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DETERMINATION OF SELENIUM IN WINE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Julyjana D. Cvetkovic[1], Sonja H. Arpadjan[2*], Irina B. Karadjova[2] Trajce Z. Stafilov[3]

[1]Institute of Agriculture, Bull. A. Makedonski bb., 1000 Skopje, Macedonia
[2]Faculty of Chemistry, University of Sofia, 2 James Bourchier Bul., 1126 Sofia, Bulgaria
[3]Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia
E-mail: SGaneva@chem.uni-Sofia.bg

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A procedure for electrothermal atomic absorption spectrometry (ETAAS) determination of selenium in wine is described. The method includes decomposition of the wine sample in presence of nitric acid and hydrogen peroxide followed by extraction of Se as dithiocarbamate complex into isobutylmethyl ketone and ETAAS measurement of Se in the organic phase. Silver is proposed as effective chemical modifier. The described method permits the determination of lowest concentration of 0.2 μg/l Se in wine. The relative standard deviation of multiple measurements ranged from 8% (1.3 μg/l Se) to 15% (0.2 μg/l Se). The concentration of Se in wines from Macedonia and Bulgaria was found to be between 0.4 and 1.3 μg/l.

Key words: selenium, wine; extraction; electrothermal atomic absorption spectrometry.

INTRODUCTION

The essential role of Se as a trace metal, its toxic effect at higher concentrations and its influence on the metabolism of other toxic heavy metals are well known [1, 2]. Therefore reliable methods for routine analysis of Se in human diet are of interest.

Little has been published concerning Se determination in wine, but uncontaminated wine probably contains only a few μg/l of this element (0.5 – 1.0 μg/l) [3, 4]. Potential sources of Se in wine include the soil, fertilisers, insecticide sprays. The techniques used for analysis of wine for the presence of Se are inductively coupled plasma emission spectrometry [3], inductively coupled plasma mass spectrometry [4] and hydride generation atomic absorption spectrometry (HG-AAS) [5].

Traditionally the sample preparation procedures for determination of trace amounts of elements in various kinds of wine include simple sample dilution with diluted nitric acid [6 – 12], mineralization with conc. HNO_3 and H_2O_2 [13 – 15], microwave digestion [16], evaporation to dry residuals [17, 18]. In the present paper digestion with HNO_3/H_2O_2 is proposed for wine decomposition prior to the extraction of Se as dithiocarbamate complex. Electrothermal atomic absorption spectrometry (ETAAS) was chosen as an alternative method to the HG-AAS because most laboratories are equipped with this instrumentation.

EXPERIMENTAL

Apparatus

The experiments were carried out using a Perkin Elmer model 3030 Zeeman atomic absorption spectrometer with a HGA-600 atomizer, electrodeless discharge lamp for Se, AS-60 autosampler, Anadex printer. Uncoated graphite tubes, pyrolytic graphite-coated graphite tubes and pyrolytic graphite L'vov platform were used as atomizers. Organic solutions obtained after the extraction of selenium (10 μl) were introduced into the atomizer manually using micropipettes (Eppendorf). A spectral bandwidth of 0.7 nm was selected to isolate the 196.0 nm Se line. The Zeeman 3030 Perkin Elmer graphite furnace operating parameters are presented in Table 1. Only integrated absorbance values (peak areas) were used for quantitative evaluation.

Reagents

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout the experimental runs. A stock standard solution for AAS (Titrisol Merck, Darmstadt) for selenium with a concentration of 1 g/l was used for the preparation of working standard solutions by appropriate dilution. The standard solutions for calibration in the organic phase were prepared by extraction of the dithiocarbamate complex of selenium into isobutylmethyl ketone (IBMK) as follows: 1 ml of aqueous standard solution containing 5 – 50 ng/ml Se was diluted in an extraction tube with 1 ml conc. HCl and 25 ml doubly distilled water. Then, 2 ml of 2% ammonium pyrrolidin-*1*-yl-dithioformate [ammonium pyrrolidinedi-

thiocarbamate (APDC)] and 1.0 ml isobutylmethylketon (IBMK) were added and extracted for 2 min.

The matrix modifiers used were 1 g/l Ag as silver nitrate and 0.3 g/l Pd as ammonium tetrachloropalladate(II) (Fluka AG). The silver nitrate was produced in the Institute for High Purity Substances, Sofia, Bulgaria.

Table 1. Temperature programme for ETAAS determination of Se in wine with silver as matrix modifier (10 µl 0.1 % Ag) after preliminary preconcentration by evaporation and extraction.

