

## POTENTIAL OF ARSENIC SPECIATION FOR GEOGRAPHICAL ORIGIN DISCRIMINATION OF RED WINES

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**Abstract** - The speciation of arsenic (As) in red wines has been developed and validated by HPLC – ICP MS. Four species were addressed, namely As(III), As(V), DMA and MMA. They could be determined at the (sub) µg As/L level depending on the species with repeatability, reproducibility and accuracy parameters consistent with the use of the method for discrimination studies. The method developed has then been applied to red wines from different origins. The results of Principle Component Analysis clearly show that even if As speciation does not allow a complete discrimination of the red wines as a function of the geographical origin, it is much more discriminant than the single total As determination.

**Keywords:** geographic origin, As speciation, HPLC – ICP MS

### 1. INTRODUCTION

Wine traceability and authenticity are of primary importance for both consumers and producers. As a matter of fact, wine is one of the most studied food commodities for authentication [1] probably due to its high market price that makes it attractive for fraud. The approaches used for food and beverages authentication have recently been reviewed [1, 2]. They generally include microbial fingerprinting, sensory analysis, isotopic ratios determination and metabolites fingerprinting, this latter including both metabolites and trace element determination.

Arsenic (As) is usually present in wine either because the vine has grown on a soil naturally containing As and has accumulated it [3] or consequently to the use of As-containing herbicides and insecticides during grape production [4]. In

general, concentrations of a few µg/L of As have been reported [4]. At this level, the amount of As may not produce acute intoxication. But the different potential sources of As may lead to differences in As speciation depending on the geographical origin.

Most of the studies related to As speciation in wine are based on liquid chromatography (HPLC) coupled to element specific detectors [5, 6, 7] such as inductively coupled plasma mass spectrometry (ICP MS). The aim of this study was to determine both total As and As speciation in a variety of red wines to assess the potential relationships between the As speciation and the geographical origin and therefore to evaluate the relevancy of using As speciation for red wines authentication.

### 2. MATERIALS AND METHOD

**Samples.** Samples of red wines were collected with provenance information : China (n = 14), Bordeaux (n = 35) and California (n = 8).

**Total As determination.** Samples were digested by HNO<sub>3</sub> 69% on a hot plate (DigiPrep, SCP Sciences). The total As concentration was determined by ICP MS equipped with a collision cell filled with H<sub>2</sub> (7500cx, Agilent) by the method of the standard additions.

**As speciation.** The red wines were diluted two times by ultrapure water and filtered at 0.45 µm. An aliquot of the diluted wine was injected on the Hamilton PRP-X100 HPLC column directly connected to the ICP MS (7500cx, Agilent). The chromatographic separation was performed using a Model 1100 HPLC pump (Agilent) using a gradient of ammonium carbonate from 20 to 50 mM.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optimization of As speciation in red wine

Direct analysis of the red wine by HPLC – ICP MS was not possible due to the alcohol content and the possible presence of particules. Dilution by a factor two by ultrapure water and filtration at 0.45 µm were necessary before injection on the HPLC column. In order to check whereas this protocol was not leading to any As loss, the total As content in the diluted/filtered wines was compared to the total As in the raw wines. In average, the recovery of As was of 101 ± 5% (n = 15) showing that As was not lost during this pre-treatment step.

As speciation was then performed by HPLC – ICP MS on the diluted/filtered red wines. In average the most abundant species were the inorganic ones (taking into account the possible oxidation of As(III) into As(V) within the time, the sum of both species was considered rather than both individual species). It was accounting for in average *ca.* 76% of the total As. Most of the remaining As was present in the form of methylated species (mainly DMA, but also MMA from time to time). An example of chromatogram is shown Fig. 1.

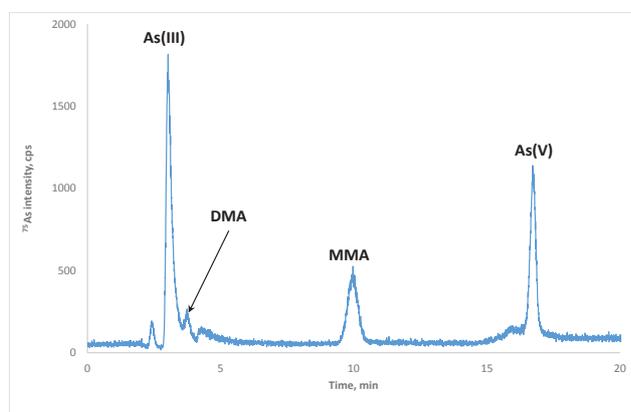


Fig. 1. Typical HPLC – ICP MS chromatogram obtained for a red wine

#### 3.2. Validation of As speciation in red wine

The method developed was then validated using a mixture of red wines from different origins in order to cover the whole potential matrices. The figures of merit obtained this way are shown Table 1. It can be seen that both repeatability and reproducibility were below 10%. Accuracy (at a level close to the quantification limits and a level 5 times higher) was in the range 93 – 107%. Quantification

limits were evaluated according to the IUPAC recommendations as 10 times the standard deviation of the blanks. They were evaluated at the (sub) µg As/L level depending on the species. These figures of merit are consistent with the use of As speciation for authentication purpose by HPLC – ICP MS.

