# PRELIMINARY DETERMINATION OF ESSENTIAL AND TOXIC ELEMENTS IN BUCKWHEAT (*Fagopyrum Esculentum*) BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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**ABSTRACT**

This paper describes the preliminary determination of some element concentration in buckwheat and commercial buckwheat flour determined by ICP-MS. The results indicate how essential and toxic elements added in the soil were absorbed by the buckwheat seeds planted and how the elements concentration of the new seeds was affected by this intentional addition. Results showed limits of detection and quantification range from 0.008 to 1.085 µg/Kg. Correlation coefficients (r) were calculated in the range of 0.9920 to 0.9999. The data obtained described that some elements are far below LOD and LOQ in µg/Kg concentrations in the grains. and that ICP-MS was a very precise method to determinate simultaneously many elements at the same time.

**Keywords:** *Buckwheat, ICP-MS, microwave digestion, mineral elements*.

## 1. INTRODUCTION

Lately this decade the number of allergic people to some types of proteins like gluten. soy or dairies are considerable risen (1). In the search of alternatives to supply the food that those people can't eat. the buckwheat (*Fagopyrum esculentum*) appeared from the family of pseudo cereals seeds with high concentration of proteins. vitamins and fatty acids (2-5) which most important feature is the absence of gluten same as quinoa (Chenopodium quinoa) and amaranth (*Amaranthus sp*.). Buckwheat arrives to Chile in the decade of 90 from northern Asia (6). Specifically, to the southern region of the country since the climate allows the optimal growth of this type of plants like a rainy but not too cold winter and good temperatures in the beginning of spring season.

Knowing the properties and alimentary values of proteins and minerals have become very important in the life of people who are allergic to gluten or have a vegan style of life (7-8). eating this pseudo cereal as grain or flour. Buckwheat has reported pharmacological activity showing cardiovascular benefits reacting with cholesterol and glucose present in blood (9-10) and oxidative stress (11).

Also. its reported that the flowers of the buckwheat plants are used to produce honey with beehives only interact with them with almost the same elements concentration as seeds. The elements that are going to be determined by ICP-MS analysis are Li. Cr. Co. Ni. Ga. Ag. Cd. In. Pb and Bi were divided by two groups. essential and toxic. The toxicity of an element is ambiguous and determined by its concentration in the ingest of it. but they were classified as toxic in this paper as the elements that needs low concentration to affect the health of humans (12-14). These elements are going to be analyzed in acidic solutions after an oxidizing microwave digestion (15-17).

There are many variables on the absorption of minerals and elements of the plant. like the quality and quantity of the fertilizer if it's used (18-19). the characteristics of the irrigation water and soil (pH. ORP and proper concentration of the elements) could affect the growing of the buckwheat plant.

It is known that adding heavy metals on soils before planting some vegetables. will affect the absorption and accumulation capacity of the plant (20). So this work will be focused on this theory with another type of seed like buckwheat instead of the plants used in that investigation. The soil that was treated here is classified as *trumao* type that its commonly found in southern Chile. a volcanic ash derived type of soil with high organic content and acidic pH (21-22).

## II. MATERIALS AND METHODS

Materials.

Samples of buckwheat (Fagopyrum esculentum) used for line base were obtained from Universidad de Concepción. Chile and Universidad Autónoma de Chile of Temuco. Chile. Buckwheat flour was obtained from a local supermarket.

Reagents

$HNO_3$ (superior grade of pure. Merck). $H_2O_2$ (suprapur. Merck). Ultrapure water with conductivity down to 0.057 uS/cm for analysis.

Samples preparation.

The buckwheat seeds samples were ground and put in the microwave digestion tubes with 10mL of $HNO_3/H_2O_2$ (9:1) for approximately 2 hours for digestion at 140°C same as buckwheat flour samples (23). All samples were filtered and adjusted to a final volume of 50mL with deionized water before determination by ICP-MS (THERMO FISCHER iCAP).

The multielement standard solution IV were obtained by Merck. Standard curves ranged from 1.00. 3.00. 5.00 and 10 ug/L for Li. Cr. Co. Ni. Ga. Ag. Cd. In. Pb and Bi were prepared by diluting 1000 mg/L mixed standard solution.

## III. RESULTS AND DISCUSSION

Selection of elements isotopes

Working with ICP-MS concerns knowing that it will be some interferences due reactions caused by the matrix or the plasmogen gas. So, to analize an interference free determination as possible it is necessary to choose the best isotope to determinate. some elements have and abundant isotope that its commonly chosen but in some cases that isotope have many interferences. The isotopes chosen were showed in Table 1.

**Table 1**. Elements isotopes chosen to the determination.

| Element | Isotope | Abundance |
|---|---|---|
| Li | $^{7}$ Li | 93% |
| Cr | $^{52}$ Cr | 85% |
| Co | $^{59}$ Co | 100% |
| Ni | $^{60}$ Ni | 68% |
| Ga | $^{69}$ Ga | 60% |
| Ag | $^{107}$ Ag | 52% |
| Cd | $^{114}$ Cd | 29% |
| In | $^{115}$ In | 96% |
| Pb | $^{208}$ Pb | 52% |
| Bi | $^{209}$ Bi | 100% |

**Detection linearity. regression equation and correlation coefficients.**

For the analysis for elements. calibration curve of multi-element standard solution was used to define LOD (3 SD/m. where SD is standard deviation of blanks and m the slope of the regression equation). same as LOQ (10 SD/m). these were showed in Table 2.