Step	wall atomization	platform atomization
Drying 120		
Temperature (°C)	120	120
Ramp time (s)	15	15
Hold time (s)	10	10
Ar (ml/min)	300	300
Pre-treatment		
Temperature (°C)	1400	1400
Ramp time (s)	15	15
Hold time (s)	10	10
Ar (ml/min)	300	300
Atomization		
Temperature (°C)	2400	2400
Ramp time (s)	0	0
Hold time (s)	3	2
Ar (ml/min)	0	0
Cleaning		
Temperature (°C)	2500	2500
Ramp time (s)	2	2
Hold time (s)	3	2
Ar (ml/min)	300	300

Sample Preparation

The wine samples were in 0.7 l bottles, commercially available in Macedonia and Bulgaria. The samples were analysed shortly after the bottles had been opened. A 20 ml portion of wine sample was processed with a mixture of HNO_3+H_2O_2 till a clear solution was obtained. After evaporation of this solution to a wet residue, the latter was dissolved in hydrochloric acid and Se was extracted with APDC into IBMK.

RESULTS AND DISCUSSION

Atomization Parameters

The optimal pyrolysis and atomization temperatures for Se as dithiocarbamate complex in IBMK were determined by recording the pretreatment and atomi-zation curves using Ag [19, 20] or Pd as chemical modifiers. No significant difference in the thermal behaviour and sensitivity of Se was observed for uncoated and pyrolytic graphite-coated graphite tubes. However the measurement reproducibility for the investigated organic extracts was better for uncoated graphite tubes due to better mixing with the aqueous matrix modifier solution. The curves obtained are presented in Fig 1. As it can be seen from this figure silver (10 μg) as a matrix modifier stabilizes selenium in organic phase up to a pretreatment temperature of 1400°C and requires an atomization temperature of 2400°C independent of the type of atomization - from the wall or from a platform. Palladium (0.3 μg) stabilizes Se up to a pretreatment temperature of 1000°C. A higher amount of Pd (3 μg) increased the loss-free pretreatment temperature for Se up to 1300°C, but this temperature stabilization is connected with sensitivity losses (see Fig. 1).

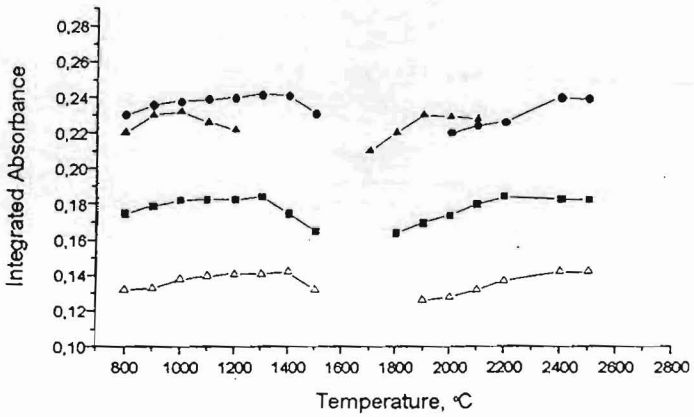

Fig. 1. Pre-treatment and atomization curves for Se as dithiocarbamate complex in organic phase: wall atomization in the presence of 10 μg Ag (Δ), platform atomization in the presence of 10 μg Ag (•). 0.3 μg Pd (♦) and 3 μg Pd (■).

The effect of the masses of silver and palladium on the absorbance signal of Se is shown in Fig. 2. Unlike Pd, even 100 μg of Ag do not lead to a substantial change of the registered integrated absorbance signal for selenium (Fig. 2A). Probably Pd forms intermetallic compounds with Se that are more difficult to atomize than Ag. It can be concluded that silver is a more appropriate modifier for ETAAS determination of selenium as dithiocarbamate complex in IBMK. Silver allows

higher pre-treatment temperature without sensitivity losses. The optimal temperature programme is summarised in Table 1. The atomization from a platform with Ag as a matrix modifier leads to about 1.7 fold enhancement of the sensitivity for Se.

