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Determination of trace element concentrations in tomato samples at different stages of maturation by ICP OES and ICP-MS following microwave-assisted digestion

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ABSTRACT

The concentrations of 15 elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Se, Sn, Sr, V and Zn) were determined in three tomato species (Khaki, Cherry and Italy) at different stages of maturation by ICP OES and ICP-MS following microwave-assisted acid digestion. The digestion efficiency was evaluated on the basis of the determination of residual carbon content and trace element recoveries. Diluted nitric acid solutions were used for the efficient digestion of 300 mg of tomato samples, with a considerable reduction in the residual acidity when compared with a procedure that employed a concentrated nitric acid solution. The good agreement between the measured and certified concentrations of a National Institute of Standards and Technology (NIST) Certified Reference Material 1573a (Tomato Leaves) indicated that the developed analytical method was well suited to determine the trace elements contents in similar matrices. The analytical parameters, such as the limits of quantification, the accuracy and the precision of the overall procedure, were assessed statistically. Moreover, the measured trace element concentrations were used to distinguish between conventional and organic cultivation. According to the data, the species of tomato, the form of cultivation and the stage of maturation of the fruit influenced the concentrations of the trace elements that are found in the tomato samples. Tomatoes in the final stage of maturation showed higher concentrations of most of the elements that were measured in the three species studied. Regarding the type of cultivation, organic tomatoes contained higher levels of micronutrients and less contaminants when compared with conventionally grown tomatoes.

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1. Introduction

Tomatoes (*Lycopersicon esculentum*) are an excellent source of many nutrients and secondary metabolites that are important for human health, including mineral matter, vitamins, lycopene, flavonoids, organic acids, phenolics and chlorophyll [1]. Additionally, tomato fruits contain several antioxidants, such as vitamin C, carotenoids, phenolic compounds, flavonoids and phenolic acids. The presence of nutritive and toxic elements in tomato samples depends on the growing conditions and the utilization of pesticides and fertilizers. In addition, the accumulation of metals varies greatly both between species and cultivars [2].

Elemental food composition data are important to both consumers and health professionals, and recent food labeling legislation has highlighted this importance. Several analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) [3–10], inductively coupled plasma mass spectrometry (ICP-MS)

[11–13], flame atomic absorption spectrometry (F AAS) and electrothermal atomic absorption spectrometry (ET AAS) [14–17], are available for determining trace element contents in food samples.

Several studies have reported the trace element concentrations in tomato samples. Kelly and Bateman determined by ICP-MS the mineral concentrations in commercially grown organic and conventional crops [18]. Micronutrients and heavy metal contents were determined employing F AAS and graphite furnace atomic absorption spectrometry (GF AAS) [14]. The determination of trace metals in tomatoes by GF AAS was performed after closed vessel microwave digestion [15]. High performance liquid chromatography (HPLC)–ICP OES hyphenation technique was used to determine the concentration of some organic (i.e., carbohydrates, carboxylic acids) as well as inorganic (metals and anions) compounds in tomato samples [3].

To determine trace element contents using atomic spectrometry techniques, food samples typically need to be digested to convert the solid samples into a solution form prior to the measurements. Many procedures have been developed to shorten the analysis time and to minimize problems that are associated with solid sample pretreatment, such as sample contamination and analyte loss [19,20]. For example, the microwave digestion of solid samples followed by an ICP OES or ICP-MS analysis is a powerful approach to the complete

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decomposition and accurate determination of metals in food samples [10–13,15–17,19,20].

The aim of this study was to develop multi-element ICP OES and ICP-MS methods to analyze tomato samples after microwave-assisted acid digestion. The analytical performance of the entire procedure, such as the limit of detection, precision and accuracy were assessed statistically to evaluate the developed procedures. The elemental contents of various commonly consumed commercial tomato samples were also determined to establish whether these products are safe to be consumed by the population.

2. Materials and methods

2.1. Instrumentation

The acid digestion of the tomato samples was performed using a commercial high-pressure laboratory microwave oven (Milestone Ethos 1600 Microwave Labstation, Sorisole, Italy) operating at a frequency of 2450 Hz with an energy output of 900 W. This microwave digestion system was equipped with ten 100 mL tetrafluoromethoxy vessels and a ceramic vessel jacket. The maximum operating temperature and pressure were 300 °C and 100 bar, respectively.

