APPLICATION NOTE

Atomic Absorption

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The Analysis of Copper, Iron, and Manganese in Wine with FAST Flame Atomic Absorption

Introduction

With the growing popularity of wine consumption in China, regulations on the safety and quality of wine are being implemented. Recent wine imports into China are required to meet mandated elemental limits and are subject to local testing upon arrival. If a wine does not meet the specifications listed in Table 1, it can be subject to destruction or return to its point of origin.

These elements are naturally occurring in wine grapes and, as such, are normally present in the wine produced from them. Concentrations of these elements can vary from region to region and from variety to variety due to the presence of nutrients in the soil the grapes are grown in, the uptake of these nutrients by the vine itself, and the process by which the wine is made. Because of this great variability, there is no way to ensure that a given wine meets the import specifications without undertaking analytical testing. Due to the possibility of the wine being rejected upon arrival into China and the financial impact this represents, wine producers and exporters are interested in a simple and accurate method for determining the concentrations of elements of interest in their wine.

Table 1. Elemental limits on wines imported into China.

Element	Limit (mg/L)
Copper (Cu)	1
Iron (Fe)	8
Manganese (Mn)	2

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Experimental

Nine different wines were acquired (Table 2) for the analysis of copper (Cu), iron (Fe), and manganese (Mn) using the conditions outlined in Table 3. All analyses were performed on a PerkinElmer PinAAcle™ 900T atomic absorption spectrometer operating in flame mode. A high-efficiency nebulizer was used with the standard spray chamber and a 10 cm burner head. External calibrations were created using a single intermediate standard made in 2% HNO_3/deionized water which was then diluted in-line using the capabilities of the PerkinElmer FAST Flame 2 sample automation accessory. The highest standard exceeded the concentrations of the upper regulatory limit for each element to ensure a broad range of detection capability. The wine samples were run directly without preparation other than spiking and were introduced with the use of the FAST Flame 2 accessory.

The FAST Flame 2 accessory is a combination of high-speed autosampler, peristaltic pumps and switching valve. It provides quick sample turnaround with fast rinse-out, short signal stabilization times and no sample-to-sample memory effect. The FAST Flame 2 sample automation accessory rapidly fills a sample loop via vacuum and then switches to inject the sample loop while the autosampler moves to the next sample. This removes the wait time associated with self-aspiration or peristaltic pumping and the long rinse-in and rinse-out times associated with autosampler movement and flushing, resulting in sample-to-sample times as short as 15 seconds.

Table 2. Wines analyzed.

Type	Country of Origin	Identifier
Cabernet	Argentina	AR Cab
Cabernet	Australia	AU Cab
Cabernet	USA	USA Cab A
Cabernet	USA	USA Cab B
Chardonnay	Argentina	AR Chard
Chardonnay	Australia	AU Chard
Chardonnay	USA	USA Chard A
Chardonnay	USA	USA Chard B
Red Zinfandel	USA	USA Zin

Table 3. PinAAcle 900T instrument and analytical conditions.

Parameter	Copper (Cu)	Iron (Fe)	Manganese (Mn)
Wavelength (nm)	324.75	248.33	279.48
Slit (nm)	0.7	0.2	0.2
Air Flow (L/min)	2.5	2.5	2.5
Acetylene Flow (L/min)	10	10	10
Integration Time (sec)	3	3	3
Replicates	3	3	3
Sample Flow Rate (mL/min)	6	6	6
Intermediate Standard	20	40	20
Auto-Diluted Calibration Standards (mg/L)	0.5, 2, 5	1, 4, 10	0.5, 2, 5
Calibration Curve Type	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero

The ability of the FAST Flame 2 accessory to mechanically pump the sample during injection allows for ideal optimization of nebulizer and flame conditions, eliminates variability due to changes in sample viscosity, dissolved solids and tubing length, and also provides long-term sample flow stability. The in-line dilution capability allows the analyst to create a single intermediate standard, and then the FAST Flame 2 accessory automatically generates all calibration standards in-line, as required. In addition, the instrument can be set to identify QC over-range samples and then utilize the in-line dilution capability to automatically re-run a sample that falls outside the calibration range at an increased dilution factor to bring the signal within the calibration and provide accurate measurement along with a passed QC check.

Each wine sample was spiked at levels both below and above the regulatory limit to assess accuracy. The highest spike in each case was purposefully out of range of the calibration, and the instrument software identified and then auto-diluted the samples using the in-line capabilities of the FAST Flame 2 accessory. This demonstrates the ability of the PinAAcle 900 AA spectrometer coupled with FAST Flame 2 accessory to accurately and quickly assess samples at a wide range of concentrations without user intervention.

Results and Discussion

The calibration curves were created using the in-line dilution capabilities of the FAST Flame 2 accessory. Calibration results are shown in Table 4. The excellent correlation for the calibration standards demonstrates the value of the automatic in-line sample and standard dilution available on the FAST Flame 2 accessory. The independent calibration verification recoveries ensure that the calibration is valid and that the creation of standards via the dilution system is very accurate.

Table 4. Calibration results.

