African J. Biol. Sci., 20 (1): 131-139(2024)
ISSN 1687-4870 **e- ISSN 2314-5501 (online)**
www.ajbs.journals.ekb.eg **E-mail:**aasdjournal@yahoo.com

Comparative analysis of mineral content in conventional and organic vegetable using ICP-MS

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Received: April 24, 2024; Accepted: May 23, 2024; Available Online: May 24, 2024
DOI: 10.21608/AJBS.2024.354493

ABSTRACT

Minerals are essential nutrients for plant growth and development. However, the mineral composition of agricultural produce can vary significantly due to factors such as cultivation practices, soil quality, and the use of agrochemicals. Inductively coupled plasma with mass spectrometry detectors (ICP-MS) is a reliable analytical technique for accurately measuring multiple elements in various samples. This study aimed to compare the mineral content of organic and conventional vegetables grown in Egypt using ICP-MS. In the current study samples were analyzed using a PerkinElmer NexION 1000 ICP-MS following closed-vessel microwave digestion. The results indicated excellent performance with low detection limits for Fe, Na, K, P, and Ca (0.02-0.311 mg/L), high recovery rates (97-102%), and low relative standard deviations (RSDs < 5%). Organic vegetables exhibited significantly higher levels of Fe, Na, P, and Ca compared to conventional vegetables, while K levels were comparable. It was concluded that the optimized ICP-MS method offers superior accuracy, precision, sensitivity, and multi-element capability compared to traditional techniques. The findings highlight the potential health Gains of consuming organic vegetables, particularly in terms of essential mineral content.

Keywords: Organic and conventional vegetables- fruits - ICP-MS- minerals-microwave-digestion validation.

INTRODUCTION

Humans need more than 20 minerals and a deficiency in any of these minerals causes various malnutrition problems around the world. In developing countries lack of availability or access to nutrient dense foods has increased overall risks of infection, stunting, underweight and infant mortality (Rakhi *et al.*, 2020). The nutritional composition of vegetables is a critical factor influencing human health. Minerals, essential micronutrients, play a vital role in various physiological functions, including enzyme activity, bone health, and immune system functions. The cultivation practices employed in vegetable production can potentially impact the mineral content of these crops. These discrepancies may be attributed to factors such as soil composition, climate, and specific farming practices. Organic and conventional vegetable are two primary methods of growing procedure. While both aim to provide nutritious food. organic farming is often considered more sustainable and environmentally friendly (Seufert *et al.*, 2012). Organic farming practices adhere to strict guidelines that minimize or eliminate the use of synthetic pesticides, fertilizers, and genetically engineered organisms. Conventional farming, on the other hand, often utilizes these inputs to enhance crop yields and control pests (Smith-Spangler *et al.*, 2012). The differences in agricultural practices between conventional and organic farming raise the question of whether they influence the mineral composition of vegetables.

Various analytical techniques can be employed for this purpose. ICP-MS is the most common methods for determination of mineral in vegetable (Ahmad *et al.*, 2021; Janja *et al.*, 2021). A flame absorption spectrophotometer method for the analytical determination of mineral in fruits grown was used (Antonia *et al.*, 2010). An atomic absorption spectrophotometer method for analytical determination the amount of element in vegetable was described (Teslima *et al.*, 2016). ICP-OES method for analytical determination of elements in different plants was described (Panel *et al.*, 2019). ICP-AES method for determination of elements in different plants was used (Başgel *et al.*, 2006; Panel *et al.*, 2013). A fluorescence method for analytical determination of mineral in the leaves of spinach was described (Mittal et al. 1993). The main Principle for Ion Chromatography (IC) is separating ions based on their affinity for a stationary phase. It is using for determining anions and cations in vegetables (Judith et. al. 2023). The choice of method depends on the specific minerals of interest, the desired sensitivity, and the available equipment and expertise. A new method for determination of trace amount of phosphorus was established by solid phase spectrophotometry (Yuan et al. 2017 and Dorota et al. 2022).

MATERIALS AND METHODS

1. Experimental

1.1 **Reagents and standard**

All materials and reagents used in this work were laboratory pure chemicals. They include potassium hydroxide pellets [KOH] (Merck), ultrapure water (H_2O): Purified H_2O (18 MΩ) generated by a Milli-Q system (EMD Millipore Corp., Billerica). Nitric acid (HNO_3): 65% (w/v) super pure or equivalent was used for digestion. Hydrochloric acid, (HCl): 37% (w/v) ultrapure (Merck) or equivalent. Hydrogen peroxide (H_2O_2): 30% (w/v) for analysis (Merck).

