



ICP - Mass Spectrometry Analytics

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Geographical Differences of Trace Elements in Wines – Analysis with NexION 300X/350X ICP-MS and Visualization with TIBCO Spotfire® Software

Introduction

Traceability of the wine origin is important for brand protection. Elemental profiles of wines have been shown to be specific for their geographic origin^{1,2}, since the levels of trace metals in wines are related to the soil in the grapevine cultivation area.

In this study, a total of 75 Italian red wines from different regions and grape types were analyzed by ICP-MS to determine whether elemental profiles correlate to the region of origin. Results were imported into TIBCO Spotfire® software for statistical calculations and to display geospatial distribution.

Methods

All wines in this study were red wines produced in different regions of Italy and from various grape types, the majority bottled in 2011 or 2010, with a few older wines. Regions were Lombardy (Lombardia), Abruzzo, Tuscany (Toscana), Trentino-Alto Adige, Apulia (Puglia), Sicily (Sicilia) and Sardinia (Sardegna).

All analyses were performed on a PerkinElmer NexION® 300X ICP-MS in both Standard and Collision modes.

Table 1. Instrumental Conditions

Parameter	Condition
Instrument	NexION 300X ICP-MS
Nebulizer	Glass concentric
Spray chamber	Glass cyclonic
Sample uptake rate	0.25 mL/min
RF power	1500 W
Internal standard	Ge, Rh, Re at 10 ppb
Dwell time	50 ms
Collision mode	He = 4 mL/min

All samples were filtered and diluted four times with 2% (v/v) HNO₃. Internal standards were used to compensate for possible matrix effects during sample introduction. An internal standard mix (Ge, Rh, and Re) was added on-line by merging flows of the sample and internal standard mix.

Results for all samples were compiled into a single table in Microsoft® Excel, with columns of elements, and the ICP-MS values (in cps) for each sample in rows. For most of the samples, information on the region and city of origin, the type of grape, and year of production were available, and added as additional category columns to the table. The table was opened in TIBCO Spotfire® software and the data used for various calculations and visualizations. Standard S Plus statistical algorithms such as Principal Component Analysis (PCA) were used. The category columns enable different grouping and sorting options for raw data and the resulting statistical outputs, and for color coding of graphs.

Results

The levels of 39 elements were measured for each sample; these vary widely, from phosphorus at high mg/L levels to rare earth elements at sub µg/L levels. PCA was used to investigate the relationship between the geographic origin of wines and their elemental profiles.

PCA is a data analysis method used to reduce the dimensionality of multivariate data and to derive meaningful patterns from the complex information.

PCA transforms or projects the variables for each sample into a lower dimensional space, while retaining the maximal amount of information about the variables. Resulting principal components for each sample are a combination of the original variables after the transformation. The largest difference in the combined variables between the samples is described by Principle Component 1 (PC1), the next largest by component 2 and so on.

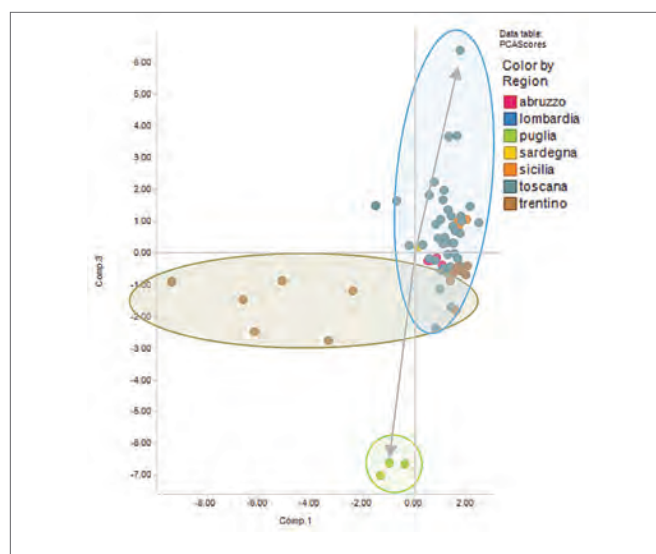


Figure 1. Scores Plot for PC1 vs. PC3 showing separation of the Puglia (Apulia) wines in green from the Toscana (Tuscany) wines in blue and the Trentino wines in brown.

