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Dedicated to Professor Ivan Petrov on the occasion of his 80th birthday

DETERMINATION OF MAJOR AND TRACE ELEMENTS IN WINE BY k_0-INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Julijana Cvetković[1], Radojko Jaćimović[2], Trajče Stafilov[3], Sonja Arpadjan[4], Irina Karadjova[4]

[1]*Institute of Agriculture, Bull. A. Makedonski bb, 1000 Skopje, Republic of Macedonia*
[2]*Jožef Stefan Institute, Jamova 39, POB 3000, SI-1000 Ljubljana, Slovenia*
[3]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, The "Sv. Kiril i Metodij" University, POB 162, MK-1001 Skopje, Republic of Macedonia*
[4]*Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

In this work, a method for the determination of major and trace elements in different types of wine samples based on k_0-instrumental neutron activation analysis (k_0-INAA) is presented. Results for the content of major and trace elements in different wines from the Republic of Macedonia are presented. Some data were compared using atomic absorption spectrometry (AAS). Mineralized wine samples were irradiated in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute. The samples were irradiated with a thermal neutron flux of $1.1 \cdot 10^{12}$ cm^{-2} s^{-1} for 20 hours. The carousel facility was not rotated during the irradiations. For f (thermal to epithermal flux ratio) and α (parameter which measures the epithermal flux deviation from the ideal (1/E) distribution) determination the "Cd-ratio" method for multi monitor was used. Thin foils or low-concentration alloys were used to minimize self-shielding effects (foils: 125 μm Zr and 50 μm Zn; wires: Al – 0.1 % Au and Al – 1.0 % Co). The following results were obtained in the CF: $f = 27.5$ and $\alpha = -0.015$. The values f and α obtained in this way were used to calculate element concentrations. The activities of irradiated samples were measured on a HPGe detector (ORTEC, USA) with 40% in relative efficiency. The detector was connected to a CANBERRA S100 multichannel analyser. For the peak area evaluation, the HYPERMET-PC programme was used. For elemental concentrations and effective solid angle calculations a software package called KAYZERO/SOLCOI®, operated on an IBM-compatible PC, was applied.

Key words: major and trace elements; wine; determination; instrumental neutron activation analysis; atomic absorption spectrometry

INTRODUCTION

During wine production, analysis is very important, especially with the development of technology and legal regulation. Analyses of wine are performed for a number of reasons: quality control (ripening, processing, ageing), spoilage reduction and process improvement, blending, export certification or global requirements. The analysis of trace elements in wines is of great importance for the quality control of wine [1], wine metal toxicity, bioavailability, etc. These elements might be essential or toxic [2] in the human body, they can influence the wine making process, and they can change the taste and quality of wine. The presence of trace elements in wine is the consequence of atmospheric deposition of airborne particulate matter on grapes, natural intake from soil and ground water, and from viticultural practices [3, 4]. The contact with the equipment during the fermentation and post-fermentation process and the usage of fining agents have also an important influence on their amount.

Atomic absorption spectrometric techniques are the most commonly used, such as those based on inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). k_0-Instrumental neutron activation analysis (k_0-INAA) [5, 6] is also a potentially interesting technique for determination of trace elements in wine. This multi-elemental technique is widely used in reference material certification, and has several advantages for direct sample measurement after irradiation (without radiochemical treatment).

The main objective in this paper was to apply the k_0-standardization method for determination of major and trace elements in different types of wine samples. Some of the data obtained were compared with those from flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS).

EXPERIMENTAL

Sample preparation

The wine samples (100 ml) were decomposed with 5 ml conc. HNO_3 and 10 ml 30 % H_2O_2 by heating on water bath, at 100 °C. If necessary, mainly for red wines, some additional drops of H_2O_2 were added until the solution remained clear and then evaporated almost to dryness. Then, the residue was disolved with doubly distilled water up to 10 ml.

k_0-Instrumental neutron activation analysis

Mineralized wine samples (about 2 ml) were sealed in pure polyethylene ampoules. A sample and a standard (Al–0.1 %Au IRMM-530 disk of 6 mm in diameter and 0.2 mm high) were stacked together and irradiated for 20 hours in the carousel facility of the TRIGA Mark II reactor of the Jožef Stefan Institute (IJS) at a thermal neutron flux of $1.1 \cdot 10^{12}$ $cm^{-2} \cdot s^{-1}$. After irradiation the sample and the standard were transferred to clean 5 ml polyethylene mini scintillation vials for measurement. Each sample was measured three times on a calibrated coaxial HPGe detector [7, 8] with 40 % relative efficiency, after 2–3, 8–10 and 30–40 days of cooling time. Measurements were performed at such distances that the dead time was kept below 10 %. For the peak area evaluation, the HYPERMET-PC [9, 10] program was used. For elemental concentrations and effective solid angle calculations a software package called KAYZERO/SOLCOI® [11], operated on an IBM-compatible PC, was applied.

