

Determination of Multiple Elements in Foods using Automated Fast Sequential-Flame AAS Analysis

Increase sample throughput using an Agilent 280FS FAAS and SIPS 20 pump system



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Introduction

Atomic absorption spectrometry (AAS) techniques are widely used for the analysis of foods. Flame AAS (FAAS) can easily quantify nutritional elements in a variety of samples, which is an important application for product labeling and the quality control of foods. While AA is a well-established technique, there are ways to improve the analytical workflow, enabling labs to accurately analyze as many as 100 food samples a day. Automating sample preparation, instrument calibration, and lamp selection using a fast sequential FAAS fitted with a sampling pump, avoids potential sources of error, improves sample throughput, and reduces the cost-per-sample.

The Agilent 280FS AAS with Agilent Fast Sequential (FS) mode combines eight lamps, including multi-element lamps, so eight, nine, ten, or more elements can be determined from a single aspiration. In FS mode, all elements are determined sequentially in the first sample before the next sample is analyzed. Measuring all elements in one solution before proceeding to the next solution reduces the delay time between measurements and the total analysis time. All eight lamps are operated simultaneously, and a fast, motorized mirror enables rapid lamp selection. The instrument's monochromator has a fast slewing speed of 2,025 nm/min, ensuring minimal delay when switching from one wavelength to another. The Agilent hammer gas control system of the 280FS enables gas flows to be changed within 30 ms, so that an optimum gas flow is used for every element.

To further enhance productivity, the 280FS AAS can be fitted with an Agilent Sample Introduction and Preparation System, double pump (SIPS 20) accessory (1). The SIPS 20 automatically prepares the calibration solutions from a single bulk solution and allows for consistent matrix modification with automatic addition of a matrix modifier. Remeasurement of samples is minimized by automatically diluting overrange samples and extending the working range of the method.

In this study, the Agilent 280FS AAS with SIPS 20 accessory was used to measure K, Na, Ca, Cu, Mg, Mn, Fe, Ni, and Zn in a High Purity Standards (HPS) Orchard Leaves certified reference material (OL CRM).

Experimental

Instrumentation

The Agilent 280FS AAS was used in this study. The instrument was fitted with a Mark 7 flame atomization system comprising a Mark 7 spray chamber with integrated nebulizer and air/acetylene burner. The nebulizer flow rate and glass impact bead position were optimized by maximizing the signal for a 5 mg/L Cu solution.

Three Agilent multi-element hollow cathode lamps, which have cathode compositions that enable the same lamp to be used for the determination of multiple elements, and a single element lamp were used (Table 1). All four lamps were element "coded" for automatic recognition by the instrument, simplifying operation and avoiding errors when changing the lamp position.

The wavelengths, operating conditions, and concentration of the bulk standard listed in Tables 1 and 2 were selected to give absorbances of approximately 0.7–1 for each element. The gas stoichiometry, mix of air and acetylene, was adjusted and optimized almost instantaneously (30 ms) for each element using the hammer gas box. The gas control system is vital for the fast sequential determination of multiple elements in a single solution aspiration. A higher fuel flow was used to cool the flame slightly for the determination of easily ionized elements (EIEs), K and Na. A lower fuel flow (slightly hotter flame) was used for the other elements, as shown in Table 1.

The 280FS AAS is fully controlled using Agilent SpectrAA software, which uses a method wizard and automated features to simplify method development and sample analysis, improving data quality. The FS wizard automatically builds a sequential method from individual methods. The software selects the optimal order of the elements to be analyzed based on wavelength, allowing all required elements to be analyzed from a single solution introduced to the instrument.

The 280FS allows analysts to save analysis time without compromising on precision using the PReCision Optimized Measurement Time (PROMT) function of the SpectrAA software. PROMT allows the operator to set the level of precision (%RSD) needed for the results. The software automatically optimizes read times by measuring the solutions to a specified precision level, rather than for a specified time. With PROMT, higher concentration samples are read more quickly, while blank or low concentration samples are measured for the maximum set time. Compared to conventional analysis, PROMT reduces the sample-to-sample read time by 8%, as shown in the results section of this note.

