

## Measurement and Analysis of Mineral Components in Grape Wine by Inductively Coupled Plasma-Optical Emission Spectrometer

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**Abstract:** A direct measuring method for the determination of mineral components in grape wine by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was developed. It was applied to six grape wines from China's 2 major wine-producing regions-Changli in Hebei Province and Yantai in Shandong Province. Here in this study, eleven elements (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn) were analyzed. The analysis was performed by heating the wine sample in an oven with acid digestion method using concentrated nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>), followed by sequential determination of the elements by ICP-OES. Typical patterns of elements obtained by the multicomponent analyses can be evaluated by multivariate data analysis to recognize the wine origins.

**Keywords:** Grape wine, ICP-OES, mineral component

### INTRODUCTION

Grape wine is an alcoholic beverage, typically made of fermented grape juice. Its compositions and properties are related to the wine origin and age. The constituents of wine are water, ethanol, saccharides, amino acids, phenolic compounds and other pigments, and trace metals (Roig and Thomas, 2003; Katalinic *et al.*, 2004; Nilsson *et al.*, 2004; Monaci *et al.*, 2003). Moderate wine consumption can provide significant amounts of several human essential elements, i.e., Se, Mo, Mn, etc. However, excess metals are undesirable, and in some cases prohibited (such as Pb or As) due to potential health risks and legal requirements, though the metal concentrations in wine are low and usually do not affect the product taste (Grindlay *et al.*, 2009; Aceto *et al.*, 2002). In addition, the concentration pattern of most metals in wine has been used for determination of wine origin. Therefore, elemental determination of the metal levels not only contributes to human health, but also prevents adulteration and fraud.

To determine the mineral components in wine, several analytical methods were previously developed. However, most methods produce imprecise results, require large sample preparation, and are time-consuming. Although atomic spectroscopy is the most sensitive and rapid one of several methods for metal determination, the matrix composition of wines strongly affect the test accuracy due to both spectral and non-spectral interferences. Two points must be considered to perform the wine analysis: the low

analyte concentrations and the risk of matrix interferences (Grindlay *et al.*, 2009). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a multi-element method with very good detection power and offers the right conditions for reliable and rapid determination. By using ICP-OES, the wine organic matrix components do not contribute to interferences and have no effect on the final measurements, due to high plasma temperature.

The goal of this study is to measure and analyze the mineral components in grape wine by ICP-OES. Firstly, we applied ICP-OES to sequentially determine Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn in six red or white wine samples from Changli in Hebei Province or Yantai in Shandong Province. Secondly, the elemental concentration patterns were evaluated by multivariate data analysis to recognize the wine origins.

### MATERIALS AND METHODS

**Materials:** The investigation included 6 wines (4 red and 2 white) from China's major wine-producing regions (Changli in Hebei Province and Yantai in Shandong Province). These samples were selected to cover different origins. Samples were acquired at local supermarkets. All information regarding the analyzed samples was summarized in Table 1.

**Reagents:** The standard stock solutions of elements were as follows: 50 mg/L of K, Fe and Ca; 200 mg/L of

Table 1: Wine samples

Sample No.	Producer/region	Grape variety	Wine types
1	Yantai	Cabernet franc	Dry red
2	Yantai	Reisling	Dry white
3	Changli	Cabernet sauvignon	Dry red
4	Changli	Cabernet franc	Dry red
5	Changli	Cabernet gernischt	Dry red
6	Changli	Cabernet merlot	Dry white

Table 2: Lines used for determination of elements with ICP-OES

Element	ICP-OES $\lambda$ (nm)
Ca	317.933
Cd	228.802
Cr	267.716
Cu	324.752
Fe	238.204
K	766.490
Mg	285.213
Mn	259.372
Ni	231.604
Pb	220.353
Zn	213.857

Mg, Cu and Mn; 5 mg/L of Ni, Cd, Cr, Pb and Zn (Perkin-Elmer Instruments Co., Ltd. USA). The Working solutions were prepared by serial dilution of stock solutions with high purity water. The range of concentrations used depended on the elements determined. All other reagents were analytical grade or better. High purity water (i.e., with conductivity lower than 10 M $\Omega$ /cm) was obtained from a Milli-Q water purification system (Millipore. Co., USA).

