



MOLDAVIAN WINE ANALYSIS BY ICP-AES AND NAA TECHNIQUES: COMPARISON STUDY

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The determination of inorganic elements in wines is of great concern both from enological and toxicological points of view. The comparison of two analytical techniques using as example eight matrix and trace elements: Al, Ba, Ca, Fe, K, Mg, Na, and Zn in red and white wines from the Republic was done. Analyses were performed by inductively coupled plasma atomic emission spectroscopy and neutron activation analysis. The content of all determined elements was below the maximum value recommended by the Office International de la Vigne et du Vin (OIV). Data obtained by the two analytical techniques presented strong evidence supporting their effectiveness in wine analysis.

	Normal	Alkali
RF Power, kW	1.2	0.8
Plasma Gas, L/min	10	10
Auxiliary Gas, L/min	0.6	0.6
Carrier Gas, L/min	0.7	0.8
Nebulizer	Co-axial	
Chamber	cyclone	
Torch	mini	
Exposure, sec	30	
Integration Point	3 pixel	

INTRODUCTION

The Republic of Moldova is a well-known producer of world-class wines, which play a critical role in the economy of the country. Wine has a complex composition which includes a variety of organic as well as inorganic components.^{1,2}

Consumption of wine in moderate quantities can contribute significantly to the daily requirements of the human organism for essential elements, such as Ca, Cr, Co, K, Se, Zn.³ On the other hand the excessive presence of Al, Cu, K, Fe, Mn, Zn can have a negative effect on the organoleptic properties of the wine, such as contributing to haze formation and even color, aroma and taste defects, and is also directly related to its destabilization and oxidative evolution,⁴⁻⁶ while As, Cd, Pb, and Br are known to be potentially toxic.³

The sources contributing to the elemental composition of wine can be traced to two separate groups: natural and anthropogenic. These sources allow for the formation of a representative "fingerprint" which is especially important for high quality wines produced in specific regions, such as protected designation of origin (PDO) wines. Natural factors influencing endogenous metallic content involve: the degree of grape maturity, climatic conditions, the nature of soil, water quality, vinification conditions, must fermentation and storage.^{7,8} Technological factors influencing metallic content include fertilizers, inorganic pesticides, wine-making equipment, steel containers, and pollution of the surrounding environmental industries.^{1,9}

Analysis of wine is of great interest for wine consumers and producers, since it can provide influential information for wine price, quality, and the identification of a wine's geographical origin.

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Large set of analytical techniques have already been applied to quantify the elemental content of wines, such as inductively coupled plasma mass spectrometry,^{3,8} atomic absorption spectrometry,^{1,4,6,9,10} inductively coupled plasma optical emission spectrometry,¹¹ stripping voltammetry,¹² and neutron activation analysis.¹³ In 2011 the International Organization of Vine and Wine (OIV) for the first time introduced in its booklet concerning the methods recommended for wine elemental analysis – inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).¹⁴

ICP-AES is one of the multi-element analysis methods that has the proper selectivity, sensitivity, and robustness suited for the direct multi-element analysis of solutions.⁸ However, the increase in the quantity of the solution alongside the increase in the number of determined elements, requires the use of acids or other solvents, interferences of organic components often preclude its widespread use. In this case, neutron activation analysis (NAA), which allows for the determination of both very high and low concentrations of a wide range of elements with high precision, using small samples, is very useful. The main drawbacks of NAA are high cost, strict safety requirements and the rarity of irradiation facilities. At the same time its proven accuracy makes NAA indispensable as a reference technique.¹⁵

The purpose of the present study was to compare the applicability of NAA and ICP-AES techniques for wine analysis using as example eight elements Al, Ba, Ca, Fe, K, Mg, Na, and Zn determined in 22 samples of Moldavian wine.