1.2 ICP Standard Solutions:

Certified reference standards for Ca, Na, K, P and Fe (1,000 mg/L) were obtained from a reputable supplier and diluted to working concentrations.

1.3 Apparatus

- Microwave Digestion Systems for Sample Preparation ETHOS™ UP: (Milestone, Italy) with Teflon® vessels.
- Analytical balance: Readability to 0.1 mg (AT200, Switzerland).
- Pipettes: Micropipette variable 50–200 µL and 200–1000 µL
- Electronic digital Pipettes 50–1000 µL (SLV, tests MD1 and MD 2).
- Polypropylene (PP) tubes: Assorted sizes, single-used as received equivalent.
- PP bottles and flasks uses for storage of reagents.
- Fume hood: A fume hood acid-resistant was used (SLV, tests MD1 and MD2).
- A Heraeus 6120T drying oven (Heraeus, Hanau, Germany) was utilized for the SLV, as well as tests MD2.
- Mixer or grinder for homogenization: A Retsch (Haan, Germany) mixer GM200 was used for the SLV, tests MD1 and MD2.

1.4 Vegetables:

The widely consumed vegetables in Egypt, during summer and winter seasons and all over the year in the period 2022 and 2023 were used for determination of their mineral content. The selected vegetables were:

- **Carrots and cabbages** represent winter vegetables.
- **Eggplants and squashes** represent summer vegetables.
- **Lettuces and tomatoes** represent vegetables which are grown all over the year.

Vegetables were bought fresh from the Cairo Agriculture Ministry and frozen organic vegetable were bought fresh from Harm Metro market. Samples were transferred to laboratory for analysis.

2. Sample preparation of P, Ca, K and Na, and method of determination:

2.1 Microwave Digestion:

Samples were digested using a closed-vessel microwave digestion system (Model: Ethos UP, Milestone).

The digestion process was as follows:

- Reagents: 8 mL of concentrated HNO_3 and 2 mL of H_2O_2 were added to each vessel.
- Temperature Program: The temperature was ramped to (180°C) over 10 minutes and held for 30 minutes.
- Cooling: After digestion, the containers were cooled to room temperature and the digested solution was diluted to 50 ml with ultra pure water.

2.2 ICP-MS Analysis:

The PerkinElmer NexION 1000 ICP-MS was used for the determination of Ca, Na, K, and Fe. The instrument was calibrated using multi-element standard solutions prepared in 2% HNO_3 Instrument parameters were optimized for sensitivity and precision:

- RF Power: 1600 W
- Nebulizer Gas Flow: 1.0 L/min
- Dwell Time per Isotope: 50 ms
- Monitoring Masses: m/z 43 (Ca), m/z 23 (Na), m/z 39 (K), m/z 57 (Fe)