Table 1. Figures of merit of As speciation in red wines by HPLC – ICP MS

	As(III)	DMS	MMA	As(V)
Repeat.	0.9%	1.4%	0.5%	2.7%
Reprod.	2.3%	3.4%	3.6%	7.0%
Accuracy (low level)	105%	102%	107%	103%
Accuracy (high level)	93%	97%	100%	94%
LOQ (µg As/L)	1	0.4	1	0.6

#### 3.3. Statistical approach for discrimination purpose

In a first approach, the boxplots corresponding to the total As content in the whole set of samples were built to check the presence of outliers (Fig. 2).

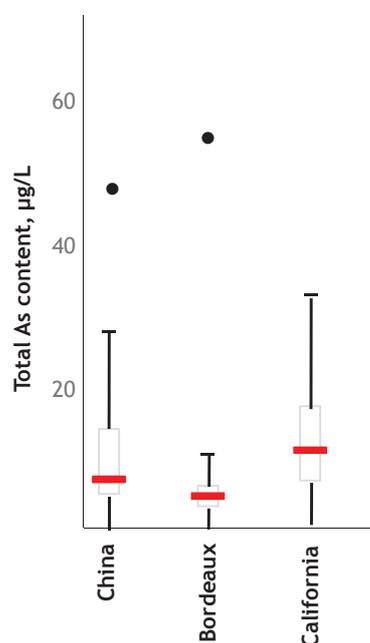


Fig. 2. Boxplots for total As content of red wines from different geographical origins

The boxplots indicate an outlier in the Bordeaux and China wines group. The Bordeaux sample was from 1969 when the grape was

probably subjected to a mildew treated by an As-containing fungicide. This sample was removed for further statistical treatment. In addition, the boxplots clearly show a higher dispersion of the total As concentration for the China and California wines than for the Bordeaux ones. For this reason, and because of a low amount of samples available in this group, the China wines outlayer point was kept for further statistical treatment.

The relevancy of combining total As and As speciation to discriminate the geographical origin was then investigated. Using only total As concentration (Fig. 3a) is not enough to even start to discriminate the geographical origin (this was already suggested by the boxplots presented Fig. 2 that were overlapping). However, using a combination of total As and As speciation (Fig. 3b) clearly improves the distinctiveness for geographical origin discrimination.

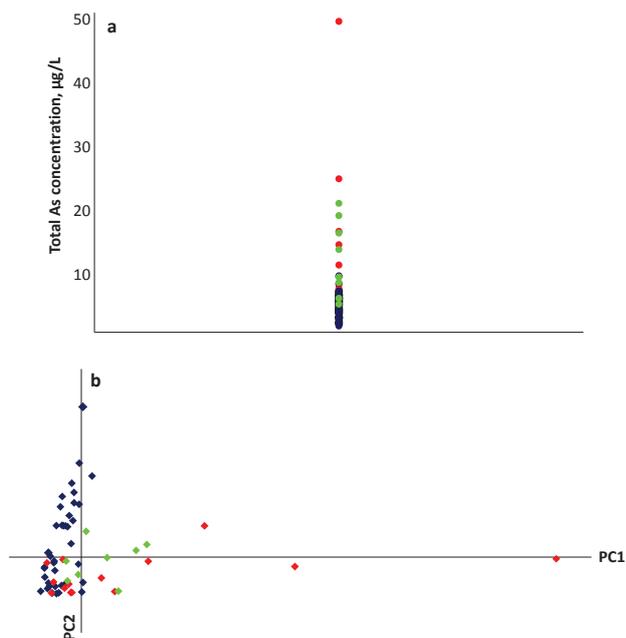


Fig. 3. (a) Repartition of total As concentration. (b) Results of Principal Component Analysis with total As and As speciation. Red signs : China wines. Blue plots : Bordeaux wines. Green plots : California wines.

It has however to be pointed out that the discrimination is not comprehensive. This can be, at least partly, due to the fact that total As and As speciation are not independent parameters. It would also be necessary to complete this study with additional samples to get results statistically more relevant. However these results tend to show that

As speciation would be a more discriminant parameter than total As in view of building models for tracking the geographical origin of red wines.

#### 4. CONCLUSIONS

The method developed and validated for As speciation in red wine presents analytical performances consistent with its use to evaluate the relevancy of using As speciation for geographical discrimination of red wines. Even if only an incomplete discrimination of the samples can be achieved using As speciation, this parameter appears to be more discriminant than the total As content for geographical authentication purpose. It has however to be pointed out that the study should be completed with the analysis of additional samples.

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2<sup>nd</sup> IMEKOFOODS  
*Promoting Objective and Measurable Food Quality & Safety*  
October, 2<sup>nd</sup>-5<sup>th</sup> 2016 Benevento (Italy)

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