Metal analysis in rice flour

A A Stakheev, T P Stolboushkina

The Federal State Unitary Enterprise «Russian metrological institute of technical physics and radio engineering» (VNIIFTRI), 141570, Russian Federation, Moscow region, Solnechnogorsk district, Mendeleovo

E-mail: stakheev@vniiftri.ru , stolboushkina@vniiftri.ru

Abstract. The principal goal of present work was to develop a precise method of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method to measure trace toxic elements (Cd and Pb) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method to measure macro and micro elements (K and Cu respectively) in rice flour, the sample preparation method using a system for microwave-assisted pressure digestion and the preparation of laboratory plasticware. The parameters of the sample preparation method, of the spectrometers and measurement results are given.

1. Introduction

Industrialization leads to an increase in man-made environmental pollution. An increase in the content of heavy metals and toxic elements in water and soil leads to an increase in their concentration in agricultural products. This leads to the fact that food products from plant raw materials can be a source of components that are dangerous for human health [1].

Rice is one of the most consumed cereals in the world. Studies have shown that rice accumulates higher concentrations of toxic elements compared to other plants. The accumulation is associated with the peculiarities of rice cultivation. Rice is grown in flooded or very humid areas, which promotes the transfer of toxic elements and heavy metals from the soil to the plant [2]. In order to protect the environment and public health it is often necessary to analyze food for the presence of a number of elements in accordance with the norms of national and international regulatory authorities. The regulation of the content of hazardous elements is becoming more stringent, so that the requirements for food safety are increasing. When using analytical equipment for food analysis, it is becoming increasingly important to obtain highly reliable data on the elemental composition in a wide range of concentrations, whether it is hazardous elements in trace amounts or mineral components in high concentrations. Therefore, it is important to monitor macro, micro and toxic elements and their concentration in the rice and rice products.

Pb and Cd are among the extremely toxic metals for human health. K and Cu are one of the key minerals necessary for the normal functioning of the human body. [3]. Various methods are used to measure the content of these elements in food. Since its introduction ICP-OES and ICP-MS has significantly changed the capabilities of elemental analysis. Today these methods are highly precision and sensitive methods of physicochemical analysis, which are often used for food analysis [4-8]. The success of the measurements and the reliability of the results depends upon the quality of the methods that are developed. Thus, the scope of this research work was to investigate a suitable method for rice flour sample preparation and the method for measuring the concentration of potassium, copper, cadmium and lead in rice flour using ICP-MS and ICP-OES for participating in key comparison.
2. Materials and methods

2.1 Reagents and standards
High purity deionized water (>18 MΩ) from a Adrona Crystal B Ultrapure water purification system (ADRONA SIA Process and Laboratory Systems, Riga, LATVIA) was used throughout this work for preparation and dilution of samples. Lead (Pb), cadmium (Cd), potassium (K) and copper (Cu) solutions directly traceable to the State Primary Standard of the unit of mass fraction and unit of mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods GET 217–2018 were used for preparation standard additions [9].

All of the employed chemical reagents used were analytical grade. Concentrated 65 % HNO₃ purified twice by sub-boiling distillation in a DST-1000 Acid Purification System (Savillex, LLC, USA) was used for digestion procedures and sample dilution. Suprapure 30.0 % H₂O₂ (Merck, Germany) used in the digestion procedures in order to help oxidation of the organic matter. The accuracy of the methods was assessed by analyzing of the certified reference material of rice flour (NIST 1568B), the obtained results compared with the certified value.

2.2 Sample preparation
Sample preparation procedure is an important step in the analysis. This is one of the important sources of errors in method development. In order achieve high-quality blank and to reduce the risks of contamination of the samples the procedure for treatment of plasticware in an ultrasonic bath in four stages using 5 % HNO₃ and deionized water was carried out. The PTFE vessels were cleaned by cleaning run (with 65 % HNO₃ and 30 % H₂O₂) in microwave-assisted digestion system prior to each sample digestion run.

The samples of rice flour were dried in a drying chamber (Binder FED53, Germany) at (60 ± 2) °C until constant weight. Afterward, the samples were stored in a desiccator until analysis.

For the sample preparation assisted by microwave-assisted acid digestion used a mixture of high purity deionized water, 65 % HNO₃ and 30 % H₂O₂. All dry samples (0.5 g) were weighted and transferred to the PTFE vessels of the system for microwave-assisted pressure digestion TOPwave (Analytik Jena, Germany ). 4 mL of HNO₃, 1 mL of H₂O₂, and 4 mL of H₂O were added to the sample in the vessel. For complete decompose of the samples a five-stage digestion program was used. The overall program of the microwave digestion is presented in Table 1.

Table 1. Steps and parameters of microwave digestion

| Step | Temperature (°C) | Time (min) | Ramp (min) | Power (%) |
|------|-----------------|------------|------------|-----------|
| 1    | 150             | 5          | 5          | 80        |
| 2    | 180             | 5          | 5          | 80        |
| 3    | 200             | 5          | 20         | 90        |
| 4    | 150             | 5          | 1          | 40        |
| 5    | 50              | 10         | 4          | 0         |

At the end of the microwave heating steps and after cooling to room temperature the digests were then quantitatively transferred to precleaned 50 mL centrifuge tubes. The digests were diluted 50 and 100 times with 2 % HNO₃ before they were measured.

