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THE RELATIONSHIP BETWEEN METAL IONS RELEASED FROM AISI304 AND AISI321 STAINLESS STEELS IN FOOD SIMULANT SOLUTIONS AT VARIOUS WORKING PARAMETERS

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Abstract: *The aim of this study was to apply statistical techniques to analyze the experimental data obtained from accelerated migration tests of metal ions from different stainless steels grades in simulated environments foods. For this purpose it was used principal component analysis (PCA) to the metal ions analyzed in acetic acid solutions (3%, 6% and 9% in double-distilled water) at different working parameters, in order to get an overview of the data obtained and to find which variables are related, and which variables are the most important in distinguishing between samples. For AISI304 stainless steel grade was studied the migration of Cr, Mn, Fe and Ni ions and for AISI321 stainless steel grade was studied the migration of Cr, Mn, Fe, Ni and Ti ions. The correlations between all determined varibles were studied using Pearson's coefficients with statistical significance at $p<0.05$. Significant correlations between metal ions released in food simulant solution of 3%, 6% and 9% concentrations for AISI304 and AISI321 were found. This study demonstrated that the principal component analysis (PCA) is useful for interpreting data set, providing informations about the relationships between metal ions analyzed release in food simulant solutions from both stainless steel grades, at various working parameters. The results indicate a high Cr and Mn content comparatively with iron and nickel content released from AISI304 in food simulant 6% concentration. High iron content comparatively with chromium and nickel content was realeased from AISI321 in acid food simulant 3% concentration and a high Fe and Ni content comparatively with Cr and Mn content was realeased from same stainless steel grade in food simulant 9% concentration.*

Keywords: *acetic acid, metal migration, principal component analysis, correlation matrix*

1. Introduction

Although the presence of metal ions in food plays often an essential role in metabolic processes, they can easily exceed toxicity limits, if the choice of metallic material is not done correctly, taking into account the specific conditions of work.

Current research on food contamination led to an increased awareness of the behavior of metal ions that are released into food during their industrial processing or storage. At the same time, the consumer concerns about food safety have greatly increased. Thus, at national and international level, this result has led to strictly impose of the new higher limits on the migration of chemical elements that can contaminate the food raws in the food chain and processed food [1], [2], [3]. AISI304 and AISI321 stainless steel grades are the most common metallic alloys, both in the manufacture of food processing equipment components, as well in the construction of various storage containers. To study the behavior of these materials in food corrosive environments, the tests were performed under accelerated conditions and the release of metal ions provides quickly and relevant informations. In these migration tests a great importance has the choice of working parameters, taking into account their influence on the migration process. In order to distinguish between different compounds who migrate into food corrosive environments, various authors have used different statistical techniques [4], [5], [6]. Mathematical modeling was performed to assess the concentration of metallic elements migrated in acetic acid solution of various concentration as function of working parameters [7].

The aim of this study was to apply of the principal component analysis (PCA) to some metal ions that migrated in acetic solution at 3%, 6% and 9% concentration at diferent working parameters, to get an overview of the data obtained and to find which variables are related, and which variables are most important in distinguishing between samples.

2. Materials and methods

The present study was carried out for 27 samples of each grades of stainless steel, AISI304 and AISI321. As corrosive environments were used solutions of 3%, 6% and 9% acetic acid in double-distilled water, which it is recommended as a simulant solution in the migration testing of metal alloys in contact with acidic foods [8], [9]. In order to prevent the contamination of corrosive environment with foreign compounds from the surface of metal samples, they were washed with a solution of detergent at 40°C, rinsed in double-distilled water and then subjected to ultrasonic at a temperature of 45°C in the ultrasonic bath Elma D-78224 for 15 min. The samples were then dried in oven at a temperature of 40°C. For AISI304 stainless steel was studied the migrations in the solution of Cr, Mn, Fe and Ni ions and for AISI321 stainless steel was studied the Cr, Mn, Fe, Ni and Ti ions.

In the immersion tests the following working parameters were used: the testing temperature ranged from 22 to 34ºC, the stiring environment varied from 0 to 250 rot/min and the exposure time ranged from 30 to 90 min. The concentrations of metal ions in solution were analyzed by inductively coupled plasma mass spectrometry (*ICP-MS*). The concentrations of metal ions obtained by *ICP-MS* were used in multivariate analysis. The interdependence among all determined varibles - metal ions release in food simulant solutions of 3%, 6% and 9% concentration from AISI304 stainless steel grade, respectively AISI321 grade at various working parameters – were studied using Pearson's coefficient with statistical significance at $p < 0,05$ and Principal Component Analysis (PCA). PCA is a multivariate analysis technique that can be applied to original data to reduce the number of variables by preserving as much as possible the variance of the original data. This technique transforms the variables under investigation into new variables, namely *principal components* (PCs) minimizing the correlation among the original variables. The new variables are arranged in decreasing order of importance, are determined and expressed as linear combination of the original variables: the first PC has maximum variance, while the second principal component has a variance as high as possible but less than that of the first principal component. It will retain the PCs that have an eigenvalue > 1 because they bring a lot more information than the initial variables [10]. The variables were compared and interpreted through two dimensional bi-plots that show the position of determined variables and identify how the variables relate to both the PCs and other input. The elements of PCs can be divided into fewer groups, underlining the differences between the variables and similarities between them. Pearson's correlation analysis and PCA were carried out using SPSS v.16.0 software.

