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Photochemical investigation of elements in *Oryza sativa*

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ABSTRACT

Short white rice grains produced locally from Mahaica, Guyana were collected from the rice farm and analyzed for ten trace elements by flame atomic absorption spectrometer. The concentrations of the trace elements investigated are as follows: - Ca (76.81), Mg (54.30), Fe (28.2), Cu (4.90), Zn (71.16) and Mn (14.33) mg/Kg. There had been controversial reports about the toxic elements normally present in the rice produced in different areas and conditions. The other four toxic elements As, Co, Pb and Al were also analyzed but not detected. With reference to the literature on the maximum daily intakes for human consumption, the concentration levels were all below the literature except for zinc and manganese.

Keywords: *Oryza Sativa*; Rice Grains; Human Consumption; Trace Elements; AAS

1. INTRODUCTION

Oryza sativa commonly known as rice is a member of the grass family, *Gramineae* and belongs to the genus *Oryza* under the tribe *Oryzaceae* [1]. Rice is an important food commodity for most people all over the world. Rice provides 20% of the world's dietary energy supply and is also a good source of thiamine, riboflavin, niacin and dietary fibre [2].

In addition to the presence of vitamins, elements can also be found in rice due to their uptake medium such as water and soil through their roots. Their presence in human body provides different important metabolic functions and can also lead to human health risks.

Certain trace elements are necessary for the maintenance of certain physicochemical processes which are very important for optimal health and they play important roles to in many activities of the body [3]. Trace elements are required by humans in amounts ranging from 50 micrograms to 18 milligrams per day [4]. These elements are the simplest substances that cannot be broken down by chemical methods.

Trace elements can be categorized as major, minor and ultra-trace elements. Major trace elements include sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg), are required by humans above 50mg per day. Minor trace elements such as iron (Fe), iodine (I), zinc (Zn), copper (Cu), manganese (Mn), chromium (Cr), selenium (Se) and cobalt (Co) are required by humans less than 50 mg per day. Lastly, arsenic (As), aluminum (Al), lead (Pb) and barium (Ba) are the ultra-trace elements not essential for human intake. If present in more than 50mg quantity these trace elements can lead to toxic problems in humans. Toxicity and importance of these trace elements are:-

