Determination of nickel in wine by electrothermal atomic absorption spectrometry

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Abstract. A method is described for electrothermal atomic absorption spectrometric (ETAAS) determination of nickel in untreated wine samples. Pyrolytic graphite tubes and centre fixed platform tubes are tested as atomizers. The optimal temperature program is defined according to the pre-treatment and atomization curves constructed in the presence of different types of wines. The calibration procedure is proposed taking into account matrix interferences evaluated through the slopes of calibration curves obtained for aqueous standard solutions and untreated wine samples. The detection limit achieved is 1.0 µg L^{-1} Ni in wine. The relative standard deviation for the concentration range from 4 to 50 µg L^{-1} Ni is 2-5 %. 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 wine samples. The method was applied for the analysis of wines produced in different regions of Macedonia. A total of 31 wine samples from different regions of Macedonia were analyzed and nickel levels ranged from 14.2 to 61.4 µg L^{-1} for red and from 9.2 to 61.4 µg L^{-1} for white wines.

Keywords: nickel, wine, determination, electrothermal atomic absorption spectrometry.

1. Introduction

Nickel is one of the essential trace elements naturally present in the human body, considered as an element that is involved in the stabilization process of DNA and RNA [1]. However, in excessive intake, particularly it's compound nickel tetracarbonil, $Ni(CO)_4$, it is considered to be highly toxic, allergenic and carcinogenic [1]. The maximum allowed dietary intake of Ni is up to 250 µg/day. Nickel enters the human body chain via plants and animal food products. It's content in food and beverages origins from the natural absorption of plants from the soil, but also it can be increased by the presence of industrial capacities. As widely consumed beverage, wine could contribute an important fraction of dietary intake of Ni. 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 [2-4], and some methods are proposed for Ni either [5-7]. Also, other methods can be employed, such as ICP-AES [8] and MS-ICP [9-11]. In the present paper, method based on ETAAS for direct determination of nickel in untreated wines is described. Optimal instrumental parameters: temperature programs, modifiers, atomizers and calibration procedure are 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

Instrumentation

A Varian 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.

Table 1. Instrumental condition for determination of nickel by ETAAS

Condition				
Wavelength	232.0 nm			
Slit	0.2 nm			
Lamp current	4 mA			
Calibration mode	Absorption, peak area			
Background correction	D_2			
	Ni in water		Ni in wine	
	platform	wall	wall	platform
Drying				
Temperature/°C	95	95	95	95
Ramp time/	40	40	40	40
Temperature/°C	120	120	120	120
Ramp time/	10	10	10	10
Pre-treatment				
Temperature/°C	800	800	900	800
Ramp time/s	5	5	5	5
Hold time/s	5	1	1	5
Atomization				
Temperature/°C	2400	2400	2400	2400
Ramp time/s	1	1	1	1
Hold time/s	2	2	2	2
Cleaning				
Temperature/°C	2500	2500	2500	2500

Reagents

Standard solutions were prepared from 1000 mg L^{-1} nickel 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 palladium solutions with different concentrations, prepared by appropriate dilution of palladium standard solution (1000 mg L^{-1}, Merck, Darmstadt, Germany) and silver 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.

Procedure

Nickel 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 Ni was proved by the analysis of the decomposed wine samples. The decomposition procedure was performed with mixture of hydrogen peroxide and nitric acid.

