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ICP-Optical Emission Spectroscopy

Analysis of Micronutrients in Fruit Juice Using the Avio 200 ICP-OES

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Introduction

Fruit juice continues to be a popular and refreshing beverage and can be a better nutritional alternative than typical carbonated beverages. The nutritional content of 100% fruit juices is derived from the fruit itself, and these valuable nutrients are displayed on the detailed bottle label. Customers use these labels to inform themselves on the nutritional content of the juice and for comparative shopping. While these labels provide a valuable reference for customers, they are also legally required in North America, and the veracity of these labels is the responsibility of the manufacturer.

For food manufacturers and processors, it is imperative that there is a means to quantify the content of food products, including micronutrients, for both safety and quality reasons along with regulatory label-claim requirements. Screening raw materials for elemental contaminants prior to use and then confirming the micronutrient content of the final product are two basic examples of the benefits of analytical testing. Accurate and precise analysis can also help improve the production process by providing rapid results and allowing optimization of the production process to maximize nutrient yield or production volume where appropriate.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is generally favored in a multi-element analytical environment with detection capabilities appropriate for nutritional analysis as demonstrated in this application. Flame atomic absorption (AA) systems, which provide cost savings, simplicity, and single- element analytical speed, can be attractive alternatives[1]. However, measuring a large number of elements by Flame AA requires each sample to be re-analyzed individually for each element, which can eliminate the speed advantage of Flame AA.

This work will focus on the analysis of micronutrients in a variety of commercial juice products using a PerkinElmer Avio™ 200 ICP-OES with sample preparation performed using a PerkinElmer Titan MPS™ Microwave Sample Preparation System.

Experimental

Samples and Sample Preparation

With the tremendous variety of fruit juice and fruit juice blends available on the market, samples were selected to be representative of commonly available and purchased juices. During selection,a preference for samples that were made from 100% juice (as accepted under current labeling guidelines) was used, though this still meant that, in many cases, the juice was reconstituted from concentrate. The samples analyzed represent two different brands of orange juice, apple juice, and grape juice, as well as a cranberry juice and a cranberry juice cocktail. The analytical elements selected are representative of micronutrients that commonly appear on product labels for these juices.

Juice samples were prepared for analysis by closed-vessel microwave-assisted digestion using a PerkinElmer Titan MPS microwave digestion system. The digestion method, sample parameters, and reagents used are listed in Tables 1 and 2. Samples were delivered by volume into the digestion vessels, and then the digestion reagents and any sample spikes were added. The samples and reagents then sat open in the vessels for 10 minutes, which allowed any early reactions to occur safely. After this time, the vessels were closed and placed into the Titan MPS for heating and digestion. When the digestion had completed, the samples were transferred out of the digestion vessels by triple-rinsing with deionized (DI) water into sample vials and then brought up to the final solution volume with DI water (18 MΩ-cm).

Instrumental Conditions

All analyses were performed on an Avio 200 ICP Optical Emission Spectrometer equipped with a PerkinElmer S10 Autosampler. The elements of interest and instrument conditions for the analysis of the juice samples are outlined in Tables 3 and 4. A Meinhard® glass nebulizer was used with the standard cyclonic spray chamber. External calibration standards were created from a

Table 1: Titan MPS Digestion Method.

Step	Target Temp (°C)	Pressure Limit (bar)	Ramp Time (min)	Hold Time (min)	Power Limit (%)
1	150	30	8	5	90
2	200	30	2	20	100
3	50	30	1	20	0

Table 2: Digestion Information.

Parameter	Volume
Reagents Used	8 mL of HNO_3 (70%), 2 mL H_2O_2 (30%)
Initial Sample Volume	5 mL
Final Solution Volume (after dilution)	50 mL

Table 3: Avio 200 ICP-OES Instrumental Parameters.

Parameter	Value
Nebulizer	Meinhard® Glass Type K1 (Part No. N0777707)
Spray Chamber	Glass Cyclonic Baffled (Part No. N0791352)
Sample Uptake Rate (mL/min)	0.8
RF Power (W)	1500
Nebulizer Gas (L/min)	0.68
Auxiliary Gas (L/min)	0.2
Plasma Gas (L/min)	8

custom PerkinElmer multi-element standard and were diluted with DI water and trace metal grade nitric acid to the final elemental concentrations listed in Table 5. The final nitric acid concentration of the standards was approximately 10% to match the relatively high concentration of acid in the digested and diluted samples.

Analysis was performed with standard 2-point background correction and no other spectral correction formulas. Yttrium was used as an internal standard for all elements analyzed using axial and radial plasma view.