RESULTS AND DISCUSSION

Two high sensitivity multi-elemental techniques were applied to determine the concentrations of eight elements in 22 red and white wine samples. The comparison of concentration values is presented in Table 1. The content of the investigated elements in studied wines was consistent with values reported for other viticulture areas.^{1,16}

Sodium

The sources of sodium in wine can be natural or industrial.¹⁷ Grapes contain high potassium and low sodium content, and this relationship remains relatively unaltered in wine.¹⁸ Data obtained in present work support this fact. The concentration of sodium was approximately 20 times lower than

that of potassium. The sodium content was found to be between 9 and 30 mg/L (ICP-AES) and 8-32 mg/L (NAA), with highest concentrations coming from Cabernet, Regent and Uniblanc wines. Obtained results are in close agreement with literature data^{6,13,18,19} and lower than the limit set for sodium (60 mg/L) by the OIV.²⁰

Potassium

Potassium is the most abundant of the inorganic constituents of the wine, comprising about 75% of the total cation content of wines. High K levels affect the stability of wine with respect to the potassium hydrogen L-(+)-tartarate precipitation.⁶ Its concentration in wines is influenced by soil, climate, grape variety, time of harvest, temperature of fermentation, storage conditions, percentage of alcohol, pH, ion-exchange resins, and fining agents.¹⁷ Potassium concentration in the studied samples ranged from 276 to 768 mg/L (ICP-AES) and from 253 to 843 mg/L (NAA). The highest content of potassium was determined in Syzar and Malbec wine samples by both techniques. Potassium content in white wines was lower than in red. This can be explained by the fact that white wines require a shorter period of contact during the fermentation process with the skins. Obtained concentrations are lower than results reported by Cvetkovic *et al.*¹³ and Sauvage *et al.*,¹ and approximately the same as those reported by Salvatore & Marjorie.¹⁸

Magnesium

Magnesium concentration in wine depends on the grape variety, winemaking process, wine storage, the relative concentration of alcohols and other constituents, and the use of ion-exchange resins.¹⁷ Magnesium concentrations in studied wines were between 42.2-108 mg/L ICP-AES data and 65-118 mg/L for NAA. Obtained values well correlate with data obtained by Taylor *et al.*²¹

Calcium

Calcium is a natural constituent of musts and wines, necessary for the normal course of alcoholic fermentation. Calcium sources for wines include soil, the treatment of the musts with calcium salts, and ion exchange treatment.¹⁷ Calcium concentration in studied wines constituted 38-90 mg/L for ICP-AES and 39-92 mg/L for NAA. These values are lower than data obtained by Interesse *et al.*¹⁹ and comparable to data presented by Cvetkovic *et al.*,¹³ Sauvage *et al.*,¹ and Taylor *et al.*²¹