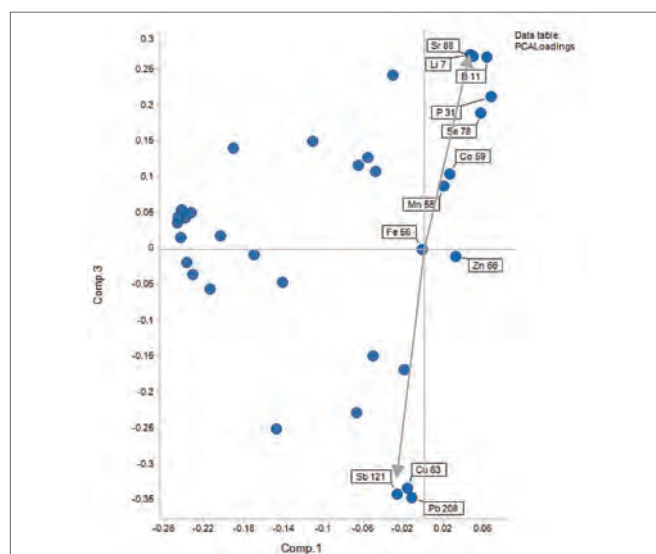


Figure 2. Loadings Plot of PC1 vs. PC3 showing that the strongest contributors to the separation of the Puglia (Apulia) wines are the higher levels of Sb, Cu and Pb, with some Toscana (Tuscany) wines having higher levels of Sr, Li and B.

A Scores Plot summarizes the relationship between the samples, a plot of PC1 vs. PC2, or PC1 vs. PC3 will show the samples grouped according to the larger differences between them; this information is displayed in TIBCO Spotfire® software scatter plots. A Loadings Plot of the same components shows the weighting for each variable as a distance from the origin. The plot is a means of interpreting the patterns seen in the Scores Plot.

For these wine analyses, the levels of the 39 different elements from the ICP-MS results are the variables. PCA calculations used the functions within the TIBCO Spotfire® Statistics Services, including autoscaling of values in each element column, thus giving the same variance ranges across the samples, independent of concentration and ICP-MS instrument response.

The Scores Plot from the initial autoscaled PCA results show a strong separation of the three Puglia wines from all other wines using PC1 vs. PC3 (Figure 1). The corresponding Loadings Plot (Figure 2) indicates that this separation was most strongly

correlated to the higher levels of Cu, Sb and Pb in these wines. Other wines, particularly those from Tuscany, are partly grouped by having higher levels of Sr, Li and B. Trentino wines correlate to increased levels of a number of elements, which will be described for the PC1 vs. PC2 interpretation that follows.

A bar chart of the levels of Cu and Pb for each sample, sorted by region, confirms the higher levels for the Puglia samples (Figure 3). It is not known whether these relatively high levels are due to the soil type, grape type, or cultivation and production methods for these wines. For example, high levels of Cu may be due to the use of copper compounds as mildewcides and fungicides. Increased levels may also relate to the use of brass equipment during production and bottling.

The various wines from the Trentino region were also partly grouped in a Scores Plot of PC1 vs. PC2; the loadings plot (Figure 4) suggests that these wines have higher levels of a number of rare earth elements. These elements have been reported previously^{3,4}, as having variable levels in wines due to the use of bentonite, an absorbent clay, to precipitate proteins from the wine. Thus, these elements are not considered to be reliable indicators of geographic origin.

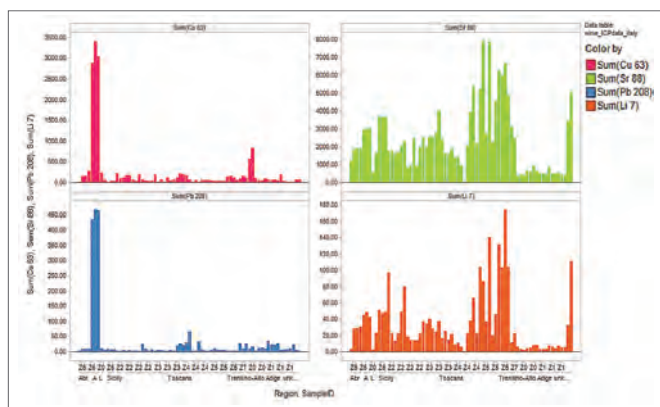


Figure 3. Bar chart of the concentration of Cu (red), Pb (blue), Sr (green), and Li (orange) for each sample, grouped by region, shows that the wines from Puglia (Apulia) have higher levels of Cu and Pb, while several of the wines from Toscana (Tuscany) have higher levels of Sr and Li.

