Multivariate characterization of fresh tomatoes and tomato-based products based on mineral contents including major trace elements and heavy metals

SEBNEM OZTURKOGLU-BUDAK – INCI AKSAHIN

Summary

The contents of five minerals (Na, K, P, Ca and Mg) and nine trace elements (Se, Fe, Zn, Cu, Mn, Mo, Pb, Cd and As) have been determined in 80 fresh tomato and tomato-based products: tomato paste, tomato juice, minced tomato, tomato puree, grated tomato and dried tomato. Analyses were performed by inductively coupled plasma mass spectrometry (ICP/MS). In order to characterize and classify the samples, chemometric analyses were performed by combining principal component analyses (PCA), hierarchical cluster analyses (CA) and variance analyses (ANOVA). The application of multivariate analyses tended to categorize samples according to product variety, establishing nutritional relationships of products and identifying healthy nutritional sources. The results of the mineral measurements revealed that tomato juice and minced tomato are the best substitutes for fresh tomato. Moreover, there were considerable differences in trace element composition among the tomato samples. Heavy metal levels varied among samples.

Keywords

fresh tomatoes; tomato-based products; minerals; trace elements; heavy metals; multivariate analyse

Tomato (*Lycopersicon esculentum*) is one of the most widely consumed fresh vegetables in the industrialized world. Worldwide production of fresh tomato was 123 million tons in 2013 and approximately 10% (11.80 million tons) of this production came from Turkey [1]. Tomato is an excellent source of many nutrients and secondary metabolites that are important for human health, namely, mineral matter, vitamins, antioxidants, phenolics and organic acids [2]. Thus, consumption of tomatoes is considered a nutritional indicator of good dietary habit and a healthy life style [3]. Because its consumption contributes to the intake of fibre, antioxidants and several minerals, it reduces the risk of certain types of cancer and chronic degenerative diseases [4]. Major and trace element contents of tomatoes depend on cultivar, cultivation method, region of cultivation, sampling period and growing conditions [2, 4].

Minerals are involved in many important functions in the body, such as enzymatic reactions, bone mineralization, as well as the protection of cells and lipids in biological membranes. Low intake or reduced bioavailability of minerals may lead to deficiencies, which causes impairment of body functions [5]. The mineral and trace element contents of plants are affected by the plant cultivar, soil and weather conditions during plant growth, use of fertilizers and the plants maturity at harvest [6].

All mineral elements and most of the trace elements (Mn, Cu, Fe, Zn and Se) present in foodstuffs are considered as essential to a certain extent. However, from the analysed elements, Cu, Fe and Zn are reported as potentially toxic in case of an overdose by the Joint FAO/WHO Codex Alimentarius Commission. For that reason, it is important to establish the composition of mineral and trace elements in tomatoes and to elucidate the main factors influencing this composition.

Several studies have been carried out to assess mineral and heavy metal contents of foodstuffs

Sebnem Ozturkoglu-Budak, Department of Dairy Technology, Faculty of Agriculture, University of Ankara, Irfan Bastug Street 24, 06110 Ankara, Turkey.
Inci Aksahin, The Scientific and Technological Research Council of Turkey, Tunus Street 80, 06100, Ankara, Turkey.

Correspondence author:
Sebnem Ozturkoglu-Budak, e-mail: budak@ankara.edu.tr

e.g. cows' milk [7], infant food [5], wheat [8], wines [9], cereals, fruits and vegetables [6], treated liver pastes [10] and tobacco [11]. Although studies of mineral, trace element and heavy metal levels in tomatoes were published [2–4], there are no studies on tomato-based products.

