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DETERMINATION OF CHROMIUM IN MACEDONIAN WINE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

A method is described for the electrothermal atomic absorption spectrometry determination of chromium in untreated samples of wine. The optimal temperature program is defined according to pretreatment and atomization curves constructed in the presence of different types of wines from Macedonia. Pyrolytic graphite tubes and centre fixed platform tubes are tested as atomizers. Matrix matched (tartaric acid) aqueous standards are proposed for calibration. The detection limit achieved is 0.5 μg l^{-1} Cr in wine. The relative standard deviation for the concentration range 30 - 100 μg l^{-1} Cr is 2-3 %. The accuracy of the method was confirmed by comparing the results obtained with those found for wine samples previously digested with HNO_3–H_2O_2 mixture and by analysis of spiked samples. The analytical procedure developed was applied for the analysis of wines produced in different regions of Macedonia. The chromium content ranged from 8 to 38 μg l^{-1} for white wines and from 10 to 20 μg l^{-1} for red wines.

Key words: chromium, wine, ETAAS

1. Introduction

Chromium(III) is one of the essential trace elements in the human body that is involved in glucose and lipid metabolism [1,2]. However in excessive intake, particularly those of Cr(VI) it is considered to be highly toxic [3]. The estimated safe and required dietary intake of Cr(III) is 0.05–0.20 mg/day [4]. Food and beverages are the most important source for Cr(III) intake by humans. Wine could contribute an important fraction of the dietary intake of Cr [5,6]. It is a complex matrix containing various mineral and organic substances, such as organic acids, polyphenols, proteins, aminoacids, polyhydroxy alcohols and polysaccharides. Therefore increased bioavailabilty could be expected for chromium species in wines. Trace chromium content in wines may originate from natural sources (soil, grapes) as well as from environmental contamination, fertilizers, pesticides, industrial processing and containers [7,8]. Several studies have investigated the chemistry of chromium in soils and its uptake by plants [9,10]. It was shown that the plants growing on high-chromium soils contained higher chromium concentration than similar plants growing on low-chromium soils.

The electrothermal atomic absorption spectrometry (ETAAS) is probably the most frequently used technique for determination of low concentration of trace elements expected in wine samples. In the present paper, method for direct determination of chromium 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 HNO_3 – H_2O_2 mixture was used as comparative method and good agreement of the results obtained is achieved.

2. Experimental

2.1. 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. The atomization cell was purged with argon. Optimum instrumental conditions for ETAAS measurements are given in Table 1.

Table 1 Instrumental conditions for determination of chromium by ETAAS

Condition		Setting	
Wavelength		357.9 nm	
Slit		0.2 nm	
Lamp current		4 mA	
Calibration mode		Absorbency, peak area	
Background correction		D_2	
Step No.	Temperature, ^oC	Time, s	Gas flow, l/min
1	85	5	3.0
2	95	40	3.0
3	120	10	3.0
4	1300	5	3.0
5	1300	1	3.0
6	1300	2	0
7	2600	1.2	0
8	2600	2	0
9	2600	2	3.0

2.2. Reagents

Standard solutions were prepared from 1000 mg l^{-1} chromium atomic absorption standard (Merck, Darmstadt, Germany). Working standard solutions were prepared daily by diluting appropriate aliquots of the stock solution in double-distilled water. The matrix modifiers used were: 10 % aqueous solution of tartaric acid, 10 g l^{-1} Ag as silver nitrate dissolved in double-distilled water and Pd solutions with different concentrations are prepared by appropriate dilution of palladium standard solution (1000 mg l^{-1}, Merck, Darmstadt, Germany). Tracepur hydrogen peroxide and nitric acid, provided by Merck, were used for decomposition of the wine matrices.

2.3. Procedure

Chromium was directly determined by ETAAS in different types (red, white, rose) wines by injections of 10 -20 µl samples and 5-10 µl of modifier solutions. In order to check the matrix effect and to present the accuracy of the direct determination, ETAAS analysis of the decomposed wine samples was also performed. Decomposition procedure: portions of 50 ml wine samples were placed in a 100 ml bakers 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 transparent and clear solution was obtained. The watch glasses were then removed and the samples were further heated till 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.

3. Results and discussion

3.1. Optimization

The furnace program was optimized according to the pretreatment and atomization curves for aqueous standard solution of Cr (10 µg/L) and undiluted wine sample, using pyrolytically coated tubes and centre fixed platform tubes, without modifier (Fig. 1). As can be seen identical thermal behaviour of Cr was observed for aqueous standard solutions and wine samples (all types of wines white, red and rose). Maximum loss-free pretreatment temperature by using wall atomization is 1300 ^{o}C and optimal atomization temperature is 2600 ^{o}C. Centre fixed platform tube enables the use of higher pretreatment temperature, up to 1500 ^{o}C, but the measurement sensitivity was the same (Fig. 1).

