ORIGINAL PAPER

DETERMINATION OF HEAVY METALS CONTENT FROM CITRUS FRUIT PEELS

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Abstract. *This study aims to determine the concentrations of heavy metals and other metals of safety concern in citrus fruit peel extracts. Different types of citrus fruits (i.e., lemon, mandarin, orange, grapefruit, and lime) were collected randomly from markets, during the spring of the year 2024. The inductively coupled plasma mass spectrometry technique was used to determine the concentrations of Al, Cr, Mn, Ni, Cu, Zn, Sr, Cd, and Pb in citrus peel extracts. The obtained data have not exceeded the maximum allowed limits provided by European legislation. The statistical analysis results show that Cu and Zn were correlated positively. Likewise, a strong positive correlation (>0.500) can be observed between Al and Sr, Cr and Ni, Cr and Zn, Cr and Pb, Mn and Zn, Ni and Cd, Ni and Pb, Cd, and Pb. To check if the sample data are adequate, the Kaiser-Meyer-Olkin test was used. The principal component analysis contains a maximum of three components responsible for 74.872% of the total variation, while cluster analysis revealed the approximate HMs content of the 17 analyzed samples.*

Keywords: *citrus; heavy metals; food safety; ICP-MS; statistical analysis.*

1. INTRODUCTION

Citrus fruits, such as sweet oranges (*Citrus sinensis*), lemons (*Citrus limon*), limes (*Citrus aurantifulia*), mandarins (*Citrus reticulata*), and grapefruits (*Citrus paradisi*), are among the most significant and popular fruit crops in the world [1]. The production of oranges, lemons, limes, mandarins, tangerines, clementines, pomelos, grapefruits, and other citrus was estimated to be approximately 166.4 million tonnes annually [2]. Moreover, oranges production for over 50% of the total annual global output, i.e., 76.4 million tonnes in 2022 [2]. In Romania, the number of imports and intra-union exchanges of fruits, especially citrus, increased considerably between 2017 and 2021 [3]. Several studies revealed that the main portion of valuable organic active compounds (i.e., flavonoids, including naringenin, hesperidin, eriocitrin, and rutin, phenolic acids, such as chlorogenic, p-coumaric, ferulic, and sinapic acids, condensed tannins, ascorbic acid, tocopherols, carotenoids, dietary fiber, minerals, etc.), commonly known as natural antioxidants, are found in the peel, not in the pulp

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of the citrus fruits [1, 4-10]. On the other hand, these antioxidants contribute to color and predator protection [9,10]. Furthermore, they have anti-inflammatory and antioxidant capabilities, which promote human health [11-13]. Due to its high nutritional value, citrus peel is used as animal compost. However, xenobiotic substances, including pesticides and heavy metals, are one emerging concern about citrus peels used as animal feed [14-19]. On the other hand, a large quantity of by-products known as citrus pomace, which consists of peels, seeds, pulps, and membrane scraps, is considered food waste, accounting for more than half of the degraded fresh fruit, and must be recycled and reused in the context of circular economy [4,5]. In this respect, citrus by-products have been used in various food products, including bakery [20-22], meat [23-25], and dairy [26]. Even though these citrus by-products have been used in various research to create functional foods, their food safety must still be properly evaluated.

