Determination of Pb, Cd, Cr and Ni in Grains Based on Four Chinese National Methods via Zeeman GFAAS

Application Note

Food Testing

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Introduction

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.

Features such as high sensitivity, low running costs, and accurate correction for complex backgrounds make GFAAS with Zeeman background correction suitable for the determination of trace levels of Pb, Cd, Cr and Ni in grain.

The procedures set out in four Chinese National Methods relate to the determination of Pb, Cd, Cr and Ni in many food products using GFAAS.

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In this study, Pb, Cd, Cr and Ni were determined in the Wheat Flour Standard Reference Materials (SRM) using the Agilent 280Z Zeeman GFAAS. The study was conducted in accordance with the following 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.

Experimental

An Agilent 280Z AAS with transverse Zeeman background correction was used for all measurements to determine Pb, Cd, Cr and Ni in wheat flour. The instrument features the highly sensitive and accurate Agilent GTA 120 Graphite Tube Atomizer (GTA) and an Agilent PSD 120 Programmable Sample Dispenser (PSD) autosampler, as shown in Figure 1. The PSD automatically delivers measured volumes of the sample to the furnace.

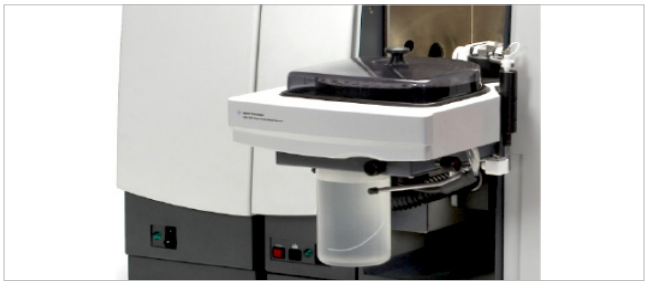

Figure 1. Agilent PSD 120 programmable sample dispenser

The Agilent PSD 120 provides the capacity for up to 135 solutions and performs automatic standard preparation, modifier addition and overrange dilution.

The 280Z AA comprises patented longitudinal graphite tube heating and a Constant Temperature Zone (CTZ) design. In addition to prolonging the graphite tube lifetime, these features provide consistent, uniform heating, which is essential for the accurate low-level determination of complex samples. The Tube-CAM furnace viewing camera, which is standard on the 280Z AA, provides real time viewing inside the graphite tube via the Agilent SpectrAA Software that controls the instrument. Still images and videos can be recorded to set the probe dispensing height and confirm optimum drying conditions, simplifying method development.

For reduced baseline noise and increased sensitivity due to higher emission intensity, a single-element UltrAA hollow cathode lamp light source was used for Pb and Ni. A single-element hollow cathode lamp light source was used for Cd and Cr. For all elements, a partition tube (coated) was used.

Instrument operating conditions are listed in Table 1.

Materials and reagents

The PSD 120 autosampler rinse solution comprised a 0.01 % v/v non-ionic surfactant and 2% v/v of high purity nitric acid. Chemical modifiers were used to reduce matrix interferences and to stabilize analyte signals.

Table 1. Agilent 280Z GFAAS instrument operating conditions.

Parameter	Setting			
Element	Pb	Cd	Cr	Ni
Instrument mode	Absorbance	Absorbance	Absorbance	Absorbance
Calibration mode	Concentration	Concentration	Concentration	Concentration
Measurement mode	Peak height	Peak height	Peak Height	Peak Height
Wavelength (nm)	283.3	228.8	357.9	232.0
Lamp type	UltrAA lamp	Hollow cathode lamp	Hollow cathode lamp	UltrAA Lamp
Lamp current (mA)	10	4	7	7
Slit width (nm)	0.5	0.5	0.2	0.2
Replicates	2	2	2	2
Calibration standards (µg/L)	10, 30, 50	1, 2, 3	2, 4, 8	10, 25, 50
Sample volume (µL)	10	10	10	10
Sample introduction	Auto-mix	Auto-mix	Auto-mix	Auto-mix
Background correction	On	On	On	On
Modifier	Premixed 2000 µg/mL $NH_4H_2PO_4$ + 120 µg/mL $Mg(NO_3)_2$	2000 mg/L $NH_4H_2PO_4$	300 mg/L Pd	150 mg/L Pd
Modifier injection Type	Co injection	Co injection	Co injection	Co injection
Modifier volume (µL)	5	5	5	5

The following reagents were used for the preparation of calibration standard solutions and samples:

