ICP–MS Analysis of Multi-Elemental Profile of Greek Wines and Their Classification According to Variety, Area and Year of Production

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Abstract: Major, minor and trace elements in wines from Greece were determined by inductively coupled plasma–mass spectrometry (ICP–MS). The concentrations of 44 elements (Na, Mg, P, K, Ca, Cu, Co, Cr, Zn, Sn, Fe, Mn, Li, Be, B, V, Sr, Ba, Al, Ag, Ni, As, Sn, Hg, Pb, Sb, Cd, Ti, Ga, Zr, Nb, Pd, Te, La, Sm, Ho, Tm, Yb, W, Os, Au, Th, U) in 90 white and red wines from six different regions in Greece for two consecutive vinification years, 2017 and 2018, were determined. Results for the elements aforementioned were evaluated by multivariate statistical methods, such as discriminant analysis and cluster analysis, and the wines were discriminated according to wine variety and geographical origin. Due to the specific choice of the analytes for multivariate statistical investigation, a prediction rate by cross-validation of 98% could be achieved. The aim of this study was not only to reveal specific relationships between the wine samples or between the chemical variables in order to classify the wines from different regions and varieties according to their elemental profile (wine authentication), but also to observe the annual fluctuation in the mineral content of the studied wine samples.

Keywords: elemental analysis; inductively coupled plasma–mass spectrometry; annual variation; chemometrics; wine authenticity

1. Introduction

Wine is a complex matrix and, it contains low-level concentrations of mineral elements [1]. Data on mineral elements as probe of origin determination must be carefully interpreted because mineral content in wines depends on many factors that can easily mask vital elemental information [2]. Many of these factors are natural sources (vineyard soil geochemistry), external contamination of the grapevine during growth, contamination through the winemaking process, as well as grape variety, maturity, and climatic conditions [3,4]. Other potential sources that affect mineral content are soil amendments, atmospheric pollution, pesticides, fertilizers, irrigation water, contact materials during transport, vinification and aging processes, enological processing aids, and additives [5–7]. For these reasons, wine classification reflects not only the geographical provenance but also anthropogenic factors. Metals are the best-placed descriptors to perform differentiation according to the geographical origin due to the direct relationship with the composition of the soil in which the vine is grown, with Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr, and Zn being the most common metal ions determined [8]. Some of these elements, such
as Fe, Zn, Cu, Cr, Se, Ca, Co, and Ni, are essential for the human organism in that they form an integral part of one or more enzymes involved in a metabolic or biochemical process [9,10]. Elements are also important for efficient alcoholic fermentation and for the prosthetic metallo-enzyme activation of yeast. In addition, mainly Zn and Fe can contribute to stability and clarity in the wine and its color, and they may affect the organoleptic characteristics of the wine [11]. Depletion of some elements occurs over time, especially during alcoholic fermentation. Precipitation of K and Ca as tartrate salts begins during alcoholic fermentation and continues during the aging period [12]. Alkaline elements, Rb, Li, and Cs, are good indicators of geographical provenance, as they are not included in the group of contaminant elements of wines, while B and Sr are natural elements that originate from their presence in the soil [13]. Mn, Mg, Sr, Ba, and rare-earth elements are also listed as useful elements, although the first two should be considered carefully, as they can be introduced through viticultural practices such as the use of fertilizers and pesticides, while rare-earth element content in wines can increase due to treatment with bentonites [14]. Wine minerals are also useful because of the possibility of toxicological risk, such as Cd and Pb [15,16]. All these factors may markedly change the multi-element composition of the wine, thus precluding their use for authentication purposes [17].

Several studies on this subject have been carried out in most wine producing-countries, such as Argentina [18], Australia [19], Brazil [20,21], Greece [22], Italy [23], Portugal [24], Romania [25], South Africa [26], and Spain [27], indicating that the multi-elemental determination of wines can enable their successful discrimination.

Many multi-element techniques have been employed in elemental analysis in foods, such as atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), inductively coupled plasma–mass spectrometry (ICP–MS), and inductively coupled plasma optical emission spectrometry (ICP–OES) [28]. Inductively coupled plasma–mass spectrometry (ICP–MS) is considered a very potent discriminant technique regarding metal content in wine samples since it provides high detection power due to low detection limits as well as high selectivity and sensitivity [29]. This technique also provides the simultaneous determination of several elements present in low concentrations in the samples [11]. In addition, chemometric analysis (cluster analysis (CA) and discriminant analysis (DA)) was performed to present specific correlations between the chemical variables that characterized the wine samples.

The main goal of this study was to develop a simple, robust, and rapid analytical method with minimum sample pretreatment and low risk of loss of analytes or contamination for the authentication (characterization and differentiation) of Greek wines based on their elemental profile. For this purpose, the direct determination of 44 metals employing ICP–MS instrumentation was carried out for wine samples produced in six different regions of Greece from nine different varieties.