A quadrupole ICP-MS XseriesII (Thermo, Germany) equipped with a hexapole collision cell (CC) was used for Cd, Co, Cr, Hg, Ni, Se and V determinations. Internal standards (Ge, Rh, Tl, In, Bi, and Sc) were added to compensate for any effects from acid or instrument drift. The instrument software allowed the rapid switch between standard mode (no gas, cell vented to mass analyzer chamber) to CC mode while continuously aspirating the sample. The premixed gasses H₂ (7%) in He (H₂O and other impurities < 5 ppm) were admitted into the CC under flow control through stainless steel lines. The measurements were made with nickel sampler and skimmer cones (1.0 mm and 0.7 mm diameter orifices) and a standard concentric nebulizer. A glass impact bead spray chamber that was cooled to 4 °C by a Peltier cooler and a shielded Fassel torch were used to minimize the plasma potential and thereby obtain a low and narrow initial ion energy distribution. The ICP-MS operational conditions are summarized in Table 1.

An inductively coupled plasma optical emission spectrometer (ICP OES) with an axially viewed configuration (VISTA PRO, Varian, Mulgrave, Australia) that was equipped with a solid-state detector, Stumar-master mist chamber, and V-groove nebulizer was employed for Al, Ba, Cu, Fe, Mn, Sn, Sr, and Zn determinations. The operating conditions are summarized in Table 2. The emission lines for the analysis by ICP OES were chosen according to previous interference studies. The lines that exhibited low interference and high analytical signal and background ratios were selected. The emission lines that were employed were Al (I) 237.312, Ba (II) 233.527, Cu (I) 324.754, Fe (II) 234.350, Mn (II) 260.568, Sn (I) 235.485, Sr (II) 460.733 and Zn (I) 213.857 nm.

Table 1Instrumental conditions of the ICP-MS.

Parameter	Value
RF incident power	1300 W
Plasma argon flow rate	13 L min ⁻¹
Auxiliary argon flow rate	0.7 L min ⁻¹
Nebulizer argon flow rate	0.87 L min ⁻¹
Scanning mode	Peak jump
Resolution	Standard
Dwell time	10 ms
Sweeps	100
Number of readings per replicate	3
Conditions	$^{140}\text{Ce}^{16}\text{O}^{+}/^{140}\text{Ce}$ and $^{137}\text{Ba}^{++}/^{137}\text{Ba}^{+}{<}2\%$

Table 2Instrumental conditions of the ICP OES.

Parameter	Value
RF incident power	1.3 kW
Plasma argon flow rate	15 L min ⁻¹
Auxiliary argon flow rate	1.5 L min ⁻¹
Nebulizer argon flow rate	0.7 L min ⁻¹
Mist chamber	Stumar-master
Nebulizer	V-groove

2.2. Reagents, solutions and samples

All labware was soaked in a 10% (v/v) HNO_3 solution bath for 24 h and was rinsed with high-purity water. Subsequently, all materials were dried under clean-air conditions at ambient temperature.

All solvents and reagents were of the highest commercially available purity grade. Deionized water (resistivity $18\,M\Omega\,cm^{-1}$) that was obtained from a Milli-Q Pluswater purification system (Millipore Molsheim, France) was employed to prepare all standard and sample solutions. Suprapur grade 65% (m/m) HNO $_3$ and 30% (m/m) H $_2$ O $_2$ (Merck, Germany) were used for sample dissolution. Monoelemental, high-purity grade 1 g L $^{-1}$ stock solutions of Al, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Se, Sn, Sr, V, and Zn and a multielement solution of 100 mg L $^{-1}$ of Bi, Ge, In, Tl, Rh and Sc were purchased from Merck (Darmstadt, Germany). The purity of the plasma torch argon was greater than 99.99%.

The three tomato species (Khaki, Cherry and Italy) were randomly collected at two different ripening stages from municipal markets in Salvador, Bahia. Organic samples were obtained directly from certified organic growers, assuming that the production has avoided the use of synthetic fertilizers and pesticides.

