TXRF

Rapid ultra trace analysis of arsenic in rice by TXRF spectroscopy

Application Note # XRF 460

Introduction

Almost half of the world's population eats rice every day, in many cases even several times a day. Rice contains up to ten times more inorganic arsenic than any other food plant. The reasons for this are the cultivation in an aqueous medium containing arsenic, the growing area and the processing.

Therefore, it is considered that rice is the dominant source of toxic inorganic arsenic in the human diet. Upcoming regulations in many countries will increase the demand for monitoring arsenic in rice products routinely.

This report describes a procedure for the analysis of rice samples using Total Reflection X-ray Fluorescence (TXRF) which is especially suited for small laboratories or at remote locations.

Figure 1
A variety of wild, brown and white rice

Figure 2
Under water rice fields

Where does the arsenic come from?

Arsenic (As) is a metalloid because it features properties intermediate of those typical for metals and non-metals.It occurs in the same group of the periodic table of elements as nitrogen and phosphorus. Consequently, the chemistry of arsenic is similar in many respects to that of these two dietary elements. This might be the reason for high As levels in many marine organisms and in marine algae and plants.

Arsenic naturally occurs worldwide in soil and water. Concentrations of arsenic in groundwater, an important source of drinking water, are usually lower than 10 µg/l (ppb), but they can reach 5000 µg/l in some areas. Arsenic is especially common in the rocks of the Himalayas, from where the Ganges and other rivers carry it to the heavily populated plains of India, Bangladesh and other Asian countries.

Globally, about 80% of the rice is harvested from fields under water (see the top five rice producing countries in Table 1), which leads to ten times higher uptake of arsenic in rice compared to other cereal grains. In addition, flooding makes soil conditions anaerobic which causes arsenic to convert from bound and stable forms into more mobile ones.

Rice contains significant amounts of inorganic arsenic with concentrations often between 0.1 to 0.4 mg As/kg dry mass or higher. Although fish and other seafood often contain a higher total arsenic concentration, most of it is converted to less or non-toxic organic species.

Health effects of high arsenic exposure

Studies have shown evidence that chronic arsenic exposure is linked to cancers of bladder, lungs, skin and prostate, as well as to heart diseases. In the short term, it can cause gastrointestinal problems, muscle cramping and lesions on hands and feet.

Therefore, most countries have set a maximum level for total arsenic in drinking water of about 10 ppb, whereas only few countries have established maximum levels in food products like cereals, rice or seafood (Table 2).

Rank	Country	Production (million tons per year)
1	P. R. China	203.29
2	India	159.20
3	Indonesia	71.28
4	Bangladesh	51.50
5	Vietnam	44.04

Table 1

List of the five most important rice producing countries

Country	Regulatory	Maximum level	Type of As and type of product
Australia	FSANZ	1 ppm	total As, in cereals
China	Ministry of Health	0.2 ppm	inorganic As in rice and rice products
European Union	European Commission	0.2 ppm	polished rice
		0.1 ppm	infants rice products
India	–	1.1 ppm	total As, in all products
Singapore	Agri-Food and Veterinary Authority	1 ppm	total As, in all products
UK	Food Standard Agency	1 ppm	total As, in all products
–	World Health Organisation (WHO)	0.2 ppm	total As, in all products

Table 2

List of countries already applying maximum levels of inorganic arsenic in rice and rice products

Rapid and cost-effective analysis of arsenic in rice

Even though many different analytical methods are available for the analysis of arsenic in rice, there is a strong demand for a convenient, easy-to-use approach for daily routine operation. Since the analysis of arsenic in rice is becoming an important task in developing countries and in remote areas, the use of complicated sample preparation procedures, calibrations and data evaluation must be avoided.

During the last years TXRF was established as a standard method for the measurement of trace elements in environmental and biological samples [1]. In this report the straight-forward analysis of rice samples with TXRF is described.

