

# Flame and Graphite Furnace Atomic Absorption Spectroscopy

Application Compendium



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Agilent Technologies is a leading manufacturer of analytical instruments. Since the introduction of the world's first atomic absorption spectrometer in the 1960s, Agilent has invested in research and development in the field of atomic absorption analysis. We have patented many technologies associated with atomic absorption spectrometers and provide fast, accurate and sensitive instrumentation for elemental analysis. Agilent Atomic Absorption Spectroscopy (AAS) instruments can be found in laboratories around the world. They are used for testing food, pharmaceuticals, materials, and chemical, biological and environmental samples.

To promote the exchange of research interests and experience, we invited customers who use our AAS instruments to submit technical articles related to elemental analysis. The selected articles in this compendium represent common applications of AAS instruments. Technology advances that reduce common causes of wasted time during elemental analysis are also presented.



## Solutions for Common AAS Problems

When using an AAS instrument, you may encounter issues such as:

- Time-consuming multi-element analysis
- Inaccurate results caused by a complex sample matrix
- Unstable readings

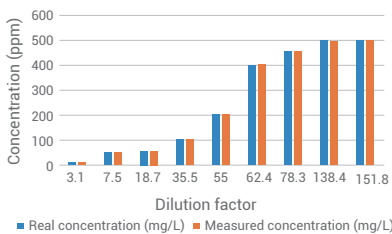
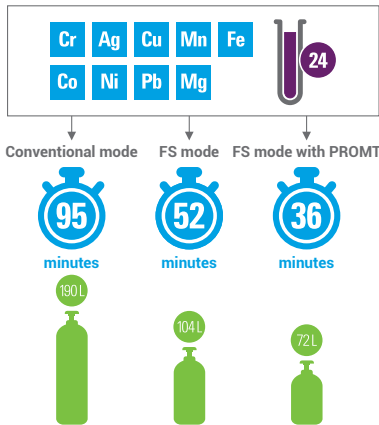
This compendium uses typical application examples to present solutions for these common causes of wasted time. We also address three of the most common frustrations analysts face when using an AAS instrument, below:



**Time wasting concern: Switching between flame and graphite furnace consumes a lot of time and raises concerns about the system stability.**

**The solution: [Agilent AA Duo Products](#) enable true simultaneous analysis using flame and graphite furnace**

The [Agilent AA Duo atomic absorption system](#) includes both a flame instrument and a furnace instrument, controlled by one computer. They can be operated at the same time, providing high sample throughput. Both instruments can be setup, ready for any analysis without the time wasting requirement to changeover and re-align atomizer workheads when switching between methods.



Dilution performance of a SIPS 20 at different dilution factors. Excellent dilution accuracy was obtained with a maximum of only 1.2% dilution error.

**Time wasting concern: Measuring a lot of samples or elements using AAS is inefficient. The sample preparation is tedious and time-consuming, and over-range samples need to be remeasured, causing more wasted time.**

**The solution: Fast Sequential mode, the PROMT feature, and the Sample Introduction Pump System**

**Fast Sequential mode**

The Agilent 240FS and 280FS AAS instruments feature a measurement mode called Fast Sequential. It can achieve the same productivity and speed as a sequential ICP-OES by measuring multiple elements from one sample aspiration. Fast Sequential mode uses a spinning mirror to switch between each hollow cathode lamp, and a unique gas box able to instantaneously change the gas flows for each elements ideal ratio.

By analyzing multiple elements with one aspiration, FS mode offers:

- High analytical efficiency
- Low running costs (less gas and electricity)
- Less sample consumption

**PROMT feature**

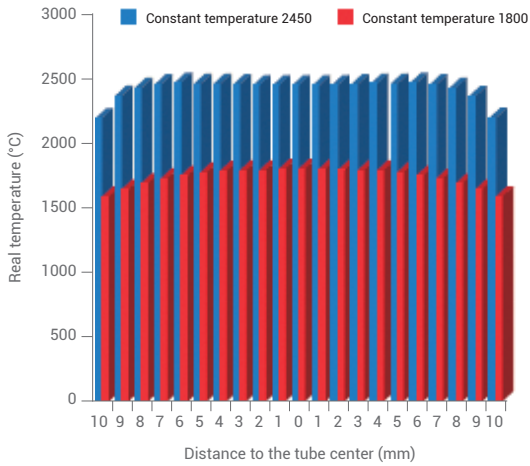
The PROMT software feature saves even more time and sample volume. Rather than setting one signal read time that will be used for every sample, you simply set the measurement precision (%RSD) you require. The PROMT feature will then automatically adjust the signal read time for each sample to achieve the required precision. The signal read time will be a longer time for samples with lower concentrations and made shorter for higher concentrations.

Using both Fast Sequential mode and PROMT allows you to measure 10 elements in one sample in 2 minutes using only 10 mL of sample.

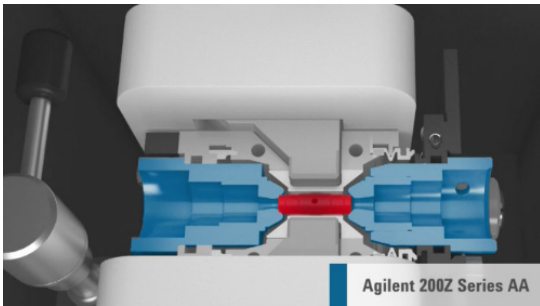
**Sample Introduction Pump System**

The Sample Introduction Pump System (SIPS) is an optional accessory for Agilent AAS instruments. The SIPS accessory connects to the sample uptake tube and is controlled by the instrument software. A SIPS accessory uses one or two pumps to:

- Automatically create a multi-point calibration curve by preparing several dilutions of the highest concentration standard
- Automatically perform inline pre-dilution of samples and dilute over-range samples so they can be remeasured during the run
- Automatically add matrix modifiers and internal standards to samples during the run



CTZ technology ensures a constant temperature in the middle of the graphite tube, where the sample sits.



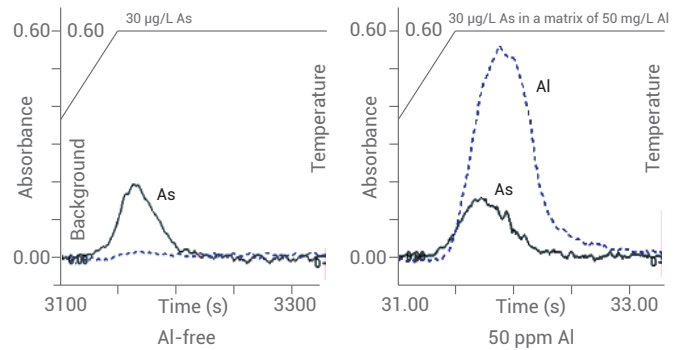
The Agilent Zeeman systems feature the transverse Zeeman configuration and constant temperature zone furnace design.

## Time wasting concern: How to overcome interferences in complex matrix samples? How to ensure stable and accurate testing results using a graphite furnace system

### The solution: An Agilent graphite furnace system with Zeeman background correction

The Agilent 240Z and 280Z graphite furnace AAS instruments feature:

- Outstanding performance at ppb levels from the constant temperature zone (CTZ) furnace design. CTZ features long, end-heated atomization tubes, which are uniformly and rapidly heated to achieve fast sample analysis
- High correction accuracy with Agilent’s unique magnetic waveform providing background correction at double the speed of longitudinal Zeeman systems, featuring three point polynomial interpolation for an 11-fold improvement in accuracy



Agilent Zeeman Graphite Furnace: Comparing the analysis of a sample containing 30 µg/L As without any matrix (left) and another containing 30 µg/L As in a matrix of 50 mg/L (right) The As could still be accurately determined, despite high background absorption caused by the Al.

# Determination of Cu, Fe, K, Mg, Mn, Na and Zn in Food Using AAS in Fast Sequential mode



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## Efficient elemental analysis of food samples

As more food products are imported and exported around the globe, greater quality control methods are needed. Some laboratories are looking for optimized systems that can efficiently and accurately analyze up to eight elements or more in as many as 100 samples per day. Such optimization is essential because it is inefficient to dedicate one analyst to manually running large numbers of samples every day.

Cu, Mn, Fe, K, Na, Mg, and Zn are seven elements most commonly measured in food testing. Flame atomic absorption spectrophotometry continues to be an appealing technique for this analysis due to its low purchase price, simple hardware and lower operational costs.

In this study, an Agilent AA 280FS flame atomic absorption spectrometer featuring Fast Sequential (FS) mode and PRecision Optimized Measurement Time (PROMT) was used to determine seven elements, Cu, Mn, Fe, K, Na, Mg, and Zn, in a wheat flour reference material.

To analyze 100 samples per day, up to 10 calibration standards would need to be prepared, as well as diluting samples and also adding a ionization buffer, or modifiers, as required. These steps would be typical in a food lab and can introduce contamination and error into the analysis. The Agilent SIPS 10 Sample Introduction Pump System was used to automatically dilute and prepare the standards and samples, in order to maximize the efficiency of this analysis.

Remeasurement often occurs in food labs when results show errors. Errors caused by incorrectly prepared standards and sample preparation errors can all force sample remeasurement. Again, the SIPS 10 can avoid these errors, by removing the manual preparation of standards and samples.

## Analysis of Cu, Mn, Fe, K, Na, Mg, and Zn

The method conditions for the each of the elements: wavelength, gas flow, lamp and lamp current, and slit width were all adjusted by the 280FS instrument. In Fast Sequential mode, instantaneous gas flow changes ensure optimized flame stoichiometry for each element. All the required hollow cathode lamps are illuminated, with a spinning selection mirror selecting the light from each lamp in the sequence. A high speed wavelength drive rapidly moves to the right wavelength for each element. This allowed all elements to be measured from one sample aspiration.

The gas flow stoichiometry for each element was controlled by the Hammer Gas Box, built into the instrument. The gas flows recommended in the [Agilent Flame Atomic Absorption Spectroscopy Method Development Primer](#) were used.

The seven elements were assayed using only one stock solution, the SIPS 10 prepared 5 calibration standards for each element. Table 1 lists method conditions for each element. The precision of each measurement was controlled by the PROMT function, where measurement time is adjusted for a set level of precision i.e. 1% RSD. Higher concentrations achieve the precision target more quickly than lower concentrations elements, so measurement time is reduced to save time and gas during analysis.

**Table 1.** Instrument conditions.

Element	Cu	Mn	Fe	K	Na	Mg	Zn
Lamp current (mA)	4.0	5.0	5.0	5.0	5.0	4.0	5.0
Wavelength (nm)	324.8	279.5	248.3	766.5	589.0	285.2	213.9
Slit width (nm)	0.5	0.2	0.2	1.0	0.5	0.5	1.0
No. of standards	5						
Measurement mode	PROMT						
Inline diluter type	SIPS 10						

## Results

Figures 1 and 2 show the standard curves for two of the seven elements. Table 2 shows the measurements of wheat flour standard GBW08503b.