2.3. Digestion procedure

All tomato samples were chopped into small pieces, washed with water and then dried at 65 °C for 72 h. Approximately 300 mg of each tomato sample was inserted directly into a microwave-closed vessel. One milliliter of 30% (m/m) $\rm H_2O_2$ and 7.0 mL of HNO₃ solution were added to each vessel. Three nitric acid solutions were tested for the digestion procedure, including 14.2, 7.1 and 4.0 mol L⁻¹ HNO₃. The heating program was performed in four successive steps. In the first step, the temperature was increased linearly from 25 to 90 °C in 4 min. In the second step, the temperature was held at 90 °C for 2 min. In the third step, the temperature was increased linearly to 180 °C over 6 min, and in the last step, the temperature was held at 180 °C for 10 min. After the digestion procedure and subsequent cooling, the digested samples were diluted to a final volume of 25.0 mL with water. Blanks were prepared in each lot of samples. All experiments were performed in triplicate.

2.4. Determination of the acidity and residual carbon of the digests

Acid–base titrations of the digests were performed to determine the final acidity of the samples. The titration was performed with a standard solution of sodium hydroxide (0.0997 mol L $^{-1}$) and phenolphthalein (1.0% m/v in ethanol). The standard solutions for the calibration curves were prepared at the same acid concentration of each digestion procedure.

The residual carbon was measured by ICP OES at 193.027 nm. To determine the residual carbon content (RCC) [21], the digested solutions were sonicated with an ultrasonic bath before the determination by ICP OES to remove any volatile carbon compounds that may have existed. The standard solutions for the calibration curves of the residual carbon were prepared with citric acid [21].

2.5. Validation studies

The accuracies of the measurements were assessed using a tomato leaf Certified Reference Material 1573a (CRM 1573a) from National Institute of Standards and Technology (Gaithersburg, MD, USA). The precision of the method, defined as the closeness of agreement between mutually independent test results, was determined in terms of the percentage of the variation coefficient. The limits of detection (LOD) and quantification (LOQ) of each analyte were calculated as the analyte concentration that corresponded to three and ten times, respectively, the standard deviation of ten independent measurements of the blank, divided by the slope of the calibration curve.

3. Results and discussion

3.1. ICP OES and ICP-MS performance

The concentrations of 15 elements were determined in three species of tomato samples at different stages of maturation by ICP OES and ICP-MS following a microwave-assisted digestion procedure. Initially, ICP OES was used to attempt to determine all of the elements. However, ICP-MS was then employed because the determination of all the elements by ICP OES was not possible because of LOD limitations.

The determination of Al, Ba, Cu, Fe, Mn, Sn, Sr, and Zn was performed by ICP OES. Because ICP OES parameters can influence the signal intensities and the sensitivity of the method [22], the employed incident power and nebulizer argon gas flow rate were 1.3 kW and 0.70 L min⁻¹. These values were optimized previously [23].

The determination of Cd, Co, Cr, Hg, Ni, Se and V were monitored in standard (STD) and collision cell technology (CCT) modes in the presence of 7% premixed $\rm H_2$ in He as the reaction gas. Considering that the determinations of some elements by ICP-MS suffered from polyatomic isobaric interferences, collision/reaction cells were used to remove or reduce those polyatomic species. For example, this was the case for the nickel signal at m/z 58 by 23 Na 35 Cl, the selenium signal at m/z 80 by 40 Ar 40 Ar $^{+}$ and the vanadium signal at m/z 51 by 35 Cl 16 O [11,13].

The LODs for Cd, Co, Cr, Hg, Ni, Se and V, the elements determined by ICP-MS, were 0.008, 0.019, 0.077, 0.128, 0.049, 0.115 and 0.052 $\mu g \, g^{-1}$, respectively. When ICP OES was employed, the LODs for Al, Ba, Cu, Fe, Mn, Sn, Sr and Zn determinations were 0.022, 0.025, 0.098, 0.043, 0.006, 0.073, 0.010 and 0.028 $\mu g \, g^{-1}$, respectively. The accuracies of the determinations were evaluated by the analysis of tomato leaf Certified Reference Material (CRM 1573a). The results, which are shown in Table 3, showed good agreement with the reference values

Table 3 Analysis of tomato leaf Certified Reference Material (CRM 1573a) by ICP-MS and ICP OES ($\mu g g^{-1}$, n=3, at 95% of confidence level).