2. Materials and Methods
2.1. Reagents and Materials

Multi-element stock solutions containing 1000 mg/L were used to prepare external standard solutions. TraceSelect concentrated HNO3 was purchased from Fluka. MilliQ water (Millipore, Burlington, MA, USA) was used for dilutions.

2.2. Wine Samples

A total of 90 wine samples from 9 varieties—white and red—were collected from 6 different regions and various producers in Greece (Figure 1) [4]. The wines were derived from 2 consecutive harvests, 2017 and 2018. An overview of grape varieties, type, and the origin of the Greek wines is given in Table 1, while the mineral concentration of each wine sample is given in the Supplementary File.
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**Figure 1.** Hierarchical dendrogram for 44 chemical variables for the vintage year 2017. The clustering led to the following 4 significant clusters: K1 (K, Tl, Os, Au, Se, Pd, Ba, P, Mg, B, Fe, Sr), K2 (Ca, Cu, Na, V, Li, Co, Mn, Cr, Ni, Zn, Sn, Te, La, Pb, Sb), K3 (Tm, Hg, Al, As, Ag, Cd), and K4 (Be, Ga, Zr, Yb, Sm, Ho, Th, U, Ti, Nb, W).

**Table 1.** An overview of the Greek wine samples (number of samples, vinification year, origin, variety, type of wine).

| Number of Samples | Year of Production | Origin | Variety | Type  |
|-------------------|--------------------|--------|---------|-------|
| 32                | 17                 | Arkadia | Moschofilero | white |
| 28                | 18                 | Attika  | Syrah   | red   |
| 2                 | 17                 | Attika  | Asyrtiko | white |
| 4                 | 17                 | Attika  | Malagouzia | white |
| 5                 | 18                 | Attika  | Malagouzia | white |
| 7                 | 17                 | Attika  | Roditis  | white |
| 7                 | 17                 | Attika  | Roditis  | white |
| 2                 | 18                 | Attika  | Savatiano | white |
| 3                 | 17                 | Naousa  | Syrah   | red   |
| 1                 | 18                 | Naousa  | Xinomavro | red   |
| 8                 | 17                 | Nemea   | Agiorgitiko | red   |
| 18                | 18                 | Samos   | Muscat  | white |
| 4                 | 17                 | Santorini | Asyrtiko | white |

Table 2 summarizes the analytical results (mean concentration ± standard deviation) for the whole set of samples. Considering the mean concentrations, the elements were
divided into “macro elements” (concentration > 0.1 mg/L), “trace elements” (concentration ranging from 99.9 µg/L to 0.1 µg/L) and “ultra-trace elements” (concentration < 100 ng/L).

Table 2. An overview of metal content (mean ± standard deviation) of Greek wine samples for the two consecutive vinifications, 2017 and 2018.

| Macro Elements (mg/L) | Vinification Year 2017 | Vinification Year 2018 |
|-----------------------|------------------------|------------------------|
|                       | Mean Concentration ± Standard Deviation | Mean Concentration ± Standard Deviation |
| K                     | 705 ± 265              | 774 ± 264              |
| Ca                    | 81 ± 18                | 85 ± 17                |
| P                     | 150 ± 47               | 153 ± 37               |
| Na                    | 23 ± 19                | 18 ± 13                |
| Mg                    | 87 ± 17                | 103 ± 20               |
| Zn                    | 0.52 ± 0.23            | 0.57 ± 0.18            |
| Fe                    | 0.86 ± 0.56            | 1.70 ± 0.81            |
| Mn                    | 1.3 ± 0.43             | 1.9 ± 0.97             |
| B                     | 5.4 ± 1.5              | 5.7 ± 1.2              |
| Sr                    | 0.29 ± 0.09            | 0.39 ± 0.12            |
| Al                    | 0.57 ± 0.39            | 0.61 ± 0.39            |
|                       |                       |                        |
| Trace elements (ug/L) |                       |                        |
| Cu                    | 87 ± 50                | 67 ± 46                |
| Co                    | 3.8 ± 2.1              | 6.3 ± 3.8              |
| Cr                    | 13 ± 7.1               | 14 ± 5.1               |
| Se                    | 0.38 ± 0.22            | 0.80 ± 0.35            |
| Li                    | 13 ± 12                | 11 ± 7.9               |
| Be                    | 0.37 ± 0.59            | 0.86 ± 0.77            |
| V                     | 2.1 ± 1.5              | 4.1 ± 2.6              |
| Ba                    | 62 ± 25                | 87 ± 28                |
| Ag                    | 0.19 ± 0.16            | 2.4 ± 0.76             |
| Ni                    | 29 ± 14                | 34 ± 14                |
| As                    | 2.1 ± 1.6              | 1.8 ± 1.6              |
| Sn                    | 0.02 ± 0.01            | 0.84 ± 0.55            |
| Hg                    | 1.1 ± 1.0              | 13 ± 2.6               |
| Pb                    | 18 ± 14                | 24 ± 14                |
| Sb                    | 0.73 ± 0.55            | 0.37 ± 0.42            |
| Cd                    | 0.30 ± 0.32            | 0.40 ± 0.27            |
| Ti                    | 16 ± 5.9               | 19 ± 8.1               |
| Ga                    | 0.15 ± 0.11            | 0.13 ± 0.11            |
| Zr                    | 1.1 ± 0.74             | 2.5 ± 2.1              |
| La                    | 1.2 ± 1.1              | 0.43 ± 0.26            |
| W                     | 0.15 ± 0.08            | 0.43 ± 0.23            |
| Tl                    | 0.25 ± 0.14            | 0.29 ± 0.13            |
|                       |                       |                        |
| Ultra-trace elements (ng/L) |                   |                        |
| Nb                    | 57 ± 45                | 104 ± 57               |
| Pd                    | 92 ± 59                | 195 ± 99               |
| Te                    | 40 ± 39                | 107 ± 22               |
| Sm                    | 29 ± 24                | 131 ± 131              |
| Ho                    | 11 ± 8.2               | 17 ± 8.2               |
| Tm                    | 4.4 ± 2.7              | 24 ± 14                |
| Yb                    | 44 ± 21                | 101 ± 62               |
| Os                    | 67 ± 41                | 230 ± 163              |
| Au                    | 61 ± 34                | 258 ± 202              |
| Th                    | 41 ± 50                | 170 ± 80               |
| U                     | 61 ± 41                | 162 ± 102              |

