Quantitative Analysis of Metals in Wine Using ICP-MS Spectrometry

Uwe Oppermann[1], Ludivine Fromentoux[2], and Jan Knoop[1]
[1]Shimadzu Europa GmbH, Spectroscopy, Duisburg, Germany, [2]Shimadzu France SAS, Marne La Vallee, France

1. Overview

Strict and steady control from the origin of the food to the final product is needed to protect consumers against undesired contaminations and guarantee a high level of quality. This is achieved by controlling limits of maximum allowable concentrations of hazardous substances. Recent examples are the European drinking water regulation, the European food safety regulations, the recent food and packaging directive, and the European wine regulation, which includes the classification of wines from different locations, but also the production process, alcohol concentrations and the classification of organic and inorganic contaminants.

2. Sample Preparation and System Setup

Figure 1: Wine – a popular drink in Europe

For simultaneous quantitative determination of the inorganic contaminants in wine, ICP-MS is the most preferable tool for quality control because of a high sensitivity (trace detection), a wide dynamic range and a high sample throughput. Shimadzu ICPMS-2030 is an easy and fast system to meet this requirement. Due to the unique Eco-mode system associated with Mini-torch, ICPMS-2030 is able to drastically reduce running cost. Even though, wine is regarded as a difficult matrix because of the high number of constituents, the octopole collision cell assures a high accuracy for all element measurement. Using Helium gas and Kinetic Energy Discrimination principle, this cell suppressed most of the spectroscopic interferences (polyatomic interferences). Efficiency of interferences suppression and sensitivity are improved by a cooled cyclonic chamber and well controlled torch positioning. In this study some commercially available red and white wines are used: three white wines Gavi, Critone, Lugana and three red wines Montalcino, Chianti, Magliano. Thanks to the ICPMS-2030 system, analysis of wine could be performed with a minimum effort on sample preparation. All samples analyzed here are only diluted 1:3 with 1 % Nitric acid to decrease the ethanol levels around 4%. After this treatment they are directly aspirated for analysis by ICPMS-2030.

3. Multi Element Analysis

14 different elements are simultaneously quantified : As, Cd, Cs, Cu, Cr, V, Fe, Mn, Ni, Pb, Se, Sn, Tl and Zn. Analytical measurements conditions are resumed in table 1.

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxilliary gas	1,1 l/min
Carrier gas	0.7 l/min
Nebulizer type	MicroMist
Sampling depth	6 mm
Spray Chamber temperature	5°C
Coll. Cell gas flow (He)	4 ml/min (std) 8 ml/min for As^{75} and Se^{78}
Quantified Isotopes	V^{51}, Cr^{52}, Mn^{55}, Fe^{56}, Ni^{60}, Cu^{63}, Zn^{66}, As^{75}, Se^{78}, Cd^{111}, Sn^{118}, Cs^{133}, Tl^{205}, Pb^{208}
Internal Standards (ISTD)	Sc^{45}, Ge^{72}, Y^{89}, In^{115}, Tb^{159}, Ho^{165}, Lu^{175}, Bi^{209}

Table 1: ICPMS 2030 measurement parameters

The element distribution can show significant differences based on the geographic origin, as the levels of major-, minor-, and trace elements in wines are related to the soil of the vineyards. The essential trace elements and especially the undesired heavy metals are present based on the geochemical composition of rocks and soil and the corresponding mineral uptake of the grapevine from the soil, and finally through anthropogenic sources such as environmental pollution and agricultural treatment by fertilizers, pesticides and fungicides. Last not least the metal content in wine can be influenced during wine production, wine processing, conservation and bottling, which is more than expected, as during the wine making process the grape material is often in long contact with various materials, such as stainless steel, wood from a variety of barrels, glass bottles and other equipment and many more.

Elements like Zn, Cu, and Fe have an influence on the wine quality. Elevated copper concentrations higher than 1 mg/L results in a metallic bitter taste and might generate turbidity, that's why during the production process the concentrations are always kept below 0.5 mg/L. Copper in wine is coming from the Bordeaux mixture, which is a mixture of copper sulfate ($CuSO_4$) and calcium hydroxide ($Ca(OH)_2$) solution used as a fungicide in vineyards, to protect against downy mildew, powdery mildew and other fungi. Since the Bordeaux mixture has been applied in large quantities the copper has been accumulated in the soil and becomes a pollutant, that´s why in the European community the Bordeaux mixture will be banned most probably during 2016.