**Apparatus:** All glassware and plastic ware were washed with deionized water, soaked in 2% HNO<sub>3</sub> overnight, rinsed with deionized water, and air-dried. ICP-OES determinations were performed with Perkin-Elmer Optima 2100DV spectrometer (Perkin-Elmer Instruments Co., Ltd. USA). Emission lines utilized were shown in Table 2. Argon (purity higher than 99.99%) was employed as plasmogen and carrier gas.

**Sample preparation:** In order to be able to use aqueous calibration standards the organic components of the wine, in particular the alcohol must be removed from the samples. The wine samples were prepared according to the following instructions: 5 mL volume of sample with 5 mL concentrated HNO<sub>3</sub> and 1 mL HClO<sub>4</sub> were transferred into a 100 mL conical beaker covered with a ribbed watch glass and heated on an oven for digestion. After cooling to room temperature, the remaining solution was transferred to a 25 mL volumetric flask and diluted to volume with deionized water. The blank solution that was prepared from 5 mL concentrated HNO<sub>3</sub> and 1 mL HClO<sub>4</sub> was used as a control for wine sample. The solutions were then filtered through filter paper into a triangular flask, followed by analysis with the ICP-OES.

Table 3: Instrumental conditions employed in ICP-OES for the elemental analysis of samples

Parameter	Value
RF power	1300 W
Gas	Argon
Plasma gas	15 L/min
Auxiliary gas	0.2 L/min
Nebuliser gas	0.8 L/min
Sample aspiration rate	1.5 mL/min
View	Axial
Background correction	2-Point
Number of replicates	1
Nebuliser	Mein hard

**Analytical methods:** The ICP-OES instrument was initialized and allowed to achieve thermal equilibrium over 30 min. The operating conditions of the ICP-OES equipment were summarized in Table 3.

**Statistical analysis:** Evaluation and analysis of data were performed by SPSS 11.5 software package for Windows (SPSS Inc, USA). Hierarchical cluster analysis and discriminant analysis were carried out.

## RESULTS AND DISCUSSION

Wine digestion destroys matrix components mitigating matrix effects due to organic compounds (Grindlay *et al.*, 2009). Plasma spectrometers are not very popular within food analysis laboratory in the developing countries because the cost of purchase and maintenance are well beyond their finances. However, routine use of ICP-OES could prove, in the long-term, to be more advantageous than expected. The wide linear dynamic range of this technique allows the concomitant determination of several analytes from major elements down to trace elements (Aceto *et al.*, 2002). A high temperature plasma yields optimal conditions for the efficient breakage of organic matter present in wine, thus the interferences ICP-OES are usually much lower than that in other atomic techniques. The precision of ICP-OES in wine samples is usually good for most elements and >2% at the mg/L.

**Interpretation of the results:** The ICP-OES was employed to determine 11 elements (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn) in grape wine. The maximum allowable concentrations of the elements were expressed in milligrams per liter in Table 4. Measuring the decomposed wines provides a wide variability and altogether lower values caused by losses during digestion in the conical beaker, viscosity influences by the perchloric acid during nebulization and contamination by the instruments and chemicals. The ICP-OES is fairly unsuitable to determine alkali elements, because the high temperature of the plasma

Table 4: Maximum allowable concentrations (mg/L) of elements in wine

Wine	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	Pb	Zn
1	107.2	Nd	0.03	0.37	1.59	1952.44	97.770	3.98	0.16	Nd	0.650
2	88.20	Nd	0.01	0.01	0.85	1593.04	103.54	4.26	0.08	Nd	0.460
3	83.70	Nd	0.01	0.17	Nd	510.150	80.160	1.12	0.54	Nd	5.440
4	147.0	Nd	0.02	0.06	0.89	1168.65	108.50	2.15	0.07	Nd	12.36
5	75.60	Nd	0.02	0.06	0.79	451.400	43.710	2.68	0.09	Nd	0.180
6	83.60	Nd	0.03	Nd	1.00	1014.37	91.020	5.12	0.10	Nd	0.050

Nd: Not detected

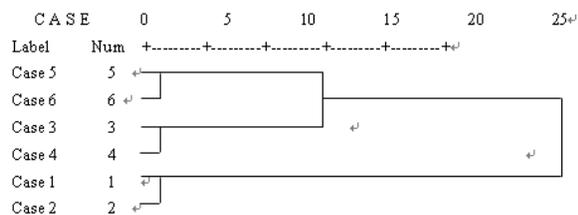


Fig. 1: Dendrographic classification of the six red and white wine samples based on their contents of Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn in mg/L, determined by ICP-OES

reduces the sensitivity of the arc lines for these easily ionized elements (Thiel and Danzer, 1997).

