Using ICP-MS to Determine the Effect of Storage Temperature and Packaging on the Trace Metal Composition of Wine

Application Note

Food Testing and Agriculture

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Introduction

The metal composition of finished wine is a function of the metals present in the grapes as well as those introduced by viticultural and enological practices [1]. Most research so far has focused on elemental profiling for the potential determination of the geographical origin of wine. However, in previous studies, the correlation between the trace element profile of vineyard soil and wine made from the grapes grown on the soil was poor, indicating a significant change in the elemental composition due to wine making and wine storage [2].

This fact is not too surprising, as during wine making the grape material is often in long contact with various materials, such as stainless steel, oak wood, glass, and so forth. A study has shown that the rare earth element concentrations differed significantly between wines stored in glass bottles, oak barrels, or stainless steel tanks [3]. Unfortunately, the same authors did not provide further information about the storage containers used (for example, type of glass bottles, history and type of barrels and tanks, cleaning regimes, and so forth). However, these results indicate a possible change of the elemental profile of wine due to the storage vessel.

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These findings lead to the question of whether there are other factors that may have an impact on the trace element profile of wine as well. This application note describes a study of the effect of wine packaging materials and storage temperatures on the trace elemental profile of red wine that has been published previously [1]. It uses ICP-MS analysis to determine the levels of more than 20 trace metals. Statistical analysis using Mass Profiler Professional software revealed patterns in the concentrations of trace elements that were indicative of the packaging and storage conditions used for a particular sample. It was found that storage temperature has less of an effect on trace element composition than packaging type, and wine packaged with screw caps showed elevated levels of tin.

Experimental

Chemicals and standards

All solutions were prepared using deionized water with resistance >18 MW•cm with a Milli-Q system (Millipore).

Table 2. Agilent 7700x ICP-MS operating conditions

Chemical/Standard	Source
Nitric acid, ultrapure	Fisher Scientific
Claritas PPT Grade Internal Standard Mix 1	SPEX CentriPrep
Claritas PPT Grade Multi-Element Calibration Standards, Solution 2A and 3	SPEX CentriPrep
Ethanol, 200 proof	GoldShield

Instrumentation

This study was performed using an Agilent 7700x ICP-MS. The instrument conditions used are listed in Table 1.

Table 2. ICP-MS Instrument Parameter Conditions

RF power	1,550 W
Carrier gas flow	1.03 L/min
Nebulizer gas flow	1.1 L/min
Nebulizer type	MicroMist
Sampling depth	10 mm
Spray chamber temperature	2 °C
OSR^3 collision cell gas flow (He)	4.3 mL/min and 10 mL/min for ^{75}As and ^{78}Se
Monitored and quantified isotopes	^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{111}Cd, ^{117}Sn,^{118}Sn, ^{119}Sn, ^{120}Sn, ^{133}Cs, ^{205}Tl, ^{208}Pb
Sweeps/replicate	100, three replicates

Samples

The same commercially available Cabernet Sauvignon from the Californian Central Coast, vintage 2009, was used for 12 different treatments. These included all combinations of three storage temperatures (10 °C, 20 °C, 40 °C) and four wine packaging types:

1. 0.75 L green glass bottles with a natural cork closure (24 × 49 mm AC-1 grade, ACI Cork, Fairfield, CA)

2. 0.75 L green glass bottle with screw cap closures filled with two filling heights (aluminum Stelvin cap 30 × 60 mm, Federfin Tech S.R.L., Tromello, Italy, with 28.6 × 2 mm tin-polyvinylidene chloride (PVDC) liner, Oenoseal, Chazay, France)

3. Bag-in-box (3 L DuraShield 34ES, Scholle Packaging, Northlake, IL)

All samples were stored upright during the entire storage period, which was 6 months. The experimental design is depicted in Figure 1.

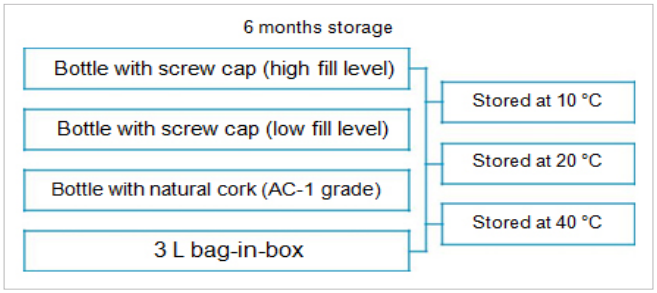


Figure 1. Experimental design.

