thermo scientific

APPLICATION NOTE 43019

Determination of trace elements in rice products by flame and graphite furnace atomic absorption spectrometry

Authors

Dr. Jianfeng Cui,
Application Specialist,
Thermo Fisher Scientific,
Bremen, Germany

Keywords

Atomic absorption, Essential elements, Flame, Graphite furnace, Rice, Toxic elements

Goal

The Thermo Scientific™ iCE™ 3000 Series Atomic Absorption Spectrometers are the ideal tool for the accurate and rapid determination of multiple trace elements in rice products. Flame atomic absorption can be used as a fast screening tool for the analysis of nutritional elements such as copper, manganese and zinc, while graphite furnace atomic absorption can be used for the accurate determination of toxic elements such as cadmium and lead.

Introduction

Rice is the second most prevalent cereal crop in the world with an annual global production of approximately 600 million tons. It is the staple food of most Asian countries, with a daily consumption per person of between 200 and 400 g. Trace elemental analysis of this crop and its products is therefore important on an essential, nutritional and toxicological level. The analysis of heavy metals is of particular relevance to human health following numerous incidents such as the mass cadmium poisoning of hundreds of people in the Toyama Prefecture, Japan.

During the early 20th Century, cadmium was released into the Jinzu River, Japan by mining companies in the mountains. The river water was used to irrigate rice fields and cadmium was subsequently absorbed by the growing rice. The effect on local people was softening of bones, anemia and kidney failure. It became known as “Itai-Itai Byo”, a phrase adopted by the locals to represent the pain caused by the poisoning. Global legislation now exists to regulate the permissible levels of cadmium in foodstuffs, with both China and the EU setting an upper limit of 0.2 $mg \cdot kg^{-1}$ of cadmium in rice[1,2]. Such legislation has produced a requirement to monitor rice and other foodstuffs for trace metal content and this application note discusses the analysis of copper, zinc, manganese, cadmium and lead in rice products by flame and furnace atomic absorption for this purpose.

ThermoFisher SCIENTIFIC

Method

Reagents

For flame analysis:

- Nitric acid, Trace analysis grade
- Copper, manganese and zinc master standards, 1000 mg·L^{-1}
- Multi-element standards prepared at 0, 0.5, 1, 2 and 5 mg·L^{-1} copper, manganese and zinc using master standards. Diluted to volume with 1% nitric acid

For graphite furnace analysis:

- Nitric acid, Trace analysis grade
- Cadmium and lead master standards, 1000 mg·L^{-1}
- Cadmium standard prepared at 5 µg·L^{-1} using master standard. Diluted to volume with 1% nitric acid
- Lead standard prepared at 10 µg·L^{-1} using master standard. Diluted to volume with 1% nitric acid
- Furnace matrix modifier: ammonium nitrate, 20 µg in 10 µl injection for cadmium, 50 µg in 10 µl injection for lead

All standards and reagents from Fisher Scientific, Loughborough, UK.

Sample preparation

Three samples were analyzed: rice flour CRM (IRMM-804, LGC, Teddington, UK) and two samples of retail products from a local supermarket, rice flour and whole white rice. Samples were dried for 12 hours at 85 ˚C. The samples were cooled and portions of approximately 0.25 g were accurately weighed and transferred to microwave digestion vessels. 4 ml nitric acid was added to each vessel and left uncovered for 1 hour. A further 4 ml nitric acid was added to each vessel, the vessels sealed and samples digested in a high pressure closed microwave digestion system, by ramping over 20 minutes to 170 ˚C. Samples were left to cool before being made up to 250 ml with deionized water for cadmium analysis. Duplicate samples were prepared for the analysis of copper, lead, manganese and zinc (from the same sample) with the digests made up to 50 ml with deionized water.

A spiked sample of the supermarket rice flour was prepared to assess the sample preparation and subsequent analysis of cadmium and lead by graphite furnace. Spikes were added to obtain a final concentration approximately 75% of the CRM rice flour standard.