- Single element standard solutions for Pb, Cd, Cr and Ni, 1000 mg/L (Agilent);
- Non-ionic surfactant, Trition X-100 surfactant (Agilent);
- Mixed GFAA matrix modifiers:
  - 10 mg/mL ammonium phosphate,
  - 600 µg/mL magnesium nitrate,
  - 10% ammonium phosphate,
  - 1% palladium nitrate (Agilent);
- High-purity nitric acid (Ultrapur, Merck);
- NIST 1567b Wheat Flour SRM,
- NRC-CNRC Durum wheat flour DUWF-1 (NRC-CNRC),
- 18 MΩ de-ionized water prepared using a Milli-Q purification system (Merck Millipore).

Sample preparation

To validate the method for Pb and Cd, NIST 1567b Wheat Flour SRM (Gaithersburg, USA) was prepared for analysis by microwave digestion.

To validate the method for Cr and Ni, NRC-CNRC Durum wheat flour DUWF-1 (NRC-CNRC) was prepared for analysis by wet digestion.

Microwave digestion for Pb and Cd

Digests were prepared in triplicate using a Milestone UltraWAVE Single Reaction Chamber (SRC) microwave digestion system. The system, which serves both as a microwave cavity and reaction vessel, can reach high temperatures. Sealing of the vials was not required since the SRC was pressurized using nitrogen gas at 40 bar. Approximately 1.0 g of the sample was weighed into a quartz reaction vessel. 1 mL of hydrogen peroxide 30% Emsure (Merck) and 5 mL nitric acid 60% Ultrapur (Merck) were added. Each sample was thoroughly mixed using a vortex mixer. The samples were then digested and made up to a volume of 20 mL using 18 MΩ de-ionized water. The temperature program used for the microwave digestion process is shown in Table 2.

Table 2. Parameters used for microwave digestion (where t is the time in minutes, and T1 and T2 are the programmed initial and final vessel temperatures).

Step	t (min)	T1 (°C)	T2 (°C)	Power (W)
1	5.5	Ambient	200	1500
2	4.5	200	200	1500

Wet digestion for Cr and Ni

For preparation of digests for the determination of Cr and Ni, approximately 0.5 g of the sample was weighed into a Pyrex test tube. 1 mL of hydrogen peroxide 30% Emsure (Merck) and 5 mL nitric acid 60% Ultrapur (Merck) were added and thoroughly mixed using a vortex mixer.

The test tubes were placed in a hot block at 80 °C. They were removed when the solution level began to rise. The temperature was increased to 120 °C for 1 hour and the test tubes were covered with a watch glass to allow reflux. Once the temperature had risen to 150 °C, the watch glasses were removed to allow the water to boil off for 1 hour. The digests were made up to a volume of 20 mL using 18 MΩ de-ionized water. Samples were prepared in triplicate.

Calibration standards

Bulk standards of Pb, Cd, Cr and Ni were prepared from 1000 µg/L single element standards. All calibration standards were automatically prepared by the PSD 120 autosampler from 100 µg/L Pb, 5 µg/L Cd, 20 µg/L Cr and 50 µg/L Ni. The bulk standards were matrix matched to 20% HNO_3 to ensure consistency with the acid content of the digested samples.

Results and Discussion

The furnace programs used for the analysis of Pb, Cd, Cr and Ni in wheat flour are given in Table 3. Inert high-purity gas was used throughout all furnace programs. Gas flow rates were the same for all elements and were the default values in the SpectrAA Software.

The Constant Temperature Zone (CTZ) of the GTA 120 graphite tube atomizer allows rapid heating, with a maximum ramp rate of 2000 °C/s. The pre-emptive sampling capabilities of the PSD 120 ensure optimum analysis times as the autosampler proceeds to the next sample while the previous sample is still reading. The combination of these features means that analysis times were significantly decreased without compromising tube lifetime.

To verify the four methods, Pb, Cd, Cr and Ni were analyzed in three replicate digests of a wheat flour SRMs. The results are given in Table 4. The agreement between the certified values and the measured results (average of three runs) confirm the accuracy of the methods.

Table 3. Furnace program for the analysis of Pb, Cd, Cr, and Ni in wheat flour.