Several studies revealed that heavy metals (HMs) and metalloids (Ms) including cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), manganese (Mn), copper (Cu), mercury (Hg), beryllium (Be), aluminum Al), and arsenic (As) respectively is a serious concern for the environment and human health [27-37]. More precisely, Waleed and Hamad (2023) related that heavy metals are a group of dense and harmful elements even in low concentrations, consisting of metals and metalloids with densities greater than 5 g/cm3 and atomic masses ranging from 60 to 200 [35]. Heavy metals are usually classified into essential metals and non-essential metals. Other studies classified HMs into four specific classes such as toxic, precious, radionuclides, and nutrients (micro and macronutrients) [35,38]. Metals play an important role in the biological processes of life. Essential heavy metals are important to living organisms and may be required in the body in fairly low concentrations, and non-essential heavy metals have no known biological role in living organisms [39]. Thus, Mn, Fe, Cu, Co, and Zn are considered essential metals, in terms of required micronutrients/trace elements of plants. Low concentrations of these metals can help the growth, stress resistance, biosynthesis, and functioning of various biomolecules (i.e., carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites). For humans, the deficiency or excess in the body of an essential metal can lead to abnormal conditions, even diseases. It can be concluded that the essential heavy metals content may vary in the case of plants, animals, and microorganisms [40]. Non-essential metals, known as xenobiotic metals, have no biological role in living organisms, being considered toxic metals regardless of the concentration in which they are found. Obvious, metals such as Cd, Pb, Ni, and Hg, can modify the concentration of an essential element in the body, leading to an equilibrium loss in terms of human health [32]. Other research revealed that HMs such as Zn, Cu, Ag, Fe, Cr, As, Pd, U, and Pt have harmed health, even at low levels [33-36]. According to their carcinogenic level, HMs are classified as [41] (i) carcinogenic metals (Al, As, Cd, and their inorganic compounds, compounds of Cr(VI) and Ni, as well); (ii) potentially carcinogenic metals (Pb, V, Hg, Co, and their inorganic compounds); (iii) carcinogenicity cannot be classified (Cr(III) compounds, Cu, Hg and its inorganic compounds, Se, and its compounds, arsenic organic compounds not metabolized by humans); (iv) potentially non-carcinogenic metals (Mn, Zn, Ag). Heavy metals and pesticides are chemical contaminants that may be present in citrus fruits, posing a significant health risk due to potential toxicity effects on humans, specifically neurological [42] and carcinogenic effects [41]. Thus, is critical to ensure that citrus fruits are safe for human consumption. Starting from these considerations, this study aims to determine the concentration of nine HMs including Cd, Pb, Cr, Mn, Ni, Cu, Zn, Al, and Sr in citrus fruit peel extracts (i.e., orange, lemon, grapefruit, mandarin, and lime). Statistical analysis was used to assess the correlation between metals and potential toxic effects on the human health of HMs from citrus.

2. MATERIALS AND METHODS

2.1. MATERIALS AND REAGENTS

All reagents (Merck KGaA, Germany, and Sigma-Aldrich, Saint Louis, USA) were of analytical grade, and the liquid samples were filtered before use to avoid accidental contamination of the samples or potential interference in analyses. Deionized water (conductivity < 0.5 µS/cm at 25°C) was used for sample dilution. In March 2024, 17 samples of citrus fruits (lemons, mandarins, oranges, grapefruits, and limes, Table 1) were collected randomly from the market of southern Romania to determine the concentration of heavy metals in their peel. Citrus samples were collected following the sampling procedure described in Commission Regulation (EC) No 333/2007 [43]. Six samples were collected from storage, one from an import warehouse, and ten from the retail (Table 1). Two samples collected from the retail were identified for sale with the "organic label".

Table 1. Data related to samples collected in the spring of the year of 2024.

Sample cod	Sampling place	The sample	Origin Country
1G -I	Warehouse	Grapefruit	non-EU
1Li-I	Storage	Limes	non- EU
1L-SI (organic)	Retail	Lemons (organic)	EU
1M-SI (organic)	Retail	Tangerines (organic)	EU
1P-SI	Storage	Oranges	EU
2G-I	Retail	Grapefruit	non-EU
2L-I	Storage	Lemons	non-EU
2Li-I	Retail	Limes	non-EU
2M-I	Storage	Tangerines	non-EU
2M-SI	Retail	Tangerines	EU
2P-SI	Storage	Oranges	EU
3G-I	Retail	Grapefruit	non-EU
3L-I	Storage	Lemons	non-EU
3LI-I	Retail	Limes	non-EU
3M-I	Retail	Tangerines	non-EU
3P-SI	Retail	Oranges	EU
4L-I	Retail	Lemons	non-EU

EU – European Union; non-EU - countries that are not a member of the European Union.

2.2. SAMPLE PREPARATION

Citrus peel extracts were prepared as follows: 100 g of peeled citrus were weighed on an analytical balance, then were added into a sterile glass with 1000 mL of ultrapure water for maceration for 72 hours at 20°C; after that, the samples were filtered under vacuum. It is important to mention that each fruit was washed separately at 60–70°C and dried to remove impurities that could affect the assay result. The citrus extracts were stored at a temperature of 40°C till digestion. The chemical digestion of the citrus samples was performed using a TOPWAVE microwave-assisted digester (Analytik Jena, Jena, Germany). 20 mL extract sample was inserted into a PTFE tube type PM 60 (Analytik Jena, Jena, Germany), then were added 4 mL of 65% pure nitric acid and 1 mL of hydrogen peroxide 30-35%. After 40 minutes of rest, samples were digested to destroy the inorganic matrix. The parameters of digestion are shown in Table 2.