Element	Reference value	Found
ICP-MS determination		
Cd	1.52 ± 0.04	1.41 ± 0.06
Co	0.57 ± 0.02	0.52 ± 0.01
Cr	1.99 ± 0.06	1.85 ± 0.16
Hg	0.034 ± 0.004	0.036 ± 0.017
Ni	1.59 ± 0.07	1.63 ± 0.10
ICP OES determination		
Al	598 ± 12	512 ± 26
Ba	(63)	53 ± 1
Cu	4.70 ± 0.14	3.87 ± 0.23
Fe	368 ± 7	322 ± 8
Mn	246 ± 8	244 ± 3
Sr	(85)	84 ± 1
Zn	30.9 ± 0.7	28.1 ± 3.9

Values in parentheses are not certified values.

of the CRM sample. The lower recoveries observed for Fe and Al might be due to incomplete release of these elements from the sample since they are normally associated with the aluminosilicate matrix as noted previously by Krishna and Arunachalam [24].

3.2. Optimization of the sample digestion procedure

Sample digestion is a critical step in most analytical methods for the routine determination of chemical elements in food samples. The use of nitric acid for organic matrix digestion is the most common approach used for sample pretreatment during the analysis of trace elements. Ideal digestion should lead to the complete decomposition of organic material using minimal amounts of acid. Acid solutions should be as diluted as possible to decrease the final acid concentration and to protect certain instrument parts, such as nebulizers and nebulization chambers [10].

The digestion procedure was evaluated at three different HNO₃ concentrations (14.2, 7.1 and 4.0 mol L⁻¹) by comparing the residual carbon content, the residual acidity of the digests and the element recoveries by analyzing the CRM 1573a. The degree of dissolution varied with the treatment that was used. In general, the digestion solutions appeared to be clearest, i.e., free from particles in suspension, when the three nitric acid solutions were used. The residual carbon contents ranged from 6.00 ± 0.50 to $12.0\pm0.8\%$ (n = 3). The residual acidities obtained after the digestions with 14.2, 7.1 and 4.0 mol L $^{-1}$ HNO₃ were 3.8 ± 0.2 , 1.7 ± 0.1 and 0.8 ± 0.1 mol L $^{-1}$, respectively.

Despite the lower residual acidity that was obtained with the 4.0 mol L^{-1} solution, the low recoveries of the analytes showed that the digestion procedure using this solution was not appropriate. The best recoveries were obtained from a microwave digestion with a mixture composed of 3.5 mL of HNO3, 3.5 mL of H2O and 1.0 mL of H2O2 30% (m/m) for 0.300 g of sample, which corresponded to a final concentration of approximately 7.1 mol L^{-1} HNO3. Moreover, this concentration resulted in solutions with adequate carbon contents and low residual acidity when compared with the 14.2 mol L^{-1} experiment. The use of diluted solutions of HNO3 improved the performance of the ICP OES and ICP-MS, avoiding the wear of the equipment components that made contact with the digested samples.

3.3. Determination of the element concentrations in tomato samples

3.3.1. Study of type of tomato and the maturation stage

A study was conducted to evaluate the concentrations of trace elements in the initial and final states of maturation of three types of tomato (Khaki, Cherry and Italy) that had been obtained from conventional cultivation. The concentrations obtained for the elements studied are shown in Table 4. According to these data, the concentrations of the analytes in samples of conventionally grown tomatoes varied with the species. For most elements that were quantified by ICP OES, the analyte concentrations were highest in the Khaki species and were lowest in the Cherry species in the early stage of maturation. An exception to this statement was observed for Sr and Ba, whose concentrations were lowest in the Italy species.

For most elements that were quantified by ICP-MS, the Cherry species contained the highest concentrations of Cr and Se in the initial stage of maturation. The Khaki species showed the highest values for Hg, while Cd, Co, Ni and V were highest in the Italy species. No significant differences were observed in the concentrations of Se between the Khaki and Italy species or in Hg between the Italy and Cherry species.

