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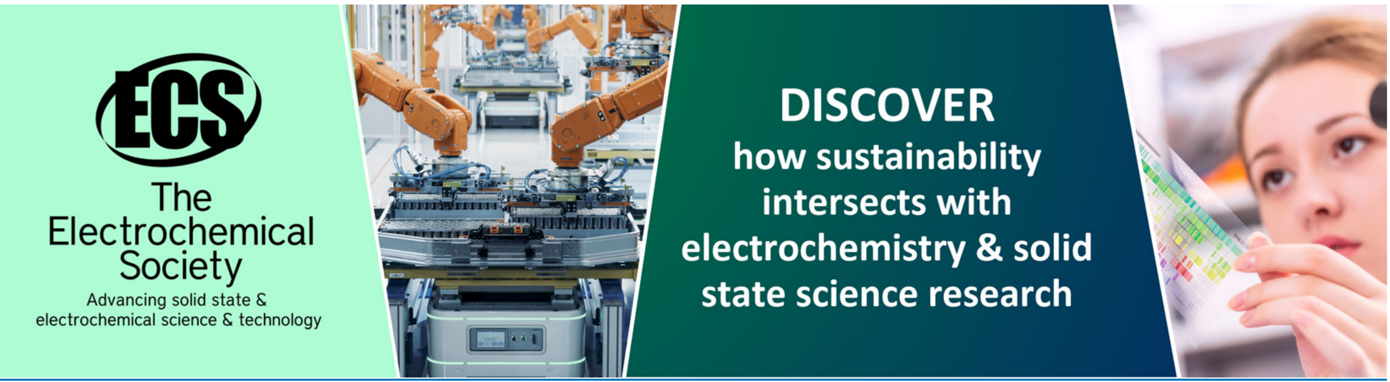

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Nuclear and analytical methods for investigation of high quality wines

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Abstract. Nuclear and analytical methods can help to determine the year of production – vintage and the geographical provenance of high quality wines. A complex analytical investigation of Melnik fine wines from "Artarkata" vineyards, Vinogradi village near Melnik in Southwest Bulgaria using different methods and equipment were performed. Nuclear methods, based on measured gamma-ray activity of ^{137}Cs and specific activity of ^{3}H can be used to determine the year of wine production. The specific activity of ^{137}Cs was measured in wines from different vintages using Low-Background High-Resolution Gamma-Spectrometry. Tritium measurements in wine samples were carried out by using a low level liquid scintillation counting in a Packard Tri-Carb 2770 TR/SL liquid scintillation analyzer. The identification of the origin of wines using their chemical fingerprints is of great interest for wine consumers and producers. Determination of 16 chemical elements in samples from soil, wine stems, wine leaves and fine wine from the type Shiroka Melnishka, which are grown in typical Melnik vineyard was made, using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

1. Introduction.

Fine wines in the world are nowadays subject to increased demand driving up prices and creating environment of limited supply and high value that make these products attractive for counterfeiting. Recent studies estimated counterfeit wine market between 6 and 30 million US $ [1]. 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 is said to be Sir Winston Churchill.

A nuclear method, based on the measurement of the gamma-ray activity of the radioisotope ^{137}Cs have been utilized to control the authenticity of an old wine [2]. It occurs in the wine from fruit contamination, which can result from direct deposition on fruit surfaces, absorption by the fruit skin and transport to the pulp, deposition to soil, root uptake and transfer to fruit [3]. ^{137}Cs decays into ^{137}Ba, which emits a single gamma-ray with an energy of 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, the radioisotope is accumulated in soil and measurable amount of it 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 [2].

The present lack of any research facility for irradiation (a research reactor or/and a research accelerator) in Bulgaria opens a possibility for such interesting experiments like the present one. The new TR24 cyclotron project in Bulgaria [4] will give many new possibilities for experiments in Bulgaria in the field of nuclear physics.

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 [5]. Later studies of ^{137}Cs in soil from South-West Bulgaria have shown mean value of 30 Bq/kg at the time of investigation [6].

It is possible to date a wine through the activity measurement of the radioactive isotope ^{3}H using the low level liquid scintillation spectrometry technique. Dating wines with ^{3}H dates back to 1954 when it was investigated by Kaufman and Libby [7]. Measurement of wine with ^{3}H by Schöhofer was also performed in the early 1990s [8]. However, tritium measurements are hampered by nuclear fallouts and the spreadout of nuclear power plants.

^{3}H, is a low-energy beta emitter ($E_{\beta max}$ = 18.6 keV) with a period of half live equal to 12.43 years. Its presence in the nature is a consequence of the interactions of cosmic rays in the Earth atmosphere. It can also be produced in human activities. It is released into the atmosphere from weapons manufacturing, operation of nuclear power plants, and reprocessing of nuclear fuels. The ^{3}H environmental level increased in the period from 1945 to 1963 as a result of nuclear weapon tests [9-11]. This radionuclide shows slight differences in the chemical and physical characteristics in comparison with hydrogen, and for this reason can replace it in water samples. Tritiated water (HTO) moves through the environment like ordinary water, cycling readily through the hydrologic components in the environment and as a consequence it is in abundance in the atmospheric fallout [9].

