

## Determination of Essential Elements in Indian Rice Samples Before and After Washing by ICP-MS

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In this study, a simple analytical technique was established to determine the content of essential elements (K, P, Mg, Ca, Zn, and Cu) in four samples of Indian rice. The influence of soaking, washing, and cooking on the essential elements concentration was determined. Twenty samples employed in this study, were contained in closed vessels and subjected to microwave-assisted digestion. Six elements (K, P, Ca, Mg, Zn, and Cu) were analyzed and determined through inductively coupled plasma mass spectrometry (ICP-MS). In the analyzed elements, the concentration of potassium elements and phosphate was the highest and that of zinc and copper was the lowest. The low values of the limits of detection (LOD) and limits of quantification (LOQ) with a relative standard deviation (%RSD) of 0.2-3% were observed.

**Keywords:** Rice, essential elements, Microwave-assisted digestion, ICP-MS.

### INTRODUCTION

Worldwide, rice is an important food product and necessary diet component of >1000 million consumers. Almost 90% of rice produced worldwide is cultivated and consumed in Asia [1]. Recently, safety concerns regarding agricultural foods caused by the presence of heavy metals, including cadmium, zinc, copper, arsenic and lead have become an environmental problem [2-6]. Heavy metal toxicity results from the consumption of the crops accumulated with these elements and consequently pose a health hazard to humans. In food chains, this pattern causes a gradual increase in the amount of certain metals through bioaccumulation.

The consumption of key trace elements over the safe limit essential for humans, including Cu and Zn, may lead to toxicity. Copper overdose causes immuno and developmental toxicity and an excess of Zn can lead to neurotoxicity [7]. Because of phosphorus deficiency, leaves become short, narrow and considerably erectile, while phosphorus deficiency may develop if a variety has a tendency to generate anthocyanin. Initially in potassium deficiency, on the tips of older leaves, dark-brown necrotic spots or dark-green colour with yellowish-brown leaf

margins appear. Additionally, in severe potassium deficiency, the tips of leaves turn yellowish-brown, and the colour of older leaves changes to brown from yellow [8]. Potassium is one of three macronutrients required in a large amount for plant growth and yield [9]; however, mostly, potassium is eliminated from soil through burning and leaching or plant residue removal. Large amounts of potassium (14.5 kg) are required to produce a ton of rice [10]. Food quality assurance evaluates heavy metal contamination as a main parameter of the procedure [11]. The risks associated with heavy metals present in food products and their recognized negative influence on human health lead to a decrease in permissible toxic element levels in foods in both global and local food quality regulations [12]. An excess of the intake of such metals through food products presents a serious threat to human health [13].

Halim *et al.* [14] reported that the contaminated soil produces rice grains containing high concentrations of heavy metals. In Saudi Arabia, families use rice as the main meal and rice is treated through different means before cooking. Some people use only wash rice. The traditional method followed in Saudi Arabia is soaking rice before cooking it for different time periods. With the influence of each factor on essential elements

known, whether increase or decrease was observed, element concentrations were measured after each treatment.

Differences in rice quality produced by various agriculture regions in terms of metals and essential elements were caused by the differences in rice brand types selected for evaluation (even when the producer country was the same), fertilization type (chemical or organic), irrigation source, the type of poison used, the conditions of spraying, the soil characteristics (pH, humidity, redox potential), rice genus and geographical conditions [15,16]. Additionally, other less important parameters, including sample extraction and preparation methods, measuring instrument accuracy and sample size can be mentioned [17,18].

In this study, the concentration of six metals and essential elements, namely K, Mg, Cu, P, Zn, and Ca, in four rice brands (produced in India) used in Saudi Arabia were analyzed through scanning electron microscopy (SEM) and ICP-MS. These methods are based on the study of the effect of five factors on element concentrations in the samples obtained before analysis. The factors included no washing, washing for three times, soaking for 2 h, soaking overnight and cooking for 20 min.

## EXPERIMENTAL

Nitric acid (69% v/v) and hydrogen peroxide (30% v/v) were procured from Merck, Germany. High purity water was obtained from Millipore Milli-Q water purification system and used throughout the work. A single standard solution for ICP-MS of six elements (P, K, Ca, Mg, Cu and Zn) (Aristar grade, BDH laboratory supplies, England). The ICP-MS (NexION™ 300 D (Perkin-Elmer, USA) instrument employed in the present work was a laboratory constructed unit. Instrument components and operating conditions are given in Table-1.

