

DETERMINATION OF CONTAMINANTS IN WINE USING GCMS AND ICP MASS SPECTROMETRY

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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

Analysis of Inorganic Contaminants 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. The Shimadzu ICPMS-2030 constitutes an easy and fast system to meet these requirements. Due to the unique Eco-Mode associated with Minitorch, ICPMS-2030 is able to drastically reduce running costs by half. 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 elements measurement. Using Helium gas and Kinetic Energy Discrimination principle (KED), this cell suppresses most of the spectroscopic interferences (polyatomic interferences). The efficiency of interferences suppression and enhancement of sensitivity are improved by a cooled cyclonic chamber and well controlled torch positioning.

In this study some commercially available red and white wines are regarded:

- 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 analysed samples are only diluted by factor of 4 using 1 % Nitric acid to decrease the ethanol levels to appr. 4%. After this treatment they are directly aspirated to the 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 summarized 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 include 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 are measured as quality control (Gavi, white wine and Montalcino, red wine), spiked with 1 ppb or 10 ppb resp., depending on the natural element concentration.

An internal standard solution of 1µg/L in 1% nitric acid was mixed using online mixing with sample, before it is aspirated (Sc⁴⁵, Ge⁷², Y⁸⁹, In¹¹⁵, Tb¹⁵⁹, Ho¹⁶⁵, Lu¹⁷⁵, Bi²⁰⁹).

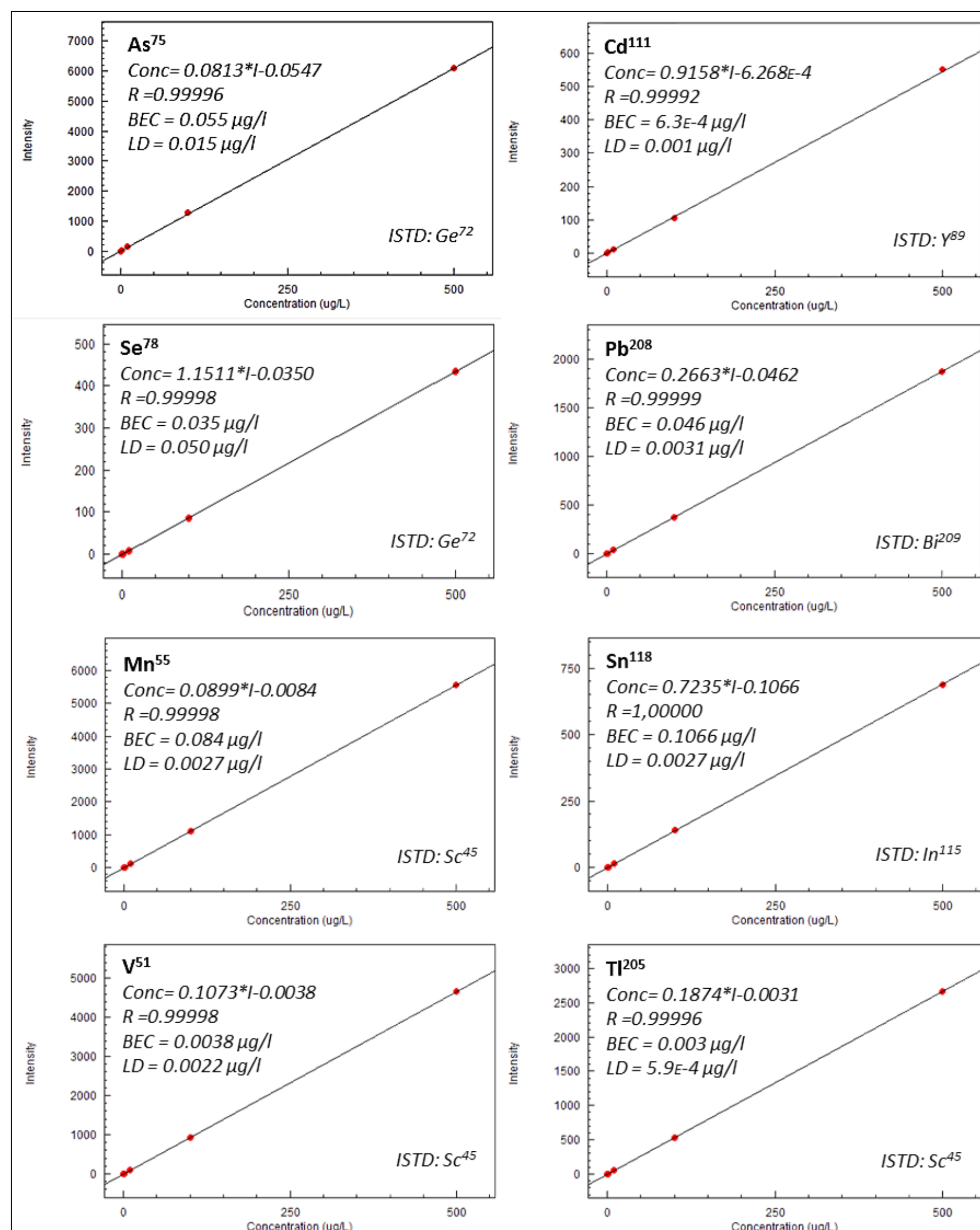


Figure 2: Examples of calibration curves using 1% HNO₃ and 4% EtOH.

