MICROANALYTICAL AND RADIOLOGICAL INVESTIGATION OF FINE MELNIK WINES

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Abstract

Chemical fingerprint and radiological methods can use to determine the geographical provenance or designation of origin and the year of production – vintage of high quality wines. Chemical and radiological investigations are performed on Bulgarian Melnik fine wine, as well as, on vineyard soil.

The concentrations of sixteen chemical elements have been measured in samples from soil and fine wine from the type Shiroka Melnishka, which are grown in typical Melnik vineyard by means of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

The gamma-ray activity of the radioisotope ^{137}Cs has been measured in wines from different vintages using low background, high resolution gamma-ray spectrometry.

For the first time we report results obtained for fine Bulgarian wines from Melnik region and vineyard soil.

Derived chemical and radiological correlations can be used as initial data base for eventual proof of designation of origin of Melnik fine wine and for determination of vintage back to 1986.

Key words: *ICP-OES elemental analysis, Broad-Leaved Melnik grape; wine; gamma-spectroscopy; ^{137}Cs*

Introduction.

Nowadays fine wines are subject to increased demand driving up prices and creating a threat of counterfeiting. Recent studies estimated counterfeit wine market between 6 and 30 million US $ [6]. Due to their high quality, Bulgarian fine wines are eventually also objects of counterfeiting.

The Melnik region is world renowned for its red wine, produced since 1346 from the endemic grape Broad-Leaved Melnik (Shiroka Melnishka loza). The special flavour of this grape, the aging in unique dry underground caverns and the secrets of the local vintners gives the Melnik wine its extraordinary quality. Wines from this particular grape variety were the most popular Bulgarian wines in Western Europe in the 19th and 20th century. One of the most famous connoisseurs of the red wine from Melnik was Sir Winston Churchill, who regularly ordered barrels of it.

Recent studies were directed on methods indicating the geographical provenance or designation of origin of high quality wines using their chemical „fingerprints" (unique combination of elements present in wine). Microelements (trace elements) are good indicators of wine origin and their concentrations can be used as criteria for guaranteeing authenticity [1].

The identification of the geographical origin of wines is of great interest for wine consumers and producers, since it may provide determinant criteria for wine price and guarantees of quality [1].

Provenance establishment of wine is based on the principle that elements in wine are derived mainly from the soil and environment, and that the concentration of the majority of elements is not significantly changed during the wine production. Additionally, the element content depends on grape variety, weather and agricultural practices. Therefore, these methods involve analysis of the element and microelement concentrations, not only of certain wine, but also of vineyard soil [2, 7], vine stems and leaves.

A nuclear method, based on measured gamma-ray activity of the radioisotope ^{137}Cs can use to determine the year of wine production. [3]. ^{137}Cs isotope is a secondary product of uranium nuclear

fission. ^{137}Cs decays in ^{137}Ba, which emits a single gamma-ray with energy 661 keV. It was released into the environment in the 20th century as a result of nuclear weapons testing (1946-1961) and the Chernobyl power plant accident in 1986. In both cases, nuclear fallout is accumulated in soil and measurable amount of long-living isotopes can be detected by means of high-resolution gamma-ray spectrometry. ^{137}Cs with a half-life of 30 years is well suited for radiometric determination of age of wine because its activity is strongly correlated with the year of production of wine form certain geographic region [1].

In Bulgaria, as in all countries in South-Eastern Europa, the ^{137}Cs deposition originates mainly from fallout from Chernobyl accident.

The total ^{137}Cs fallout in Bulgaria was estimated to 1.3 x 10^{15} Bq, or 1/30 of the total released ^{137}Cs [6]. Later studies of ^{137}Cs in soil from South-West Bulgaria have shown mean value of 30 Bq/kg at the time of investigation [4].

The aim of this study was to investigate the possibility for control of designation the origin and vintage of high quality Melnik wines by means of chemical „fingerprints“ and radiological methods.

Material and methods.

The object of the research is fine Melnik wine – „Baba Ivanka Wine” produced from local Broad-Leaved Melnik grape variety in a single vineyard near the village Vinogradi (5 km south of Melnik), community Sandanski, province Blagoevgrad, in „Artarkata“ site with coordinates 41^{o}29’ 49.45” N, 23^{o} 23’ 20.99” E, altitude 390 m.