Element	Correlation Coefficient	ICV Concentration (mg/L)	ICV (% Recovery)
Copper (Cu)	0.99999	2	101
Iron (Fe)	0.99999	4	99.4
Manganese (Mn)	0.99983	2	102

Tables 5-7 show the results for the analyses for copper, iron, and manganese, respectively. The results indicate that the wines are under the regulatory limits with the exception of the Australian chardonnay which is over the limit for manganese. From the limited samples analyzed, it appears that the 2 mg/L specification for manganese could be a critical parameter for qualification of a wine for importation into China. Spike recoveries for all elements are within 10% of the spiked values, even when spiked at or below half the regulated values and when diluted via the in-line dilution capability of the FAST Flame 2 sample automation accessory, demonstrating the excellent accuracy needed to ensure successful analysis.

The addition of the FAST Flame 2 accessory reduced the creation of standards from one intermediate and three final standards to a single intermediate standard with a commensurate reduction in human error during standard creation. The FAST Flame 2 accessory was also able to react to the over-range spikes and auto-dilute the samples accurately and consistently without interaction from an analyst, saving time and eliminating additional sample handling and re-prep.

These results demonstrate the robustness and accuracy of the analysis and the speed and increased productivity available from the PinAAcle 900 AA spectrometer and the FAST Flame 2 accessory.

Table 5. Copper in wine (regulated limit = 1 mg/L).

Wine	Measured Conc. (mg/L)	Measured Spikes			Spike Recoveries %		
		0.5 mg/L	1.0 mg/L	10.0 mg/L *	0.5 mg/L	1.0 mg/L	10.0 mg/L *
AR Cab	0.046	0.558	1.08	10.4	103	104	104
AU Cab	0.603	1.11	1.61	10.8	100	101	102
USA Cab A	0.088	0.579	1.11	10.3	98.3	102	102
USA Cab B	0.088	0.611	1.12	10.8	105	103	107
AR Chard	0.013	0.527	1.03	10.5	103	101	105
AU Chard	0.478	0.969	1.38	10.3	98.2	90.3	98.6
USA Chard A	0.120	0.637	1.15	10.7	104	103	106
USA Chard B	0.099	0.609	1.13	10.8	102	103	1076
USA Zin	0.256	0.746	1.20	10.1	98.0	94.2	98.6
					* = 5X Online Dilution		

Table 6. Iron in wine (regulated limit = 8 mg/L).

Wine	Measured Conc. (mg/L)	Measured Spikes			Spike Recoveries %		
		1.0 mg/L	5.0 mg/L	20.0 mg/L *	1.0 mg/L	5.0 mg/L	20.0 mg/L *
AR Cab	1.80	2.72	6.78	21.4	92.1	99.5	97.9
AU Cab	2.18	3.20	7.35	22.8	103	104	103
USA Cab A	2.32	3.24	7.69	21.9	92.7	1085	98.1
USA Cab B	2.31	3.25	7.42	22.1	93.9	102	98.8
AR Chard	1.65	2.61	6.69	21.0	95.5	101	96.7
AU Chard	2.92	3.91	7.86	23.6	99.2	98.8	103
USA Chard A	1.68	2.67	6.62	21.3	98.7	98.8	98.1
USA Chard B	1.16	2.15	6.17	21.0	99.5	100	99.3
USA Zin	2.80	3.77	7.70	23.7	97.6	98.1	104
					* = 5X Online Dilution		

Table 7. Manganese in wine (regulated limit = 2 mg/L).

Wine	Measured Conc. (mg/L)	Measured Spikes			Spike Recoveries %		
		1.0 mg/L	4.0 mg/L	10.0 mg/L *	1.0 mg/L	4.0 mg/L	10.0 mg/L *
AR Cab	1.36	2.31	5.20	11.0	95.0	95.9	96.0
AU Cab	1.93	2.90	6.07	12.3	97.1	104	104
USA Cab A	1.51	2.45	5.41	11.0	94.3	97.6	94.7
USA Cab B	1.50	2.45	5.45	10.9	94.5	98.8	93.9
AR Chard	1.01	1.98	5.03	10.5	97.2	101	94.4
AU Chard	2.09	3.07	6.29	12.4	97.2	105	103
USA Chard A	1.07	2.04	5.05	10.6	97.2	99.6	95.6
USA Chard B	0.968	1.94	4.96	10.8	97.1	99.8	97.8
USA Zin	1.67	2.66	5.85	11.9	98.6	105	102
					* = 5X Online Dilution		

Conclusion

This work has demonstrated the ability of the PinAAcle 900 AA spectrometer to accurately measure Cu, Fe, and Mn in a variety of wine samples at levels which meet the regulations imposed by China for imported wine. Using the FAST Flame 2 sample automation accessory minimizes user errors when performing dilutions and making calibration standards, increasing sample throughput. For labs with low sample throughput, these same analyses can also be performed without the FAST Flame 2 sample automation accessory[1].

References

1. Neubauer K., Lim S., "The Analysis of Copper, Iron, and Manganese in Wine with the PinAAcle 500", PerkinElmer Application Note.

Consumables

Component	Part Number
Red/Red PVC Pump Tubing	N8145158
Black/Black PVC Pump Tubing	N8145153 (unflared) N8145202 (flared)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Cu Hollow Cathode Lamp	N3050121
Fe Hollow Cathode Lamp	N3050126
Mn Hollow Cathode Lamp	N3050145
Pure-Grade Cu Standard (1000 mg/L)	N9300183 (125 mL) N9300114 (500 mL)
Pure-Grade Fe Standard (1000 mg/L)	N9303771 (125 mL) N9300126 (500 mL)
Pure-Grade Mn Standard (1000 mg/L)	N9303783 (125 mL) N9300132 (500 mL)

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