3. Results and Discussion

Minimum and maximum values, mean and standard deviation for each of metal ions of chromium, manganese, iron and nickel which migrated from stainless steel samples AISI304 and for each of metal ions of titanium, chromium, manganese, iron and nickel which migrated from AISI321 stainless steel samples in the acid food simulant solution of 3%, 6% and 9% concentration are showed in Table 1 and 2.

Correlation coefficients between ions released in simulant solution of 3%, 6% and 9% concentration from AISI304 are presented in Table 3.

Table 1. Specific values of metal ions which released from the AISI304 stainless steel samples in 3%, 6% and 9% acetic acid solutions

Metal ions released in solutions	* Notations used for metal ion released in the solutions 3%, 6% and 9% acetic acid	Calculated value [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{x}$	Standard deviation, *SD*
Chromium	Cr_3	4.00	238.00	33.51	58.23
	Cr_6	5.00	42.00	18.22	8.45
	Cr_9	1.00	36.00	6.33	7.01
Manganese	Mn_3	1.80	43.00	8.77	11.15
	Mn_6	1.47	15.67	4.45	4.07
	Mn_9	0.72	9.72	2.03	1.91
Iron	Fe_3	100.00	4450.00	865.18	1159.47
	Fe_6	100.00	610.00	304.07	149.31
	Fe_9	10.00	1140.00	178.88	254.30
Nickel	Ni_3	6.80	237.20	38.59	50.96
	Ni_6	121.00	561.00	326.77	118.67
	Ni_9	3.30	16.80	7.53	2.85

* Cr_3, Mn_3, Fe_3, Ni_3 – metal ions of chromium, manganese, iron and nickel which release in 3% acetic acid; Cr_6, Mn_6, Fe_6, Ni_6 – metal ions of chromium, manganese, iron and nickel which release in 6% acetic acid; Cr_9, Mn_9, Fe_9, Ni_9 – metal ions of chromium, manganese, iron and nickel which release in 9% acetic acid;

Table 2. Specific values of metal ions which released from the AISI321 stainless steel samples in 3%, 6% and 9% acetic acid solutions

Metal ions released in solutions	* Notations used for metal ion released in the solutions 3%, 6% and 9% acetic acid	Calculated value [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{x}$	Standard deviation, *SD*
Titanium	Ti_3	0.40	3.50	167	0.99
	Ti_6	0.58	8.28	2.24	1.70
	Ti_9	0.68	2.28	1.33	0.44
Chromium	Cr_3	5.00	36.00	13.03	7.31
	Cr_6	1.00	22.00	9.77	5.69
	Cr_9	0.00	49.00	13.59	12.42
Manganese	Mn_3	3.77	16.57	7.47	3.20
	Mn_6	2.93	19.73	6.42	3.37
	Mn_9	2.49	8.99	5.36	2.15
Iron	Fe_3	140.00	1370.00	579.62	272.40
	Fe_6	110.00	760.00	337.77	155.20
	Fe_9	140.00	710.00	452.96	165.66
Nickel	Ni_3	13.30	58.30	32.00	11.54
	Ni_6	306.00	806.00	536.37	162.25
	Ni_9	7.70	77.70	27.73	18.09

* Ti_3, Cr_3, Mn_3, Fe_3, Ni_3 – metal ions of titanium, chromium, manganese, iron and nickel which release in 3% acetic acid; Ti_6, Cr_6, Mn_6, Fe_6, Ni_6 – metal ions of titanium, chromium, manganese, iron and nickel which release in 6% acetic acid; Ti_9, Cr_9, Mn_9, Fe_9, Ni_9 – metal ions of titanium, chromium, manganese, iron and nickel which release in 9% acetic acid.