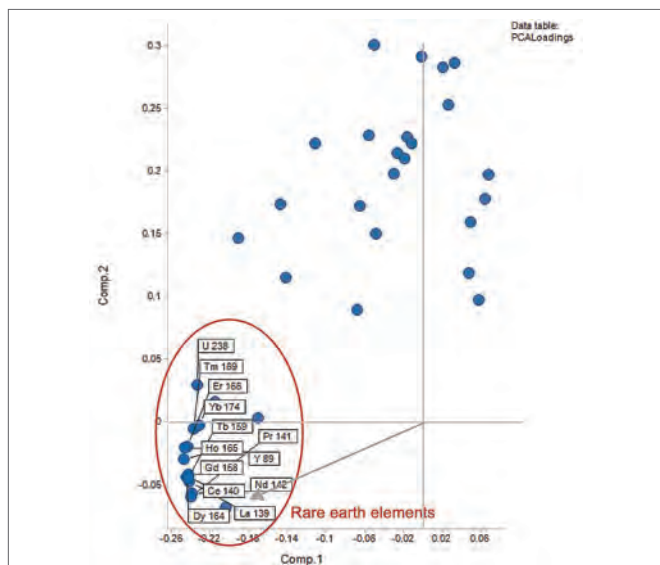


Figure 4. Loadings Plot of PC1 vs. PC2 showing that the increased levels of many rare earth elements differentiate the Trentino wines.

A new PCA analysis of the data was made, after excluding the data columns for the rare earth elements. The new Scores Plot of PC1 vs. PC2 (Figure 5) gave a clearer differentiation of the groupings for the Tuscany and Trentino regions.

The differentiators in the loadings plot (Figure 6) are clustered into groups of elements, which may be classified by geochemistry. This grouping has been reported for other wines⁵, and may relate to the local rainfall and climate of the grapevines. The chalcophilic elements (Cu, Zn, Sb, As, Sn) have a lower affinity for oxygen and prefer to bind to sulfur as insoluble sulfides. These elements are at higher levels in Tuscany wines, as are siderophilic elements such as Ni and Co which track with Fe. Lithophilic elements (Li, Ba, Cs, Sr etc.) are highly soluble and associate with the soil; these are at lower levels in Trentino wines.

TIBCO Spotfire® software visualizations allow the user to quickly group information in the element data table in different ways.

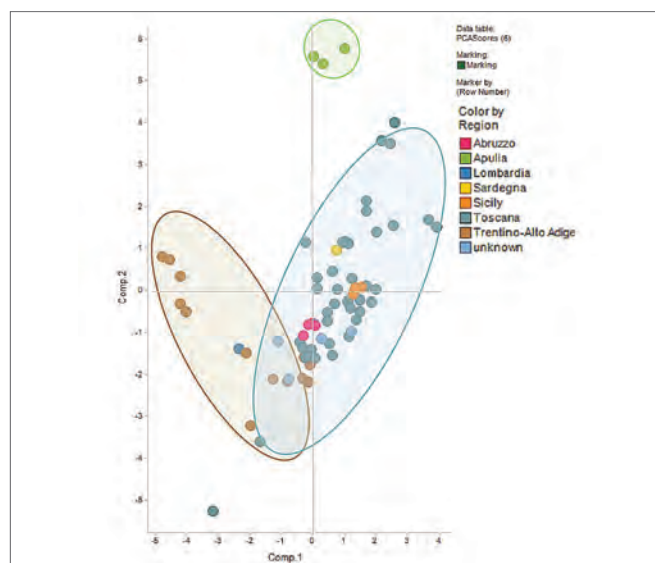


Figure 5. Scores Plot for PC1 vs. PC2 using only the non-rare-earth elements, showing separation of the groups of the Puglia (green), Trentino (brown), and Toscana (blue) wines.