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). Individual vineyard areas have unique trace element “signatures” that permit the identification of the provenance of a wine. This suggests that trace elements could play some role in determining the distinctiveness of wine that differentiates wines of one region from those of another. The analysis of trace metals in wines is of great importance for quality control of wine, authenticity control of wine, wine metals toxicity, bioavailability etc [12]. 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 [13].

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 [14].

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

2. 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),

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community Sandanski, province Blagoevgrad, in „Artarkata" site with coordinates 41°29' 49.45" N, 23° 23' 20.99" E, altitude 390 m.

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

2.1. *Gamma activity*

For the Gamma measurements wine samples of fine Melnik 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 carried out using 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. For data acquisition a multichannel analyzer was used at 8192 channels with dead time/pileup correction.

2.2. *^{3}H activity*

Wine samples were purified by distillation as a pre-treatment step to remove the content of organic compounds and reduce quenching, which might adulterate the results. An aliquot of 10 ml from the second fraction of the distillate was transferred in a polyethylene vial, mixed to 10 ml of ULTIMA GOLD LLT scintillation cocktail for measurement. The samples were measured by us using a Liquid Scintillation Counter, Packard TRI-CARB 2770 TR/SL. All measurements were performed using 300 minutes counting time. Efficiency calibration was performed automatically during the procedure of normalization with internal unquenched standard – ^{3}H and ^{14}C.

2.3. *Inductively Coupled Plasma – Optical Emission Spectrometry*

For the geographical characterization of the wine 16 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.

3. Results and discussion

3.1. *Gamma activity*

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

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 (figure 1). 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.

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][b]	^{40}K [Bq/l]
1985	< 0.10[a]	-	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[a]	-	19.30 (1.80)

[a] minimum detected ^{137}Cs gamma-activity
[b] ^{137}Cs gamma-activity corrected for the year of production

A strong correlation was established between ^{137}Cs gamma activity of different vintages and the year of production (figure 2).

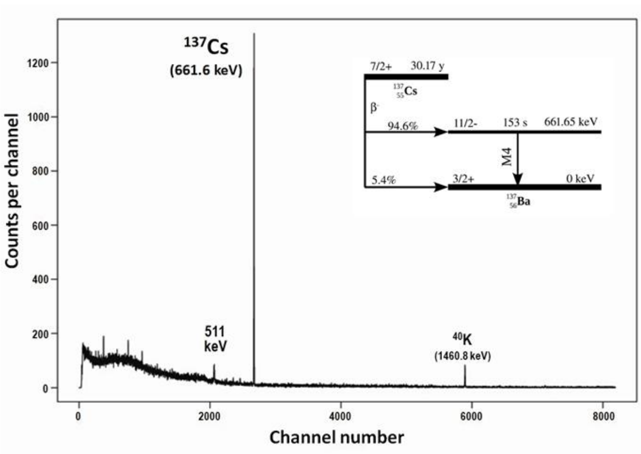

Figure 1. Gamma-ray spectrum of Melnik fine wine, 1986 vintage

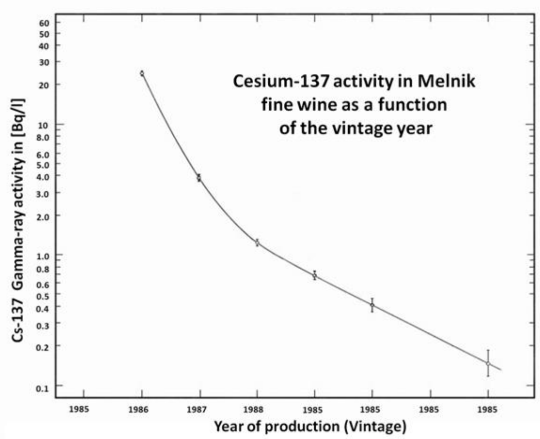

Figure 2. ^{137}C [Bq/l] in Melnik fine wine as a function of the year of production

3.2. ^{3}H *activity*

^{3}H determinations can provide information about the natural origin of many substances including wine, which can be used to determine the age of wine of a certain vintage [8]. The tritium content in the wine is that of the rain which nourished the vineyard. The specific activity of ^{3}H for different vintages of Melnik fine wine are given in table 2.