Dangers of lead and arsenic poisoning

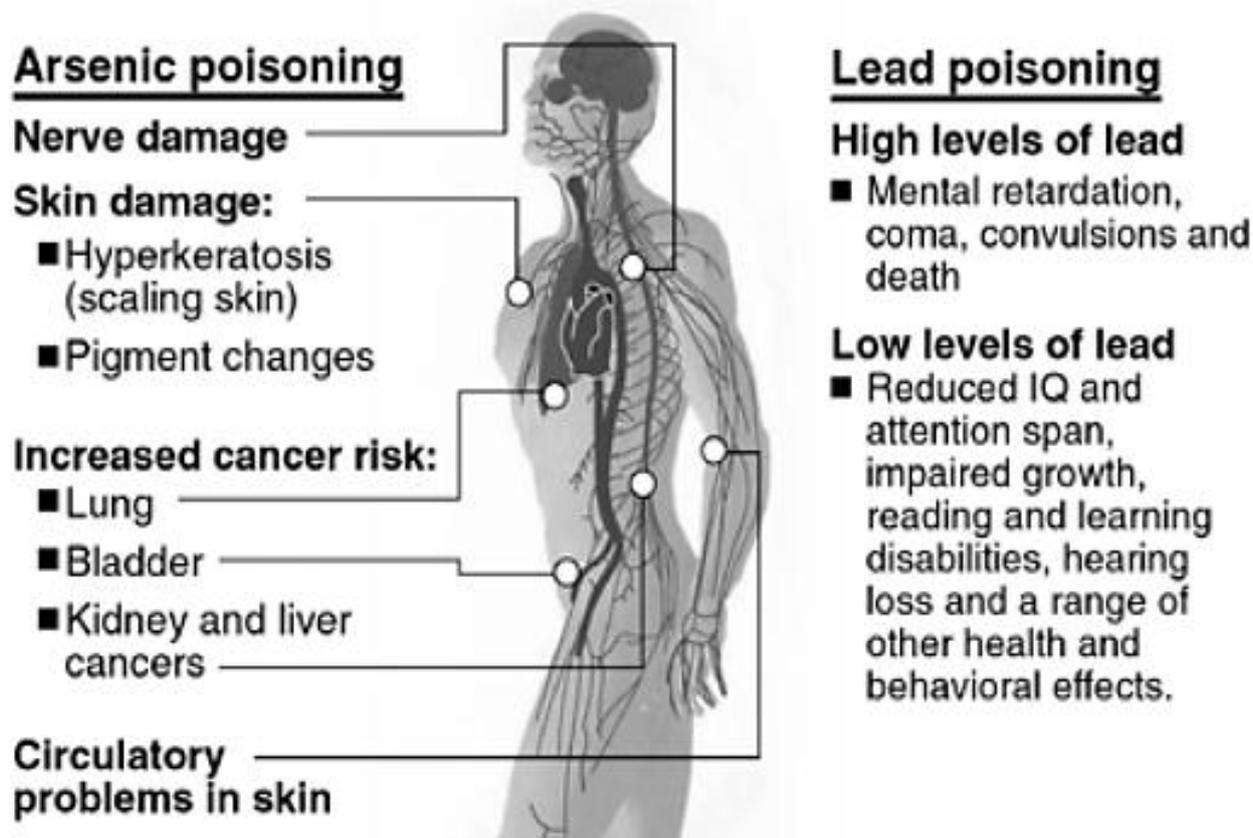


Fig. 1. Showing the effects of lead and arsenic on the different parts of body.

Aluminum (Al) Recent studies implicate aluminum toxicity in Alzheimer's disease, other brain and senility syndrome. The amount of aluminum an average is found around 65mg mostly in the lungs, brain, kidney, liver and thyroid.

Arsenic (As) is considered to be one of the most carcinogenic, dangerous and toxic element. Long term exposure of arsenic to humans has been shown to increase the risk of cancer of the skin, lungs, urinary bladder possibly even kidney, liver and prostate cancer. The most toxic forms of arsenic are inorganic arsenic(III) and (V), with ethylated form having acute toxicity. Arsenic can cause a characteristic pattern of skin changes that involve a darkening of the skin and the appearance of small 'wart-like' outbreaks on the palm, soles and torso. Arsenic can also affect the peripheral nervous system and the blood count. Although some studies suggest that arsenic may also contribute to poor circulation, high blood pressure, heart disease, liver toxicity, diabetes, and reproductive effects its role in these illnesses has not been clearly defined [5,6].

The "consumer Reports" in 2012 reported that the rice contains high level of arsenic. The studies were further made on number of different varieties of rice produced in different locations and countries. Another report was presented in 2015 that only the Basmati rice produced in California, India and Pakistan has a very minimal quantity of arsenic which is safe to consume.



Fig. 2. A few varieties of rice grains.

Rice absorbs more arsenic than the other grains because the way it is produced in more water where the fertilizers and pesticides are contributors of arsenic. It has been advised to rinse the rice properly to remove some percentage of the arsenic before cooking and the eating.

Calcium (Ca) is needed for the construction and maintenance of teeth and bones [3].

Cobalt (Co) is present in the component of cobalamine commonly known as vitamin B2 [7].

Copper (Cu) needed for the development of connective tissues, nerve coverings and bone, acts as reductant in enzyme superoxide dismutase and cytochrome oxidase. Toxicity is very rare in humans but can be associated with liver damage and can lead to gastrointestinal effects characterized by vomiting and diarrhea [7].

Iron (Fe) aids in functioning of red blood cells to transport oxygen to the body. Chronic intoxication occurs frequently associated to genetic and metabolic diseases and repeated blood transfusion [7].

Magnesium (Mg) needed for healthy bones and blood vessels, muscle and energy formation. Low magnesium intake resulting in magnesium loss will intensify the magnesium depleted state [8,9].

Manganese (Mn) associated with bone development, present in the active site of cytosolic mitochondrial enzyme and can cause Parkinson-type syndrome [7].

Lead (Pb) influences biological enzyme systems. Organs or systems which may be affected at such exposures can be haemopoietic, nervous, cardiovascular, reproductive and immune systems [10].