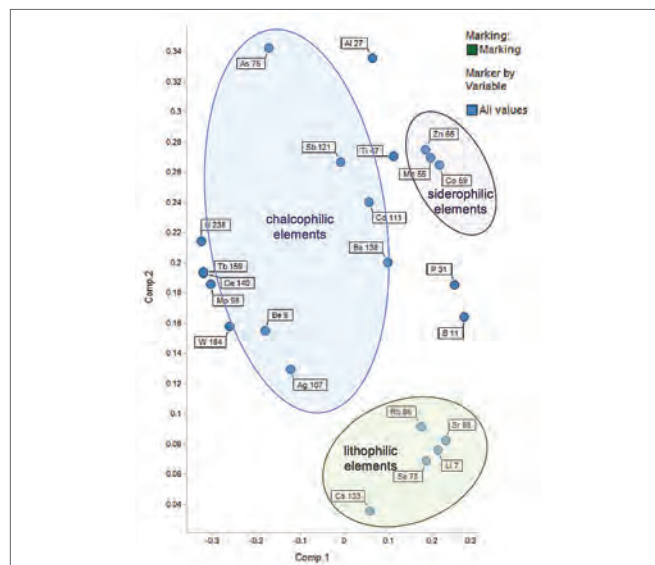


Figure 6. Loadings Plot showing a partial grouping of elements that differentiate the wines into the categories of the Goldschmidt geochemical classification of elements.

For example, a bar chart showing concentrations of Li for each sample (Figure 7), is ordered first by region, and then color-coded by city. This view of the data highlights the difference in Li levels by region. The higher levels in many wines from Florence in Tuscany are clearly visible.

Custom expressions are easily created to show the levels for a combined group of elements. A category for various chalcophilic elements (the sum of concentration for Zn, Sb, As, and Sn but not Cu) gives a clear view of the differences in concentration of this group of elements for all the samples (Figure 8).

