

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

## Application note

Food Safety

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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  $\mu\text{g L}^{-1}$ , depending on the country in question [1]. However, there are countries, such as the United States, that do not regulate levels

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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.

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. This application is also applicable for Agilent's 4210 MP-AES instrument.

The MP-AES offers high sensitivity, with superior performance in comparison to Flame Atomic Absorption Spectroscopy. The instrument uses nitrogen to sustain the plasma, either extracted from the ambient air (using a nitrogen generator) or supplied via a nitrogen Dewar. Compared with acetylene-based instruments, the MP-AES is much safer to run, as no flammable gases are required. Operating costs are also significantly less. The addition of the MSIS accessory assists with the production of hydride species which are separated from the liquid and introduced to the plasma, delivering better performance and lower detection limits, than with conventional nebulization.

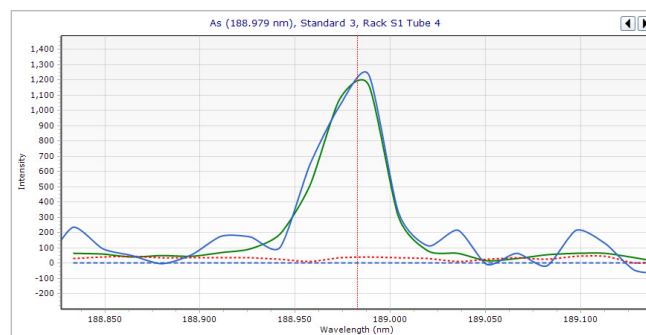
## Experimental

### 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.

The Agilent MP Expert software allows for correction of background and spectral interferences. The Fast Linear Interference Correction (FLIC) background correction (refer to Figure 1) was used to correct for the complex structured background by modeling with the solution blank of 10% HCl and 5% ethanol as the interferent.



**Figure 1.** FLIC background correction applied to As (188.979 nm) calibration standard. Background and analyte peak (blue line), FLIC model applied to background and analyte peak (green line).

**Table 1.** Agilent 4200 MP-AES operating and method conditions.

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 (sec)	20
Number of Replicates	3
Sample uptake delay (s)	40
Nebulizer flow (L/min)	0.45
Fast pump during uptake	On
Stabilization time (s)	20
Background correction	FLIC
Calibration Fit	Linear
Nitrogen gas source	Agilent 4107 Nitrogen Generator

### Samples

Forty commercially available wines, originating from various areas in California, were analysed in this study (Table 2). The wine varieties included: Pinot noir, Merlot, Cabernet Sauvignon, Rosé, Chardonnay, white Zinfandel, Sauvignon blanc, a white blend, sparkling wine and port-style wine.

**Table 2.** Wine samples used in the study, with corresponding sample number and regional origin.

Sample#	Wine type	Region
1	Cabernet Sauvignon	South Coast
2	Cabernet Sauvignon	Sonoma County
3	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
4	Cabernet Sauvignon	South Coast
5	Cabernet Sauvignon	Sierra Foothills
6	Cabernet Sauvignon	Napa County
7	Cabernet Sauvignon	Sierra Foothills
8	Cabernet Sauvignon	Napa County
9	Cabernet Sauvignon	Greater Bay Area
10	Cabernet Sauvignon	North Coast
11	Cabernet Sauvignon	North Coast
12	Cabernet Sauvignon	South Central Coast
13	Cabernet Sauvignon	Greater Bay Area
14	Cabernet Sauvignon	Sonoma County
15	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
16	Cabernet Sauvignon	North Central Coast
17	Cabernet Sauvignon	South Central Coast
18	Cabernet Sauvignon	South Coast
19	Cabernet Sauvignon	South Central Coast
20	Cabernet Sauvignon	Sonoma County
21	Cabernet Sauvignon	Sierra Foothills
22	Cabernet Sauvignon	South Central Coast
23	Cabernet Sauvignon	North Central Coast
24	Cabernet Sauvignon	North Coast
25	Cabernet Sauvignon	Greater Bay Area
26	Cabernet Sauvignon	Napa County
27	Cabernet Sauvignon	Sierra Foothills
28	Pinot Noir	Appellation Central Coast
29	White Blend	San Joaquin County
30	Rosé	Contra Costa County
31	Rosé	Lodi/San Joaquin County
32	Chardonnay	Santa Barbara County
33	White Zinfandel	Napa and Sonoma
34	Chardonnay	Central Coast
35	Chardonnay	Napa County
36	Merlot	Napa County
37	White Zinfandel	Napa and Lodi
38	Sauvignon Blanc	Oakville/Napa County
39	California Brut sparkling wine	Sonoma County
40	Petite Sirah port-style wine	Clarksburg/Yolo County

### Sample preparation

All wine samples were diluted by a factor of three with Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany) then further diluted with hydrochloric acid (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) for a total acid concentration of 10%. This resulted in a final 3.3-fold wine dilution. Each wine was prepared in triplicate with the exception of sample 37, which was prepared with 5 replicates due to high residual sugar content.

Four wine samples were selected and prepared as spiked samples for additional analysis. Low and high concentration spikes were used at 10 µg/L and 50 µg/L and prepared in triplicate.