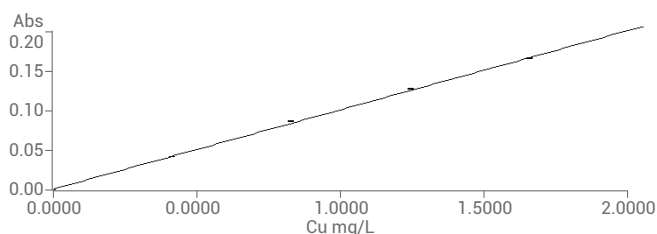
**Table 2.** Comparison of the measured concentration of elements in a wheat flour standard GBW08503b, versus the certified concentrations.

Element	Certified value (mg/kg)	Measured value (mg/kg)	Recovery (%)
Cu	3.98±0.43	3.70	93
Mn	22.0±2.0	20.89	95
Fe	37.7±9.4	37.17	98
K	2370±100	2290	97
Na	8.3±1.1	9.10	109
Mg	616±44	598	97
Zn	20.6±1.7	19.34	94

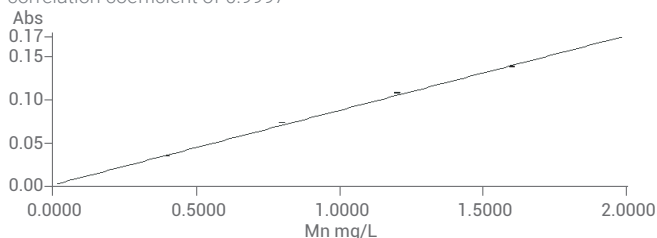
The SIPS 10 was able to prepare accurate calibration curves with correlation coefficients exceeding 0.999 for all elements. This automation of standard preparation significantly reduced the labour associated with manual standard preparation. The use of the SIPS 10 single pump sampling system also enabled the automatic dilution of over-range samples, removing this common source of wasted time. For those sample results that were above the range of the calibration, the SIPS 10 was able to reduce remeasurement by automatically performing inline dilutions, removing the need for user intervention.

The PROMT function reduced the measurement time and the sampling volume, thus improving efficiency and reducing sample consumption.

Compared with conventional flame atomic absorption spectrometry, using the 280FS, PROMT and the SIPS 10 increased the workflow efficiency by more than three times, and reduced the analysis time by over 70%. This means more samples can be measured in less time.



**Figure 1.** The calibration curve for Cu shows excellent linearity, with a correlation coefficient of 0.9997



**Figure 2.** The calibration curve for Mn shows excellent linearity, with a correlation coefficient of 0.9995.



# Rapid Determination of Seven Elements in Milk Powder by Microwave Digestion and Flame Atomic Absorption Spectrometry



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## Introduction

Flame Atomic Absorption Spectrometry (FAAS) can be used to determine the concentration of nutrient elements in milk and milk products. It is a low cost and simple technique to own and operate. Being a long established analytical technique, FAAS is included in many standard methods and regulations, so the analytical parameters and requirements are well documented.

FAAS analysis can be slow, compared to newer techniques such as ICP-OES. Samples must be measured multiple times—once for each element being measured. This makes the technique inefficient and may introduce errors.

There have been technology developments that have improved the efficiency of FAAS. In this study, seven elements; K, Na, Ca, Mg, Fe, Zn and Cu, were determined in milk powder from a single sample measurement with an Agilent 280FS Flame AAS using Fast Sequential (FS) mode.

## Fast Sequential mode

The Agilent 280FS is a high performance flame atomic absorption spectrometer. It combines eight lamps with the Agilent Fast Sequential mode which doubles sample throughput and dramatically reduces running costs. The 280FS is ideal for labs wanting the best performance.

Fast Sequential mode operates all eight lamps simultaneously. A fast lamp selection mirror and high speed wavelength drive are used to switch between the lamp and wavelength required to measure each element. The mode allow the rapid determination of the seven nutrients in milk powders from a single sample aspiration into the flame. This compares to conventional FAAS where only one element is measured with each aspiration of a sample—measuring seven elements would require the sample to be presented to the instrument seven times, increasing analysis time, gas consumption and the risk of errors. FS mode saves time, reduces gas consumption and occurrence of operator error.

## Instrument setup

Seven single element, Agilent-coded, hollow cathode lamps were used for this analysis: K, Na, Ca, Mg, Fe, Zn, and Cu.

All the glassware for the experiment were soaked in nitric acid (1 in 4 dilution) for 24 h, rinsed with distilled water and then with deionized water, and air dried for later use.

Calibration standards are shown in Table 1.

**Table 1.** Concentrations of standards (mg/L).

Element	1	2	3	4	5
K	0.050	0.10	0.20	0.40	0.80
Na	0.050	0.10	0.20	0.40	0.80
Ca	0.50	1.0	2.0	4.0	8.0
Mg	0.050	0.10	0.20	0.40	0.80
Cu	0.50	1.0	2.0	4.0	8.0
Fe	0.50	1.0	2.0	4.0	8.0
Zn	0.10	0.20	0.50	1.0	2.0

The instrument settings are shown in Table 2. The blank and standard solutions were measured to create calibration curves. The correlation coefficient of the standard curve for each element is shown in Table 3.

**Table 2.** Instrument settings.

Element	Wave-length (nm)	Slit Width (nm)	Lamp Current (mA)	Air Flow Rate (L/min)	Acetylene Flow Rate (L/min)
K	766.5	0.5	5	13.50	2.0
Na	589.0	0.5	5	13.50	2.0
Ca	422.7	1.0	10	13.50	2.0
Mg	285.2	0.2	4	13.50	2.0
Cu	324.8	0.5	10	13.50	2.0
Fe	248.3	0.2	10	13.50	2.0
Zn	213.9	0.2	4	13.50	2.0

**Table 3.** Correlation coefficient of the standard calibration curve created for each element.

Element	Correlation coefficient
K	0.9991
Na	0.9987
Ca	0.9994
Mg	0.9996
Cu	0.9998
Fe	0.9989
Zn	0.9993

## Microwave digestion procedure

0.500 g of the sample was weighed into a microwave digestion vessel into which 5 mL of nitric acid was then added. The sample was then placed in a microwave digestion system, using the following conditions: Heating to 120 °C in 5 min and then holding for 5 min; heating to 160 °C in 5 min and then holding for 10 min; heating to 180 °C in 5 min and then holding for 10 min. The acid was then boiled off at 140–160 °C until the sample volume was reduced to 1 mL. The sample was transferred into a 50 mL volumetric flask, with the digestion vessel being rinsed 2 to 3 times with a small amount of water. The rinse solutions were added to the volumetric flask and 5.0 mL of lanthanum oxide solution was added. The final dilution factor was 100.

## Precision and accuracy

Six replicates of 0.500 g of a milk powder standard reference material were accurately weighed, digested using a microwave digestion system, and analyzed. Results are shown in Table 4.

Excellent recoveries (within  $\pm 10\%$ ) were obtained for each of the seven elements, based on the certified values of the reference material. The RSD% was  $< 2.5\%$  for each element, except Ca, which was 3.7%.

The results demonstrate the high accurate and precision of the 280FS when using FS mode.

**Table 4.** Precision and recovery (n = 6).

Element	Measured value (mg/ 100 g)	RSD (%)	Certified value (mg/ 100 g)	Mean recovery (%)
K	693.6	2.35	717.0	97
Na	141.5	1.48	157.0	90
Ca	628.2	3.67	616.5	102
Mg	67.41	0.74	70.94	95
Cu	418.9	0.32	434.5	96
Fe	7.214	1.01	7.440	97
Zn	4.027	0.63	4.310	93

# High Sensitivity Determination of Pb in Soy sauce using Graphite Furnace AAS



## Regulated levels of heavy metals in food

Soy sauce is a traditional Chinese condiment, with a unique flavor and delicious taste. Soy sauce can be divided into light (thin), dark, and thick soy sauce, according to the fermentation process. The China National Health Commission and the State Administration of Market Regulation have prepared The National Standard for Food Safety for the Maximum Levels of Contaminants in Foods GB 2762-2017. This standard specifically states the limits for heavy metals in food for lead, cadmium, mercury and arsenic, tin, nickel and chromium. The analysis of food samples can prove challenging due to the complex matrices that are present, often being high in salts and sugars.

In this study, Pb was analyzed in soy sauce by the Agilent 280Z AA Graphite Furnace Atomic Absorption Spectrometer (GFAAS).

## Instrumentation

The Agilent 280Z AA features a Transverse Zeeman Background Correction technology to ensure the highest sensitivity for Pb in soy sauce. The Agilent PSD 120 autosampler automatically prepares the calibration curve, adds modifier and accurately and reliably delivers samples to the furnace. The Hot Injection capability in the software was used to control the conditions of injection for effective delivery of the sample droplets to the Omega platform tube. The Omega platform tube ensures improved performance and the highest sensitivity for Pb. The Tube-CAM furnace viewing camera, standard on the 280Z AA, provides real time viewing inside the graphite tube. This is used to confirm the deposit position of the sample. It is also used to control the drying program, which is essential when analyzing samples like soy sauce that have a complex matrix.

To assist in the development of a robust furnace program, the Surface Response Methodology (SRM) tool in the SpectrAA software was used to find the optimum ash and atomization temperature. The tool guides the operator to find the maximum absorbance in just a few experiments, significantly simplifying method development and saving time.

The optional local fume extraction accessory ensures that any harmful vapors are removed at the source ensuring they don't escape into the lab. It also includes a convenient LED lighted mirror to provide a clear view of the graphite tube injection hole assisting in the easy insertion and removal of graphite tubes (Figure 1).

## Standard and modifier preparation

A 50 µg/L bulk standard of Pb was prepared from a 1000 mg/L Pb stock standard and diluted with 1% nitric acid (HNO<sub>3</sub>). The working calibration standards were prepared with the PSD 120 Autosampler with the concentration 0, 10, 20, 30 and 40 µg/L. The prepared chemical modifier consisted of 1% magnesium nitrate + 0.2% palladium nitrate in 1% HNO<sub>3</sub>.



**Figure 1.** Agilent's optional extraction/LED accessory for the Agilent GTA 120 graphite tube atomizer.

### Sample preparation

An accurately weighed soy sauce sample of 0.10 g and was diluted to 5.0 g using 1% HNO<sub>3</sub> and thoroughly mixed with a vortex mixer for one minute, to have a final dilution factor of 50.

### Instrument conditions

Table 1 lists the instrument operating conditions. Table 2 lists the furnace settings used for the analysis.

**Table 1.** Agilent 280Z AA instrument operating conditions.

Element	Pb
Lamp current (mA)	10
Wavelength (nm)	283.3
Slit Width (nm)	0.5
Type of tube	Omega platform tube
Background correction	Zeeman
Modifier	5 µl 1% Magnesium nitrate + 0.2% Palladium nitrate (Co-inject)
Sample Volume (µL)	10
Lamp type	Hollow Cathode Lamp
Hot injection Temp (°C)	60
Injection Speed	8

**Table 2.** Furnace program for the analysis of Pb in soy sauce.

Step	Temp (°C)	Time (s)	Argon Flow (L/min)	Reading
1	95	50.0	0.3	-
2	120	20.0	0.3	-
3	400	30.0	0.3	-
4	500	20.0	0.3	-
5	805	15.0	0.3	-
6	805	10.0	0.3	-
7	805	1.0	0.0	-
8	2132	0.6	0.0	Yes
9	2132	2.0	0.0	Yes
10	2500	2.0	0.3	-

### Optimization

To ensure accuracy and precision of analysis in GFAAS, control over the furnace temperature program is critical. The Tube-CAM on the 280Z AA provides real time viewing inside the Omega platform tube to correctly optimize drying step. This internal view is valuable for the high salt matrix of the soy sauce samples. The Tube-CAM showed an additional heating step to 400 °C, was required to sufficiently remove salts and sugars common with food type samples, prior to ashing and to complete the matrix removal.