Atomic absorption spectrometry

The AAS measurements were carried out on a Varian SpectraAA 880 spectrometer with a GTA 100 graphite furnace and a D_2 corrector; a Varian SpectraAA 640Z spectrometer with a GTA 100 graphite furnace and a Zeeman corrector; a Perkin-Elmer 3030 spectrometer with a HGA-700 graphite furnace and a Zeeman corrector and a Varian SpectraAA 220Z spectrometer with a hydride system and a Zeeman corrector. The light source used for each element was the corresponding hollow cathode lamp. During the ETAAS measurements, 10 μl of the sample solution and 10 μl of the modifier (if necessary) were introduced in the graphite furnace, using an autosampler. Pyrolyticaly coated graphite tubes and coated graphite tubes with pyrolytic platforms (Perkin Elmer) and with center fixed platforms (Varian) were used as atomizers. The optimal graphite furnace parameters for each element were employed. Only peak areas were used for quantification.

Reagents

All reagents and solvents were of an analytical-reagent grade (E. Merck, Darmstadt, Germany). Aqueous standard solutions were prepared daily by appropriate dilution of 1 $g \cdot l^{-1}$ stock solutions (E. Merck, Darmstadt, Germany).

Procedures

Determination of Ca, Fe, K, Mg, Na and Zn. Calcium, iron, potassium, magnesium, sodium and zinc were determined by a direct determination in wine samples by flame atomic absorption spectrometry. The air-acetylene gas mixture was used for the flame.

Determination of Co, Cr, Cu and Ni by direct ETAAS. After the opening of the bottle, wine was filtered, diluted with redistilled water and injected in the atomizer. It was evident that tartaric acid is an efficient modifier for Co, Cr, Cu and Ni ETAAS determination. Their determinations could be performed without adding the modifier.

Determination of As, Cd, Pb, Se and Tl by ETAAS after wine digestion. A 50 ml wine sample with 2 ml conc. HNO_3 + 5 ml H_2O_2 in a baker covered by watch glass was heated on a water bath until clear. The watch glass was removed and the sample was evaporated to dryness until NO_2 fumes. After cooling it was transferred to extraction cylinders. The pH was adjusted to 4 by NH_4OH. The excess H_2O_2 was eliminated by adding Na_2SO_4 (20 mg). For determination of As, Cd and Pb the wet residue was dissolved by 1–2 ml 10 % (*V/V*) HNO_3, while for Se and Tl 1–2 ml conc. HCl were used.

Determination of Se by ETAAS after extraction. The wine sample (50 ml) was heated on a water bath in a baker covered by watch glass until clear. The watch glass was removed and the sample was evaporated to dryness until NO_2 fumes. Conc. HCl (2 ml) and 2 ml water were added and after heateding (10–15 min) on a water bath to provide the reduction of Se(VI) in Se(IV). Then it was transferred to the extraction cylinder. 20 ml redistilled water and 2 ml 2 % (*m/V*) APDTC were added to complex Se and to extract analyte into MIBK (2 ml).

Determination of Tl by ETAAS after extraction. The wine sample (50 ml) was heated on a water bath in a baker covered by watch glass until clear. The watch glass was removed and the sample was evaporated to dryness until NO_2 fumes. Conc. HCl (1 ml) was added and the solution was heated. Then it was transferred to the extraction cylinder. 20 ml redistilled water and 2 ml 2 % (*m/V*) APDTC were added to complex Se and to extract analyte into MIBK (2 ml).

RESULTS AND DISCUSSION

Five different samples (white, rosé and red) of Macedonian wines were analyzed by k_0-INAA at the the TRIGA Mark II reactor of the Jožef Stefan Institute. The samples were irradiated after their ten-fold concentration by mineralization and evaporation. The data obtained are presented in Table 1. As it can be seen 30 elements could be analyzed by this method from a single irradiation in the CF. For those elements (Cd, Hg, Mo, Se, Ta, U and Zr) not visible in the gamma spectra, the limits of detection are presented.