Zinc (Zn) supports normal growth and development in pregnancy, childhood and adolescent. Also, involves in the activity of about 100 enzymes such as carbonic anhydrase and RNA polymerase. Toxicity occurs in acute and chronic forms [7].

2. INSTRUMENTATION OF FLAME ATOMIC ABSORPTION SPECTROMETRY

FAAS is a common, widely established and accepted analytical technique capable of quantitative detection of trace and ultra-trace elements and metals in a wide variety of sample solutions.

In order to carry out an analysis, the element of interest must be compatible to the hollow cathode lamp used. The liquid sample is fed into the flame via a nebulizer which converts the sample into atoms at approximately 2300 °C. Radiation released from the hollow cathode lamp passes through the flame. Some of the radiation is absorbed by the atomized element and then passes through the monochromator. The light that reached the detector is then measured to the intensity of the light that hit the detector when the sample was not present. The processor then calculates the results obtained by the detector and the amount is outputted on the display screen.

A study on sixteen essential and trace elements in polished rice produced in South Korea were reported [10]. The method used by Jung et al included sixty-three samples from eight administrative areas. The collected samples were washed with deionized water and dried at 20 °C for five days. Two grams of dried sample was added to 5 mL concentrated 70% nitric acid and heated on a block at 100 °C and 50 °C for three hours each, 150 °C for ten hours and 160°C for one hour. Upon cooling, 3 mL concentrate perchloric acid was added to the sample and slowly heated for the second time at 150 °C for eighteen hours.

The dried residue was leached at 70 °C in 2mL 5M hydrochloric acid for one hour with an attached condenser. Finally, it was leached with added 8mL deionized water and shaken via vortex mixer. The solution was then analyzed via inductively coupled plasma atomic emission spectrometry. Successful completion of the study they obtained the following results with a median level.