Table 2. Parameters of digestion method.

Steps	Temperature [°C]	Pressure [bar]	Power [%]	Ramp [min]	Time [min]
1	170	40	80	5	10
2	200	40	90	1	15

After digestion, the tubes were removed from the digestor and cooled to 20-22°C. After cooling, the samples were filtered into 25 mL volumetric flasks, using a qualitative filter paper with 8-12 µm porosity; finally, the samples were brought to 25 mL with ultrapure water.

2.3. INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Metal concentrations (*i.e.*, Al, Cr, Mn, Ni, Cu, Zn, Sr, Cd, and Pb) were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an iCAP™Q spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The high sensitivity of this technique allows the determination of metals at the ppb-ppt level (µg/kg or µg/L-ng/kg or ng/L), as well as isotope analysis and determination of multiple elements on a single sample. ICP-MS separation and detection are based on the *m/z* ratio, where *m* is the ion's mass and *z* is its charge. Measurements were performed in triplicate in standard (SD) mode, with Qtegra Intelligent Scientific Data Solution software automatically correcting for known isobaric interference. Blank solutions were used to determine the limits of detection (LOD) and quantification (LOQ) of the metals such as LOD ranged from 0.620±0.136 to 96.766±8.384 µg/L and LOQ ranged from 0.892±0.136 to 113.535±8.384 µg/L (Table 3). Metal calibration curves showed satisfactory linearity from 0.01 to 10.0 mg/L, with R^2 coefficients ranging from 0.991 to 0.999. The accuracy and precision of the method ranged from 92-105% and 1-8%, respectively.

Table 3. Limits of detection and limits of quantification.

ppb	Al	Cr	Mn	Ni	Cu	Zn	Sr	Cd	Pb
Blank 1	59.558	63.344	0.621	0.714	6.820	6.471	0.331	0.366	6.063
Blank 2	57.723	71.391	0.105	0.434	5.531	8.723	0.798	0.111	7.888
Blank 3	50.446	80.108	0.738	0.888	6.711	7.809	1.159	0.156	5.300
Average	55.909	71.614	0.488	0.678	6.354	7.668	0.763	0.211	6.417
SD	4.819	8.384	0.337	0.229	0.715	1.132	0.415	0.136	1.330
LOD	70.365	96.766	1.498	1.365	8.498	11.064	2.007	0.620	10.405
LOQ	80.003	113.535	2.171	1.823	9.928	13.329	2.837	0.892	13.065

2.4. STATISTICAL ANALYSIS

Statistical methods through descriptive analysis, Pearson correlation coefficient, principal component analysis (PCA), and cluster analysis were performed using IBM SPSS Statistics for Windows, Version 26.0. Armonk, NY: IBM Corp to determine the correlation or dependencies between metals presented in citrus fruit peel extracts.

3. RESULTS AND DISCUSSION

The results show that all the analyzed samples contain heavy metals in different concentrations, including the two organic samples (Table 4). It is observed that the 2Li-I sample has the highest content of aluminum and strontium. The samples 1L-Si (organic) and 1M-Si (organic) have detected different concentrations of heavy metals, and the sample 2P-Si appears to be the least contaminated sample (Table 4). The 3P-Si sample showed high concentrations of chromium, lead, and nickel, while the 3Li-I sample showed a high cadmium concentration. Commission Regulation (EU) 2023/915 sets limit values for heavy metals in fruit for lead and cadmium [44]. According to data from Table 4 *vs.* Table 5 it should be noted that in the analyzed samples no exceeding of the maximum limits allowed for lead and cadmium.

Table 4.Concentrations of heavy metals and other metals of safety concern.