Sample preparation

Wine samples were prepared as described previously [1]. They were diluted 1:3 with 1% nitric acid to decrease the ethanol levels to around 4%. Wines were sampled directly out of the packaging and special care was taken not to shake the bottles, as the wine closure would have been in contact with the wine during that step.

Data analysis

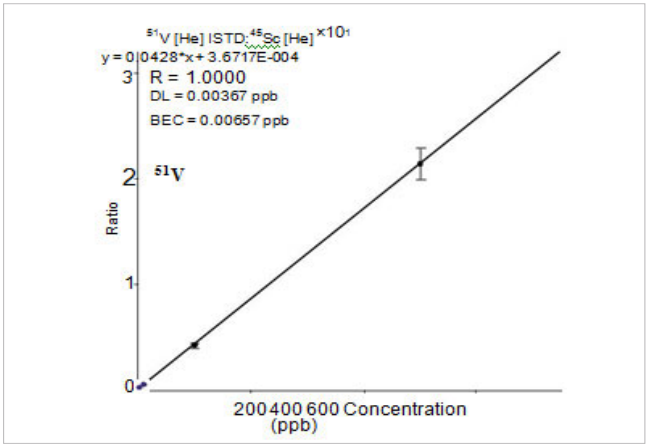
Agilent ICP-MS MassHunter software was used to acquire the mass data, and Mass Profiler Professional was used to perform statistical analysis, including principal component analysis (PCA) and heatmap analysis.

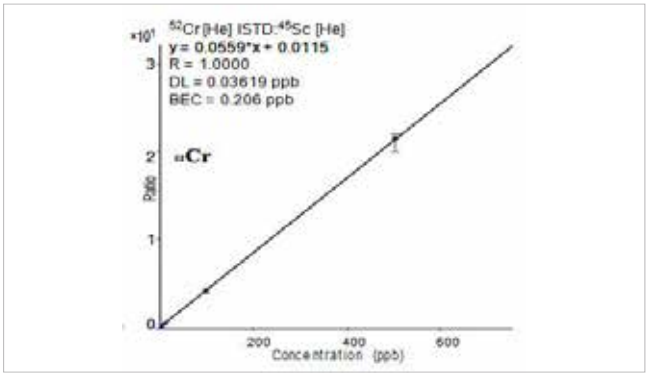
Results and Discussion

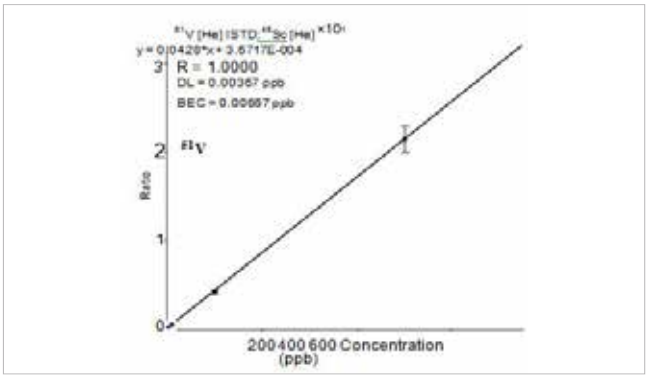
Trace element detection and quantitation

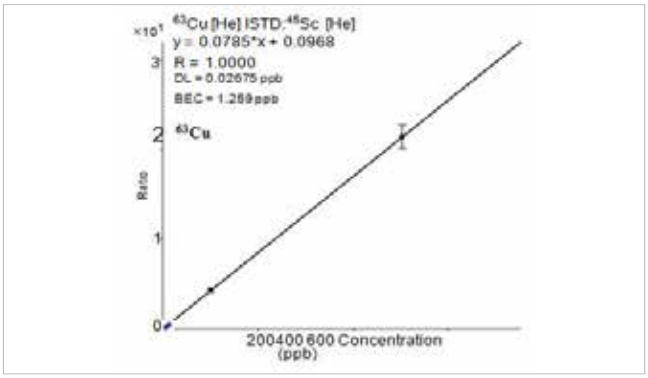
All calibrated elements were quantified using five-point calibration curves for each element in the concentration range from 0.1 to 500 µg/L in matrix-matched solutions (1% HNO_3 and 4% ethanol). Examples of the calibration curves are shown in Figure 2, with R2 (coefficient of correlation) values over 0.999. Wines were measured in triplicate, and spiked wine samples containing 0.5, 1, or 10 µg/L tin (Sn) were measured as quality control samples throughout the sample queue.