Tomato fibre was reported to be rich in minerals, such as K (112.5 $mg\cdot kg^{-1}$), Mg (15.73 $mg\cdot kg^{-1}$), Ca (14.05 $mg\cdot kg^{-1}$), and low in Na (7.83 $mg\cdot kg^{-1}$), Fe (0.17 $mg\cdot kg^{-1}$) and Zn (0.053 $mg\cdot kg^{-1}$) [12]. In another study, higher contents of minerals such as K (470.88 $mg\cdot kg^{-1}$), Na 140.72 $mg\cdot kg^{-1}$), Fe (3.79 $mg\cdot kg^{-1}$), Zn (2.08 $mg\cdot kg^{-1}$) and Mg (8.16 $mg\cdot kg^{-1}$) were detected in conventionally grown tomatoes [13]. The differences could have originated from intrinsic components in soil.

Among the techniques in element analysis, inductively coupled plasma mass spectrometry (ICP/MS) excels in true multi-element capabilities together with extremely low detection limits [9]. For screening trace-metal contents of foodstuffs, atomic absorption spectrometry (AAS) is generally used [5–10]. Rare studies use ICP/MS for determination of microchemical elements [14].

In the present work, minerals (Na, K, P, Ca, Mg), trace elements (Se, Fe, Zn, Cu, Mn, Mo) and heavy metals (As, Pb, Cd) were determined in fresh tomato and tomato-based products. The objectives were to evaluate the element composition in relation to product variety and the changes in mineral value during processing. Multivariate analysis was performed to classify samples and to identify the more healthy product types. This is the first surveillance report of mineral and trace element contents not only in fresh tomato but also in six different kinds of tomato-based products, in which the results also presents a comparison between different groups.

MATERIAL AND METHODS

Tomato sampling and sample preparation

A total of 80 samples from unpackaged fresh tomato and six different product categories from eleven brands, which were packaged in five different ways, (1) can, (2) cardboard, (3) glass, (4) vacuumed plastic and doy-pack, and (5) nylon bag, were randomly collected in retail outlets in Turkey. Samples were maintained at refrigeration temperature (4 °C) prior to the study. Fresh tomatoes were washed in distilled water for removal of residues of soil and gently dried with a paper towel before preparation. Each tomato was cut in four slices before blending in an Ultra-Turrax blender (Heidolph, Schwabach, Germany). Fresh tomatoes were then mixed based on their brands and homogenized to a puree. Tomato paste, tomato puree, tomato juice, minced tomato, grated tomato and dried tomato were used directly after being removed from their package. All samples were desiccated under nitrogen gas, homogenized again and stored in a polyethylene tube at room temperature until acid digestion for the determination of mineral and trace elements.

Equipment

An Anton PAAR Multiwave 3000 (Perkin Elmer, Waltham, Massachusetts, USA) was used to digest the tomato samples. An Agilent 7500a benchtop ICP/MS (Agilent Technology, Santa Clara, California, USA) equipped with ASX-510 Autosampler (Cetac Technologies, Omaha, Nebraska, USA) fitted with a cross-flow nebulizer and a quartz spray chamber was used for all element analyses throughout the study. Operational parameters and acquisition parameters are listed in Tab. 1.

Reagents and solutions

All chemicals used in the sample treatments were of ultrapure grade. All materials were soaked in 20% (v/v) HNO_3 overnight, rinsed several times with deionized water, and blanks were read before use. Solutions of 65% HNO_3, 35% HCl and 30% H_2O_2 from Merck (Darmstadt, Germany) were used throughout the analytical procedures.

Tab. 1. Operational parameters for Mg, K, Na, Ca, Se, Fe, Cu, Mn, P, Mo and Zn determination in digested tomato samples.

Parameter	Value
Radio-frequency power	1 270 W
Carrier gas flow	1.18 $l\cdot min^{-1}$
Torch-strength (H)	0.4 mm
Torch-velocity (V)	–0.7 mm
Sampling depth	7 mm
Nebulizer	Babington
Spray chamber	Quartz
Spray chamber temperature	2 °C
Peristaltic pump	0.1 Hz
Analyte	Selected 5 minerals and 6 trace elements
Internal standards	^{103}Rh, ^{45}Sc, ^{89}Y, ^{71}Ga
Number points per mass	3
Acquisition time per mass	0.20 s
Number of repetitions	3

Tab. 2. Recovery assays, analysis of the certified reference material CRM 1573a and detection limits.