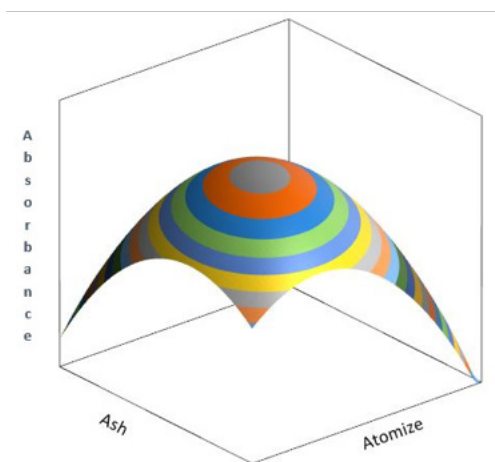
The ash and atomize temperatures in GFAAS are not independent variables. The SRM Wizard tool is unique in its ability to simultaneously find the relationship between ashing and atomization. This ensures the maximum absorbance, highest sensitivity and excellent %RSD of replicates. Once the initial Ash and Atomize temperatures and steps were defined (Table 2), the tool automatically derived the experiments needed to find the optimum ash and atomization temperature with the schematic showing the stability of the vapor phase (Figure 2).

**Table 3.** SRM, experimental design factors.

Step	Temperature (°C)	Step (°C)
Ash	1000	300
Atomization	2000	300

The optimum temperatures found by the SRM Wizard were:

- Ash: 805 °C
- Atomization: 2132 °C



**Figure 2.** The SRM tool in the SpectrAA software uses a mathematical model to automatically optimize ash and atomize temperatures. Shown here the schematic for a spiked soy sauce sample.

### Method detection limit

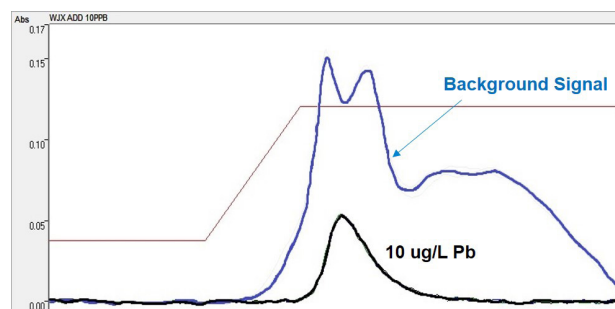
The Method detection limit (MDL) was determined from the 3 sigma measurement of 10 matrix blank solutions and multiplying by the dilution factor. The food safety standard GB 2762-2017 specifies the maximum allowable content of Pb in condiments to be  $\leq 1.0$  mg/kg. The limits show that the 280Z AA are well below the requirements of the standard (Table 3).

**Table 4.** The method detection limits and limit of quantification achieved were well below the maximum allowable limit of Pb.

	MDL in solution ( $\mu\text{g}/\text{kg}$ )	MDL in sample ( $\mu\text{g}/\text{kg}$ )	LOQ in sample ( $\mu\text{g}/\text{kg}$ )	Maximum allowable Limit ( $\mu\text{g}/\text{kg}$ )
Limit	0.35	18	59	1000

### Sample analysis and method robustness

The stability of the 280Z AA was investigated by analyzing a soy sauce sample spiked with  $10 \mu\text{g}/\text{kg}$  of Pb, each sample was measured in triplicate. Figure 3 shows the Pb analyte absorbance peak in the spiked soy sauce sample, recovered accurately and precisely (1.0 %RSD) even with in the complex background (pale grey line) with Agilent's effective Zeeman background correction.



**Figure 3.** Absorbance peak for a soy sauce sample spiked with  $10 \mu\text{g}/\text{kg}$  Pb (dark lines) in a complex background (pale grey line).

The method robustness was examined by repeating it in four Centers of Excellence (COEs) in China with different operators/instruments. The results across the four sites were almost identical (Table 4) with excellent precision of  $<2.0$  %RSD and recovery of the spike  $98 \pm 4\%$  demonstrating the robustness of the method and reliability of the Agilent 280Z AA.

**Table 5.** Repeatability Pb analysis in soy sauce across the four COEs.

COE	# of Samples Measured	Unspiked Soy Sauce ( $\mu\text{g}/\text{kg}$ )	Spiked Sauce ( $\mu\text{g}/\text{kg}$ )	RSDs	Recovery
Shanghai HS	n=10	<MDL	9.66	1.7%	97%
Shanghai LYX	n=10	<MDL	10.4	1.2%	102%
Chubang	n=7	<MDL	9.62	0.7%	98%
LiJinji	n=7	<MDL	9.35	1.2%	94%

### Conclusion

The Agilent 280Z AA using the Omega platform tube provided high sensitivity, accuracy and precision quantify Pb in soy sauce according to GB 2762-2017. The SRM Wizard ensured the optimum ash and atomization temperatures, producing a robust method for the maximum absorbance. The method robustness was validated across four different laboratories where it was shown that the method exceeds the GB 2762:2017 requirements for Pb in soy sauce.

With its excellent precision and accuracy for such a difficult matrix, the Agilent 280Z is ideally suited for laboratories that require sensitive and cost-effective instrumentation.

# Determination of Cr, Cu, Ni and Zn in Soils Using Fast Sequential Mode



## High throughput analysis

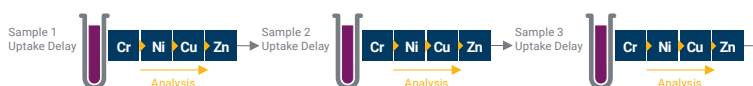
Laboratories testing soils using Atomic Absorption Spectroscopy (AAS) face pressure due to the number of elements to be measured and large numbers of samples. It is not uncommon to measure from 4 to 10 different elements in each soil sample. Conventional flame AAS systems can only detect one element per one sample aspiration, which means multiple aspirations are needed for multi-element testing. It is time-consuming and laborious when there are a large number of elements and samples waiting for analysis.

The Agilent 240FS is a high performance flame atomic absorption spectrometer. It combines four lamps with the Agilent [Fast Sequential \(FS\) mode](#) which doubles sample throughput and dramatically reduces running costs. Fast Sequential mode operates all four lamps simultaneously. A fast lamp selection mirror and high speed wavelength drive are used to switch between the lamp and wavelength required to measure each element. The Hammer gas control system initiates instantaneous changes to the gas flows, ensuring each element is analyzed under optimal conditions. This results in much higher analytical efficiency, lower operating cost, minimized sample consumption, as well as reduced reagent and handling costs.

In this study, the Agilent 240FS Flame AA was used to measure four elements: Cu, Zn, Ni and Cr in Geochemical Soil Certified Reference Samples (GSS series). The method used FS mode to quickly measure the four elements in a sample before moving onto the next sample (as shown in Figure 1).

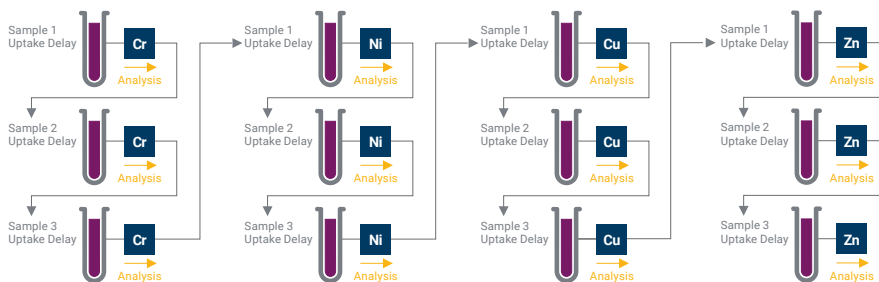
### Fast Sequential mode

Using Fast Sequential mode, samples are only aspirated once, with all elements being measured before the next sample is aspirated.



### Conventional mode

Conventional AA determines only one element from each sample aspiration, so samples are analyzed time and time again during a multi-element sequence.



**Figure 1.** In Fast Sequential mode, all elements are measured in each sample before moving onto the next sample. This compares with conventional AAS, where a single element is measured in each sample at a time.

Table 1 displays the instrument operating conditions for Cu, Zn, Ni and Cr. The results in Table 2 show that the measured results compare well with the certified values. It took only about 15 minutes to determine 4 elements in 8 samples, saving about 50% of the time and gas consumption compared with conventional AA system.

Using FS mode, it took only 15 minutes to determine four elements in eight samples. This was a 50% reduction in time and gas consumption, compared with a conventional AA system. The 240 FS is an efficient flame AAS instrument, able to measure large numbers soil samples quickly and accurately.

**Table 1.** Operating conditions of using FS Mode to determine Cu, Zn, Ni and Cr in soil.

	Cu	Zn	Ni	Cr
Lamp current (mA)	10	10	10	10
Wavelength (nm)	324.8	213.9	232.0	357.9
Slit Width (nm)	0.5	0.2	0.2	0.2
Flame Type	Air-acetylene			
Acetylene Flow (L/min)	2.0	2.0	2.0	2.0
Air Flow (L/min)	13.5	13.5	13.5	13.5

The measured concentrations of the samples show excellent accuracy. Each result was within  $\pm 10\%$  of the certified value (see Table 2).

**Table 2.** A comparison of the measured concentrations for Cu, Zn, Ni, and Cr against the certified concentrations for the soil samples.

Sample		Cu (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
GSS-4	Measured value	40.97	199.08	60.77	371.48
	Certified value	40 $\pm$ 3	210 $\pm$ 13	64 $\pm$ 5	370 $\pm$ 16
GSS-8	Measured value	24.67	67.77	29.97	64.51
	Certified value	24.3 $\pm$ 1.2	68 $\pm$ 4	31.5 $\pm$ 1.8	68 $\pm$ 6
GSS-9	Measured value	25.20	59.78	32.74	72.92
	Certified value	25 $\pm$ 3	61 $\pm$ 5	33 $\pm$ 3	75 $\pm$ 5
GSS-11	Measured value	21.41	63.81	24.89	57.02
	Certified value	21.4 $\pm$ 1.2	65 $\pm$ 5	25.4 $\pm$ 1.3	59 $\pm$ 3
GSS-13	Measured value	22.29	65.56	28.65	63.26
	Certified value	21.6 $\pm$ 0.8	65 $\pm$ 3	28.5 $\pm$ 1.2	65 $\pm$ 2
GSS-21	Measured value	24.52	67.78	27.30	50.68
	Certified value	24 $\pm$ 1	66 $\pm$ 3	28 $\pm$ 1	55 $\pm$ 5
GSS-23	Measured value	31.61	94.61	37.73	82.34
	Certified value	32 $\pm$ 1	97 $\pm$ 3	38 $\pm$ 1	82 $\pm$ 4
GSS-24	Measured value	27.20	80.28	24.86	62.36
	Certified value	28 $\pm$ 1	81 $\pm$ 2	24 $\pm$ 1	62 $\pm$ 2

# Measuring Multiple Elementals in Steel Samples Using FAAS With Automated Standard Preparation and Sample Dilution



## Ensuring the quality of steel

Steel manufacturers test the quality of their products by measuring several elements in the steel to ensure the grade and performance of their final product. Different grades of steel have different specifications for elemental content.