Sample preparation

Two certified reference materials (rice flour samples NIST 1568a and NIST 1568b) and 12 rice samples from different locations in Southeast Asia and Australia were analyzed with TXRF.

- All samples were ground in a laboratory bench top mill (Retsch MM400), equipped with a zirconium vessel and ball for 3 min at 30 Hz.

- Subsequently amounts of 100 ± 5 mg ground rice were weighed into centrifugation tubes and suspended in 5 ml aqueous Triton X-100 solution (1 vol.-%).

- For internal standardization 30 µl of a Y solution (1 g/l) were added. After thorough homogenization the samples were placed in an ultrasonic bath for 5 min.

- Afterwards the samples were fixed in an automatic sample shaker and slowly agitated at about 800 r/min to avoid precipitation.

- While constantly agitating, 10 µl of each suspension were transferred to a siliconized quartz glass carrier and dried. The reference samples were prepared tenfold and the other rice samples as duplicates.

- All measurements were performed for 1000 s using a S2 PICOFOX spectrometer, which was equipped with a 50 W X-ray tube with Mo target and a XFlash® silicon drift detector with 60 mm² active area.

Figure 3

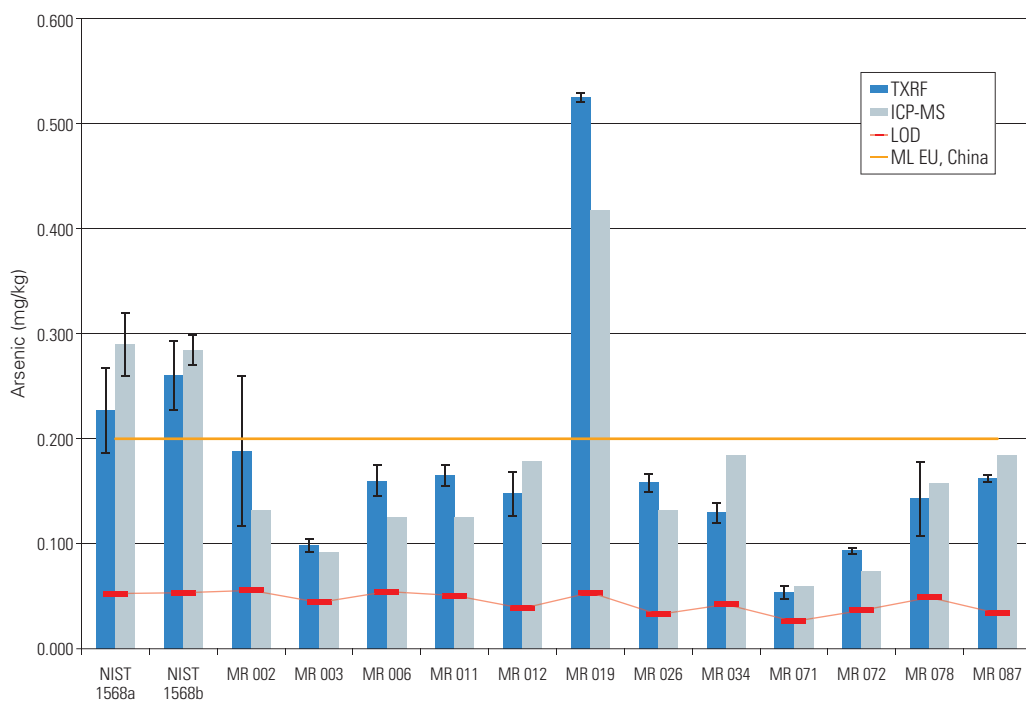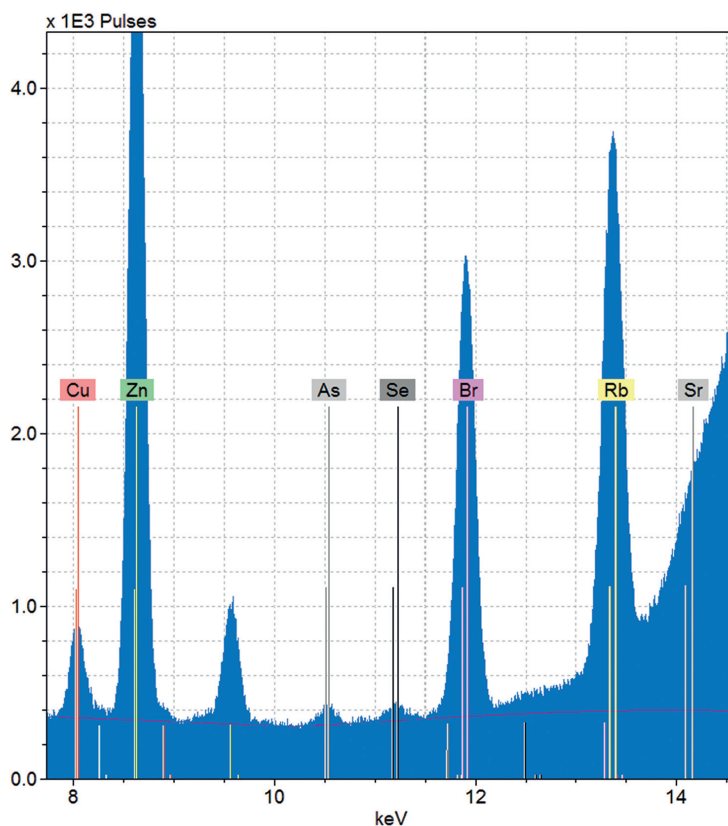Spectrum of rice flour standard NIST 1586a, detail view of the high energy range above 8 keV.