TABLE-1  
CONDITIONS OF INSTRUMENT OPERATION  
FOR DETECTING METALS IN RICE

RF power	1600 W
Nebulizer gas flow	0.65 L/min
Lens voltage	9.55 V
Analog stage voltage	-1745 V
Pulse stage voltage	950 V
Number of replicates	3
Reading/replicates	20
Scan mode	Peak hopping
Dwell time	40 ms
Integration	1200 ms

**Samples collection:** In this study, four different rice samples were collected randomly from the local markets of Riyadh, Saudi Arabia in 2019. The collected samples were kept in plastic bags at room temperature for further analysis. Before measurement, each rice sample was divided into five parts: the first sample was digested without washing, second sample was washed with deionized water thrice, third sample was washed and soaked for 2 h with deionized water, fourth sample was washed and soaked for whole night with deionized water and finally the last sample was cooked with deionized water.

**Sample preparation:** Dry samples (60-80 mg) were digested in 2 mL of HNO<sub>3</sub> and then 1 mL H<sub>2</sub>O<sub>2</sub> was added using a dry and clean digestion microwave (Milestone Ethos 1600) vessel. The digested sample was then transferred to 10 mL volumetric flasks and made up the volume using deionized water. The rice samples were analyzed using ICP-MS. For Zn and Cu analysis with open digestion, 2 g of clean and dried rice was weighed, placed into a ceramic crucible then heated on an electric cooker until no fume appeared. The contents were placed into a high temperature oven. The substance was firstly carbonized at low temperature, then incinerated at 800 °C for 10-12 h and cooled down. Nitric acid (10 mL of 3% v/v) was added and heated gently to near dryness. After cooling, it was transferred into a 100 mL volumetric flask and diluted to the constant volume with deionized water. The solution was shaken well, then the rice samples were analyzed using ICP-MS [19].

**Determination of essential elements by ICP-MS:** The ICP-MS calibration was carried out by external calibration. The calibration curves of six elements: Mg, K, P, Cu, Ca and Zn were obtained using the blank and three working standards 0, 0.5, 1.0 and 2 mg/L. The calibration curves exhibit excellent linearity for all elements (figures not shown).

**Determination of elements concentration on the surface of rice grains using SEM:** Samples of rice were air-dried at room temperature for a few days and then analyzed using a filtered electron magnifying lens (JEOL 76105 field outflow SEM) in order to estimate the presence of essential elements on the surface of the rice samples [15,20,21].

## RESULTS AND DISCUSSION

Four types of the rice samples from India were analyzed. Table-2 presents the obtained concentrations. For 20 samples, microwave-assisted digestion was conducted in closed vessels to prepare the samples for the ICP-MS analysis. Six elements (K, P, Ca, Mg, Zn and Cu) were analyzed and determined after the sample treatment (no washing, washing three times, soaking for 2 h, soaking overnight and cooking). For comparison, open acid digestion was performed for copper and zinc. The concentration of potassium and phosphate elements was the highest and that of zinc and copper was the lowest among the analyzed elements. After the application of four treatment methods and the measurement of all sample concentrations, a decrease in the phosphate levels was observed after washings. Two hours and overnight soaking resulted in a slight decrease in the phosphate concentrations and after cooking, phosphate concentrations increased to the similar level observed before washings.

Potassium concentrations increased after washing and a drastic loss was observed with 2 h or overnight soaking. Subsequently, after cooking the concentration returned to the highest level. The concentration of magnesium was lower than that of potassium and phosphate, and the highest level of magnesium was obtained in sample-2 among all Indian rice types. The magnesium concentration slightly decreased on applying three treatment methods (soaking and washing), but it increased substantially with cooking. The washing samples showed a decrease in zinc and calcium levels, and the declining effect was higher in zinc because zinc concentration decreased by