In the final stage of maturation, the highest concentration of Cu, Fe and Sr were observed in the Khaki species, while Sn was highest in the Cherry species. The lowest concentrations of Sr and Zn were measured in the Italy and Cherry species, respectively. There were no significant differences in the concentrations of Cu between the Italy and Cherry species. The elements Al and Fe were highest in the

Table 4Trace element determinations in conventionally cultivated tomato samples (n = 3, 95%) confidence level, (n = 1, 95%) in the early and final maturation stages (dry weight).

Analyte	Khaki		Italy		Cherry	
	Early maturation	Final maturation	Early maturation	Final maturation	Early maturation	Final maturation
Al	21.6 ± 2.3	39.2 ± 1.2	9.92 ± 0.15	36.6 ± 3.8	5.96 ± 0.69	57.8 ± 2.2
Ba	3.40 ± 0.08	< 0.025	< 0.025	< 0.025	0.51 ± 0.01	< 0.025
Cu	5.54 ± 0.18	9.19 ± 0.10	2.94 ± 0.10	5.13 ± 0.07	2.44 ± 0.04	5.40 ± 0.19
Fe	39.0 ± 1.5	47.9 ± 2.3	39.8 ± 0.8	43.1 ± 2.8	15.0 ± 0.2	43.8 ± 3.4
Mn	13.1 ± 0.6	13.3 ± 0.2	12.6 ± 0.2	18.2 ± 0.4	10.6 ± 0.2	5.64 ± 0.15
Sn	18.2 ± 2.6	19.9 ± 1.6	16.1 ± 0.9	18.9 ± 1.0	6.12 ± 0.60	25.4 ± 1.6
Sr	10.5 ± 0.5	11.9 ± 0.1	0.68 ± 0.06	2.66 ± 0.08	4.64 ± 0.03	9.30 ± 0.12
Zn	15.5 ± 1.2	22.3 ± 0.9	11.1 ± 0.3	29.5 ± 1.1	5.22 ± 0.21	19.7 ± 1.7
Cd	< 0.008	0.0092 ± 0.0009	0.0362 ± 0.0007	0.21 ± 0.02	0.027 ± 0.002	< 0.008
Co	0.366 ± 0.005	0.634 ± 0.004	1.81 ± 0.06	4.39 ± 0.46	0.65 ± 0.03	1.36 ± 0.04
Cr	0.18 ± 0.01	0.26 ± 0.01	0.12 ± 0.01	0.395 ± 0.009	0.21 ± 0.02	0.25 ± 0.01
Hg	0.396 ± 0.006	0.41 ± 0.01	0.165 ± 0.035	0.13 ± 0.01	0.174 ± 0.012	0.288 ± 0.009
Ni	0.28 ± 0.02	0.63 ± 0.01	0.52 ± 0.01	0.775 ± 0.051	0.499 ± 0.002	0.55 ± 0.10
Se	0.35 ± 0.08	0.94 ± 0.12	0.35 ± 0.06	0.489 ± 0.029	0.63 ± 0.09	0.62 ± 0.02
V	0.101 ± 0.004	0.42 ± 0.01	0.15 ± 0.02	0.325 ± 0.021	0.094 ± 0.006	0.16 ± 0.01

Khaki species and were lowest in the Cherry species, whereas Cr, Ni and Cd were highest in the Italy species and were lowest in the Cherry species.

According to the results shown in Table 4 for the Khaki samples, the elements Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Se, V and Zn exhibited their lowest concentrations in the early stage of maturation; Ba was lowest at the final stage of maturation and concentrations of Hg, Sr, Sn and Mn did not differ between the stages. An ANOVA confirmed the influence of the fruit stage of maturation on elemental composition because significant differences between the two stages were found for all of the elements except for Hg, Sr, Mn and Sn.

The Cherry samples showed significant differences (95% confidence level) in all of the elements between the initial and final stages. Additionally, the Italy samples showed significant differences (95% confidence level) in all of the elements except Ba, Fe and Sn between the initial and final stages of maturation of the tomatoes. According to Rodrigues et al. (2002) [25], an increase in absorption of micronutrients by tomato plants is expected between 21 and 105 days of cultivation, which may explain the higher concentrations of these elements in the mature tomatoes.

