APPLICATION NOTE

Atomic Absorption

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Analysis of Micronutrients in Fresh and Dried Fruits by Flame Atomic Absorption Using Microwave Digestion and FAST Flame Sample Automation

Introduction

As an addition to a morning breakfast, a snack throughout the day or even as a meal itself, fruit is a delicious and healthy food choice. With an increased focus on healthy living and the consumption of healthy foods, interest in the nutritional quality of the fruit has become more important. When fresh fruit is not available, dried fruit is often substituted, and manufacturers and customers would like to know that the dried fruit has not lost some nutritional value during processing when compared to fresh fruit.

One way of monitoring the quality of fresh or dried fruit is by measuring the micronutrient concentration contained within. Micronutrients are represented by trace elements considered to be nutritionally valuable, and it is these elements that can be analyzed via various inorganic analytical methods.

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While inductively coupled plasma optical emission spectroscopy (ICP-OES) is generally favored as a multi-element analytical method, the cost savings, simplicity and speed of operation of a flame atomic absorption (AA) system provides an attractive alternative. Measuring multiple elements by flame AA requires a sample to be analyzed once for each element of interest, with each re-analysis impacting the throughput advantage of flame AA.

To address the speed issue, a fast, high-throughput sample automation system can be used. Although samples still need to be analyzed multiple times, the analysis time per sample is significantly reduced, thus increasing sample throughput compared to manual sample introduction. In addition, an automated sample introduction system increases the precision of the analysis by reducing technique problems and frees the chemist to perform other tasks.

In this work, we demonstrate the ability of PerkinElmer's PinAAcle™ 900 atomic absorption spectrometer operating in flame mode coupled to a FAST Flame sample automation accessory to analyze common nutritional elements in a variety of fresh and dried fruit.

Experimental

All analyses were performed on a PinAAcle 900T atomic absorption spectrometer operating in flame mode using a FAST Flame 2 sample automation accessory. The elements of interest and instrument conditions for the analysis are outlined in Table 1. The sample introduction system consisted of a high-sensitivity nebulizer, the standard spray chamber and a 10 cm burner head. External calibrations were performed using a single intermediate standard made in 10% HNO_3/deionized water which was then diluted in-line using the capabilities of the FAST Flame 2 accessory. To control ionization during the analysis of potassium (K), sodium (Na), and calcium (Ca), La_2O_3 was added to the solutions, standards, and diluent at a concentration of 0.5% by weight.

The FAST Flame 2 accessory is a combination of high-speed autosampler, peristaltic pump and switching valve which provides quick sample turnaround with fast rinse-out, short signal stabilization times, and no sample-to-sample memory effect. The FAST Flame 2 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 time delay associated with self-aspiration or peristaltic pumping and eliminates the long rinse-in and rinse-out times associated with autosampler movement and flushing, resulting in complete sample-to-sample analytical times as short as 15 seconds.

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 lets the FAST Flame 2 automatically generate 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 bringing the signal within the calibration range and providing accurate measurement along with a successful QC check.

For accurate analysis of the fruit samples, the elements of interest must be extracted from the fruit into an instrument-ready solution. Open-vessel digestion using nitric acid and a simple heating block can be effective, but may leave undigested matter behind requiring

Table 1. PinAAcle 900 Instrument and Analytical Conditions

Element	Cu	Fe	Mg	Mn	Zn	K	Na	Ca
Mode	Absorption	Absorption	Absorption	Absorption	Absorption	Emission	Emission	Absorption
Wavelength (nm)	324.75	248.33	285.21	279.48	213.86	766.49	589.00	422.67
Slit (nm)	0.7	0.2	0.7	0.2	0.7	0.2	0.2	0.7
Acetylene Flow (L/min)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.7
Air Flow (L/min)	10	10	10	10	10	10	10	10
Burner Head Rotation	0°	0°	0°	0°	0°	45°	0°	0°
Acquisition Time (sec)	1	1	1	1	1	1	1	1
Replicates	3	3	3	3	3	3	3	3
Sample Flow Rate (mL/min)	6	6	6	6	6	6	6	6
Intermediate Standard (mg/L)	1	5	1	1	5	200	10	10
Auto-Diluted Calibration Standards (mg/L)	0.05 0.1 0.2 0.5 1	0.25 0.5 1 2.5 5	0.05 0.1 0.2 0.5 1	0.05 0.1 0.2 0.5 1	0.25 0.5 1 2.5 5	10 20 40 100 200	0.25 0.5 1 8 10	0.5 1 2.5 5 10
Calibration Curve Type	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero

further filtration or centrifugation prior to introduction into the instrument and can result in reduced recovery with corresponding poor accuracy. Closed-vessel microwave digestion delivers complete sample digestion, eliminating the need for any additional steps and ensuring maximum element recovery while providing higher throughput and increased safety.