TABLE-2  
CONCENTRATION OF ESSENTIAL ELEMENTS IN FOUR TYPES OF INDIAN RICE WITH DIFFERENT PROCESSING METHODS

Sample No.	Element	Conc. $\pm$ %RSD ( $\mu\text{g/g}$ )				
		Without washing	Washing 3 times	Soaked for 2 h	Soaked all night	Cooked for 20 min
Sample 1	P	1332.640 $\pm$ 1.8	1284.551 $\pm$ 1.0	1076.369 $\pm$ 2.4	1178.483 $\pm$ 1.2	1309.706 $\pm$ 1.2
	K	1181.120 $\pm$ 1.5	1296.346 $\pm$ 1.2	759.510 $\pm$ 3.4	688.390 $\pm$ 1.2	1205.588 $\pm$ 1.6
	Mg	279.520 $\pm$ 2.4	260.133 $\pm$ 2.2	199.424 $\pm$ 2.0	187.926 $\pm$ 2.2	292.206 $\pm$ 2.4
	Ca	103.200 $\pm$ 0.8	97.310 $\pm$ 0.4	120.920 $\pm$ 1.0	123.080 $\pm$ 1.0	127.060 $\pm$ 1.0
	Cu	6.240 $\pm$ 1.9	10.130 $\pm$ 0.9	2.880 $\pm$ 0.8	3.170 $\pm$ 1.5	3.530 $\pm$ 0.4
	Zn	8.480 $\pm$ 1.6	2.970 $\pm$ 0.7	7.640 $\pm$ 0.7	17.150 $\pm$ 1.4	5.940 $\pm$ 0.7
Sample 2	P	2939.655 $\pm$ 3.0	2855.162 $\pm$ 0.8	2817.236 $\pm$ 0.4	2572.887 $\pm$ 2.1	2817.357 $\pm$ 1.6
	K	1927.429 $\pm$ 2.9	2181.858 $\pm$ 1.1	1901.398 $\pm$ 0.8	1817.863 $\pm$ 3.0	2296.656 $\pm$ 1.0
	Mg	1124.451 $\pm$ 2.7	1136.431 $\pm$ 2.5	1129.596 $\pm$ 0.5	1116.874 $\pm$ 3.7	1431.529 $\pm$ 0.7
	Ca	115.990 $\pm$ 1.9	98.820 $\pm$ 0.7	128.110 $\pm$ 1.2	130.940 $\pm$ 1.8	133.590 $\pm$ 0.6
	Cu	3.760 $\pm$ 1.0	3.240 $\pm$ 1.7	4.970 $\pm$ 1.0	4.630 $\pm$ 1.8	4.780 $\pm$ 1.6
	Zn	23.820 $\pm$ 0.7	18.140 $\pm$ 1.9	26.860 $\pm$ 0.2	43.860 $\pm$ 0.7	15.790 $\pm$ 0.7
Sample 3	P	1174.629 $\pm$ 2.2	1074.806 $\pm$ 0.6	1121.09 $\pm$ 2.4	917.414 $\pm$ 0.5	1327.576 $\pm$ 2.9
	K	1417.004 $\pm$ 2.2	1543.669 $\pm$ 0.6	982.287 $\pm$ 2.4	621.767 $\pm$ 0.5	1462.900 $\pm$ 2.9
	Mg	269.366 $\pm$ 2.6	230.103 $\pm$ 1.5	228.824 $\pm$ 1.7	131.754 $\pm$ 1.9	269.811 $\pm$ 1.5
	Ca	101.210 $\pm$ 1.4	69.640 $\pm$ 1.6	124.960 $\pm$ 0.5	124.140 $\pm$ 1.3	127.140 $\pm$ 1.2
	Cu	3.640 $\pm$ 0.5	3.620 $\pm$ 0.4	5.480 $\pm$ 1.2	2.560 $\pm$ 1.3	12.710 $\pm$ 0.4
	Zn	37.520 $\pm$ 2.1	9.170 $\pm$ 0.5	23.030 $\pm$ 0.8	28.180 $\pm$ 1.3	24.880 $\pm$ 0.5
Sample 4	P	1027.023 $\pm$ 0.8	1161.846 $\pm$ 2.3	943.876 $\pm$ 1.7	1024.370 $\pm$ 1.1	1022.489 $\pm$ 0.2
	K	873.282 $\pm$ 0.9	835.846 $\pm$ 1.3	535.935 $\pm$ 1.6	559.104 $\pm$ 1.2	938.081 $\pm$ 1.5
	Mg	239.542 $\pm$ 2.0	288.462 $\pm$ 0.3	209.556 $\pm$ 1.6	235.434 $\pm$ 1.1	273.013 $\pm$ 3.0
	Ca	118.320 $\pm$ 1.3	97.850 $\pm$ 0.8	129.090 $\pm$ 1.4	143.690 $\pm$ 0.3	139.880 $\pm$ 0.4
	Cu	3.210 $\pm$ 0.4	3.080 $\pm$ 0.4	3.500 $\pm$ 1.0	3.920 $\pm$ 0.8	4.040 $\pm$ 1.0
	Zn	37.860 $\pm$ 0.6	12.920 $\pm$ 0.8	23.960 $\pm$ 0.9	69.190 $\pm$ 0.9	27.440 $\pm$ 2.0

