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EVALUATION OF THE RELATIONSHIPS BETWEEN METALLIC IONS MIGRATED FROM AISI304 AND AISI321 STAINLESS STEEL SAMPLES INTO FOOD SIMULANT SOLUTIONS AT VARIOUS STIRRING DEGREES

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Abstract: *The objective of this work was to assess through statistical methods the relationship between metallic ions migrated from AISI304 and AISI321 stainless steel food samples into acid simulant solutions depending on the stirring degrees of corrosive environments. Principal Component Analysis method (PCA) was used to fulfill the purpose aimed at. The metallic samples were immersed into corrosive solutions at diferent stirring degrees: 0 r/min (stationary environment), 125 r/min and 250 r/min. Acetic acid solutions in bidistilled water were used as food simulant environment. After conducting the migration tests, the concentration of Cr, Mn, Fe and Ni ions migrated from AISI304 stainless steel samples into corrosive solutions and Ti, Cr, Mn, Fe and Ni ions concentration migrated from AISI321 stainless steel samples were analyzed. These concentrations were analyzed by mass spectrometry with inductively coupled plasma (ICP-MS). In order to characterize the diffusion processes occurring under accelerated corrosion, the experimental data obtained were statistically processed in two steps: analysis of the correlation between variables based on Pearson's correlation matrix and analysis of relationships between variables through the Principal Component Analysis. PCA method has identified the two significant principal components that explain more than 93% of the original data variance. Significant correlations between the metallic ions migrated into corrosive solutions stirred at 125 and 250 r/min were found.*

Keywords: *stainless steel, food simulant solution, Pearson correlation matrix, Principal Components Analysis*

1. Introduction

The study on the diffusion of metallic elements in foods is an area of interest for many scientists and technologists in this field. A statistical method frequently used to study the phenomenon of diffusion is Principal Component Analysis (PCA). Principal components analysis is a multivariate analytical statistical technique that can be applied in qualitative and quantitative analysis in order to reduce the dependent variables to a smaller number of variables based on correlations between the initial data [1]. Therefore, many researches have been undertaken to explain this complex phenomenon, often leading to the alteration of the final quality of food products [2], [3], [4], [5]. This paper carries on previous studies in the field: over the last two years we have published other studies on the relationship between metallic ions from metal samples at different working parameters [6], [7]. The objective of this work was to assess through statistical methods the relationship between the metallic ions migrated from AISI304 and AISI321 stainless steel food samples into acid simulant solutions depending on the stirring degrees of corrosive environments.

2. Materials and methods

Taking into account that the most aggressive environment found in the food industry is the acidic environment, acetic acid solutions in bidistilled water were used in the present research.
The metal samples were made of AISI304 (X5CrNi18-10) and AISI321 (X6CrNiTi18-10) stainless steel food grade, with a side of 40 mm.
The argument of choosing the two grades of stainless steel is that AISI304 stainless steel grade is the most used of the 300 series, in that they have a good corrosion resistance in a very wide range of food environments. Compared to AISI304 stainless steel, AISI321 stainless steel has in its composition added titanium (Ti), metallic element that has the ability to prevent the precipitation of chromium carbides, thus eliminating the risk of corrosion at the grain boundaries.
The metal samples of two stainless steel grades were tested under the same working conditions. The experimental conditions are shown in Table 1.
Mass spectrometry with inductively coupled plasma method (*ICP-MS Agilent 7500*) was used to analyse the chemical composition of corrosive environments, before and after performing the corrosion tests. In order to characterize the diffusion processes occurring under accelerated corrosion, the experimental data obtained were statistically processed in two steps: analysis of the correlation between variables based on the Pearson correlation matrix, and analysis of the relationships between variables through the Principal Component Analysis, using the trial version of SPSS v16.0 software.

Table 1.
Experimental conditions of accelerated migration tests

Experimental conditions	Levels
Solution conc., [%, wt]	3
	6
	9
Testing temperature, [ºC]	22
	28
	34
Immersion time, [min.]	30
	60
	90
Stirring degree, [r/min]	0
	125
	250

The Pearson correlation matrix was performed using the values of the *stirring dregree* variable of corrosive solutions.
The adequacy of variables was verified in order to apply the principal component analysis. For this purpose the *Kaiser-Meyer-Olkin* (KMO) statistic test and *Bartlett* test of sphericity were applied.
By applying the PCA method, a reduction of the number of variables to a smaller number of components, unrelated to each other, called *principal components*, was obtained. The first principal component extracted (PC1) represents the linear combination of variables that take the maximum possible variance of the original data, and the second principal component (PC2) takes a smaller variance compared to the first component. The number of components chosen have to explain more than 70% the total variance of the data [8].