For comparison with the k_0-INAA results, the atomic absorption spectrometry with flame (FAAS) or graphite furnace (ETAAS) was applied for the determination of some major (Ca, Mg, Na, K and Fe) and trace elements (As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl and Zn). The results are given in Table 2. AAS determinations were performed either by a direct measurement or with a matrix modifier [12–14]. The elements which could not be determined by INAA (Cu, Mg, Ni, Pb, Se and Tl) were analyzed only by AAS, Table 2.

As it can be seen from the results given in the Tables 1 and 2, very similar data were obtained for Ca, Co, Cr, K and Na. Some differences were found in the results for As, Fe and Zn. The concentrations for alkali and earth-alkali elements are in the range of $mg{\cdot}l^{-1}$: from 0.062–0.31 $mg{\cdot}l^{-1}$ for Ba; from 0.30–0.84 $mg{\cdot}l^{-1}$ for Sr; from 0.82–2.68 $mg{\cdot}l^{-1}$ for Rb, from 3.13–12.0 $mg{\cdot}l^{-1}$ for Na, from 31.6–49.8 for Mg (obtained only by AAS); from 13.2–91.8 $mg{\cdot}l^{-1}$ for Ca and the highest value from 730–940 $mg{\cdot}l^{-1}$ is obtained for K. High concentration values were also obtained for Zn (0.10–0.56 $mg{\cdot}l^{-1}$) and Fe (3.41–7.13 $mg{\cdot}l^{-1}$). In one sample (Rose) copper concentration was found to be higher than in the other wine samples (230 $\mu g{\cdot}l^{-1}$).

All other elements have the concentrations in the range of $\mu g{\cdot}l^{-1}$. The concentrations of Ag, Cs, Hf, Hg, La, Sc, Sm, Ta, Tb, Th and Yb are bellow 1 $\mu g{\cdot}l^{-1}$. The concentration ragne for As, Cd, Co, Se and Tl is between 1 to 10 $\mu g{\cdot}l^{-1}$, and for Cr, Cu, Ni and Pb it is between 10 to 20 $\mu g{\cdot}l^{-1}$.

The obtained data show that the content of major and trace elements in wine samples from different Macedonian vineries are well below the maximal allowed concentrations according to the Office International de la Vigne et du Vin (OIV) [15].

Table 1

Content of major and trace elements in different wine samples determined by the k_0-INAA method. Results are expressed in $\mu g \cdot l^{-1}$ if not given otherwise

Element	Joska	Kratošija	T'ga za jug	Gamay	Rosé
Ag	0.29	< 0.1	0.10	0.55	0.08
As	3.53	2.93	3.43	1.13	5.13
Ba, $mg \cdot l^{-1}$	0.062	0.078	0.166	0.31	0.116
Br, $mg \cdot l^{-1}$	0.051	0.087	0.060	0.14	0.025
Ca, $mg \cdot l^{-1}$	91.80	13.20	65.80	54.90	73.80
Cd	< 20	< 20	< 15	< 15	< 15
Ce	3.5	< 1	< 2	< 2	1.10
Co	4.85	3.05	2.75	4.85	6.45
Cr	20.1	19.2	21.1	6.55	19.5
Cs	1.40	0.15	< 0.1	9.50	3.10
Fe, $mg \cdot l^{-1}$	5.27	3.76	3.41	3.46	7.13
Hf	< 0.08	< 0.08	0.23	< 0.1	0.80
Hg	< 0.5	< 0.4	< 0.4	< 0.5	< 0.5
K, $mg \cdot l^{-1}$	730	804	769	884	940
La	2.60	< 0.3	0.50	< 0.3	0.68
Mo	< 10	< 10	< 10	< 10	< 8
Na, $mg \cdot l^{-1}$	8.59	9.19	12.2	2.87	6.13
Rb, $mg \cdot l^{-1}$	0.98	0.88	0.82	2.68	1.46
Sb	1.40	0.90	0.81	0.27	2.70
Sc	0.21	<0.01	0.15	<0.01	0.14
Se	< 1	< 1	< 1.5	< 1	< 1
Sm	0.40	< 0.3	< 0.2	< 0.2	0.17
Sr, $mg \cdot l^{-1}$	0.30	0.74	0.76	0.84	0.63
Ta	< 0.05	< 0.05	< 0.05	< 0.1	< 0.08
Tb	0.06	< 0.05	< 0.05	< 0.05	< 0.05
Th	0.19	< 0.1	0.16	< 0.1	0.07
U	< 1	< 1	< 1	< 1	< 1
Yb	0.21	< 0.1	< 0.1	< 0.2	0.44
Zn, $mg \cdot l^{-1}$	0.43	0.10	0.075	0.43	0.56
Zr	< 50	< 30	< 50	< 50	< 40

