APPLICATION NOTE:	AN1803
TECHNOLOGY:	ICP
INDUSTRY:	Food/Bev

Analysis of Brewer's Hops Using the Teledyne Leeman Labs' Prodigy Plus ICP-OES

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Introduction

It has been scientifically proven that plants absorb contaminates and residues during their growth, which in turn are passed onto the humans and animals who consume them. The contamination can come directly from the soil, surface or groundwater sources or as a result of human activities such as industry, waste disposal, agriculture or mining. Contamination can include the presence of heavy metals, radionuclides, explosives, pesticides and fertilizers.

Hops, the flower of the Humulus Lupulus plant, are used in the brewing process to add flavor and bitterness to beer. Hops is also added for its antibiotic properties to suppress the growth of bacteria.

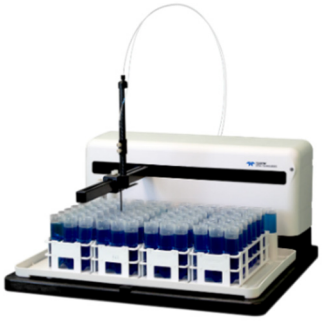
Small quantities of metals such as Cu, Mn and Zn in barley and hops are normal and necessary for plant growth. During the brewing process, these metals assist in the metabolism of yeast and affect the physical properties of the final beer product. At higher levels however, these metals can be toxic to the yeast and give the finished beer a metallic taste. Consequently, metal content in hops and the brewing process is directly related to its success and quality. Other metals such as Cd and Pb are toxic to humans at low levels.

Instrument

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer equipped with an axial view torch (Figure 1) and a 240-position Teledyne CETAC ASX-560 autosampler (Omaha, NE) (Figure 2) were used to generate the data for this application note.

Figure 1 Prodigy Plus ICP-OES

Figure 2 Teledyne CETAC ASX-560 Autosampler



The Prodigy Plus is a compact benchtop simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel Large Format CMOS (L-CMOS) detector. At 28 x 28 mm, the active area of the L-CMOS is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy Plus to achieve higher optical resolution than other solid-state detector-based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading, without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than six orders of magnitude. The Prodigy Plus uses a 40.68 MHz rugged, free-running RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

Sample Introduction

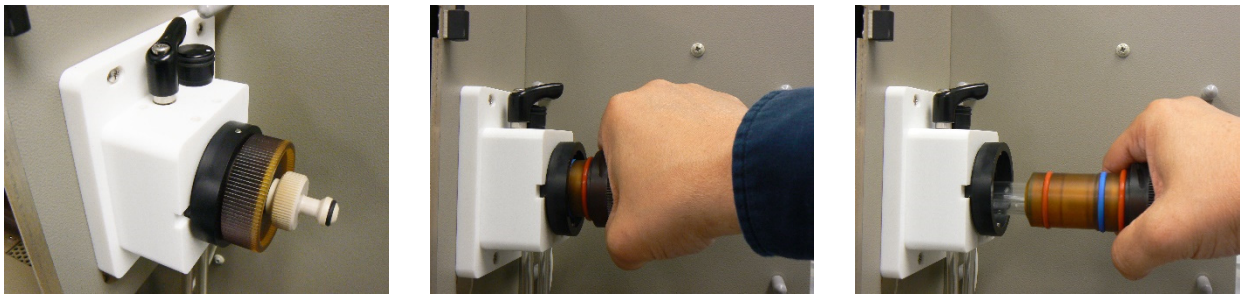
A high-sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer.

The sample introduction system consisted of:

- Cyclonic spray chamber no knockout tube
- Conikal™ Concentric nebulizer
- Four-channel peristaltic pump

The Prodigy Plus's torch is mounted using an innovative twist-n-lock cassette system, shown in Figure 3. This design permits operators to remove and replace the torch to the exact same position, providing day-to-day reproducibility and simplified training. Additionally, the twist-lock design automatically connects the coolant and auxiliary gas flows, eliminating potential errors.

Figure 3 Axial Twist-n-Lock Sample Introduction System



Method

The Prodigy Plus operating parameters used for this study are shown in Table I. Wavelengths used are shown in Table II. The analytical viewing zone was set using the 0.25 ppm Mn standard. The optimum viewing position is automatically selected by the Prodigy Plus's Salsa software. All data was acquired using an axial-view torch orientation.