Step		Pb		Cd		Cr		Ni		
		Temp (°C)	Time (s)	Temp (°C)	Time (s)	Temp (°C)	Time (s)	Temp (°C)	Time (s)	Read
1	Drying	85	10.0	85	10.0	85	10.0	85	10.0	-
2	Drying	95	25.0	95	25.0	95	25.0	95	30	-
3	Drying	120	5.0	120	5.0	120	5.0	120	5.0	-
4	Ashing	500	5.0	400	5.0	1300	5.0	1200	5.0	-
5	Ashing	500	10.0	400	5.0	1300	5.0	1200	5.0	-
6	Ashing	500	2.0	400	2.0	1300	2.0	1200	2.0	-
7	Atomization	2100	0.8	1800	0.7	2650	0.6	2800	0.8	Yes
8	Atomization	2100	1.0	1800	1.0	2650	1.0	2800	1.0	Yes
9	Clean out	2700	2.0	2300	2.0	2650	2.0	2800	2.0	-

Table 4. Results for analysis of NIST 1567b Wheat Flour (Pb and Cd) and DUWF-1 (Cr and Ni) Durum Wheat Flour by GFAAS.

Element	Certified value (ppb)	Measured value (mean, n=3) (ppb)	Standard deviation (ppb)	Recovery (%)
Pb	10.4 ± 2.4	10.9	1.4	105
Cd	25.4 ± 0.9	23.4	0.22	92
Cr	23.0 ±- 9.0	21.5	2.1	93
Ni	170 ± 80	172	7.5	101

Method detection limits

Method detection limits (MDLs) for each method required only 10 µL of sample and were calculated from 7 replicate analyses of a 0.3 ppb standard solution for Pb, 0.05 ppb standard solution for Cd, 0.1 ppb standard solution for Cr and 0.5 ppb solution for Ni. The absorbance peaks for Pb and Cd are shown in Figures 2 and 3 respectively. The calculated MDLs for Pb, Cd, Cr and Ni and the required MDLs specified in 5009.12—2010, GB 5009.15—2014, GB 5009.123—2014 and GB 5009. 138—2003 are given in Table 5. The MDLs for both elements obtained using the Agilent 280Z Zeeman GFAAS are lower than the MDLs specified in the GB methods.

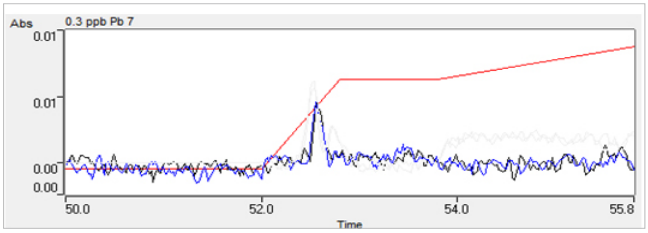

Figure 2. Absorbance peak from the measurement a 0.3 ppb Pb standard solution

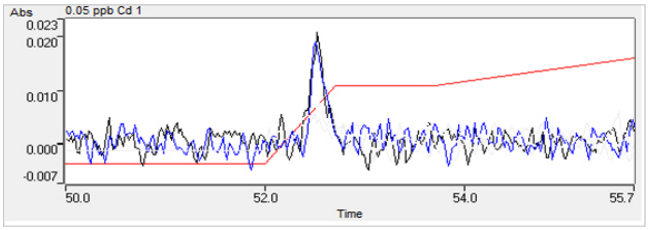

Figure 3. Absorbance peak from the measurement of a 0.05 ppb Cd standard solution

Table 5. MDLs acquired per GB 5009.12—2010, GB 5009.15—2014, GB 5009.123—2014 and GB 5009. 138—2003 guidelines. A Student t factor of 3.143 was applied to give a 99% confidence.

Element	MDL[1] (µg/L)	MDL[2] (µg/kg)	MDL[2] (mg/kg)	GB specified MDL (mg/kg)
Pb	0.13	2.6	0.0026	0.005
Cd	0.019	0.37	0.00037	0.001
Cr	0.038	1.5	0.0015	0.01
Ni	0.16	6.0	0.006	0.06

1. Calculated MDL in solution
2.Calculated MDL in sample

Calibration range

The calibration curves for Pb, Cd, Cr and Ni are shown in Figures 4, 5, 6 and 7, respectively. All elements display excellent calibrations with correlation coefficients greater than 0.999. All standards were prepared automatically via the PSD 120.

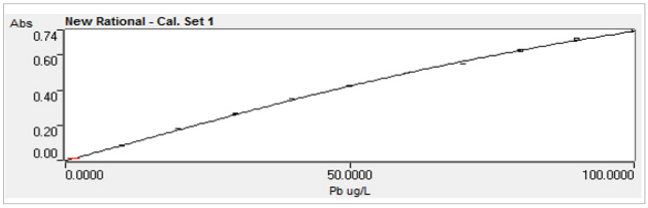

Figure 4. Calibration curve for Pb from 0 to 100 µg/L.