3. Results and discussion

Minimum and maximum values, mean values and standard deviation values for each of Ti, Cr, Mn, Fe and Ni metal ions migrated from AISI304 and AISI321 stainless steel samples into the simulant solutions stirred at 0, 125 and 25 r/min are shown in Table 2 and 3.

Table 2.
Specific values of metal ions that migrate from AISI304 stainless steel into the simulated acid solutions stirred at 0, 125 and 250 r/min

Metal ions migrated into solutions	* Notations used for metal ions released into solutions stirred at 0, 125 and 250 r/min	Calculated value, [ppb]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Standard deviation, *SD*
Chromium	Cr_0	1.00	20.00	8.22	5.30
	Cr_125	1.00	79.00	13.40	15.04
	Cr_250	3.00	238.00	36.44	56.34
Manganese	Mn_0	0.72	14.67	2.74	2.79
	Mn_125	1.02	16.00	3.76	3.25
	Mn_250	1.42	43.00	8.74	11.36
Iron	Fe_0	10.00	560.00	192.22	156.21
	Fe_125	10.00	1950.00	328.88	366.23
	Fe_250	50.00	4450.00	827.03	1148.21
Nickel	Ni_0	3.30	411.00	99.62	139.60
	Ni_125	5.30	531.00	120.37	168.59
	Ni_250	5.90	561.00	152.91	177.87

*Cr_0, Mn_0, Fe_0, Ni_0 – metal ions of chromium, manganese, iron and nickel migrated into simulant solution at 0 r/min;
Cr_125, Mn_125, Fe_125, Ni_125 – metal ions of chromium, manganese, iron and nickel migrated into simulant solution at 125 r/min;
Cr_250, Mn_250, Fe_250, Ni_250– metal ions of chromium, manganese, iron and nickel migrated into simulant solution at 250 r/min;

Table 3.
Specific values of metal ions migrated from AISI321 stainless steel into the simulated acid solutions stirred at 0, 125 and 250 r/min

Metal ions migrated into solutions	* Notations used for metal ions released into solutions stirred at 0, 125 and 250 r/min	Calculated value, [ppb]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Standard deviation, *SD*
Titanium	Ti_0	0.58	3.50	1.66	0.91
	Ti_125	0.50	5.28	1.81	1.09
	Ti_250	0.40	8.28	1.77	1.56
Chromium	Cr_0	1.00	24.00	7.51	5.48
	Cr_125	2.00	37.00	12.00	7.84
	Cr_250	4.00	49.00	16.92	10.52
Manganese	Mn_0	2.49	14.57	6.01	2.72
	Mn_125	2.69	16.57	6.69	3.14
	Mn_250	2.93	19.73	6.54	3.32
Iron	Fe_0	110.00	770.00	361.11	176.33
	Fe_125	130.00	1370.00	518.14	282.55
	Fe_250	190.00	870.00	491.11	174.80
Nickel	Ni_0	7.70	716.00	167.81	222.26
	Ni_125	9.70	756.00	204.62	267.34
	Ni_250	13.70	806.00	223.66	286.09

*Ti_0, Cr_0, Mn_0, Fe_0, Ni_0 – metal ions of titanium, chromium, manganese, iron and nickel migrated into simulant sol. at 0 r/min; Ti_125, Cr_125, Mn_125, Fe_125, Ni_125 – metal ions of titanium, chromium, manganese, iron and nickel migrated into simulant solution at 125 r/min; Ti_250, Cr_250, Mn_250, Fe_250, Ni_250 – metal ions of titanium, chromium, manganese, iron and nickel migrated into simulant solution at 250 r/min;

The correlation matrix of the variables studied - ions migrated from AISI304 samples into solutions - shows significant positive correlations between some of the variables (Table 4). A moderate correlation (*r* = *0.499*), significant at *p* = *0.01*, between the chromium and nickel ions migrated in stationary corrosive environment (*0 r/min*), was obtained.

Strong correlations *(r > 0.7, p = 0.01)* were obtained between chromium and manganese ions, between manganese and iron ions, at 125 and 250 r/min., according to Table 4.