Cu and Zn are considered phytotoxic elements if the concentrations are greater than 15 and 400 mg kg⁻¹, respectively, independent of the maturation stage [26]. In the analyzed samples, the concentrations of these elements did not exhibit values that suggested phytotoxicity.

Table 5 Trace element determinations in Italy tomato samples ($n\!=\!3$, 95% confidence level, $\mu g \, g^{-1}$) from conventional and organic cultivation in the early and final maturation stages (dry weight).

Analyte	Organic cultivation		Conventional cultivation		
	Early maturation	Final maturation	Early maturation	Final maturation	
Al	< 0.022	57.03 ± 1.46	9.92 ± 0.15	36.6 ± 8.8	
Ba	< 0.025	< 0.025	< 0.025	< 0.025	
Cu	1.22 ± 0.07	5.25 ± 0.02	2.94 ± 0.10	5.13 ± 0.07	
Fe	18.4 ± 0.8	43.7 ± 1.3	39.8 ± 0.8	43.1 ± 2.8	
Mn	6.01 ± 0.07	8.48 ± 0.27	12.6 ± 0.2	18.2 ± 0.4	
Sn	7.06 ± 0.51	16.8 ± 0.8	16.1 ± 0.9	18.9 ± 1.0	
Sr	< 0.010	3.61 ± 0.09	0.68 ± 0.06	2.7 ± 0.1	
Zn	6.76 ± 0.09	12.1 ± 0.8	11.1 ± 0.3	29.5 ± 1.1	
Cd	0.083 ± 0.004	0.061 ± 0.002	0.0360 ± 0.0007	0.21 ± 0.02	
Co	0.770 ± 0.060	0.40 ± 0.04	1.81 ± 0.06	4.39 ± 0.46	
Cr	0.207 ± 0.018	0.15 ± 0.01	< 0.077	0.395 ± 0.009	
Hg	0.297 ± 0.027	0.154 ± 0.004	0.165 ± 0.035	0.13 ± 0.01	
Ni	0.264 ± 0.002	< 0.049	< 0.049	0.77 ± 0.05	
Se	0.48 ± 0.06	< 0.115	0.350 ± 0.060	< 0.115	
V	0.215 ± 0.008	0.092 ± 0.003	0.150 ± 0.020	0.32 ± 0.02	

According to Fayad et al. (2002) [27], the nutrient content in tomato samples varies with the method of cultivation. This absorption depends on biotic and abiotic factors, such as air and soil temperature, light and humidity, planting time, genotype and concentration of nutrients in the soil. Additionally, other factors, such as drip irrigation, vertical conduction of plants and plastic cover, influence the absorption of nutrients.

3.3.2. Study of the type of cultivation

This study was conducted to evaluate the concentrations of elements in Italy tomato samples that were cultivated both by organic and conventional farming. According to the results shown in Table 5, at the initial stage of maturation, the elements Al, Cd, Co, Cu, Fe, Mn, Sn, Sr and Zn had lower concentrations in the organically farmed tomatoes, while Cr, Hg, Ni, Se and V had lower concentrations in the conventionally farmed tomatoes. During the final stage of maturation, Cd, Co, Cr, Mn, Ni, Se, Sn, V and Zn exhibited lower concentrations in the organically farmed tomatoes, while Al, Hg and Sr showed lower concentrations in the conventionally farmed tomatoes.

In the organic crops at the final maturation stage, the micronutrients Cu and Zn were higher in concentration, while Mn was present at a lower concentration. These results were expected because these elements are identifiers of the authenticity of organic farming, and variations in their concentrations can be explained by the presence of arbuscular mycorrhizal fungi (AMF), which is present, in general, in soils from organic farming [18].

A paired Student t-test (95% confidence level) was used to verify the differences between the concentration means of each element for the organic and conventional tomatoes. The statistical test confirmed the influence of the method of cultivation on elemental composition because significant differences between the two types of cultivation were found for all of the elements, except for iron in the final stage of maturation of the tomatoes.

In general, the elemental contaminations were lower in tomatoes that had been subjected to organic farming, a factor that can be used to determine the authenticity of this type of cultivation. When comparing the effects of the production system on food safety, there is evidence that, with respect to pesticide residues, organic foods have a clear advantage over conventionally grown foods [28,29]. The results of this study are consistent with this statement because the organic tomatoes were richer in micronutrients and contained lower concentrations of toxic elements.

