Reduced Plasma Flow ICP-OES Method for the Analysis of Fruit Juices

Fast, stable and accurate analysis using the Agilent 5110 ICP-OES

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Introduction

Analytical testing of food and beverage products is fundamental to product-safety, regulatory compliance, and product labeling. To meet strict quality control (QC) measures for inorganic components, regular testing is performed to identify and quantify nutrients, micronutrients, and heavy metals.

To ensure that food testing laboratories follow the correct measurement requirements, they are closely examined by regulatory bodies. As a result, regulated methods have guided the procedures and instrumentation adopted by laboratories in the food industry. Traditionally, many food-related regulated methods specified atomic absorption spectrometry (AAS). However, more recent publications of regulated methods, including ILNAS-EN 16943:2017 and AOAC Official Method 2011.14, have described the analysis of food and beverages by Inductively Coupled

Plasma-Optical Emission Spectrometry (ICP-OES) (*1, 2*). The benefits of ICP-OES compared to AAS range from enhanced analytical speed to greater performance capabilities enabling multi-element, high throughput, unattended analysis of many sample-types. With its extensive range of software and hardware features that facilitate a fast, stable, and efficient analysis, the Agilent 5110 ICP-OES is ideally suited to meet the evolving needs of the food industry.

In this study, the Agilent 5110 Vertical Dual View (VDV) ICP-OES was operated with an argon plasma flow rate under 10 L/min to measure Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sn, Zn in a range of fruit juices.

Experimental

Instrumentation

All measurements were performed using the Agilent 5110 VDV ICP-OES configured with an SPS 4 autosampler. The sample introduction system consisted of a Seaspray glass concentric nebulizer, double-pass glass cyclonic spray chamber, and an Easy-fit VDV demountable 1.8 mm injector torch.

Compared to other ICP-OES instrumentation, the 5110 VDV ICP-OES analyzes samples in significantly less time due to the Vista Chip II CCD detector (*3*). Fast analysis times lead to improved sample throughput, lower consumption of utilities and consequently, significant cost savings. The Vista Chip II's speed arises from its 1 MHz pixel processing speed and ability to measure the full wavelength range in a single exposure without the need for multiple detectors or slits. In addition, the Vista Chip II can actively adapt using integration times ranging from 1 to 100 s, providing a full eight orders of dynamic range. This wide analytical range assists food laboratories handling unknown samples, which may contain elements over a wide concentration range.

Typically, the 5110 uses a plasma flow rate of 12 L/min. However, the vertically oriented torch and the solid-state radio frequency (SSRF) system, allows for robust, stable measurement of a wide variety of fruit juices with a plasma flow rate of only 9.5 L/min (*4*). Even complex-food digests can be measured with less torch cleaning, fewer replacements, and lower overall argon gas-usage, leading to significant cost-savings for laboratories handling these types of samples.

Increasingly, labs are demanding instrumentation that is simple-to-use and easy for new or occasional users to operate. To ensure reproducible performance irrespective of the analyst, the 5110 ICP-OES uses a simple and effective torch loader mechanism that automatically aligns the torch and connects gases for fast start-up. Once loaded there is no need for further adjustment of the torch, or optical alignment of the axial viewing position.

In addition to simplifying data analysis, the ICP Expert software includes an automatic Fitted Background Correction (FBC) technique that models the background signal under the analyte peak (*5*). FBC not only provides accurate correction of both simple and complex background structures, it requires no method development. Yttrium was selected as the internal standard (IS) at 5 mg/L. The IS was added on-line using a tee piece.

Instrument operating conditions are given in Table 1.

Table 1. Instrument operating parameters.

Parameter	Setting	
Viewing mode	Axial	Radial
Replicate read time (s)	10	5
Stabilization time (s)	10	
Replicates	3	
Sample uptake delay (s)	15	
Rinse time (s)	30	
Pump speed (rpm)	12	
Fast pump during uptake and rinse	Yes	
RF power (kW)	0.9	
Plasma flow (L/min)	9.5	
Aux flow (L/min)	1	
Nebulizer flow (L/min)	0.5	
Viewing height (mm)	10	
Background correction	Fitted	
Sample pump tubing	White/white	
Internal standard pump tubing	Black/black	
Waste pump tubing	Blue/blue	

Standard and sample preparation

All working calibration standards were prepared using Agilent single element standard solutions. Information regarding the concentration of all standards and the QC solution is provided in Table 2. The solutions were matrix matched using nitric acid (Emsure, Merck) and diluted with 18.2 MΩ Millipore water to form a final matrix of 2% nitric acid. The yttrium 371.092 nm IS was prepared at 5 ppm from an Agilent 10,000 ppm stock solution using a 2% nitric acid matrix.