Results and discussion

Flame: Copper, manganese and zinc

Copper, manganese and zinc were analyzed by flame atomic absorption as these elements can be found as natural constituents in soils and water, therefore detection within the low mg·kg^{-1} range was required. The transverse and lateral burner position and the impact bead were manually optimized using a 5 mg·kg^{-1} copper standard prior to analysis. Burner height and fuel gas flow were optimized for each element using the *Optimize Gas Flow and Burner Height* Wizard in the Thermo Scientific SOLAAR software, as shown in Figure 1. This allowed quick and easy method development with optimized parameters entered automatically into the analytical method.

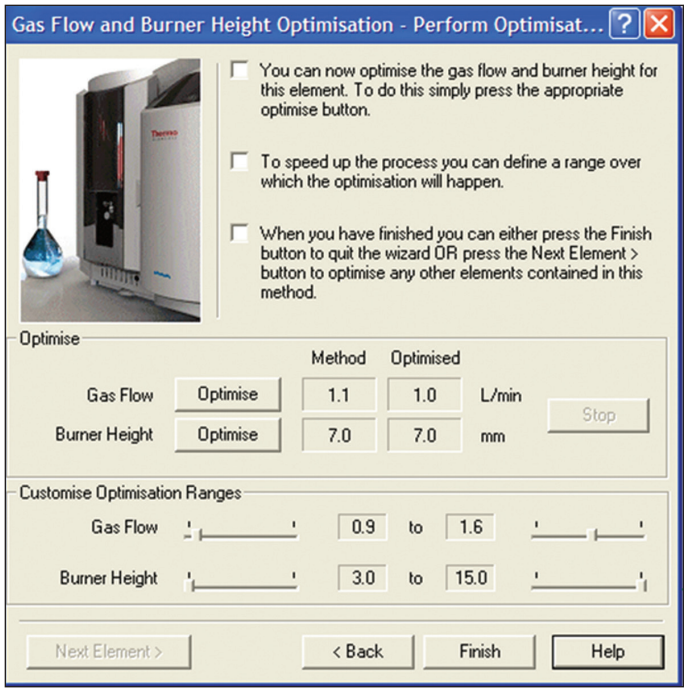

Figure 1. Gas flow and burner height optimization wizard.

The samples prepared to total volume of 50 ml were analyzed for copper, manganese and zinc. Each standard and sample was analyzed in triplicate using the fast re-sampling option. A continuous signal was measured for 4 seconds for each resample. The total analysis duration, including optimization, calibration and analysis of samples was 25 minutes. This included a 5 point calibration and analysis of the three samples for each element (Cu, Mn and Zn). Calibration curves for copper, manganese and zinc are shown in Figure 2.

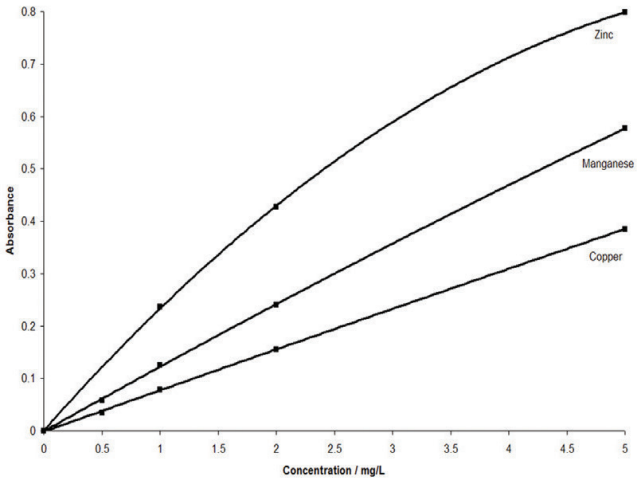

Figure 2. Calibration curves for the determination of copper, manganese and zinc in rice products.