As the different curves show in Figure 2, all correlation coefficients r achieve a 0.9999 level. Moreover, low values of detection limits (LD), calculated automatically by LabSolution ICPMS software with 3σ method, indicate the highly suitability and ability of ICPMS-2030 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: ICPMS-2030 results for each wine sample

The quantitation results in table 2 demonstrate that ICPMS-2030 is able to quantify simultaneously many various elements present 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). The achieved results are mentioned in table 3 an calculated according to:

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

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: Spike-Recovery rates in white and red wines. ¹ spike of 1 ppb. ² spike of 10 ppb.

The recovery rate for all the elements are between 95% and 105%, indicating the suitability of the developed method in point of accuracy, independent from initial element concentration.

Determination of 2,4,6-Trichloroanisole in Wine

Cork stoppers used for wine bottles can effect the taste of 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 TCA by cork stoppers measures the quantity released by a sample of cork stoppers macerated in a aqueous-alcoholic solution.

The aim of this method is to evaluate the value of released TCA by analyzing different cork stoppers and as final step 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.

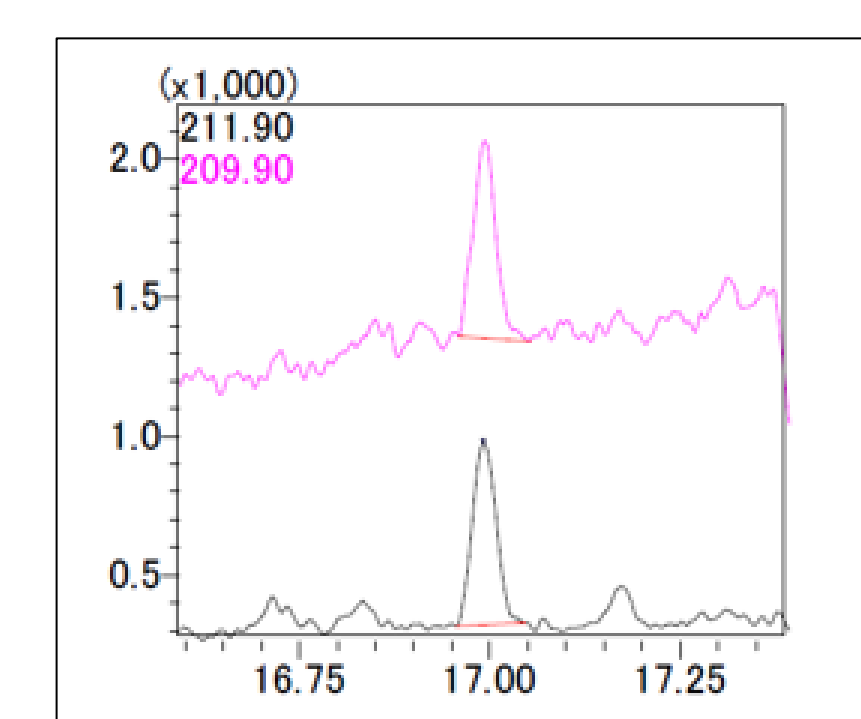


Figure 4: SIM Chromatogram of TCA in Wine using HS-Trap (wine spiked with 1 ng/L TCA)

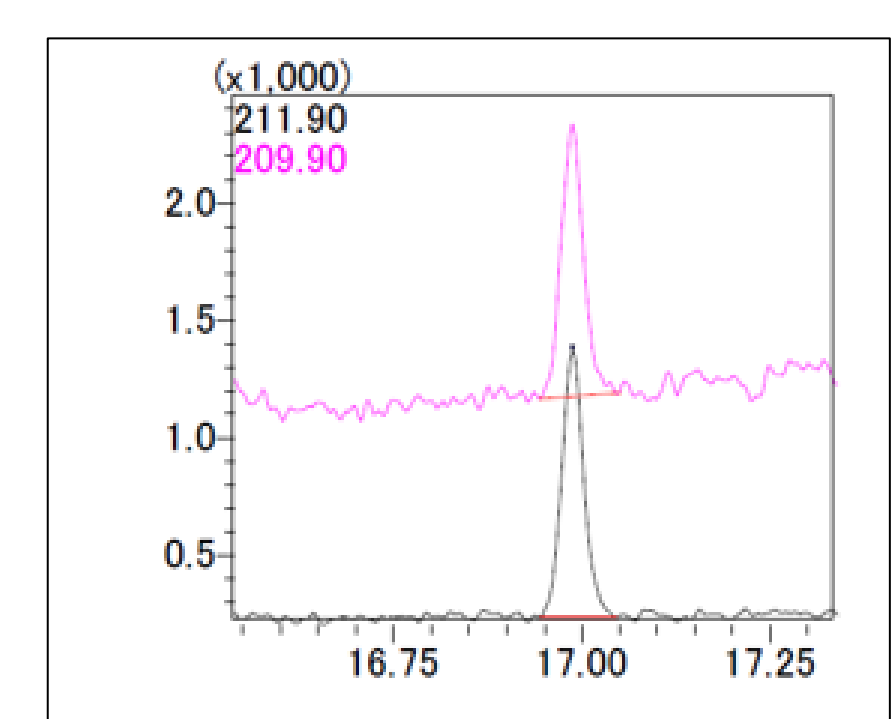


Figure 5: SIM Chromatogram of TCA in Wine using conventional headspace GCMS (wine spiked with 100 ng/L TCA)

Summary

ICP-MS is a fast and reliable tool for determination of heavy metals in wine and 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.