For each element, calibration curves are built using 5 points in the concentration range from 0.1 to 500 µg/l in a matrix-matched solution using 1% nitric acid and 4% ethanol. Wine samples are measured in triplicate and two of them, one white (Gavi) and one red wine (Montalcino) are spiked with 1 ppb or 10 ppb depending on the element and measured as quality control. An internal standard of 1µg/L in 1% nitric acid was mixed using tee with sample before the nebulizer and contained Sc^{45}, Ge^{72}, Y^{89}, In^{115}, Tb^{159}, Ho^{165}, Lu^{175}, Bi^{209}.

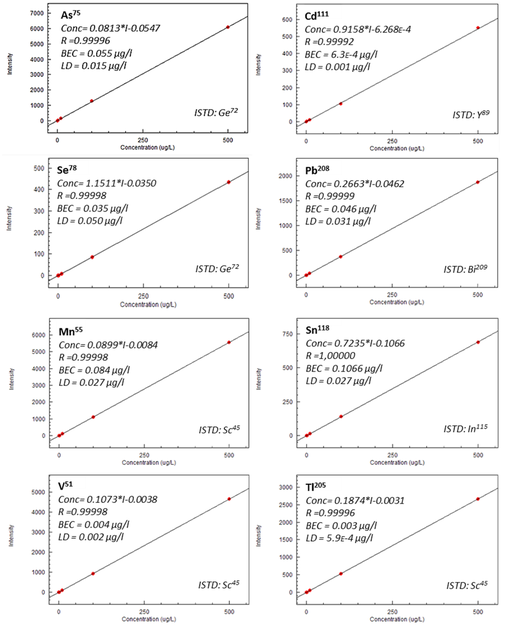

Figure 2: Examples of calibration curves obtained for 8 elements

As the different curves show in Figure 2, all correlation coefficients r are better than 0.9999. Low values of detection limits (LD), calculated automatically by *LabSolution ICPMS* software with 3σ method indicate ICPMS 2030 high ability for trace contaminant analysis. For each wine sample, the results are summarized in table 2.

Element	Red wines (ppb)			White wines (ppb)		
	Montachino	*Chianti*	Magliano	Gavi	*Critone*	Lugana
V^{51}	3.5	*3.5*	5.3	2.5	*1.4*	3.1
Cr^{52}	15.6	*14.7*	16.5	1.3	*4.0*	4.2
Mn^{55}	4160	*2808*	4660	2208	*844*	528
Fe^{56}	1176	*2660*	1660	152	*720*	289
Ni^{60}	105	*76.4*	92.8	77.6	*15.8*	11.3
Cu^{63}	162	*281*	540	56,0	*7,7*	34,8
Zn^{66}	652	*800*	1068	540	*484*	440
As^{75}	1.8	*1.0*	1.8	1.4	*2.6*	2.0
Se^{78}	6.5	*2.8*	4.8	0.5	*0.8*	0.5
Cd^{111}	2.8	*0.8*	0.8	0.3	*0.2*	0.1
Sn^{118}	12.0	*4.4*	1.2	1.8	*2.5*	1.4
Cs^{133}	12.8	*21.4*	71.2	4.4	*1.5*	28.0
Tl^{205}	0.9	*1.0*	1.7	0.2	*0.2*	0.7
Pb^{208}	14.4	*8.9*	8.7	3.6	*7.0*	16.2

Table 2: Element concentration in red and white wine

The results in table 2 demonstrate that ICPMS 2030 is able to quantify simultaneously all the elements present in the wine samples: major elements like Fe, Mn and Zn as well as trace element concentrations of As, Tl, Cd, Pb, and V. In order to demonstrate the method accuracy, some spike of each element (1 ppb or 10 ppb) is done in a white wine (Gavi) and in a red wine (Montalciano). Then recovery percentage is calculated according following formula :

$$recovery(\%) = \frac{value\ after\ spike - initial\ value}{initiale\ value} \times 100$$

The recovery values for all the elements are between 95 and 105%. This point strongly demonstrates that ICPMS-2030 developed method has a high accuracy, regardless of element concentration.

4. Conclusion

The ICPMS-2030 allows a fast and sensitive determination of heavy metals in wine and is a reliable tool in order to guarantee the highest level of quality and safety according to the European wine regulations.