Fresh fruit and dried fruit samples were prepared (both spiked and unspiked) using a PerkinElmer Titan MPS™ microwave sample preparation system, a sample digestion oven that utilizes unique vessel and system design with an emphasis on safety, throughput, and ease of use. With non-contact temperature control for every vessel and pressure control via a reference vessel, the Titan MPS system ensures accurate digestion method control and zero sample contamination regardless of the sample type. Details of the microwave digestion method are listed in Table 2; each vessel contained 0.5 g dried fruit or 1 g of fresh fruit and 10 mL concentrated nitric acid. All spiking was performed prior to sample digestion with spike concentrations selected based on expected sample concentrations.

Results and Discussion

The calibration curves for individual elements were created from a single intermediate standard with the in-line dilution capabilities of the FAST Flame 2 accessory preparing the final standards in real-time. Calibration results are shown in Table 3. The excellent correlation for the calibration standards demonstrates the value of the automatic in-line sample and standard dilution capabilities. The independent calibration verification recoveries ensure that the calibration is valid and that the creation of standards via the dilution system is accurate.

Figure 1 shows the results obtained for the analyzed fruit samples, with the dried fruits being in blue and the fresh fruits in orange. From this plot, it is obvious that all of the dried fruits contain significantly higher concentrations of nutrients than the fresh fruits. The elemental concentrations also vary greatly among fruits, but in all cases, the potassium levels are the highest among the elements measured. The FAST Flame 2 accessory automatically diluted the samples by the factors shown in Table 4 so that the results were within the calibration range.

Table 2. Titan MPS System Digestion Method

Method Step	Target Temp (°C)	Pressure Limit (bar)	Ramp Time (min)	Hold Time (min)	Power Limit (%)
1	140	35	10	2	60
2	195	35	3	25	100
3	50	35	1	20	0

Table 3. Calibration Results

Element	Correlation Coefficient	ICV Concentration (mg/L)	Measured ICV (mg/L)	ICV (% Recovery)
Cu	0.99985	0.500	0.494	98.8
Fe	0.99999	2.00	1.98	99.0
Mg	0.99999	0.500	0.517	103
Mn	0.99995	0.500	0.495	99.0
Zn	0.99991	2.00	1.95	97.5
K	0.99860	100	96.7	96.7
Na	0.99865	5.0	4.55	91.0
Ca	0.99975	5.0	5.02	100

Table 4. In-Line Dilution Factors

Fruit	Cu	Fe	Mg	Mn	Zn	K	Na	Ca
Dried Blueberry	1	1	20	1	2	2	1	5
Dried Strawberry	1	1	20	1	2	2	1	5
Dried Raspberry	1	1	20	1	2	2	1	5
Fresh Raspberry	1	1	20	1	2	2	1	5
Fresh Blueberry	1	1	20	1	2	2	1	5
Fresh Strawberry	1	1	20	1	2	2	1	5
Fresh Kiwi	1	1	20	1	2	2	1	5