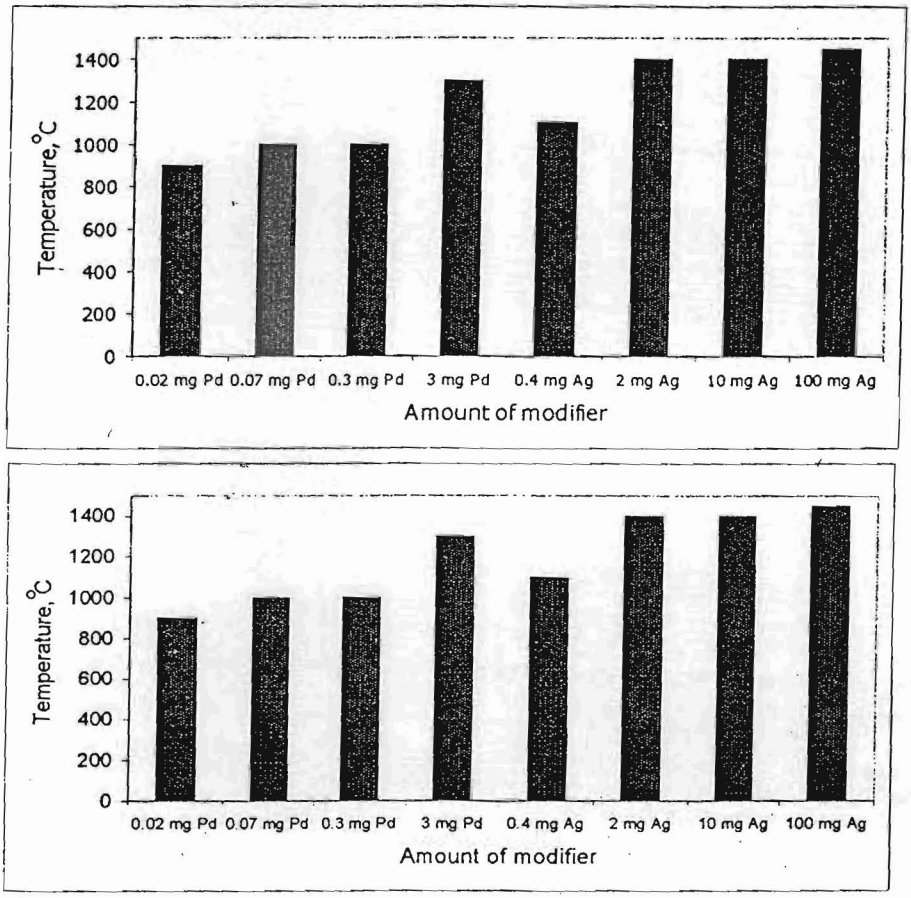

Fig. 2. Dependence of the integrated absorbance signal for Se (A) and of the maximum loss free pretreatment temperature (B) on the amount and type of modifier

Analysis of Wine Samples

Two parallel 10 ml portions of a wine sample were placed in a dry and clean 50 ml borosilicate beaker. To one of the beakers 1.0 ml 20 ppb Se aqueous standard solution was added (final concentration 2 μg/l Se). Then to both parallel samples 0.5 ml conc. HNO_3 and 2 ml 30% H_2O_2 were added, the beakers were covered with watch glasses and heated at 120°C on a sand bath. If necessary, aliquots of H_2O_2 were additionally added until the solutions became transparent and clear. Then the watch glasses were removed and the samples were further heated till moisture

residue was obtained in order to eliminate the excess of nitric acid and hydrogen peroxide. The residue was dissolved in about 1 ml conc. HCl, heated for 1 min and quantitatively transferred to a 30 ml polypropylene extraction tube and diluted to 28 ml with water. To each extraction tube 2 ml 2% aqueous APDC solution and 1.0 ml IBMK were added and Se was extracted for 2 min. The resulting organic phase was analysed for selenium by ETAAS introducing 10 µl from the obtained extract and 10 µl chemical modifier solution (1000 ppm Ag) into the graphite furnace with L'vov platform and starting the optimised temperature programme (Table 1). The blank sample was passed through the whole described procedure. The content of Se was calculated from the recorded peak area of absorbance signals for the samples with and without addition of 20 ng Se according to the standard addition method for calibration. The calibration curve is linear up to 10 µg/l Se in wine. The detection limit (3σ criteria) is 0.2 µg/l Se. The relative standard deviation of repeatability ranged from 8% (1.3 µg/l Se) to 15% (0.2 µg/l Se).

Table 2. Comparative results for concentration of selenium (µg/l ± SD) in wine determined by ETAAS and HG-AAS. Number of parallel determinations $n = 3$. $t\ (P = 0.95; f = 4) = 2.78$

Wine	Extraction ETAAS	HG-AAS	t
red(Tga za Jug)	0.66 ± 0.06	0.72 ± 0.04	1.47
white (Kresna)	0.58 ± 0.07	0.53 ± 0.05	1.02
rose (Kavadarzi)	0.48 ± 0.06	0.42 ± 0.05	1.33

For checking any loss of Se during the decomposition, samples of red, white and rose wine were analysed for Se after sample decomposition with HNO_3+H_2O_2 mixture in a closed system under reflux. The values thus obtained were not significantly different from those, obtained by the usual procedure.

