

# Spectroscopy Focus

## TRACE ELEMENT ANALYSIS OF RICE BY XRF

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*The analysis of trace elements in rice is a vitally important area of research, given the vast numbers of people who depend on it as a major food source. X-ray fluorescence (XRF) spectrometry has emerged as an invaluable tool for this application. XRF delivers many advantages over conventional trace element measurement techniques, including rapid, accurate and precise analysis; together with very simple sample preparation.*

*Worldwide, more than 415 million metric tonnes of rice was consumed in 2006-2007, making it one of the world's most important crops. Rice is a staple food for around half the world's population. It provides the major source of calories, particularly in Asian countries. In Korea, for example, around 400g of rice is consumed per person per day [1].*

*With more than 30 billion people dependent on rice as a substantial part of their diet, the analysis and monitoring of its composition is vital. The determination of trace elements is a particularly important area in terms of both nutrition and toxicology. This article presents data on the use of XRF spectroscopy for the analysis of trace elements in rice.*

### INFLUENCES ON TRACE ELEMENT COMPOSITION

Many factors affect the types and amounts of trace elements and micronutrients in rice. Uptake of trace elements is greatly affected by environmental conditions, such as soil pH.

A further factor is pollution, which can result in the introduction of heavy metals to the soil, which in turn are taken up by crops and enter the human food chain. Milling – the process of removing the husk from the grain – also alters the nutritional value of rice. The process converts brown rice to white, stripping many nutrients in the process.

### GOOD AND BAD

Some trace elements are beneficial – such as iron and zinc. Iron and zinc deficiencies are extremely widespread in humans, and also some farm animals. Therefore, the study of these two micronutrients in rice is extremely important for monitoring improvements in nutrition in the developing world.

The presence of other trace elements in rice is often an indication of pollution. Copper, for example, while an essential micronutrient for rice and humans, can occur in elevated levels in polluted soils.

Too much copper in rice can cause conditions such as black roots and a decrease in tillering efficiency, resulting in yield reductions of around 18-25% [2].

The levels of the heavy metal cadmium in rice are of particular concern. Cadmium enters the soil in a variety of ways, including from operational and former extractive mines, untreated sewage and combustion by-products. Readily taken up by rice and other crops, cadmium presents a major hazard to human health.

The affects of cadmium ingestion are wide ranging. It damages the liver and kidneys and also softens and weakens bones. Cadmium may also be a risk factor in the development of prostate or lung cancer.

A well-documented outbreak of cadmium poisoning through rice consumption occurred in Japan in the first half of the 20th century. The disease, which became known as 'itai-itai' disease, was caused by significant emissions of cadmium from mining operations in the Toyama Prefecture.

The pollution entered the Jintsu River basin, which was used to irrigate rice fields. Cadmium uptake by the rice crop exposed the local population to high levels of the metal over a period of several decades. As a consequence, many people suffered the characteristic symptoms of chronic cadmium poisoning, including renal dysfunction and osteomalacia.

### LEGISLATION

Regulatory organisations across the world are involved in making environmental policies to reduce emissions of heavy metals into the environment. For example, Japan's Food Product Hygiene Law prohibits the selling or processing of unpolished rice containing 1.0 mg kg<sup>-1</sup> or more of cadmium. This is a further reason why accurate and precise trace element determination in rice is essential.

*\*CODEX Norm defines that more than 14mg kg<sup>-1</sup> of Cd should not be contained in rice for food.*

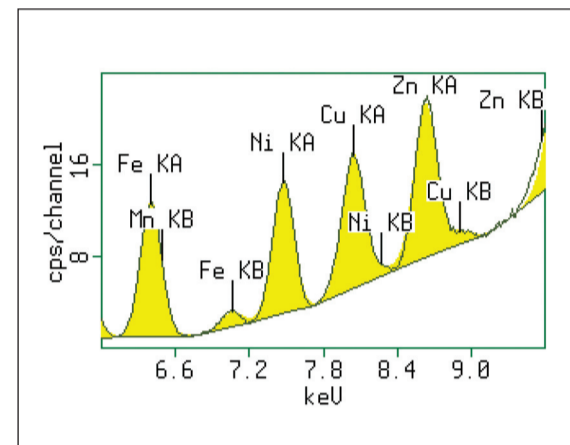


Figure 1. XRF spectrum of a rice standard showing the excellent resolution of the detector. Spectrum deconvolution in the MiniPal software calculates the net intensities for all elements of interest

### WHY XRF?

Atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrophotometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are the conventional methods of trace element analysis in food products. However, these methods usually require the conversion of food samples into solution. This can involve pre-treatment such as acid decomposition. For example, cadmium measurement using AAS requires laborious solvent extraction.