Table 4.
Pearson correlation matrix of ions migrated from AISI304 stainless steel into the simulated acid solutions stirred at 0, 125 and 250 r/min

	Cr_0	Cr_125	Cr_250	Mn_0	Mn_125	Mn_250	Fe_0	Fe_125	Fe_250	Ni_0	Ni_125	Ni_250
Cr_0	1.000											
Cr_125	0.534[a]	1.000										
Cr_250	0.039	0.173	1.000									
Mn_0	0.282	0.395[b]	0.236	1.000								
Mn_125	0.482[b]	**0.876[a]**	0.275	0.561[a]	1.000							
Mn_250	0.053	0.227	**0.973[a]**	0.236	0.353	1.000						
Fe_0	0.301	0.520[a]	0.637[a]	0.364	0.622[a]	0.657[a]	1.000					
Fe_125	0.364	**0.898[a]**	0.211	0.417[b]	**0.854[a]**	0.274	0.635[a]	1.000				
Fe_250	0.016	0.369	**0.843[a]**	0.299	0.448[b]	**0.888[a]**	0.649[a]	0.468[b]	1.000			
Ni_0	**0.499[a]**	0.162	-0.160	0.190	-0.036	-0.241	-0.026	-0.059	-0.216	1.000		
Ni_125	0.515[a]	0.211	-0.159	0.195	-0.004	-0.236	-0.027	-0.014	-0.202	0.993[a]	1.000	
Ni_250	0.508[a]	0.193	0.099	0.257	0.015	0.006	0.126	-0.018	-0.017	0.962[a]	0.962[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

Table 5.
Pearson correlation matrix of ions migrated from AISI321 stainless steel into the simulated acid solutions stirred at 0, 125 and 250 r/min.

	Ti_0	Ti_125	Ti_250	Cr_0	Cr_125	Cr_250	Mn_0	Mn_125	Mn_250	Fe_0	Fe_125	Fe_250	Ni_0	Ni_125	Ni_250
Ti_0	1.000														
Ti_125	0.719[a]	1.000													
Ti_250	0.266	0.823[a]	1.000												
Cr_0	**0.468[b]**	0.530[a]	0.318	1.000											
Cr_125	0.364	**0.459[b]**	0.308	0.551[a]	1.000										
Cr_250	0.421[b]	0.373	0.138	0.434[b]	0.901[a]	1.000									
Mn_0	**0.700[a]**	0.549[a]	0.149	**0.609[a]**	0.565[a]	0.582[a]	1.000								
Mn_125	0.705[a]	**0.654[a]**	0.297	0.600[a]	**0.535[a]**	0.569[a]	0.906[a]	1.000							
Mn_250	0.444[b]	0.833[a]	**0.833[a]**	0.549[a]	0.533[a]	**0.381[b]**	0.491[a]	0.645[a]	1.000						
Fe_0	**0.554[a]**	0.419[b]	0.105	**0.530[a]**	0.557[a]	0.674[a]	**0.671[a]**	0.594[a]	0.303	1.000					
Fe_125	0.720[a]	**0.459[b]**	0.009	0.471[b]	**0.430[b]**	0.595[a]	0.791[a]	**0.829[a]**	0.311	0.767[a]	1.000				
Fe_250	0.458[b]	0.539[a]	0.348	0.476[b]	0.600[a]	**0.735[a]**	0.641[a]	0.654[a]	**0.545[a]**	0.786[a]	0.670[a]	1.000			
Ni_0	0.106	0.556[a]	0.727[a]	0.077	-0.014	-0.216	0.030	0.027	0.464[b]	-0.230	-0.331	-0.105	1.000		
Ni_125	0.019	**0.435[b]**	0.611[a]	0.041	-0.016	-0.214	0.038	-0.009	0.383[b]	-0.241	-0.364	-0.104	0.964[a]	1.000	
Ni_250	0.032	0.461[b]	**0.636[a]**	0.048	-0.002	-0.201	0.018	-0.014	0.397[b]	-0.238	-0.368	-0.101	0.973[a]	0.996[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

The correlation matrix between ions migrated from AISI321 stainless steel samples into the simulant solution stirred at 0, 125 and 250 r/min (Table 5) shows significant correlations between some variables. Thus, significant correlations were obtained between:

- Titanium and chromium ions ($r = 0.468$), titanium and manganese ions ($r = 0.700$), titanium and iron ions ($r = 0.554$) migrated into the simulant solutions stirred at 0 rpm;
- Titanium and chromium ions ($r = 0.459$), titanium and manganese ions ($r = 0.654$), titanium and iron ions ($r = 0.459$), titanium and nickel ions ($r = 0.435$) migrated into the simulant solutions stirred at 125 r/min;
- Titanium and manganese ions ($r = 0.833$) and titanium and nickel ions ($r = 0.636$) migrated into the simulant solutions stirred at 250 r/min;
- Chromium and manganese ions and between chromium and iron migrated into the simulant solution stirred on all three levels;
- Manganese and iron ions migrated into the simulant solution stirred on all three levels.