Atomic Spectroscopy with Flames

Atomic Absorption Spectroscopy

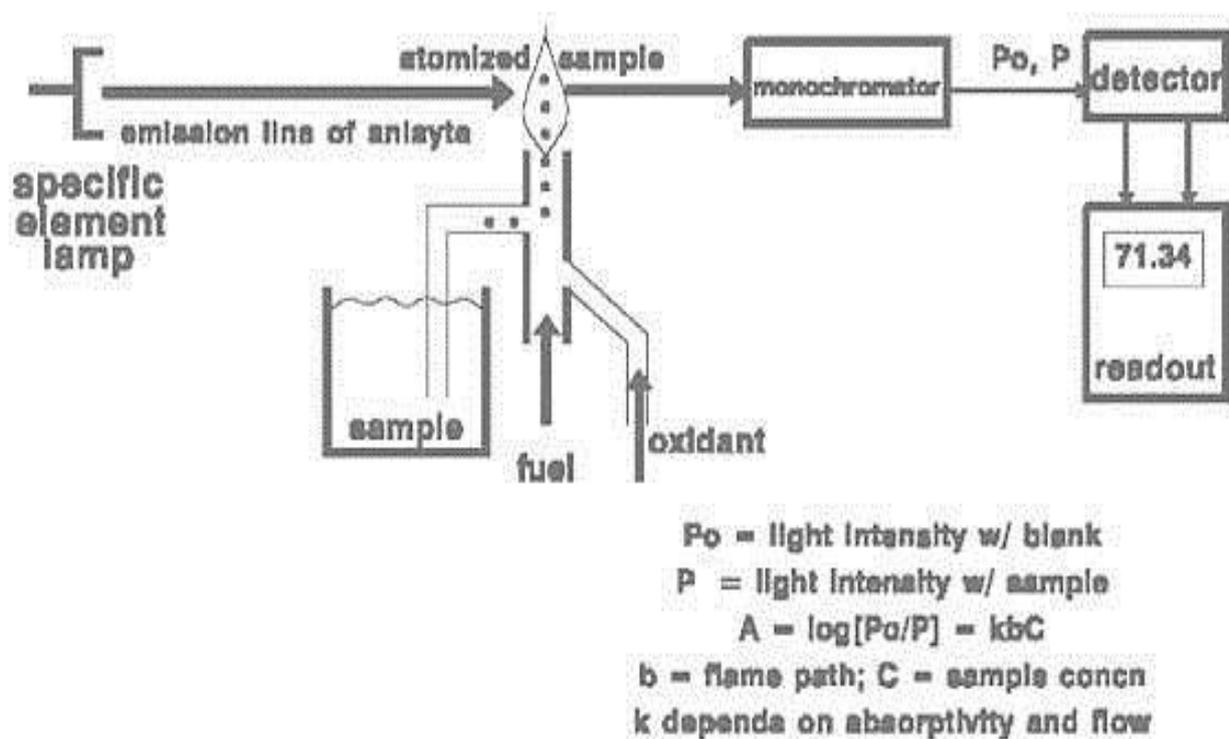


Fig. 3. Showing a typical setup for flame atomic absorption spectra of rice grains solution.

Table 1. Showing essential elements in rice grains.

Essential elements (mg/kg)	
Potassium	2190
Calcium	94.7

Aluminum	10.9
Iron	10.5
Sodium	14.0
Zinc	16.9
Silicon	51.1
Magnesium	94.6
Trace elements (mg/kg)	
Copper	1.850
Barium	0.970
Lead	0.190
Arsenic	0.124
Chromium	0.093
Nickel	0.090
Cadmium	0.021
Cobalt	0.006

In conclusion, the baseline study of essential and trace elements in polished rice found that potassium had the highest context followed by magnesium, calcium, silicon, zinc, sodium, aluminum and iron. Among the eight administrative areas, analysis of essential elements and trace elements for possible inter area variation by ANOVA showed no statistically significant difference in all areas ($p > 0.05$).

There are many digestion methods that can be applied for different elements. For instance, the determination of total arsenic was done via acid digestion.

In the present investigation an aliquot of sample 0.5g was quantitatively digested in 5 mL concentrated nitric acid using a microwave-assisted digested system. The digestion solution was quantitatively transferred to a graduated test tube and made up to volume with 10mL water. An aliquot of resulting solution was quantitatively transferred to a test tube and an aqueous solution of 4 mL Rhenium, an internal standard. [12]. The main aim of the study was to determine heavy metals on Swedish market. The total arsenic was determined with the use of inductively coupled plasma mass spectrometry (Axion, Thermo Elemental, UK) with a resolution setting of 11000. The recovery of total arsenic was quite small and the researchers' mean level of total arsenic was as follows:

Table 2. Showing concentration of arsenic in different varieties.

Rice type	mg/kg
Parboiled	0.21
White	0.10
Long grain	0.24

2. 1. Description of experiment

Table 3. Trace element concentrations in white rice in present study.

Trace elements	Concentration levels (mg/kg)
Major	
Ca	76.81
Mg	54.30
Minor	
Cu	4.90
Co	ND
Fe	28.26
Zn	71.16
Ultra-trace	
Al*	ND
As	ND
Mn	14.33
Pb	ND

In our present study approximately 15 g white rice grains were washed with deionized water to remove dust and dirt present. The sample was then bloated to remove excess water.

Approximately 10 g of sample was weighed into a crucible and dried in oven at 90-100 °C for approximately 10 hours. 1.0 g finely ground sample was accurately weighed into a conical flask. Aqua regia, a digestion mixture containing 15 mL concentrated hydrochloric acid and 5 mL concentrated nitric acid, was slowly added to the dried sample and allowed to react in fume hood for about 1 hour with continuous stirring with applied heat. The digested sample was allowed to cool and made up to mark in 100 mL volumetric flask with deionized water.

Al, Ca, Co, Fe, Mg, Mn, Pb and Zn were all analyzed by Flame Atomic Absorption Spectrometer (Varian AA240 series).

For the study of arsenic, 1.0 g finely ground sample was suspended in 20 mL hydrochloric-sulfuric mixture. Approximately 0.5 g potassium iodide was added to reduce arsenic followed by 20% stannous chloride to clear the liberated iodine solution with frequent stirring. The solution was then transferred to 100 mL volumetric flask and made up to make with hydrochloric-sulfuric acid (50% v/v). The test for arsenic was analyzed by Flame AAS (Thermo Scientific iCE 3000 series).

