Determination of Metals in Wort and Beer Samples using the Agilent 5110 ICP-OES

Application

Food and Beverages

Authors

Dana Sedin[1], Stacey Williams[1], Elizabeth Kulikov[2], Jenny Nelson[3], Greg Gilleland[3]

1. New Belgium Brewing Company, Fort Collins, CO, USA

2. Agilent Technologies, Melbourne, Australia

3. Agilent Technologies, Santa Clara, CA, USA

Introduction

The analysis of metals during the beer brewing process is important as certain elements can affect the quality and taste of final beer products. Metals can originate from a range of sources including the brewing water, malt grains, hops, adjuncts, fruits, and spices. They can also be introduced through the brewing and packaging process. Brewers deliberately introduce metals in the form of salts ($CaSO_4$, $MgSO_4$, $ZnSO_4$, $CaCl_2$) to control pH, adjust taste, improve efficiency, and enhance fermentation performance. Metals that can be detrimental to the overall taste of beer include iron, which can impart a metallic taste. As a result, the concentration of Fe must be kept as low as possible in the finished product.

Typical techniques used for the identification of metals in beers include Flame Atomic Absorption Spectroscopy (FAAS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The Agilent 5110 Vertical Dual View (VDV) ICP-OES is a suitable option for food and beverage testing laboratories. The instrument's vertically oriented torch and solid-state RF (SSRF) system, which operates at 27 MHz, deliver a stable and robust plasma that can handle a range of complex sample types.

The 5110 ICP-OES uses a high-speed Vista Chip II CCD detector that provides good precision and fast analysis times. The high productivity of the 5110 ensures that argon consumption per sample is low. The instrument's large dynamic range of 8 orders allows the measurement of essential nutrients at high concentrations and minor elements at trace levels. This range of concentration levels is typical in food and beverage testing.

In addition to quantification of selected elements, IntelliQuant, a semiquantitative feature in the ICP Expert software, can identify and calculate an approximate concentration for up to 70 elements in a sample. IntelliQuant allows analysts in beverage labs to monitor the additional elements in their samples, without changing their routine methods. IntelliQuant can acquire data across all wavelengths from 167 to 785 nm with a further reading of Agilent's VistaChip II CCD detector, in as little as 15 additional seconds per sample.

This study focused on the determination of Ca, K, Mg, Na, Cu, Fe, Mn, and Zn in wort and finished beer samples using the Agilent 5110 VDV ICP-OES.

Experimental

Instrumentation

All measurements were performed using an Agilent 5110 VDV ICP-OES. The sample introduction system consisted of a SeaSpray nebulizer, double-pass cyclonic spray chamber, and a 1.8 mm i.d injector torch. Using a combined run, some elements were measured in radial mode and others in axial. The user can set up multiple conditions in the ICP Expert software and for each sample analyzed, two sets of conditions are measured and the results are combined in a single report. Instrument operating parameters are shown in Table 1.

Table 1. Agilent 5110 ICP-OES instrument and method parameters.

Parameter	Setting							
	Cu	Fe	Mn	Zn	Ca	K	Mg	Na
Read time (s)	10				5			
Replicates	3							
Sample uptake delay (s)	35							
Stabilization time (s)	25				3			
Rinse time (s)	35							
Pump speed (rpm)	13							
Fast pump during uptake and rinse (rpm)	On							
RF power (kW)	1.20							
Auxillary flow (L/min)	1.00							
Plasma flow (L/min)	12.0							
Nebulizer flow (L/min)	0.70							
Viewing mode*	Axial				Radial			
Viewing height (mm)	-				8			
Sample pump tubing	Black/black							
Internal standard pump tubing	Orange/green							
Waste pump tubing	Blue/blue							
Background correction	Fitted							

*Combined run of two viewing modes.

Standards and sample preparation

Wort and beer samples were obtained from the New Belgium Brewing Company (Fort Collins, CO, USA). Sample details are listed in Table 2. All in-process and finished beer samples were sonicated for 20 mins to remove CO_2. Following sonication, 10 mL of beer was diluted in 10 mL of 14% HNO_3.

All wort samples were filtered through Whatman paper before preparation. 8 mL of wort was diluted in 32 mL of 8.8% HNO_3 and 3.8% ethanol. All beer and wort samples were stored at 4 °C before analysis.

Table 2. New Belgium Brewing Company wort and finished beer samples.

Sample code	Sample description
W1	Voodoo Ranger IPA wort
W2	Fat Tire wort
W3	Voodoo Ranger 8 Hop Pale Ale wort
W4	Voodoo Ranger Imperial wort
B1	Voodoo Ranger IPA finished beer
B2	Fat Tire finished beer
B3	Voodoo Ranger 8 Hop Pale Ale finished beer
B4	Voodoo Ranger Imperial finished beer

Multi-elemental calibration standards were prepared at 0.1 and 0.5 ppm for Cu, Fe, Mn, and Zn; and at 15.0 and 50.0 ppm for Ca, K, Mg, and Na. All standards were prepared in 7% HNO_3 and 3% ethanol.