By applying the method of principal component analysis and the graphical representation of principal components, allows the visualization of the relationship between variables and identification the possible groups.

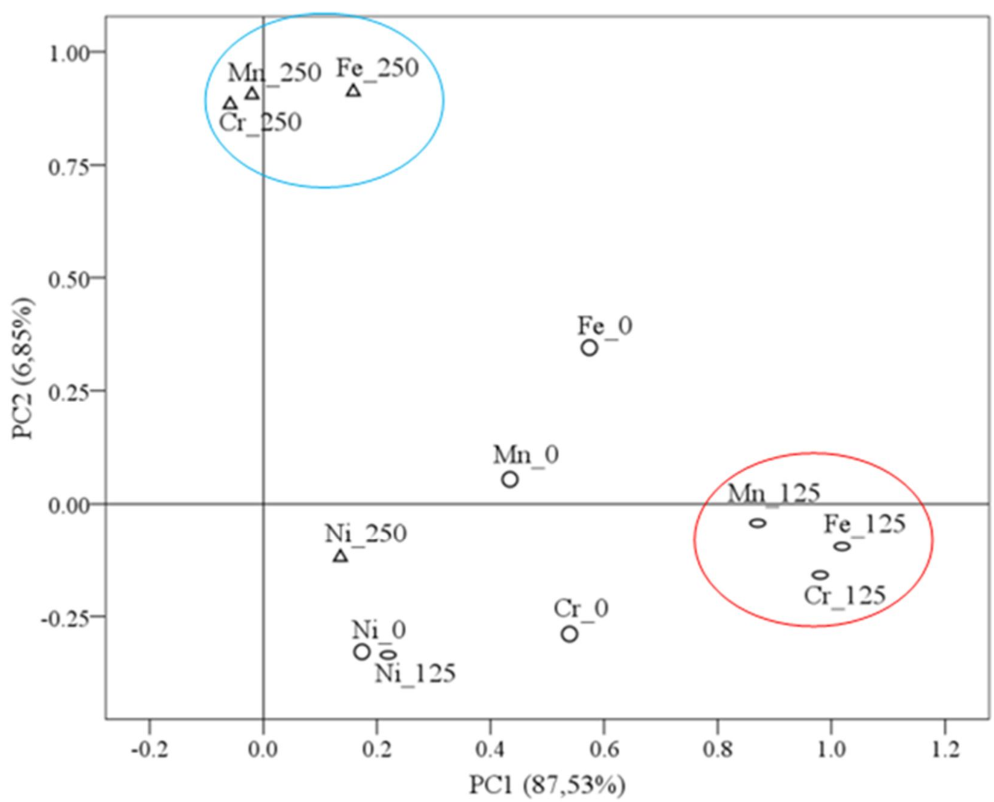

Figure 1. PCA loadings plot for the Cr, Mn, Fe and Ni ions migrated from AISI304 stainless steel samples into the simulated acid solutions. Symbols and definition: ○ - stirring degree 0 r/min; - ⬭ stirring degree 125 r/min; Δ - stirring degree 250 r/min.

After carrying out the statistical data analysis on AISI304 stainless steel grade, the first two principal components explain 94.38% of the original data variance, *PC1*

= 87.53 % and *PC2 = 6.85%*, according to Figure 1. The graphical representation shows that the ions contained in AISI304 stainless steel migrated into simulant solution can form three distinct groups, each group containing the same ions: manganese, iron and chromium the groups being differentiated only by the stirring degree of the solution.

Figure 1 presents along the first principal component (PC1) that there is a strong association between the manganese, iron and chromium ions, migrated into the simulant solution stirred at 125 r/min (encircled in red). These variables indicate a strong correlation with PC1.

The second principal component (PC2) is strongly correlated with the manganese, iron and chromium ions migrated into the simulant solution stirred at 250 r/min (encircled in blue). The second principal component (PC2) highlights the contrast between the iron and nickel ions migrated into the simulant solution at 0 and 250 r/min.