The above concentrations are shown in the chart below

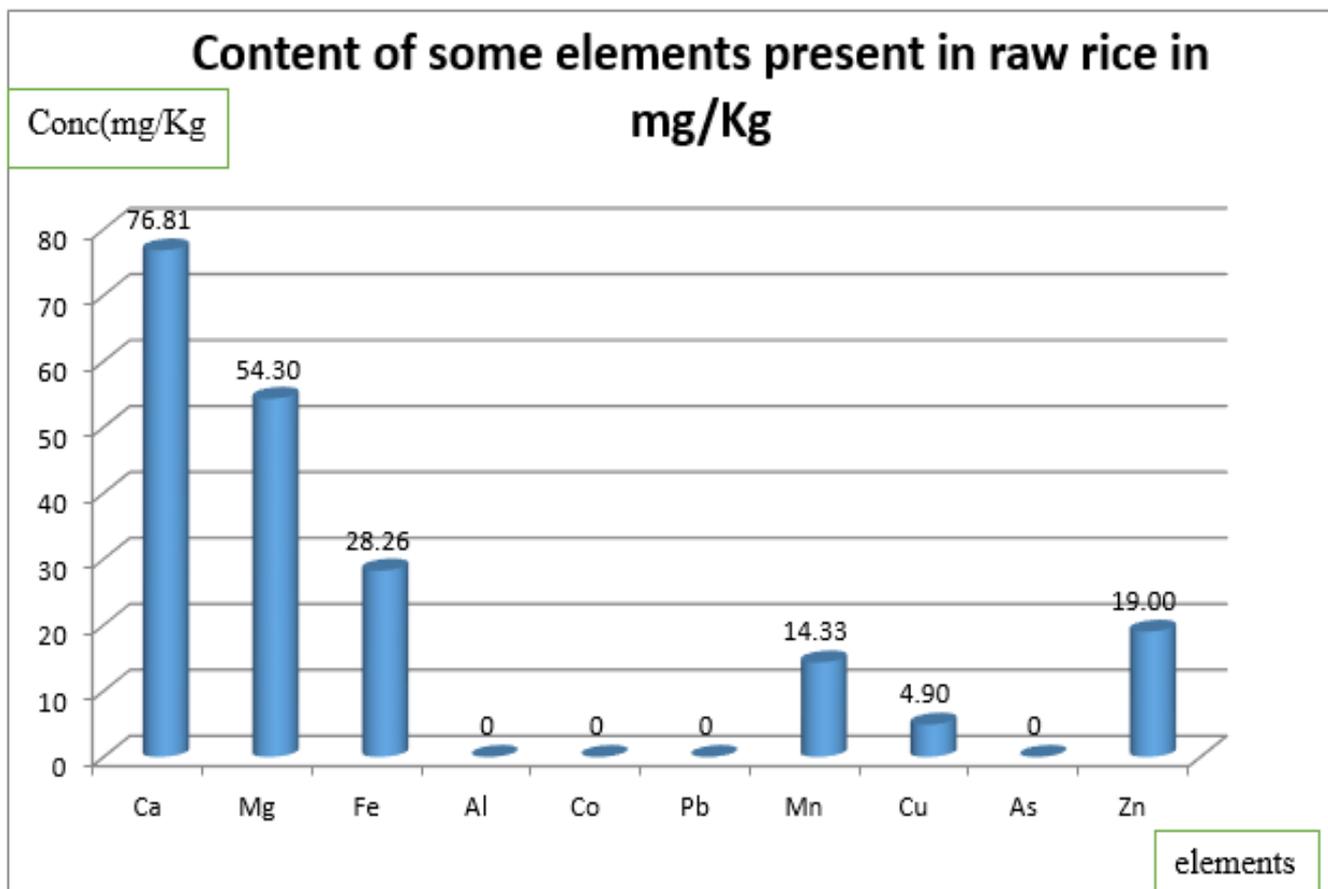


Fig. 4. Showing the comparative concentration of different elements in white rice.