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 Discussions
Optimization

The furnace program was optimized according to the pretreatment and atomization curves for aqueous standard solution of Ni (5 µg/L) and diluted wine samples (1:1), using pyrolytically coated tubes and centre fixed platform tubes, without modifier. The results from the investigation run on pyrolytically coated tubes are shown on Fig. 1. As can be seen identical thermal behaviour of Ni 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 800 °C and 900 °C for wine sample. Optimal atomization temperature is 2400 °C.
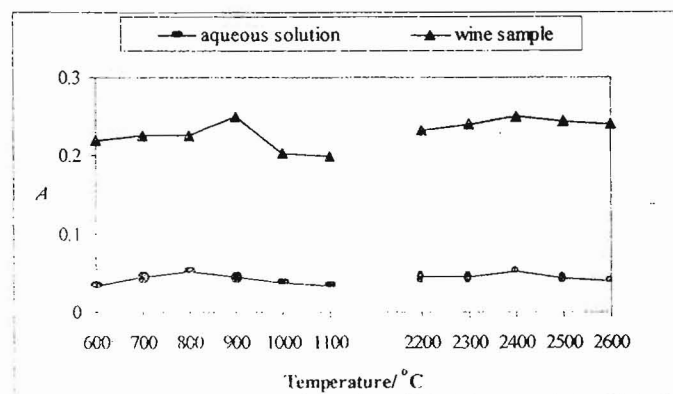
Fig. 1. Thermal pretreatment and atomization curves using pyrolytically coated tubes

Three modifiers were tested during the optimization procedure: Pd (various concentrations), Ag (500 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 Ni.
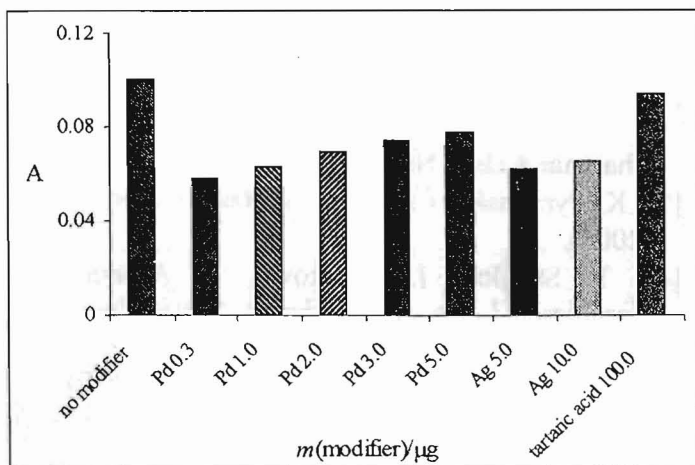

Fig. 2. Effect of the mass of modifiers on 0.05 ng Ni using pyrolytically coated tubes

Similar investigations were run with centre fixed platform tubes. The procedure of the temperature optimization is shown on Fig. 3. The optimal pre-treatment temperature, in both cases (aqueous solution and diluted wine sample) is 800 °C and the optimal atomization temperature is 2400 °C.

The effect of the modifiers mass on the absorbance signal was also investigated and the results are shown in Fig. 4. It is obvious that similar results are achieved as those when pyrolytically coated tubes were used. 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 Ni determination.
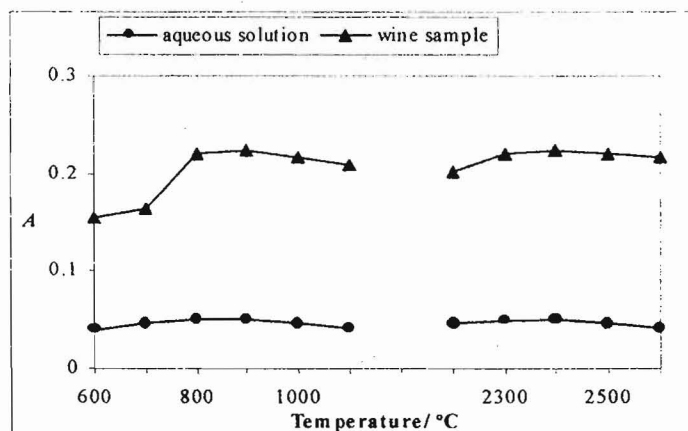