Operating the 280FS AAS in FS mode also reduces sample-to-sample read times, as measurements for all elements are taken from a single aspiration. FS is achieved by having all the lamps operating simultaneously throughout the run. Rather than acquiring measurements for one element in all samples, FS measures all elements for one sample before moving to the next sample. FS eliminates extra uptake delay, stabilization delay, and rinse times for each element that is analyzed in the sequence. For the analysis of nine elements, as measured in this study, FS mode reduces the read time by approximately 50% compared to conventional analysis.

For correct operation of the SIPS 20 accessory, the nebulizer flow rate was set to 5 mL/min using the capillary adjustment screw and in the SIPS tab of the SpectrAA method editor. The SIPS 20 was used to automatically add a matrix modifier (1.0% Cs, 5.0% Sr) during the analysis to provide the necessary ionization suppressant required for calibration of EIEs, Na and K. The pump speed for the addition of the ionization buffer was set relatively low (10%) to maintain a low dilution effect from this addition. SIPS 20 was also used for the automated addition of a releasing agent for Ca.

Compared to just using PROMT and FS mode of the 280FS, the SIPS 20 further reduces time per sample by 15 to 20%, depending on the number of elements being analyzed.

Standard and sample preparation

A bulk standard solution containing the elements at the concentrations and absorbances listed in Table 2 was prepared from Agilent single element stock solutions in 5% nitric acid (Merck, Emsure). The 18.5 MΩ de-ionized water (DIW) was supplied by a Merck Milli-Q IQ 7010 Water Purification System. The 5% HNO₃ blank solution was used as the bulk diluent.

Table 2. Bulk standard concentration, approximate absorbances, and SIPS 20 calibration points, automatically calculated by the software.

Element/ Wavelength (nm)	Bulk Standard Conc (mg/L)	Approx. Max Absorbance	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)
K 404.4	200	0.4	66.6	133.3	200.0
Na 589.0	1	1	0.333	0.667	1.000
Ca 422.7	60	0.7	20.00	40.00	60.00
Cu 324.8	7.5	0.9	2.500	5.000	7.500
Mg 285.2	1.0	1	0.333	0.667	1.000
Mn 279.5	5	1	1.667	3.333	5.000
Fe 248.3	20	0.8	6.667	13.33	20.00
Ni 232.0	12.5	0.9	4.167	8.333	12.50
Zn 213.9	2.5	1	0.833	1.667	2.500

Table 1. 280FS AA operating conditions.

	Na	Ca	K	Cu	Mg	Mn	Fe	Ni	Zn
Wavelength (nm)	589.0	422.7	404.4	324.8	285.2	279.5	248.3	232.0	213.9
Slit Width (nm)	0.5		1	0.5		0.2			1
Deuterium Correction	No			Yes					No
Lamp*	1	2	1	3	2	3		4	
Burner Used	Air/acetylene								
Acetylene Flow (L/min)	3.0	2.2	3.0	1.8	2.0				
Air Flow (L/min)	13.5								
Burner Height (mm)	13.5	18.0	13.5	17.0	13.5	20.0	20.0	18.0	20.0
Instrument Mode	Absorbance								
PROMT Precision (%)	1								

*Key to lamps:

1. Sodium/potassium (Na/K) coded multi-element hollow cathode (HC) lamp, Agilent part number (p/n) 5610107000
2. Aluminum/calcium/magnesium (Al/Ca/Mg) high intensity UltrAA coded multi-element HC lamp, Agilent p/n 5610133600
3. Cobalt/chromium/copper/iron/manganese/nickel (Co/Cr/Cu/Fe/Mn/Ni) high intensity UltrAA coded multi-element HC lamp, Agilent p/n 5610134500
4. Zinc (Zn) coded single element HC lamp, Agilent p/n 5610106800

The SIPS 20 was used to automatically dilute the bulk standard for calibration based on three equally distant calibration points for each element (Table 2). Representative calibration curves for K and Ca are shown in Figures 1 and 2, respectively. The calibration fit used for all elements was New Rational.