Table 3. Selenium content in some Macedonian (Mc) and Bulgarian (Bg) wines.Number of parallel determinations $n = 3$.

Wine	Se (µg/l) ± SD
Zilavka (Mc, white)	1.24 ± 0.08
Belan (Mc, white)	1.33 ± 0.08
Cabernet Sauvignon (Mc, red)	0.86 ± 0.06
Smederevka (Mc, white)	0.67 ± 0.04
Merlot (Bg, red)	0.57 ± 0.04
Donkey milk (Bg, white)	0.72 ± 0.05
Cabernet Sauvignon (Bg, red)	0.64 ± 0.04

The accuracy of the proposed method is not easily established, since there is no standard wine with reference values for Se available. Comparative results, obtained with the described extraction ETAAS procedure and with HG-AAS for red (Tga za Jug), white (Kresna) and roze (Kavadarzi) wines are presented in Table 2. As it can

be seen no significant difference between the results for Se in wine was observed. In all cases the calculated values for t (Student test) are less than the tabulated value for $t(P, f)$.

In Table 3 the results for Se in some wines produced in Macedonia and Bulgaria are given.

CONCLUSION

Selenium in wine can be determined by electrothermal atomic absorption spectrometry after preliminary concentrating it by extraction of the selenium dithiocarbamate complex in IBMK. It turned out that silver is an appropriate matrix modifier for selenium determination in wine allowing high pretreatment temperature of up to 1400 °C.

REFERENCES

1. Selenium, Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, Washington DC, 1976.
2. Nordberg G. (ed.), Factors influencing metabolism and toxicity of metals, *Environ. Health Perspect.*, 1, 25 (1978).
3. ESCNAUER H., L. JAKOB, R. WEEB, *Mikrochim. Acta*, **III**, 291 (1989).
4. GREENOUGH J., H. LONGERICH, S. JACKSON, *Australian J. Grape and Wine Res.*, **3**, 75 (1997).
5. BALUJA-SANTOS C., A. GONZALEZ-PORTAL, Talanta, **39**, 329 (1992).
6. ALMEIDA A., J. CARDOSO, J. LIMA, *At. Spectrosc.*, **15**, 73 (1994).
7. GOOSSENS J., T. DE SMAELE, L. MOENS, R. DAMS, *Fresenius J. Anal. Chem.*, **347**, 119 (1993).
8. STROH A., P. BRUECKNER, U. VOELLKOPF, *At. Spectrosc.*, **15**, 100 (1994).
9. ANDREY D., H. BEUGGERT, M. CESCHI, C. CORVI, M DE ROSSA, A. HERMANN, B. KLEIN, N. PROBST-HENSCH, *Mitt. Geb. Lebensmittelunters. Hyg.*, **83**, 711 (1992).
10. MATTHEWS M., P. PARSONS, *At. Spectrosc.*, **14**, 41 (1993).
11. WANGKARN S., S. PERGANTIS, *J. Anal. At. Spectrom.*, **14**, 657 (1999).
12. BRUNO S., R. CAMPOS, A. CURTIS, *J. Anal. At. Spectrom.*, **9**, 341 (1994).
13. CABRERA C., Y. MADRID, C. CAMARA, *J. Anal. At. Spectrom.*, **9**, 1423 (1994).
14. KILDAHL B., W. LUND, *Fresenius J. Anal. Chem.*, **354**, 93 (1996).
15. SEGURA M, Y. MADRID, C. CAMARA, *J. Anal At. Spectrom.*, **14**, 131(1999).
16. TEISSEDRE P., M CABANIS, J. CABANIS, *Analusis*, **21**, 249 (1993).
17. GREENOUGH J., H. LONGERICH, S. JACKSON, *Canadian J. Appl. Spectrosc.*, **41**, 76 (1996).
18. MANNINO S., M BRAMBILLA, *Ital. J. Food Sci.*, **4**, 47 (1992).
19. KIRKBRIGHT G. F., S. HSIAO-CHUAN, R. D. SNOOK, *At. Spectrosc.*, **1**, 85 (1980).
20. ALEXANDER J., K. SAEED, Y. THOMASSEN, *Anal. Chim. Acta*, **120**, 377 (1980).