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**Table 2.** Calibration and detection limits of the elements by ICP-MS.

| Element | Regression equation | Correlation coefficient (r) | LOD (ug/L) | LOQ (ug/L) |
|---|---|---|---|---|
| Li | Y = 4914X+ 1219 | 0.9989 | 0.023 | 0.077 |
| Cr | Y = 82011X+25130 | 0.9983 | 0.026 | 0.085 |
| Ni | Y = 43234X+ 30795 | 0.9958 | 0.091 | 0.304 |
| Co | Y = 85905X+10109 | 0.9994 | 0.012 | 0.041 |
| Ga | Y = 97931X+ 17765 | 0.9969 | 0.018 | 0.062 |
| Ag | Y = 43737X + 2015768 | 0.9920 | 0.065 | 0.218 |
| Cd | Y = 26557X + 3294 | 0.9999 | 0.018 | 0.060 |
| In | Y = 159777X+ 14226 | 0.9990 | 0.008 | 0.027 |
| Pb | Y = 48867X+ 65778 | 0.9951 | 0.325 | 1.085 |
| Bi | Y = 117763X – 190549 | 0.9982 | 0.029 | 0.096 |

**Concentration of elements in buckwheat grains and flour**

From a nutritional point of view. some plants have elements that meats do not have. that is the importance of the ingestion of vegetables and cereals in the diary diet. the bioavailability of some elements depends on the climate and soil where the plant is growing. So the quality of the grain will depend on these characteristics and will determinate it is able to consume or if it's not recommendable to eat it. The concentration of the elements of this work in ppb were showed in Table 3.

The data presented herein are means (n=3) and standard deviation (SD) of measured values. There was an intentional addition of some elements to have an approximate concentration of 100 ppb in the soil. by adding 5 mL per 500 g of soil of a multielement solution of 10 mg/L of Ba. B. Bi. Ca. Cr. Cu. Fe. K. Mg. Mn. Na. Ni. Pb. Sr and Zn. The soil characteristics was pH = 6.32 ± 0.12 and the was ORP 442 ± 33 mV for a n = 23 soil samples of a *trumao* type soil that its commonly founded in southern Chile. a volcanic ash derived type of soil with high organic content and acidic pH.

**Table 3.** Concentration of elements by ICP-MS

| Element | Concentration (µg/Kg) | | | | | |
|---|---|---|---|---|---|---|
| | S | H | CH | C | F | P |
| $^{7}$Li | ND | ND | ND | ND | ND | ND |
| $^{52}$Cr | 3.2 ± 1.8 | 4.4 ± 0.3 | 1.0 ± 0.7 | ND | 1.0 ± 0.8 | ND |
| $^{59}$Co | 0.26 ± 0.02 | 0.04 ± 0.18 | ND | ND | ND | ND |
| $^{60}$Ni | 9.7 ± 3.0 | 5.4 ± 1.9 | 6.8 ± 1.0 | 8.5 ± 0.6 | 8.8 ± 0.3 | 7.4 ± 0.8 |
| $^{69}$Ga | 0.46 ± 0.01 | ND | ND | 0.70 ± 0.02 | 1.1 ± 0.3 | 1.0 ± 0.1 |
| $^{107}$Ag | ND | ND | ND | ND | ND | ND |
| $^{114}$Cd | ND | ND | ND | ND | ND | ND |
| $^{115}$In | ND | ND | ND | ND | ND | ND |
| $^{208}$Pb | 2.7 ± 0.3 | 0.7 ± 0.8 | 1.7 ± 0.3 | 3.9 ± 0.1 | 1.5 ± 0.3 | 2.3 ± 0.3 |
| $^{209}$Bi | 9.2 ± 0.9 | 6.3 ± 0.5 | 8.4 ± 0.1 | 8.6 ± 0.1 | 7.2 ± 0.4 | 7.1 ± 0.1 |

ND: not detected

The identification of the six types of samples are 2018 seeds (S), market flour (H), 2019 seeds (C), humid 2019 seeds (CH). fine sieved 2019 seeds (F) and ultrasonic 2019 sieving powder (P).

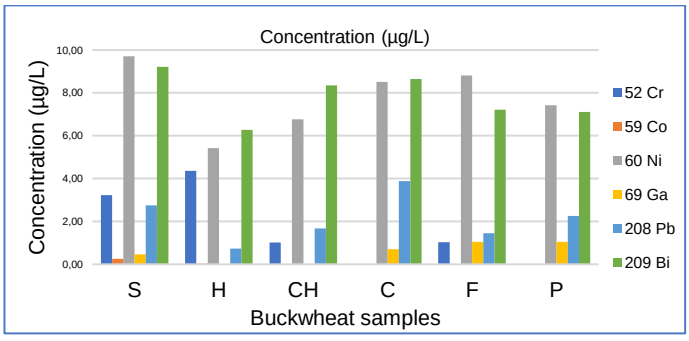


**Figure 1.** Concentration of elements in µg/L in 0.2500 g of sample showing low concentrations for Co. Ga. intermediate concentrations for Cr and Pb. and near 10-µg/L for Ni and Bi.