half. By contrast, zinc concentration increased with 2 h or overnight soaking.

Cooking leads to an increase and a decrease in calcium and zinc concentration levels in all samples. In all the samples, the influence of treatment on the copper concentration was weak because no change in its concentration was observed and it remained nearly constant. Moreover, no considerable increase was observed after cooking, except for sample-3.

Table-3 presents the comparison between closed-digestion microwave and open digestion through acid. The concentration of zinc and copper was higher when the closed digestion system was used. The similar results were acquired when the concentration of elements on the rice grain surface was determined using SEM by weight (%). Tables 4-6 present the concentrations of the study metals on the rice sample surface and SEM images. The results showed a high concentration of potassium and phosphate on the rice grain surface in all the samples. The concentrations of magnesium, copper, calcium and zinc were low. Cooking highly influenced potassium and phosphorus concentrations, and washing and 2 h or overnight soaking mildly affected their concentrations. Washing was considered the preferred option to maintain the concentration of potassium and phosphorus constant. Moreover, cooking results in consid-

erable loss of magnesium, and 2 h or overnight soaking positively affects the preservation of this important element.

Short (2 h) and long periods (overnight) soaking contribute to a substantial increase in calcium and copper concentrations compared with the unwashed rice samples. In samples 2 and 3, with a few unexpected results for cooking, it led to a higher Ca concentration, and in samples 1 and 3, copper concentration increased after cooking. The effect of treatment on zinc concentration in all the samples somewhat varied, where cooking led to an increase in zinc concentration by half in the half of the samples and simultaneously zinc concentration was found to be lacking after cooking in the remaining half samples, which showed 2 h soaking can lead to high concentrations of zinc in all the samples.

The LOQ was calculated by determining the lowest concentrations measured according to the recommendations of ICH Q2(R1). Below these concentrations, the calibration graph was non-linear [22]. The LOD was measured by determining the lowest concentration of the readily detected analyte. Table-7 presents the results.  $\text{LOQ} = (10 \times \text{SD})/100$  and  $\text{LOD} = (3.3 \times \text{SD})/100$ . In these two expressions,  $\text{SD} = \text{SE} \cdot \sqrt{N}$ ,  $\text{SE} = \text{RSD}/\sqrt{N}$ . The relative standard deviation is represented by three blank measurements of the standard deviation corresponding to %RSD and SD.