For the geographical characterization of the wine sixteen elements (Al, Fe, Ba, Ca, Co, Cr, Cu, Pb, K, Li, Mg, Mn, Na, Ni, Zn and Ga) were analyzed.

Chemical analysis was also performed on samples from the vineyard soil.

The wine sample was prepared by mixing wines from several recent vintages. Soil samples of 15 points within the vineyard were collected from a depth of 0 to 20 cm. The representative soil sample was then prepared by removing plant residue, air drying, mixing, finely grounding and passing through a 20 mesh filter to obtain very fine particles.

Samples were subjected to microwave digestion in a closed PTFE vessel (Anton Paar) according to U.S. EPA Method 3052 and subsequently analyzed by Inductively Coupled Plasma – Optical Emission Spectrometry. Measurements are made using ICP-OES Optima 7000 model of the company Perkin Elmer with dual-view configuration. ICP Multi Element Standard Solution IV CertiPUR® (Merck) was used as reference material. Emission lines utilized are given in Table 1.

Table 1: Lines used for determination of elements with ICP-OES

Element	**Al**	**Fe**	**Ba**	**Ca**	**Co**	**Cr**	**Cu**	**Pb**
λ (nm)	396.15	238.20	233.53	317.93	228.61	267.72	327.39	220.35
Element	**K**	**Li**	**Mg**	**Mn**	**Na**	**Ni**	**Zn**	**Ga**
λ (nm)	766.49	670.78	285.21	257.61	589.59	231.60	213.86	417.21

The radiological study includes gamma-ray measurements of natural and artificial radioactive isotopes in studied wine.

For the radiometric examination wine samples of Melnik fine wine were placed in standard 0.5 L Marinelli beakers. The measurement took 24 to 48 hours depending on the specific activity of the

samples.

The activity measurement was performed by means of a low-background lead shielded gamma-spectrometer, lined with cadmium, copper and plexiglass, equipped with High Purity Ge-detector of 20 % relative efficiency and 1.9 KeV resolution for the 1332 keV peak of ^{60}Co was used. The background counting rate was less than 2 cps in the energy range 50 – 2000 keV, and less than 0.005 cps in the peak area of ^{13} Cs. For data acquisition a multichannel analyzer was used at 8192 channels with dead time/pileup correction.

Results and discussion. **Chemical examination**.

The presence of trace elements in wine is the consequence of the atmospheric deposition of airborne particulate matter on grapes and/or of the intake of these elements by the grapevine from ground water and soil, pesticides and fertilizers [8].

The ICP-OES element analysis provides the content of sixteen elements, all available in soil, active and capable of migration in stems, leaves and wine. The concentration of some other elements in the wine samples are below the detection limit.

The data could help to identify chemical "fingerprint" for Melnik wines, because Melnik fine wines are produced mostly from the same variety – the endemic Broad-Leaved Melnik grape vine, grown in the same isolated geographical region in Southwest Bulgaria. The measured element concentrations are shown on Figure 1. For comparison, the concentrations measured in soil sample are also indicated.