Comparisons to the CRM expected concentration were made to assess the suitability of the method. Results for the CRM, rice flour and whole rice are shown in Table 1, along with the method detection limits (MDLs) and characteristic concentrations (CCs) determined using the automated *Instrument Performance* Wizard in the SOLAAR software.

Furnace: Cadmium and lead

As toxic elements with no nutritional benefit, detection of cadmium and lead was required. As this was at trace level, graphite furnace atomic absorption was selected as the appropriate analysis technique. While a longer analysis time is required per sample, the use of the integrated autosampler allowed samples to be run unattended. Ammonium nitrate matrix modifier was used for both the analysis of cadmium and lead. A working volume of 20 µl was used for standard and sample injection, with an additional 10 µl aliquot of matrix modifier added in a combined wet injection. 20 µg of ammonium nitrate was added for cadmium and 50 µg for lead. Graphite Furnace TeleVision (GFTV) was used to observe injection deposi¬tion and the drying phase. This unique feature of the iCE 3000 Series Atomic Absorption Spectrometers allows direct visualization of the inside of the cuvette, displaying a high resolution image on the PC monitor for enhanced method development. The *Optimize Furnace Parameters* Wizard in the SOLAAR software was used to optimize the ash and atomize phases. Zeeman background correction was selected for all analyses to eliminate the effect of potential structured background interferences. Furnace parameters for cadmium and lead are shown in Table 2.

Table 2. Furnace parameters for the analysis of cadmium and lead in rice products.

Phase	Temp. ˚C	Time / s	Ramp ˚C/s
1: Drying	100 Cd, 115 Pb	30	10
2: Ashing	700 Cd, 1000 Pb	20	150
3: Atomizing	1300 Cd, 1500 Pb	5 Cd, 3 Pb	n/a
4: Cleaning	2500	3	n/a

Table 1. Table of results and percentage recoveries of copper, manganese and zinc in rice products. Method detection limits and characteristic concentrations shown are based on an initial mass of 0.25 g sample.

	Expected concentration mg·kg^{-1}	Measured concentration mg·kg^{-1}	Percentage recovery (%)	Method detection limit µg·L^{-1}	Characteristic concentration mg·kg^{-1}
Copper					
CRM	0.013	0.012	108.3	0.0042	0.0646
Rice flour		0.007			
Whole rice		0.014			
Manganese					
CRM	0.163	0.162	100.6	0.0379	0.0102
Rice flour		0.038			
Whole rice		0.026			
Zinc					
CRM	0.110	0.111	99.1	0.0019	0.0187
Rice flour		0.091			
Whole rice		0.063			

Calibrations within the range 0-5 µg·L^{-1} for cadmium and 0-10 µg·L^{-1} for lead were obtained using the master standards. Standards were automatically diluted using the fixed volume standard preparation option in the SOLAAR software as shown in Figure 3.

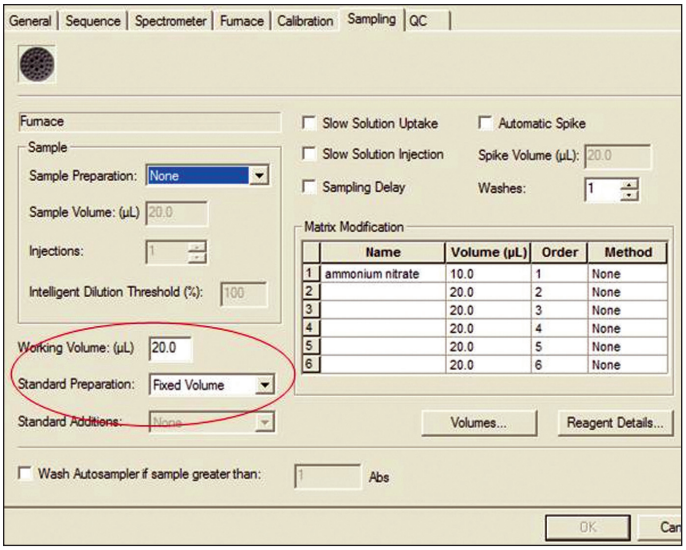

Figure 3. Sampling conditions for the analysis of cadmium and lead in rice products.