Table 1

The concentrations of the investigated elements determined in wine samples, mg/L

Type of wine	Elements											
	Na		Mg		Al		K		Ca		Fe	
	NAA	ICP-AES	NAA	ICP-AES	NAA	ICP-AES	NAA	ICP-AES	NAA	ICP-AES	NAA	ICP-AES
Cabarnet	23±0.09	26.3±0.4	118±0.6	107±2	1.6±0.005	1.2±0.04	666±67	598±14	47±5	48±1.2	6.1±0.04	6±0.02
Regent	32±0.13	30.2±0.4	105±0.5	106±2	0.78±0.002	0.9±0.03	695±70	608±15	70±7	63±1.6	0.4±0.002	0.5±0.002
Pinot Noir	17±0.07	23.2±0.3	116±0.6	109±2	2.1±0.006	1.9±0.06	698±70	654±16	54±5	52±1.3	8.8±0.05	7.9±0.02
Nero	29±0.11	26.3±0.5	110±0.6	105±2	0.8±0.002	1.05±0.03	563±56	548±14	73±7	70±1.7	0.9±0.005	0.9±0.003
Syzar	21±0.09	21.3±0.3	89±0.4	103±2	1±0.003	1.2±0.04	820±82	699±17	35±3	38±0.9	1.4±0.01	1.5±0.005
Merlot	16±0.07	18.7±0.2	89±0.4	99±1.9	2.3±0.007	2±0.06	723±72	686±17	51±5	53±1.3	3.6±0.02	3.4±0.01
Malbec	14±0.06	22.5±0.3	104±0.5	107±2	2.4±0.007	2.1±0.06	844±84	768±19	50±5	51±1.3	5.9±0.04	5.5±0.02
Sauvignon p1	15±0.06	17.8±0.2	74±0.4	80±1.6	1.3±0.004	1.3±0.04	290±29	304±8	69±7	70±1.8	1.3±0.009	1.9±0.006
Riesling	19±0.08	16.8±0.2	91±0.5	84±1.7	2.2±0.007	1.9±0.06	299±30	289±7	93±9	90±2.2	1.7±0.01	1.9±0.006
Sauvignon p2	17±0.07	17.9±0.3	82±0.4	80±1.6	2.4±0.007	2±0.06	253±25	276±7	80±	80±2.0	1.7±0.01	1.7±0.005
Pinot Gris	18±0.07	18±0.3	97±0.5	90±1.8	1.5±0.004	1.6±0.05	329±33	307±8	64±6	60±1.5	1.2±0.007	1.8±0.005
Muscat	17±0.07	16.8±0.07	74±0.4	70±1.4	1.4±0.004	1.3±0.04	285±29	276±7	70±7	69±1.7	1.1±0.007	1.3±0.004
UniBlank	210.09	20±0.3	86±0.4	79±1.6	2.5±0.007	2.1±0.06	339±34	307±8	81±8	79±2.0	1.2±0.007	1.3±0.004
Pinot C-18	13±0.05	10.5±0.1	68±0.3	48±1	1.2±0.004	1.1±0.03	600±60	569±14	52±5	48±1.2	1.1±0.006	0.9±0.003
Pinot C-42	10±0.04	11.3±0.1	81±0.4	53±1	1±0.003	1.4±0.04	434±43	497±12	72±7	70±1.7	0.7±0.004	0.9±0.003
Pinot C-191	8±0.03	10±0.1	76±0.4	56±1.1	0.9±0.003	1.2±0.04	441±44	541±13	64±6	60±1.5	1.2±0.007	1.4±0.004
Pinot C-197	15±0.06	11.9±0.2	83±0.4	54±1.1	1.4±0.004	1.3±0.04	458±46	499±12	72±7	69±1.7	2.2±0.013	1.8±0.005
Chardonnay C-13	10±0.04	10.2±0.1	95±0.5	42±1	2.2±0.007	1.9±0.06	594±59	467±12	78±8	74±1.8	1.7±0.01	1±0.003
Chardonnay C-179	8.5±0.03	12.7±0.2	89±0.4	54±1	1.8±0.005	2±0.06	561±56	513±13	72±7	76±1.9	1.5±0.009	1.3±0.004
Chardonnay C-163	15±0.06	14.5±0.3	94±0.5	67±1.3	2.5±0.008	2.6±0.08	636±64	568±14	79±8	76±1.9	1.3±0.008	1.3±0.004
Chardonnay C-173	9.5±0.04	11±0.2	65±0.3	69±1.4	1.9±0.006	2.4±0.07	644±64	573±14	82±8	80±2.0	1.6±0.01	1.2±0.004
Type of wine	Elements											
	Zn		Ba									
	NAA	ICP-AES	NAA	ICP-AES								
Cabarnet	1.27±0.08	1.2±0.03	0.13±0.01	0.2±0.01								
Regent	0.23±0.01	0.4±0.01	0.32±0.02	0.3±0.02								
Pinot Noir	0.63±0.04	0.8±0.02	0.22±0.015	1±0.05								
Nero	0.27±0.016	0.4±0.01	0.1±0.007	0.4±0.02								

Table 1 (continued)

Syzar	0.8±0.05	0.8±0.02	0.09±0.006	0.2±0.01
Merlot	0.43±0.026	0.5±0.01	0.14±0.01	0.2±0.01
Malbec	0.63±0.04	0.6±0.01	0.08±0.005	0.2±0.01
Sauvignon p1	0.52±0.03	0.5±0.01	0.15±0.01	0.12±0.01
Riesling	0.53±0.03	0.5±0.01	0.1±0.007	0.2±0.01
Sauvignon p2	0.53±0.03	0.6±0.01	0.1±0.007	0.2±0.01
Pinot Gris	0.58±0.03	0.5±0.01	0.09±0.006	0.17±0.01
Muscat	0.54±0.03	0.6±0.01	0.12±0.008	0.2±0.01
UniBlank	0.44±0.026	0.5±0.01	0.12±0.008	0.17±0.01
Pinot C-18	0.67±0.04	1.1±0.03	0.12±0.009	0.16±0.01
Pinot C-42	1.30±0.08	1.2±0.03	0.09±0.006	0.3±0.02
Pinot C-191	1.1±0.07	1.1±0.03	0.11±0.007	0.2±0.01
Pinot C-197	1.2±0.07	1.2±0.03	0.12±0.009	0.2±0.01
Chardonnay C-13	0.5±0.03	0.7±0.02	0.11±0.007	0.2±0.01
Chardonnay C-179	0.67±0.04	0.8±0.02	0.07±0.005	0.2±0.01
Chardonnay C-163	0.56±0.03	0.7±0.02	0.11±0.007	0.2±0.01
Chardonnay C-173	0.62±0.04	0.7±0.02	0.12±0.009	0.2±0.01

