DETERMINATION OF CONTAMINANTS IN WINE USING GCMS AND ICPMS SPECTROMETRY

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

■ 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.

Figure 1: Wine – one of the most popular drinks in Europe

■ Inorganic contaminants analysis using ICP-MS

For simultaneous quantitative determination of the inorganic elements 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 constitutes 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. 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.

For each studied 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 solution of 1 µg/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}.

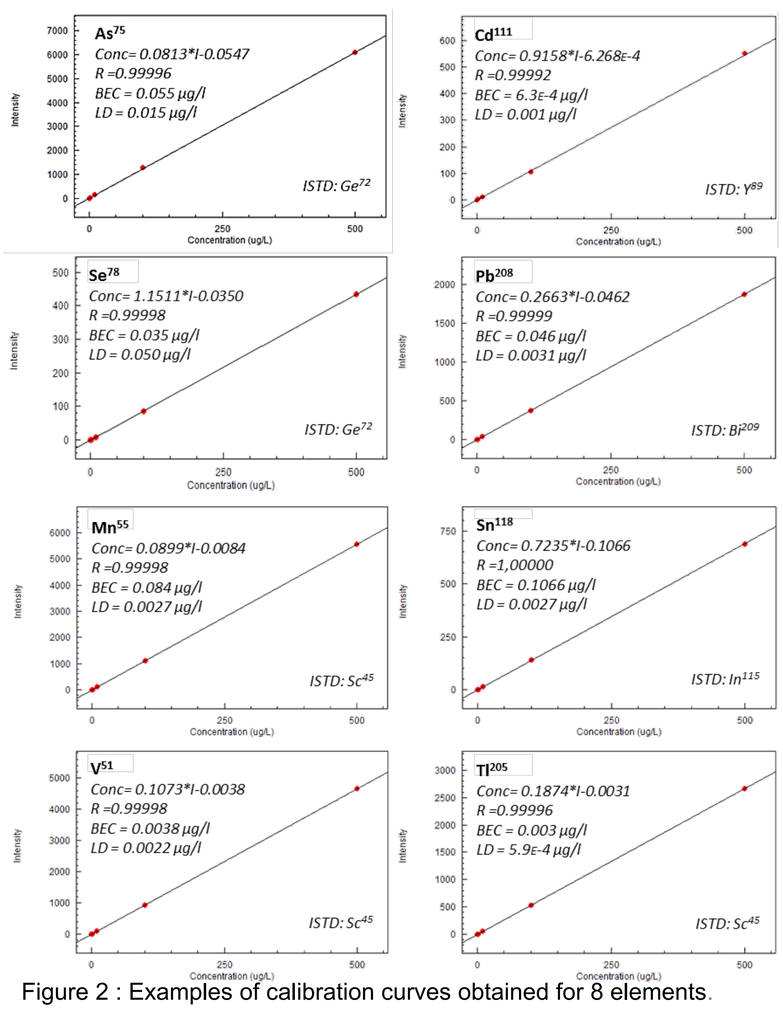

Figure 2 : Examples of calibration curves obtained for 8 elements.

As the different curves show in Figure 2, all correlation coefficients r are better than 0.9999. Moreover, 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, results are summarized in table 2.

Element	Red wines (ppb)			White wines (ppb)		
	Montalcino	*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 : Elements concentrations for each wines

The results in table 2 demonstrate that ICPMS 2030 is able to quantify simultaneously all the elements presented in wine samples: major elements like Fe or Mn and traces of As, Tl, V as well.

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 (Montalcino). Then recovery percentage is calculated according following formula :

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

Results of the calculations are shown in Table 3.

Element	Recovery value (%)	
	Gavi (white)	Montalcino (red)
V^{51}	103 [1]	99 [1]
Cr^{52}	95 [1]	101 [1]
Mn^{55}	100 [2]	100 [2]
Fe^{56}	96 [2]	100 [2]
Ni^{60}	95 [2]	101 [1]
Cu^{63}	97 [2]	101 [2]
Zn^{66}	100 [2]	100 [2]
As^{75}	99 [1]	97 [1]
Se^{78}	98 [1]	97 [1]
Cd^{111}	101 [1]	105 [1]
Sn^{118}	105 [1]	96 [2]
Cs^{133}	95 [2]	96 [2]
Tl^{205}	103 [1]	104 [1]
Pb^{208}	101 [2]	99 [2]

Table 3 : Recovery values for each element in white and red wines. [1] spike of 1 ppb. [2] spike of 10 ppb.

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.

■ Determination of 2,4,6 Trichloroanisole in Wine

Cork stoppers used for wine bottles can effect the taste of the wine. The main contaminant is the well known 2,4,6-Trichloroanisole (TCA). This is an off-flavor which is believed to be produced by methylation of phenols of the cork tree and final bleaching of the cork. Human nose and taste can trace back down to about 5-10 ng/L (5-10 ppt). The odor detection threshold in wine is 1.4 ng/L TCA. The method of determination of releasable 2,4,6-trichloroanisole by cork stoppers measures the quantity of TCA released by a sample of cork stoppers macerated in a aqueous-alcoholic solution. The aim of this method is to evaluate the risk of releasing by the lot of analyzed cork stoppers and to provide a method for controlling the quality of cork stoppers. The analytical procedure is done using an HS-trap GC/MS system consisting of the Shimadzu GCMS-QP2010 Ultra with the HS-20 headspace sampler including a trap function that is able to concentrate headspace gases. A wine sample spiked with the equivalent of 1 ng/L TCA was measured by selected ion monitoring (SIM) using the HS-trap method (Fig. 4).
The results show how the system was able to analyze low concentrations of TCA with high sensitivity. Figure 5 shows the same wine sample spiked with the equivalent of 100 ng/L TCA measured by SIM using the conventional headspace-GC/MS method. The comparison of both shows that the HS-trap method provides significantly higher sensitivity.

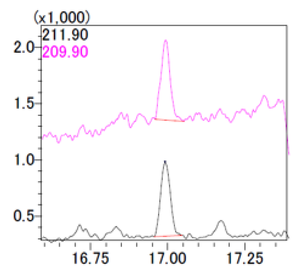

Figure 4: SIM Chromatogram of TCA in Wine using HS-Trap (wine spiked with 1 ng/L TCA

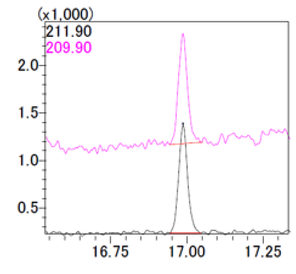

Figure 5: SIM Chromatogram of TCA in Wine using conventional headspace GCMS (wine spiked with 100 ng/L TCA

■ Summary

ICP-MS is a fast and reliable tool for determination of heavy metals in wine. Furthermore the HS-trap GC/MS system is a high sensitivity method for monitoring trichloroanisole in wine in order to guarantee the highest level of quality and safety according to the European wine regulations.

Shimadzu Europa GmbH

Albert-Hahn-Str. 6-10
D-47269 Duisburg
+49(0)203/7687-0

www.shimadzu.eu
shimadzu@shimadzu.eu