	Recovery [%]		Content [mg·kg^{-1}]		Limit of detection
	CRM 1573a (n = 3)	Internal standard (n = 3)	CRM 1573a		
			Certified value	Found value	
Na	100.4	101.6	4.97 ± 0.10	4.93 ± 0.02	0.025 mg·kg^{-1}
K	98.8	100.4	15.90 ± 0.30	15.84 ± 0.24	0.027 mg·kg^{-1}
P	96.9	97.8	12.80 ± 0.50	12.73 ± 0.35	0.182 mg·kg^{-1}
Ca	99.1	98.8	10.50 ± 0.12	10.98 ± 0.16	0.115 mg·kg^{-1}
Mg	103.2	104.0	1.78 ± 0.06	1.81 ± 0.03	0.019 mg·kg^{-1}
Se	100.6	99.9	110.00 ± 10.00	108.00 ± 3.00	0.026 μg·kg^{-1}
Fe	98.8	98.6	1.98 ± 0.10	2.01 ± 0.04	0.010 mg·kg^{-1}
Zn	96.9	97.4	45.50 ± 2.50	45.10 ± 0.67	0.020 mg·kg^{-1}
Cu	99.7	102.1	0.90 ± 0.10	0.84 ± 0.20	0.032 μg·kg^{-1}
Mn	102.0	101.3	240.00 ± 60.00	252.00 ± 28.00	0.010 μg·kg^{-1}
Mo	104.2	103.0	9.40 ± 0.80	9.45 ± 0.50	0.010 μg·kg^{-1}
Pb	95.9	97.7	19.00 ± 2.00	18.60 ± 2.00	0.098 ng·kg^{-1}
Cd	97.8	99.0	0.80 ± 0.30	0.88 ± 0.10	0.087 ng·kg^{-1}
As	98.6	100.4	0.50 ± 0.10	0.47 ± 0.20	0.051 ng·kg^{-1}

Tuning solutions of 10 μg·kg^{-1} Li, Y, Ce, Tl, Co were supplied by Agilent (Agilent Technology). The ICP/MS internal standard was obtained from Accu Standard (New Haven, Connecticut, USA).

Analytical procedures and quality assurance

Samples of 1 g from each product type were dried in a clean oven at 100 °C for 24 h. An amount of 0.5 g from these samples was weighed into microwave bombs and digested by using a mixture of $HNO_3:HCl:H_2O_2 = 6:2:2$. The microwave digestion program applied included the following steps: 250 W for 15 min ramp 15 min hold, 500 W for 15 min ramp 15 min hold, and 750 W for 20 min ramp 20 min hold. The digested sample solution was brought to a volume of 25 ml with deionized water. Triplicate digestions were performed for each sample. Working standard solutions were prepared fresh each day from stock standard solution in 2% HNO_3 (1 000 μg·ml^{-1}). Calibrations were performed using direct calibration against aqueous standards. All samples were measured by a standard addition method using ICP/MS. Standard additions were also applied to 100× diluted digested samples. The external calibration samples were diluted 10–100 fold.

Limit of detection and quality control

Trueness of the method was verified by analysing the certified reference material CRM 1573a (tomato leaves) of NIST (National Institute of Standards and Technology, Gaithersburg, Maryland, USA). The contents found were within 95.9–104.2% of the certified values. The results obtained are presented in Tab. 2 and show good agreement between the found values and the certified ones. To assess possible contamination during sample preparation, blank samples of ultrapure water were prepared using the same procedure as for the samples. All blank levels obtained were negligible. An internal standard was used for all ICP/MS measurements in order to quantify the elemental composition of the samples and correct for any instrument drift during analysis. Limit of detection (*LOD*) was calculated for each element as three standard deviation (*SD*) values of the contents determined in the blank solutions (i.e. ultra pure water containing 1% (v/v) HNO_3 and 1% (v/v) HCl). Tab. 2 shows the results of *LOD* determination as well as certified and found values for CRM 1573a.