2.3. Sample Reparation

Microwave-assisted digestion was used as it is a very effective technique in extracting the metal ions bound in stable complexes. Microwave sample digestion was carried out in a CEM Mars 5 (CEM Microwave Technology, Buckingham, UK) instrument and the samples were digested using the program recommended by the manufacturer. Table 3
shows operational parameters for microwave digestion. Digestion of wine samples was carried out in polytetrafluoroethylene (PTFE) vessels, which were previously cleaned in concentrated nitric acid to avoid any kind of contamination. Each time, 2.5 mL of wine sample and 5 mL of HNO$_3$ were transferred to the vessel, where the acid was added in portions, as the addition of the entire amount at once would cause a loss of the analyte due to the excessively rapid reaction of organic matter in wine and heating [30]. After the digestion step was completed, the digestion vessels were cooled to room temperature. Then, the solutions were transferred to vials and diluted with Millipore water to a final volume of 20 mL.

### Table 3. Microwave digestion conditions.

| Power (W) | Ramp Time (min) | Temperature (°C) | Stirrer Hold Time (min) |
|-----------|-----------------|-------------------|-------------------------|
| Stage     | Maximum %       |                   |                         |
| 1         | 1600 100        | 2 165             | 0 0                     |
| 2         | 1600 100        | 3 175             | 0 5                     |

#### 2.4. ICP–MS Analysis

Multi-element determination was performed on an Agilent 7700 ICP–MS instrument. In accordance with the analytes of interest, the collision/reaction cell was in “He and No gas mode”. For the ICP–MS analysis, the following mass-to-charge ratios (m/z) were recorded: 23Na, 24Mg, 31P, 39K, 44Ca, 63Cu, 59Co, 52Cr, 64Zn, 78Sn, 56Fe, 55Mn, 7Li, 9Be, 11B, 51V, 88Sr, 137Ba, 27Al, 109Ag, 60Ni, 75As, 118Sn, 202Hg, 208Pb, 121Sb, 111Cd, 47Ti, 71Ga, 90Zr, 93Nb, 105Pd, 125Te, 139La, 146Nd, 147Sm, 165Ho, 169Tm, 172Yb, 182W, 189Os, 197Au, 205Tl, 232Th, 238U. Here, 45 Sc (lg/L) was used as an internal standard to correct instrument drift. Two spiked wine samples were prepared with selected elements in order for the method’s accuracy to be accessed through the recovery. The selected metals were Pb, Cd, As, Cr, Ni, Fe, Mn, Zn, Se, Hg, and Sb, cited in Table 4. The recovery of all selected metals was within the accepted limits of 80–120% according to Table 4. The instrument and accessories were PC-controlled by Mass Hunter software.

### Table 4. Recovery percentage for selected metals in spike dilutions.

| Type | Cr | Mn | Fe | Ni | Zn | As | Se | Pb | Cd | Sb | Hg |
|------|----|----|----|----|----|----|----|----|----|----|----|
| white| 107| 103| 105| 109| 114| 110| 112| 104| 107| 105| 111|
| red  | 110| 92 | 100| 109| 115| 111| 114| 105| 104| 103| 106|