Table 2. Concentration of working calibration standards and QC solution.

Element	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	QC (mg/L)
Al	0.5	2			0.7
As	0.5	2			0.7
Ca			2	20	7
Cd	0.5	2			0.7
Cu	0.5	2			0.7
Fe	0.5	2			0.7
K			10	100	35
Mg			2	20	7
Mn	0.5	2			0.7
Na			2	20	7
Ni	0.5	2			0.7
P	5	20			7
Pb	0.5	2			0.7
S	5	20			7
Sn	0.5	2			0.7
Zn	0.5	2			0.7

Nine different commercially available fruit juices, varying in consistency were bought for analysis. “Smooth” fruit juices, which contained no solid matter, were prepared using a simple ‘dilute and shoot’ method. These samples included apple, apple blackcurrant, blackcurrant, cranberry, and pomegranate juices. The remaining juices, which contained solid matter, including grapefruit, pulp-free orange, orange with pulp, and a tropical juice, were prepared by microwave digestion.

For the 'dilute and shoot' method, samples were diluted by a factor of 40 in 2% nitric acid. For microwave digestion (CEM MARS 6 Microwave Digestion System, Buckingham, UK), 4 mL nitric acid and 1 mL 30% hydrogen peroxide (Emsure, Merck) were added to 5 g of sample. The solution was digested according to the temperature program listed in Table 3. The digests were then diluted to a final volume of 200 mL using 18.3 MΩ Millipore water, giving a final matrix of 2% nitric acid. Using a dilution factor of 40 for all samples ensures that the results from both sample preparation procedures are directly comparable.

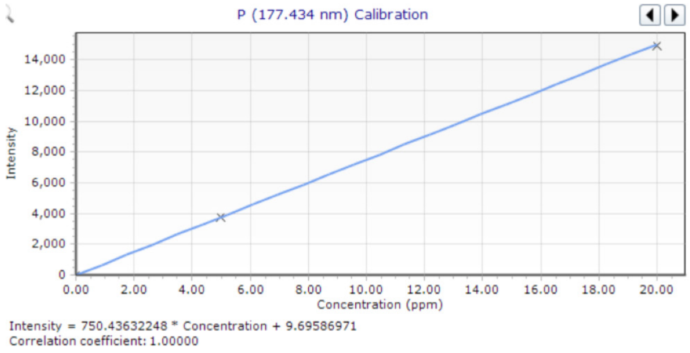
Table 3. Temperature program for acid microwave digestion.

Steps	Power (W)	Ramp time (min)	Hold time (min)	Temperature (°C)
1	1030–1800	20–25	15	210
2	290-1800	20	15	210
3	400-1800	15	15	210
4	700-1800	30	15	210

Results and discussion

Calibration linearity

Linear calibrations were obtained for all elements, with calibration coefficients greater than 0.99998 (Table 4). A representative calibration curve for P 177.434 nm is shown in Figure 1.



Intensity = 750.43632248 * Concentration + 9.69586971
Correlation coefficient: 1.00000

Figure 1. Calibration graph for P 177.434 nm.

Automated FBC was used for background correction for all elements and wavelengths. An example of FBC is shown in Figure 2. FBC has accurately modeled the background for the Cu 177.421 nm interference peak on P 177.434 nm. This modeling allows for easy interference and background correction by eliminating the need for a user to manually determine off-peak background correction points.

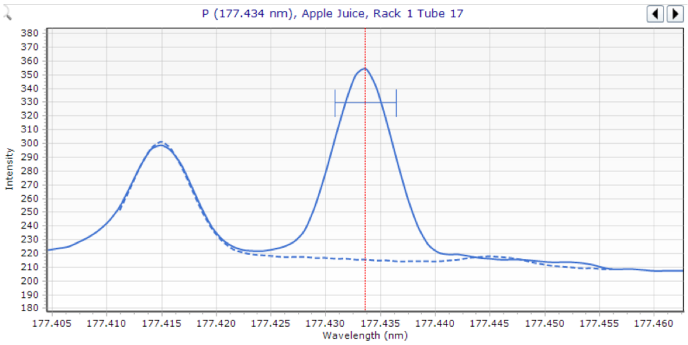


Figure 2. Fitted background correction of P 177.434 nm.