Sample cod	Heavy metals concentrations [μg/L]								
	Al	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Sr**	**Cd**	**Pb**
1G-I	194.368±2.020	196.733 ±0.513	460.803 ±9.211	3.211 ±0.074	63.206 ±0.773	153.951 ±0.395	165.548 ±1.630	2.995 ±0.128	56.128 ±1.718
1Li-I	156.833 ±0.905	131.586 ±0.144	65.839 ±1.363	2.096 ±0.084	88.989 ±1.225	77.145 ±1.578	319.934 ±1.524	0.271 ±0.020	46.778 ±1.493
1L-SI (organic)	126.131 ±1.369	136.523 ±2.781	28.330 ±0.419	1.855 ±0.246	37.968 ±1.065	51.850 ±0.944	460.683 ±3.565	0.398 ±0.049	39.930 ±1.005
1M-SI (organic)	131.475 ±1.148	85.628 ±0.575	102.679 ±1.103	2.544 ±0.268	33.463 ±0.660	45.531 ±0.654	231.131 ±0.254	2.865 ±0.255	49.380 ±1.843
1P-SI	210.829 ±45.936	146.346 ±0.836	46.986 ±0.635	3.109 ±0.144	28.298 ±0.384	40.838 ±0.464	343.140 ±4.439	2.044 ±0.074	46.014 ±1.596
2G-I	194.779 ±4.023	196.093 ±2.016	21.353 ±0.193	1.839 ±0.029	28.529 ±0.258	42.759 ±0.326	159.029 ±2.410	0.413 ±0.114	57.569 ±1.548
2L-I	326.875 ±5.120	93.294 ±0.606	75.563 ±0.711	1.569 ±0.193	81.026 ±0.596	47.935 ±1.546	199.099 ±2.180	0.151 ±0.048	37.834 ±0.543
2Li-I	891.001 ±9.579	139.319 ±0.506	63.198 ±0.263	3.768 ±0.098	58.433 ±0.656	66.988 ±1.395	1055.499 ±12.174	1.256 ±0.135	55.391 ±0.750
2M-I	319.299 ±4.748	185.546 ±0.900	67.460 ±0.338	3.459 ±0.011	77.095 ±0.418	101.828 ±2.266	311.040 ±2.239	3.773 ±0.259	73.498 ±0.536
2M-SI	268.160 ±1.439	74.548 ±0.775	41.814 ±0.290	2.986 ±0.365	79.581 ±0.319	52.850 ±0.533	458.264 ±6.011	0.170 ±0.211	41.659 ±0.330
2P-Si	178.994 ±2.464	106.935 ±0.600	19.553 ±0.399	0.881 ±0.049	46.254 ±0.273	41.519 ±0.034	144.288 ±1.933	0.318 ±0.046	41.243 ±0.614
3G-I	129.934 ±2.086	83.223 ±0.800	43.665 ±0.654	2.894 ±0.219	33.978 ±0.096	41.244 ±0.714	244.959 ±5.880	0.363 ±0.011	37.639 ±1.016
3L-I	242.136 ±3.106	88.133 ±0.255	33.115 ±0.635	1.661 ±0.020	41.164 ±0.576	56.588 ±1.279	192.971 ±1.373	5.993 ±0.153	57.831 ±0.160
3Li-I	146.758 ±1.864	75.314 ±0.405	43.606 ±0.396	3.830 ±0.356	50.213 ±0.235	60.445 ±0.389	256.161 ±1.046	12.018 ±0.594	56.025 ±0.434
3M-I	222.240 ±3.948	186.913 ±2.469	71.738 ±0.361	3.990 ±0.146	57.065 ±0.221	120.544 ±4.233	279.888 ±5.889	0.001 ±0.135	41.909 ±0.699
3P-SI	175.148 ±3.475	234.678 ±0.204	68.131 ±0.566	5.248 ±0.175	63.316 ±1.001	53.671 ±1.311	176.689 ±2.240	11.835 ±0.520	84.148 ±1.433
4L-I	305.046 ±3.178	218.768 ±3.153	43.769 ±0.744	3.744 ±0.354	59.590 ±1.238	89.844 ±2.324	502.509 ±7.653	3.973 ±0.160	67.810 ±1.113

Lead accumulates over time in the body's "reservoir tissue", such as bone, and cadmium, chromium, and lead specifically accumulates in target tissues such as the kidney, causing chronic toxicity. For Al, Cu, Cr, and Ni were not yet expressed values in 2023/915/EU [44].

Table 5. Maximum levels for heavy metals according to 2023/915/EU [44].