2.3 Instrumentation
The concentrations of K and Cu were determined by ICP-OES and the concentrations of Cd and Pb were analyzed by ICP-MS. All of the measurements were conducted using an ICP-MS and an ICP-OES, which are part of GET 217–2018 – the State Primary Standard of the unit of mass fraction and unit of mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods.
3. Elemental analysis

The standard addition method was used to prevent matrix effects. To select the optimal concentrations of additions, a preliminary measurement of the target elements concentrations was carried out by the external calibration a five-point analytical curve, prepared by diluting the mono cadmium, potassium, copper and lead standards with 2 % (v/v) HNO$_3$. All solutions were prepared gravimetrically. The parameters of the spectrometers are shown in the Table 2 and Table 3.

3.1 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES operating parameters are shown in Table 2.

| Parameter                        | Value                  |
|----------------------------------|------------------------|
| RF power, Watt                   | 1200                   |
| Plasma gas flow rate, L min$^{-1}$| 12                     |
| Auxiliary gas flow rate, L min$^{-1}$ | 0.5                 |
| Nebulizer gas flow rate, L min$^{-1}$ | 0.5                |
| Sample uptake rate, mL min$^{-1}$ | 1.0                   |
| Lines monitored                  | 327.396Cu, 766.491K    |

3.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS operating parameters are shown in Table 3.

| Parameter                        | Value                  |
|----------------------------------|------------------------|
| RF power                         | 1200                   |
| Plasma gas flow rate, L min$^{-1}$| 9                     |
| Auxiliary gas flow rate, L min$^{-1}$ | 1.2                 |
| Nebulizer gas flow rate, L min$^{-1}$ | 0.9                |
| Integration time, ms             | 1250 (per isotope)     |
| Isotopes monitored               | 111Cd, 206Pb*, 207Pb*, 208Pb* |

*The values of lead concentration are expressed as the mean between of the three isotopes

3.3 Analytical results

The results of analysis are consistent with the reference values of the reference material which proves the applicability of the standard additions method for measuring cadmium, potassium, copper and lead in rice flour. Good agreements between the certified and measured values were achieved for certified reference materials. The analytical method was validated by measuring limit of detection (LOD), limit of quantification (LOQ), linearity, precision and relative bias. Eurochem requirements [10] were applied for all calculations. The obtained results compared with the certified value and the relative bias was assessed. Repeatability calculated using ten independent runs of rice flour were better than 5% relative standard deviation (RSD) for all elements. LODs obtained for K, Cu, Cd and Pb were 12.0, 0.24, 0.0004 and 0.0006 mg kg$^{-1}$, respectively. LOQs obtained for K, Cu, Cd and Pb were 50.0, 0.89, 0.0015 and 0.0020 mg kg$^{-1}$, respectively.

The linearity of the calibration curve was evaluated by investigating the correlation coefficient ($r$) of the calibration curves. The $r$ values higher than 0.9990 for all of the analytes were obtained.

Analytical results of reference materials obtained by ICP-OES and ICP-MS in comparison with the certified values are shown in Table 4 and Table 5.
Table 4. Analytical results obtained by ICP-OES

| Element | Measured Value (mg kg\(^{-1}\)) | Certified Value (mg kg\(^{-1}\)) | % Error |
|---------|---------------------------------|---------------------------------|---------|
| K       | \(1261 \pm 54\)                | 1282                            | 1.6     |
| Cu      | \(2.38 \pm 0.08\)              | 2.35                            | 1.3     |

Note: Values are as mean ± SD (n = 10)

Table 5. Analytical results obtained by ICP-MS

| Element | Measured Value (mg kg\(^{-1}\)) | Certified Value (mg kg\(^{-1}\)) | % Error |
|---------|---------------------------------|---------------------------------|---------|
| Cd      | \(0.0218 \pm 0.001\)            | 0.0220                          | 2.7     |
| Pb      | \(0.0084 \pm 0.0004\)           | 0.0080                          | 5.0     |

Note: Values are as mean ± SD (n = 10)

4. Results and Discussion

In this work, we developed and validated ICP-MS method of cadmium and lead levels and ICP-OES method of copper and potassium levels in rice flour. The rice flour were processed using a system for microwave-assisted pressure digestion.

The high concentrations of K and Cu and the trace contents of Cd and Pb were observed for rice flour samples. Both methods are reliable to use for precise analyze the elements in rice flour sample in follow-up studies.

References

[1] Korotkova T G et al 2017 Determination of metals consists in Regul, the raw rice sort KubGAU Scientific Journal 132 (08)
[2] Sauvé S 2014 Time to revisit arsenic regulations: comparing drinking water and rice BMC Public Health 14 (1):465
[3] Glenske K et al 2018 Applications of Metals for Bone Regeneration Int. J. Mol. Sci. 19:826
[4] Voica C, Dehelean A, Kovacs M H, Lazar M D 2012 The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples Food Chem pp 110–113.
[5] Cubadda F 2004 Inductively coupled plasma-mass spectrometry for the determination of elements and elemental species in food: a review J AOAC Int. Jan-Feb 87(1) 15084102
[6] Oto Miedico, Marco Iammarino, Marina Tarallo and A Eugenio Chiaravalle 2017 Application of inductively coupled plasma–mass spectrometry for trace element characterisation of equine meats International Journal of Food Properties 20:12 pp 2888-2900
[7] Jackson BP Punshon T 2015 Recent Advances in the Measurement of Arsenic, Cadmium, and Mercury in Rice and Other Foods Curr Environ Health Rep 2(1):15-24
[8] A González S Armenta M. De La Guardia 2008 Trace elemental composition of curry by inductively coupled plasma optical emission spectrometry (ICP-OES) Food Additives & Contaminants: Part B 1:2 pp 114-121
[9] Dobrovolskiy V I Stakheev A A Stolboushkina T P 2018 National primary standard for the units of mass fraction and mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods GET 217–2018 Measurement Techniques (11):3-5 (In Russ.)
[10] B Magnusson and B Örnemark 2014 Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics (2nd ed.)