Table 3. Pearson correlation matrix of ions released in 3%, 6% and 9% acetic acid solution from AISI304 stainless steel grade

	Cr_3	Cr_6	Cr_9	Mn_3	Mn_6	Mn_9	Fe_3	Fe_6	Fe_9	Ni_3	Ni_6	Ni_9
Cr_3	1.000											
Cr_6	0.259	1.000										
Cr_9	0.219	0.787[a]	1.000									
Mn_3	**0.984[a]**	0.290	0.263	1.000								
Mn_6	0.082	**0.638[a]**	0.588[a]	0.128	1.000							
Mn_9	0.274	0.791[a]	**0.941[a]**	0.325	0.664[a]	1.000						
Fe_3	**0.855[a]**	0.336	0.437[b]	**0.911[a]**	0.220	0.506[a]	1.000					
Fe_6	0.483[b]	**0.648[a]**	0.387[b]	0.492[a]	0.300	0.454[b]	0.467[b]	1.000				
Fe_9	0.331	0.819[a]	**0.930[a]**	0.391[b]	0.660[a]	**0.971[a]**	0.573[a]	0.469[b]	1.000			
Ni_3	**0.977[a]**	0.299	0.262	0.959[a]	0.092	0.298	**0.799[a]**	0.480[b]	0.329	1.000		
Ni_6	0.011	-0.285	-0.306	-0.007	-0.412[b]	-0.377	-0.022	0.014	-0.425[b]	0.055	1.000	
Ni_9	0.126	0.864[a]	0.876[a]	0.175	0.527[a]	0.810[a]	0.308	0.401[b]	**0.830[a]**	0.169	-0.324	1.000

Bold values represent correlation with significance
[a] Significant correlations at a 0.01 level
[b] Significant correlations at a 0.05 level

Among the ions released from stainless steel samples grade AISI 304 in the acidic solution of concentration 3%, Table 3, the ions of manganese, iron and nickel showed significant positive correlations, at a level of significance p = 0.01, with chromium ions. Significant correlations were obtained at a level p = 0.01 between the manganese, iron and chromium ions that were released in solution of 6% concentration and between manganese, iron, nickel and chromium ions that were released in the solution of 9% concentration was found.

The interdependence among metalic ions migrated from stainless steel grade AISI304 in acid simulant solution of 3%, 6% and 9% concentration are represented in Figure 1. The first two PCs represent 98.13 % of the total variance (PC1 = 94.76% and PC2 = 3.37%).

The plot of PC1 vs. PC2 loadings shows, along the PC1 axis, a close association between ions of manganese and chromium which were released in the acidic solution of concentration 6% and ions of manganese, chromium, iron and nickel which were released in acetic solution of concentration of 9%, variables strongly associated with the specific axis.

The correlations between this varaibles is positive, so as shown by their position in the same quadrant.

The second principal component PC2 show a strong association between the metal ions of chromium, manganese, nickel and iron which migrated in the acidic solution of concentration 3%, variables perfectly differentiated from the rest, since they have lower values on the first component.

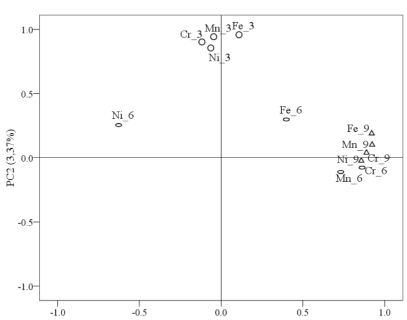

Figure 1. PCA loadings plot for ions released in the 3%, 6% and 9% acetic acid solutions from AISI304. Symbols and definition: ○ - ions released in solution of concentration 3%; ⬭ - ions released in solution of concentration 6%; ∆ - ions released in solution of concentration 9%.

Also, PC2 underlines the opposition between the nickel, chromium and manganese ions which migrated in the 3% acetic solution and same metal ions which migrated in the 9% acetic solution. Chromium and manganese metal ions were more predominantly released in 6 % acetic acid comparatively with some metals like iron and nickel.

From the correlation matrix of metal ions that migrate from AISI321 stainless steel grade in acid simulant solution of 3%, 6% and 9% concentrations, Table 4, it can be noted that was obtained significant positive correlations at a significance level of 0.01 between the manganese, nickel and titanium ions that migrate in acid food simulant of 3% concentration.

Table 4. Pearson correlation matrix of ions released in 3%, 6% and 9% acetic acid solution from AISI321 stainless steel grade