In comparison, X-ray fluorescence (XRF) spectrometry is a rapid analysis method that offers non-destructive testing and requires little or no sample preparation. In recent years, advances in X-ray technology have enabled highly sensitive trace element analysis to be conducted routinely using XRF instrumentation.

Two examples of the use of XRF for the analysis of trace elements in rice are presented below:

### TRACE ELEMENT ANALYSIS OF IRON, COPPER AND ZINC IN WHITE RICE

This study demonstrates the use of an energy dispersive XRF (EDXRF) spectrometer for the analysis of iron, copper and zinc in rice samples at trace levels.

#### Instrumentation

Measurements were performed using a MiniPal 4 EDXRF spectrometer (PANalytical), equipped with a 30 kV rhodium anode tube, five filters, a helium purge facility, a high-resolution Silicon Drift Detector, a spinner and a 12-position removable sample changer.

#### Sample preparation

Secondary rice standards were prepared by doping rice with different amounts of iron, copper and zinc. The precise concentrations of these elements in the standards were obtained by ICP and AAS.

These rice grains were pulverised in a tungsten carbide swing mill and then pressed into pellets of 30 mm in diameter (20 tons pressure, 30 s dwelling time). No binder material was applied. The samples were placed in standard sample holders and loaded into the MiniPal 4.

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**Measurement procedure**

Nine secondary rice standards were used to set up the calibrations. Only one measurement condition was required to measure the elements of interest (see Table 1). The total measurement time per sample was five minutes. Matrix corrections were applied using a backscattering intensity ratio. Figure 1 shows the resolution of the MiniPal 4 detector.

**Calibration accuracy**

Figures 2, 3 and 4 show calibration plots for iron, copper and zinc in rice, respectively. These plots show a good correlation between the certified concentrations and the measured intensities. Detailed calibration results are listed in Table 2. The Lower Limits of Detection (Table 2) are based on the measurement times listed in Table 1 and for 100 s counting time.

**Precision**

One white rice sample was measured 20 times consecutively, using the conditions given in Table 1. The average concentration, the RMS (1 sigma standard deviation), the relative RMS and the relative CSE (counting statistical error) are expressed in Table 3. These data are also illustrated in Figure 5. Very reproducible results are obtained with the MiniPal 4.

Table 1. Measurement conditions

Element	kV	µA	Filter	Medium	Measurement time (s)
Fe, Cu, Zn	30	130	Thick Al	Air	300

