Routine analysis of total arsenic in California wines using the Agilent 4200/ 4210 MP-AES

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Introduction

Arsenic (As) is a naturally occurring element found throughout the world. The environmental levels of As have been increasing due to natural sources, such as volcanic activity, and anthropogenic sources, such as smelting. The continuous release of As into the ecosystem has formed an accumulation of the element in the food chain.

Wine is a globally consumed beverage where total levels of As are regulated between 100-200 µg L^{-1}, depending on the country in question. However, there are countries, such as the United States, that do not regulate levels of all elements in wine. This necessitates investigating total As levels in wine produced in the United States to identify potential contamination, beyond the levels regulated by other countries.

Measuring total arsenic levels in wine with various spectrometric techniques typically deliver insufficient sensitivity due to the element's relatively high ionization potential. However, the use of vapor generation techniques to form volatile forms of As allow for a more sensitive detection of As.

The MP-AES offers:

- High sensitivity, with superior performance to FAAS
- Lower operating costs as the instrument uses nitrogen to sustain the plasma, either extracted from the ambient air (using a nitrogen generator) or supplied via a nitrogen Dewar
- Safer to run, compared to acetylene-based instruments, as no flammable gases are required
- Addition of MSIS accessory assists with hydride species, delivering lower detection limits, than with conventional nebulization

This study investigates the use of the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) coupled with the Multimode Sample Introduction System (MSIS) accessory to measure total As in wine samples from the California region.

The Agilent MP-AES fitted with Multimode Sample Introduction System

Experimental

Instrumentation

All measurements were performed using the Agilent 4200 MP-AES fitted with the MSIS accessory, MicroMist glass nebulizer and Easy-fit torch.

The As 188.979 nm line was selected for analysis and the read time optimized in the easy to use MP Expert software that controls the instrument. The instrument operating and method settings are given in Table 1.

Experimental

Table 1. Agilent 4200 MP-AES operating and method parameters

Parameter	Setting
As wavelength (nm)	188.979
Pump Speed (rpm)	20
Sample pump tubing	Black/black
Hydride reagent tubing	Black/black
MSIS waste tubing	Black/white
Read time (s)	20
Replicates	3
Sample uptake delay (s)	40 (Fast pump:ON)
Stabilization time (s)	20
Nebulizer flow (L/min)	0.45
Background correction	FLIC
Calibration fit	Linear
Nitrogen gas source	Agilent 4107 Nitrogen Generator

Sample preparation

Forty commercially available wines from various areas in California, were analysed. Wine varieties included: Pinot noir, Merlot, Cabernet Sauvignon, Rosé, Chardonnay, white Zinfandel, Sauvignon blanc, a white blend, sparkling wine and port-style wine (for sample list see full application note at Agilent.com).

All wine samples were diluted by a factor of three with Millipore ultrapure water then further diluted with hydrochloric acid (34-37.5%) for a total acid concentration of 10%. This resulted in a final 3.3-fold wine dilution. Each wine was prepared in triplicate.
Four wine samples were selected and prepared as spiked samples for additional analysis. Low and high concentration spikes were used at 10 µgL^{-1} and 50 µgL^{-1} and prepared in triplicate.

Calibration standards and reagents

Working standards at 5, 10, 25, 50 and 100 µgL^{-1} prepared from 1,000 µgL^{-1} As single element calibration standard. As (III) and As (V) calibration standards were used as check standards to validate the method at 20 µgL^{-1} each. All calibration standards were matrix-matched with a 10% hydrochloric acid (34-37.5%) and 5% ethanol (v/v) solution.

Hydride generation solutions: 1.2% Sodium Borohydride ($NaBH_4$, 98%,) and 1.0% Sodium Hydroxide (NaOH) in Millipore ultrapure water. The second was a 1:1 solution of HCl (34-37.5) and Millipore ultrapure water.

A reduction solution: 25% (w/v) potassium iodide, added to all samples and standards to create a final concentration of 1%, was used to reduce As species prior to analysis to change the valence state of As from As (V) to As(III). As (V) does not readily form a metal hydride.
The setup of the MSIS (in Vapor Generation mode) is displayed in Figure 1.