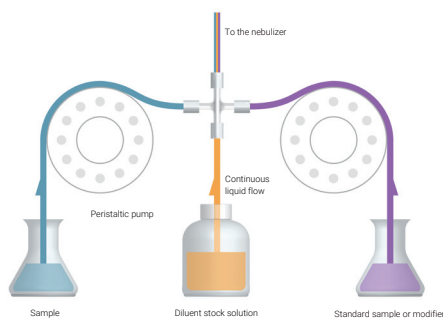
Laboratories are looking beyond whether an instrument can 'do the job' to whether a specific instrument can improve their sample throughput, lower their costs, simplify sample preparation and instrument operation, and deliver reliable results throughout the analysis of a large batch of samples.

Complex matrices, such as steel samples, introduce a lot of chemical or physical interferences to flame atomic absorption spectroscopy measurements. Manual dilution of samples is the conventional way to prevent these interferences causing incorrect results. Unfortunately, such dilutions can be complex and tedious. Manually diluting samples can also cause sample contamination.

Standard addition is a calibration method that can replace the conventional standard curve calibration method to help eliminate chemical and physical interferences. Manually preparing standard additions is time-consuming and laborious due to the need to prepare multiple solutions for each sample, with variable amounts of known concentrations of the analyte.

The Agilent Sample Introduction Pump System (SIPS) accessory provides automation for flame AA analysis, increasing sample throughput, simplifying sample preparation and instrument operation. The accessory is available in a single pump version (SIPS 10) and a dual pump version (SIPS 20). The SIPS 10 enables automatic preparation of standard solutions from a single standard solution and auto dilution of over-range samples. The SIPS 20 also automates the preparation of standard additions and spikes (for spike recovery measurements) and can add matrix modifiers and internal standards.

The SIPS 20 is ideal for the analysis of steel samples with complex matrices, as it automates and simplifies the standard addition calibration method. An operator needs to prepare just one bulk standard solution and present it to the right pump of the SIPS 20. The desired additions amounts are entered into the SpectrAA software and the right pump on the SIPS 20 automatically adds the standard to the samples as they are presented. It significantly reduces the manual labour of preparing large batches of samples and improves the analysis efficiency and increases the sample throughput.



How the SIPS accessory works (left) and the accessory mounted on the front of an AA instrument (right).



**Table 1.** The instrument settings for the analysis.

Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Oxidant gas/gas	Oxidant flow (L/min)	Acetylene flow (L/min)
Co	240.7	0.2	7.0	Air/Acetylene	13.5	2.0
Mn	403.1	0.2	5.0	Air/Acetylene	13.5	2.0
Ni	352.5	0.2	4.0	Air/Acetylene	13.5	2.0
Cr	429.0	0.5	7.0	Nitrous oxide/ Acetylene	11.0	6.6
Mo	313.3	0.5	7.0	Nitrous oxide/ Acetylene	11.0	7.6

### Sample preparation

0.1000 g of two reference steel samples; NIST-348a and BCS-336 was accurately weighed into a digestion vessel. 2 mL of HCl and 1 mL of HNO<sub>3</sub> was added, and the reaction proceeded to take place. After approximately 10 minutes, when the reaction was complete, 2 mL of perchloric acid was added and the sample heated on a hot plate until white smoke was generated. The solution was then diluted to 100 mL with distilled water.

Molybdenum can experience interferences from the high concentration of Iron (Fe) in steels, it was therefore necessary to add 0.5% AlCl<sub>3</sub> to remove the interference.

### Instrument setup

Table 1 lists the instrument operation parameters. The analysis used the default gas flows as provided in the SpectrAA instrument software.

### Result accuracy

Recoveries of the measured values were within ±10% of the certified values, as shown in Table 2. Compared with the conventional standard addition method, the SIPS accessory removed most of the solution preparation work, improving analytical efficiency.

In this example, the use of the SIPS 20 accessory enabled automated inline standard addition, saving manual dilution and other tedious work required by the conventional standard addition method, resulting in a much higher analytical efficiency.

**Table 2.** Measured concentration versus the certified concentration of two of reference steel samples.

Element	NIST-348a Measured value (%)	NIST-348a Certified value (%)	Recovery (%)	BCS-336 Measured value (%)	BCS-336 Certified value (%)	Recovery (%)
Co	0.15	0.15	100%	0.069	0.063	109%
Mn	0.62	0.64	97%	0.77	0.81	95%
Ni	23.2	24.2	96%	9.36	9.48	99%
Cr	14.0	14.8	95%	17.0	17.6	96%
Mo	1.15	1.18	97%	2.25	2.43	93%

# Measurement of Multiple Heavy Metals in Plating Wastewater Using Flame AAS



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**Figure 1.** A SIPS accessory, fitted to the front of an Agilent AA 240FS flame atomic absorption spectrometer.

## Complying with environmental standards

Metal plating is a process that uses electrochemical methods to treat material surfaces. As the process varies with the material to be plated, the pollutants in the liquid waste, and their concentrations, vary considerably. Plating wastewater is generally complex in composition, often containing elements such as Cr, Cd, Pb, Cu, Zn, and Ni.

Plating companies must comply with environmental standards for discharges from their facilities. These standards for wastewater include the Integrated Wastewater Discharge Standard (GB 8978-2002), Emission Standard of Pollutants for Electroplating (GB 21900-2008) and others. These standards require the concentration of these elements to be within the range of 0.1–2.0 mg/L. This concentration makes the analysis suitable for flame AAS or by ICP-OES. AAS instruments are popular due to their low capital cost and low running costs. However, analysts working in the plating industry or those in labs providing discharge sample testing, face a large number of samples containing varying concentrations of elements, complex test requirements and a heavy workload. Conventional AAS is slow as each sample must be measured multiple times, once for each element.

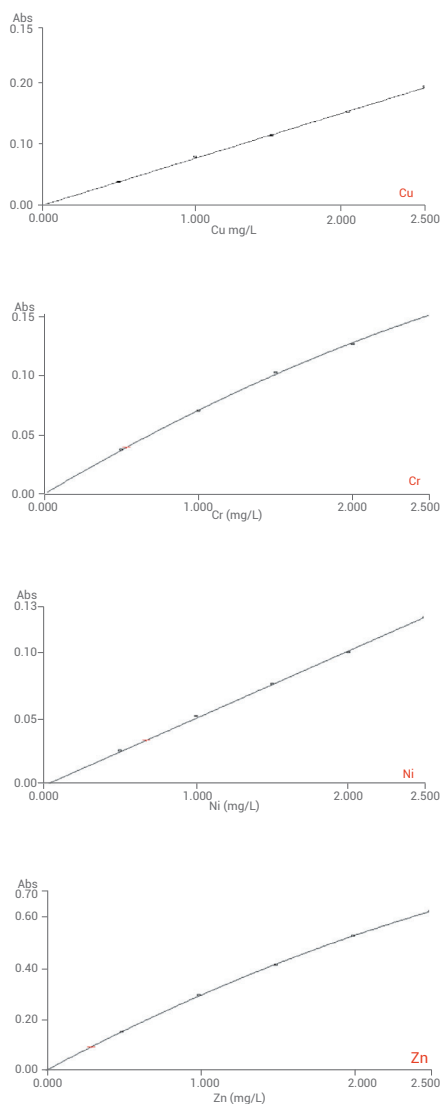
The Agilent AA 240FS flame atomic absorption spectrometer enables rapid sequential analysis of multiple elements in a single sample aspiration. The Agilent Sample Introduction Pump System (SIPS) accessory provides automation for flame AA analysis, increasing sample throughput, simplifying sample preparation and instrument operation. The accessory is available in a single pump version (SIPS 10) and a dual pump version (SIPS 20). The SIPS 20 enables automatic preparation of standard solutions from a single standard solution and auto dilution of over-range samples. The SIPS 20 also automates the injection of standard additions and spikes (for spike recovery measurements) and can add matrix modifiers and internal standards.

## Analysis of four elements in a certified reference material

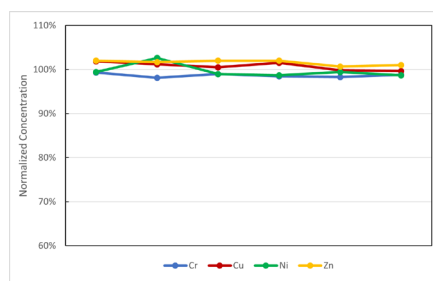
In this study, an Agilent 240FS instrument, fitted with a SIPS 20 accessory, was used to determine the concentrations of Cr, Cu, Ni and Zn in samples of a mixed water certified reference material 200931 (Institute of Reference Materials, China Ministry of Environmental Protection) and real plating bath waste water discharge samples. The samples were evaluated in accordance with the requirements of the measurement standards: Integrated Wastewater Discharge Standard (GB 8978-2002) and Emission Standard of Pollutants for Electroplating (GB 21900-2008). Table 1 summarizes the instrument settings used for the analysis.

**Table 1.** Instrument settings for the determination of the four elements.

Test item	Air flow (L/min)	Acetylene flow (L/min)	Characteristic wavelength (nm)	Slit width (nm)	Lamp current (mA)
Cr	13.5	3.3	357.9	0.2	7.0
Cu	13.5	2.0	324.8	0.5	4.0
Ni	13.5	2.1	232.0	0.2	4.0
Zn	13.5	2.0	213.9	1.0	5.0



**Figure 2.** Standard curves for the four elements show excellent linearity (the highest concentration point of each element is 2.5 mg/L).



**Figure 3.** Short term precision of six measurements, with %RSDs for all elements between 0.5 and 1.5%.

The standards were prepared by the SIPS 20 accessory from one multielement stock solution and used to create a calibration curve for each element. All calibrations had excellent linearity, as shown in Figure 2 and the correlation coefficients in Table 2.

**Table 2.** Correlation coefficients for each calibration curve.

Element	Correlation Coefficient ( $r^2$ )
Cr	0.9999
Cu	0.9998
Ni	0.9996
Zn	1.0000

### Sample analysis

The results from the analysis of the Mixed Water 200931 CRM as well as the plating bath waste water samples are shown in Table 3. The concentrations of the four elements were determined sequentially in a single aspiration, providing high analytical efficiency. The sample results showed excellent accuracy, with all four elements for the CRM recovered within  $\pm 2\%$ . The plating wastewater sample was measured, as received, for the four elements Cr, Cu, Ni and Zn. A spike recovery test (1.5 mg/L spike) on the sample was performed to ensure the accuracy of the method. Recovery rates for the plating wastewater samples were between 91-99% demonstrating the suitability of the 240FS and SIPS 20 when analyzing real wastewater samples. A precision of 0.45%–1.52%, met the QC requirements of the wastewater standard. The method showed many advantages such as fast analysis, excellent repeatability, and low cost.