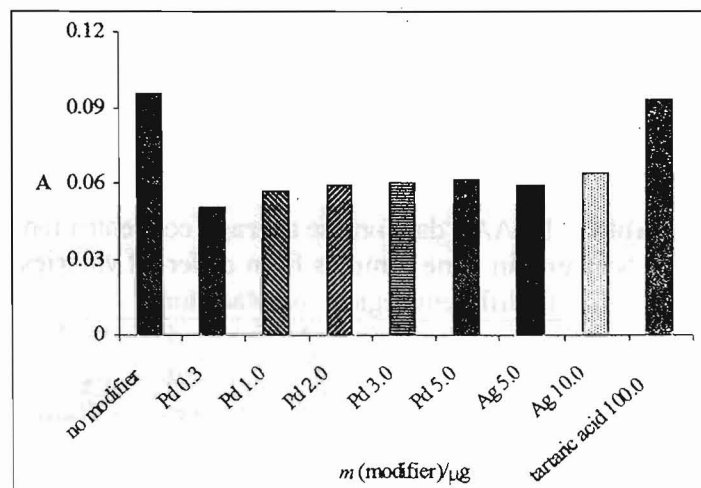**Fig.3**. Thermal pretreatment and atomization curves using centre fixed platform tubes

Fig.4. Effect of the mass of modifiers on 0.05 ng Ni using centre fixed platform tubes

The detection limit (3*s*-criteria) achieved is 1 µg L^{-1} Ni in wine. The relative standard deviation (s_r) for the concentration range 4 -50 µg L^{-1} Ni is 2 -5 %.

Since there is no standard wine with reference values for Ni available, the accuracy of the proposed method was established with the method added-found. Comparative results obtained are presented in Table 2.

Nickel concentration in Macedonian wines

The content of Ni in 31 wine samples analyzed by the recommended procedure varied in the range 14.2 to 61.4 µg L^{-1} in red wines and from 9.2 to 61.4 µg L^{-1} in white wines. Table 2 shows the average concentration of Ni found in wine samples from different vineries and different regions in Macedonia.

Table 2. Comparative results from Ni determination in wine with added-found method

n = 5; $t_{(0.95; 4)}$ =2.78

Type of wine	White	Rose	Red
Determined value, $[\gamma(Ni)_{av.} \pm s]/\mu g\ L^{-1}$	13.3±0,2	16.7±0.2	18,3±0.2
Added value/$\mu g\ L^{-1}$	10.0	10.0	10,0
Calculated value, $[\gamma(Ni)_{av.} + \gamma(Ni)_{ad.}]/\mu g\ L^{-1}$	23.3	26.7	38.2
Found value, $[\gamma(Ni)_{av.} \pm s]/\mu g\ L^{-1}$	23.3	26.4±0.3	38.5±0.4
$t_{(0.95; 4)}$	0,0	2.68	1.49

It can be seen that Ni levels are slightly higher in red wines. These values are in conformity with those obtained for wines from Japanese market (16.1-68.0 $\mu g\ L^{-1}$) [12] or for German red wines (56-60 $\mu g\ L^{-1}$) [13].

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

Vinery, Location	White wines, Ni content, $\mu g\ L^{-1}$		Red wines, Ni content, $\mu g\ L^{-1}$	
	Average	Range	Average	Range
Tikveš, Kavadarci	18.3	9.2-31.4	28.9	18.3-38.8
Povardarie, Negotino	32.1	22.4-45.2	29.2	14.2-48.4
Bovin, Negotino	17.1	15.8-18.3	25.3	16.7-60.8
Vinojug, Gevgelija	18.2	12.4-23.6	25.12	19.9-40.9
Strumica	20.8	19.3-23.1	26.4	18.2-42.4
Lozar, Veles	61.1	59.4-62.8	56.5	48.5-61.4

4. Conclusions

Optimal conditions for direct ETAAS determination of Ni in wines are: pyrolytically coated tube as atomizer, pretreatment temperature of 800 °C, atomization temperature of 2400 °C and calibration against aqueous standard solution with tartaric acid. Applying this method it was found that the concentration of Ni in Macedonian wines ranges from 9.2 to 62.8 $\mu g\ L^{-1}$.

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6. References

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