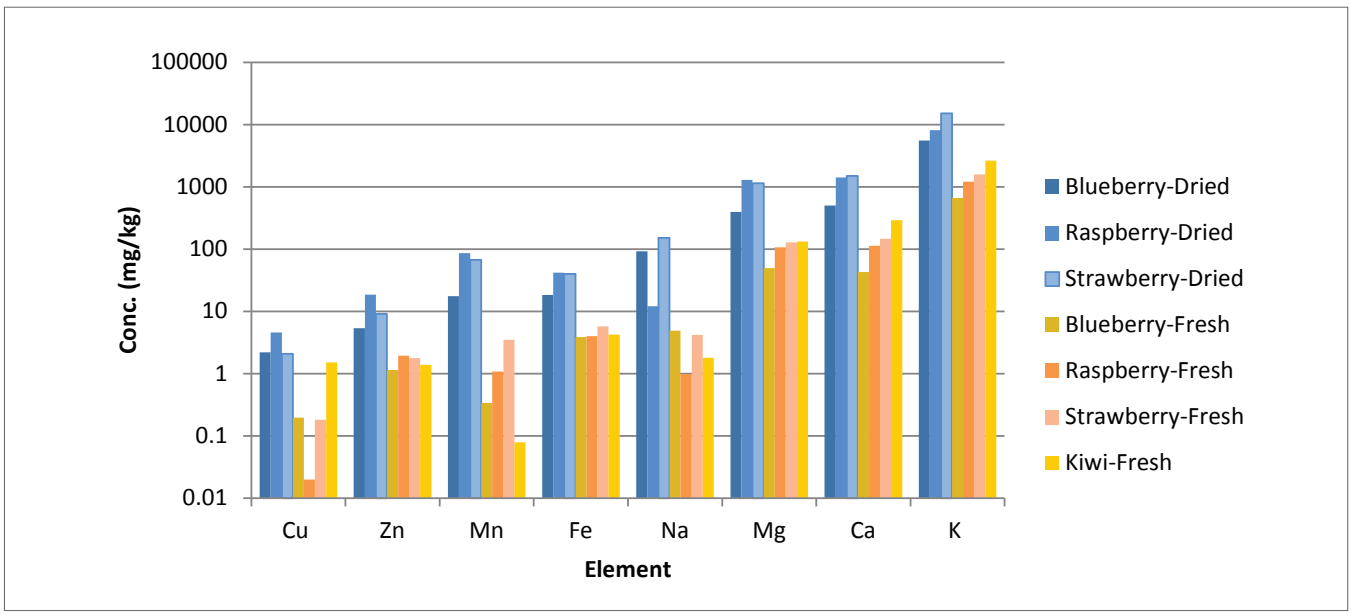

Figure 1. Results for dried (blue) and fresh (orange) fruit samples.

Table 5. Spike Levels (all units in mg/kg)

Fruit	Cu	Fe	Mg	Mn	Zn	K	Na	Ca
Dried Blueberry	49.3	197	493	98.6	197	4880	195	488
Dried Strawberry	46.6	186	466	93.1	186	4930	197	493
Dried Raspberry	50.1	201	501	100	201	5236	209	524
Fresh Raspberry	19.6	78.6	196	39.3	78.6	2078	83.1	208
Fresh Blueberry	18.9	75.7	189	37.9	75.7	1850	74.0	185
Fresh Strawberry	21.0	83.9	210	42.0	83.9	1744	69.8	174
Fresh Kiwi	19.7	78.7	197	39.4	78.7	1991	79.6	199

To assess accuracy, all samples were spiked (pre-digestion) at the levels indicated in Table 5. The recoveries of all sample method spikes are within 10% of the calculated values for all elements, as shown in Figure 2. The spike recovery studies did not require per-sample matrix matching, demonstrating the value and labor savings of using the Titan MPS system to digest the samples safely and completely. The variety of fresh and dried fruit types all exhibited spike recoveries within 10%, further demonstrating the robustness of the sample preparation and instrument methods.

The addition of the FAST Flame 2 accessory reduced the creation of standards from one intermediate and five final standards to a single intermediate standard with a commensurate reduction in human error during standard creation. The measured concentrations of many of the elements in the samples varied enough to fall outside the calibration curve. The in-line dilution capability of FAST Flame 2 allowed real-time dilution of these samples so that the absorbance fell within the calibration curve, and the results represented accurate analysis. The ability of FAST Flame 2 to react to the over-range samples and auto-dilute the samples accurately and consistently without interaction from an analyst saved time and eliminated additional sample handling and lengthy re-prep.

These results validate the accuracy and value of fresh and dried fruit analysis via flame AA along with the speed and increased productivity available from the PinAAcle 900 AA spectrometer coupled with the FAST Flame 2 accessory.

Conclusion

This work has demonstrated the ability of PerkinElmer's PinAAcle 900 AA spectrometer to reliably and effectively analyze fresh and dried fruit samples for Cu, Fe, Mg, Mn, Zn, K, Na, and Ca over a wide range of concentrations. Using the FAST Flame 2 accessory along with the PinAAcle 900 minimizes user error when performing dilutions and making calibration standards, increases throughput, and provides excellent long-term stability, increasing productivity for the laboratory. (Equivalent results would also be obtained with the PinAAcle 500 AA spectrometer). Use of the Titan MPS for sample digestion eliminated sample and matrix problems and permitted the use of external standards without the need for matrix matching or specialized analytical parameters. The same analyses can also be done without the use of a FAST Flame 2 accessory when analyzing smaller sample batches.