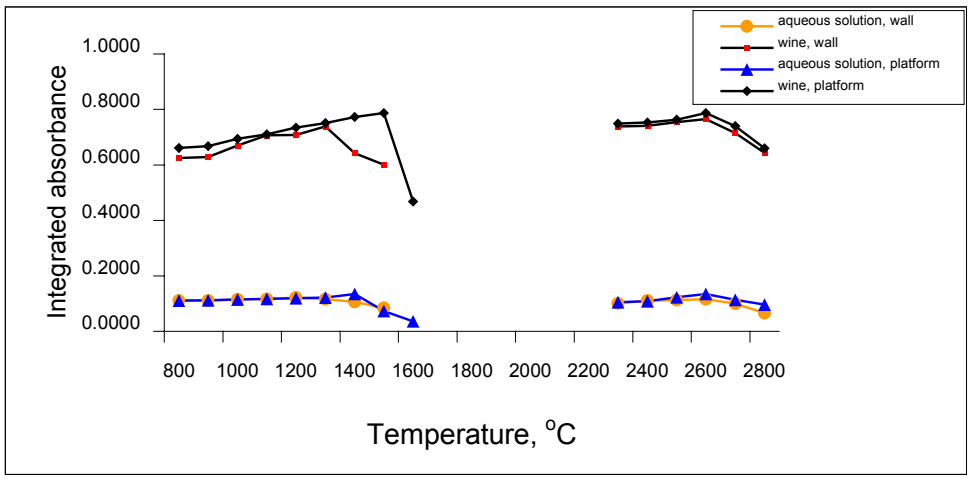

Fig. 1 Thermal pretreatment and atomization curves using wall and center fixed platform tubes

Three modifiers were tested during the optimization procedure: Pd (various concentrations), Ag (500 µg ml^{-1} and 1000 µg ml^{-1}) and 10 g l^{-1} tartaric acid. The modifiers do not change the pretreatment and atomization temperatures. They influenced the shape of the absorbance signals and only in the presence of tartaric acid the enhancement of the measurement sensitivity is observed. For all other modifiers the same or lower sensitivity is achieved (Fig. 2). Since tartaric acid is a natural ingredient (5-6 g l^{-1}) of the wine, it can be considered that wine samples have their own suitable matrix modifier for the determination of Cr. It should be pointed only that obviously matrix matched standard solution should be used for calibration which mean that tartaric acid should be added to all aqueous standard solutions to ensure the same sensitivity for Cr determination.

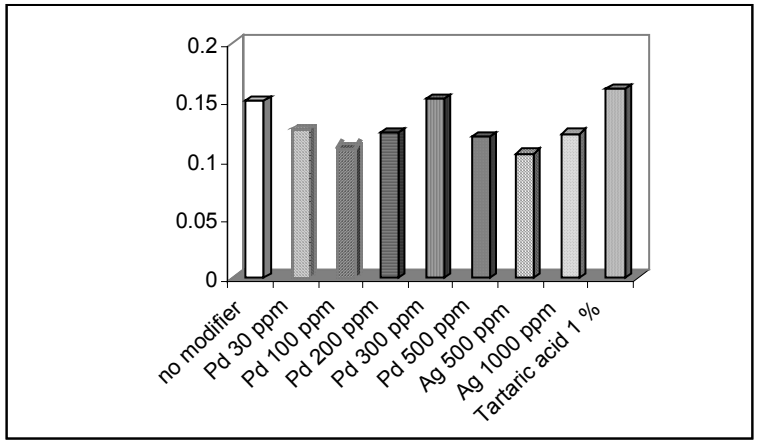

Fig. 2. Effect of the type of the modifier on 0.1 ng Cr

In this case the slope of standard addition curve for wine sample is equal to the slope with aqueous standard solutions matched with tartaric acid.

The method proposed for direct determination of Cr in wine samples was compared with Cr determination in previously decomposed samples, using the same furnace conditions (Table 1). The results obtained agreed very well, but the sensitivity of Cr measurement in the decomposed samples is slightly lower than this obtained from direct determination ($p \leq 0.05$, F test) and as can be expected the reproducibility of the former method is lower. Analysis of the same wine samples was performed also by using Zeeman background correction (SpectrAA 640Z) and very well agreement of the results obtained was observed again. This means that simple and fast method developed for direct determination of Cr in wines is characterized with good accuracy. The detection limit achieved is 0.5 μg l^{-1} Cr in wine. The relative standard deviation for the concentration range 30 - 100 μg l^{-1} Cr is 2-3 %.

3.2. Chromium concentration in Macedonian wines

A total of 31 wine samples were analyzed by application of the previously described method. Chromium content ranged from 8.6 to 23,1 μg/l in red wines (x = 13.8 μg/l) and from 8.9 to 48.6 μg/l (x = 28.7 μg/l) in white wines.

Table 2 shows the average concentration of Cr found in wine samples from different vinaries and different regions in Macedonia. It is obvious that Cr levels were higher in white wines (from 19.3 μg/l in Tikves Vinary to 37.8 μg/l in Povardarie Vinary). Since those two vinaries are settled in few kilometers distance and use grapes grown in almost identical conditions, it is obvious that the contamination appears during the wine production and storage. But, the causes of differences in wine chromium levels, such as possible differences in soils, wine varieties, winemaking, conservation processes and environmental pollution, should be further studied.

Table 2. ETAAS data on the average concentration of Cr found in wine samples from different vineries in different regions of Macedonia

Vinary/Location	Average content of Cr in white wines, μg/l	Average content of Cr in red wines, μg/l
Tikves/Kavadarci	19.3	9.9
Povardarie/Negotino	37.8	11.9
Bovin/Negotino	37.1	19.3
Lozar/Veles	30.9	11.3
Lozar/Bitola	8.9	10.2

4. Conclusions

Two atomization techniques (wall and platform) have been tested for determination of Cr in wine using ETAAS. Wall atomization was found to be most convenient technique.

Three modifiers (Pd, Ag and tartaric acid) were tested and compared with the results obtained without modifier. Best results, for aqueous standard solution, were obtained when tartaric acid was used. Since the wine samples ingrate about 5-6 g/l tartaric acid, it is not necessary to use any external chemical modifier.

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