Statistical data analysis

Multivariate analyses of minerals, trace elements and heavy metals were performed using SPSS version 18.0 for Windows (SPSS, Chicago, Illinois, USA). A data matrix, of which rows are the different tomato product type (analysed samples, cases) and columns are descriptors corresponding to mineral and trace element contents determined (variables), was built for further multivariate analysis. Eighty cases divided into seven product types and 11 variables (Na, K, P, Ca, Mg, Se, Fe, Zn, Cu, Mn, Mo, Pb, Cd and As) were taken into consideration.

Classification was performed by principal component analysis (PCA) and hierarchical cluster analysis (CA), and the results obtained from these analyses were subjected to one-way analysis of variance (ANOVA) to determine differences between the results [15].

PCA is a powerful tool for pattern recognition, classification, modelling and other aspects of data evaluation [8]. PCA reduces the dimensionality of the original data matrix while retaining the maximum amount of variability. It reveals the relationship between variables and observations, as well as recognizes the data structure by a new set of variables (principal components, PCs). It facilitates the discovery of patterns in the dataset [7]. PCA will show contents of which elements and which products correlate with each other [10].

CA measures either the distance or the similarity between objects to be clustered. Objects are grouped in clusters in terms of their similarity. The initial assumption is that nearness of objects in the space defined by the variables reflects the similarity of their properties. In our study, the Ward's method as the amalgamation rule, and squared Euclidean distance as metric were used [16].

ANOVA was used for showing if there are significant differences between contents of minerals or trace elements and product categories. Mean values obtained for the variables studied in the different groups were compared by a one-way ANOVA test (Duncan's multiple range) assuming that there were significant differences among them when the statistical comparison gave $p < 0.05$.

Pearson correlation analysis was used in order to quantitatively analyse and confirm the relationships among mineral and trace element content in selected tomato samples. The Pearson correlation analysis was applied to the obtained data. The Pearson correlation coefficient is a common parameter used to quantify the strength of linear association between pairs of variables by calculating a summary index.

RESULTS AND DISCUSSION

Based on current knowledge, several elements are recognized as essential for human health, such as Zn, Mg, Se, Fe, K, P or Ca. The basic source of essential elements for humans is food. Their beneficial levels do not cause any disorders and have no harmful effect. However, the line between the quantity being beneficial (and/or therapeutic) and toxic is very important. In addition to environmental effects such as chemical, physical and biological processes, other sources of influence and contamination should definitely be considered as well (rainfall, atmospheric dust, plant protection agents and fertilizers etc.). These have special importance for toxic elements. In that order, the chemometric approach is recognized as a useful way to provide additional and complementary information [16].

In the present work, minerals (Na, K, P, Ca, Mg), trace elements (Se, Fe, Zn, Cu, Mn, Mo)