Figure 4

Recovery of TXRF results (blue bars) in comparison with ICP-MS values (grey bars). The red line represents the achieved TXRF detection limits (LOD), the yellow bar shows maximum allowed levels (ML) of As in rice in selected countries.

Results

Figure 3 shows a magnified detail of a typical TXRF spectrum of a rice sample with trace amounts of arsenic. A simultaneous detection of major components (P, S, Cl, K, Ca) as well as of other trace elements (Cr, Mn, Fe, Ni, Cu, Zn, Se, Rb, Sr, Ba, Hg) is possible.

Figure 4 presents the TXRF measurement results and the ICP-MS data for the 12 rice samples and the two reference standards. Considering the standard deviation of the values, it shows that the TXRF results of the rice samples are in good concordance with the certified reference materials.

For the ICP-MS data of the rice samples no standard deviations were available. The TXRF values are in good agreement with the ICP-MS data, even in the concentration range below 0.2 ppm.

Figure 4 also shows the maximum levels accepted in the European Union and in China. Since the detection limits of TXRF are about a factor of 4 to 5 lower, a safe control of the legal limit values is definitely possible. For rice products for infants the maximum levels of arsenic can be even lower. When applying longer measurement times even detection limits below 0.03 ppm can be achieved.

Conclusion

Due to its high sensitivity, TXRF is a suitable method for the determination of arsenic in rice products. It offers a rapid and cost-effective solution for the control of the arsenic amount with regard to legal limit values. The technique is suitable for small laboratories and a valuable analytical technology for developing countries.

Summarized, the TXRF spectrometer S2 PICOFOX offers the following advantages in comparison to AAS, ICP-OES and ICP-MS:

- TXRF does not require complicate and time-consuming sample preparation methods like acid digestion.

- The compact S2 PICOFOX spectrometer can be used on site and at remote locations.

- The installation of a sophisticated laboratory infrastructure with exhausts and gas supplies is not necessary.

- Frequent maintenance of the spectrometer is not required.

- Lab personal with basic analytical skills can be easily trained to operate the S2 PICOFOX.

References

[1] ISO 18507 "Surface chemical analysis — Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis", First edition, 2015-07-15.

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