Application Note

Food and Agriculture

Routine Measurement of Multiple Elements in Food using an ICP-OES Fitted with a Switching Valve

Cost-effective approach meets requirements of Chinese standard method for 16 elements

Author

Peter Riles

Agilent Technologies,
Melbourne, Australia

Introduction

Elemental contamination of food can come from many sources, including irrigation, elements in the soil, elements in the air, and air-based pollution settling into the water and/or soil, to name a few. Accurate low-level analysis of trace elements is required and is especially important in foods that are consumed regularly.

China's GB5009.268-2016 Determination of Multiple Elements in Food method specifies the measurement of 16 elements by ICP-OES following a nitric acid digestion. The required accuracy of the method for some additional elements such as arsenic, mercury, and cadmium requires trace analysis by ICP-MS.
In this study, aluminum, boron, barium, calcium, copper, iron, potassium, magnesium, manganese, sodium, nickel, phosphorus, strontium, titanium, vanadium, and zinc were determined in a rice flour standard reference material (SRM) using an Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES fitted with a 6-port switching valve, the Advanced Valve System (AVS 6). The aim was to develop a high throughput and cost-effective method, while still meeting the regulated method's requirements for accuracy.

Experimental

Instrumentation

An Agilent 5110 SVDV ICP-OES fitted with an AVS 6 six port switching valve was used for the analysis and validation of the GB5009.268-2016 method. The 5110 uses a plug-and-play torch that automatically aligns and connects all gases. The simple-to-fit torch removes operator-to-operator variability when setting up the instrument and allows for fast startup. Mass flow controllers are used on three argon lines to provide excellent plasma stability and reproducible results over extended periods.

As a regulated method, GB5009.268-2016 specifies the performance and quality control (QC) tests required to verify the quality of the data. The detection limit requirements outlined in GB5009.268-2016 for the 16 specified elements are easily achieved using the 5110 ICP-OES. The instrument's SVDV configuration provides higher sensitivity for less abundant elements by analyzing them axially, while using radial viewing for more abundant elements. SVDV also provides a wide linear dynamic range while maintaining excellent detection limits.

The 5110 SVDV ICP-OES uses a Dichroic Spectral Combiner (DSC) to combine the light emitted radially with light emitted axially for truly simultaneous measurements. This unique ability of the 5100 SVDV ICP-OES reduces sample-to-sample analysis times, while also reducing the amount of argon and other reagents used for analysis [2].

The Agilent AVS 6 was used to further enhance the speed and performance of this application. The switching valve features a high-speed positive displacement pump (PDP) to reduce uptake and rinse times. The system uses carefully controlled bubble injection into the sample stream to maximize read times and optimize analytical precision. The PDP is reliable and requires less maintenance than the typical vacuum pump found on other valve systems. The AVS 6 is simple to set up and operate, as it is fully integrated within the ICP-OES hardware and controlled through the ICP Expert software. The valve system automatically delivers the sample to the nebulizer.

Boron is an analyte required by GB5009.268-2016. Since B is typically present in ICP glassware that is manufactured from borosilicate glass, an inert spray chamber and nebulizer were used. A 1.8 mm quartz injector was used in the standard Agilent SVDV torch. The spray chamber was a double pass cyclonic spray chamber manufactured from PTFE, and the MiraMist nebulizer was manufactured from PEEK. Typically, inert materials are used when HF is required in sample preparation. However, they are also used to minimize boron memory effects and contamination from laboratory or ICP glassware.

Instrument operating parameters are outlined in Tables 1, 2 and 3.

Table 1. Instrument parameters.

Parameter	Setting
Read time (s)	10
Replicates	3
Sample uptake delay (s)	0
Stabilization time (s)	15
Rinse time (s)	0
Pump speed (rpm)	12
Fast pump during uptake and rinse (rpm)	12
RF power (kW)	1.20
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.70
Viewing height (mm)	8

Table 2. AVS 6 switching valve parameters.

Parameter	Setting
Loop uptake delay (s)	4.0
Uptake pump speed (refill) (rpm)	35
Uptake pump speed (inject) (rpm)	10
Sample loop size (mL)	0.5
Time in sample (s)	2.5
Bubble inject time (s)	1.0

Table 3. Sample Introduction and background corrections.

Parameter	Setting
Nebulizer	MiraMist
Spray chamber	Inert Double Pass Cyclonic
Torch	Standard Quartz, 1.8 mm injector
Sample pump tubing	Black-Black
Waste pump tubing	Blue-Blue
Ar/O_2 addition	No
Ar/O_2 (%)	NA
Background correction	Fitted/FACT

A combination of fitted background correction (FBC) and Fast Automated Curve Fitting (FACT) modeling was used for background correction. An example of fitted background correction is shown in Figure 1. FBC simplifies method development by eliminating the need to determine off-peak background correction points for some elements [3].

