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## Fast Digestion Analysis of Lead and Cadmium in Rice Using GFAAS with Deuterium Background Correction

thereby seriously endangering human health through diet.<sup>1,2</sup> These toxic element levels need to be carefully monitored. Maximum levels of Pb and Cd are strictly regulated in Asian countries, especially in China; therefore, it is extremely important to develop a simple, reliable method for trace levels of Pb and Cd in rice.

The allowable maximum levels of Pb and Cd in grains in EU and China are required to be below 0.2 mg/kg (Commission Regulation EC 1881/2006 and Chinese GB 2715-2016 Hygienic Standard). Graphite furnace atomic absorption spectroscopy (GFAAS) is the officially recommended technique for detection of trace elements in various food stuffs (GB/T 5009.15-2017, GB/T 5009.12-2017 and EN 14083:2003). Food samples are usually pretreated before GFAAS analysis using various methods: microwave digestion, hot block digestion, dry ashing, and hot plate digestion. These conventional digestion procedures are usually complicated and time-consuming (2-4 hours or longer). Plus, they require large quantities of corrosive and oxidizing reagents, increasing the chance for contamination which could lead to inaccurate results. However, fast digestion (already introduced and validated in a previous application note<sup>3</sup>) can effectively speed up the sample preparation procedure while reducing the use of corrosive reagents and the chance for contamination.

### Introduction

Toxic elements, such as lead (Pb) and cadmium (Cd), are entering the food chain through environmental contamination. Rice, as the most widely consumed cereal grain in Asia, can quickly pick up Pb and Cd from soil,

In this work, rice powder was first pretreated by fast digestion, followed by analysis with the PerkinElmer PinAAcle™ 900H graphite furnace atomic absorption spectrometer. A rapid, economical, and accurate method for trace level analysis of Pb and Cd in rice grains is established and verified.

## Experimental Conditions

### Sample Preparation

The samples were conveniently and rapidly pretreated by fast digestion: approximately 0.5 g of each rice flour sample was accurately weighed in duplicate and transferred to 50 mL polypropylene autosampler tubes for fast digestion. Next, 1.5 mL concentrated nitric acid was added, and the loosely capped vial was then heated in the sample preparation block digestion system (SPB series, PerkinElmer) at 120 °C for 30 minutes, yielding a clear solution which did not require filtering as shown in Figure 1. The digested samples were then diluted with DI water and brought up to 25 mL. The overall time to produce an instrument-ready solution was substantially reduced to a half hour.

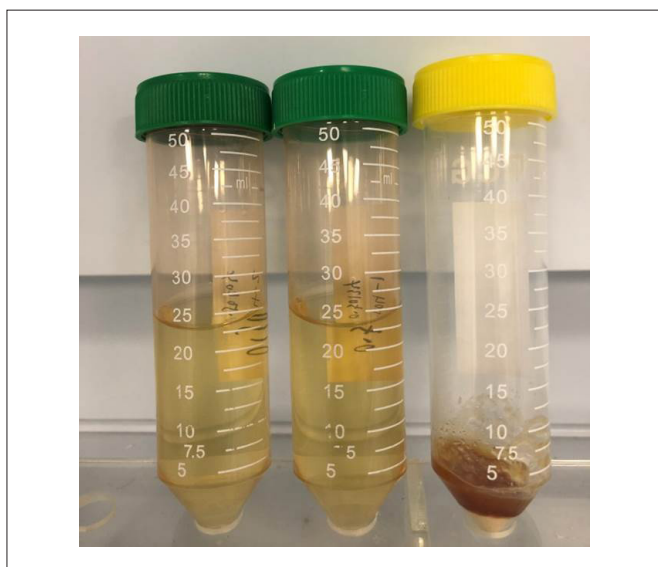


Figure 1. Transparent solution (green caps) yielded from rice flour and acid slurry (yellow cap) by fast digestion.

### Instrumentation

The measurements were performed using a PinAAcle 900H atomic absorption (AA) spectrometer (PerkinElmer, Inc., Shelton, Connecticut, USA) - PinAAcle 900T and 900Z spectrometers may also be used for this application.<sup>3</sup> The PinAAcle 900H was equipped with Syngistix™ for AA software for sample analysis, data reporting and archiving results - Syngistix™ for AA Express™ software may also be used. The PinAAcle 900H was also equipped with HGA graphite furnace and deuterium continuum source background correction, AS900 autosampler, water re-circulator system, high-speed automatic wavelength drive, automatic lamp selection, and Electrodeless Discharge Lamp (EDL) power supply. The use of cutting-edge fiber optics in the PinAAcle 900 spectrometers maximizes light throughput for improved detection levels.