#### 2.5. Statistical Analysis

Statistical analysis of the multi-element data was carried out to evaluate the effect of the year of production on mineral composition and the effect of the variety and region of the wine samples on the mineral content. The statistical analysis of the multi-element composition of the wine samples was first performed by one-way analysis of variance (one-way ANOVA) and comparison of means (Tukey’s HSD tests at 95% confidence level). Moreover, a normality test (Anderson Darling test), test for equal variances (Levene test), and a run test were carried out in order to check if the results met the requirements of the one-way ANOVA. Whenever the parametric test assumptions were not verified, a data transformation was attempted with Box–Cox or Johnson transformation and a non-parametric test (Kruskal–Wallis test) was applied. In these cases, comparison of means was not carried out. Correlations between metal concentrations were carried out (Pearson correlations). The data were then processed using multivariate chemometric methods, namely cluster analysis (CA) and discriminant analysis (DA), in order to determine, for each element, the main effect of the region and variety, using the Statistica software package (Statsoft Inc., Tulsa, Version 12, OK, USA), IBM SPSS Statistics 25, SIMCA (Umetrics, version 15.0.2, Umeå, 907 29, Sweden), Minitab 19, and R.
To validate the classification model based on the ICP-MS method, external and internal validation were performed. For classification of the samples regarding variety and area of production, OPLS-DA and O2PLS-DA methods were used. A separate data set (as a test set) from the experimental data set (training set) was used to validate the discrimination ability [31,32]. Training and test sets were randomly generated by keeping in both sets samples from all the groups. Approximately 70% of the overall samples (N = 90) were kept in the training sets and the remaining 30% in the test sets. UV scaling was used throughout this study. The confidence level of parameters was set to 95% and the significance level for distance to the model and Hotelling’s T2 was set to 0.05.

3. Results and Discussion

3.1. Preliminary Classification of Wines According to Elemental Composition

Cluster analysis displays the similarity of objects and classifies them into clusters, so that they are similar within a class but different from those in other classes with respect to the predetermined selection criterion. Hierarchical cluster analysis is the most common approach, and all the data are illustrated by a dendrogram. Cluster analysis is also used to group variables into homogenous and distinct groups. The grouping of the variables by means of cluster analysis helps to identify redundant variables and reduce their number [15]. The HCA was performed after standardizing the input raw data and finding the Euclidean distance measure and Ward’s linkage method. The data were standardized according to the equation:

\[
\frac{X - X}{S}
\]

where

- \(X\): sample;
- \(X\): average;
- \(S\): standard deviation.

For the vintage year 2017 (Figure 1), the unsupervised clustering led to the formation of four significant clusters:
- K1 (K, Tl, Os, Au, Se, Pd, Ba, P, Mg, B, Fe, Sr);
- K2 (Ca, Cu, Na, V, Li, Co, Mn, Cr, Ni, Zn, Sn, Te, La, Pb, Sb);
- K3 (Tm, Hg, Al, As, Ag, Cd);
- K4 (Be, Ga, Zr, Yb, Sm, Ho, Th, U, Ti, Nb, W).

Concerning the vintage year 2018 (Figure 2), the clustering led to the following four significant clusters:
- K1 (K, Tl, P, Sn, Mg, Sr, B, Te, Ca, Cu, Cr, Pd, Hg, Ba, Ni, Pb);
- K2 (Co, Mn, Os, Cd, Zn, Sb, Se, W, Ti, Nb);
- K3 (Li, La, Sm, Ho, Th, Ag);
- K4 (Na, Fe, Au, Be, Zr, U, V, Al, As, Tm, Yb, Ga).
K2 (Co, Mn, Os, Cd, Zn, Sb, Se, W, Ti, Nb); K3 (Li, La, Sm, Ho, Th, Ag); K4 (Na, Fe, Au, Be, Zr, U, V, Al, As, Tm, Yb, Ga).

Figure 2. Hierarchical dendrogram for 44 chemical variables for the vintage year 2018. The clustering led to the following 4 significant clusters: K1 (K, Tl, P, Sn, Mg, Sr, B, Te, Ca, Cu, Cr, Pd, Hg, Ba, Ni, Pb), K2 (Co, Mn, Os, Cd, Zn, Sb, Se, W, Ti, Nb), K3 (Li, La, Sm, Ho, Th, Ag), and K4 (Na, Fe, Au, Be, Zr, U, V, Al, As, Tm, Yb, Ga).

After this grouping, a correlation matrix plot was produced in order to distinguish the relations between the metals. Figures 3 and 4 clearly show the positive (with blue shading) and negative (with red shading) correlation of metals, which corresponds with the clusters that are mentioned above. In particular, suitable forecasting models were created with 95% continuous integration (CI) and a 95% prediction interval (PI), and we selected those that had an average up to 30% R-sq. R-squared (R2) is a statistical measure that represents the proportion of the variance for a dependent variable that is explained by an independent variable or variables in a regression model. Whereas correlation explains the strength of the relationship between an independent and dependent variable, R-squared explains the extent to which the variance of one variable explains the variance of the second variable. Therefore, if the R2 of a model is 0.50, then approximately half of the observed variation can be explained by the model’s inputs [33]. Considering Figure 3, it is clearly observed that the maximum correlation results from cluster (K1) are between the metals K, Tl, Mg, Fe, and B; from (K2), they are Co, Mn, V, and Na, and from (K4), they are Zr, Ho, Yb, Sm, Th, and U, whereas Figure 4 distinguishes the correlations between the pairs from cluster (K1) Mg with Sr, from cluster (K2) Co, Mn, and Os, from cluster (K3) Li, La, and Sm, and from cluster (K4), Na, Fe, Be, V, Zr, Yb, Au, U, Ga, and Tm.
Figure 3. Correlation matrix plot for vintage year 2017, indicating the positive (with blue shading) and the negative (with red shading) correlation between metals.
3.2. Classification of Wines According to Their Grape Variety