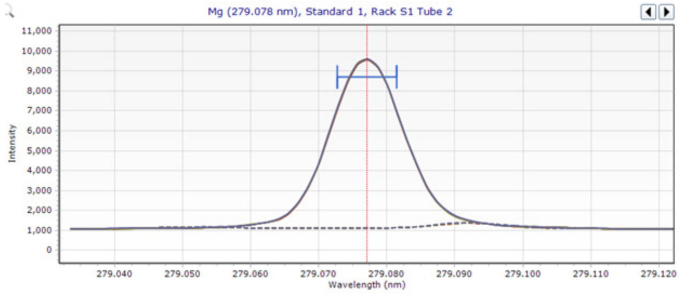


Figure 1. Fitted background correction of magnesium 279.078 nm.

FACT modeling is used to correct for highly complex background structures, where background interferences can have a significant effect. FACT achieves lower detection limits for some elements than other correction techniques [4]. An example of FACT correction is illustrated in Figure 2. ICP Expert software determines the background correction that needs to be applied to all samples in the analyses.

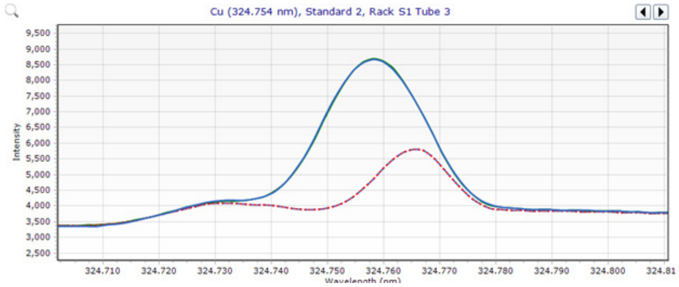


Figure 2. FACT model for background correction on copper 324.754 nm.

Method GB5009.268-2016 recommends which wavelengths to use for each element based on analytical evidence. These wavelengths were used in this study.

Table 4. Elements, wavelengths, and background correction techniques.

Element	Wavelength (nm)	Background Correction
Al	396.152	Fitted
B	249.772	FACT
Ba	455.403	Fitted
Ca	315.887	Fitted
Cu	324.754	FACT
Fe	259.940	Fitted
K	766.491	FACT
Mg	279.078	Fitted
Mn	257.610	Fitted
Na	589.592	FACT
Ni	231.604	FACT
P	213.618	FACT
Sr	407.771	FACT
Ti	323.452	FACT
V	292.401	FACT
Zn	213.857	FACT

Standard and sample preparation

Working standards of varying concentrations were prepared from Agilent single element stock solutions. The standards and QC solution listed in Table 5 were prepared by matching the acid concentration to the digested samples using nitric acid (Emsure, Merck), diluted with 18.2 MΩ Millipore water. Also, as boron is an element of interest, all solutions were diluted using plastic volumetric flasks.

Table 5. Concentrations of working calibration solutions and QC solution.

Element	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)	QC Soln (mg/L)
Al	0.5	1	2	5	10	2.5
B	0.05	0.1	0.2	0.5	1	0.25
Ba	0.05	0.1	0.2	0.5	1	0.25
Ca	5	10	20	50	100	25
Cu	0.025	0.05	0.1	0.25	0.5	0.125
Fe	0.25	0.5	1	2.5	5	1.25
K	5	10	20	50	100	25
Mg	5	10	20	50	100	25
Mn	0.025	0.05	0.1	0.25	0.5	0.125
Na	5	10	20	50	100	25
Ni	0.25	0.5	1	2.5	5	1.25
P	5	10	20	50	100	25
Sr	0.05	0.1	0.2	0.5	1	0.25
Ti	0.05	0.1	0.2	0.5	1	0.25
V	0.025	0.05	0.1	0.25	0.5	0.125
Zn	0.25	0.5	1	2.5	5	1.25

Detection limits (DLs) were determined by analyzing blank samples and calculating the standard deviation. Measurements were taken on two instruments over three days, and 120 method blank sample results were used to determine the Method Detection Limits (MDLs). The average of the standard deviation of six sets of 20 blanks was multiplied by three to give the MDL with greater than 99% confidence. As can be seen in Table 6, the MDLs obtained on the 5100 SVDV ICP-OES are below the limits specified in the GB method.

Table 6. MDLs for all elements, and specifications as outlined in GB5009.268-2016. The MDLs were calculated based on sample preparation (0.50 g sample in 50 mL final volume).