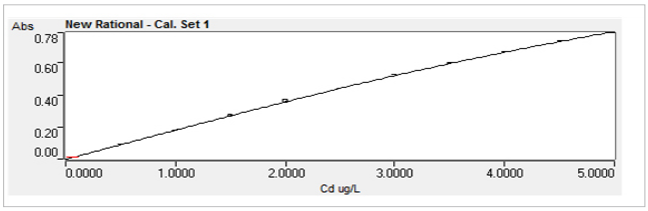

Figure 5. Calibration curve for Cd from 0 to 5 µg/L.

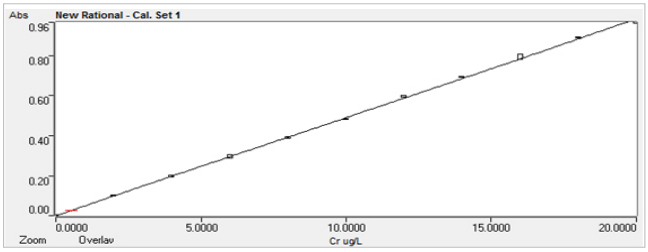

Figure 6. Calibration curve for Cr from 0 to 20 µg/L.

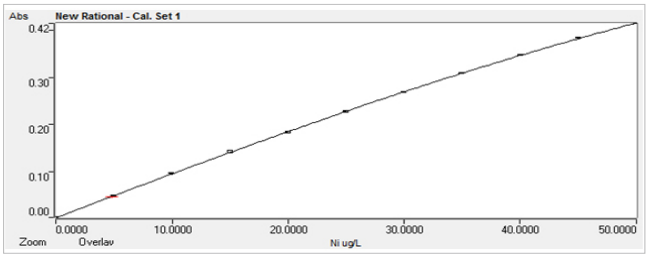

Figure 7. Calibration curve for Ni from 0 to 50 µg/L.

Instrument stability

The stability of the 280Z Zeeman GFAAS was investigated by analyzing a digest of a commercial wheat flour sample multiple times, interspersed with a 5 ppb Pb standard that was measured after every five samples (without recalibration or reslope). The measured results for the 5 ppb Pb standard were used to determine the long-term stability of the instrument. The %RSD was 1.6 over a seven-hour period. The results are given in Table 6 and with the stability plot displayed in Figure 8. There was only a 4% deviation in concentration from the initial reading.

Table 6. %RSD of a 5 ppb Pb standard measured periodically over 7 hours.

Sample	Measured value, (mean, n=26) (ppb)	RSD (%)
Wheat Flour	5.22	1.6

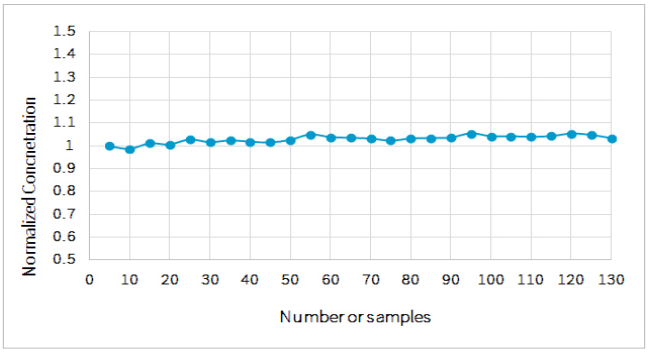

Figure 8. Long-term stability plot for a 5 ppb Pb standard measured periodically during the analysis of a wheat flour digest run over a 7-hour period.

Conclusions

The Agilent 280Z GFAAS was used to determine Pb, Cd, Cr and Ni in digested wheat flour SRMs according to Chinese National Methods GB 5009.12—2010, GB 5009.15—2014, GB 5009.123—2014 and GB 5009. 138—2003. Calibrations were achieved over a large calibration range for all three elements. Good agreement with the certified values was obtained, demonstrating the accuracy of the method. The study showed that the Agilent 280Z GFAAS exceeds the Chinese method requirements for the determination of Pb, Cd, Cr and Ni in food products.

With its excellent precision, faster analysis times when used in conjunction with the PSD 120 autosampler, long graphite tube lifetime and low argon gas usage, the 280Z GFAAS is ideally suited to meet the needs of food testing labs. Especially for labs that require accurate, sensitive, and cost effective instrumentation.

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