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# Characterization and Quantification of Heavy Metals in Wine Using ICP-OES Spectrometry

Uwe Oppermann[1], Ludivine Fromentoux[2], Marion Egelkraut- Holtus[1], and Jan Knoop[1]
[1]Shimadzu Europa GmbH, Spectroscopy, Duisburg, Germany
[2]Shimadzu France, Marne-la-Vallee, France

## ■ Overview

Food and drinks are always a hot topic discussion and in the focus of “state of the art” analytical techniques. Food scandals all around the world from eggs to horsemeat, tainted wine, oil, and milk forces the European community to establish an integrated approach on food control. The target is a high level of food safety, animal health, animal welfare and plant health within the European Union through so called “farm-to-table” measures and monitoring, ensuring the effective functioning of the European market.

Figure 1: Grapes – the source of wine

## ■ European regulations

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.

## ■ Quantitative Analysis using ICP-OES

The quality standards are fixed in the national wine regulations such as the German “Weinverordnung” (Bundesgesetzblatt Teil 1 Nr. 32) from 22nd May 2002, with the latest revision of 2012 which includes the classification of wines from different locations but also the production process, alcohol concentrations and the maximum allowable concentrations of the elements as listed in Table 1.

Table1: Maximum allowable concentrations in Wine

| Element | Max. Concentration [mg/L] |
|---|---|
| Al | 8 |
| As | 0.1 |
| B | 80 |
| Cd | 0.01 |
| Cu | 2 |
| Pb | 0.25 |
| Sn | 1 |
| Zn | 5 |

For quantitative determination of the elements in the required concentration range, ICP is the most preferable tool for quality control because of a high sensitivity, a wide dynamic range and a high sample throughput. Figure 2 shows the Shimadzu ICPE-9820 which is a simultaneous spectrometer with CCD (charge-coupled device) detector, which has been used for all determinations. This instrument configuration is equipped with a unique optical system which sets new standards with respect to performance and speed and can be optimized for a wide variety of different applications.

The vacuum systems allows precise analysis of elements in the lower UV range under extremely stable conditions. The use of a vertical mounted mini torch allows a cooling gas flow rate of only 10 L/min. The system setup for determination of low concentration heavy metals in wine has been optimized using the mini torch in the dual view mode for axial and radial plasma observation, which allows the determination of high concentration elements such as alkaline and alkaline earth and the heavy metals at the same time. The wine samples have been simply diluted 4 times with deionized water, and aspirated in the same way as aqueous solutions in the cyclone chamber and straight into the minitorch. The standard solutions have been prepared including an ethanol concentration of 3,5% in order to match the matrix. Table 2 shows a summary of the system parameters.

Table 2: Analytical conditions for wine analysis

| Parameter | Setting |
|---|---|
| RF generator power | 1.2 kW |
| Cooling gas | 10 l/min |
| Plasma gas | 0.6 l/min |
| Carrier gas | 0.7 l/min |
| Nebulizer | Coaxial |
| Plasma observation | Axial/Radial |
| Sensitivity | Wide Range |
| Exposure time | 15 sec. |
| RF generator power | 1.2 kW |

## ■ Copper in wine

The concentration of copper in wine is limited to a maximum level of 2 mg/L. In case of higher copper concentrations the wine may have a metallic bitter taste and furthermore the fermentation process will be influenced by higher copper concentrations as well. Copper in wine is coming from the Bordeaux mixture, which is a mixture of copper(II) 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 from 2016.

The calibration curve in Figure 2 shows the standards with concentrations starting at 250 µg/L up to the maximum concentration of 1000 µg/L. The limit of detection is calculated with <0,02 µg/L (3 s). Furthermore the determination of arsenic and lead is important, as those elements still can be found in the environment generated from lead arsenate ($PbHAsO_4$) which has been used as an inorganic insecticide until 1988, when it was officially banned.