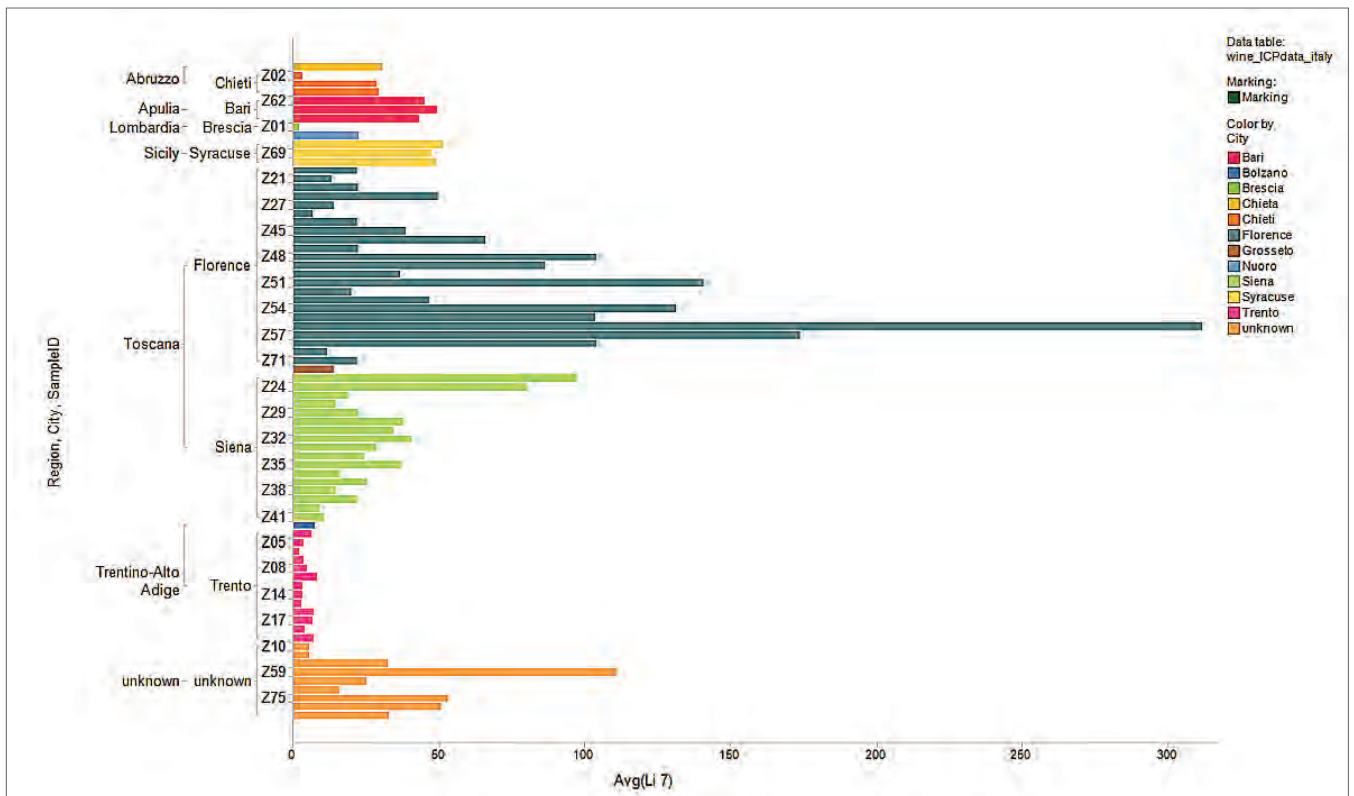


Figure 7. Bar chart showing the Li level for each sample, with samples ordered by region, then grape type and colored by city. Highest levels are for the wines from Florence in Tuscany, shown in blue.