Unknown Sample A and proficiency test Sample B were measured in this experiment. The certified reference material (CRM) NIST 1568 Rice Flour was also analyzed to validate the digestion and analysis methods. Each sample was subjected to two replicates by fast digestion. Cd determination in the CRM was also replicated twice following the same procedure. The GFAAS analytical conditions were the same throughout the whole process. The instrumental conditions are given in Table 1, and the optimized graphite furnace temperature programs are listed in Table 2 and 3.

Table 1. Instrumental conditions for analyzing Pb and Cd in rice grains on the PinAAcle 900H spectrometer.

Parameter	Lead (Pb)	Cadmium (Cd)
Wavelength (nm)	283.31	228.80
Slit Width (nm)	0.7	0.7
Lamp Type*	HCL	EDL
Measurement Type	Peak Area	Peak Area
Read Time (sec)	5	5
Sample Volume (µL)	12	12
Diluent Volume (µL)	12	12
Matrix Modifier	0.05% Pd(NO <sub>3</sub> ) <sub>2</sub>	0.3% Pd(NO <sub>3</sub> ) <sub>2</sub>
Matrix Modifier Volume (µL)	5	5
Calibration Equation	Standard Addition	Standard Addition
Standard Concentration (µg/L)	0, 5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0

\*The determination of Cd level in rice can be obtained by both HCL and EDL. However, Cd EDL was used for better detection limit and sensitivity.

Table 2. Optimized temperature program for Pb analysis in rice grains on the PinAAcle 900H spectrometer.

Lead (Pb)				
Temp. (°C)	Ramp (s)	Hold (s)	Internal Gas Flow (mL/min)	Gas Type
120	5	30	250	Normal
150	30	30	250	Normal
700	10	20	250	Normal
1800	0	5	0	Normal
2600	1	5	250	Normal

Table 3. Optimized temperature program for Cd analysis in rice grains on the PinAAcle 900H spectrometer.

Cadmium (Cd)				
Temp. (°C)	Ramp (s)	Hold (s)	Internal Gas Flow (mL/min)	Gas Type
120	5	30	250	Normal
150	30	30	250	Normal
650	10	20	250	Normal
1900	0	5	0	Normal
2600	1	5	250	Normal

## Results and Discussion

The standard addition calibration curves of Pb and Cd are presented in Figure 2, which were constructed in Sample A1 and B1 as representative sample respectively, showing an  $R^2$  value  $\geq 0.999$  in both cases, demonstrating the linearity of the analysis. The peaks for all calibration standards and the samples are shown in Figures 3 and 4. The same appearance time and peak shape demonstrates that matrix effects were effectively eliminated by using the standard addition method.

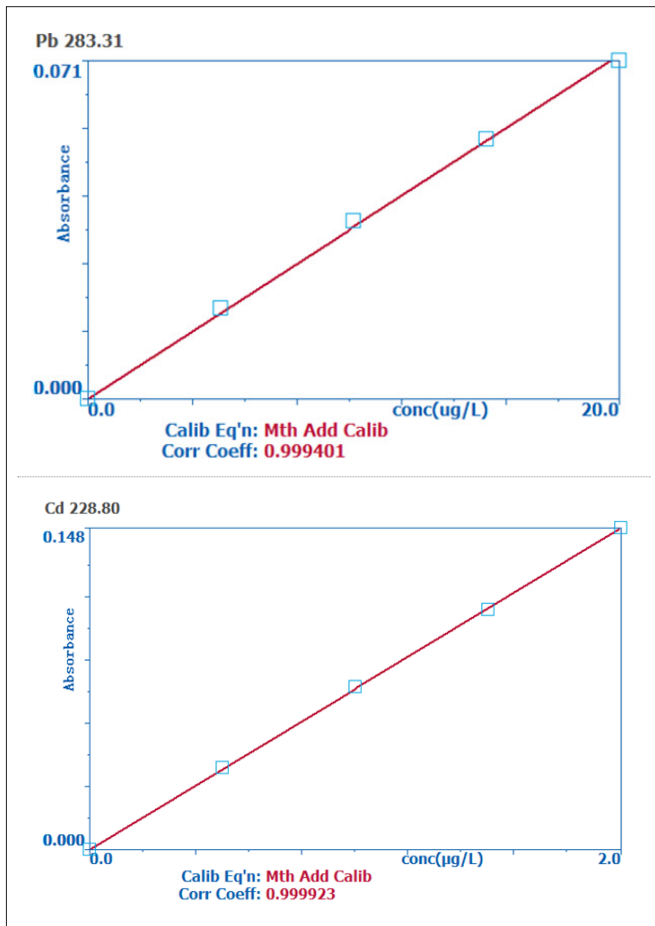


Figure 2. Standard addition curves of Pb (top) and Cd (bottom) in rice.