**Table 3.** Sample measurement results.

	200931 CRM			Plating Wastewater Sample		
	Certified Value (mg/L)	Measured Value (mg/L)	Recovery	Measured Value (mg/L)	Measured Spike (mg/L)	Spike Recovery
Cr	0.590	0.582	99%	0.06	1.42	91%
Cu	0.591	0.596	101%	0.12	1.55	95%
Ni	0.681	0.679	100%	0.08	1.49	94%
Zn	0.297	0.302	98%	0.31	1.79	99%

Multiple analyses of the mixed water CRM were performed to investigate the precision over time. Figure 3 shows the short term precision of six measurements, with %RSDs for all elements between 0.5 and 1.5%, demonstrating excellent repeatability.

It took less than one minute to measure all four elements in a sample. The method showed many advantages; fast, high efficiency analysis, excellent repeatability and low cost, making the Agilent 240FS instrument, fitted with a SIPS accessory, ideal for monitoring of multiple heavy metal elements in plating wastewater.

# Determination of Multiple Elements in Aquatic Products Using a Graphite Furnace Atomic Absorption Spectroscopy



## Monitoring pollutants in ecosystems

The measurement of heavy metals in fish and other seafood is required to monitor the presence of contaminants in the ecosystem as well as prior to consumption. Seafood products have a complex, salty composition. This complex matrix causes significant matrix effects when analyzing samples with a graphite furnace AA system (GFAAS), requiring accurate background correction.

In this study, Pb, Cd, Cu, Co, and Ni were measured in two standard reference materials: Tort 2 Lobster pancreas and CRM No 278R Mussel tissue. To optimize the analytical signal and remove chemical interferences, two matrix modifiers were used.

## Removing matrix effects and automating standard and sample preparation

The samples were frozen and then dried and homogenized. 10 mg of the dried sample was added to 100  $\mu\text{L}$  of nitric acid. The mixture was placed in a closed vessel and digested at 80  $^{\circ}\text{C}$  for 3 hours, prior to cooling and diluting with ultra-pure water to bring the volume to 2 mL. The concentration of nitric acid in the sample solution was about 3% after the dilution.

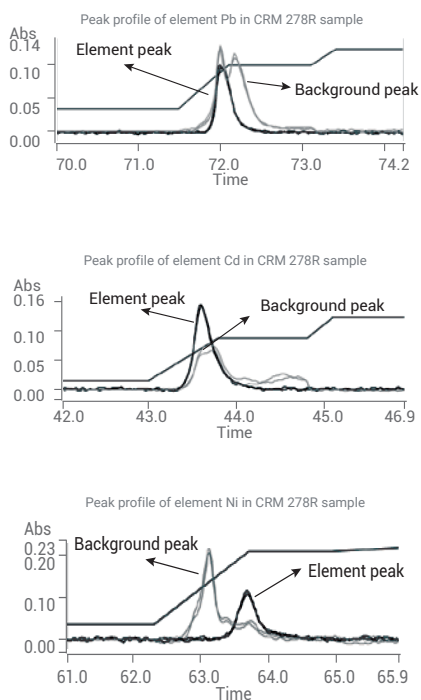
An Agilent 240Z graphite furnace AA system with Transverse Zeeman Background Correction technology was used for the analysis, with the conditions shown in Table 1. The longitudinally heated graphite furnace with the Constant Temperature Zone (CTZ) design creates a constant temperature in the graphite tube, providing uniform heating of the sample. The transverse AC modulated Zeeman background correction applies a uniform magnetic field across the atomizer, correcting the background absorption caused by complex samples.

The Agilent 240Z includes the PSD 120 autosampler, a standard feature on all Agilent GFAAS instruments. The PSD 120 can accurately prepare calibration standards and perform sample preparations including modifier addition and sample dilution. The operator simply prepares a single stock standard of the highest standard concentration, and the PSD 120 will automatically prepare the other standards to create a calibration curve. The PSD 120 can also automatically dilute overrange samples and present them for repeat analysis.

## Result accuracy

Table 2 compares the measured concentrations with the certified concentrations supplied with the reference materials. The measured concentrations showed a high level of accuracy, being within  $\pm 10\%$  of the certified values.

Figure 1 shows the signal from three of the analyte elements; Pb, Cd, and Ni in the mussel tissue sample. The complex matrix of seafood samples results in a large background signal (grey line). This background varies for each analyte at the different wavelengths and the different ash and atomization temperatures used. The Agilent 240Z using the transverse Zeeman background correction is able to correct this large background signal across the full wavelength range. The analyte peak (black line) shows the high sensitivity performance of the 240Z achieved using the CTZ with furnace optimized geometry



**Figure 1.** Peak signals for Pb, Cd and Ni in CRM 278R Mussel Tissue.

Figure 2 shows the calibration curves for Pb, Cd and Ni, which were all prepared from a single bulk standard by the PSD 120 autosampler. Each calibration shows a high degree of linearity.

The results from about multiple replicate runs (as indicated in Table 2) were stable and reliable. The method is applicable to the determination of trace heavy metals in complex matrices such as aquatic products. As a minimal amount of sample was required for the preparation procedure, the method is very suitable for applications such as the monitoring of heavy metals in biological samples with a small portions of samples.

**Table 1.** Instrument conditions.

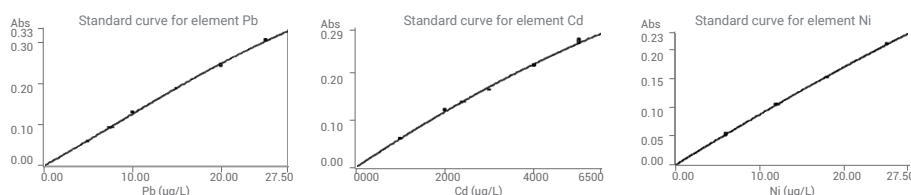
	Cd	Cu	Pb	Co	Ni	Cr
Wavelength (nm)	228.8	327.4	283.3	242.5	232.0	357.9
Lamp current (mA)	4.0	4.0	10.0	7.0	4.0	7.0
Slit width (nm)	0.5	0.5	0.5	0.2	0.2	0.2
Sample volume (µL)	5	10	20	40	20	10
Modifier 1* (µL)	5	-	5	-	8	5
Modifier 2** (µL)	5	-	5	-	4	5

Notes: Modifier 1: 0.4 mg/mL Pd(NO<sub>3</sub>)<sub>2</sub>  
 Modifier 2: 2 g/L Mg(NO<sub>3</sub>)<sub>2</sub>

**Table 2.** The certified concentrations and the measured concentrations of the two seafood reference materials.

Element	Tort-2 Certified value (mg/kg)	Tort-2 Measured value (mg/kg)	n*	Recovery (%)	CRM 278R Certified value (mg/kg)	278R Measured value (mg/kg)	n	Recovery (%)
Cd	26.7±0.6	25.7±0.92	45	96	0.348±0.007	0.31±0.01	54	90
Cu	106±10	109±4	50	103	9.45±0.13	9.1±0.4	53	96
Pb	0.35±0.13	0.36±0.04	47	103	2.00±0.04	1.8±0.1	51	91
Co	0.51±0.09	0.55±0.02	49	107	n/a	0.34±0.01	56	n/a
Ni	2.5±0.19	2.30±0.05	49	92	n/a	0.94±0.04	52	n/a

Notes: n: number of replicate runs



**Figure 2.** Calibration curves for Pb, Cd and Ni prepared using the PSD 120 autosampler.

# Analysis of Pb and Cr in Soil using Graphite Furnace Atomic Absorption Spectrometry



## Heavy metal pollution

Heavy metal pollution is a serious environmental problem. Heavy metals enter soil through wastes, irrigation water, air pollution, and settling of airborne particles. By migrating and accumulating in crop products, they can work their way through the food chain.

The major heavy metal pollutants, lead (Pb) and chromium (Cr) are required to be quantified in soil during annual monitoring in China. The limits of these two elements in soil is strictly specified in the environmental standards for soil.

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## Quantifying Cr in soil

The large number of soil samples to be measured and the importance of accurate results drives the need for a simple, precise, and reliable analysis method. The determination of Cr in soil is often conducted by diphenylcarbazide spectrophotometry, flame atomic absorption spectrophotometry, inductively coupled plasma atomic emission spectrometry, or inductively coupled plasma mass spectrometry. The first two methods are the standard methods in China and the United States for determining Cr in soil.

Flame atomic absorption spectrophotometry is characterized by simple, easy, and fast operation, and is a standard method widely applied in the determination of Cr in soil. However, this method requires high flame temperature, leading to serious interference. Ammonium chloride can be added to eliminate such interference, resulting in relatively low measured values for Cr. Graphite furnace atomic absorption spectroscopy (GFAAS) features high atomization temperature and high sensitivity. This method has become a standard method for the determination of Cr in food, aquatic products, and drinking water. The determination of Cr in soil and other media using the graphite furnace technique is specified in US EPA Method 7010. So far, China has not yet established a standard method for the determination of Cr in soil by graphite furnace atomic absorption method.

## Quantifying Pb in soil

Graphite furnace atomic absorption spectrophotometry is commonly used to measure trace levels of Pb in soil. However, the analysis by graphite furnace atomic absorption often suffers from heavy interference due to background absorption caused by the complex composition of the soil matrix. This high background introduces error into measurements.

Agilent 280Z AA graphite furnace atomic absorption spectrometer was used to determine the Pb content in the soil. During the detection, the Zeeman background correction was applied to remove the background interference from the soil matrix and measure accurately the response for Pb in the soil samples.

This study aimed to establish a method for the determination of Cr in soil using GFAAS, which may fill the gap in existing standards. The study also aimed to improve the analysis of Pb in soil by addressing the matrix interference problems.

## Analyses of Pb and Cr

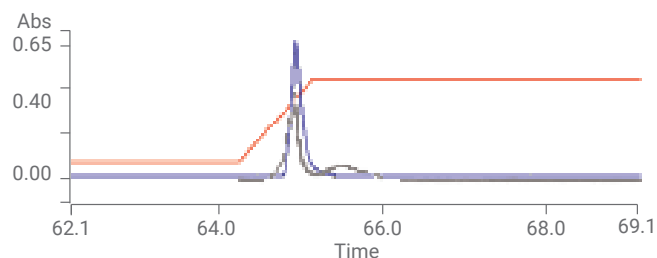
In this study, a nitric acid–hydrogen peroxide–hydrofluoric acid mixture was used for the microwave digestion of a Chinese certified reference material of soil (GBW07409), followed by acid removal, and analysis on Agilent 280Z graphite furnace atomic absorption spectrometer, using the conditions listed in Table 1.