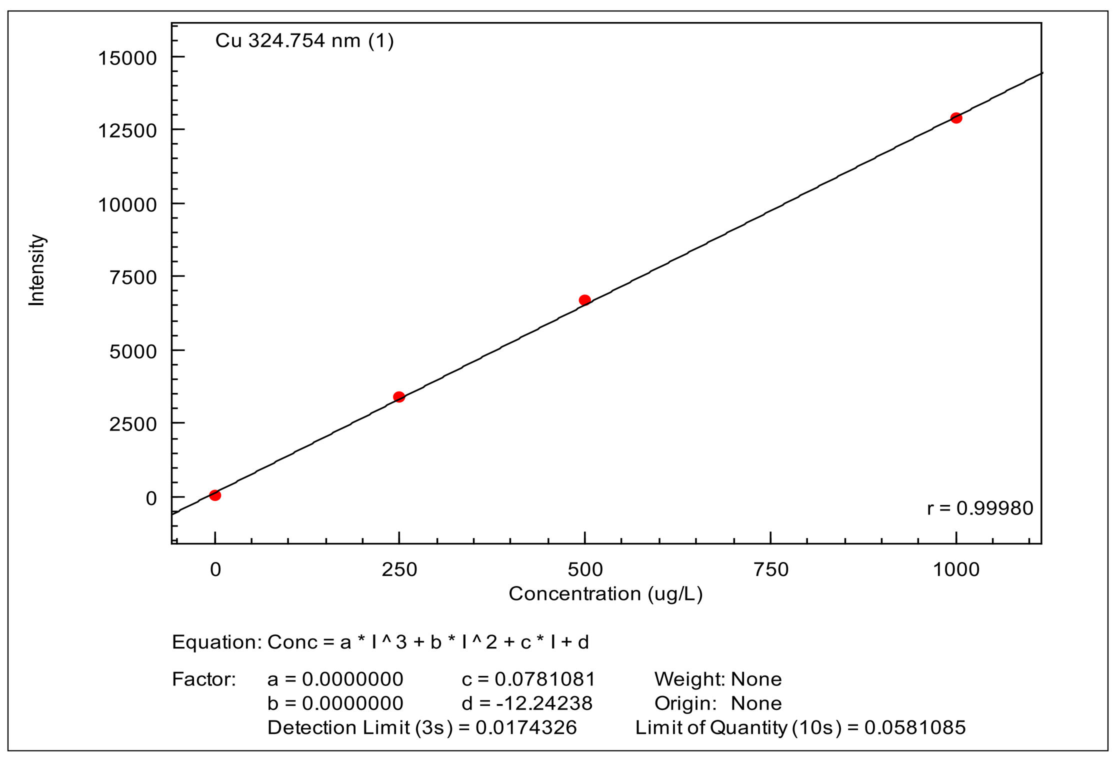


Figure 2: Calibration Curve of Copper

## ■ Antimony in Food and Food Packaging

One more element in the focus is Sb. The annual consumption of antimony trioxide in the United States and Europe is approximately 10,000 and 25,000 tons, respectively. The main application is as flame retardant synergist in combination with halogenated materials. Furthermore Antimony trioxide is used as a catalyst in the production process for PET bottles. Elevated concentrations of Sb have been found in soft drinks such as cola- and orange juices which are stored in PET bottles, as the Sb migrates from the plastic to the liquid and so accumulates in the drinks. The migration process is accelerated in alcoholic beverages. Vodka samples from glass and PET bottles have been compared according to their Sb-levels and it was found that the Sb concentration in vodka from a PET bottle can go up to 20 µg/L in comparison to less than 1 µg/L in a glass bottle. The maximum allowable concentration of Sb in drinking water is 5 µg/L.

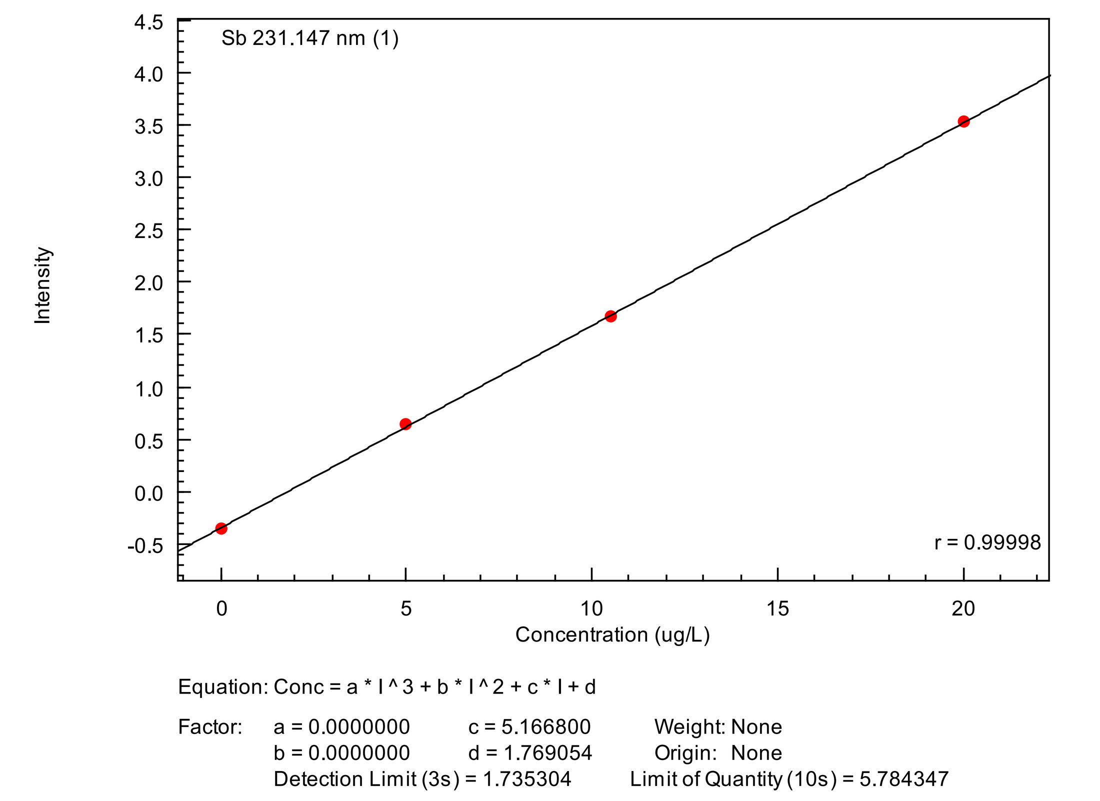


Figure 3: Calibration Curve of Antimony

## ■ Outlook

As the latest development in the wine industry is the appearance of 75 cl and 1,5 L PET bottles in the supermarket shelves with wines from New Zealand, Australia, and France further analytical investigations are in process to evaluate the Sb concentration in wines.

***Shimadzu Europa GmbH***

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

*shimadzu.eu/home/*
*shimadzu@shimadzu.eu*