2.3 Method Validation:

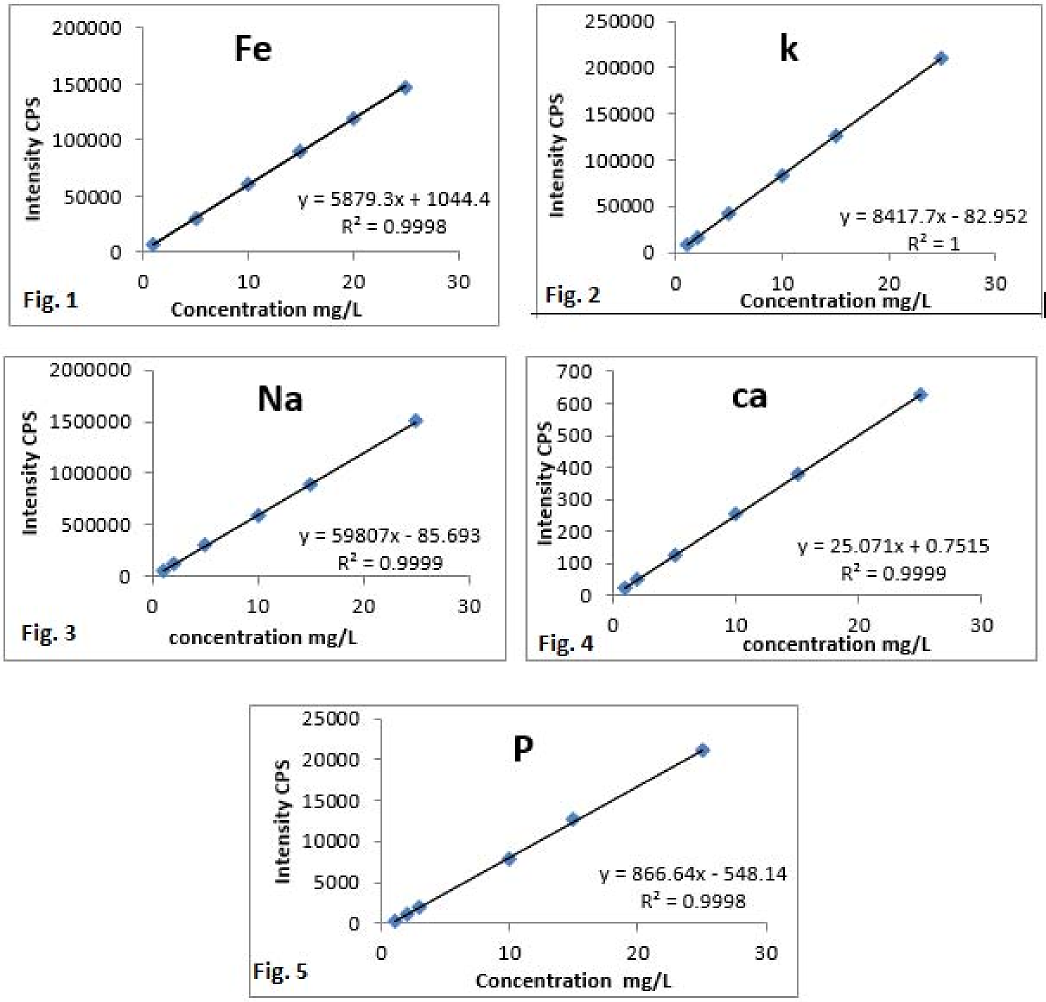
The method was validated according to guidelines from AOAC International and the International Conference on Harmonisation (ICH).

Validation was performed to characterize the method for sensitivity, limit of detection (LOD), limit of quantification (LOQ), linearity, selectivity, accuracy, precision, recovery, ruggedness and uncertainty.

RESULTS AND DISCUSSION

1. Linearity and Calibration

The method exhibited excellent linearity for P, Na, K, Ca and Fe, with correlation coefficients (R^2) greater than 0.999 across the calibration range (1-25 mg/L) as shown in Figures (1-5).



Figs. (1, 2, 3, 4 and 5): Linear regression curve of Fe, K, Na, Ca and P standards.

Validation sheet of Fe, K, Na, Ca and P in the conventional and organic vegetables:

The validation of measuring the mean concentration of Fe, K, Na, Ca and P in all collected samples of the conventional and organic vegetables during the investigated period were performed by measuring the basic parameters such as precision, accuracy, linear regression constants. The results are shown in Table (1).

Table (1): Validation sheet of mean concentration of mineral salts (Fe, K, Na, Ca and P) in the conventional and organic vegetables collected during 2022-2023 from Egypt.

Parameter	Fe	k	Na	ca	p
Accuracy	99.56±1.9	99.46±1.02	100.83±2	99.46±1.02	100.14±1.14
Slope	5879.3	25.07	59807	25.07	866.64
Intercept	1044.4	0.751	85.69	0.751	548.14
Linear Range	1-25	1-25	1-25	1-25	1-25
Correlation Coefficient (r)	0.9998	1	0.9999	0.9999	0.9998
LOD (mg/L)	0.018	0.049013	0.041717	0.311841	0.345319
LOD (mg/L)	0.056	0.148524	0.126416	0.944972	1.035957

2. Limits of Detection (LOD) and Quantification (LOQ)

The LOD and LOQ were calculated as three and ten times the signal-to-noise ratio, respectively. The LOD values were 0.018 mg/L for Fe, 0.041 mg/L for Na, 0.049 mg/L for K, 0.345 mg/L for P and 0.311 mg/L for Ca. These low detection limits demonstrate the method's sensitivity. The values of the limits of quantification for Fe, Na, K, P and Ca were 0.056, 0.13,0.15, 1.04, 0.94 mg/L respectively (Table 1)

3. Accuracy and Precision

Accuracy was assessed by analyzing the spiked samples at three different concentration levels (high, medium, low). The recovery rates ranged from 97% to 102% for all the investigated elements, indicating high accuracy. Precision, expressed as RSD (the relative standard deviation), was below 5% for intra-day and inter-day analyses, demonstrating the method's reliability (Table 1).

