FAST ARSENIC SPECIATION ANALYSIS OF WINES AND RICE WITH LC-ICP-QQQ

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Introduction
This fit-for-purpose method was designed in response to recent and proposed food standards, both international and national, that limit inorganic arsenic rather than total, organic, or individual arsenic species such as arsenite (As(III)) and arsenate (As(V)). In this method, As(III) is intentionally oxidized to As(V) with H2O2 during sample preparation, converting all inorganic arsenic (the sum of As(III) and As(V)) to the As(V) form. Arsenic species were separated in less than 2 minutes using a short, narrow bore, 5 µm chromatography column. This analysis time is 10x faster than the current FDA regulatory method. The use of O2 reaction gas with inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ with MS/MS capability) avoided spectral interferences and dramatically increased sensitivity, allowing for low volume injections. The small injection volume and modified mobile phase composition mitigate non-spectral interferences such as carbon enhanced ionization. Furthermore, the shortened analysis time significantly increases sample throughput. Validation data from two laboratories demonstrate the method’s accuracy and reproducibility of both wine and rice matrices in a single analytical batch.

Results and Discussion
For this study, the focus of the method development was to reduce the analysis time per sample. In the development of this method, we followed Jackson’s use of a small injection volume, short ion-exchange column, oxygen cell gas, and a high mobile phase linear velocity. Figure 1 shows a representative calibration set of overlaid chromatograms for the 0.5, 1.0, and 5.0 µg/kg standards. All As species are clearly separated in less than two minutes. Simply by oxidizing As(III) to As(V) in the form of As(V), the analysis time was reduced significantly compared to the current FDA regulatory method.

Experimental

Samples
• Five different California wines were used for the validation (VI) study. Each wine represented one of the five main styles of wine: red, white, rosé, sparkling, and dessert. Five additional California wines were analyzed for a commercial market basket (MB) study.
• Calibration standards were prepared at 0.1, 0.5, 1.0, 5.0, 10.0, and 20.0 µg/L (ppb) for each of DMA, MMA, and total As (sum of As(III) and As(V)).
• H2O2 was added to all samples at a 1:1 ratio to oxidize As(III) to As(V). Each sample was further diluted with de-ionized water to a total dilution factor of 5 or 6 (there were no differences in results between the two dilution factors). Each wine sample was then passed through a 0.45 µm syringe filter to remove any particulates. Samples V-1, V-5, V-6 were spiked with all As species in duplicate at three concentration levels: 5.10, and 30.0 µg/kg.

Data Collection
8800/8900 ICP-MS/MS (Agilent)
1 Concentric nebulizer, double-glass spray chamber at 27°C
2 1550 W RF power, 1.8 V RF matching voltage, 8 mm volume sampling, 0.95 ml/min Ar carrier gas, 0.20 ml/min Ar makeup gas, 0.28 ml/min Ar makeup gas, 0.31 ml/min

Table 1: Wine style, cultivar, region, vintage, and alcohol content of the wine samples for the validation and commercial market basket studies.

Table 2: Limits of detection (LOD) and limits of quantitation (LOQ) given in Table 2 are based on repeated measurements of the 0.05 µg/kg (ppb) mixed standard, n=15.

Table 3: Comparison of data measured at 2 labs using the fast LC method to reference FDA method 4.10 for 5 wine samples.

Table 4: Analyses of rice reference materials. Uncertainty shown as 1 standard deviation (N = 3), % recovery shown in parentheses.

Conclusions
The method presented here has been shown to work for both wine and rice matrices. Runtime has been decreased to 20 minutes, which is a factor of 10x faster than previous methods. The method also showed improved sensitivity and limits of detection and quantification compared to the current FDA method. Small injection volumes and addition of methanol in the mobile phase increased robustness to non-spectral interferences and makes this method more suitable for wine speciation. If needed, analysis time and results could be further improved by decreasing injection volume, increasing mobile phase flow rate and using a small volume, fast-washout spray chamber.

Acknowledgments and References
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References