Detection limits

Method Detection Limits (MDLs) and Limits of Quantitation (LOQs) were determined by analyzing six sets of 10 blank solutions on two separate instruments over two days (n=60). The MDLs and LOQs are shown in Table 4. MDLs are based on 3 sigma of 10 replicate measurements of the blank solution. The LOQs for all elements were below the requirements given in standard methods ILNAS-EN 16943:2017 and AOAC Official Method 2011.14.

Table 4. MDLs and LOQs for all elements, calculated to account for the 40x dilution factor used in sample preparation.

Element and wavelength (nm)	Viewing mode	Calibration range (mg/L)	Correlation coefficient	MDL (mg/L)	LOQ (mg/L)
Al 396.152	Axial	0–2	1	0.13	0.42
As 188.980	Axial	0–2	1	0.32	1.07
Ca 317.933	Radial	0–20	1	0.43	1.43
Cd 226.502	Axial	0–2	1	0.017	0.06
Cu 327.395	Axial	0–2	1	0.049	0.16
Fe 238.204	Axial	0–2	1	0.034	0.11
K 766.491	Radial	0–100	0.99999	12.08	40.27
Mg 280.270	Radial	0–20	0.99999	0.053	0.18
Mn 257.610	Axial	0–2	1	0.0040	0.010
Na 589.592	Radial	0–20	0.99999	1.39	4.63
Ni 216.555	Axial	0–2	1	0.094	0.31
P 177.434	Axial	0–20	1	0.30	0.99
Pb 220.353	Axial	0–2	1	0.29	0.96
S 181.972	Axial	0–20	1	0.80	2.67
Sn 189.925	Axial	0–2	0.99998	0.34	1.14
Zn 202.548	Axial	0–2	1	0.021	0.070

Spike recoveries

To validate the method, a cranberry juice sample was spiked with varying concentrations of all elements. The spike recoveries reported in Table 5 are the average results obtained from six analytical runs performed on two instruments, on two consecutive days. All recoveries are within ±10%, demonstrating the ability of the 5110 ICP-OES to accurately determine major and trace elements in fruit juice samples.

Table 5. Spike recovery results for cranberry juice.

Element and wavelength (nm)	Measured spiked sample (mg/L)	Spike concentration (mg/L)	Measured sample* (mg/L)	Recovery (%)
Al 396.152	0.05	0.05	0.003	94
As 188.980	0.1	0.1	<MDL	97
Ca 317.933	1.96	0.98	0.96	102
Cd 226.502	0.05	0.05	<MDL	100
Cu 327.395	0.05	0.05	0.001	98
Fe 238.204	0.06	0.05	0.008	104
K 766.491	13.4	10.33	3.38	97
Mg 280.270	1.27	1.06	0.26	95
Mn 257.610	0.06	0.05	0.0083	103
Na 589.592	1.49	1.02	0.47	100
Ni 216.555	0.05	0.05	<MDL	98
P 177.434	0.67	0.5	0.18	99
Pb 220.353	0.1	0.1	<MDL	101
S 181.972	0.66	0.51	0.16	98
Sn 189.925	0.2	0.2	<MDL	97
Zn 202.548	0.26	0.19	0.058	106

** '<MDL' indicates result was less than method detection limit*

Long-term stability

Approximately 300 diluted samples were run over 8.5 hours without recalibration. During the run, a QC sample was analyzed every 10 samples and plotted to demonstrate the stability of the 5110 VDV ICP-OES. Figure 3 shows the recovery of all elements to be within ±4 % of the initial measurement. Excellent precision was obtained, with <1 %RSD for all elements over the duration of the run.