An internal standard solution diluted to 1 µg/L in 1% nitric acid was mixed using a mixing tee with the sample before the nebulizer, and contained ^{6}Li, ^{45}Sc, ^{72}Ge, ^{89}Y, ^{115}In, ^{159}Tb, and ^{209}Bi. Seven sample blanks were run to determine limits of detection and quantitation (LOD, LOQ) as suggested by the International Union of Pure and Applied Chemistry (IUPAC). The LODs, LOQs, and detection limits (DLs) are shown in Table 2.









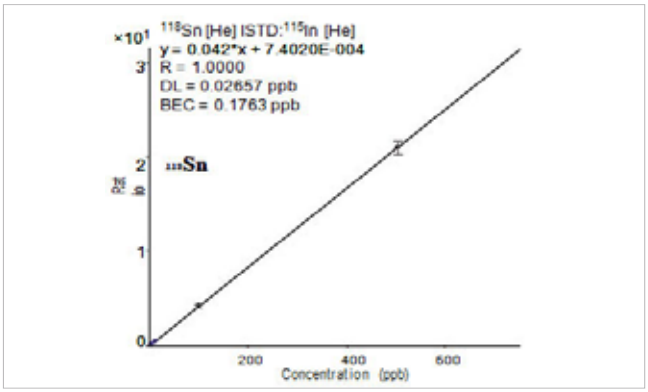


Figure 2. Calibration curves for all five significantly different elements between 0.1 and 500 µg/L (n = 3).

Table 2. Limits of Detection (LOD), Limits of Quantitation (LOQ), and Detection Limits (DL) for the Five Significantly Different Elements in µg/L (n = 7)

	^{51}V	^{52}Cr	^{63}Cu	^{118}Sn	^{208}Pb
LOD*	0.001	0.007	0.044	0.018	0.001
LOQ†	0.003	0.023	0.14	0.057	0.003
DL‡	0.004	0.036	0.027	0.027	0.006

*LOD = 3.14*sd (standard deviation)

† LOQ = 10*sd

‡ DL was reported by the Agilent ICP-MS MassHunter Workstation software (v. A.01.02)

Differences in trace metal concentrations attributed to packaging and storage temperatures

Table 3 shows that concentrations of five elements, V, Cr, Pb, Cu, and Sn, differed significantly across the samples depending upon the packaging and storage temperatures used. Not surprisingly, the bag-in-box packaging showed the lowest trace metal concentrations. The higher chromium levels in the bottled samples versus the bag-in-box samples may have been due to storage of wine destined for the bottles in a stainless steel keg for 2 days, prior to bottling.

With higher temperatures, the Sn levels increased in the screw cap samples, while V and Cu decreased with increasing storage temperature. The decreased levels in Cu were also found in all other wine packaging types (natural cork and bag-in-box). The high-fill, screw cap bottle samples gave the highest concentrations of V, Cu, and Sn for all storage temperatures. All elements were below available legal limits.

Elevated tin levels were measured in the screw cap samples only, a strong indicator that tin leached out of the tin-PVDC liner into the stored wine. This effect was pronounced at the highest storage temperature of 40 °C, due to the volumetric expansion of the wine when being warmed up, thus being in contact with the screw cap liner during the storage period. It is not clear how the tin leached into the wine at the lower storage temperatures, as the wine was not in contact with the liner.

Significant differences in lead levels due to the different packaging types and storage temperatures were observed, with the highest levels of lead in the high fill screw cap samples stored at 10 °C (Table 3). These differences are most likely a result of the different packaging types, with an additional temperature-driven effect of metal complex formation with other wine components.