4. Conclusions

ICP OES and ICP-MS techniques were demonstrated to be suitable for trace element determinations in tomato samples following microwave assisted acid digestion. According to the data, the species of tomato, the form of cultivation and the stage of maturation of the fruit influenced the concentrations of the trace elements that are found in the tomato samples. Tomatoes in the final stage of maturation showed higher concentrations of most of the elements that were measured in the three species studied. Regarding the type of cultivation, there appeared to be advantages in the consumption of organic tomatoes because these samples contained higher levels of micronutrients and less contaminants when compared with conventionally grown tomatoes.

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References

- G. Giovanelli, A. Paradiso, Stability of dried and intermediate moisture tomato pulp during storage, J. Agric. Food Chem. 50 (2002) 7277–7281.
- [2] E. Miteva, S. Maneva, D. Hristova, P. Bojinova, Heavy metal accumulation in virus-infected tomatoes, J. Phytopathol. 149 (2001) 179–184.
- [3] E. Paredes, M.S. Prats, S.E. Maestre, J.L. Todolí, Rapid analytical method for the determination of organic and inorganic species in tomato samples through HPLC-ICP-AES coupling, Food Chem. 111 (2008) 469–475.
 [4] I. Jarić, Ž. Višnjić-Jeftić, G. Cvijanović, Z. Gačić, L. Jovanović, S. Skorić, M. Lenhardt,
- [4] I. Jarić, Ž. Višnjić-Jeftić, G. Cvijanović, Z. Gačić, L. Jovanović, S. Skorić, M. Lenhardt, Determination of differential heavy metal and trace element accumulation in liver, gills, intestine and muscle of sterlet (*Acipenser ruthenus*) from the Danube River in Serbia by ICP-OES, Microchem. J. 98 (2011) 77–81.
- [5] W.P.C. dos Santos, V. Hatje, D.S. Santil, A.P. Fernandes, M.G.A. Korn, M.M. Souza, Optimization of a centrifugation and ultrasound-assisted procedure for the determination of trace and major elements in marine invertebrates by ICP OES, Microchem. J. 95 (2010) 169–173.
- [6] M.A. Hamilton, P.W. Rode, M.E. Merchanj, J. Sneddon, Determination and comparison of heavy metals in selected seafood, water, vegetation and sediments by inductively coupled plasma-optical emission spectrometry from an industrialized and pristine waterway in Southwest Louisiana, Microchem. J. 88 (2008) 52–55.
- [7] A. Meche, M.C. Martins, B.E.S.N. Lofrano, C.J. Hardaway, M. Merchant, L. Verdade, Determination of heavy metals by inductively coupled plasma-optical emission spectrometry in fish from the Piracicaba River in Southern Brazil, Microchem. J. 94 (2010) 171-174.
- [8] I.J. Cindrić, M. Zeiner, M. Kröppl, G. Stingeder, Comparison of sample preparation methods for the ICP-AES determination of minor and major elements in clarified apple juices, Microchem. J. 99 (2011) 364–369.
- [9] A.A. Fallah, S.S. Saei-Dehkordi, A. Nematollahi, T. Jafari, Comparative study of heavy metal and trace element accumulation in edible tissues of farmed and wild rainbow trout (*Oncorhynchus mykiss*) using ICP-OES technique, Microchem. J. 98 (2011) 275–279.
- [10] J.T. Castro, E.C. Santos, W.P.C. Santos, L.M. Costa, M. Korn, J.A. Nóbrega, M.G.A. Korn, A critical evaluation of digestion procedures for coffee samples using diluted nitric acid in closed vessels for inductively coupled plasma optical emission spectrometry, Talanta 78 (2009) 1378–1382.