The results of table 3 were converted to daily intake (µg/100g) to compare with the allowed daily intake per element.

| Element | Concentration (µg/100g) daily intake | | | | | | Daily intake |
|---|---|---|---|---|---|---|---|
| | S | H | CH | C | F | P | (µg/day) |
| $^{7}$Li | ND | ND | ND | ND | ND | ND | 1000 |
| $^{52}$Cr | 64 ± 36 | 87 ± 6 | 20 ± 13 | ND | 21 ± 15 | ND | 200-300 |
| $^{59}$Co | 5.2 ± 0.3 | 0.8 ± 3.7 | ND | ND | ND | ND | 6-12 |
| $^{60}$Ni | 193 ± 60 | 108 ± 37 | 135 ± 20 | 170 ± 11 | 176 ± 6 | 148 ± 16 | 1800-2000 |
| $^{69}$Ga | 9.1 ± 0.3 | ND | ND | 14 ± 0.3 | 21 ± 5 | 21 ± 2 | 700 |
| $^{107}$Ag | ND | ND | ND | ND | ND | ND | 50 |
| $^{114}$Cd | ND | ND | ND | ND | ND | ND | 0.3 |
| $^{115}$In | ND | ND | ND | ND | ND | ND | 1000-1500 |
| $^{208}$Pb | 55 ± 6 | 15 ± 16 | 33 ± 6 | 78 ± 1 | 29 ± 7 | 45 ± 6 | 100 |
| $^{209}$Bi | 183 ± 18 | 125 ± 10 | 167 ± 3 | 169 ± 3 | 144 ± 8 | 142 ± 2 | 500 |

Nd: not detected

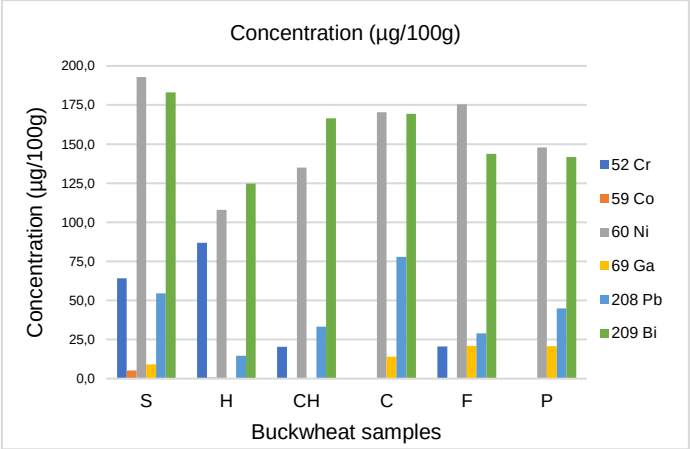


**Figure 2.** Concentration of elements in µg/100g considering as a daily intake. showing low concentrations for Co. Ga. intermediate concentrations for Cr and Pb. and near 200 µg/100g for Ni and Bi.

Some elements were not detected at this level of concentrations such as Li. Ag. Cd and In. surely could be found under 1 µg/Kg. Cr. Co. Ga was detected in some samples and for Ni. Pb and Bi. there were detected in all six types of samples.

There was not a significant increase in the concentration values of the elements considering a 100 µg/Kg addition in these cases. and they all were under the daily intake limits of consumption. this could be explained by the plant not absorbing the elements presents in the soil or absorbing them and not having the mobility inside the plant to go up to the seeds. flowers or leaves and staying concentrated in the roots as the bibliography said. Also. the acidic volcanic ash soil presents high porosity and high infiltration rate of water. due to this it is possible that the intentional addition of 100 µg/Kg was accumulated in the bottom of the pots and not interacted with the sprout or roots of the plant in germination state and not being absorbed.

## CONCLUSION

The ICP-MS multielement analysis are found to be very convenient due its quickness and speed to analyze many elements isotopes simultaneously. and the microwave digestion applied are necessary to the preparation of the samples for the determination of any element by the ICP-MS since it avoids the presence of suspension solids that may affect the analysis by capillary obstructing.

The elements analyzed in buckwheat grains and flour confirms that these are trace elements (under 10 µg/Kg). and its concentration is not toxic to the daily consumption of a person compared to other cereals or pseudo cereals.

Due the soil nature (volcanic ashes). it is a very commonly used type of soil to plant cereals and pseudo-cereals for its nutritional values and properties. but its well known that with this kind of soil cannot forficate the element concentration of the plants or seeds. due to the high porosity and filtration of the soil. losing high amounts of nutrients through the drain.

Also. it is possible that due to the characteristics of the plant. it would be not able to bioaccumulate an excess of some metals and other elements in seeds and retain them in the roots or the lower part of the plant. or not absorbing them.

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