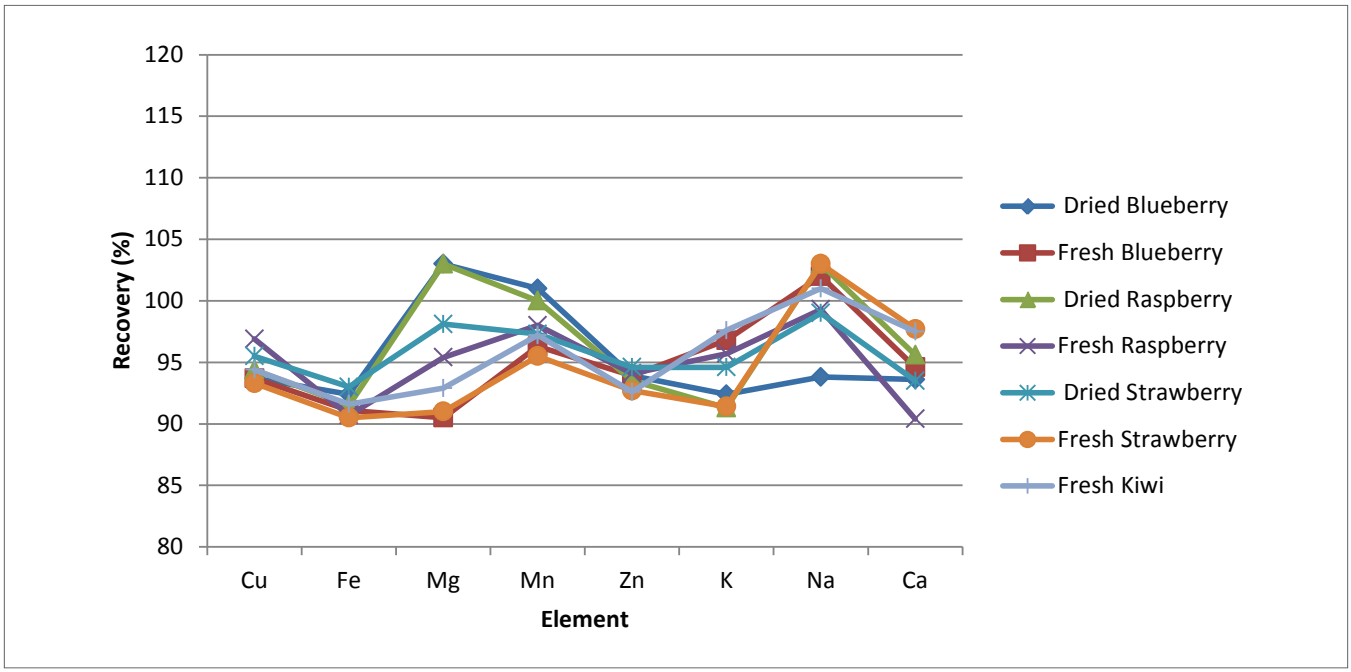

Figure 2. Recovery of pre-digestion spikes for fresh and dried fruit samples.

Consumables

Component	Part Number
Red/Red PVC Pump Tubing	09908585
Black/Black PVC Pump Tubing	09908587
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Ca Hollow Cathode Lamp	N3050114
Cu Hollow Cathode Lamp	N3050121
Fe Hollow Cathode Lamp	N3050126
Mg Hollow Cathode Lamp	N3050144
Mn Hollow Cathode Lamp	N3050145
Zn Hollow Cathode Lamp	N3050191
Pure-Grade Ca Standard (1000 mg/L)	N9303763 (125 mL) N9300108 (500 mL)

Component	Part Number
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 K Standard (10,000 mg/L)	N9304121 (125 mL) N9304120 (500 mL)
Pure-Grade Mg Standard (1000 mg/L)	N9300179 (125 mL) N9300131 (500 mL)
Pure-Grade Mn Standard (1000 mg/L)	N9303783 (125 mL) N9300132 (500 mL)
Pure-Grade Na Standard (1000 mg/L)	N9303785 (125 mL) N9300152 (500 mL)
Pure-Grade Zn Standard (1000 mg/L)	N9300178 (125 mL) N9300168 (500 mL)

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