Determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Food Testing and Agriculture

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Introduction

The concentrations of certain metals in wine are of great interest because of their influence on the wine-making process. Strict analytical control of the trace element content is required during the entire wine making process. For example, metals such as potassium, calcium, and iron can produce precipitates, cause cloudiness, or affect the taste.

The wine maker needs to properly control the production process so that the quality of the product can be assured. During vintage, when monitoring trace elements is most critical, sample turnaround time (and to a lesser extent sample throughput) becomes important. Most wine labs are small to medium in size, and hence value ease of use and reduced infrastructure requirements.

Metals in wine can be determined by a number of analytical techniques[1-10]. The most common technique used is Flame Atomic Absorption (FAA), while ICP-OES is sometimes used in larger central laboratories where extra sample throughput is required, although having elemental analysis capabilities close to the winery during vintage is generally preferred.

This work describes an alternative, safer and cheaper analytical method for the determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES).

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs.

The MP-AES offers significantly reduced on-going operating costs over both FAA and ICP-OES by running on nitrogen that can be supplied via a nitrogen generator. This eliminates the need for on-going gas resupply and avoids flammable gases (required for FAA), enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well suited to remote sites where supply of expensive specialty gases can be difficult.

The 4100 MP-AES fits between FAA and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAA and ICP-OES.

These features make the MP-AES an attractive technique for many small to medium size laboratories, particularly those at remote locations, and for an increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The measurements were performed on an Agilent 4100 MP-AES using a dewar nitrogen supply. The 4100 MP-AES is a compact bench-top microwave plasma atomic emission spectrometer that generates a robust, magnetically-excited nitrogen plasma. Operating the instrument with the optional Agilent 4100 Nitrogen Generator further reduces the operating costs.

The sample introduction system used for this application consisted of a standard torch, a double pass glass cyclonic spraychamber and an inert OneNeb nebulizer.

The determination of Ca, K, Na and Mg benefits from the use of an ionization suppressant. The ionization suppressant was mixed with the sample via a T piece placed before the nebulizer. The on-board three channel peristaltic pump was used to deliver the sample through the sample introduction system. A 0.1% w/v Cs (CsCl Analar, Merck) solution was used as an ionization suppressant.

The External Gas Control Module (EGCM) was used to inject air into the plasma when running the diluted wine matrix that contained a small amount of alcohol. The air injection prevents any carbon build up in the torch, ensuring stable results when running these samples over a long time period.

The air injection also reduces the background emissions generated by the organics present in the sample. The EGCM is automatically controlled by the instrument software, and as such requires minimal user interaction.

Because the amount of alcohol in diluted wine samples is low, the air injection rate is selected at a lower rate than the default setting for each wavelength.

The instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Parameter	Value				
Element	Ca	K	Na	Mg	Fe
Wavelength (nm)	396.847	769.897	589.592	285.213	371.993
EGCM setting	Low	Low	Low	Low	Medium
Nebulizer	OneNeb				
Spraychamber	Double pass glass cyclonic				
Pump rate	15 rpm				
Sample tubing	Orange/green				
Waste tubing	Blue/blue				
Read time	1-10 seconds*				
Number of replicates	3				
Sample uptake delay	15 seconds				
Stabilization delay	20 seconds				
Fast pump during uptake	On				
Background correction	Auto				

*Can be varied based on sample concentrations

For comparison purposes, the samples were also measured on an Agilent 725 radially-viewed ICP-OES instrument and an Agilent 240FS FAA spectrometer.

Standard and Sample Preparation

A variety of wine samples were selected for this study, covering both red and white varieties.

- Wine 1 : Shiraz
- Wine 2 : Cabernet Sauvignon
- Wine 3 : Chardonnay
- Wine 4 : Sauvignon Blanc
- Wine 5 : Viognier

Additionally, two certified reference materials were analyzed to validate the method:

- Red wine: TM-Wine-R1A (Spex CertiPrep)
- White wine: TM-Wine-W1A (Spex CertiPrep)

For MP-AES and ICP-OES analysis, the samples were degassed in an ultrasonic bath, then diluted 1 in 10 (v/v) with 5% HNO_3 (Suprapur, Merck). Standards and blank were prepared in 5% v/v HNO_3 and 2% v/v ethanol (Merck) to matrix match the alcohol content of the wine samples. Care must be taken when adding ethanol into 5% HNO_3. Ethanol should be added gradually drop-wise with a Pasteur pipette.