The samples were all injected into the graphite tube using the PSD 120 autosampler. The solution injection was monitored by the HD Tube-CAM that provides real time viewing of the samples throughout the analysis, important to control the drying and ashing steps. 20 g/L ammonium dihydrogenphosphate was used as the matrix modifier, which removed a large amount of organic matrix during the ashing process, and optimized the ashing temperature of Pb and Cr. The Agilent Zeeman background correction was applied to separate the Pb analytical signal from the background adsorption that couldn't be removed using modifiers. Optimum analytical conditions were found using the Surface

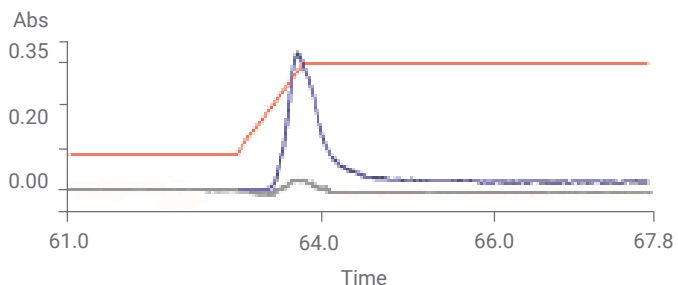
Response Methodology tool in the SpectrAA software supplied with the Agilent 280Z. The tool finds the optimal relationship between the ashing temperature, atomization temperature and analyte absorbance. Figure 1 shows the a signal profile of the Pb peak, displaying the high sensitivity response for Pb (blue line) with freedom from the significant background interferences (gray line) that occur in soil samples.

The spectra of Cr in the sample are shown in Figure 2, which too shows high sensitivity and freedom from interferences.

The measured concentrations, compared to the certified Pb and Cr concentrations for the sample are shown in Table 2. The measured results were within  $\pm 10\%$  of the certified values. These results show the effectiveness of the Agilent Zeeman background correction and the importance of an optimized furnace method.



**Figure 1.** The signal generated by total Pb in 10  $\mu\text{L}$  of the digest of reference soil material GBW07409 on Agilent 280Z graphite furnace atomic absorption spectrometer.



**Figure 2.** The signal generated by total Cr in 10  $\mu\text{L}$  of the digest of reference soil material GBW07409 on Agilent 280Z graphite furnace atomic absorption spectrometer.

**Table 1.** Instrument conditions and temperature program.

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Drying temperature ( $^{\circ}\text{C}$ )/Time (s)	Ashing temperature ( $^{\circ}\text{C}$ )/Time (s)	Atomization temperature ( $^{\circ}\text{C}$ )/Time (s)	Temp during interference elimination ( $^{\circ}\text{C}$ )/Time (s)	Argon flow rate ( $\text{mL}\cdot\text{min}^{-1}$ )	Injection volume ( $\mu\text{L}$ )
Pb	283.3	0.5	8.0	85–120/55	600/9.2	2100/2.9	2100/2	300	10
Cr	429.0	0.5	7.0	85–120/55	1000/8	2600/2.8	2600/2	300	10

**Table 2.** Analytical results of national certified reference material of soil (GBW07409).

Element	Certified value (mg/kg)	Mean measured value (mg/kg)	Recovery (%)
Pb	16.3±2.4	17.5	107
Cr	26.4±2.1	25.0	95

The results show the high sensitivity and accuracy of the method. The results also demonstrate that the Agilent 280Z graphite furnace atomic absorption spectrometer is capable of accurately quantifying samples with volumes as low as 10 µL. This method is able to complete the detection of one element in 3 minutes, which meets the needs of typical soil laboratories.

The analytical conditions developed with Surface Response Methodology tool and Tube-Cam feature provide the correct furnace method with the optimal drying, ashing, and atomization temperatures. This optimization ensures high sensitivity, high accuracy, and high reproducibility of analysis. The strong elimination of matrix interferences by Zeeman background correction makes Agilent 280Z graphite furnace system ideal for determining Pb and Cr in complex soil matrices. The instrument serves as a reliable and secure monitoring technology that supports the prevention and controlling efforts against soil pollution and helps make solid progresses in soil treatment and remediation.



# Determination of Pb and Cd in *Porphyra tenera* using Microwave Digestion and Graphite Furnace Atomic Absorption Spectrometry



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## Measuring the impacts of offshore pollution

Urban industries are developing fast in China, especially the accelerated offshore deployment of heavy chemical industries, as well as petroleum and mining industries. These industries can discharge waste water and waste residues containing a large amount of heavy metals into the ocean, exacerbating marine pollution, especially in offshore waters.

*Porphyra tenera* is a type of algae that grows on offshore rocks. It contains abundant iodine, multiple vitamins, and microelements. Apart from being edible, it is also used in Chinese traditional medicine.

However, offshore pollution has caused serious threats to the *porphyra tenera* farming industry in recent years. Measuring the concentration of some elements in *porphyra tenera* is useful to evaluate the level of heavy metal pollution and the nutrient value of *porphyra tenera*.

Commonly used methods for detecting Pb and Cd in food include atomic absorption spectrometry (AAS), spectrophotometry–colorimetry, and inductively coupled plasma mass spectrometry (ICP-MS).

Graphite furnace atomic absorption spectrometry (GFAAS) has advantages of high precision and sensitivity in instrument detection, low detection limits, and using low sample volumes. GFAAS instruments are also relatively low cost.

When analyzing dehydrated marine products such as *porphyra tenera*, high levels of microelements and heavy metal elements can interfere with signal of the target elements. This interference results in large deviations in results.

The Agilent AA 280Z graphite furnace atomic absorption spectrometer features Zeeman background correction, which can correct for structured backgrounds and spectral interferences over the full wavelength range. The instrument can also add matrix modifiers online, which change the matrix composition of a sample. Modifiers can be used to adjust the volatility of the target elements to lower interferences, or to convert those elements to different chemical forms, thereby separating the background signal from the atomic absorption signals of the target elements. For complex matrices, matrix modifiers can be used to enhance the atomic absorption signal and reduce the background signal during the atomization stage.

In this study, samples of a certified reference material (GBW08521) were prepared using microwave digestion before graphite furnace atomic absorption method was used to determine the concentration of lead (Pb) and cadmium (Cd). The study aimed to determine if GFAAS can perform stable and accurate assay of elements in complex matrix food samples such as *porphyra tenera*.

## Sample preparation

0.500 g of the sample was weighed into a microwave digestion vessel into which 5 mL of nitric acid was then added. The sample was digested according to the microwave digestion procedure under following conditions:

1. Heating to 120 °C in 5 min hold for 5 min;
2. Heating to 160 °C in 5 min hold for 10 min;
3. Heating to 180 °C in 5 min hold for 10 min.

The digestion vessel was removed after cooling, placed on an electric hotplate and heated to 140–160 °C until the sample was nearly dry, removing the acid. The digest was transferred to a 50 mL volumetric flask. The digestion vessel was rinsed 2 to 3 times with a small amount of water. The rinse solutions were then combined in the volumetric flask. The flask was then filled up to the mark with ultra pure water, and the solutions were well mixed for later use. A reagent blank was also prepared.

## Standard curves

The Agilent AA 280Z Graphite Furnace Atomic Absorption spectrometer can automatically prepare multiple standard solutions from a single bulk concentration stock solution. Stock solutions of Pb and Cd (50 µg/L and 5.0 µg/L, respectively) were prepared using China national standard solutions of Pb and Cd. Ultra pure water was then used to prepare all the standards at the concentrations shown in Table 2.

Zeeman background correction mode was used to remove spectral interferences. 5 µL of palladium nitrate was introduced as the matrix modifier with the sample solution.

The instrument operating conditions shown in Table 1 were used.

**Table 1.** Instrument operating conditions.

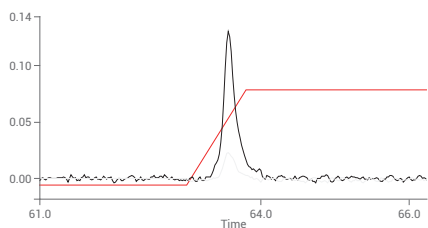
Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Integration method	Ashing temperature (°C)	Atomization temperature (°C)
Pb	283.3	0.5	10	Peak area	600	2300
Cd	228.8	0.5	5	Peak area	500	2000

Analysis results of the standards can be seen in Table 3.

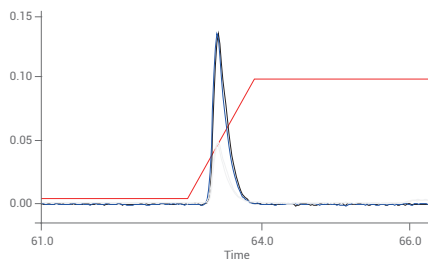
**Table 2.** Concentrations of standards (µg/L) and linearity of the calibration curves.

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Correlation coefficient
Pb	5.0	10	20	40	50	0.9998
Cd	0.5	1.0	2.0	4.0	5.0	0.9993

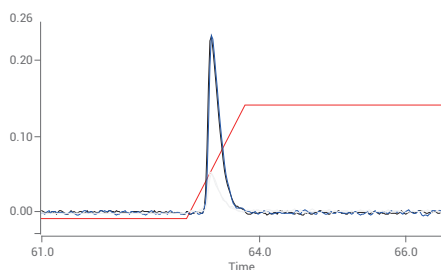
The peak signal of the *porphyra tenera* samples were consistent with those of the standard solutions, and the absorbance of replicates had a relative standard deviation of less than 1%, indicating that the method is effective in controlling and reducing interferences. The results are shown in Figures 1 to 4.



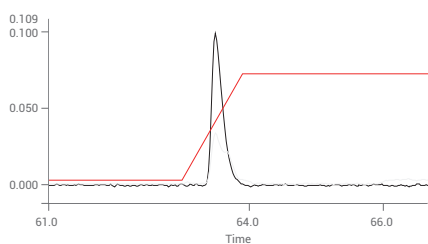
**Figure 1.** Measured signal of Pb standard solution.



**Figure 2.** Measured signal of Cd standard solutions.



**Figure 3.** Measured signal of Pb in *Porphyra tenera* samples.



**Figure 4.** Measured signal of Cd in *Porphyra tenera* samples.

### Precision and accuracy

Ten samples of the *porphyra tenera* reference material (0.500 g each) were accurately weighed, digested, and analyzed. The relative standard deviation (%RSD) of the measurement of these replicate samples was then calculated, see Table 4.

**Table 4.** Precision and recovery (n = 6).

Element	Measured Value (mg/kg)	RSD (%)	Certified Value (mg/kg)	Mean Recovery (%)
Pb	0.78	1.35	0.81	96.3
Cd	5.1	0.48	5.2	98.0

### Method suitability

The study results demonstrate that the Agilent 280Z method is able to effectively measure elements in complex dehydrated matrices using Zeeman background correction. The results of the national certified reference materials demonstrate high precision and accuracy, making the method suitable for monitoring coastal marine ecosystems as well as the quality and safety of *porphyra tenera* products.

# Determination of Cd, Cr, Ni and Pb in Grains using Zeeman Graphite Furnace Atomic Absorption Spectroscopy



## Measuring trace levels of elements in food

Trace elemental analysis of foods is essential to ensure that products are suitable for consumption. Accurate low-level determination of metals is especially important for foods that are consumed on a regular basis, such as grain products like wheat and rice. Analysis of elements such as Pb, Cd, Cr and Ni is important for ensuring product quality. When trace element analysis is required, a high sensitivity technique such as graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction is often used. This technique offers high sensitivity, low running costs, and accurate correction for complex backgrounds. GFAAS is specified in procedures set out in four Chinese National Methods relating to the determination of Pb, Cd, Cr and Ni in many food products.