3. RESULTS AND DISCUSSION

Ten trace elements, magnesium and calcium, iron, copper, zinc, arsenic, cobalt, aluminum, lead and manganese were investigated in short white grain rice from Mahaica Guyana. The rice sample was prepared and analyzed via flame atomic absorption spectrometers in IAST and GuySuCo laboratories in Guyana. The mean concentration levels of the elements of the white rice short grains from Mahaica Guyana are shown in Table 3 .

For the individual elements analyzed, Ca showed the mean highest concentration 76.81 mg/Kg, followed by Zn 71.16 mg/Kg, Mg 54.30 mg/Kg, Fe 28.26 mg/Kg, Mn 14.33 mg/Kg and lastly Cu 4.90 mg/Kg. The other four elements Al, Co, Pb and As were not found in the rice sample and so were listed as ND (not detected) and as zero mg/kg on the graphs

The graph below shows the experimental findings of all the elements studied in a side by side comparison to the literature for human consumption. With the exception of manganese and zinc concentrations, all the other concentrations were lower than the maximum intakes per adult per day, safe for human consumption.

The average concentrations for Mg and Ca were determined to be 54.30 mg/Kg and 76.81 mg/Kg, respectively. The concentrations levels for the two elements were all lower than the literature but also showed major deviations. Calcium had the larger deviation of 1573.19 mg/Kg and magnesium 625.70 mg/Kg.

The literature for Co, Pb and As showed very small concentrations safe for human consumption. The experimental concentrations for the listed micronutrients showed no sign of absorption. The concentration for Al also showed no sign of absorption; however, the maximum intake for human consumption is listed as 17 mg/Kg in the literature. *According to Joint Expert Committee in Food Additives [12], aluminum compounds have potential to affect the reproductive systems but appear to be poorly absorbed by humans.

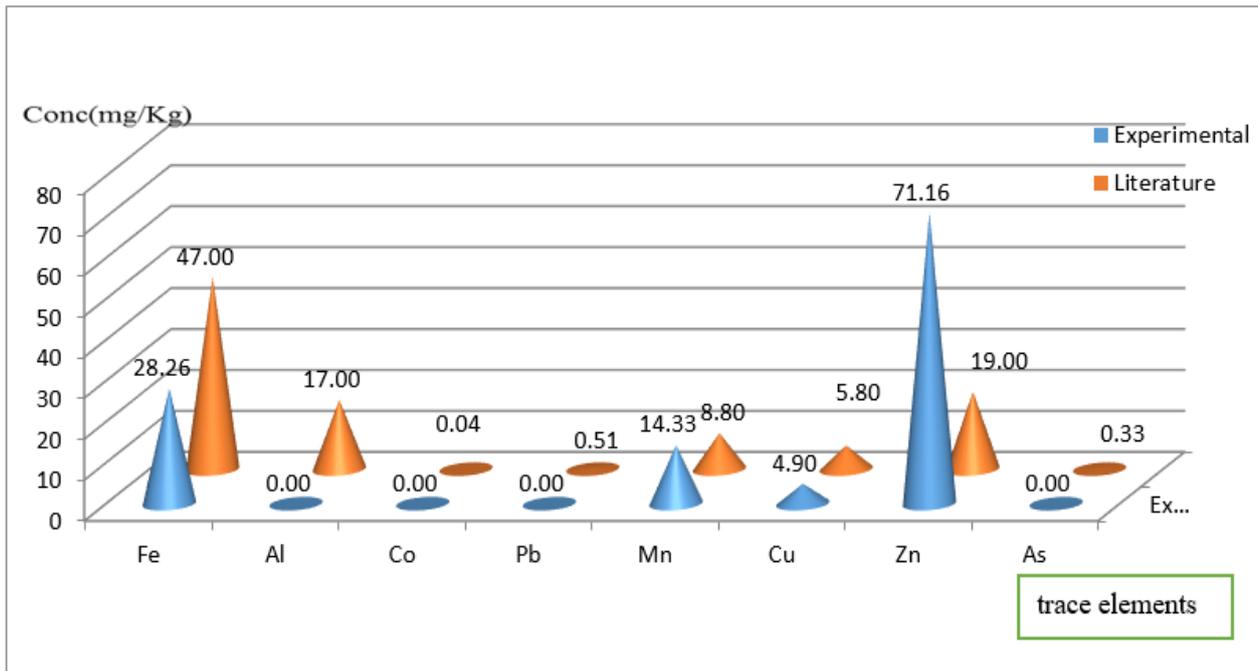


Fig. 5. Showing comparative concentrations of elements of present study and literature values

The concentrations of zinc and manganese in rice sample exceeded the literature. For zinc the concentration was found to be 71.16 mg/Kg, more than three times the literature. On the other hand, manganese concentration level is about two times the daily intake for humans. But the present study shows a very low values for calcium and magnesium than the reported values for them as shown in Fig. 6.