Along with PerkinElmer's proven track record of ICP performance, the Avio 200 spectrometer benefits from a number of unique capabilities as well. The patented Flat Plate™ plasma technology delivers a robust plasma with zero maintenance and requires no cooling while using nearly half the argon plasma gas of helical load-coil systems. The entire sample introduction system and torch assembly are packaged into a single cassette that is simple to use and maintain. Plus, Avio's Dual View capability allows automated axial or radial viewing and teamed with its outstanding optical resolution, delivers a large linear dynamic range and exceptional stability and detection limits. All instrument control and analyses were done through PerkinElmer's Syngistix™ software.

Results and Discussion

Calibration results and calibration verification check (ICV) results are shown in Table 6. The excellent correlation for the calibration standards demonstrates the accuracy and precision of the Avio 200 ICP-OES. The independent calibration verification recoveries ensure that the calibration is valid, and that the creation of the standards was accurate.

The analytical results of the juice samples are shown in Figure 1. Using the Titan MPS digestion system, the samples were simply and quickly prepared for analysis. This delivered major time savings over the typical process of open vessel digestion, and, as demonstrated by the sample data and spike recoveries, microwave digestion delivers very consistent sample preparation performance. The analytical data for the samples themselves match the amounts provided on the juice labels and demonstrate the capability of the Avio 200 ICP-OES to accurately analyze samples with a large variation of elemental concentrations in a single analysis. It is interesting to note that one of the orange juices selected was fortified with Ca and that the analysis does indeed show a significantly higher amount of Ca for this sample. The results also show the difference between a juice cocktail (Cranberry A), which is a sweetened and blended fruit juice drink, and a pure fruit juice (Cranberry B), where the pure fruit juice had consistently higher concentrations of elements when compared to the juice cocktail. The elemental distributions among the various samples highlights how the different balance of nutrients in the raw fruit can translate to the nutrients present in the final product and how monitoring and measuring these can be critical for product quality and labeling accuracy.

With the large dynamic range available and the Dual View capability of the Avio 200 system, it was not necessary to make additional sample dilutions to lower any high-element concentrations. This meant that all elements were measured in a single analysis with no need to prepare sam-

Table 4: Method Parameters.

Element	Wavelength (nm)	Plasma View	Integration Range (sec)
Ca	317.933	Radial	0.1 - 5
Cu	327.393	Axial	0.1 - 5
Fe	238.204	Axial	0.1 - 5
K	766.490	Radial	0.1 - 5
Mg	285.213	Radial	0.1 - 5
Mn	257.610	Axial	0.1 - 5
Na	589.592	Radial	0.1 - 5
P	178.221	Axial	0.1 - 5
S	181.975	Axial	0.1 - 5
Zn	206.200	Axial	0.1 - 5
Y (int std)	371.029	Radial	0.1 - 5
Y (int std)	371.029	Axial	0.1 - 5

Table 5: Calibration Standards.

Element	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)
Ca	-	-	10	50
Cu	0.1	1	-	-
Fe	0.1	1	-	-
K	-	-	10	50
Mg	-	-	10	50
Mn	0.1	1	-	-
Na	-	-	10	50
P	-	-	10	50
S	-	-	10	50
Zn	0.1	1	-	-

Table 6: Calibration Results.

Element	Correlation Coefficient	ICV Concentration (mg/L)	Measured ICV	ICV (% Recovery)
Ca	0.99998	10.0	10.8	108
Cu	0.99995	0.100	0.106	106
Fe	0.99999	0.100	0.099	99
K	0.99999	10.0	10.6	106
Mg	0.99989	10.0	10.9	109
Mn	0.99999	0.100	0.098	98
Na	0.99999	10.0	10.6	106
P	0.99969	10.0	10.6	106
S	0.99991	10.0	10.5	105
Zn	0.99995	0.100	0.098	98

ples using multiple dilutions or measure the elements over multiple analytical acquisitions. This results in increased productivity and sample throughput. With the incredible linearity of the Avio 200 ICP-OES over a large concentration range, a simple calibration covering the appropriate concentration range for each element ensured that each sample could be analyzed in a single analytical pass.

To assess any remaining matrix effects from the various juices and to verify the entire sample prep method, all juice samples were spiked prior to digestion with all elements at the levels shown in Table 7; the resulting spike recoveries appear in Figure 2. The potassium levels in the juice samples were very high in relation to the spike concentration level, so recovery values for potassium are not included. All other spike recoveries are within 10% of the calculated values, verifying the capabilities and quality of digestion of the Titan MPS and eliminating the need for per-sample matrix- matching or use of a method of standard addition for accurate and precise results.

Table 7: Pre-Digestion Spike Levels.

