivanja bila je 0,08 μg L^{-1} kadmija. Relativna standardna devijacija za koncentracijsko područje od 0,2 do 10 μg L^{-1} bila je između 1 i 7%. Točnost metode potvrđena je usporedbom rezultata s rezultatima dobivenim iz vlažno digeriranih uzoraka i nacijepljenih uzoraka. Pomoću ove metode određeno je da se koncentracija kadmija u makedonskim vinima kreće u rasponu od 0,10 do 0,90 μg L^{-1}.

Ključne riječi: kadmij, vino, ETAAS

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