The Agilent 280Z GFAAS with Zeeman background correction offers some key features for determining trace elements in food products such as grains, including:

- High sensitivity: Combining an Agilent GTA 120 Graphite Tube Atomizer with the 280Z GFAAS and Agilent UltrAA hollow cathode lamps improves the signal-to-noise ratio, ensuring high sensitivity and low detection limits.
- Reduced running costs: The GTA 120 offers outstanding furnace performance and low running costs. The fast heating and short run time of the GTA 120 requires less argon, and extends tube lifetime.
- Increased accuracy: Agilent UltrAA lamps reduce baseline noise and produce high, sharp emission intensities, resulting in excellent calibration linearity. Zeeman background correction handles the spectral interferences and high background absorbances associated with complex samples.
- Ease-of-use: The Agilent PSD 120 autosampler automates standard preparation, standard additions, and dilution of overrange samples. Accurate volumes are delivered to the furnace and, when coupled to pre-emptive sampling, optimum analysis times are achieved.

## Analysis example

Two wheat flour samples were analyzed in accordance with Chinese methods: GB Method 5009.12–2010 for Pb, GB 5009.15–2014 for Cd, GB 5009.123–2014 for Cr, and GB 5009.138–2003 for Ni.

Three replicate digests of the wheat flour standard reference materials (SRMs) were measured. The results were in good agreement with the certified values, confirming the accuracy of the method. The results are shown in Table 1.

**Table 1.** Results for the analysis of NIST 1567b Wheat Flour (Pb and Cd) and DUWF-1 (Cr and Ni) Durum Wheat Flour by GFAAS.

Element	MDL* (n=7) (ppb)	Certified Value (ppb)	Measured Value (mean, n=3) (ppb)	Standard Deviation (ppb)	Recovery (%)
Pb	2.6	10.4 ± 2.4	10.9	1.4	105
Cd	0.37	25.4 ± 0.9	23.4	0.22	92
Cr	1.5	23.0 ± 9.0	21.5	2.1	93
Ni	6.0	170 ± 80	172	7.5	101

\*Method Detection Limit (MDL) based on 10 µL sample and 0.3, 0.05, 0.1, and 0.5 ppb standard solution for Pb, Cd, Cr, and Ni, respectively, for each of the GB methods tested.

## Calibration and stability

A representative calibration curve is shown in Figure 1. All elements displayed excellent calibrations with correlation coefficients greater than 0.999. A 5 ppb Pb standard was analyzed periodically over 7 hours to determine the long-term stability of the instrument (Figure 2).

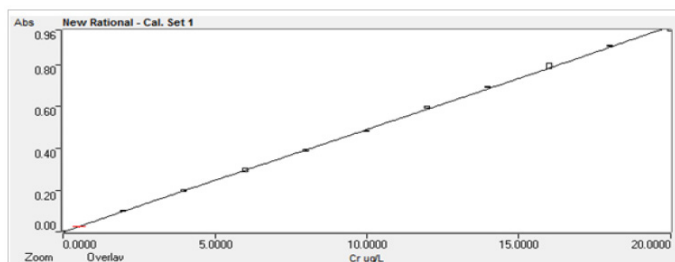
## Results

The results of the analysis demonstrate:

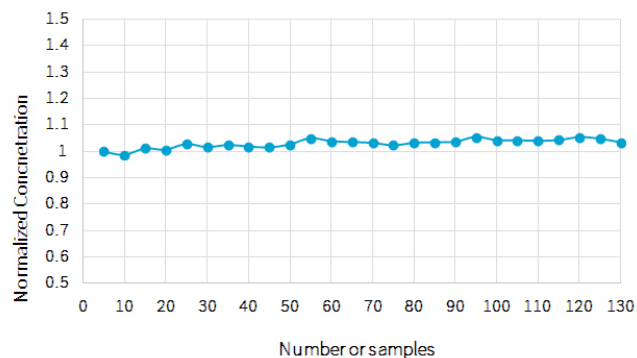
- Outstanding performance of the 280Z Graphite Furnace AA spectrometer, fitted with a GTA 120 atomizer. The method delivered good accuracy and precision of target analytical values for Pb, Cd, Cr, and Ni.
- The method detection limits exceeded the values specified in the GB methods.
- Excellent linearity was achieved across the calibration range for Pb, Cd, Cr, and Ni. All standards were automatically prepared using the PSD 120 sample preparation system.
- Excellent long-term stability, with 1.6% RSD over a 7-hour period and only 4% recovery deviation from the initial reading.

## Download the full application note

[Determination of Pb, Cd, Cr and Ni in Grains Based on Four Chinese National Methods via Zeeman GFAAS](#), Agilent publication number 5991-8144EN.

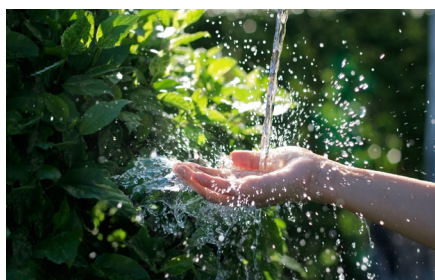


**Figure 1.** Calibration curve for Pb from 0 to 20 µg/L. All standards were prepared by the PSD 120 sample preparation system.



**Figure 2.** Long-term stability plot for a 5 ppb Pb standard measured periodically during the analysis of a wheat flour digest run over a 7-hour period.

# Measuring As in Water Utilizing GFAAS with Intelligent Optimization of Analysis Parameters



## As analysis using graphite furnace AAS

Arsenic is introduced into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition. In 2011, the [World Health Organisation \(WHO\) set the guideline value for arsenic in drinking water at 10 µg/L](#).

With its great sensitivity, graphite furnace atomic absorption spectroscopy (GFAAS) is a cost-effective technique for such analysis. The Agilent 240Z and 280Z instruments simplify graphite furnace method implementation through intelligent ashing and atomization optimizations. The instruments also feature the Stabilized Temperature Platform Furnace (STPF) concept. The instruments' Tube-CAM furnace-viewing camera can be used to control the injection and dry steps of the measurement. The SRM Wizard, an integrated feature of the instrument software, can [automatically determine the best ash and atomize temperatures](#).

## Example analysis

In this study, a standard reference material: NIST 1640a was analyzed to determine the concentration of As.

Furnace measurements were performed using an Agilent 240Z GFAAS with transverse Zeeman background correction. The instrument features the highly sensitive and accurate Agilent GTA 120 Graphite Tube Atomizer and an Agilent PSD 120 Programmable Sample Dispenser autosampler. Instrument settings are shown in Table 1.

A single stock solution of 50 µg/L As was presented to the PSD 120 autosampler, which automatically prepared multiple standard solutions to create a calibration curve.

The 240Z GFAAS utilizes the Zeeman effect, with longitudinal graphite tube heating and a Constant Temperature Zone (CTZ) design.

Atomization for arsenic was from a pyrolytic platform Omega tube. The inert gas used was 99.99% pure argon.

**Table 1.** Instrument operation conditions.

Parameter	Setting
Lamp	UltrAA Lamp Arsenic (Part no. 5610108100)
Graphite Tube Platform	Omega Platform (Part No. 6310003700)
Wavelength	193.7 nm
Slit Width	0.5 nm
Lamp Current	10 mA
Mode	Peak Area

## Method optimization

The furnace drying steps were optimized by using the integrated camera (Figure 1). Ash and atomize temperatures were optimized by a chemometric method included in the instrument software (the Surface Response Methodology tool). Tests were performed on a standard and on a spiked water sample. All measurements were made using the Peak Area calculation.



Figure 1. The view inside the tube, using the integrated camera.



Figure 3. The optional fume extraction accessory includes an LED lighted mirror to provide a clear view of the graphite tube injection hole. Alignment of the autosampler capillary is worry-free while the exhaust system removes ashing vapors at their source. The extraction accessory provides flexibility of the furnace placement eliminating the need for direct position under the exhaust fan.

Based on the results of the chemometric analysis, the Surface Response Methodology tool determined the optimum conditions, shown in Tables 2 and 3, and Figure 2.

Table 2. SRM, experimental design factors.

Step	Temperature (°C)	Step (°C)
Ash	1000	250
Atomization	2400	250

Table 3. The optimum conditions determined for the standard and sample were very similar, indicating that the modifier mix was ideally suited for the application.

Temperature	Standard	Sample
Ash (°C)	926	952
Atomize (°C)	2448	2497

## Results

- Characteristic concentration in peak area: 0.58 µg/L
- Characteristic Mass in peak area: 18.6 pg
- Method Detection Limit for 20 µL: 0.26 µg/L
- Validated quantification limit for 20 µL: 1.0 µg/L
- % recovery NIST 1640a: 100.4 % (certified concentration of As was 8.075 ± 0.070 µg/L)
- % recovery bottled water spiked with 10.0 µg/L: 102.4 %

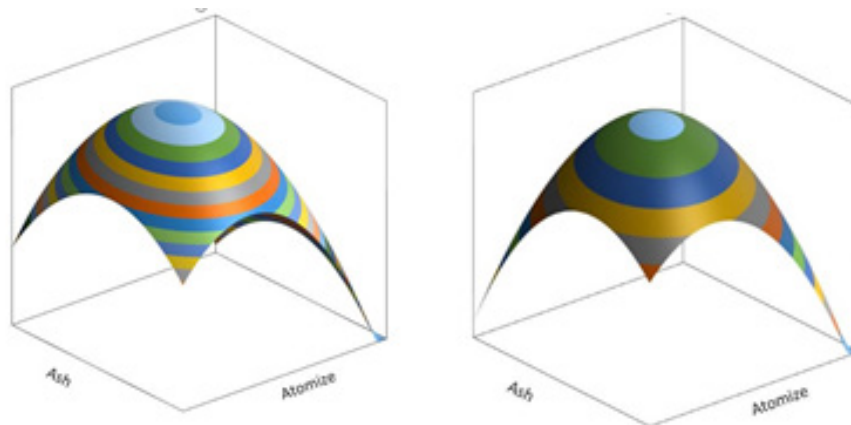


Figure 2. The Surface Response Methodology tool in the software uses chemometrics to automatically optimize the ash and atomize temperatures. Shown here is the plot for the standard reference material (left) and the spiked sample (right).

## Method suitability

The arsenic in drinking water method, applicable for a wide range of worldwide standards, was optimized automatically on the Agilent 240Z GFAA system. The method exceeded the required performance for detection limits and accuracy.

The Agilent 240Z instrument has local fume extraction, a LED lighted injection hole, Tube-Cam, and an SRM optimization wizard, delivering ease of use and method optimization.

# Measuring Cd in Water Using GFAAS with Intelligent Optimization of Analysis Parameters



## Monitoring Cd contamination

Contamination of drinking water may occur as a result of the presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers and taps. In 2011, [WHO confirmed the guideline value for cadmium in drinking water as 3 µg/L](#). With its high sensitivity, graphite furnace atomic absorption spectroscopy (GFAAS) is an ideal technique for the analysis of trace levels of Cd.