Table 3. Elements with Concentrations that Differed Significantly Across Packaging Types and Temperatures (p ~ 0.05)

		^{51}V	^{52}Cr	^{63}Cu	^{118}Sn	^{208}Pb
Bag-in-box	10 °C	14.8	14.1	21.1	0.1	4.3
	20 °C	15.4	14.7	22	0.0	4.5
	40 °C	13.9	14.1	11	0.0	4.6
Natural cork	10 °C	15.5	22	84.1	0.8	5.4
	20 °C	15.6	22.3	59.8	0.6	5.2
	40 °C	13.1	18.4	28.5	0.4	4.5
Low fill screw cap	10 °C	15.5	22.7	41.5	6.0	5.1
	20 °C	15.7	23	50.5	8.7	5.5
	40 °C	15.3	22.7	33.8	12.3	5
High fill screw cap	10 °C	34.7	22.9	152.7	6.3	8.8
	20 °C	22.1	22.1	68.7	8.3	6.5
	40 °C	20.4	22.5	50.2	16.0	6.4

The heatmap in Figure 3 and the graphs in Figure 4 illustrate the differences in the 20 metals monitored, by packaging type and temperature. It is apparent that the concentration pattern of these elements can be an indicator of the bottling and storage temperature history of a wine. The biggest differences in heatmap patterns are seen between the bag-in-box samples and the high fill screw cap bottle samples, at all three temperatures.

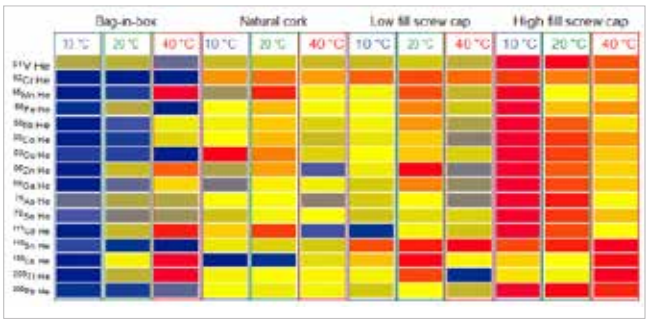


Figure 3. Heatmap of monitored elements separated by storage temperature and wine packaging type; blue = low concentration; yellow = moderate concentration; red = high concentration.

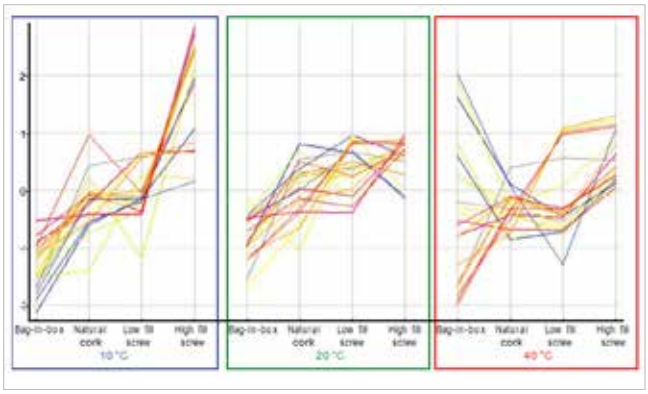


Figure 4. Log2 normalized intensities for all monitored elements separated for storage temperature and wine packaging (each line represents a different element).

Principal component analysis

Using the five significantly different elements, a graphical rep-resentation of the sample similarities and dissimilarities was obtained in a Principal Component Analysis (PCA) using Mass Profiler Professional software (Figures 5 and 6). Within the first two principal components (PCs), 93.2% of the total variance was explained, with 76.0% in the first dimension and an additional 17.2% in the second dimension.

Samples are separated by packaging type along PC 1, with the bag-in-box samples located on the left hand side of the PCA biplot (Figure 5), next to the natural cork closure bottles. The two screw cap closures (high and low fill screw cap) are positioned in the middle and right hand side of the biplot. Along PC 2, storage temperature separates the samples to different degrees, depending on packaging type. Thus PCA analysis can separate the four packaging types, again making it possible to use the elemental concentration patterns to determine the packaging history of a wine sample.

The loadings of the elements responsible for the separation of the different samples are shown in Figure 6. The distance of each element from the origin of the plot is an indication of the strength of the contribution of that element as a differentiator between package types and/or storage conditions. In this case, all five of the elements play a major role.