For AA analysis, the samples were also degassed and further sample preparation for AA depends on the element of interest.

- For Ca samples were diluted 1 in 10 with 5% HNO_3 and 2000 mg/L Sr (Strontium chloride, Laboratory reagent, BDH).
- For K and Na samples were diluted 1 in 10 with 5% HNO_3 and 1000 mg/L Cs.
- For Mg and Fe samples were diluted 1 in 10 with 5% HNO_3.

The standards and blanks were matrix matched with the samples, as described above.

Results

Method detection limit

Method detection limit (MDL) is expressed as 3 times the standard deviation of 10 replicate measurements of the blank. Analytical wavelengths used and the MDL by MP-AES are listed in Table 2.

Table 2. Method detection limits (MDL) by MP-AES

Element	Wavelength (nm)	MDL (µg/L)
Ca	396.847	8
K	769.897	110
Na	589.592	15
Mg	285.213	11
Fe	371.993	15

Certified Reference Material and Wine Samples

The accuracy of the measurement of metals in wine samples by MP-AES was verified by the analysis of the certified red and white wine reference material. Good agreement was obtained with certified values, with recoveries between 94% and 110% (see Table 3). Results for the analysis of wine samples by all three techniques can be seen in Table 4. For the five wines analyzed, the MP-AES results are in good agreement with the AA and ICP-OES results.

Table 3. Analysis of CRM samples by MP-AES

Element	Measured	Certified-TM-Wine-W1A	% Recovery
	mg/L	mg/L	
Ca	79 ± 1	82.2 ±2	96
K	980 ± 23	939 ± 142	104
Na	27.6 ± 0.4	25.1 ± 3	110
Mg	119 ± 1	123 ± 3	97
Fe	2.03 ± 0.01	1.97 ± 0.2	103
Element	**Measured**	**Certified-TM-Wine-R1A**	**% Recovery**
	mg/L	mg/L	
Ca	47 ± 0.31	50 ±2	94
K	1160 ± 32	1120 ± 142	104
Na	21.0 ± 0.4	22.4 ± 3	96
Mg	127 ± 1	123 ± 3	103
Fe	2.43 ± 0.03	2.49 ± 0.2	98

Table 4. Comparison of the analysis of wine sample by three techniques

Element	Concentration (mg/L)		
	4100 MP-AES	240FS AA	725 ICP-OES
Wine 1			
Ca	52	52	54
K	1205	1116	1112
Na	37	37	35
Mg	148	149	150
Fe	1.2	1.1	1.0
Wine 2			
Ca	6.6	6.9	6.9
K	1206	1197	1154
Na	30	34	32
Mg	103	100	102
Fe	2.2	2.2	2.0
Wine 3			
Ca	56	59	59
K	900	848	839
Na	34	33	31
Mg	87	86	90
Fe	0.9	0.9	0.7
Wine 4			
Ca	70	70	77
K	756	718	741
Na	10	11	9.0
Mg	78	77	83
Fe	0.4	0.4	0.3
Wine 5			
Ca	32	31	34
K	689	627	661
Na	48	48	45
Mg	121	125	134
Fe	1.8	1.7	1.7

Conclusion

The MP-AES is an accurate and reliable technique for this application and is an ideal alternative to FAA and ICP-OES. Results for certified samples were in good agreement with the CRM reference values and results for various wine samples were in good agreement across all three techniques.

The MP-AES also offers significant benefits over the commonly used FAA, including enhanced productivity through greatly simplified sample preparation and unattended multi-element analysis, higher performance through improved detection limits and greater linear dynamic range, and lower cost of ownership and operating costs by running on nitrogen and eliminating flammable gases such as acetylene and nitrous oxide.

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