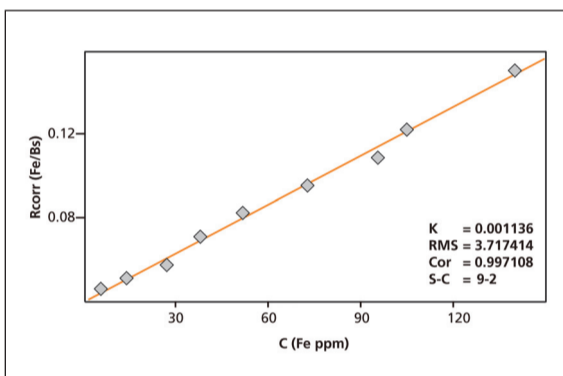


Figure 2. Calibration plot of iron in rice standards

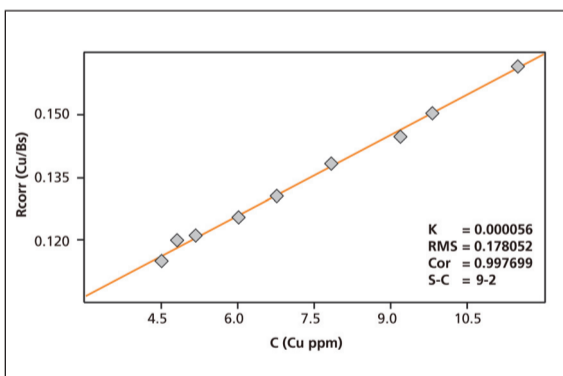


Figure 3. Calibration plot of copper in rice standards

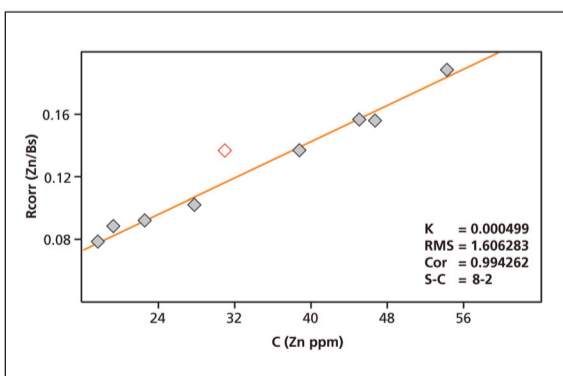


Figure 4. Calibration plot of zinc in rice standards

Table 2. Calibration details and LLD values

Element	Concentration range (ppm)	RMS (ppm)	K-value	LLD (ppm, 100 s)	LLD (ppm, measurement time)
Fe	5 - 140	3.72	0.00114	3	1.7
Cu	4.5 - 11.5	0.18	0.00006	2	1.2
Zn	17 - 54	1.61	0.00050	1.5	0.9

Table 3. Results of the repeatability test

Element	Average conc. (ppm)	RMS (ppm)	Rel. RMS (%)	Rel. CSE (%)
Fe	30.5	0.58	1.9	0.4
Cu	4.7	0.23	5.0	1.0
Zn	20.2	0.43	2.1	0.4

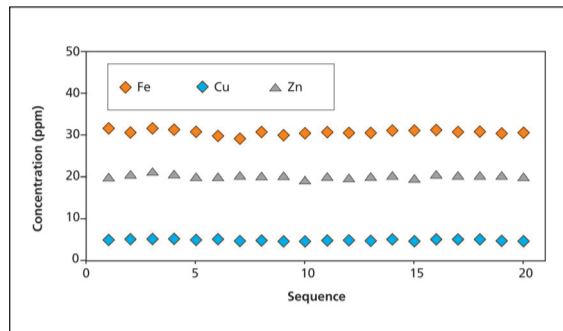


Figure 5. Repeatability results of iron, copper and zinc in a white rice sample

**RAPID ANALYSIS OF CADMIUM IN RICE**

The data shown below demonstrate the use of XRF for cadmium analysis in rice. These results are taken from a detailed investigation by Saeko Yada (Kaburagi) et al (2006) [3].

**Instrumentation**

Measurements were conducted using the Epsilon 5 EDXRF spectrometer (PANalytical). The instrument was equipped with a Gd tube at 100 kV. An Al<sub>2</sub>O<sub>3</sub> secondary target was also employed.

**Calibration**

For the calibration curve, samples of commercial non-glutinous rice flour were mixed with cadmium atomic absorption standard solution (Kanto Kagaku). The mixture was freeze-dried and adjusted to provide cadmium contents of 0.2, 0.5, 1.0 and 2.0 mg kg<sup>-1</sup> by adding non-glutinous rice flour. For the calibration, an ICP-MS system (SPQ 8000 A, SII/Nanotechnology) was used.

To confirm the accuracy of the XRF analysis values, standard rice samples NIES No. 10-a, b, c (unpolished rice flour) and NIST SRM 1568 (rice flour) were used.

**Sample preparation**

Six samples of unpolished rice with different cadmium contents were analysed. Samples were ground with a tungsten carbide grinder (800 M Mixer/Mill, SPEX Certiprep), until they passed through a 300 µm mesh sieve. A 20 mm tablet was made by adding 0.5 to 4.0 g of ground sample to a dye and applying a pressure of 20 tons for about 30 seconds. Samples were put into a standard sample cup, with polypropylene film (6 µm thick) at the bottom. A spacer with a 20 mm hole was used to fix the tablets to the middle of the cup.