Table 2

Content of major and trace elements in different wine samples determined by the AAS method. Results are expressed in $\mu g \cdot l^{-1}$ if not given otherwise

Element	Joska	Kratošija	T'ga za jug	Gamay	Rosé
As	3.86	3.22	5.86	2.83	4.96
Ca, $mg \cdot l^{-1}$	93.5	13.9	68.6	56.2	72.6
Cd	6.00	4.00	3.00	1.00	12.0
Co	4.93	3.28	2.90	4.20	6.30
Cr	22.8	18.7	38.1	6.03	61.2
Cu	12.0	32.0	7.00	28.0	230
Fe, $mg \cdot l^{-1}$	3.92	2.98	2.36	1.17	4.48
K, $mg \cdot l^{-1}$	733	801	774	893	949
Mg, $mg \cdot l^{-1}$	31.6	49.8	36.6	57.3	35.5
Na, $mg \cdot l^{-1}$	9.01	9.38	12.0	3.12	6.85
Ni	12.6	15.5	19.0	8.10	7.60
Pb	18.0	22.0	8.00	3.00	40.0
Se	4.05	4.89	6.42	5.83	6.12
Tl	4.06	7.38	4.25	6.95	5.32
Zn, $mg \cdot l^{-1}$	0.62	0.21	0.01	1.14	0.20

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Резиме

ОПРЕДЕЛУВАЊЕ НА МАКРО- И МИКРОЕЛЕМЕНТИ ВО ВИНО СО k_0-ИНСТРУМЕНТАЛНА НЕУТРОНСКА АКТИВАЦИОНА АНАЛИЗА

Јулијана Цветковиќ[1], Radojko Jaćimović[2], Трајче Стафилов[3], Соња Арпаджян[4], Ирина Караджова[4]

[1]*Земјоделски институт, бул. А. Македонски бб, 1000 Скопје, Република Македонија*
[2]*Institut „Jožef Stefan", Jamova 39, p. fah 3000, 1000 Ljubljana, Slovenija*
[3]*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“, п. фах 162, 1000 Скопје, Република Македонија*
[4]*Химически факултет, Софийски университет, 1126 София, България*

Клучни зборови: макро- и микроелементи; вино; определување; инструментална неутронска активациона анализа; атомска апсорпциона спектрометрија

Во трудот е презентиран метод за определување на макро- и микроелементи во различни типови на примероци од вино со примена на k_0-инструменталната неутронска активациона анализа (k_0-INAA). Презентирани се и резултати од определувањето на поголем број на елементи во различни вина произведени во Република Македонија. За одредени елементи извршено е споредување со податоците добиени со примена на атомската апсорпциона спектрометрија (ААС). Минерализираните примероци се озрачувани во специјален карусел (CF) на реакторот 250 kW TRIGA Mark II во Институтот „Јожеф Стефан“. Примероците се озрачувани со флукс од термички неутрони од $1{,}1 \cdot 10^{12}$ cm^{-2} s^{-1} за време од 20 часа. Каруселот не ротира за време на озрачувањето. За определување на f (односот на термалните и епитермалните неутрони) и α (параметар кој ја дава девијацијата на епитермалниот флукс од идеалната, 1/E, дистрибуција) е земен методот „Cd-ratio“. Применети се тенки фолии или нисколегирани легури за минимизација на self-shielding-ефектите (фолии: 125 μm Zr и 50 μm Zn; жици: Al – 0,1 % Au и Al – 1,0 % Co). Добиени се следните резултати за CF: $f = 27{,}5$ и $\alpha = -0{,}015$ и тие беа користени за пресметување на концентрациите на елементите. Активностите на озрачените обрасци беа мерени со детектор HPGe (ORTEC, USA) со релативна ефикасност од 40 %. Детекторот е поврзан со мултиканален анализатор CANBERRA S100. За обработка на пиковите е користена програмата HYPERMET-PC. За пресметување на концентрациите и на ефективниот агол е применет софтверскиот пакет наречен KAYZERO/SOLCOI®.