Aiming to verify if mineral content allows the classification of wines according to their variety, a discriminant analysis was performed. Figures 5 and 6 reflect the discriminating ability of the OPLS-DA model, which can be observed in the scatter plot, showing a reasonably good classification among samples according to the variety of wine. In particular, Agiorgitiko, Asystiko, Malagoyzia, Muscat, Mosxofileri, Xinomavro, Roditis, Savatiano, and Syrah are clearly separated, with a proportion of 97.78% and 96.67% for both harvest years, respectively. Tables 5 and 6 summarize all the misclassified observations and indicate the predicted groups. The results obtained with this canonical analysis show that, using the elemental composition of wines, it is possible to discriminate among these wines considering the grape variety, as the proportion of the correctly classified chemical variables is incomparable with the misclassified.

Figure 4. Correlation matrix plot for vintage year 2018, indicating the positive (with blue shading) and the negative (with red shading) correlation between metals.
Figure 5. Score scatterplots for the wine samples of 2017 classified regarding variety (i.e., 1: Syrah, 2: Agiorgitiko, 3: Asyrtiko, 4: Malagouzia, 5: Muscat, 6: Moschofilero, 7: Xinomavro, 8: Roditis, and 9: Savatiano), where (a) training set, (b) test set, (c) overall model 2D, and (d) overall model 3D.

Figure 6. Score scatterplots for the wine samples of 2018 classified regarding variety (i.e., 1: Syrah, 2: Agiorgitiko, 3: Asyrtiko, 4: Malagouzia, 5: Muscat, 6: Moschofilero, 7: Xinomavro, 8: Roditis, and 9: Savatiano), where (a) training set, (b) test set, (c) overall model 2D, and (d) overall model 3D.
Table 5. Misclassification tables produced for the OPLS-DA models of the wine samples of 2017 classified regarding variety, where (a) training set, (b) test set, (c) overall model.

(a) Variety, 2017 Training Set

| Samples  | Correct 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|-----------|---|---|---|---|---|---|---|---|
| Syrah    | 10%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Agioritiko | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Asyrtiko | 100%      | 0 | 0 | 15 | 0 | 0 | 0 | 0 | 0 |
| Malagouzia | 75%      | 0 | 0 | 0 | 3 | 0 | 1 | 0 | 0 |
| Muscat   | 100%      | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| Moschofilero | 100%  | 0 | 0 | 0 | 0 | 0 | 29 | 0 | 0 |
| Xinomavro | 100%     | 0 | 0 | 0 | 0 | 0 | 6 | 0 | 0 |
| Roditis  | 100%      | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| Savatiano | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| **Total** | **66**    | **96.97%** | | | | | | | |

(b) Variety, 2017 Test Set

| Samples  | Correct 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|-----------|---|---|---|---|---|---|---|---|
| Syrah    | 100%      | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Agioritiko | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Asyrtiko | 100%      | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Malagouzia | 100%     | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| Muscat   | 100%      | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 |
| Moschofilero | 100%  | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 |
| Xinomavro | 100%     | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 |
| Roditis  | 100%      | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| Savatiano | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| **Total** | **24**    | **100%** | | | | | | | |

(c) Variety, 2017 Overall Model

| Samples  | Correct 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|-----------|---|---|---|---|---|---|---|---|
| Syrah    | 66.67%    | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| Agioritiko | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Asyrtiko | 100%      | 19 | 0 | 0 | 19 | 0 | 0 | 0 | 0 |
| Malagouzia | 85.71%  | 0 | 0 | 0 | 6 | 0 | 1 | 0 | 0 |
| Muscat   | 100%      | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Moschofilero | 100% | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 |
| Xinomavro | 100%     | 0 | 0 | 0 | 0 | 0 | 9 | 0 | 0 |
| Roditis  | 100%      | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 |
| Savatiano | 100%     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| **Total** | **90**    | **97.78%** | | | | | | | |

Analytically, by observing the results of Table 6, it could be said that three samples (1 from Syrah and 2 from Malagouzia groups) are wrongly classified; thus, they are responsible for lowering the successful classification of the overall model (Table 6c) to 96.67%. In future, more samples from these two varieties and provinces are considered important to be added to the model, as the more samples each group contains, the better classification is obtained. As can be seen in Table 6a, in the training set, several samples were misclassified, but when they were mixed with the test set, the overall model was improved.