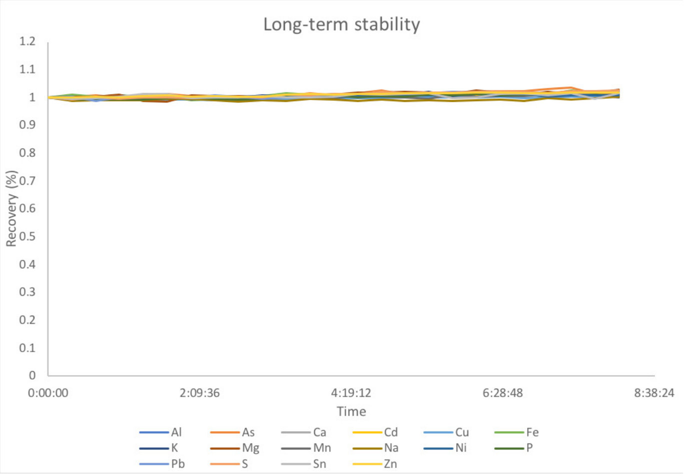


Figure 3. Long-term stability: recovery of a QC sample analyzed after every 10 samples over an 8.5 hour period.

The results show that the plasma was stable over the duration of the 8.5 hour run. The 5110 ICP-OES exhibited excellent stability due to the vertically oriented plasma and a solid-state RF system, even at a reduced plasma flow rate of 9.5 L/min.

Quantitative and semiquantitative analysis

Quantitative results of 16 elements in an orange juice sample containing pulp are shown in Table 6. If additional screening of samples is required for quality assurance purposes, a simple, quick, full wavelength semiquantitative scan can be performed. With the IntelliQuant feature of ICP Expert software, analysts can identify and obtain approximate concentration data for up to 70 elements in a sample, in an additional 15 seconds (*6*).

The software generates a periodic table heat map to visually represent the relative concentrations of elements present in a sample. A full spectrum scan of the pulpy orange juice was obtained using IntelliQuant, as shown in Figure 4. The semiquantitative analysis data is in broad agreement with the quantitative analysis data for all elements.

Table 6. Average (n=10) measured concentration in pulpy orange juice.

Element and wavelength (nm)	Concentration (mg/L)	Element and wavelength (nm)	Concentration (mg/L)
Al 396.152	<LOQ	Mn 257.610	0.0039
As 188.980	<LOQ	Na 589.592	<LOQ
Ca 317.933	2.1	Ni 216.555	<LOQ
Cd 226.502	<LOQ	P 177.434	5.8
Cu 327.395	0.0075	Pb 220.353	<LOQ
Fe 238.204	0.024	S 181.972	1.7
K 766.491	55	Sn 189.925	<LOQ
Mg 280.270	3.1	Zn 202.548	0.0091

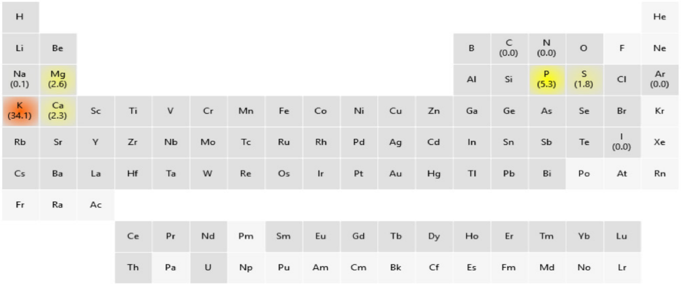


Figure 4. IntelliQuant heat map generated from the analysis of pulpy orange juice (mg/L).

Total argon gas consumption

In this study, all 16 elements were determined in 100 seconds per sample using a plasma gas flow rate of 9.5 L/min. The total argon consumption was 30 L per sample. All gas flows within the instrument were considered to ensure an accurate calculation of gas used. The fast analysis times for major and trace elements, along with the reduced plasma flow rate, cuts argon consumption per sample while ensuring data quality is uncompromised.

Conclusion

The Agilent 5110 VDV ICP-OES provides a low-cost, easy-to-implement method enabling accurate elemental analysis of fruit juice samples with simple and complex matrices. All elements could be determined in the fruit juice samples in a single analytical run, ensuring efficient argon-gas usage. Even at a reduced plasma flow rate of 9.5 L/min, the Agilent 5110 VDV ICP-OES exhibited excellent stability and precision over a long-term analysis. Also, validation and detection limit requirements specified in two standard methods were achieved.

The IntelliQuant feature in the ICP Expert software provided a quick semiquantitative scan of a fruit juice sample, identifying all elements present in the sample. This rapid screening mode can identify and quantify elements that are not present in the calibration standards—a useful tool for quality assurance in food testing laboratories.

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Printed in the USA, April 1, 2019
5994-0785EN

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