Continuing Calibration Verification (CCV) standards were prepared at 0.02 ppm for minor element checks, 15 ppm for majors, and 500 ppm for K check.

A control beer sample spiked with 0.1 ppm Zn was also prepared.

Internal standards (ISTD), gallium and yttrium, were prepared at 200 ppm (Ga) and 40 ppm (Y).

All calibration standards, Quality Control (QC) checks, and internal standards were matrix matched with 7% HNO_3 + 3% ethanol.

Results and Discussion

Detection limits

The Detection Limit (DL) for each element was based on three sigma of seven replicate measurements of the blank solution during an analytical run (Table 3). Sub-ppm (mg/L) level DLs were achieved for all elements. Method DLs (MDLs) were determined by calculating 3 x the SD of 10 replicate beer and wort samples, respectively. The MDLs are also given in Table 3.

Table 3. Element wavelengths, DLs, and MDLs.

Element & wavelength (nm)		DL (mg/L)	Wort MDL (mg/L)	Beer MDL (mg/L)
Major elements				
Ca	422.673	0.0126	13.35	10.41
K	769.897	0.6539	57.35	66.93
Mg	279.553	0.0091	8.12	15.28
Na	589.592	0.0301	2.07	2.16
Minor elements				
Cu	327.395	0.0005	0.027	0.014
Fe	238.204	0.0008	0.061	0.018
Mn	259.372	0.0001	0.015	0.020
Zn	213.857	0.0009	0.034	0.016

Calibration linearity

Linear calibrations were obtained for all elements, with calibration coefficients greater than 0.999 (Table 4) and less than 10% calibration error for each point. Figure 1 shows linear calibration curves for Fe, Cu, Mg, and Ca.

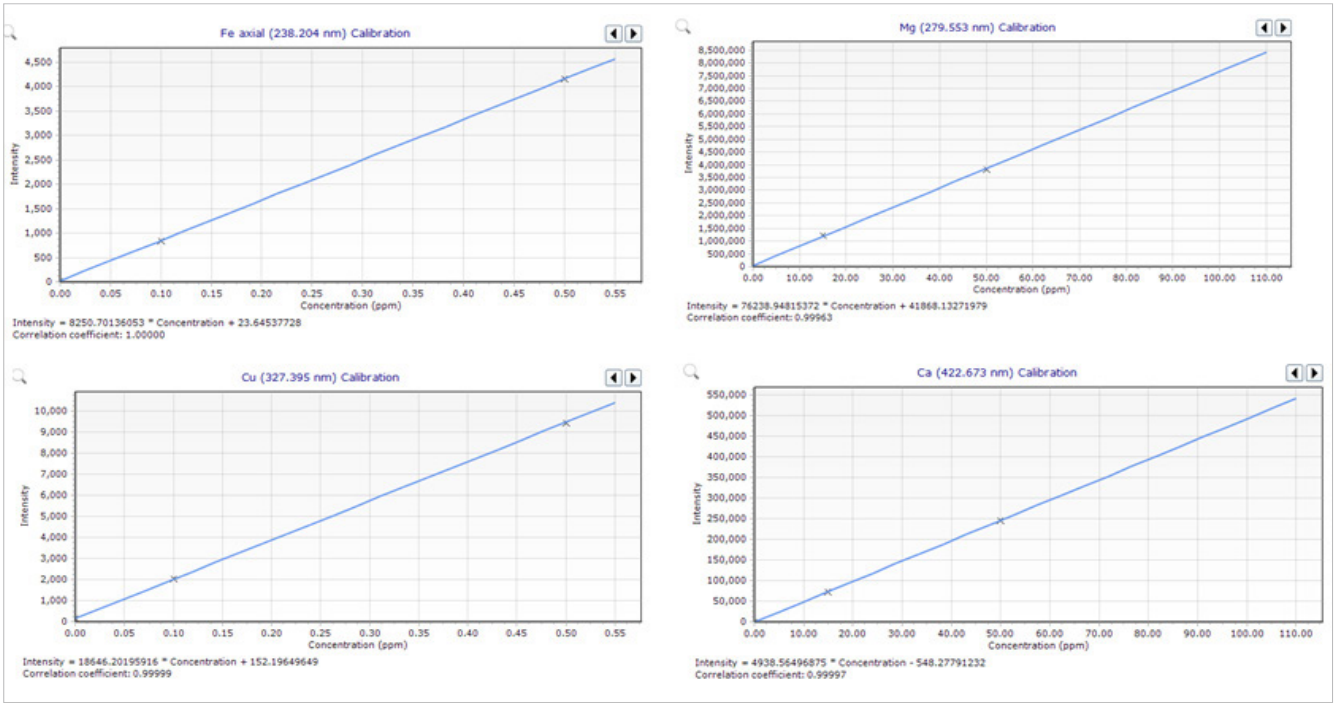

Figure 1. Calibration curves for Fe 238.204 nm, Cu 327.395 nm, Mg 279.553 nm, and Ca 422.673 nm.

Table 4. Wavelength and working calibration range.