Element and wavelength (nm)	MDL (mg/kg)	MDL Specification (mg/kg)
Al 396.152	0.169	0.5
B 249.772	0.065	0.2
Ba 455.403	0.007	0.1
Ca 315.887	0.657	5
Cu 324.754	0.042	0.2
Fe 259.940	0.160	1
K 766.491	2.14	7
Mg 279.078	0.783	5
Mn 257.610	0.010	0.1
Na 589.592	0.622	3
Ni 231.604	0.154	0.5
P 213.618	0.498	1
Sr 407.771	0.007	0.2
Ti 323.452	0.052	0.2
V 292.401	0.028	0.2
Zn 213.857	0.043	0.5

Samples were prepared for microwave digestion (CEM) by weighing 0.5000 g of reference material into a sealable PTFE test tube and adding 5 mL of concentrated HNO_3. All samples were diluted to 50 mL final volume. Digestion of each sample was carried out according to conditions provided in the GB method (Table 7).

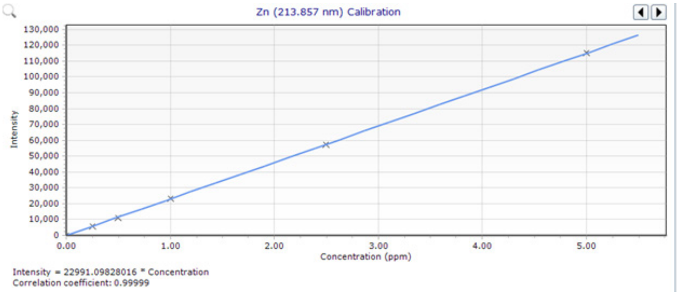
Table 7. Microwave digestion parameters.

Step	Temperature (°C)	Ramp Time (min)	Constant Temperature Time (min)
1	120	5	5
2	150	5	10
3	190	5	20

Linear calibration curves were obtained for all elements, with correlation coefficients >0.9998 (Table 8). Representative curves for Zn 213.857 nm and Cu 324.754 nm are shown in Figures 3a and b, respectively.

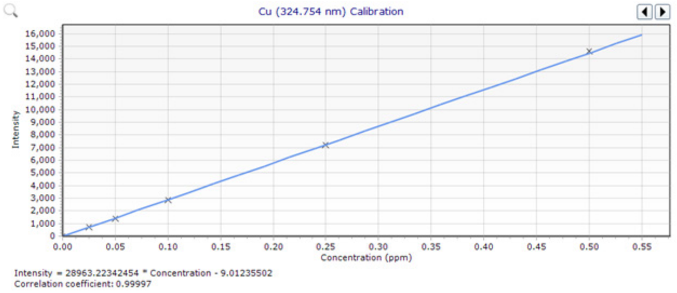
Table 8. Calibration ranges and correlation coefficients.

Element and wavelength (nm)	Concentration range (mg/L)	Correlation coefficient
Al 396.152	0–10	0.99982
B 249.772	0–1	0.99992
Ba 455.403	0–1	0.99998
Ca 315.887	0–100	1.00000
Cu 324.754	0–0.5	0.99997
Fe 259.940	0–5	0.99992
K 766.491	0–100	0.99985
Mg 279.078	0–100	0.99995
Mn 257.610	0–0.5	0.99997
Na 589.592	0–100	0.99997
Ni 231.604	0–5	0.99996
P 213.618	0–100	0.99997
Sr 407.771	0–1	0.99999
Ti 323.452	0–1	0.99997
V 292.401	0–0.5	0.99998
Zn 213.857	0–5	0.99999



Intensity = 22991.09828016 * Concentration
Correlation coefficient: 0.99999

Figure 3a. Calibration graph for Zn 213.857 nm.



Intensity = 28963.22342454 * Concentration - 9.01235502
Correlation coefficient: 0.99997

Figure 3b. Calibration graph for Cu 324.754 nm.

Table 9 outlines the results obtained for the analysis of NIST 1568b Rice Flour SRM. The recoveries for all certified elements were within ±10% of the certified value. Certified values are not available for some elements.

Table 9. Analysis of SRM 1568b - Rice Flour using the 5100 SVDV ICP-OES. Blank cells indicate no certified value.

Element and line (nm)	Certified Value (mg/kg)	Uncertainty in Certified Value (mg/kg)	Measured Value (mg/kg)	Recovery (%)
Al 396.152	4.21	0.34	3.90	93
B 249.772			0.65	
Ba 455.403			0.206	
Ca 315.887	118.4	3.1	116	98
Cu 324.754	2.35	0.16	2.19	93
Fe 259.940	7.42	0.44	6.9	93
K 766.491	1282	11	1187	93
Mg 279.078	559	10	579	104
Mn 257.610	19.2	1.8	20.05	104
Na 589.592	6.74	0.19	7	99
Ni 231.604			0.2	
P 213.618	1530	40	1518	99
Sr 407.771			0.13	
Ti 323.452			0.03	
V 292.401			0.02	
Zn 213.857	19.42	0.26	18.9	97

A digested sample of rice flour was spiked with a low concentration of each analyte to determine the recoveries of the elements. All recoveries were within ±10% of the expected concentration, as shown in Table 10. The B recovery result shows that the standard SVDV torch did not contribute to any boron memory effects.