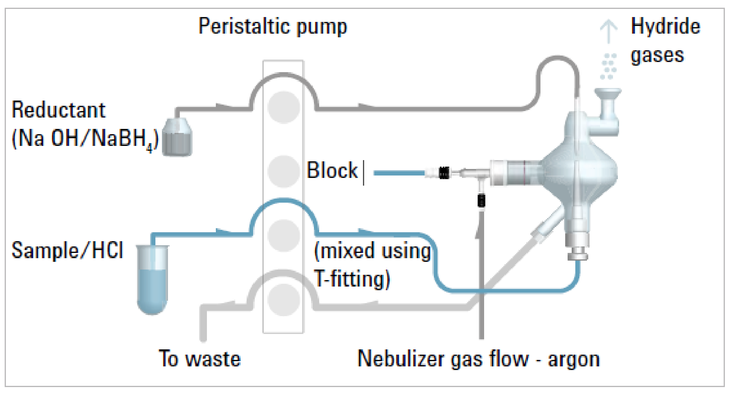

Figure 1. The setup of the MSIS (in Vapor Generation mode). The sample and HCl solution were mixed using a 'tee' fitting. Sample line to the nebulizer was blocked during analysis.

Results and Discussion

Calibration

The five-point calibration curve for As (188.979 nm) is shown in Figure 2. It shows excellent linearity with a calibration coefficient of greater than 0.999 and less than 6% error on each calibration point.

Method Detection Limit

The Method Detection Limit (MDL) for As was determined from the analysis of ten replicate measurements of the blank solution. Table 2, shows that the calculated MDL (confidence interval of 99.5%) for As was 0.34 µgL^{-1}.

Results and Discussion

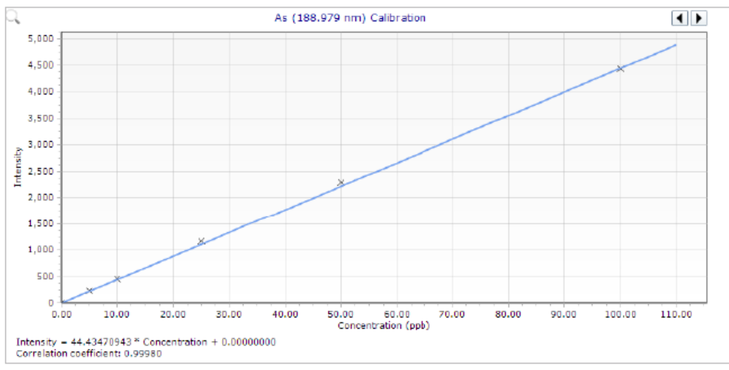

Figure 2. Calibration curve for As 188.979 nm showing excellent linearity

Table 2. The calculated MDL and standard deviation results for As 188.979 nm.

Element	Concentration (µgL^{-1})
Mean (n=10)	0.01
Standard Deviation	0.10
MDL (0.995)	0.34
MDL (0.99)	0.29
MDL (0.95)	0.19

Method Validation

Quality Control (QC) samples were run after the calibration and throughout the analytical run. The Continuing Calibration Verification (CCV) and Continuing Calibration Blanks (CCB) were measured every 10 samples. The initial calibration verification block included a 20 µgL^{-1} As (III) and As (V) sample. This was done to validate the calibration and confirm the efficiency of the KI reduction step of As (V) to As (III) prior to analysis. All recoveries were within ± 10% of the assigned values (Table 3).

Table 3. QC recoveries of CCB, CCV and 20 µgL^{-1} As (V) and As (III) samples.

Solution	Concentration (µgL^{-1})	Recovery (%)
CCB, (mean, n=7)	0.46	-
25 µg L^{-1} CCV (mean, n=7)	23.94	96
20 µgL^{-1} As (V)	20.59	103
20 µgL^{-1} As (III)	19.92	100

Analysis of wine samples

The results obtained for each sample are the average of 3 replicates. Table 4 displays some of the samples, along with the standard deviation and relative standard deviation (%RSD). As concentrations in the wine samples ranged from below the MDL to 48.81µgL^{-1}, well below the range of 100-200 µgL^{-1} regulated in many countries. For all sample results see full application note at Agilent.com.

Table 4. Quantitative results for total As (188.979 nm) concentration in Californian wines using the 4200 MP-AES, <MDL = below Method Detection Limit

Sample	Concentration (µgL^{-1}) (mean, n=3)	Standard deviation	Relative Standard Deviation (%)
1	1.03	0.88	0.85
10	43.81	1.13	0.03
15	6.09	1.45	0.24
20	<MDL	1.52	6.70
35	9.86	0.23	0.02
40	2.64	0.90	0.34

Conclusions

The Agilent 4200 MP-AES with the MSIS accessory provided an easy, accurate and cost- effective for analysis of total As in wine:

- The MSIS technology increased sensitivity to levels lower than single digit µgL^{-1}.
- All 40 wine samples analyzed were found to have As concentrations less than the levels regulated by most countries worldwide.
- The nitrogen-based plasma significantly reduces operating costs when nitrogen is supplied with the use of a Agilent 4107 Nitrogen Generator.

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