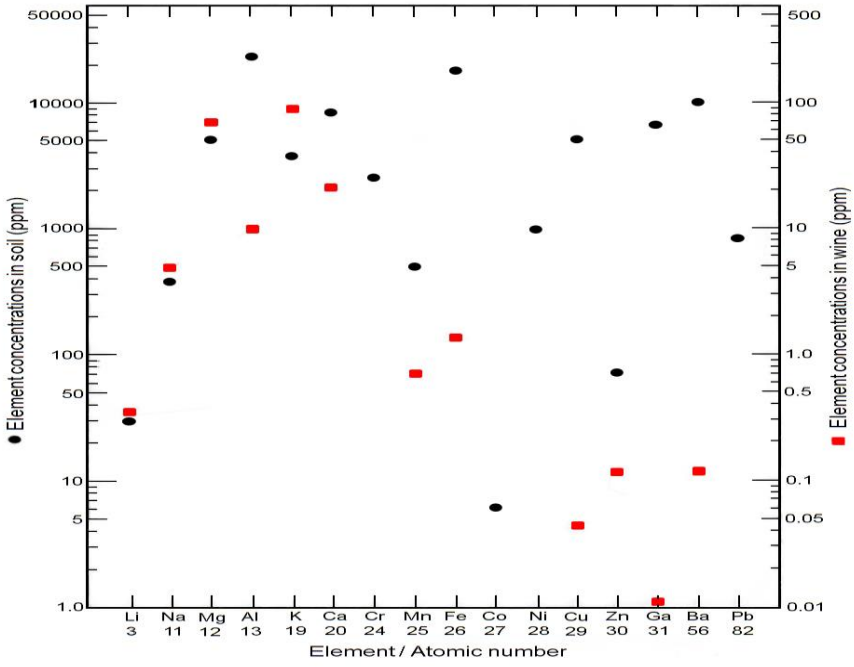

Fig. 1 Element concentrations in Melnik fine wine (squares) and element concentrations in soil samples from the vineyard (circles)

All sixteen elements detected in soil samples and fifteen in wine samples are considered for the study. From these elements, Ca, K and Na levels in wine can be influenced by regional variations in the

soil fertilization practices and in the wine making process and are therefore not sufficient reliable markers for fingerprinting. Furthermore, Fe concentration can have mostly technological origin. We consider Li, Mg, Mn and Zn as best markers for fingerprinting, because of the good correlations obtained between the element concentrations in wine and soil. These concentrations, in the relative proportion measured, can be used for determining with extreme precision the region of origin of wine (see Fig. 1).

Radiometric examination.

The results showed that samples of Melnik fine wine contain the isotopes ^{40}K at the level of 20 Bq/l and ^{137}Cs. ^{40}K is a natural isotope whose percentage in the total potassium content is estimated at 0.0119 (this value is determined by the constant isotopic ratio) [5].

The gamma-ray activities of ^{137}Cs and ^{40}K for different vintages of Melnik fine wine are given in Table 1.

Table 1 Results from gamma-ray measurements on single grape Melnik wine from different vintages [Bq/l]

Vintage	^{137}Cs [Bq/l]	^{137}Cs [Bq/l]**	^{40}K [Bq/l]
1985	< 0.10*	-	15.50 (0.88)
1986	24.9 (0.37)	44.6 (0.70)	15.40 (1.50)
1987	3.95 (0.08)	7.20 (0.14)	17.00 (1.00)
1988	1.22 (0.05)	2.08 (0.08)	16.80 (0.90)
1989	0.70 (0.04)	1.17 (0.08)	18.30 (0.90)
1990	0.43 (0.05)	0.71 (0.08)	20.75 (1.10)
1992	0.15 (0.04)	0.24 (0.07)	15.30 (0.78)
2001	< 0.15*	-	19.30 (1.80)

Notes:
1. * minimum detected ^{137}Cs gamma-activity
2. ** ^{137}Cs gamma-activity corrected for the year of production
3. Uncertainty for the confidence interval 66%

The data of radio-cesium in samples of Melnik fine wine show a reduction of the ^{137}Cs activity with time, with highest values for the vintage year 1986 (Fig.2).