Table I Instrument Operating Conditions

Parameter	Value	Part Number
RF Power	1.2 kW	
Coolant Flow	16.0 LPM	
Auxiliary Flow	0.5 LPM	
Nebulizer Pressure	34 PSI	
Pump Rate	25 RPM	
Torch	Quartz Demountable	318-00167-1
Injector	2.5 mm Bore	318-00161-ORG2
Axial Integration Time	60 sec	

Instrument Detection Limit

A study was performed to determine the Instrument's Detection Limit (IDL) in axial view for the elements of interest. Detection limits were calculated based on three times the standard deviation of 10 replicate measurements of the calibration blank. For all analytes of interest, background correction was performed simultaneously with the peak measurement, resulting in improved precision and detection limits. Results for the detection limit study are shown in Table II in units of parts per million (ppm).

Table II Wavelengths and Instrument Detection Limits		
Element	**Wavelength (nm)**	**DL (ppm)**
Cd	214.441	0.0006
Co	228.615	0.0005
Cr	206.149	0.003
Cu	324.754	0.0004
Fe	259.940	0.0002
Mn	257.610	0.0001
Ni	221.648	0.004
Pb	220.353	0.003
Zn	213.856	0.0004

Sample Preparation

Two types of dried brewer's hops, grown in Washington State, were obtained for analysis (Centennial and Nugget). Samples were digested by weighing ~0.5 g into a glass beaker and then covering with 5 ml deionized (DI) water. 5 ml of nitric acid was then added and the samples heated at 95 ˚C for one hour. Once the samples cooled, 5 ml of 30% hydrogen peroxide was added and the samples heated again for an additional half hour. Once cooled, the samples were filtered through Whatman® 50 filter paper and brought to a final volume of 100 ml with DI water. One additional sample was spiked with 0.1 mg/Kg of the elements of interest then digested using the process above, to evaluate the method. A preparation blank was also prepared.

Standards

NIST SRM1570A (Spinach Leaves) was analyzed as a Quality Control (QC) Standard and was digested/prepared in the same manner as the samples above.

The Calibration Standards shown in Table III were made from a multi-element ICP standard from VHG Labs (LGC Quality Control Standard 19, P/N VHG-QC19-500). The calibration standards were matrix matched to the acid concentration of the samples.

Table III Calibration Standard Concentrations				
Element	**Std0 ppm**	**Std1 ppm**	**Std2 ppm**	**Std3 ppm**
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	0	0.050	0.100	0.250

Results

The results of the study are shown in the tables below. All concentrations are in mg/Kg, unless noted. Results labeled "ND" are below the IDL and those labeled "NA" are not applicable. Sample results are shown in Table IV and Table V. The spiked sample results are shown in the "Spike % Recovery" Column of Table IV. The NIST SRM QC Standard results are shown in Table VI.

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Table IV Results for Centennial Hops			
Element	**Mean**	**Standard Deviation**	**Spike % Recovery**
Cd	0.24	0.02	90.1
Co	ND	NA	91.2
Cr	0.51	0.07	93.6
Cu	4.84	0.02	94.0
Fe	59.0	0.68	95.2
Mn	44.2	0.35	93.4
Ni	4.1	1.05	87.8
Pb	0.61	0.19	90.7
Zn	40.1	0.05	98.5

Table V Results for Nugget Hops		
Element	**Mean**	**Standard Deviation**
Cd	0.20	0.03
Co	ND	NA
Cr	0.39	0.052
Cu	7.48	0.02
Fe	59.5	1.20
Mn	45.3	0.29
Ni	3.31	0.16
Pb	0.65	0.24
Zn	38.5	0.09

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Table VI Results for NIST SRM1570A			
Element	**Mean**	**Certified Result**	**% Recovery**
Cd	2.79	2.89	96.5
Co	ND	-	-
Cr	0.36	0.39	91.4
Cu	11.7	12.2	95.6
Fe	125.8	-	-
Mn	73.5	75.9	96.9
Ni	2.08	2.14	97.2
Pb	ND	-	-
Zn	81.2	81.2	99.1

Conclusion

The results for NIST SRM1570A were quite good. The spiked and digested sample had acceptable recoveries indicating that the method is suitable for this sample matrix. Sample preparation and analysis was simple and fast. The analysis of metals in plant material (brewer's hops in this study) using the Teledyne Leeman Labs' Prodigy Plus High Dispersion ICP was successful. The image stabilized plasma and simultaneous data collection of both peak and background data, provided exceptionally precise and stable results.

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