	Ti_3	Ti_6	Ti_9	Cr_3	Cr_6	Cr_9	Mn_3	Mn_6	Mn_9	Fe_3	Fe_6	Fe_9	Ni_3	Ni_6	Ni_9
Ti_3	1.000														
Ti_6	0.254	1.000													
Ti_9	0.362	0.720[a]	1.000												
Cr_3	0.030	0.718[a]	0.780[a]	1.000											
Cr_6	0.420[b]	**0.663[a]**	0.911[a]	0.672[a]	1.000										
Cr_9	0.066	0.703[a]	**0.808[a]**	0.789[a]	0.727[a]	1.000									
Mn_3	**0.707[a]**	0.471[b]	0.651[a]	0.299	0.601[a]	0.485[b]	1.000								
Mn_6	0.263	**0.901[a]**	0.788[a]	0.792[a]	0.681[a]	0.825[a]	0.568[a]	1.000							
Mn_9	0.098	0.362	**0.638[a]**	0.563[a]	0.618[a]	0.702[a]	0.526[a]	0.564[a]	1.000						
Fe_3	**0.475[b]**	0.543[a]	0.699[a]	**0.464[b]**	0.601[a]	0.593[a]	**0.769[a]**	0.582[a]	0.489[a]	1.000					
Fe_6	0.338	**0.829[a]**	0.939[a]	0.823[a]	**0.856[a]**	0.824[a]	0.604[a]	**0.876[a]**	0.614[a]	0.658[a]	1.000				
Fe_9	0.184	0.506[a]	**0.863[a]**	0.733[a]	0.705[a]	**0.660[a]**	0.443[b]	0.596[a]	**0.476[b]**	0.592[a]	0.794[a]	1.000			
Ni_3	**0.571[a]**	0.770[a]	0.837[a]	**0.638[a]**	0.786[a]	0.649[a]	**0.757[a]**	0.809[a]	0.604[a]	**0.686[a]**	0.853[a]	0.602[a]	1.000		
Ni_6	0.369	**0.596[a]**	0.890[a]	0.726[a]	**0.797[a]**	0.619[a]	0.546[a]	**0.642[a]**	0.391[b]	0.601[a]	**0.818[a]**	0.882[a]	0.744[a]	1.000	
Ni_9	0.168	0.831[a]	**0.888[a]**	0.860[a]	0.832[a]	**0.816[a]**	0.457[b]	0.829[a]	**0.496[a]**	0.513[a]	0.884[a]	**0.795[a]**	0.753[a]	0.832[a]	1.000

Bold values represent correlation with significance
[a] Significant correlations at a 0.01 level
[b] Significant correlations at a 0.05 level

Significant correlations exist between the titanium, chromium, manganese, iron and nickel ions which migrate in acid solution of 6% concentration.

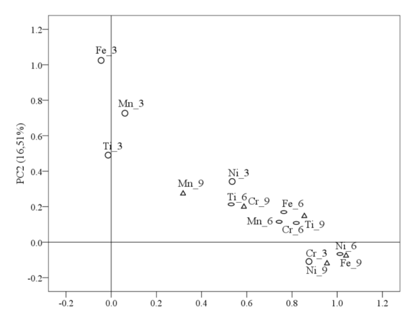

Figure 2. PCA loadings plot for ions released in acidic solution of concentration 3%, 6% and 9% from AISI321. Symbols and definition: ○ - ions released in solution of concentration 3%; ⬭ - ions released in solution of concentration 6%; ∆ - ions released in solution of concentration 9%.

For all the ions studied that migrate from AISI321 stainless steel grade in acid food simulant solution of 9% concentration, significant correlations were obtained between chromium, manganese, iron and nickel ions.

The relationship between the metal ions released from the AISI321 stainless steel grade samples in 3%, 6% and 9% acid food simulant solution are shown in Figure 2.

The first two principal components represent here 77.86% and 16.51% of the total variance. In regard to principal component PC1, we can notice a strong association between some metal ions which migrated from AISI321 stainless steel grade in acid food simulant solution of 6% and 9% concentration. These variables are closely associated with the first principal component. The second principal component is strongly correlated to the iron, manganese and titanium metal ions which migrated from AISI321 stainless steel grade in acid food simulant solution of 3% concentration. Strong significant correlations ($r > 0,7$) at a level of significance of $p < 0,01$ between titanium, iron and manganese ions was found (Table 4). With respect to PC2, this principal component distinguishes between iron and chromium metal ions released in 3% acetic acid solution. Iron ion was more predominantly released in 3% acetic acid comparatively with some metals like chromium and nickel. Nickel ion was more predominantly released in 9% acetic acid comparatively with some metals like chromium and manganese.

4. Conclusion

Correlation analysis showed that are significant correlations ($p < 0,5$) between some metal ions released in 3%, 6% and 9% solution from both stainless steel grades. The PCA method is useful for interpreting data set, providing informations about the relationships between metal ions released in 3%, 6% and 9% solution from AISI304 and AISI321 stainless steels, at various working parameters. A close relationship was found between manganese and chromium ions which were released from AISI304 stainless steel in 6% and 9% solution. The distribution of ions which were released from AISI304 in solution of concentration 3% indicated a high association between ions of nickel, chromium, manganese and iron. Regarding the ions released from AISI321 stainless steel grade, a high correlation was obtained between chromium, iron and manganese ions in acetic acid solution of 6% concentration and between nickel and iron ions which were released in 9% solution.

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