

DETERMINATION OF CADMIUM IN WINE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

A method is described for ETAAS determination of cadmium in untreated samples of wine. Pyrolytic graphite tubes and centre fixed platform tubes are tested as atomizers. The detection limit achieved is $0.08 \mu\text{g L}^{-1}$ Cd in wine. The relative standard deviation for the concentration range from 0.5 to $5 \mu\text{g L}^{-1}$ Cd is 2-3 %. The cadmium content in wines ranged from 0.2 to $0.9 \mu\text{g L}^{-1}$.

Introduction

As widely consumed beverage wine could contribute an important fraction of the dietary intake of Cd. Therefore accurate and reliable control of whole wine making process is required. The electrothermal atomic absorption spectrometry (ETAAS) is probably the most frequently used technique for the determination of low concentration of trace elements expected in wine samples [1-4]. In the present paper, method for direct determination of cadmium in untreated wines is described. Optimal instrumental parameters: (i) temperature programs, (ii) modifiers, (iii) atomizers, (iv) calibration procedure is presented. The accuracy and precision of the proposed method are evaluated. Wet digestion procedure by using $\text{HNO}_3 - \text{H}_2\text{O}_2$ mixture was used as comparative method and good agreement of the results obtained is achieved.

Experimental

Instrumentation

A Varian model SpectrAA 880 atomic absorption spectrometer with deuterium arc background correction, GTA 100 graphite furnace and autosampler were used. Pyrolytically coated graphite tubes and centre fixed platform tubes were employed as atomizers. Optimum temperature programs for ETAAS measurements are given in Table 1.

Reagents

Standard solutions were prepared from 1000 mg l^{-1} cadmium atomic absorption standard. Palladium solutions with different concentrations were used as matrix modifier. Tracepure hydrogen peroxide and nitric acid were used for decomposition of the wine matrices.

Table 1. Instrumental condition for determination of Cd by ETAAS

Parameter	Cd in water solution		Cd in wine	
	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

Procedure

Cadmium was directly determined by ETAAS in different types (red, white, rose) of wine 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 the decomposed wine samples. The decomposition procedure was performed with mixture of hydrogen peroxide and nitric acid.

Results and discussion

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

The results from the investigations run on pyrolytically coated tubes indicate that identical thermal behavior of Cd was observed for aqueous standard solutions and wine samples. Maximum loss-free pretreatment temperature by using wall atomization is 200 °C. Palladium, proposed as a modifier, has a stabilizing effect on Cd in the aqueous standard solution as well as in the wine samples. The optimal pre-treatment temperature, in this case is 300 °C, and the optimal atomization temperature is 1800 °C. The best results were obtained when 1 µg Pd was used as modifier. This amount of modifier also reduces the matrix interferences

Similar investigations were run with standard L'vov pyrolytic platform. As it can be expected, the sensitivity of the measurements is increased. Also, the optimal pre-treatment temperature, in this case is 400 °C, even in absence of the modifier. In the

presence of Pd, maximum loss-free pretreatment temperature for water solution is 600 °C and the optimal atomization temperature is 1800 °C in both aqueous solution and in the wine samples. The optimal mass of modifier in this case is 3 µg Pd. Probably palladium as modifier equalizes the thermal behaviour of different chemical species of Cd in wine samples and thus increases absorbance signals and reduces the matrix interferences. Consequently aqueous standard calibration curve could be used for quantitative determination. Comparative results obtained by the proposed procedure and procedure based on previous wine digestion showed very good agreement. Method proposed for direct determination of Cd in wine samples was compared with Cd determination in previously decomposed samples, using the same furnace conditions (Table 2) and the results obtained agreed very well.

Table 2. Results from the comparative analysis for Cd determination in wine ;
 $n_1=n_2=3$; $t_{(0,95; 4)} = 2,45$

Sample	Direct determination	Determination after mineralization	$t_{(0,95; 4)}$
	$[\gamma(\text{Cd})_{sr} \pm s] / \mu\text{g L}^{-1}$	$[\gamma(\text{Cd})_{sr} \pm s] / \mu\text{g L}^{-1}$	
White wine	2.28±0.02	2.30±0.02	1.22
Rose	3.36±0.01	3.37±0.02	0.81
Red wine	1.54±0.01	1.53±0.02	0.81

This means that simple and fast procedure developed for direct ETAAS determination of Cd in wines is characterized with good accuracy. The detection limit (3s-criteria) achieved is 0.08 µg L⁻¹ Cd in wine. The relative standard deviation (s_r) for the concentration range 0.1 - 5 µg L⁻¹ Cd is 2-3 %. The content of Cd in 31 wine samples analyzed by the recommended procedure varied in the range 0.2 to 0.9 µg L⁻¹ in red wines and from 0.1 to 0.4 µg L⁻¹ in white

Conclusion

Optimal conditions for direct ETAAS determination of Cd in wines are: L'vov platform as atomizer, total Pd in the furnace 3 µg as modifier, pretreatment temperature of 600 °C, atomization temperature of 1800 °C and calibration against aqueous standard solution.

References

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