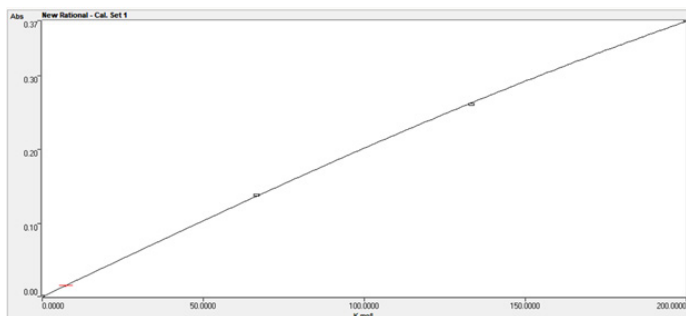


Figure 1. Calibration graph for K 404.4 nm.

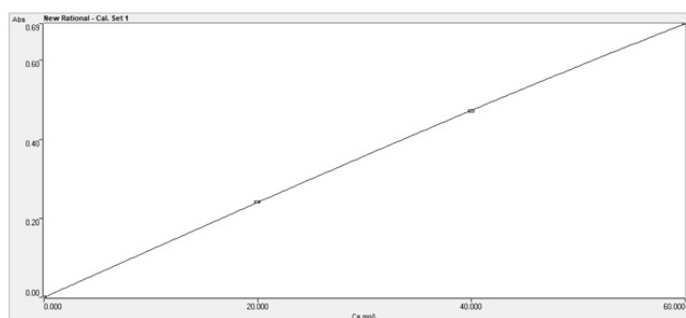


Figure 2. Calibration graph for Ca 422.7 nm.

The samples used for the instrument stability test were prepared for analysis using a MARS 6 closed-vessel microwave digestion system (CEM Corporation, NC, USA). The samples included milk powder, wheat flour, rice flour, apple leaves, and spinach leaves. Approximately 0.5 g of each food sample was accurately weighed into a PTFE-lined vessel, followed by 10 mL of concentrated nitric acid. The samples were digested using the program given in Table 3. Each sample digest was then diluted to 50 mL with DI water.

Table 3. Microwave digestion parameters.

Step	Temperature (°C)	Ramp Time (min)	Constant Temperature Time (min)
1	210	15	15

Results and discussion

Method Detection Limits and CRM recoveries

Instrument Detection Limits (IDLs) were determined by analyzing a blank solution 10 times and multiplying the standard deviation by three. A solution containing all elements at two to three times the IDL was analyzed 10 times. The standard deviation of each analyte concentration was multiplied by three to give the method detection limit (MDL). The procedure was repeated three times to ensure that a better estimate of the MDL was obtained. The results in Table 4 show the MDLs that were determined for this application.

The OL CRM was analyzed as received. The concentration of nickel in the CRM of 0.009 mg/L was below the MDL, so the solution was spiked at 0.300 mg/L. The SpectraAA software detected that some elements in the OL CRM were overrange and the SIPS 20 automatically diluted the CRM to ensure accurate measurement, without user intervention. All elements reported recoveries within $\pm 10\%$ of certified or spiked concentration, demonstrating the accuracy of the method.

Table 4. MDLs and recovery results for the OL CRM.

Element	MDL (mg/L)	Measured Concentration (mg/L)	Certified Concentration (mg/L)	Recovery (%)	SIPS Auto Dilution Factor
K	1.45	157	150	105	-
Na	0.00945	0.99	1	99	-
Ca	0.165	197	200	99	5.0
Cu	0.0537	0.11	0.1	110	-
Mg	0.00308	59.2	60	99	129
Mn	0.0421	1.02	1	102	-
Fe	0.149	3.03	3	101	-
*Ni	0.0726	0.325	0.300 (spike level)	108	-
Zn	0.0136	25.7	25	103	13.2

Instrument stability

To test the stability of the instrument over the analysis of a range of food samples, 55 samples were digested and analyzed. A QC solution that was prepared in the lab was measured after every five samples. The results in Table 5 show excellent recoveries within $\pm 10\%$. Also, good stability of measurements ($< 5\%$ RSD) were obtained for all elements over approximately 4.5 hours, with no recalibration.