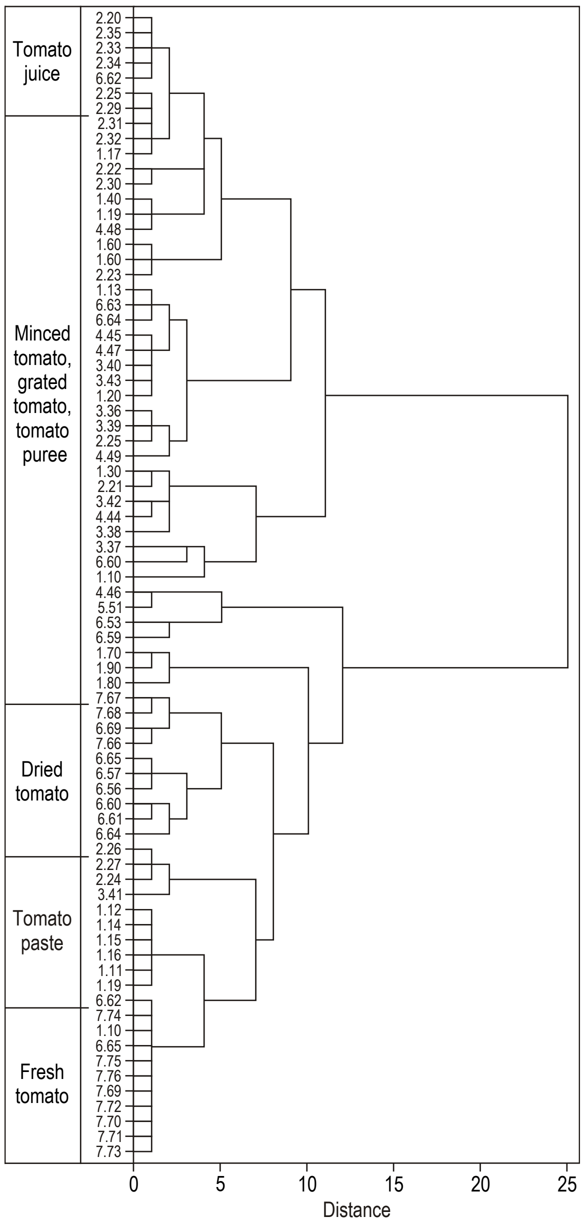

Fig. 1. Dendrogram of cluster analyses of mineral and trace element contents of fresh tomato and tomato-based products.

and heavy metals (As, Pb, Cd) were determined in fresh tomato and tomato-based products by means of ICP/MS after complete dissolution of their matrices by microwave-assisted digestion. This is the first surveillance report of mineral and trace element content not only in fresh tomato but also in six different kinds of tomato-based products.

Cluster analyses

CA provided information on what kind of classification can be made on the basis of distances only. A dendrogram was formed for autoscaled microelement contents using Ward's method as an amalgamation rule and the squared Euclidean distance as a measure of the proximity between samples. It supplied a first impression about the structure of the data and was used to find the similarity of the tomato samples by using 74 of the 80 variables determined as the input data. The results of the CA are presented as a dendrogram (Fig. 1). According to this dendrogram, dried tomato and tomato paste were more similar to the fresh tomato.

For multivariate analyses, samples were coded as; 1 – tomato paste, 2 – tomato juice, 3 – minced tomato, 4 – grated tomato, 5 – tomato puree, 6 – dried tomato and 7 – fresh tomato. Five clusters were identified from the dendrograms. The first cluster contained 10 out of 16 tomato juice samples, while the second cluster was composed of 33 samples mainly from minced tomato, grated tomato and tomato puree. These products are obtained directly from fresh tomato. Dried tomatoes are principally grouped in the third cluster, while tomato pastes are in the fourth cluster. The last cluster represents fresh tomatoes in which 8 out of 11 samples were grouped.

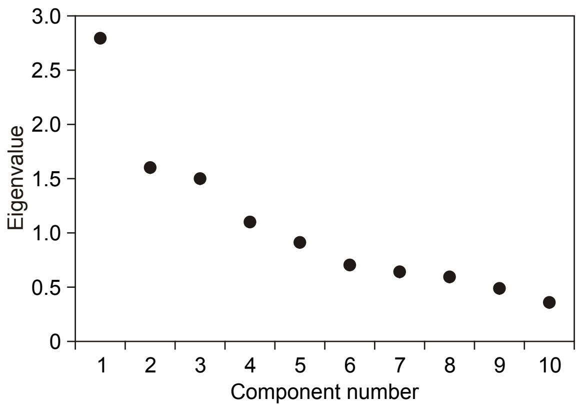

Fig. 2. Screen plot of Eigen values of the principal components.