The same pattern can be observed in Table 5. Overall, two samples (1 from Syrah and 1 from Malagouzia groups) are wrongly classified; thus, they are responsible for lowering the successful classification of the overall model (Table 5c) to 97.78%. The R2X(cum), R2Y(cum), and Q2(cum) scores of classifications for the wine samples between 2017 to 2018 regarding variety are presented in Table 7. It can be observed that the values of R2 and Q2 indicated that the model had very good fitness and prediction ability as both R2 and Q2 > 0.5, and the difference between R2Xcum and Q2cum was less than 0.2–0.3, highlighting the importance of the models. The result shows that the classification model is feasible and successful regarding variety.
Table 6. Misclassification tables produced for the OPLS-DA models of the wine samples of 2018 classified regarding variety, where (a) training set, (b) test set, (c) overall model.

| (a) Variety, 2018 Training Set | Samples | Correct    | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------------------|---------|------------|---|---|---|---|---|---|---|---|---|
| 1 Syrah                       | 1       | 0%         | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| 2 Agioritiko                  | 15      | 100%       | 0 | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 Asyrtiko                    | 5       | 100%       | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 |
| 4 Malagouzia                  | 4       | 0%         | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 |
| 5 Muscat                      | 2       | 0%         | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 |
| 6 Moschofilero                | 25      | 92%        | 0 | 2 | 0 | 0 | 0 | 0 | 23 | 0 | 0 |
| 7 Xinomavro                   | 6       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 0 |
| 8 Roditis                     | 2       | 0%         | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| 9 Savatiano                   | 6       | 0%         | 0 | 0 | 4 | 0 | 0 | 0 | 2 | 0 | 0 |
| Total                         | 66      | 74.24%     |   |   |   |   |   |   |   |   |   |

| (b) Variety, 2018 Test Set    | Samples | Correct    | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------------------|---------|------------|---|---|---|---|---|---|---|---|---|
| 1 Syrah                       | 2       | 100%       | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 Agioritiko                  | 3       | 100%       | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 Asyrtiko                    | 3       | 100%       | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| 4 Malagouzia                  | 3       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 Muscat                      | 2       | 100%       | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| 6 Moschofilero                | 3       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 |
| 7 Xinomavro                   | 3       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 |
| 8 Roditis                     | 1       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 9 Savatiano                   | 4       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| Total                         | 24      | 100%       |   |   |   |   |   |   |   |   |   |

| (c) Variety, 2018 Overall Model | Samples | Correct    | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------------------|---------|------------|---|---|---|---|---|---|---|---|---|
| 1 Syrah                          | 3       | 66.67%     | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| 2 Agioritiko                     | 18      | 100%       | 0 | 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 Asyrtiko                       | 8       | 100%       | 0 | 0 | 0 | 8 | 0 | 0 | 0 | 0 | 0 |
| 4 Malagouzia                     | 7       | 71.43%     | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 2 |
| 5 Muscat                         | 4       | 100%       | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 |
| 6 Moschofilero                   | 28      | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 28 | 0 | 0 |
| 7 Xinomavro                      | 9       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 0 | 0 |
| 8 Roditis                        | 3       | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 |
| 9 Savatiano                      | 10      | 100%       | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 0 |
| Total                            | 90      | 96.67%     |   |   |   |   |   |   |   |   |   |

Table 7. The R2X(cum), R2Y(cum), and Q2(cum) scores of classifications for the wine samples between 2017 to 2018 regarding variety by OPLS-DA.

| Vintage Year | Set    | N     | R2X(cum) | R2Y(cum) | Q2(cum) |
|--------------|--------|-------|----------|----------|---------|
| 2017         | training | 66    | 0.682    | 0.676    | 0.584   |
|              | test    | 24    | 0.833    | 0.889    | 0.600   |
|              | overall | 90    | 0.770    | 0.711    | 0.595   |
| 2018         | training | 66    | 0.804    | 0.798    | 0.525   |
|              | test    | 24    | 0.814    | 0.863    | 0.517   |
|              | overall | 90    | 0.748    | 0.687    | 0.598   |

3.3. Classification of Wines According to Their Area of Production

Taking into consideration that the mineral composition of wines reflects the elemental composition of the vineyard and is a consequence of the wine’s origin, multi-elemental analysis is an important tool in the wine industry. Several studies have been performed to find chemical markers that allow the traceability of wines [34,35].

The O2PLS-DA results of the training set displayed excellent goodness of fit (R2Y(cum)) and predictability (Q2(cum)) for the discrimination of the samples regarding the six areas of production, as shown in Tables 8 and 9. Then, the test set was imported into the training set to test the distribution of all the samples together. Therefore, the overall model was obtained and the coefficients R2 and Q2 (Table 10) as well as the % of correct classification (Tables 8 and 9) were still very good. All the test set samples could be classified into the correct area of production group. No outlier observations (in the area outside of an ellipse with a 95% confidence interval for Hotelling’s T2 on the score plots) in Figures 7 and 8 were observed and this explains the 100% excellent classification of the samples in Tables 8 and 9. From Table 10, it can be observed that the values of R2 and Q2 indicated that the model had...
very good fitness and prediction ability as both $R^2$ and $Q^2 > 0.5$, and the difference between $R^2Xcum$ and $Q^2cum$ was less than 0.2–0.3, highlighting the importance of the models. The result shows that the geographical classification model is feasible and successful.