The CRM was analyzed to assess the suitability of the method, followed by the rice flour and whole rice. Spiked rice flour was also analyzed to assess recovery performance of the method. Three repeats of each standard and sample were analyzed. The calibration line generated by the SOLAAR software for lead is shown in Figure 4, with a correlation coefficient of 0.9957. Results for the CRM, rice flour and whole rice are shown below in Table 3 along with the method detection limits (MDLs) and characteristic concentrations (CCs) determined using the automated *Instrument Performance* Wizard in the SOLAAR software. Cadmium and lead were not detected in either of the retail products displaying compliance with current international regulations.

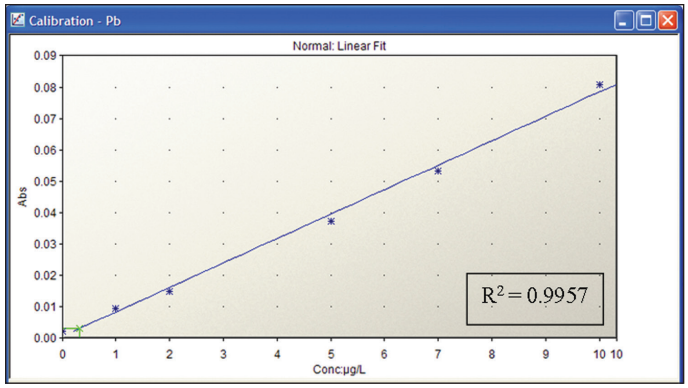

Figure 4. Calibration line for the analysis of lead in rice products.

Table 3. Table of results and recoveries of cadmium and lead in rice. MDLs and CCs shown are based on an initial mass of 0.25 g sample.

	Expected concentration mg·kg^{-1}	Measured concentration mg·kg^{-1}	Percentage recovery (%)	Method detection limit µg·L^{-1}	Characteristic concentration µg·L^{-1}
Cadmium					
CRM	1.5	1.43+/-0.07	105	0.0303	0.0600
Rice flour	<DL				
Spiked rice flour	1.06	1.00	106		
Whole rice	<DL				
Lead					
CRM	2.03	2.00+/-0.007	102	0.1960	0.7119
Rice flour	<DL				
Spiked rice flour	1.24	1.20	103		
Whole rice	<DL				

Conclusion

The results demonstrate the ease with which the Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometers can be used for the multi-element analysis of rice products. Flame atomic absorption was used as a fast analysis tool for the determination of copper, manganese and zinc. Detection limits were below 5 $\mu g \cdot kg^{-1}$ for copper and zinc and below 40 $\mu g \cdot kg^{-1}$ for manganese. Graphite furnace atomic absorption was used as an accurate analysis tool for the determination of cadmium and lead, with excellent detection limits of 0.03 and 0.2 $\mu g \cdot kg^{-1}$ obtained respectively, easily ensuring regulatory compliance.

A Certified Reference Material was used to verify both the flame and furnace methods with excellent recoveries obtained. The ease of use of the system is exemplified with the many automated wizards which enable fast accurate results regardless of analyst experience. The Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometers therefore provide an ideal solution for the accurate and rapid multi-element determination of minor and trace elements in rice at parts-per-million and parts-per-billion concentrations.

References

1. Peoples Republic of China, FAIRS Product Specific Maximum Levels of Contaminants in Food 2006
2. Commission Regulation (EC) No. 1881/2006 of 19 December 2006 setting Maximum Levels for Certain Contaminants in Foodstuffs

Find out more at **thermofisher.com/AAS**

ThermoFisher SCIENTIFIC