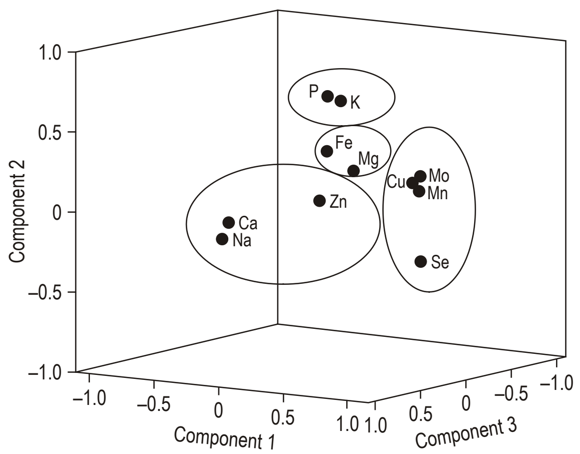

Fig. 3. Varimax rotated principal component loadings (similarities of minerals and trace elements).

Principal component analyses

Prior to performing PCA, suitability of the data for factor analysis was checked. PCA yielded four PCs with Eigen values higher than one [17] explaining 75 % of the total variance in the data, as shown in Fig. 2. The values of correlation coefficients higher than 0.50 were accepted as significant for loading factors.

The loading expresses how well the principal components correlate with the variables. The first principal component, PC1, correlated well with trace elements Mn, Mo, Se and Cu in tomato samples. Atmospheric deposition is a possible source of Mn. PC2 correlated with P and K, which are major components in food materials. PC3 correlated with Ca, Na, Zn, which originate from the soil substratum, mainly from fertilizers. PC4 correlated with Fe and Mg with highly positive loading. Fe partly originates from soil and Mg is a constituent of chlorophyll. Fe correlated negatively with PC4. PCA enabled visualization of the data set in four principal components retaining the maximum possible variability within that set as presented in Fig. 3.

The mineral composition of vegetables characterizes their nutritional value and indicates the potential yield. Excessive amounts of K and Mg in tomato inhibit Ca uptake and cause blossom-end rot as a result of Ca deficiency [18]. Ca deficiency in the growth substrate was shown to result in decreased levels of both Ca and P in tomato plants [2, 19].

Analyses of variance

To ascertain the significance of differences in mineral and trace element contents among different product categories and fresh tomato, the data were statistically evaluated by analysis of variance (ANOVA). One-way ANOVA (Duncan's multiple range) was performed on the results for each mineral or trace element by assuming that there were significant differences among them when the statistical significance gave $p < 0.05$. ANOVA showed that there were highly significant differences in the composition of fresh tomato and tomato-based products with respect to Na, P, Ca, Cu, Zn and Mo, while no significant differences were detected for Mg, K, Fe, Mn and Se. Microelement contents in foodstuffs depend on soil characteristics, such as content of organic matter, pH and clay mineralogy, which can affect the bioavailability of elements. In addition to environmental pollution, these contents can also be affected by addition of chemical products such as fertilizers, fungicides, insecticides and herbicides to crops [8].

According to the Duncan's multiple comparison test, there were no significant differences between the mean values of tomato paste and dried tomato with respect to Na content. In contrast, significant differences were observed between tomato paste and all other samples. Mean plots of the different elements were obtained that verified the comparison test results. The differences in Na are thought to result from salt supplementation in tomato paste, which is done to increase the shelf life and to prevent deterioration during the drying process (Fig. 4). With respect to P, significant differences were only observed between tomato juice and dried tomato, while significant differences in Ca were only observed between tomato juice and grated tomato. The difference is thought to be caused by the supplementation of calcium salt in tomato-based products for calcium pectate formation, which adds firmness to the structure of the product (Fig. 5).