- [11] E.P. Nardi, F.S. Evangelista, L. Tormen, T.D. Saint'Pierre, A.J. Curtius, S.S. Souza, F. Barbosa Jr., 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. 112 (2009) 727–732.
- [12] G.L. Feudo, A. Naccarato, G. Sindona, A. Tagarelli, Investigating the origin of tomatoes and triple concentrated tomato pastes through multielement determination by inductively coupled plasma mass spectrometry and statistical analysis, J. Agric. Food Chem. 58 (2010) 3801–3807.
- [13] E.J. Llorent-Martínez, P. Ortega-Barrales, M.L. Fernández-de Córdova, A. Domínguez-Vidal, A. Ruiz-Medina, Investigation by ICP-MS of trace element levels in vegetable edible oils produced in Spain, Food Chem. 127 (2011) 1257–1262.
- [14] A. Demirbas, Oil, micronutrient and heavy metal contents of tomatoes, Food Chem. 118 (2010) 504–507.
- [15] K. Bakkali, N.R. Martos, B. Souhail, E. Ballesteros, Characterization of trace metals in vegetables by graphite furnace atomic absorption spectrometry after closed vessel microwave digestion, Food Chem. 116 (2009) 590–594.
- [16] J. Naozuka, S.R. Marana, P.V. Oliveira, Water-soluble Cu, Fe, Mn and Zn species in nuts and seeds, J. Food Compos. Anal. 23 (2010) 78–85.
- [17] L.S. Nunes, J.T.P. Barbosa, A.P. Fernandes, V.A. Lemos, W.N.L. Santos, M.G.A. Korn, L.S.G. Teixeira, Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation, Food Chem. 127 (2011) 780–783
- [18] S.D. Kelly, A.S. Bateman, Comparison of mineral concentrations in commercially grown organic and conventional crops – tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*), Food Chem. 119 (2010) 738–745.
- [19] M.G.A. Korn, J.T. Castro, J.T.P. Barbosa, E.S.B. Morte, A.P. Teixeira, B. Welz, W.P.C. Santos, A.P. Fernandes, E.B.G.N. Santos, M. Korn, Sample preparation for the determination of metals in food samples using spectroanalytical methods a review, Appl. Spectrosc. Rev. 43 (2008) 67–92.
- [20] M.A.Z. Arruda (Ed.), Trends in Sample Preparation, Nova Science, New York, 2007.
- [21] S.T. Gouveia, F.V. Silva, L.M. Costa, A.R.A. Nogueira, J.A. Nóbrega, Determination of residual carbon by inductively coupled plasma optical emission spectrometry with axial and radial view configurations, Anal. Chim. Acta 445 (2001) 269–275.
- [22] L.C. Trevizan, J.A. Nóbrega, Inductively coupled plasma optical emission spectrometry with axially viewed configuration: an overview of applications, J. Braz. Chem. Soc. 18 (2007) 678–690.
- [23] W.P.C. dos Santos, D.R. Gramacho, A.P. Teixeira, A.C.S. Costa, M.G.A. Korn, Use of Doehlert design for optimizing the digestion of beans for multi-element determination by inductively coupled plasma optical emission spectrometry, J. Braz. Chem. Soc. 19 (2008) 1–10.
- [24] M.V.B. Krishna, J. Arunachalam, Ultrasound-assisted extraction procedure for the fast estimation of major, minor and trace elements in lichen and mussel samples by ICP-MS and ICP-AES, Anal. Chim. Acta 522 (2004) 179–187.
- [25] D.S. Rodrigues, A.L. Pontes, K. Mimami, C.T.S. Dias, Quantidade absorvida e concentrações de micronutrientes em tomateiro sob cultivo protegido, Sci. Agrícola 59 (2002) 137–144.
- [26] S.M. Ross, Toxic Metals in Soil-Plant Systems, First ed., John Wiley & Sons, New York, 1994, p. 496.
- [27] J.A. Fayad, P.C.R. Fontes, A.A. Cardoso, F.L. Finger, F.A. Ferreira, Absorção de nutrientes pelo tomateiro cultivado sob condições de campo e de ambiente protegido, Horticultura Bras. 20 (2002) 90–94.
- [28] B.P. Baker, C.M. Benbrook, E. Groth III, K.L. Benbrook, Pesticide residues in conventional, integrated pest management (IPM)-grown and organic foods: insights from three US data sets, Food Addit. Contam. 19 (2002) 427–446.
- [29] L. Pussemier, Y. Larondelle, C.V. Peteghem, A. Huyghebaert, Chemical safety of conventionally and organically produced foodstuffs: a tentative comparison under Belgian conditions, Food Control 17 (2006) 14–21.