Table 2. Tritium specific activity (Bq/l) of Melnik wine from different vintages

Vintage	^{3}H [Bq/l]	^{3}H [Bq/l][a]
1985	7.36 (0.91)	32.4 (4.0)
1986	16.0 (1.6)	63.0 (6.3)
1990	13.1 (1.4)	54.6 (5.8)
2000	8.75 (1.03)	16.6 (1.9)
2001	4.37 (0.60)	7.83 (1.1)

[a] ^{3}H activity corrected for the year of production

It was found that ^{3}H activity of Melnik wine was the highest during the period 1986-1990. The minimum value (7.83 Bq/L) was for a wine produced in 2001. There is no strong dependence between ^{3}H activity of different vintages and the year of production, mainly due to atmospheric variations, which prevents us to carry out precise dating. In that sense, activity measurement of the hydrogen isotope ^{3}H is complementary to the nuclear method, based on *in situ* measured gamma-ray activity of the radioisotope ^{137}Cs.

3.3. 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 [12].

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 preliminary results for chemical elemental analysis have been presented in the works [16, 17].

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 in table 3. For comparison, the concentrations measured in soil, wine stems and wine leaves, are also indicated.

Table 3. Concentrations of detected chemical elements in samples from soil, wine stems, wine leaves and fine wine from a single vineyard in the Vinogradi village near Melnik

	Element	Al	Fe	Ba	Ca	Co	Cr	Cu	Pb
Sample	λ (nm)	396.15	238.20	233.53	317.93	228.61	267.72	327.3	220.35
	Soil	22801.6	18455.3	102.8	8615.1	6.0	26.1	51.9	8.2
	Stem	10.1	9.8	4.8	2668.5	0.0	0.2	3,6	0.3
	Leave	113.8	85.5	13.9	23876.6	0.1	0.6	3,7	0.2
	Wine	9.63	1.41	0.12	21.5	0.0	0.0	0.045	0.0

	Element	K	Li	Mg	Mn	Na	Ni	Zn	Ga
Sample	λ (nm)	766.49	670.78	285.21	257.61	589.59	231.60	213.8	417.21
	Soil	3704.2	31.2	4974.9	479.8	382.4	10.2	72.6	67.7
	Stem	3430.8	0.2	1165.7	17.8	17.8	0.0	6.7	0.0
	Leave	3298.1	0.5	4957.5	90.7	52.0	0.0	10.2	0.1
	Wine	89.31	0.45	69.70	0.71	4.80	0.0	0.12	0.01

All chemical elements detected in the soil and in the 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.

4. 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.

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

It was found that ^{3}H activity of Melnik wine has higher values in the period 1986-1990, decreasing during the following years to average values.

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.

5. Acknowledgements

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References

[1] Pender R 2010 *Master of Wine Dissertation*, The Institute of Masters of Wine, London
[2] H u b e r t Ph, Perrot F, Gaye J, Médina B and Pravikoff M 2009 *C. R. Physique* **10** 622
[3] Desideri D, Roselli C and Meli M 2010 *Food and Chemical Toxicology* **48** 650
[4] Tonev D, Goutev N and Georgiev L 2016 *J. Phys: Conf. Ser.* **724** 012049
[5] V a p i r e v E, Georgiev G, Jordanov T and Hristova A 1996 *Bulgarian Journal of Physics*, **3/4** 129
[6] K o s t o v L, Kobilarov R, Kostova L, Mladenov M, Protohristov H and Stoyanov C 2007 *Nuclear Methods for Non-Nuclear Applications* Heron Press Sofia 59
[7] Kaufman S and Libby W 1954 *Phys. Rev.* **93** 1337
[8] Schönhofer F 1992 *Radiocarbon* **34** (3) 768
[9] Madruga M, Sequeira M and Gomes A 2008 *Advances in Liquid Scintillation Spectrometry* 353
[10] Palomo, M, Penalver A, Aguilar C and Borrull F 2007 *Applied Radiation and Isotopes* **65** 1048
[11] S´anchez A, Montero M, Escobar V and Vargas M 1999 *Appl. Radiat. Isotopes* **50** 1049
[12] Stafilov, T, Cvetković J, Arpdjan S and Karadjova I 2002 *BAÜ Fen Bil. Enst. Dergisi* 4.2 90
[13] Perez-Trujillo J, Barbaste M and Medina B 2012 *Journal of Wine Research*, **13** (3) 243
[14] Bentlin F, Pulgati F, Dressler V and Pozebon D 2011 *J. Braz. Chem. Soc*. **22** (2) 327
[15] Królak E and Karwowska J 2010 *Polish J. of Environ. Stud*. **19** (3) 599
[16] Tringovska I, Tonev D, Damjanova A, Grigorov T, Gutev N, Protohristov H and Kovachev N. 2016 *Acta Horticulturae* **1115** 63 DOI: 10.17660/ActaHortic.2016.1115.10
[17] Tonev D *et al.* 2016 *Comptes rendus de l'Acade'mie bulgare des Sciences*, **69** (6) 707