Table 8. Misclassification tables produced for the O2PLS-DA models of the wine samples of 2017 classified regarding area of production, where (a) training set, (b) test set, (c) overall model.

(a) Area of production, 2017 Training Set

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 5 | 100% | 5 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 16 | 100% | 0 | 16 | 0 | 0 | 0 | 0 |
| 3 Nemea | 3 | 100% | 0 | 0 | 3 | 0 | 0 | 0 |
| 4 Santorini | 11 | 100% | 0 | 0 | 0 | 11 | 0 | 0 |
| 5 Samos | 2 | 100% | 0 | 0 | 0 | 0 | 2 | 0 |
| 6 Arkadia | 27 | 100% | 0 | 0 | 0 | 0 | 0 | 27 |
| Total | 64 | 100% | 5 | 16 | 3 | 11 | 2 | 0 |

(b) Area of production, 2017 Test Set

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 5 | 100% | 5 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 5 | 100% | 0 | 5 | 0 | 0 | 0 | 0 |
| 3 Nemea | 5 | 100% | 0 | 0 | 5 | 0 | 0 | 0 |
| 4 Santorini | 4 | 100% | 0 | 0 | 0 | 4 | 0 | 0 |
| 5 Samos | 2 | 100% | 0 | 0 | 0 | 0 | 2 | 0 |
| 6 Arkadia | 5 | 100% | 0 | 0 | 0 | 0 | 0 | 5 |
| Total | 26 | 100% | 5 | 5 | 4 | 2 | 0 | 0 |

(c) Area of production, 2017 Overall Model

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 10 | 100% | 10 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 21 | 100% | 0 | 21 | 0 | 0 | 0 | 0 |
| 3 Nemea | 8 | 100% | 0 | 0 | 8 | 0 | 0 | 0 |
| 4 Santorini | 15 | 100% | 0 | 0 | 0 | 15 | 0 | 0 |
| 5 Samos | 4 | 100% | 0 | 0 | 0 | 0 | 4 | 0 |
| 6 Arkadia | 32 | 100% | 0 | 0 | 0 | 0 | 0 | 32 |
| Total | 90 | 100% | 10 | 21 | 15 | 0 | 0 | 0 |

Table 9. Misclassification tables produced for the O2PLS-DA models of the wine samples of 2018 classified regarding area of production, where (a) training set, (b) test set, (c) overall model.

(a) Area of production, 2018 Training Set

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 5 | 100% | 5 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 21 | 100% | 0 | 21 | 0 | 0 | 0 | 0 |
| 3 Nemea | 14 | 100% | 0 | 0 | 14 | 0 | 0 | 0 |
| 4 Santorini | 1 | 100% | 0 | 0 | 0 | 1 | 0 | 0 |
| 5 Samos | 2 | 100% | 0 | 0 | 0 | 0 | 2 | 0 |
| 6 Arkadia | 23 | 100% | 0 | 0 | 0 | 0 | 0 | 23 |
| Total | 66 | 100% | 5 | 21 | 15 | 2 | 0 | 0 |

(b) Area of production, 2018 Test Set

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 5 | 100% | 5 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 6 | 100% | 0 | 6 | 0 | 0 | 0 | 0 |
| 3 Nemea | 4 | 100% | 0 | 0 | 4 | 0 | 0 | 0 |
| 4 Santorini | 2 | 100% | 0 | 0 | 0 | 2 | 0 | 0 |
| 5 Samos | 2 | 100% | 0 | 0 | 0 | 0 | 2 | 0 |
| 6 Arkadia | 5 | 100% | 0 | 0 | 0 | 0 | 0 | 5 |
| Total | 24 | 100% | 5 | 6 | 2 | 0 | 0 | 0 |

(c) Area of production, 2018 Overall Model

| Samples | Correct | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|---------|---|---|---|---|---|---|
| 1 Naousa | 10 | 100% | 10 | 0 | 0 | 0 | 0 | 0 |
| 2 Attika | 27 | 100% | 0 | 27 | 0 | 0 | 0 | 0 |
| 3 Nemea | 18 | 100% | 0 | 0 | 18 | 0 | 0 | 0 |
| 4 Santorini | 3 | 100% | 0 | 0 | 0 | 3 | 0 | 0 |
| 5 Samos | 4 | 100% | 0 | 0 | 0 | 0 | 4 | 0 |
| 6 Arkadia | 28 | 100% | 0 | 0 | 0 | 0 | 0 | 28 |
| Total | 90 | 100% | 10 | 27 | 3 | 0 | 0 | 0 |
Table 10. The R2X(cum), R2Y(cum), and Q2(cum) scores of classifications for the wine samples between 2017 to 2018 regarding area of production by O2PLS-DA.