Element	Spike Concentration (mg/L)
Cu, Fe, Mn, Zn	2
Ca, K, Mg, Na, P, S	50

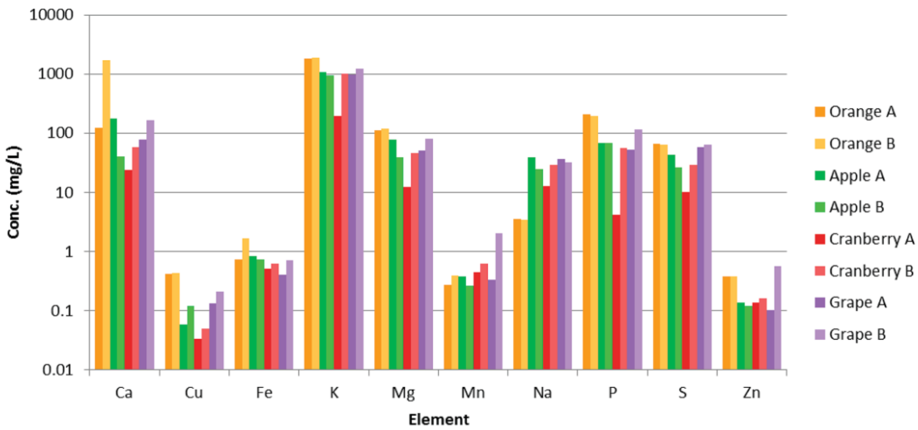

Figure 1: Results from analyses of juice samples

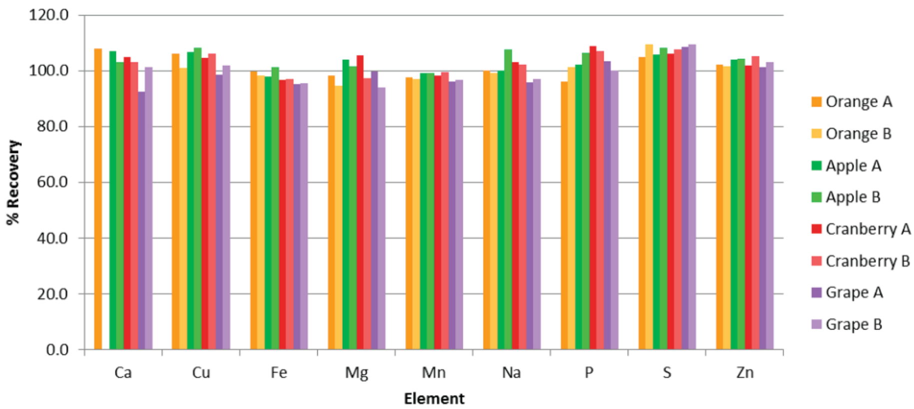

Figure 2. Spike recoveries in the juice samples

Conclusion

This work has demonstrated the ability of the Avio 200 ICP-OES to reliably and effectively analyze a variety of fruit

juice samples for an array of elements over a wide range of concentrations. With its extended capabilities, the Avio 200 system provides greater multi-element sample throughput when compared to Flame AA while allowing simple analysis of elements which are typically challenging for Flame AA (such as phosphorus and sulfur).

Using the Titan MPS microwave digestion system simplified sample preparation while increasing throughput and productivity for the laboratory, compared to hot plate or hot block digestions. The ability to completely digest the samples eliminated the need to matrix-match calibration standards or use a method of standard addition, thus simplifying the analysis.

The use of the Titan MPS for sample preparation and the Avio 200 ICP-OES for analysis is an ideal combination for fast, simple, and accurate analyses of nutritional elements in fruit juice

References

1. Spivey, Nick, “Analysis of Micronutrients in Fruit Juice Using FAST Flame Sample Automation for Increased Sample Throughput”, Application Note, PerkinElmer, 2015.

Consumables Used

Avio 200 ICP-OES	
Component	Part Number
Red/Red PVC Pump Tubing	09908585
Black/Black PVC Pump Tubing	09908587
Orange/Green PVC Pump Tubing	N0777110
Internal Standard Kit	N0774068
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Instrument Calibration Standard 2 (100 mg/L)	N9301721
Pure-Grade Phosphorus Standard (1000 mg/L)	N9303788 (125 mL) N9300139 (500 mL)
Pure-Grade Sulfur Standard (1000 mg/L)	N9303796 (125 mL) N9300154 (500 mL)

Titan MPS Digestion System	
Component	Part Number
Consumables Kit for Standard 75 mL Digestion Vessels	N3132000
Rupture Disks for Standard 75 mL Digestion Vessels (25 pieces)	N3132001
Pressure Seal for Standard 75 mL Digestion Vessels (10 pieces)	N3132002
End Cap Plug for Gas Containment Manifold	N3134004
Single Lip Seal Forming Tool for Standard 75 mL Digestion Vessels	N3132015
8-Position Lip Seal Forming Tool for Standard 75 mL Digestion Vessels	N3132014