For fresh tomatoes we can compare our results with the other results in the literature. The data obtained in this paper on Na were higher than most data published in the literature [3, 20, 21]. The high Na content in the soil is mainly due to the influence of high salinity of water used for irrigation [3]. The content of K was similar to the data indicated by Suarez et al. [3] and Holland et al. [20]. The nutritive significance of minced tomato and tomato juice is as high as of fresh tomato. Ca content is a little below the contents reported by most authors [2, 3, 6, 22]. With respect to heavy metals As, Pb and Cd, the contents determined by us were similar to the contents published by some researchers [2, 22–24]. Heavy metal contents of fresh tomato and tomato-based products showed a minimum difference. Pb was found higher than As and Cd. Fresh tomato had lower Pb content.

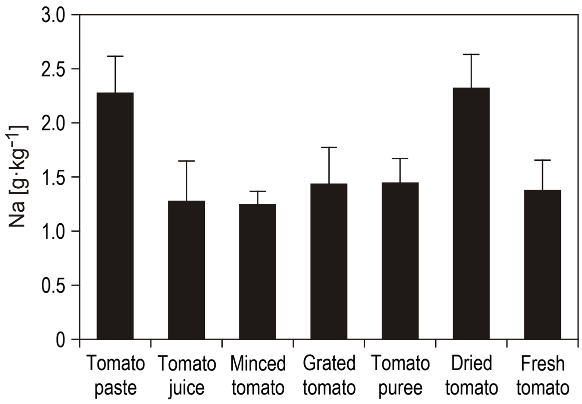

Fig. 4. Mean sodium content in fresh tomato and tomato-based products.

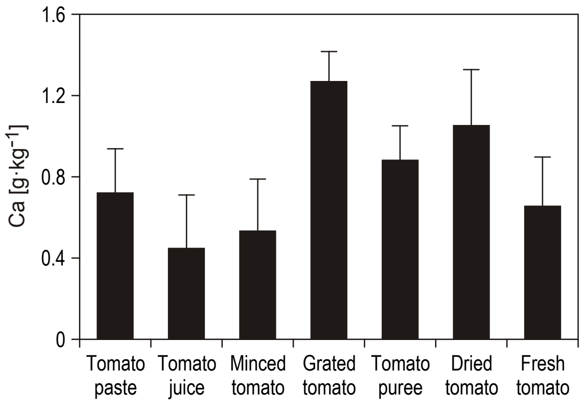

Fig. 5. Mean calcium content in fresh tomato and tomato-based products.

The levels of As and Cd in samples were close to each other.

In general, the variations observed in mineral contents of tomatoes and tomato-based products in different groups might have also originated from climate, soil conditions, cultivar, soil type, planting date, harvesting time and growing seasons, which might potentially affect the detected values.

CONCLUSIONS

Contents of 11 trace elements and minerals were used to characterize fresh tomato and tomato-based products. The chemometric approach was applied to the experimentally obtained data. By application of multivariate methods of analysis, namely, CA, PCA and ANOVA, correlations between the investigated elements were highlighted and some patterns were observed, in order to identify possible influences of outer and inner element sources. This study provides information about the similarity of processed foods to fresh foods in terms of mineral and trace element contents, or useful/harmful elements complemented during the production process. This study enables a selection of the most suitable tomato products for human diet and nutrition on the basis of identification of products most similar in mineral contents to fresh tomato, which are tomato juice and minced tomato. Tomato paste and dried tomato contain significantly more Na than fresh tomato due to salt supplementation during the production process to increase shelf life. A similar effect was observed for Ca in tomato puree and in grated tomato, which are supplemented to obtain a more firm structure. Consequently, tomato juice and minced tomato are the best substitutes for fresh tomato in human diet. The nutritive significance of tomato-based products is different from fresh tomato, but heavy metal levels were found practically the same both in fresh tomato and in tomato-based products.

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