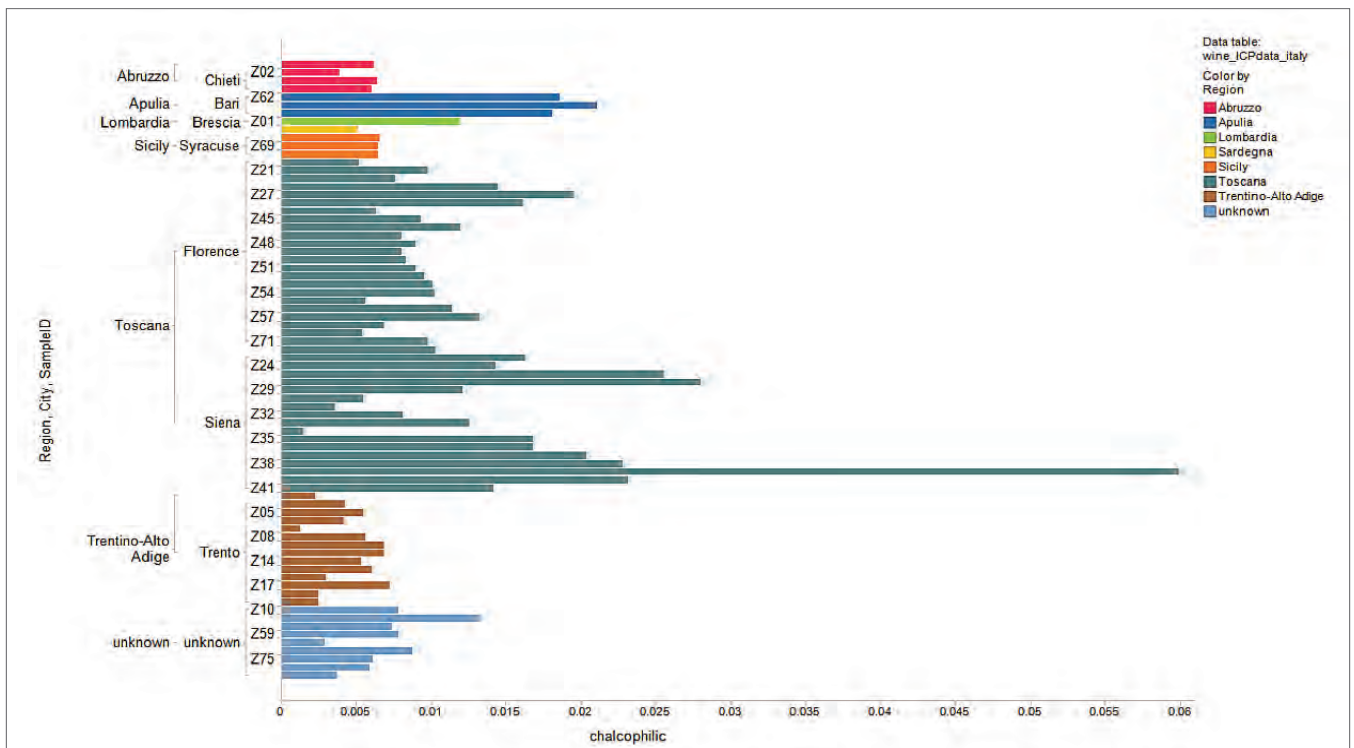


Figure 8. Bar chart for samples ordered by region then city, with bars colored by region, showing that levels for the custom chalcophilic category (sum of Zn, Sb, As, and Sn levels) are higher for the Toscana (Tuscany) wines (blue) than for the Trentino wines (brown).

Previously reported elemental analysis of Italian wines⁶ suggested that Sr and Rb levels were correlated to the soils of origin in provinces of Abruzzo in central Italy. With these results, levels of Rb were quite constant for all samples, although Sr levels did vary. The levels of Sr were highest in some of the wines from Florence in Tuscany and Syracuse in Sicily (Figure 9).

A map chart (Figure 10) shows the geospatial distribution of a selected element or customized group of elements. The region

names for a shape file of Italy are linked in TIBCO Spotfire[®] software to the region column in the data table, and regions in the map chart are color-coded by intensity for an element. Here, chalcophilic and lithophilic element groups are contrasted with high intensity levels in red and low levels in blue. Wines from the Florence area of Tuscany are relatively low in chalcophilic elements compared with other regions, but higher in lithophilic elements. Wines from Sicily are relatively high in lithophilic elements, but lower in chalcophilic elements.