Metal	Citrus fruits [μg/kg]	Citrus fruit juice [μg/kg]
Lead	100	30
Cadmium	20	NA
Chromium	NA	NA
Aluminum	NA	NA
Nickel	NA	NA

NA – not applicable

These metals are still related to human health damage and hypersensitivity, e.g., Al is a common and neurotoxic metal that poses food safety risks. Most cases of heavy metal toxicity are thought to be caused by persistent low-level exposure, often lasting decades (affecting long-term health by having a cumulative effect) [31]. Also, several studies revealed that exposure to heavy metals at the same time could have synergistic harmful effects [30-32].

Descriptive analysis provides a clear and concise picture of the collected data, providing essential information about central tendencies, the spread of data, and the shape of the distribution of identified chemical elements. Thus, from Table 6 it is possible to observe both the minimum value of the identified elements and the maximum value, the average value of the data set, the standard deviation, and the symmetry of the distribution of the data values.

Table 6. Descriptive analysis.

	Minimum	**Maximum**	**Mean**		**Std. Deviation**	**Variance**	**Skewness**		**Kurtosis**	
Al	126.131	891.001	248.23565	43.182396	178.045580	31700.228	3.246	.550	11.896	1.063
Cr	74.548	234.678	139.97529	13.081387	53.935941	2909.086	.327	.550	-1.327	1.063
Mn	19.553	460.803	76.32953	24.602127	101.437168	10289.499	3.810	.550	15.168	1.063
Ni	.881	5.248	2.86376	.270102	1.113659	1.240	.168	.550	-.160	1.063
Cu	28.298	88.989	54.59812	4.695232	19.358937	374.768	.252	.550	-1.077	1.063
Zn	40.838	153.951	67.38412	7.772168	32.045469	1026.912	1.624	.550	2.226	1.063
Sr	144.288	1055.499	323.57835	53.023355	218.620893	47795.095	2.574	.550	7.993	1.063
Cd	.001	12.018	2.87276	.927043	3.822298	14.610	1.736	.550	2.286	1.063
Pb	37.639	84.148	52.39918	3.208274	13.228052	174.981	1.009	.550	.605	1.063

In order to identify any possible correlations or dependencies between these variables, the relationship between the metals under examination was analyzed using the Pearson correlation coefficient (Table 7). A linear correlation coefficient known as the person coefficient has been used to assess the degree of relationships between two or more variables.

Table 7. Pearson Correlation.

Pearson Correlation	**Al**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Sr**	**Cd**	**Pb**
Al	1								
Cr	.074	1							
Mn	-.043	.272	1						
Ni	.212	.501*	.160	1					
Cu	.236	.101	.187	.179	1				
Zn	.089	.516*	.728**	.370	.412	1			
Sr	.843**	.011	-.167	.269	.136	.015	1		
Cd	-.141	.156	.025	.562*	-.016	.007	-.190	1	
Pb	.137	.655**	.099	.599*	.149	.247	.002	.703**	1

***. Correlation is significant at the 0.01 level (2-tailed).*
**. Correlation is significant at the 0.05 level (2-tailed).*

For significance testing, one uses the correlation coefficient, which ranges from -1 to +1 for perfect negative linear relationships, 0 for no correlation, and 1 for perfect positive linear relationships.

Table 8 shows the connection between the elements identified in the citrus samples; thus, a strong positive correlation (>0.500) can be observed between Al and Sr, Cr and Ni, Cr and Zn, Cr and Pb, Mn and Zn, Ni and Cd, Ni and Pb, Cd, and Pb. Likewise, a positive average correlation can be identified between Cu and Zn (r = 0.412). To check if the sample data are adequate, the Kaiser-Meyer-Olkin (KMO) Test was used, which having a value >0.500 (KMO = 0.687) it can be concluded that the data are adequate for statistical analysis.

Table 8. KMO and Bartlett's Test.

Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.687
Bartlett's Test of Sphericity	Approx. Chi-Square	71.811
	df	36
	Sig.	.000

The principal component analysis (PCA) contributes a maximum of three components responsible for 74.872% of the total variation. Table 9 presents the nine components and their percentage and cumulative variation.

Table 9. Total Variance Explained.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	Variance [%]	Cumulative [%]	Total	Variance [%]	Cumulative [%]	Total	Variance [%]	Cumulative [%]
1	3.055	33.946	33.946	3.055	33.946	33.946	2.563	28.479	28.479
2	1.997	22.184	56.129	1.997	22.184	56.129	2.146	23.848	52.327
3	1.687	18.743	74.872	1.687	18.743	74.872	2.029	22.545	74.872
4	.845	9.392	84.264						
5	.661	7.349	91.613						
6	.417	4.628	96.241						
7	.167	1.860	98.102						
8	.107	1.193	99.295						
9	.063	.705	100.000						

Extraction Method: Principal Component Analysis.