Element and wavelength (nm)	Background correction/ interference correction	Calibration range (mg/L)	Correlation coefficient
Ca 422.673	Fitted + ISTD (Y 371.029)	0–50	0.9999
K 769.897	Fitted + ISTD (Ga)	0–50	0.9995
Mg 279.553	Fitted + ISTD (Ga)	0–50	0.9996
Na 589.592	Fitted + ISTD (Ga)	0–50	0.9999
Cu 327.395	Fitted + ISTD (Y 360.074)	0–0.5	0.9999
Fe 238.204	Fitted + ISTD (Y 371.029)	0–0.5	1.0000
Mn 259.372	Fitted + ISTD (Ga)	0–0.5	0.9999
Zn 213.857	Fitted + ISTD (Y 360.074)	0–0.5	1.0000
Ga 417.204	Used as ISTD		
Y 371.029, 360.074	Used as ISTD		

Detectability test

To validate the method, a series of QC spike recovery tests were carried out during each analytical run. The tests consisted of a Continuing Calibration Blank (CCB), followed by two CCV solutions (low concentration for Cu, Fe, Mn and Zn, high concentration for Ca, Mg and Na), a K check, and control beer sample spiked with 0.1 ppm Zn. Each QC solution was analyzed six times and averaged, with all recoveries within ±10% of the target values. The QC results are given in Table 5.

Analysis of wort and finished beer samples

The four wort and four finished beer samples were analyzed using the developed method. The quantified concentration results are displayed in Table 6. All the results for all elements were within the specification limits set by the manufacturer. Comparing the concentration levels of the elements in wort and beer enables the analyst to monitor the beer brewing process. The data is also useful to characterize the product.

Table 5. QC spike recovery results of the low and high CCVs, and control samples.

	Element and wavelength (nm)							
	Ca 422.673	Cu 327.395	Fe 238.204	K 769.897	Mg 279.553	Mn 259.372	Na 589.592	Zn 213.857
Low conc check 0.02 ppm (mean, n=6), CCV	-	0.0215	0.0210	-	-	0.0208	-	0.0205
% Recovery	-	107	105	-	-	104	-	103
Zinc check 0.1 ppm, control sample (mean, n=6)	-	-	-	-	-	-	-	0.098
% Recovery	-	-	-	-	-	-	-	98
High conc check 15 ppm (mean, n=6), CCV	14.758	-	-	15.761	15.494	-	14.610	-
% Recovery	98	-	-	105	103	-	97	
Potassium check 500 ppm (mean, n=6)	-	-	-	464.014	-	-	-	-
% Recovery	-	-	-	92	-	-	-	-

Table 6. Concentration of major and minor elements in wort and finished beer samples.

Sample	Ca 422.673	Cu 327.395	Fe 238.204	K 769.897	Mg 279.553	Mn 259.372	Na 589.592	Zn 213.857
	Concentration (mg/L)							
W1	96	0.242	0.045	857	129	0.183	30	0.163
W2	80	0.195	0.149	675	111	0.150	26	0.167
W3	85	0.204	0.054	735	124	0.241	26	0.183
W4	74	0.357	0.055	1125	178	0.263	36	0.262
B1	90	0.099	0.029	719	134	0.287	25	0.016
B2	61	0.047	0.038	464	90	0.132	17	0
B3	101	0.076	0.023	692	106	0.308	12	0
B4	62	0.148	0.032	850	145	0.295	26	0.028

IntelliQuant semiquantitative results

A wort and finished beer sample were analyzed using IntelliQuant during the analytical run. A custom IntelliQuant calibration (1.0, 5.0 and 10.0 mg/L) was created using an Agilent QC standard solution. The semiquantitative results for all elements in the wort and finished beer samples are shown in Table 7. The results reveal the presence of high levels of silicon in the samples. Silicon is present in barley and is introduced at high levels during the beer brewing process. Levels are typically not monitored during the process but can be of interest in terms of dietary intake.

Table 7. IntelliQuant semiquantitative results of elements in wort and finished beer samples.

Element and wavelength (nm)	Wort	Finished beer
	IntelliQuant value (mg/L)	IntelliQuant value (mg/L)
Na	9.3	17.5
Mg	24.9	48.3
Si	3.35	17.6
K	136.1	309.5
Ca	20.4	30.6
Mn	0.1	0.1
Sr	-	0.1
B	0.1	-

Conclusions

Major and minor metals in wort and finished beer samples were measured with good speed and accuracy using the Agilent 5110 VDV ICP-OES. With its vertically oriented torch and 27 MHz solid-state RF system, the robust 5110 is suited to the routine analysis of complex samples, such as alcoholic beverages. The method can be used to provide valuable information to brewers at different stages of production allowing them to optimize the quality of the final product.

In addition to the quantified method results, high levels of Si were identified in the wort and beer samples using the IntelliQuant (semiquantitative) feature of the ICP Expert software.

Acknowledgements
Agilent Technologies would like to thank the New Belgium Brewing Company for their co-operation and collaboration.

www.agilent.com/chem

Published September 28, 2017
Publication number: 5991-8394EN

Agilent Technologies