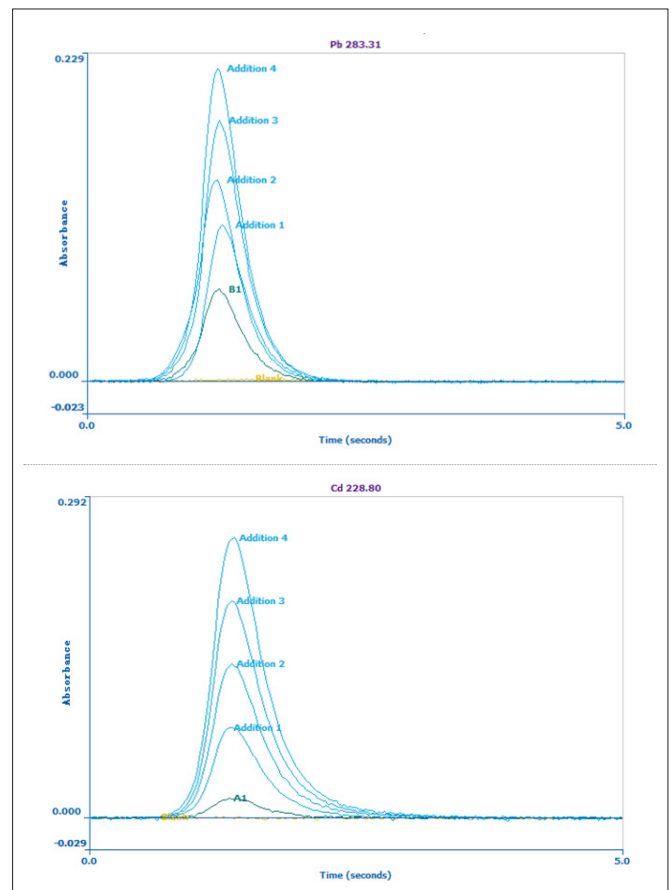


Figure 3. Overlay of spectral profiles of Pb (top) and Cd (bottom) in standard addition calibration.

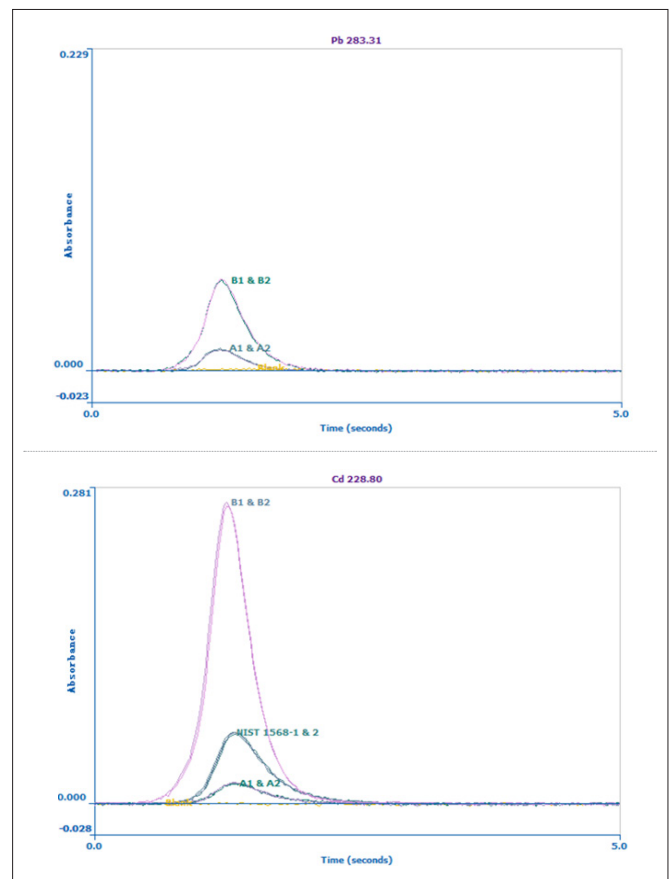


Figure 4. Overlay of spectral profiles of Pb (top) and Cd (bottom) in two samples and NIST 1568 and their duplicates.