The Venn Diagram in Figure 7 illustrates that the packaging type is the biggest differentiator in determining elemental composition, rather than storage conditions, with five entities (elements) being significantly different among the packaging types

Conclusions.

Analysis of wine using ICP-MS has shown that exogenous factors such as wine packaging and storage conditions have a clear impact on the elemental profile of wine. Packaging type has the biggest influence on elemental composition, while temperature can significantly impact the concentration of copper. Further studies that take a closer look at the different steps in wine making and storage should enable a better understanding of which elements are most influenced by the wine making processes.

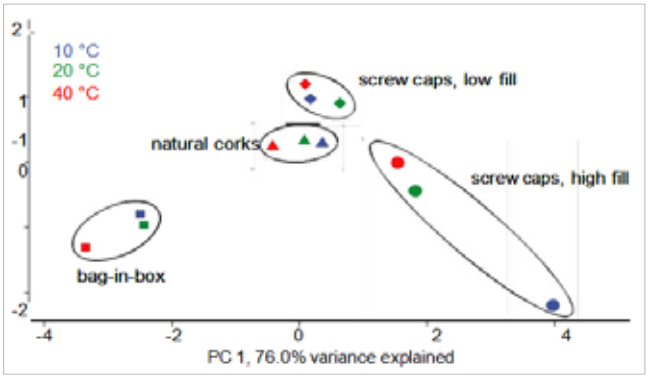


Figure 5. PCA Bi-plot, showing separation by packaging type along element PC 1, versus separation by temperature along element PC 2.

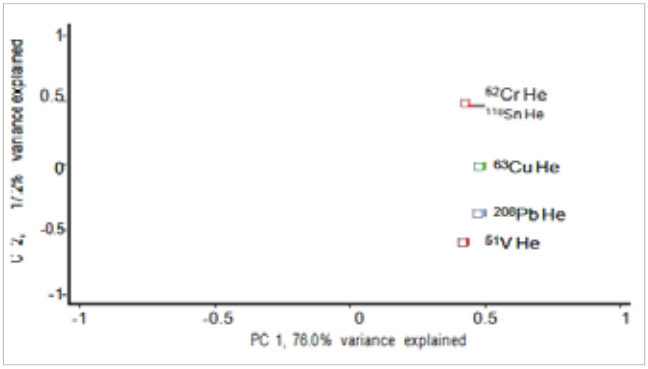


Figure 6. PCA Loading Plot illustrating the importance of each trace element in differentiating the storage and packaging conditions along the elements PC 1 and PC 2.

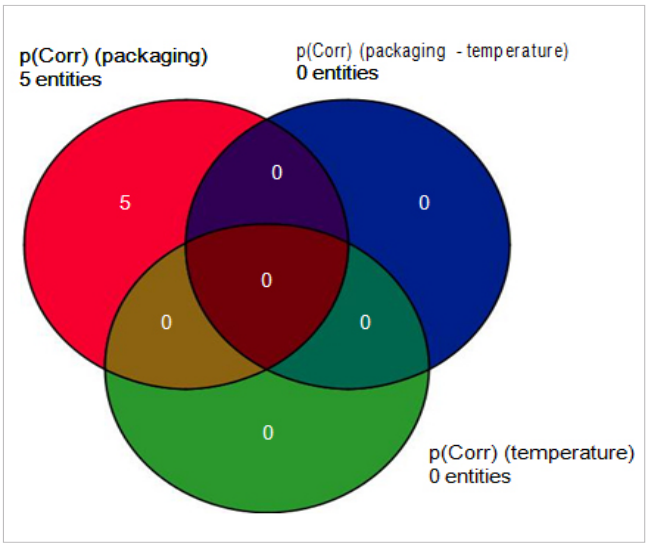


Figure 7. Venn diagram showing that the packaging determines the differentiation between trace element composition of the wine samples, rather than the temperature, or the temperature and packaging combined..

References

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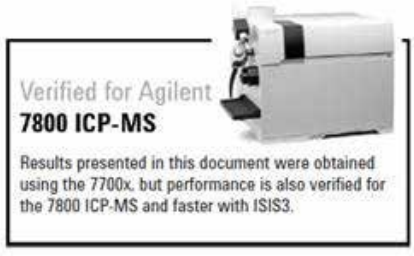

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