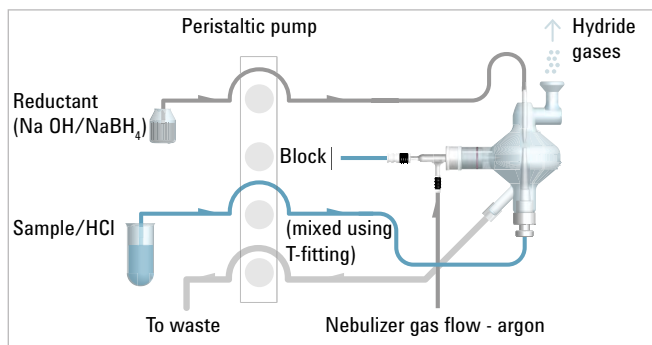
### Calibration standards and reagents

A 1,000 µg/L single element calibration standard of As (VHG Labs, Manchester, NH, USA) was used to prepare working standards at 5, 10, 25, 50 and 100 µg/L. As (III) and As (V) calibration standards from SPEX CertiPrep (Metuchen, NJ, USA) were used as check standards to validate the method at 20 µg/L each. All calibration standards were matrix-matched with a 10% hydrochloric acid (34-37.5% Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and 5% ethanol (v/v) (200 proof, Gold Shield Distributors, Hayward, CA) solution.

Two separate solutions were created for hydride generation. The first consisted of 1.2% Sodium Borohydride (NaBH<sub>4</sub>, 98%, J.T. Baker, Center Valley, PA, USA) and 1.0% Sodium Hydroxide (NaOH, ACS Grade, EMD Chemicals Inc., Gibbstown, NJ) in Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany). The second was a 1:1 solution of HCl (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany).

A reduction solution of 25% (w/v) potassium iodide (ACS Grade, BDH Chemicals, West Chester, PA) was used to reduce As species prior to analysis. As (III) and As (V) are the most prevalent forms of As in wines. This reduction step aims to change the valence state of As from As (V) to As(III), because As (V) does not readily form a metal hydride. The potassium iodide solution was added to all samples and standards to create a final concentration of 1%. Best results were obtained when it was added at least 3 hours prior to analysis.

The setup of the MSIS (in Vapor Generation mode) for this analysis is displayed in Figure 2. The sample and 50% HCl solution were mixed using a 'tee' fitting after the peristaltic pump and the combined sample/HCl line was connected to the bottom of the MSIS. The reductant, NaOH/NaBH<sub>4</sub> solution, line was attached to the top of the MSIS. The unused sample line to the nebulizer was blocked during analysis as conventional nebulization was not required.

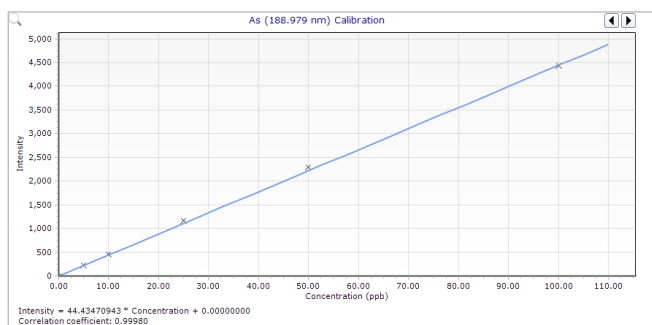


**Figure 2.** The MSIS setup for Vapor Generation mode.

## Results and discussion

### Calibration

The five-point calibration curve for As (188.979 nm) is shown in Figure 3. It shows excellent linearity with a calibration coefficient of greater than 0.999 and less than 6% error on each calibration point.



**Figure 3.** Calibration curve for As 188.979 nm showing excellent linearity across the 5-100 µg L<sup>-1</sup> concentration range, illustrating the wide analytical range of the instrument.

### Method Detection Limit

The Method Detection Limit (MDL) for As was determined from the analysis of ten replicate measurements of the blank solution. The results displayed in Table 3, show that the calculated MDL (confidence interval of 99.5%) for As was 0.34 µg L<sup>-1</sup>.

**Table 3.** The calculated MDL and standard deviation results for As 188.979 nm.

Element	Concentration (µg L <sup>-1</sup> )
Mean (n=10)	0.01
SD	0.10
MDL (0.995)	0.34
MDL (0.99)	0.29
MDL (0.95)	0.19

### Method validation

To check the validity of the method, 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 µg L<sup>-1</sup> 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 CCV recoveries were within ± 10% of the assigned values (Table 4).

**Table 4.** QC recoveries of CCB, CCV and 20 µg L<sup>-1</sup> As (V) and As (III) samples.

Solution	Concentration (µg L <sup>-1</sup> )	Recovery (%)
CCB, (mean, n=7)	0.46	-
25 µg L <sup>-1</sup> CCV, (mean, n=7)	23.94	96
20 µg L <sup>-1</sup> As (V)	20.59	103
20 µg L <sup>-1</sup> As (III)	19.92	99.6

### Analysis of wine samples

The method described above was applied to the analysis of 40 Californian wine samples. The results obtained for each sample are the average of 3 replicates and can be found in Table 5, along with the standard deviation and relative standard deviation (%RSD). As concentrations in the wine samples ranged from below the MDL to 48.81 µg L<sup>-1</sup>, well below the range of 100-200 µg L<sup>-1</sup> regulated in many countries.