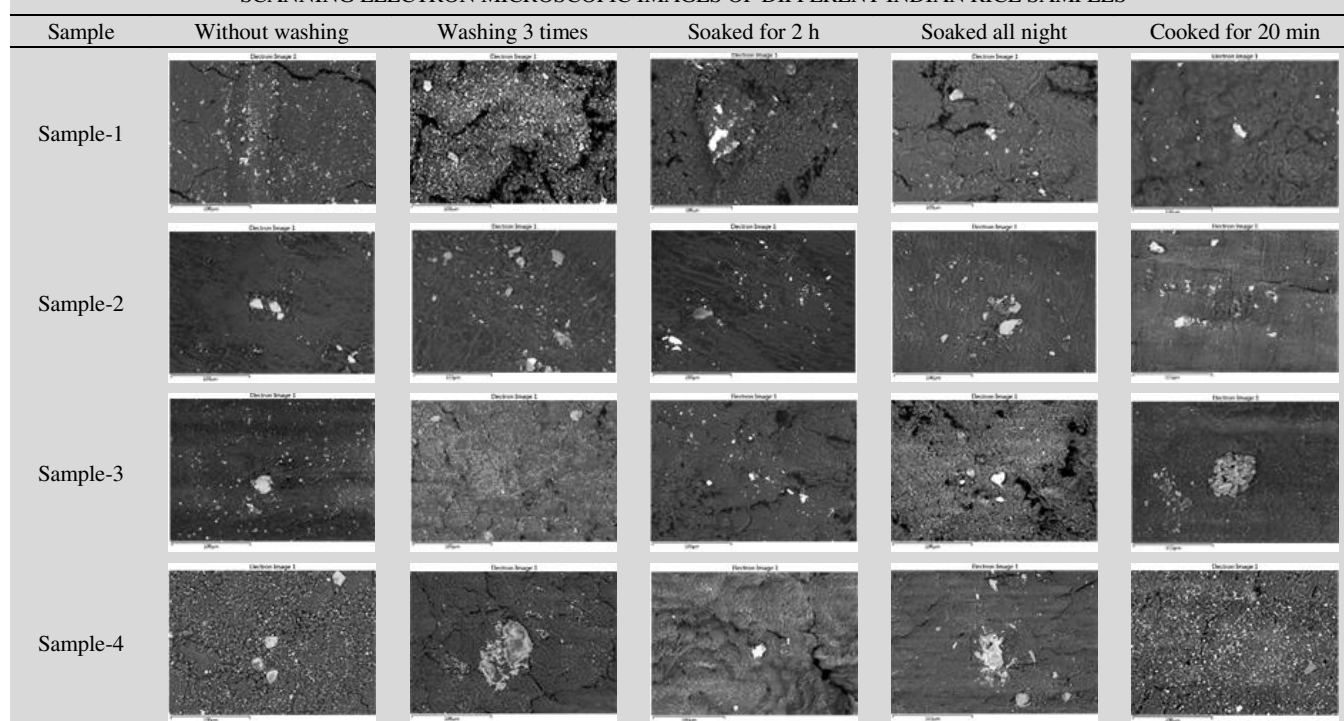
TABLE-3  
COMPARISON BETWEEN OPEN AND CLOSED DIGESTION FOR CONCENTRATION OF Cu AND Zn (mg/kg)

Sample	Cu			Zn		
	Closed digestion	Open digestion	Difference (%)	Closed digestion	Open digestion	Difference (%)
Sample 1	6.240 $\pm$ 1.9	4.891 $\pm$ 3.3	21.62	8.480 $\pm$ 1.6	7.2 $\pm$ 3.0	15.09
Sample 2	3.760 $\pm$ 1.0	2.678 $\pm$ 0.7	28.78	23.820 $\pm$ 0.7	14.688 $\pm$ 1.0	38.34
Sample 3	3.640 $\pm$ 0.5	3.21 $\pm$ 0.7	11.81	37.520 $\pm$ 2.1	28.825 $\pm$ 1.0	23.17
Sample 4	3.210 $\pm$ 0.4	3.149 $\pm$ 1.2	1.90	37.860 $\pm$ 0.6	27.423 $\pm$ 0.1	27.56