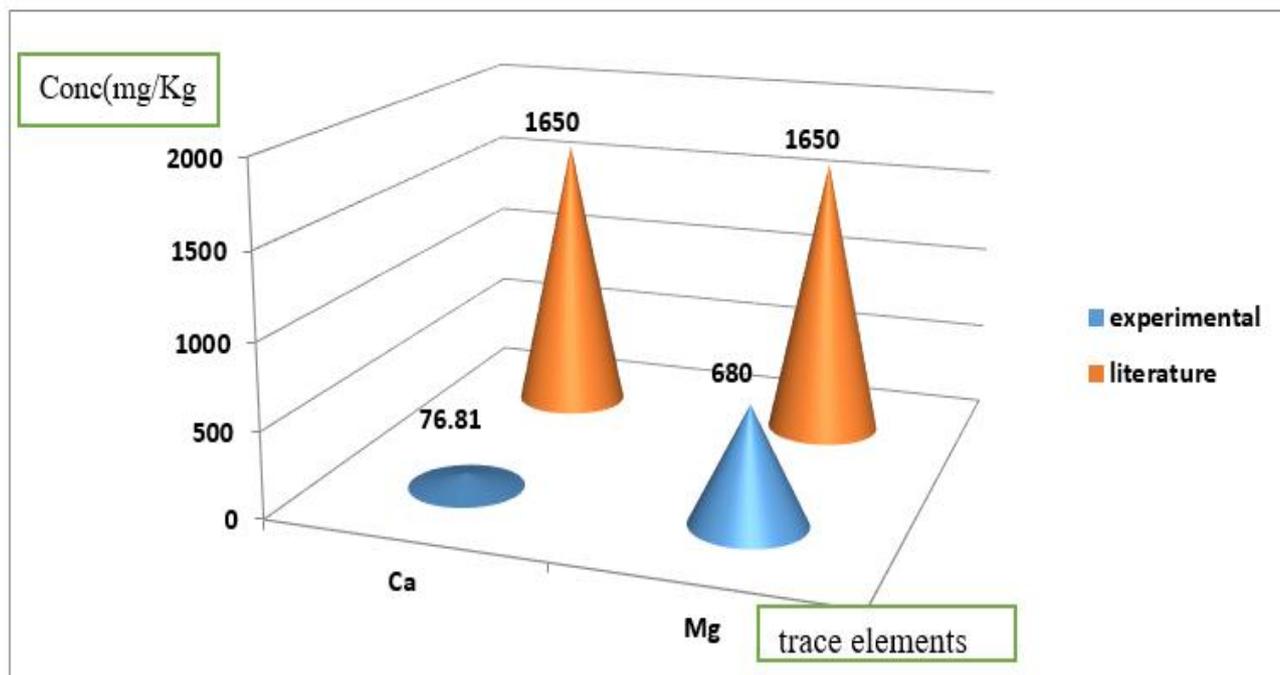


Fig. 6. Showing comparative concentrations for calcium and magnesium experimentally observed and literature values.

4. CONCLUSION

In the present study the content of ten trace elements in white rice short grains from Mahaica Guyana using flame atomic absorption spectrometer has been investigated. The concentration of Ca, Mg, Fe, Cu, Zn, and Mn are 76.81, 54.30, 28.26, 4.90, 71.16, 14.33 mg/Kg, respectively. Pb, As, Co and Al were not detected. Moreover, from the micronutrients and macronutrients found in white rice from Mahaica Guyana thus do not exceed the literature by large amounts that can cause any toxicity in humans when consumed on daily basis.

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