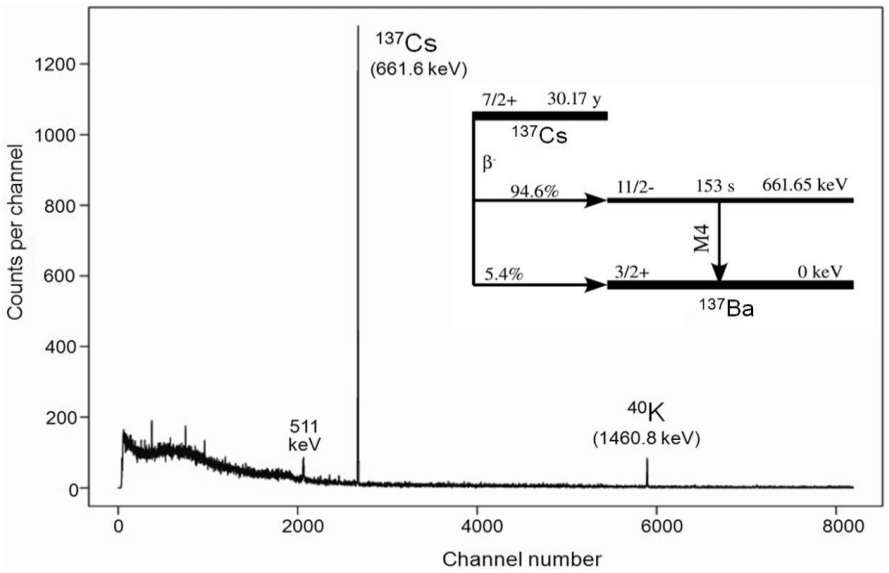

Fig. 2 Gamma-ray spectrum of Melnik fine wine, 1986 vintage

The 1986 vintage was strongly affected by radioactive contamination because in May the vines were at an advanced stage of development. Rapid decrease of the ^{137}Cs activity is observed for 1987. During 1986-1987 the cesium fallout is partly washed out or deposited and fixed in soil mostly in the upper 10 cm layer, therefore in later years only a limited amount of cesium is absorbed by the plants.

A strong correlation was established between ^{137}Cs gamma activity of different vintages and the year of production (Fig.3).

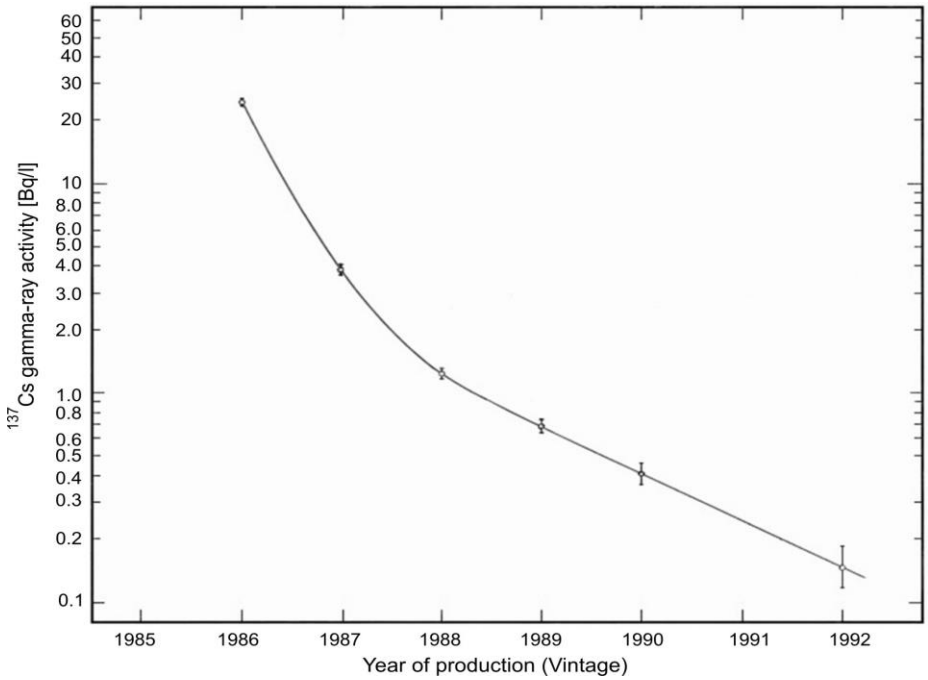

Fig. 3 ^{137}C gamma-activity in Bq/l measured in Melnik fine wine

as a function of the year of production

This correlation, studied further in detail and with more examinations, will allow determining the vintage of Melnik fine wine in the period 1986-1992. The implementation of a new ultra-low background gamma-spectrometer will increase the precision of the measurements and also allow non-destructive (in bottle) detection of vintage of fine wines. The construction of the new cyclotron center at the Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences [10] will open new opportunities for experimental nuclear physics and for measurements like reported in this work.

Conclusions.

A complex analytical investigation of Melnik fine wine from "Artarkata" vineyards, Vinogradi village near Melnik in Southwest Bulgaria using different methods and equipment, were carried out.

Sixteen chemical elements were investigated, using ICP-OES. The obtained specific concentrations of detected chemical elements in soil and wine could be used as initial database for geographical fingerprinting of Melnik fine wines.

A correlation has been established between the ^{137}Cs activity and year of production for Melnik fine wine allowing determining the vintage in the period 1986-1992.

All performed analyses conclude that the investigated fine Melnik wines are excellent for consumption and they cover all the needed parameters for bio-products.

Acknowledgements. This research has been supported by Bulgarian Science Fund under Contract No.DN08/6.

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