**Evaluation and interpretation of the results by Hierarchical Cluster Analysis (HCA):** In hierarchical cluster analysis, the similarity between samples was established using the distance concept, and calculated from mathematical relationships of numerical properties of the samples (Marengo and Aceto, 2003). In an iterative procedure, each sample was linked to the closest sample or group of samples and a distance was used to describe this union. The distances between different groups of samples could be evaluated in ways different from common linkage methods. The group formation were represented graphically in a dendrogram, which showed different groups at a normalized or rescaled distance of each sample from the others, when it was read from right to left.

As indicated in Fig. 1, HCA showed a clear discrimination between samples from Changli and Yantai. It is not difficult to explain this fact due to the region heterogeneity. The weather, the soil and the variety of grapes were distinct in Changli and Yantai, leading to the differences of wines in these two areas.

**Evaluation and interpretation of the results by Discriminant Analysis (DA):** For the integration of the classifying information individually provided by the metal composition, a multivariate statistical analysis approach, based on Discriminant Analysis (DA), was also employed. The discriminant information associated with the function derived from metal content (concentration of Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni,

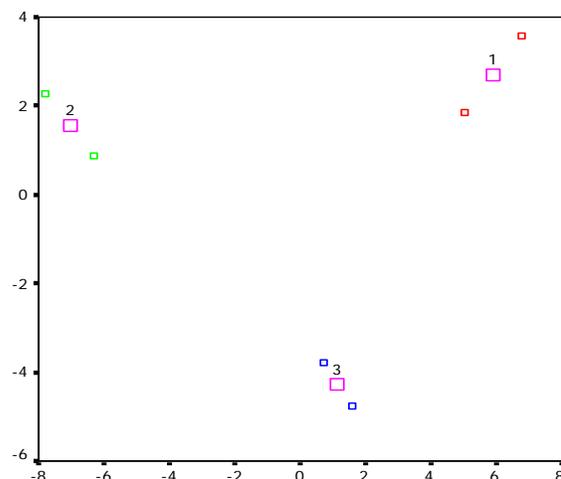


Fig. 2: DA plots of red and white wines

Class 1: Wines from Changli (Cabernet Sauvignon and Cabernet Franc); Class 2: Wines from Changli (Cabernet Gernischt and Cabernet Merlot); Class 3: Wines from Yantan

Pb and Zn, in mg L<sup>-1</sup>, determined by ICP-OES) can be grouped in the three first discriminant functions.

Once the discriminant functions were obtained, the relevant discriminant scores were calculated for each sample under research. Visualization of classification and between-group differentiation results was achieved by projecting the set of discriminant scores on the two-dimensional space defined by the first and 2<sup>nd</sup> discriminant functions (Fig. 2). The highest differentiation potential was shown to be linked to the direction of the first discriminant function, enabling the complete resolution between the different PDOs. Samples belonging to class 1, 2 and 3 were well separated from the others. The discriminant scatter plot showed that, samples belonging to class 1 were well separated from the others as expected. According to this finding that is supported by the differences of soil and grape variety, the samples of classes 1, 2 and 3 were actually considered as of different categories.

It follows that by taking a greater number of wine samples one can discover which element contents are reproducibly influenced by the wine growing and

making process and which are not been influenced at all. Therefore, this point would make it possible to judge the wine origins more effectively and still needs further investigation.

### CONCLUSION

The results showed that ICP-OES is preferable for metal determination in wine, for its fastness and simplicity of analysis. Quantitative determinations can be performed after easily overcoming interferences. Moreover, multielement analysis using ICP-OES requires little sample preparation and gives good precision analysis with low detection limits. The use of multivariate statistics is verified as a powerful tool for the examination of intercorrelations in a chemical data set and fingerprinting wine origin. Here our investigation has shown that it is feasible to directly analyze the mineral and trace elements in wine using ICP-OES, characterized by the short time required for sample pretreatment and the high level of measurement precision. In addition, by evaluating eleven elements, we clearly showed that Changli wines were distinct from Yantai wines by hierarchical cluster analysis. Furthermore, discrimination analysis using the same variables highlighted the different wine origins and grape varieties.

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