Table 2

Average, SD, RSD, RSD ratio, Pearson's correlation coefficient and coefficient of determination r^2 values for the investigated elements

Element	ICP-AES			NAA			RSD ratio	r	r^2 (%)
	Mean	SD	RSD (%)	Mean	SD	RSD (%)			
Na	17.5	6.1	34.6	16.7	6.2	37.1	0.93	0.88	77
Mg	82.5	21	25.3	91	14.5	15.9	1.6	0.77	60
Al	1.6	0.5	28.8	1.7	0.6	35	0.83	0.91	84
K	502	153	30.5	532	184	34.5	0.88	0.96	92
Ca	66	13	20	67	14	21	0.95	0.98	97
Fe	2.2	1.9	90	2.2	2	96	0.94	0.99	98
Zn	0.7	0.26	37	0.7	0.3	45	0.82	0.96	93
Ba	0.2	0.05	25	0.12	0.06	50	0.5	0.81	66

Aluminum

The high concentration of aluminum in wines can be explained by their storage in aluminum containers. The contamination of wine with aluminum may result in their spoilage due to haze formation and creation of an undesirable and unpleasant metallic taste.¹⁷ In studied wines aluminum content ranged from 0.9 to 2.5 mg/L (ICP-AES data) and from 0.8 to 2.5 mg/L (NAA data). Obtained data do not exceed the recommended value for aluminum, which should be not higher than 3 mg/L.^{17,20}

Iron

Iron content in wines is an important parameter controlling their quality and stability.^{1,22} Its content in wines depends on several factors, such as ground and redox conditions during and after alcoholic fermentation, fertilizers, corrosion of vinification equipment, and steel containers used for the transfer of berries or must.^{1,17,22} OIV rules do not define limits on the concentration of iron in wines. A major problem that appears in wines is their instability to iron concentrations greater than 10 mg/L. At concentrations greater than 10 mg/L, Fe(III) creates an insoluble suspensions with tannin and phosphates which are known as hazes or "casses".³ In the present study iron content in wines varied from 0.5 to 7.9 mg/L (ICP-AES data) and 0.4-8.8 mg/L (NAA data). The maximum values were obtained from Cabernet, Pinot Noir and Malbec wines. In these wines the concentration of iron was higher than 5 mg/L.

Zinc

In wines and musts, zinc originates from soil, fungicides, insecticides, and vinification equipment.^{4,17} Low zinc concentrations in wines play a vital role during fermentation, whereas high concentrations negatively influence organoleptic properties.¹⁷ Data obtained for Zn does not exceed values recommended by OIV and average out at 0.3 -

1.2 mg/L (ICP-AES data) and 0.2-1.3 mg/L (NAA data). Results are slightly higher than data reported by Cvetkovic *et al.*¹⁵ and lower than Dugo *et al.*,²³ Galani-Nikolakaki *et al.*,⁴ and Geana *et al.*²⁴

Barium

Barium is the element whose content in wine is not affected by the winemaking process and it originate mostly from the soil.¹⁶ From a literature search it was found that barium levels are normally low in wine (0.003–0.01 mg/100g),¹⁷ 30–115 µg/L.²⁵ In the present study, barium concentration ranged from 0.12 to 0.33 mg/L (ICP-AES data) and from 0.07 to 0.32 mg/L (NAA data).

Comparison between the methods

The average concentrations, standard deviation (SD), relative standard deviation (RSD), as well as RSD ratio of investigated elements are presented in Table 2.

As it can be seen from the obtained results the RSD ratio corresponding to two techniques varied between 0.5 (Ba) and 1.6 (Mg). The RSD ratios for Na, K, Ca, Fe, Mg, and Zn, were in the range of 1, even if the concentrations of the elements in the samples had wide ranges of variation, supporting the good agreement between ICP-AES and NAA. Data obtained for Mg and Ba show the low level of correlation between the two techniques. Relatively high Mg concentration determine by NAA can be explained by incomplete dissolution of some metal oxides during ICP-AES analysis or possible metal precipitation. In case of ICP-AES samples before analyzes are diluted or digested. Pretreatment processes have some disadvantages: high amount of reagents, potential losses of volatile elements and sample contamination due to reagent impurities.²⁶ For barium the ICP-AES data were higher than NAA data. It is suggested that barium can be introduced in sample with acids or water used for sample preparation.