| Vintage Year | Set     | N  | R2X(cum) | R2Y(cum) | Q2(cum) |
|--------------|---------|----|----------|----------|---------|
| 2017         | training| 64 | 0.766    | 0.875    | 0.719   |
|              | test    | 26 | 0.867    | 0.951    | 0.765   |
|              | overall | 90 | 0.781    | 0.844    | 0.642   |
| 2018         | training| 66 | 0.632    | 0.811    | 0.570   |
|              | test    | 24 | 0.743    | 0.898    | 0.702   |
|              | overall | 90 | 0.736    | 0.818    | 0.622   |

Figure 7. Score scatterplots for the wine samples of 2017 classified regarding area of production (i.e., 1: Naousa, 2: Attika, 3: Nemea, 4: Santorini, 5: Samos, and 6: Arkadia), where (a) training set, (b) test set, (c) overall model 2D, and (d) overall model 3D.

3.4. Annual Fluctuation in Mineral Content

Analysis of measurement results reveals how seasonal changes over the years influence the concentration of analytes. After a t-test analysis, there was not any significant variation between K (p = 0.079), Ca (p = 0.113), P (p = 0.679), Cr (p = 0.199), Zn (p = 0.104), Li (p = 0.121), B (p = 0.084), and Ga (p = 0.124). However, other elements differed statistically, particularly some rare-earth elements that indicate the minimum level of significance (p < 0.001), such as U, Th, Au, Os, W, Pd, Yb, Tm, Ho, Sm, La, Te, Pd, Nb, Zr, Ba, Sr, V, Be, Mn, Fe, Se and Co, Na (p = 0.020), Mg (p = 0.001), Cu (p = 0.005), Ti (p = 0.008), and Tl (p = 0.026). As the graphical depiction shows (Figure 9), most of the aforementioned metals displayed higher concentration levels in wine samples from vintage 2018, with the exception of Na and La, which had lower concentration levels in the same harvest year compared with the concentration levels in harvest 2017.
These statistical differences in the concentration levels of metals in the wine samples can be attributed to the significant rainfall in the early summer of the year 2018. It is widely known that wine water status depends on the climate (rainfall and potential evapotranspiration), soil (water holding capacity), and training system (canopy architecture and leaf area). Wine water uptake conditions are a key factor in understanding the effect of the terroir on grape quality potential, because the main terroir factors are involved and interact (climate, soil, grapevine). The proportions of mineral nutrients in the finished wine bear only a complex, indirect, and distant relationship with the geological minerals in the vineyard. This is why it has proven so difficult to find a reliable chemical means of using the inorganic constituents of a wine to detect the annual adulteration of the multi-element profile [36,37]. Many surveys have studied the impact of environmental factors and climatic changes on wine physiology [38]. Others have pointed out the influence of vineyard on the mineral composition of the wine [39]. However, it is very difficult to assess the joint effect of all the different geographic variables (soils, climate, microclimate, slope, etc.) that make up a vineyard; the effects caused by these parameters on wine have been independently reported.

From the comparison of results of the wine samples from the 2017 and 2018 vintages, it could be concluded that the element composition of wine is not dependent only on the year of production but on many other factors that must be studied. Of course, this result must be confirmed with a larger number of samples and other vintages so as to gain a more consolidated view.

Figure 8. Score scatterplots for the wine samples of 2018 classified regarding area of production (i.e., 1: Naousa, 2: Attika, 3: Nemea, 4: Santorini, 5: Samos, and 6: Arkadia), where (a) training set, (b) test set, (c) overall model 2D, and (d) overall model 3D).
Figure 9. Cont.
4. Conclusions

Mineral content in wines is of great importance for authenticity purposes and quality control. Minerals can influence a wine’s taste and quality, stability, and the toxicological risks associated with wine consumption, since some of them are regulated by law. In this study, an ICP–MS procedure enabled the quantification of 44 mineral elements from 90 wine samples from six different regions in Greece in two consecutive harvests. The statistical analysis of data obtained by ICP–MS has shown that a compensatory differentiation of the wine samples can be achieved concerning their multi-element composition from different varieties and cultivated regions. Therefore, the presented results suggest that the multi-element composition of the provenance also has potentialities to be used as a fingerprint of the origin of wines from the Greek wine district. Nevertheless, more wines from the same and/or other wine districts must be analyzed so as to consolidate this conclusion. A further analysis of vinification processes and fertilization practices in wine samples could be a useful tool for further differentiation concerning the provenance. Moreover, studies on the variability of soil properties could provide more details with which to understand the mineral characteristics of wines.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/separations8080119/s1, Table S1: Mineral concentrations for the wine samples for two consecutive harvests 2017–2018.

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