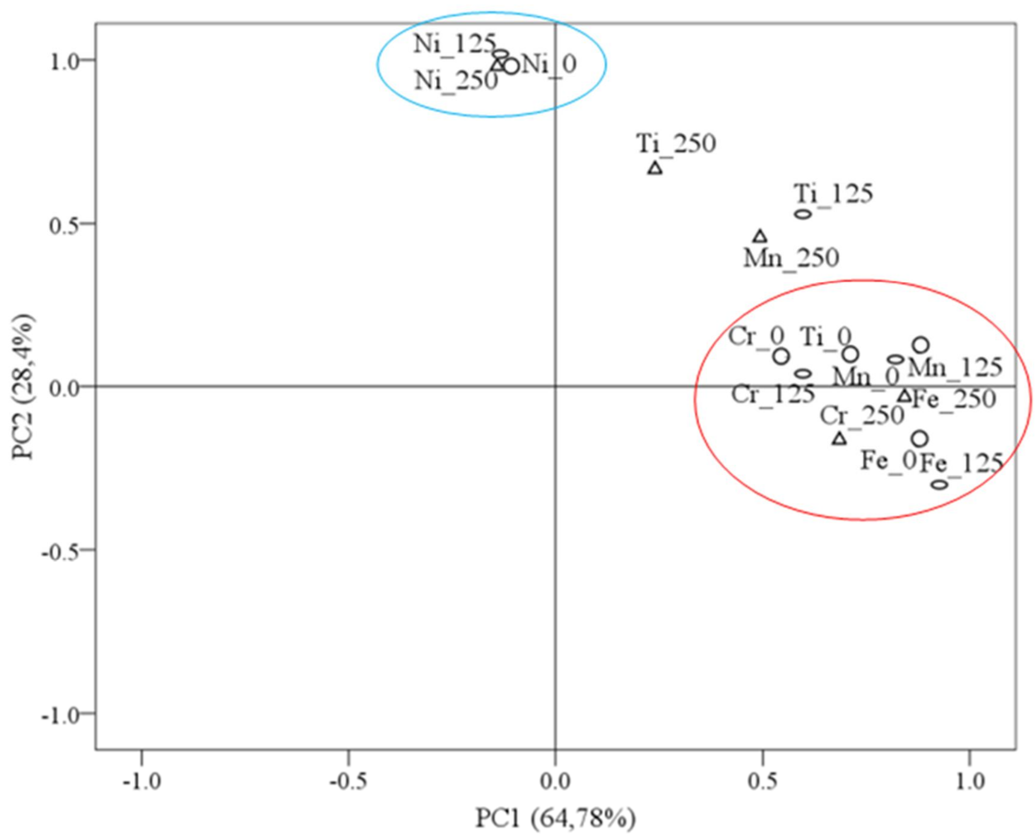

Figure 2. PCA loadings plot for the Ti, Cr, Mn, Fe and Ni ions migrated from AISI321 stainless steel samples into the simulated acid solutions. Symbols and definition: ○ - stirring degree 0 r/min; - ⬭ stirring degree 125 r/min; Δ - stirring degree 250 r/min

The correlation between the metal ions migrated from the AISI321 stainless steel samples into the simulant solution stirred at 0, 125 and 250 r/min is shown in Figure 2. The first two principal components explain 93.18% of the original data variance, *PC1 = 64.78 %* and *PC2 = 28.4%*.

Regarding the first principal component (PC1), one can notice a very good correlation between the manganese, iron and chromium ions migrated into thew simulant solution stirred at 0, 125 and 250 r/min (encircled in red). These variables are strongly correlated with the first principal component (PC1).

The second principal component (PC2) distinguishes between the nickel ions migrated into simulant solution stirred at 0, 125 and 250 r/min as well as the iron ions migrated under the same stirring conditions (encircled in blue).

4. Conclusion

After carrying out the statistical processing of experimental data, it can be concluded that the Principal Component Analysis technique is an essential tool to analyze relationships between metal ions migrated from metal samples into acid simulant solutions.

In the solution stirred at 125 r/min as well as in the solution stirred at 250 r/min, the metal ions migrated from the AISI304 stainless steel samples into simulant solutions are the chromium, iron and manganese ions as compared to the nickel ions migrated in the same stirring degrees.

Iron, chromium and manganese ions migrated into the simulant solution stirred at 125 r/min, form a distinct group from that of iron, chromium and manganese ions migrated into the solution stirred at 250 r/min. At all three stirring degrees, the iron ions are the ones which migrated from AISI321 stainless steel samples, as compared with the nickel and titanium ions.

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