The Agilent 240Z and 280Z instruments simplify graphite furnace method optimization. The instruments feature the Stabilized Temperature Platform Furnace (STPF) concept and Tube-CAM furnace-viewing camera (refer to Figure 1), which can be used to control the injection and dry steps of the measurement. An automated software tool, the SRM Wizard, can [determine the best ash and atomize temperatures](#).

## Example analysis

A standard reference material (SPS-SW1 from LGC Standards), containing  $0.50 \pm 0.01$  µg/L Cd was analyzed using GFAAS. Measurements were performed using an Agilent 240Z GFAAS with transverse Zeeman background correction. The instrument features the highly sensitive and accurate Agilent GTA 120 Graphite Tube Atomizer and an Agilent PSD 120 Programmable Sample Dispenser autosampler. An extraction/LED accessory (refer to Figure 3) removes fumes at source during the furnace operation. It also provides optimum viewing to easily align the capillary with the injection hole. Atomization for cadmium was from a pyrolytic platform Omega tube. The inert gas used was 99.99% pure argon. The instrument conditions used are shown in Table 1.

A single stock solution of 2.50 µg/L Cd was presented to the PSD 120 autosampler, which automatically prepared multiple standard solutions to create a calibration curve. A chemical modifier consisting of 1 mL  $\text{NH}_4\text{H}_2\text{PO}_4$  5 g/L + 0.2 mL  $\text{Mg}(\text{NO}_3)_2$  10 g/L was added to the samples.

**Table 1.** Instrument conditions.

Parameter	Setting
Hollow Cathode Lamp	Cadmium (part no. 5610100800)
Graphite tube platform	Omega (part no. 6310003700)
Wavelength	228.8 nm
Slit Width	0.5 nm
Lamp current	4 mA
Mode	Peak Area

## Method optimization

Sample drying steps were optimized by using the integrated camera (refer to Figure 1). Ash and atomize temperatures were optimized by a chemometric method included in the instrument software, the Surface Response Methodology tool (SRM).



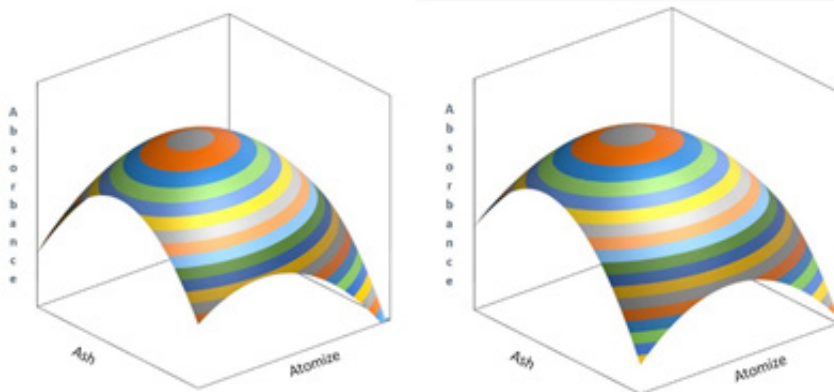


Figure 2. The Surface Response Methodology tool in the software uses chemometrics to automatically optimize the ash and atomize temperatures. Shown here is the plot for the standard reference material (left) and the spiked sample (right).

The standard reference material and on a spiked water sample were measured. All measurements were made using the Peak Area calculation. With the SRM Wizard, only 3 clicks were needed to develop the model and, based on the results of the chemometric analysis, the Surface Response Methodology tool determined the optimum conditions, shown in Tables 2 & 3 and in Figure 2.

Table 2. SRM, experimental design factors.

Step	Temperature (°C)	Step (°C)
Ash	700	200
Atomization	1600	250

Table 3. The optimum conditions determined by SRM for the standard ad sample were very similar, indicating that the modifier mix was ideally suited for the application.

Temperature	Standard	Sample
Ash (°C)	570	568
Atomize (°C)	1533	1577

## Results

- Characteristic concentration in peak area: 0.035 µg/L.
- Characteristic Mass in peak area: 0.57 pg
- Instrument Detection Limit for 20 µL: 0.011 µg/L
- % recovery SPS-SW1: 98.1 %
- % recovery bottled water spiked with 1.0 µg/L: 101.7 %

## Method suitability

The Agilent 240Z system delivered an excellent recovery and detection limit for cadmium in drinking water, with the method being applicable for a wide range of worldwide standards.

The Tube-Cam and SRM wizard make it easy to determine the appropriate furnace conditions. The system is a cost effective and accurate solution for laboratories routinely performing environmental testing.

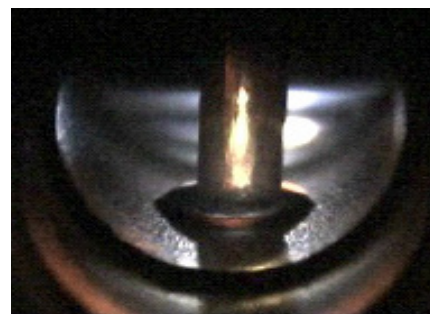


Figure 1. The view inside the tube, using the integrated camera. This shows the probe dispensing the sample into the tube



Figure 3. The optional fume extraction accessory includes an LED lighted mirror to provide a clear view of the graphite tube injection hole. Alignment of the autosampler capillary is worry-free while the exhaust system removes ashing vapors at their source. The extraction accessory provides flexibility of the furnace placement eliminating the need for direct position under the exhaust fan.

# Measuring Pb in Water Using GFAAS with Intelligent Optimization of Analysis Parameters



## Monitoring lead in drinking water

The major sources of human exposure to lead (Pb) are food and drinking water. In 2008, the [World Health Organization released a guideline value of 10 µg/L as the maximum level of lead in drinking water](#). Monitoring the amount of lead in drinking water is a critical function of governments and other organizations around the world.

In order to measure Pb within the limits required by the different regulations, atomic absorption, combined with graphite furnace methods is a popular technique. However, optimization of methods for graphite furnace systems can be difficult, due to the complexity of the atomization process.

The Agilent 240Z and 280Z instruments significantly simplify graphite furnace method implementation through intelligent ashing and atomization optimizations. Furthermore, Agilent AA instruments feature the Stabilized Temperature Platform Furnace (STPF) concept and the instruments' Tube-CAM furnace-viewing camera can be used to control the injection and dry steps of the measurement. The SRM Wizard, an integrated feature of the instrument software, can [automatically determine the best ash and atomize temperatures](#).

## Example analysis

The standard reference material: SPS SW2 (from LGC Standards), containing  $25.0 \pm 0.1$  µg/L Pb was analyzed using graphite furnace atomic absorption spectroscopy (GFAAS). The measurements were performed using an Agilent 240Z Atomic Absorption Spectrometer (AAS) with transverse Zeeman background correction. The instrument features the highly sensitive and accurate Agilent GTA 120 Graphite Tube Atomizer and the Agilent PSD 120 Programmable Sample Dispenser autosampler.

An extraction/LED accessory (see Figure 3) allows for improved fume removal compared to standard ventilation ducts. It also provides optimum viewing to easily align the capillary with the injection hole.

The instrument uses the Zeeman effect, with longitudinal graphite tube heating and a Constant Temperature Zone (CTZ) design for best sensitivity and characteristic masses. Atomization for Lead was from a pyrolytic platform Omega tube. The inert gas used was 99.99% pure argon.

A single stock solution of 50 µg/L Pb was presented to the PSD 120 autosampler, which automatically prepared multiple standard solutions to create a calibration curve.



**Figure 1.** The view inside the tube, using the integrated camera. The probe is dispensing the sample into the tube.

## Instrument Conditions

Table 1 summarizes the analytical conditions, including lamp type, tube type, and instrument parameters.

**Table 1.** Instrument conditions.

Parameter	Setting
Lamp	UltrAA Lamp Pb (Agilent part number 5610108200)
Graphite tube platform	Omega (Agilent part number 6310003700)
Wavelength	283.3 nm
Slit Width	0.5 nm
Lamp current	10 mA
Mode	Peak Area

## Method optimization

Sample drying steps were optimized by using the integrated camera. Optimization of the ash and atomize temperatures (see Figure 1) was done using the using an intelligent chemometric method, included in the instrument software (the Surface Response Methodology tool). Tests were performed on a standard reference material and on a spiked water sample. All measurements were made using the Peak Area calculation.

With the SRM Wizard, only 3 clicks were needed to develop the model. Based on the results of the chemometric analysis, the Surface Response Methodology tool determined the optimum conditions, shown in Tables 2 & 3 and in Figure 2.

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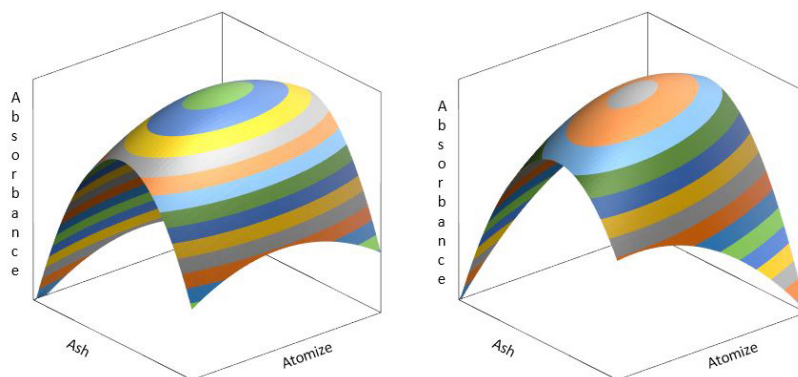
Temperature	Standard	Sample
Ash (°C)	598	614
Atomize (°C)	1435	1476

## Results

- Characteristic concentration in peak area: 0.85 µg/L
- Characteristic Mass in peak area: 13.9 pg
- Instrumental Detection limit for 20 µL: 0.15 µg/L
- % recovery of SRM SPS-SW2: 100.1 %
- % recovery of water spiked with 25 µg/L: 103.6%



**Figure 3.** The optional fume extraction accessory includes an LED lighted mirror to provide a clear view of the graphite tube injection hole. Alignment of the autosampler capillary is worry-free while the exhaust system removes ashing vapors at their source. The extraction accessory provides flexibility of the furnace placement eliminating the need for direct position under the exhaust fan.



**Figure 2.** The Surface Response Methodology software tool uses chemometrics to automatically optimize the ash and atomize temperatures. Shown here is the plot for the standard reference material (left) and the spiked sample (right). The arrows indicate the optimum temperatures.

### Method suitability

The Pb in drinking water method, applicable for a wide range of worldwide standards, was optimized automatically on the Agilent 240Z GFAA system. The method exceeded the required performance for detection limits and accuracy.

The Tube-Cam and SRM wizard make it easy to determine the optimized furnace conditions. The system is a cost effective and accurate solution for laboratories routinely performing environmental testing.

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DE44258.5634837963

© Agilent Technologies, Inc. 2021  
Published in the USA, March 5, 2021  
5994-3118EN