TABLE-4  
CONCENTRATION OF ESSENTIAL ELEMENTS (wt.%) IN INDIAN RICE SAMPLES BY SCANNING ELECTRON MICROSCOPY

Sample	Elements (wt.%)	Without washing	Washing 3 times	Soaked for 2 h	Soaked all night	Cooked for 20 min
Sample-1	P	41.58	38.06	22.37	14.46	8.51
	K	21.13	17.16	9.48	6.19	5.97
	Mg	20.99	16.79	10.08	4.67	0.0
	Ca	6.46	2.66	1.48	5.27	6.90
	Cu	0.0	5.45	18.04	18.25	34.90
	Zn	0.0	3.12	10.74	10.59	22.44
Sample-2	P	3.3	4.9	6.0	1.9	0.0
	K	26.0	15.7	18.5	12.6	26.3
	Mg	3.9	5.3	8.6	5.5	0.0
	Ca	2.1	1.6	2.6	6.8	29.6
	Cu	9.4	7.6	21.6	6.8	7.5
	Zn	5.9	4.3	13.7	6.0	0.0
Sample-3	P	29.0	43.1	19.2	21.6	10.5
	K	12.2	31.5	8.8	10.2	5.7
	Mg	13.3	0.0	8.5	4.7	6.2
	Ca	2.4	5.7	1.0	0.0	8.4
	Cu	5.7	0.0	24.4	3.4	13.4
	Zn	4.6	0.0	15.5	0.0	8.1
Sample-4	P	38.30	21.51	20.06	15.20	1.6
	K	19.75	11.82	5.6	7.24	0.72
	Mg	13.34	9.05	-	9.74	0.8
	Ca	1.57	7.64	2.8	2.05	0.1
	Cu	2.58	0.0	6.8	3.23	0.12
	Zn	1.95	0.0	5.9	0.0	0.0

TABLE-5  
SCANNING ELECTRON MICROSCOPIC IMAGES OF DIFFERENT INDIAN RICE SAMPLES



Several determinants, including temperature and time, influence the digestion efficiency. Acid, boiling points and analyte volatility were also employed to measure the temperature of open-acid digestion systems [23]. Metal dissolution is enhanced because of an increase in biological sample-acid collisions, which is caused by an increase in temperature [24].

The heating of the vessel containing a solution eventually leads to solution heating, but this heating occurs after a relatively long-time span. The boiling points of acid(s) serves as a limitation during digestion. The most volatile acids in multi-acid processes have lower boiling point. These acids are among the first components to boil [25]. Zinc and copper concentrations

TABLE-6  
EFFECT OF ESSENTIAL ELEMENTS CONTENT IN DIFFERENT RICE SAMPLES ANALYZED BY SEM

Essential elements	Different treatments effect
Phosphate	Washing several times is the best choice with this element, it maintains the ratio of it and sometimes caused a higher rate.
Potassium	Washing and soaking maintain the concentration of this element, while cooking often has a negative effect on its ratio.
Magnesium	The ratio of this element is greatly affected by all treatments specially in cooking. While soaking 2 h often has a positive effect on its ratio.
Calcium	Treatment with soaking for 2 h or one night increases the concentration of this element, while the cooking not highly effect on its ratio.
Copper	Soaking for 2 h or one-night effect a lot in this element, but treatment with cooking increases the concentration of this element some times.
Zinc	Almost this element effected with soaking and cooking.

TABLE-7  
METAL DETERMINATION METHODS FOR RICE SAMPLES AND THEIR LIMITS OF QUANTIFICATION (LOQ) AND LIMITS OF DETECTION (LOD), (WITHOUT WASHING) ( $\mu\text{g/g}$ )

Element	LOD (conc. $\mu\text{g/g}$ )	LOQ (conc. $\mu\text{g/g}$ )
P	0.247	5.050
K	34.090	103.305
Mg	0.108	0.327
Ca	0.010	0.031
Cu	0.062	0.187
Zn	0.055	0.168

were higher when the closed-digestion system was used because microwave digestion systems provide higher extraction efficiency and in open systems, digestion extraction can remain incomplete depending on the discretion of analysts. The loss of volatile elements, including lead or mercury, can occur during open digestion and in closed-digestion system, the loss of volatile elements does not occur.

The results indicated that cooking adversely affects mineral contents (Cu, Mg, K, Ca, Na, Mn and Fe). Some common household cooking methods can considerably reduce Zn bioaccessibility in rice [26,27]. Low-temperature cooking is highly effective for preserving crucial elements [28]. No considerable changes were observed in the content of Mg, Mn, Ca, Fe and Zn minerals after soaking, except in the Mn mineral in a sample because Mn and Mg flow out of rice grains during soaking and may be reabsorbed during cooking, which leads to an increase in the mineral content (compared with soaking samples) [28]. Washing grains several times after soaking led to the successful removal of several heavy metals from the rice [29].

## Conclusion

In this study, six essential elements found in four Indian rice samples were evaluated using ICP-MS. The effects of soaking, washing and cooking on the essential element concentration were studied. In all the samples after cooking, an increase in the essential element concentration was observed, except in zinc.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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