Subsequent investigation showed that the same results could be obtained when using tablets made from non-ground unpolished rice. This simplifies sample preparation even further, allowing the grinding step to be omitted.

**Measurement conditions**

Measurement conditions for XRF analysis were: 100 kV excitation voltage and a primary current of 6 mA. The K<sub>α</sub> line (23.17 K eV) was used and measurement time was 1800 seconds live time per sample.

The use of a 125 µm thick Zr primary X-ray filter between the X-ray tube and the secondary target was found to provide the lowest detection limits and best noise reduction. Using the Zr filter reduces the detection limit from 0.2 mg kg<sup>-1</sup> to 0.1 mg kg<sup>-1</sup>

**Results**

Figure 6 shows the cadmium spectral intensity and standard deviation when measuring calibration curve samples ten times. Linearity is found at high values between 0.2 to 2.0 mg kg<sup>-1</sup> cadmium content. Standard deviation was within the range of 0.01 to 0.02 cps mA<sup>-1</sup>, independent of cadmium content.

Certified rice samples were measured under the same conditions and cadmium concentrations were calculated using the calibration curve. NIES No. 10-a and NIST SRM 1568, which have a low cadmium content, were below the limit of detection. However, XRF analysis of NIES No. 10-b and 10-c by XRF confirmed the certified values. This demonstrates that precise quantitative determination of cadmium in rice samples can be achieved using XRF.

Table 4 shows the data obtained by XRF and ICP-MS for cadmium content in the rice samples (A to F). Sample (A) was below the limit of detection for XRF, but for all other samples the value obtained using ICP-MS was within the range of the standard deviation. The standard deviation of the XRF analysis values showed an almost fixed value of around 0.07 mg kg<sup>-1</sup>, irrespective of the cadmium content in the unpolished rice. Measurement accuracy was 3.4% in terms of the relative standard deviation.

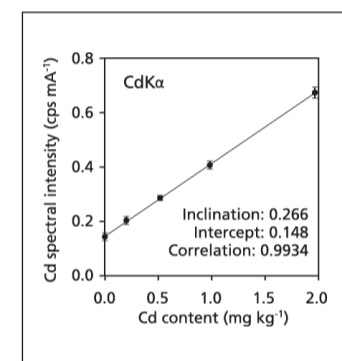


Figure 6. Relationship between Cd content and spectral intensity of calibration curve compilation sample

Table 4. Results of quantitative determination of Cd in unpolished rice samples

	Cd concentration (mg kg <sup>-1</sup> )	
	XRF*	ICP-MS**
A	n.d.***	0.06
B	0.22±0.06	0.23
C	0.40±0.05	0.41
D	0.53±0.06	0.49
E	0.93±0.07	0.98
F	1.66±0.07	1.63

\* average value of 10 measurements and standard deviation  
 \*\* average value of two series of measurements  
 \*\*\* below the limit of detection (0.1 mg kg<sup>-1</sup>)

**CONCLUSIONS**

Data presented here clearly demonstrate the suitability of the MiniPal 4 EDXRF spectrometer for trace level analysis of iron, copper and zinc in rice. Accurate, reliable and repeatable results are obtained in a measurement time of just five minutes. The analytical method benefits from very simple sample preparation.

The authors of the cadmium study used the results to develop a rapid XRF screening method for cadmium analysis in rice. With short analysis times and simple sample preparation, XRF is ideal for such an application. Rapid screening for cadmium has many benefits.

For example, in Japan the rice harvest takes place over a very short timescale. During the period between harvesting and shipping, large numbers of different rice products must be analysed to ensure that rice with a cadmium content of 0.4 mg kg<sup>-1</sup> or more is not circulated.

The data shown here verified that XRF was able to provide the necessary levels of analytical precision and accuracy for an effective, rapid and simple screen for cadmium in rice.

**References**

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- Saeko Yada (Kaburagi), Akira Kawasaki, Kenji Matsuda, Manabu Mizuhira, Hisao Oda. A rapid and simple screening analysis of cadmium in rice samples using an X-ray fluorescence spectrometer. Japanese Journal of Soil and Fertilizer Science (Nippon Dojo Hiryo Gaku Zasshi) Vol. 77 No. 2 p. 165-170, 2006.