4. Recovery Studies

Recovery studies were performed by spiking known amounts of P, Ca, Na, K, and Fe into the homogenized samples. The recoveries were within the acceptable range of 90-110%, confirming the method's accuracy.

5-The mean concentration of P, Ca, Na, K, and Fe in conventional and organic vegetables:

The data in Tables (2 & 3) showed that potassium concentration in all investigated organic vegetables was lower than that in the conventional vegetables because chemical fertilizers contain higher amount of potassium and often in excess of plant needs. Potassium is presented to plants differently by organic and conventional systems. Conventional potassium fertilizers are easily absorbed by plants, providing them with a significant amount of potassium. In contrast, organically managed soils have a more moderate supply of both potassium and magnesium in the area where plant roots grow (Havlin *et al*., 2014).

Also, the sodium, iron, phosphorus and calcium concentrations in organic vegetables were higher than the concentration of these minerals in the conventional vegetables. Organically managed soils have more microorganisms that produce many compounds including substances such as lactates and citrate that combine with soil minerals and make them more available for plant roots. For iron, in particular, this is especially important because many soils contain adequate iron but in an unavailable form. Soil organic matter chelate iron from soil and it makes more available for plants (Amarjeet *et al*., 2023).

The higher concentration of Phosphorus in organic vegetables is related to the presence of magnesium in the soil, therefore increasing of Mg causing increase in absorption of phosphorus (Bear *et al*. 1949).

Plants fertilized with chemical fertilizer are presented with large quantities of nutrients all at once (Garcia *et al*., 2018; Bear *et al*., 1949). With chemical fertilizers, there is no attempt to influence soil structure or to encourage soil microorganisms (Chauhan *et al*., 2010). These differences in the management of soil fertility affect soil dynamics and plant metabolism, which result in differences in plant composition and nutritional quality. Soil that has been managed organically has more microorganisms which produce many compounds that help plants, including substances such as citrate and lactate that combine with soil minerals and make them more available to plant roots.

Hunter *et al*. (2011) reported higher levels of certain minerals in organic vegetables, while others have found no significant differences or even higher levels in conventional vegetables. Xiaofan *et al.* (2018) reported that the mineral element contents of P, Mg, K were higher in the organic corn grain rather than those in conventional corn by about 30%, 20% and 30%, respectively Also, the organic corn had higher content of Zn, Fe, although the differences were not significant. However, they found that the conventional corn grain contained notably richer S and Mn than the organic one by 15% and 17% higher, respectively.

Moreover, it was found that the antioxidant responses were more flexible under organically improved soil, given the lower concentration of antioxidants produced in organically grown produce under no-stress environments and the higher concentrations under drought conditions compared to conventionally grown produce (Atanu *et. al*., 2020; Songul, 2023).

Table (2): Mean concentration(mg/L) of mineral salts in conventional and organic vegetables through 2022.

Conc / Vegetables	Conventional					Organic				
	K	**P**	**Ca**	**Fe**	**Na**	**K**	**P**	**Ca**	**Fe**	**Na**
tomatoes	2862.5 ±195	310.6 ±21.4	152.1 ±16.1	5.8 ±0.3	108.6 ±13.1	2503.4 ±218	367.8 ±27.5	200.8 ±18.5	7.8 ±0.5	202.8 ±17.4
Lettuces	2421.8 ±201	348.0 ±27.8	309.3 ±29.1	11.8 ±2.6	73.2 ±18.5	2284.5 ±184	456.1 ±32.1	395.7 ±26.5	21.7 ±04.8	112.8 ±13.1
carrots	3205.4 ±298	417.2 ±21.9	359.1 ±19.5	4.9 ±0.4	613.5 ±32.4	3090.5 ±245	545.6 ±31.5	460.4 ±33.7	6.7 ±0.4	736.4 ±28.5
cabbage	2500.6 ± 184	321.5 ±23.9	402.1 ±27.8	5.8 ±0.3	142.5 ±16.9	2306 ±238.5	375.4 ±27.6	448.2 32.3	8.8 ±0.7	228.3 ±23.5
eggplants	2671.9 ±217	238.1 ±18.9	172.9 ±12.7	3.9 ±0.03	85.9 ±4.1	2565.4 ±194.1	269.7 ±30.7	283.7 ±19.9	5.2 ±0.3	156 ±9.9
squashes	2006.1 ±157	316.5 ±21.4	245.1 ±17.6	5.9 ±0.4	73.5 ±6.2	1958.4 ±115	454.2 ±29	317.7 ±12.7	7.8 ±0.6	154.2 ±9.1

Table (3): Mean concentration (mg/L) of mineral salts in conventional and organic vegetables through 2023.