The first PCA component with a variation value of 33.946% shows a strong load for Cr (0.754), Ni (0.802), Cd (0.524), and Pb (0.803), while for the second PCA component, only Al and Sr have loads strong of 0.897 and 0.924 respectively. Mn (0.699), Zn (0.649), and Cu (0.635) are the elements with the predominant charge for PCA component 3 (Figure 1).

Following the cluster classification, a grouping into two classes can be observed in the case of Al and Mn elements, a grouping into three classes for Sr, four classes for Cd, five classes for Cr, Ni, Zn, and Pb, and six classes for Cu, which denotes the approximate heavy metal content of the 17 analyzed samples (Figure 2).

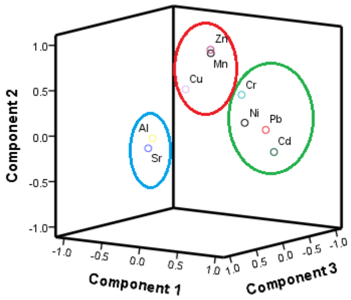
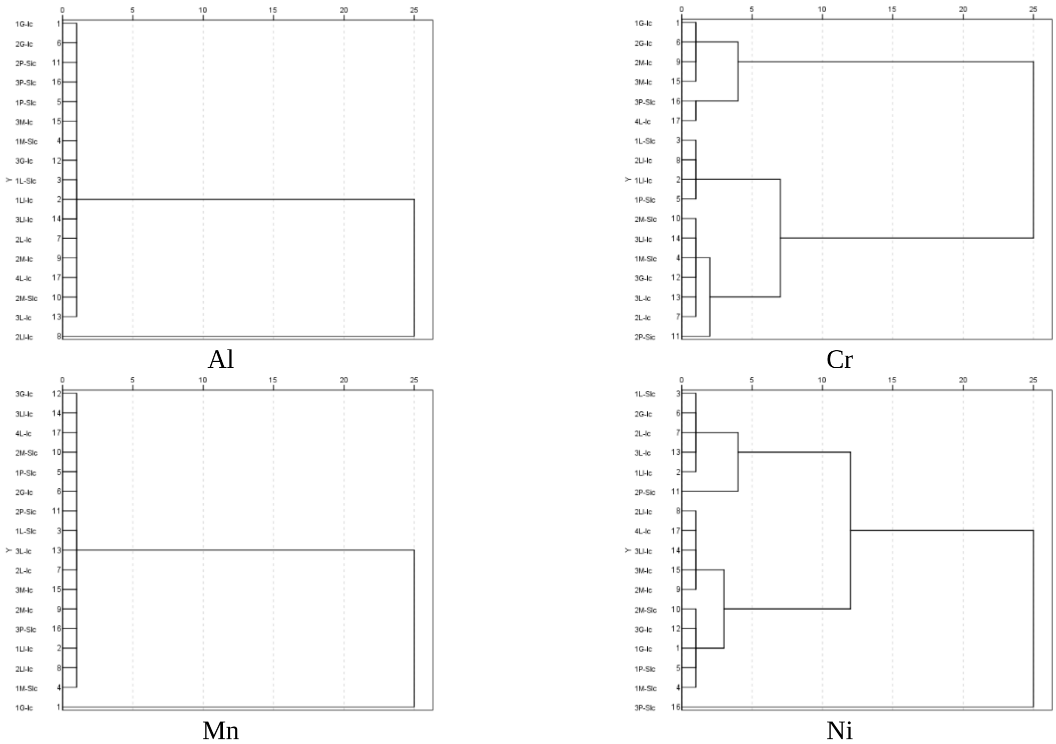


Figure 1. Component Plot in Rotated Space for investigated metals.