Long term stability is achieved due to the hammer gas box that also provides instantaneous gas flow changes, ensuring that all elements are measured at their optimal stoichiometry.

Table 5. Stability results for a QC solution measured every five samples over 4 hours 19 minutes, n=12.

Element	Average Measured Concentration (mg/L)	Expected Concentration (mg/L)	Recovery (%)	SD (mg/L)	RSD (%)
K	96.7	100	97	1.25	1.3
Na	30.6	30.0	102	1.39	4.5
Ca	32.1	30.0	107	1.46	4.6
Cu	3.67	3.75	98	0.049	1.3
Mg	51.5	50.0	103	1.41	2.7
Mn	2.48	2.50	99	0.056	2.3
Fe	10.2	10.0	102	0.29	2.8
Ni	6.26	6.25	100	0.12	1.9
Zn	1.24	1.25	99	0.017	1.4

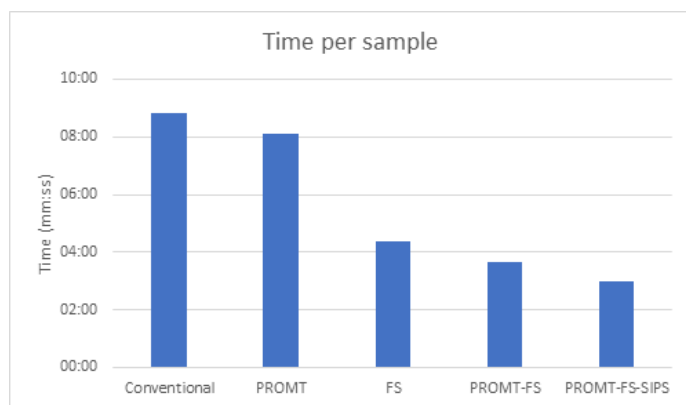


Figure 3. Measurement time per sample for nine elements in the OL CRM using conventional FAAS and the 280FS AA with various productivity tools.

Productivity

In this report, we have highlighted several features of the 280FS AAS that were used to increase the productivity of the method compared to conventional AAS. These features include PROMT, FS mode, and the SIPS 20 accessory. Conventional AAS analysis typically takes three replicate readings of an element using a fixed read time, before measuring the same element in subsequent samples. The sequence is then repeated for each individual element required by the analysis method. For the time per sample comparison study, three, 3 s replicates were measured for the conventional analysis of nine elements in the OL CRM. The results in Figure 3 show the productivity gains of the 280FS compared to conventional AAS:

- PROMT reduced the sample-to-sample read time by 8%.
- FS mode halved the sample analysis time.
- FS and PROMT reduced the time per sample by another 44 s compared to FS only.
- The SIPS accessory with PROMT and FS mode reduced analysis time by approximately two-thirds.

The 280FS with PROMT and SIPS would increase the sample throughput from 6.8 samples per hour to 20 samples per hour, on average—significantly improving productivity of the workflow.

Conclusion

The study has demonstrated the accuracy and precision of the Agilent 280FS AA with SIPS 20 accessory for the measurement of K, Na, Ca, Cu, Mg, Mn, Fe, Ni, and Zn in foods. Excellent accuracy was demonstrated with recoveries of certified elements in the OL CRM within $\pm 10\%$ of expected. A QC stability test over approximately 4.5 h showed good precision of less than 5% RSD, with no need to recalibrate.

The method was simplified using the SIPS 20 pump system to automatically calibrate the instrument, add an ionization buffer matrix modifier for Na and K, and a releasing agent for Ca. Automating manual processes minimized sources of error and contamination, and provided operators with more time to perform other tasks.

Agilent-only features of the 280FS including PROMT, Fast Sequential mode, and the SIPS 20, improved productivity by 66% compared to conventional AAS analysis. These productivity tools enabled the measurement of nine elements in 20 food samples an hour, greatly improving the sample throughput capabilities of AAS.

Reference

1. Increasing Productivity and Simplifying Sample Preparation with the SIPS Accessory, Agilent publication, [5991-6613EN](#)

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