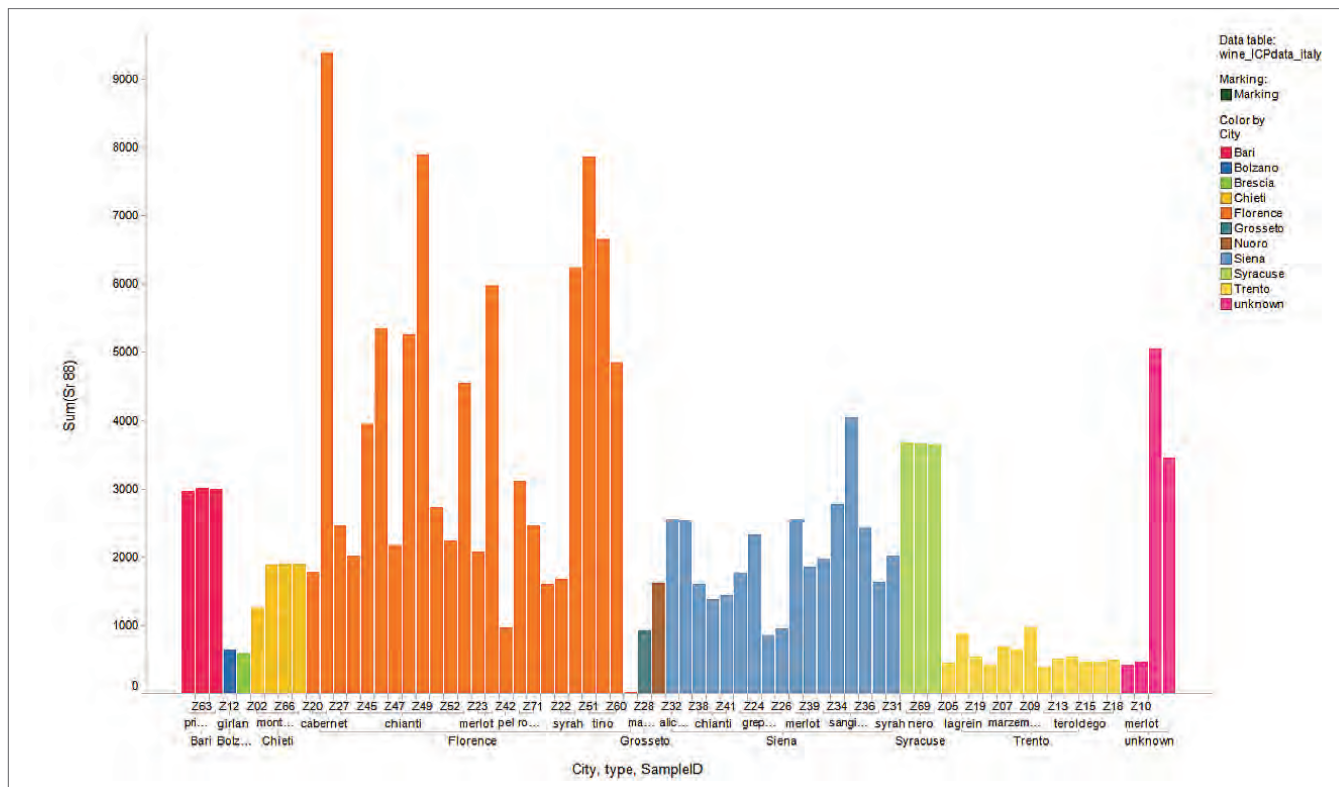


Figure 9. Bar chart showing levels of Sr for each sample, with columns colored by city, and ordered by city and grape type.

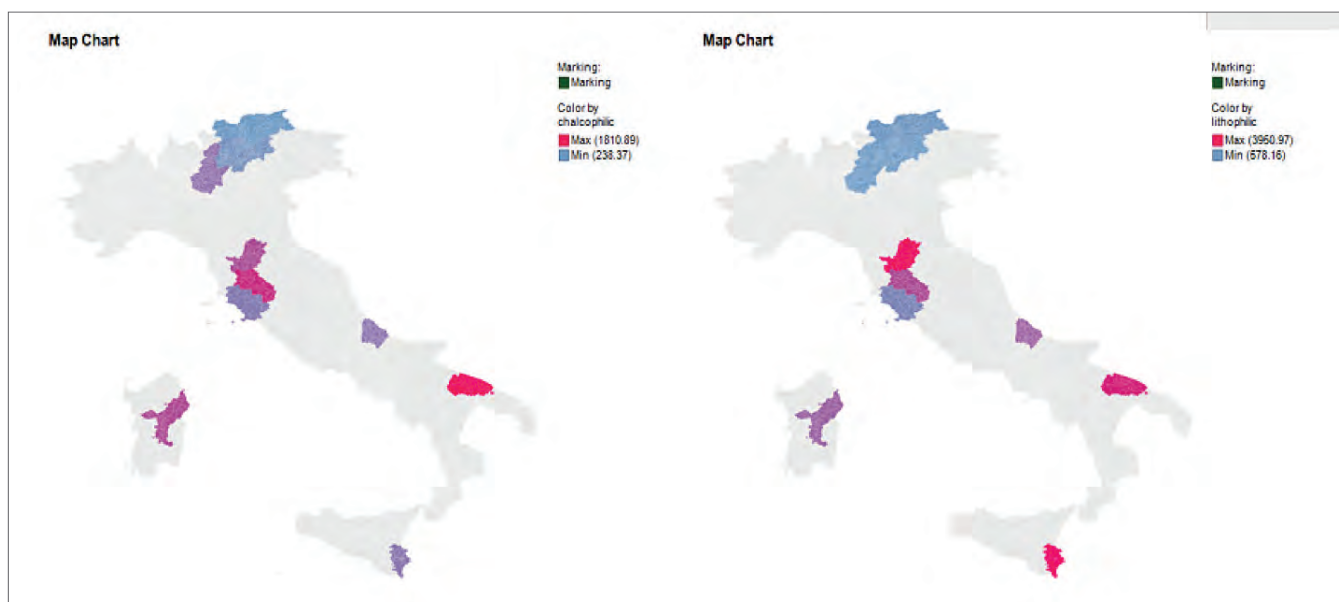


Figure 10. Map charts showing the distribution by region of the chalcophilic elements (Zn, Sb and As) on the left and lithophilic (Li, Ba, Cs, Sr etc.) elements on the right, with red for the highest intensity and blue as the lowest.

Conclusion

The ICP-MS analysis of a large number of wines from Italy provided results which were used for statistical analysis and geospatial mapping with TIBCO Spotfire® software. Results indicated significant differences in elemental levels in many of the wines, some of which were linked to specific geographical regions. Further research will be needed to investigate whether these differences relate to soil and rainfall, or are correlated to viticulture production differences.

References

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