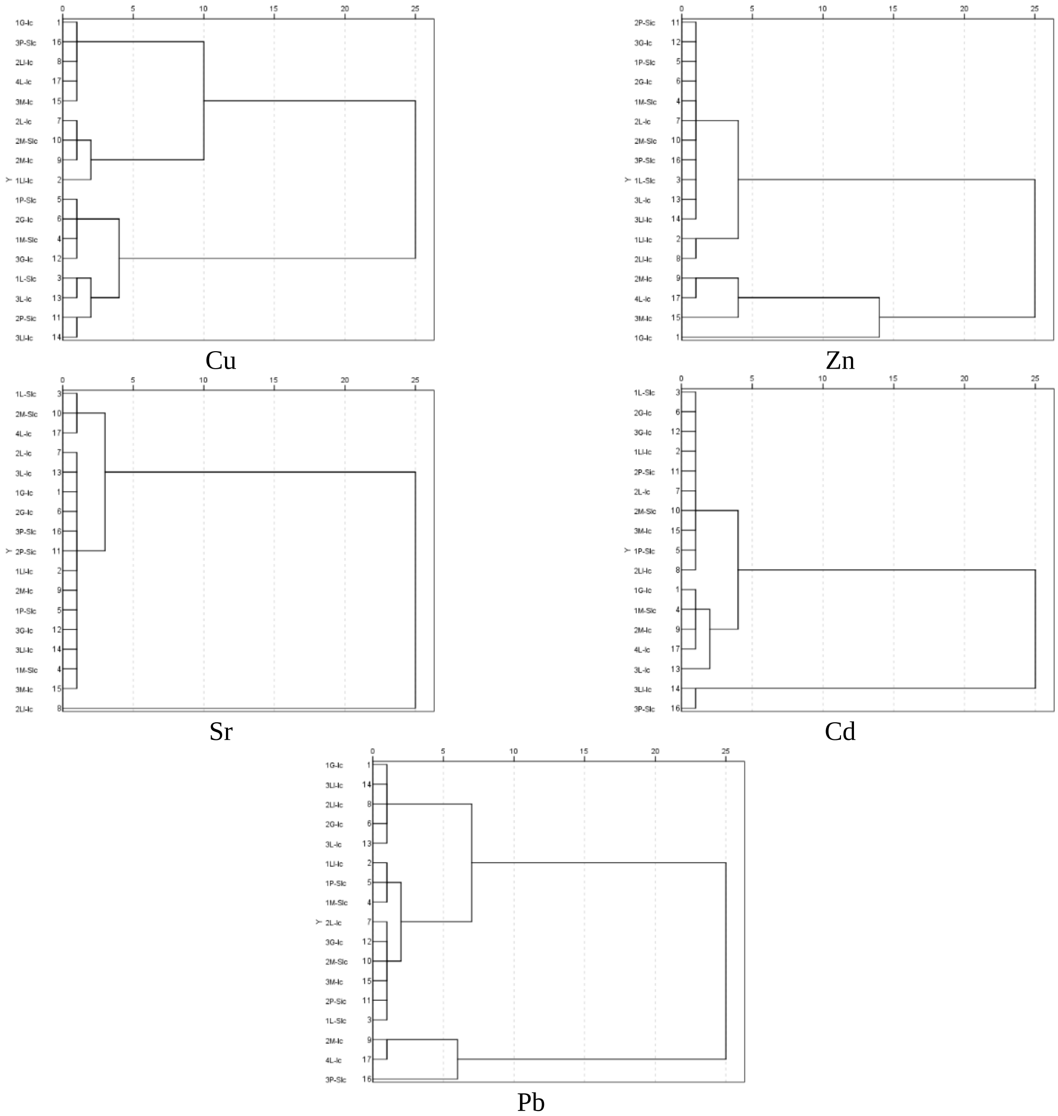


Figure 2. Cluster classification of investigated heavy metals.

4. CONCLUSIONS

Consumption of contaminated citrus fruits endangers human health and can lead to serious diseases. This research highlights issues related to heavy metal content in citrus fruits, which may pose a potential risk to human health. Consequently, the citrus peel should be well-cleansed with water and consumed in limited quantities, because some heavy metals from peel surfaces can pose a risk of cancer (e.g., Cd, Pb, Ni, and Cr) for humans. The analytical data revealed that in all analyzed citrus samples, the concentration of Cd and Pb (as carcinogenic and potentially carcinogenic metals) did not exceed the permitted limits according to European legislation. Descriptive analysis provided a clear and concise picture of the collected data, providing essential information in terms of correlation/dependencies between analyzed metals. This research revealed that there is no significant health risk to citrus consumers, in terms of heavy metals, but to counteract the effect of the concentrations of HMs, it is suggested that the citrus be well-washed before being peeled.

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