Conc / Vegetables	Conventional					Organic				
	K	P	Ca	Fe	Na	K	P	Ca	Fe	Na
tomatoes	2811.2 ±189	301.8 ±14.8	4.5 ±0.3	149.7 ±1.21	98.4 ±8.3	2227.7 ±21.8	371.4 ±32.4	214.2 ±18.5	8.4 ±0.5	215.3 ±11.9
Lettuces	2445.8 ±199	324.5 ±28.2	295.9 ±20.7	10.9 ±1.4	67.6 ±9.5	2114.1 ±192.5	460.8 ±32.1	490.8 ±29.9	24 ±6.9	124.6 ±25.3
carrots	3217.5 ±218	404.8 ±28.5	382.4 ±14.3	4.3 ±0. 4	582.4 ±29.7	3081.2 ±258	561.9 ±41.3	485.6 ±17.6	7.4 ±0.65	716.4 ±32.8
cabbage	2591.3 ±237	310.4 ±28.3	398.4 ±32.7	5.2 ±0.5	142.5 ±16.9	2285 ±272	389.7 ±31	457.6 ±21.7	9.1 ±0.48	231.9 ±27.3
eggplants	2699.5 ±180.7	224.3 ±23.3	398.4 ±17.7	3.2 ±0.6	74.2 ±8.1	2548.3 ±191.1	285.2 ±21.8	299.8 ±18.4	5.9 ±0.32	173 ±10.5
squashes	2091.8 ±184	301.4 ±24.5	226.1 ±29	5.2 ±0.6	89.8 ±4.38	1905.2 ±167	478.7 ±25.1	322.5 ±21.1	8.1 ±0.7	167.5 ±28.5

Conclusion:

The PerkinElmer NexION 1000 ICP-MS can be used to give accurate detection of Ca, Na, K, and Fe, P contents in vegetables.

The results highlight the presence of most of the essential mineral content in organic vegetables which are required for potential health benefits.

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تحليل مقارن لمحتوى المعادن في الخضروات العضوية والتقليدية باستخدام جهاز البلازما المقترنة بكاشف التحليل الطيفي الكتلي

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المستخلص

المعادن هي مغذيات أساسية لنمو النبات وتطوره ومع ذلك، يمكن أن تختلف تركيبة المعادن في المنتجات الزراعية بشكل كبير بسبب عوامل مثل ممارسات الزراعة وجودة التربة واستخدام المبيدات الزراعية .يعد التحليل الطيفي الكتلي باستخدام البلازما المقترنة بالحث (ICP-MS) تقنية تحليلية موثوقة لقياس العديد من العناصر بدقة في عينات مختلفة .هدفت هذه الدراسة إلى مقارنة محتوى المعادن في الخضروات العضوية والتقليدية المزروعة في مصر باستخدام جهاز PerkinElmer NexION 1000 ICP-MS بعد الهضم بالميكروويف في وعاء مغلق .أظهرت الطريقة أداءً ممتازًا مع حدود اكتشاف منخفضة للحديد والصوديوم والبوتاسيوم والفوسفور والكالسيوم (0 02-0.311.ملغ / لتر)، ومعدلات استرداد عالية (97-102%)، وانحرافات معيارية نسبية منخفضة (RSDs < 5%) . أظهرت الخضروات العضوية مستويات أعلى بشكل ملحوظ من الحديد والصوديوم والفوسفور والكالسيوم مقارنة بالخضروات التقليدية، في حين كانت مستويات البوتاسيوم قابلة للمقارنة .تُظهر النتائج أن طريقة ICP-MS المحسّنة توفر دقة ودقة وحساسية وقدرة متعددة العناصر تفوق الطرق التقليدية .تسلط النتائج الضوء على الفوائد الصحية المحتملة لاستهلاك الخضروات العضوية، خاصة فيما يتعلق بمحتوى المعادن الأساسية.

الكلمات المفتاحية :الخضروات العضوية والتقليدية - الفواكه - ICP-MS - المعادن - الهضم بالميكروويف - التحقق من صحة التحليل.