The method detection limit (MDL) was calculated (Table 4) based on the standard deviation of eleven replicates of the reagent blank and accounted for the dilution factor used in sample preparation. The method detection limit wasn't deteriorated by the smaller sample volume of 12 µL and is well below the regulated levels, which demonstrates the capability of the PinAAcle 900H to measure low concentrations in difficult matrices.

Table 4. MDL using the PinAAcle 900H spectrometer.

Analyte	MDL (3σ, µg/kg)		
	Calculated	Regulated	
Pb	13	20 <sup>a</sup>	20 <sup>b</sup>
Cd	0.8	1.0 <sup>c</sup>	20 <sup>b</sup>

(0.5 grams sample diluted to 25 mL; <sup>a</sup>: regulated in GB 5009.12-2017; <sup>b</sup>: regulated in (EC) No 1881/2006; <sup>c</sup>: regulated in GB 5009.15-2014.)

Table 5. Analysis of NIST 1568 pretreated by fast digestion on the PinAAcle 900H spectrometer.

Analyte	Certified Value (mg/kg)	Measured Value (mg/kg)
Pb	NA	NA
Cd	0.029 ± 0.004	0.027

The results from the analysis of Samples A and B are summarized in Table 6. Online dilution was applied during Cd analysis in Sample B due to the high concentration in the sample. The accuracy of this methodology is well aligned with previous experiments on the PinAAcle 900T GFAAS (with Zeeman background correction), and the precision is again, ascertained by RSD% < 1.0% in both Cd and Pb cases.

Table 6. Results for the detection of Pb (top) and Cd (bottom) in rice grains (mg/kg).

Sample	Pb (mg/kg)			
	FD1	RSD (%)	FD2	RSD (%)
A	0.083	<1	0.081	<1
B*	0.394	<1	0.399	<1

\*Result from proficiency test is 0.390 mg/kg.

Sample	Cd (mg/kg)			
	FD1	RSD (%)	FD2	RSD (%)
A	0.077	<1	0.082	<1
B*	0.378	<1	0.371	<1

\*Result from proficiency test is 0.370 mg/kg.

## Conclusions

Fast digestion is ascertained to be a simple, effective and accurate technique for rice grain pretreatment. The PinAAcle 900H AA spectrometer, equipped with an HGA graphite furnace and deuterium background correction, has demonstrated its ability to effectively handle digested rice sample matrix – the system provides the superior sensitivity required for heavy-metal testing in food matrices, with excellent accuracy and precision, as observed from CRM results and low RSDs. This application has the potential to be extended to heavy metal analysis in a variety of other food types, including cereal grains/flour, corn, beans and milk powder.

## References

1. IARC: [http://monographs.iarc.fr/ENG/Classification/latest\\_classif.php](http://monographs.iarc.fr/ENG/Classification/latest_classif.php).
2. U.S. ATSDR: <https://www.atsdr.cdc.gov/csem/csem.asp?csem=6&po=12>.
3. Fast Digestion Analysis of Lead and Cadmium in Rice Using GFAAS with Longitudinal Zeeman Background Correction, S. Wei, R-K. Yang, Q-L. Liu, PerkinElmer, Shanghai, China.

## Consumables Used

Component	Description	Part Number
Sample Preparation Block	SPB 50-24, 24-position 50 mL 115/230 V	N9300802
	SPB 50-48, 48-position 50 mL 115/230 V	N9300803
Cd Lamp	Hollow Cathode Lamp (HCL)	N3050115
	Electrodeless Discharge Lamp (EDL)	N3050615
Pb Lamp	Hollow Cathode Lamp (HCL)	N3050157
	Electrodeless Discharge Lamp (EDL)	N3050657
HGA Graphite Tubes	Pyrocoated Graphite Tubes with Integrated Platform	NB3001262 (5-pack) B3001264 (20-pack) N9300651 (40-pack)
Cd Standard	1000 ppm, matrix 2% HNO <sub>3</sub>	N9300176 (125 mL) N9300107 (500 mL)
	Modifier Pd(NO <sub>3</sub> ) <sub>2</sub>	1% Pd, 50 mL
Conical Centrifuge Tube	50 mL - Qty 500	B0193234