Table 10. Recoveries for spiked SRM 1568b - Rice Flour.

Element and line (nm)	Measured sample (mg/L)	Spiked (mg/L)	Measured Spike (mg/L)	Recovery (%)
Al 396.152	0.032	4.00	3.926	97
B 249.772	0.007	0.40	0.404	99
Ba 455.403	0.011	0.40	0.403	98
Ca 315.887	1.788	40.00	42.249	101
Cu 324.754	0.016	0.20	0.206	95
Fe 259.940	0.138	2.00	2.166	101
K 766.491	11.375	40.00	50.040	97
Mg 279.078	3.288	40.00	45.162	105
Mn 257.610	0.083	0.30	0.387	101
Na 589.592	0.119	40.00	40.020	100
Ni 231.604	0.002	2.00	2.169	108
P 213.618	11.616	40.00	55.214	109
Sr 407.771	0.009	0.40	0.415	101
Ti 323.452	0.009	0.40	0.408	100
V 292.401	0.000	0.20	0.204	102
Zn 213.857	0.087	2.00	2.135	102

Long-term stability

Approximately 200 digested samples were run over a six hour period without recalibrating. During the run, a QC sample was analyzed every 10 samples and plotted to show the stability of the method. Details of the QC solution are given in Table 6. Figure 4 shows the recovery of all elements over the 6-hour period to be within ±10%. The relative standard deviation of this data was less than 3% for all elements, indicating excellent precision over the extended run.

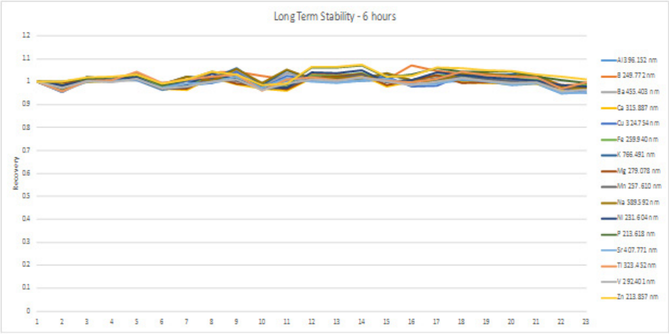


Figure 4. Long-term stability: recovery of a QC sample analyzed every 10 samples over a six hour period.

Fast sample throughput and low argon consumption

Using the AVS 6 switching valve, sample analysis times were reduced by 54 s to only 48 s per sample. Argon consumption was reduced from 37 to 17 L per sample. Argon plasma flow could be further reduced to 10 L/min with 16 L per sample, with a few other changes, while still complying to the GB method specifications.

Conclusions

Routine measurements of food sample digests can be carried out successfully using a Agilent 5110 SVDV ICP-OES fitted with an Advanced Switching Valve (AVS 6). The AVS 6 increases productivity, while the SVDV configuration provides excellent sensitivity and an extended linear dynamic range. The method also complies with the Chinese GB5009.268-2016 Determination of Multiple Elements in Food standard method.

Benefits of the Agilent ICP-OES method include:

- Reliable results with FACT correction of highly complex background structures, especially important for low concentrations, as background structures could have a large impact on results.
- Simple-to-use fitted background correction, which provides excellent correction where a highly complex background structure is not observed.

- Use of a standard torch did not affect the accuracy or sensitivity of the boron results.
- The inert spray chamber allowed for accurate and precise reporting of boron, and a low detection limit, by removing potential contamination sources from the glass cyclonic spray chamber.
- Accurate and precise results, while maintaining a low operating costs with a sample analysis time of 48 s and argon consumption of 17 L per sample.
- Possibility to reduce costs further using an argon plasma flow of 10 L/min, with a few other support changes, while still complying to the GB5009.268-2016 specifications. Analysis time remains the same with the argon consumption being reduced to 16 L per sample using AVS 6, or 35 L per sample without AVS 6.

References

1. GB5009.268-2016 Determination of Multiple Elements in Food, Published December 23, 2016.
2. Synchronous Vertical Dual View (SVDV) for Superior Speed and Performance, Agilent publication 2016, 5991-4853EN
3. Fitted Background Correction (FBC) - Fast, Accurate and Fully Automated Background Correction, Agilent publication 2016, 5991-4836EN
4. Real-time Spectral Correction of Complex Samples using FACT Spectral Deconvolution Software, Agilent publication 2016, 5991-4837EN

www.agilent.com/chem

Printed in the USA, April 16, 2018
5991-9287EN

Agilent
Trusted Answers