**Table 5.** The quantitative results for total As (188.979 nm) concentration in 40 Californian wines using the 4200 MP-AES.

Sample	Mean Concentration ( $\mu\text{gL}^{-1}$ ) (mean, n=3)	Standard Deviation	Relative Standard Deviation (%)
1	1.03	0.88	0.85
2	<MDL	0.71	N/A
3	1.48	2.12	1.43
4	1.43	0.84	0.59
5	<MDL	0.21	N/A
6	<MDL	0.40	N/A
7	<MDL	0.77	N/A
8	<MDL	0.74	N/A
9	<MDL	0.74	N/A
10	43.81	1.13	0.03
11	2.92	3.55	1.22
12	<MDL	1.17	3.95
13	<MDL	3.91	1.90
14	6.63	1.14	0.17
15	6.09	1.45	0.24
16	3.24	1.89	0.58
17	<MDL	0.22	N/A
18	2.33	1.33	0.57
19	<MDL	2.11	14.06
20	<MDL	1.52	6.70
21	0.75	0.92	1.23
22	<MDL	2.51	N/A
23	10.16	1.15	0.11
24	<MDL	1.63	N/A
25	<MDL	1.74	N/A
26	<MDL	1.66	N/A
27	<MDL	0.22	N/A
28	3.96	0.52	0.06
29	1.37	1.16	0.85
30	<MDL	0.71	N/A
31	<MDL	0.47	N/A
32	27.04	1.21	0.04
33	31.17	4.72	0.15
34	4.53	0.37	0.08
35	9.86	0.23	0.02
36	3.44	0.46	0.13
37	17.84 (mean, n=5)	0.63	0.04
38	11.23	0.28	0.02
39	9.76	0.24	0.02
40	2.64	0.90	0.34

<MDL = below Method Detection Limit

### Analysis of spiked wine samples

Four wines, representing various total As concentrations, were selected for a spike recovery study. Two spikes were completed for each sample at 10 and 50  $\mu\text{gL}^{-1}$ . This equates to spikes of 33 and 165  $\mu\text{gL}^{-1}$  in the sample. The recoveries for each spike were within  $\pm 10\%$ , with the exception of one which had a recovery of 111%. Results seen in Table 6, show excellent recovery for As using the MP-AES at low and high  $\mu\text{gL}^{-1}$  levels.

### Conclusions

The Agilent 4200 MP-AES coupled with the MSIS accessory provided an easy and accurate analysis of total As in wine. The MSIS technology increased sensitivity to levels lower than single digit  $\mu\text{gL}^{-1}$ . The resulting MDL would be approximately 100 times lower when compared to using direct nebulization. All 40 wine samples analyzed were found to have As concentrations less than the levels regulated by most countries worldwide.

The complex background on the calibration and samples was easily corrected with Agilent's Fast Linear Interference Correction (FLIC), improving analytical accuracy.

The nitrogen-based plasma significantly reduces operating costs when nitrogen is supplied with the use of a Agilent 4107 Nitrogen Generator. The generator extracts nitrogen from compressed air. Alternatively, nitrogen can be supplied by Dewar.

The Agilent 4200 MP-AES with MSIS accessory proved to be a reliable, cost-effective instrument for quantifying total As in wine.

**Table 6.** The percent recovery results for the four As spiked wine samples at 10 and 50  $\mu\text{gL}^{-1}$ , the results shown represent the concentration in the original sample, calculated accounting for the dilution factor.

Sample#	Spiked concentration ( $\mu\text{gL}^{-1}$ )		Measured spiked concentration ( $\mu\text{gL}^{-1}$ )	Measured unspiked concentration ( $\mu\text{gL}^{-1}$ )	Recovery (%)
8	33	Ave	32.25	-1.53	102.36
		%RSD	0.03	-0.48	
8	165	Ave	153.26	-1.53	93.82
		%RSD	0.01	-0.48	
23	33	Ave	42.76	10.16	98.81
		%RSD	0.01	0.11	
23	165	Ave	164.79	10.16	93.72
		%RSD	0.01	0.11	
28	33	Ave	39.54	3.96	107.82
		%RSD	0.01	0.06	
28	165	Ave	161.48	3.96	95.46
		%RSD	0.04	0.06	
32	33	Ave	57.63	27.04	92.68
		%RSD	0.00	0.04	
32	165	Ave	211.12	27.04	111.56
		%RSD	0.01	0.04	

## Reference

C. K. Tanabe, H. Hopfer, G. Gilleland, A. Liba, S. E. Ebeler and J. Nelson. Total arsenic analysis in Californian wines with hydride generation – microwave plasma – atomic emission spectroscopy (HG-MP-AES). *J. Anal. At. Spectrom*, 2016

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Results presented in this document were obtained using the 4200 instrument, but performance is also verified for the 4210 MP-AES

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