Table 3

ICP-AES operating conditions

	Normal	Alkali
RF Power, kW	1.2	0.8
Plasma Gas, L/min	10	10
Auxiliary Gas, L/min	0.6	0.6
Carrier Gas, L/min	0.7	0.8
Nebulizer Chamber	Co-axial cyclone	
Torch	mini	
Exposure, sec	30	
Integration Point	3 pixel	

To measure the linear relationship between data obtained by the two analytical techniques and to show how well the regression line represents the data Pearson's correlation coefficient (r), the coefficient of determination (r^2) were calculated (Table 3). Correlation greater than 0.8, is generally considered strong. In the present study for all eight elements r was higher than 0.8. In particular for Ca, K, Zn, and Fe, a perfect positive fit (approximately 1) was observed. The lower r values were for Mg and Ba. For magnesium, the correlation between methods increased from 0.77 to 0.88 when wines were divided in two groups (by winemaking companies). Thus, Mg can be defined as a representative "fingerprint" that can separate wines into two distinct classes. The percentage of the points fell within the regression line range between 60% (Mg) and 98% (Fe).

MATERIALS AND METHODS

Reagents

For ICP-AES analysis Fluka chemical standards of analytical grade, TraceSELECT Ultra class nitric acid and distilled water were used.

Materials

Twenty two samples of red and white wine from two major wine-production regions of Moldova were analyzed. Wines were obtained directly from producers: S.A. Romanesti and S.A. Cricova.

Inductively coupled plasma atomic emission spectroscopy ICP-AES

The ICP-AES measurements were carried out on ICPE-9000 spectrometer (ICP-AES, Shimadzu Co., Japan). The ICP-AES operating conditions are given in Table 3.

Sample preparation included wine dilution with 2% nitric acid solution (1:1) for determination of microelements. For macro-elements analysis dilution ranged from 1:25 (Na, Ca, Mg) to 1:100 (K). The concentration of nitric acid (1%) was kept.

All experimental data was processed with the use of MS ExcelTM XP and StatSoft Statistica 6.0 programs.

Neutron activation analysis

For NAA analysis, wine samples were evaporated in ultrapure quartz vials at 80°C for 24 hours and then dried in a oven until constant weight, after which the sample was irradiated simultaneously with standards at the IBR-2 reactor. The analytical scheme used has been described in detail elsewhere²⁷ and only a brief account is given here. The concentrations of elements based on short-lived radionuclides: Al, Ca, and Mg were determined by irradiation for 3 min at a thermal neutron fluency rate of $1.6 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. After decay for 3 and 15 min the samples were measured for 3 and 15 min, respectively. To determine long-lived isotopes: Ba, Fe, K, Na, and Zn, a cadmium-screened irradiation channel at a resonance neutron fluency rate of $3.31 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ was used. The samples were irradiated for 3 days, repacked, and then measured twice after decay for 4 and 20 days. The counting time varied from 30 min to 1.5 hours.

The NAA data processing and determination of element concentrations was performed using the software developed at FLNP JINR.²⁸

The quality control of the analytical measurements was carried out using certified standards—

1566b (Oysters tissue), 1633b (Coal fly ash), 1632c (Trace elements in coal), 690CC (Calcareous soil), 433 (Marine sediment). The validation of data obtained by NAA is proved by inter-laboratory studies like Wageningen evaluating programs for analytical laboratories (WEPAL) for different type of samples.^{29,30}

Data obtained by NAA in mg/kg were recalculated in mg/L using the formula:

$$C/1000*m$$

C – NAA concentration, mg/1000g

m – mass of ash in 1 L of wine, g/L

CONCLUSIONS

ICP-AES is suitable for fast and routine liquid samples analysis while NAA remains essential as a highly accurate reference method. High values of Pearson's correlation coefficient and coefficient of determination displays a strong relationship between the applied techniques. The results obtained for magnesium can be used for the confirmation of the geographical origin of wine products. Relatively low content of metals such as zinc, iron, and potassium gives evidence for the absence of exogenous metals of agronomical and technological origin. Furthermore ICP-AES and NAA can be applied to identify counterfeit wine products.

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